RADIATION-INDUCED VOIDS IN METALS

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The Cover

High-purity aluminum irradiated to 8×10^{20} neutrons/cm² at 125°C. 105,000×. (K. Farrell and J. T. Houston, Oak Ridge National Laboratory)

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RADIATION-INDUCED VOIDS IN METALS

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April 1972

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PREFACE

Voids, or three-dimensional aggregates of vacancies, occur in many materials, but the discovery in 1966 by Cawthorne and Fulton that voids are produced in the high-temperature irradiation of metals came as a dramatic surprise. From the scientific point of view, it was a surprise because the substantial amount of previous work argued that all radiation effects would have disappeared at these temperatures—clearly void formation constituted a new regime. From the engineering point of view, the surprise has substantial economic import because void formation means the material swells in size by amounts which require a substantial modification of the design of reactors operating in this temperature range. Huebotter and Bump in their paper in this volume discuss in detail how this swelling implies an additional cost of several billions of dollars in the cost of the fast breeder reactors planned for the United States alone by the year 2000.

The Cawthorne-Fulton observations were on stainless steel. Their results became generally known from a publication in 1967. Shortly thereafter Mastel and Brimhall observed voids in a pure metal, nickel; these results were particularly interesting since the voids were seen at a level of irradiation two orders of magnitude less than that used in the stainless-steel results. It thus became apparent that void formation might be a common radiation phenomenon whose details of formation depend on the detailed material parameters. This indeed turned out to be the case.

Many major research programs were promptly launched in Europe and the United States to provide more insight into the problem. A number of reactor irradiations were begun, many requiring several years of irradiation. Accelerator irradiations were begun to simulate the neutron-damage conditions and

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achieve the comparable fluence levels more quickly. A number of new tools, including high-voltage electron microscopy, were brought to bear on the problem.

Early in 1969 a small informal meeting involving United States scientists was organized at the U. S. Atomic Energy Commission headquarters in Washington. Both the engineering and scientific aspects of the problem were discussed; these results were quickly incorporated into the research programs. In early 1970 it became clear to us that June 1971 would be a propitious time to hold a major international meeting on the problem since many of the research projects would be coming to fruition then. The advisory committee was formed and the planning begun. In view of the importance of the topic (and the general lack of travel funds), our British colleagues decided to hold a European conference on the same topic; this meeting was held at Reading University, Reading, England, in March 1971.

This volume contains the papers and discussion of the International Conference on Radiation-Induced Voids in Metals which was held on the Albany Campus of the State University of New York, June 9-11, 1971. A number of speakers were invited to give review talks, the topics being chosen to give a broad, balanced perspective of all facets which might be relevant to the solution of the problem. The papers are presented in the same order they were given at Albany. Seventeen papers were invited and the remaining selected on the basis of contributed abstracts. The meeting started off with a review of research on engineering materials and pure metals irradiated with neutrons. Accelerator studies including high-voltage electron microscopy followed. Quenching experiments and other peripheral, but related, kinetic studies were then discussed. The concluding half day was devoted to theory and computer-simulation studies. Interspersed throughout the meeting were some review papers on techniques and theory thought useful for both the general meeting discussion and the proceedings.

In retrospect, the meeting clearly recorded the remarkable progress achieved in a few years on a rather formidable problem. It is interesting to note how rapidly such advanced techniques as high-voltage electron microscopy and high-energy heavy-ion accelerators were incorporated into the research activity. The availability of these new techniques and the background of understanding on defects and radiation damage have certainly been crucial to this progress.

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A number of new results appear in the proceedings, including new data and discussion on the interesting phenomena of the void lattice. Clearly the research programs have reached a substantial level of maturity. As Professor Seeger pointed out in his closing remarks, several classically minded wags had argued that all this effort on voids was "Much Ado About Nothing"; he, however, in view of the scientific and technological challenges remaining, felt Gershwin was closer to the mark with, "I got plenty of nothin' and nothin's plenty for me"!

James W. Corbett

State University of New York at Albany

Louis C. Ianniello

U. S. Atomic Energy Commission

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We were greatly aided in the organizing of this conference by the distinguished members of our Advisory Committee. The committee consisted of the following:

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A. L. Bement (Massachusetts Institute of Technology)
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B. R. T. Frost (Argonne National Laboratory)
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✓ NUCLEATION AND GROWTH OF VOIDS IN STAINLESS STEELS DURING FAST-NEUTRON IRRADIATION

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ABSTRACT

The nucleation and growth of voids and dislocation loops in austenitic stainless steels have been investigated by transmission electron microscopy and immersion density measurements. Annealed 304 stainless steel has been irradiated at 370 to 800°C to fast-neutron fluences up to about 1×10^{23} neutrons/cm² (>0.1 MeV). The effects of temperature, neutron flux, and neutron fluence on the concentration and spatial and size distribution of dislocations and voids are reviewed. Available results on the effects of composition and preirradiation microstructure are compared and related to data on annealed 304 stainless steel. The experimental observations are compared to the predictions of various void-nucleation mechanisms. The results do not appear to be in agreement with the predictions of homogeneous-nucleation theory as presently formulated. Nucleation mechanisms involving the presence of such gases as helium are capable of explaining many of the observations and trends but have not been described analytically. Void growth appears to be controlled by vacancy diffusion.

The formation of voids and dislocations during fast-neutron irradiation was first reported by Cawthorne and Fulton.^{1,2} It was recognized that the swelling and changes in mechanical properties produced by this microstructure would have significant effects on the design and operation of liquid-metal-cooled fast breeder reactors (LMFBRs). The need for models to provide estimates of the property changes outside the range of available experimental data is apparent. The complexity of the atomistic processes involved in the nucleation and growth of voids and dislocations makes it necessary to use both qualitative and quantitative experimental results for the development of these models and the determination of the various unknown parameters contained in the analytic treatments.

In the past 3 years, considerable progress has been made in characterizing the structural damage over a wide range of irradiation conditions. Available results

now allow nucleation-and-growth models to be tested critically from the standpoint of predicting not only bulk density changes but also the concentration of voids, the spatial and size distributions of voids, the effect of fast-neutron flux, the effect of transmutation products, and the effects of varying the alloy composition and microstructure.

The present paper surveys the recent experimental results on austenitic stainless steels. For convenience the paper is divided into four sections. The first section concentrates on the development of the irradiation damage in annealed 304 stainless steel since these results cover a wider range of temperature and fluence than do results for any other alloy. The next two sections deal with the effects of alloy composition and preirradiation microstructure on void formation. The last section summarizes the experimental results and compares them with the predictions of various nucleation-and-growth models.

VOID FORMATION IN ANNEALED 304 STAINLESS STEEL

Annealed 304 stainless steel has been irradiated³⁻⁹ in the Experimental Breeder Reactor II (EBR-II) at temperatures in the range 370 to 800°C and to fast-neutron fluences in the range 1×10^{18} to 1×10^{23} neutrons/cm². For irradiation temperatures between 370 and 470°C, most of the data have been obtained from examination of such EBR-II components as fuel cladding, safety- and control-rod thimbles, and portions of experimental subassemblies. Along any one component the irradiation temperature, neutron flux, and neutron-energy spectrum vary, and these variations must be considered in analyzing the results. For example, Fig. 1 shows the temperature and neutron fluences for an EBR-II safety-rod thimble (3D1). From the bottom of the thimble to the bottom of the core, the temperature is approximately constant at 370°C; through the core the temperature increases to 460 to 470°C, and then above the core the temperature again remains approximately constant. The neutron-energy-spectrum variation is obvious from the comparison of the fluences for neutrons with energies greater than 0.01, 0.1, and 1.0 MeV. Irradiation temperatures above 470°C have generally been obtained by separating test samples from the coolant by a static gas annulus. Nuclear heating produces a temperature gradient between the specimen and the experiment containment tube. The reported temperatures are calculated.

In general, dislocation and cavity structures are produced by most irradiation conditions. For convenience of the reader, the development of these structures will be discussed separately. Unless otherwise noted the reported fluences are for neutrons with energies above 0.1 MeV.

Dislocation Structure

Examples of the dislocation structures that are observed after irradiation at various conditions are illustrated in Fig. 2. No damage was observed in specimens

Fig. 1 Variation in irradiation temperature and fast-neutron fluence along the length of an EBR-II safety-rod thimble (3D1).

Fig. 2 Irradiation-produced dislocation structures in annealed 304 stainless steel.

irradiated to 1×10^{18} neutrons/cm² at 370°C. After irradiation to 1.4×10^{20} neutrons/cm², defects with diameters to about 100 Å were present. About 75% of these defects were $a/3$ $\langle 111 \rangle$ interstitial dislocation loops. The remainder were $a/2$ $\langle 110 \rangle$ dislocation loops and a defect having a symmetric three-dimensional strain field (in contrast to the two-dimensional strain field of a dislocation loop). The concentration of these defects decreased with increasing irradiation temperature, and for this fluence no damage was visible above 524°C. At relatively low fast-neutron fluences, a much higher concentration of dislocation loops has been observed in the immediate vicinity of grown-in dislocations than in the surrounding matrix, as illustrated in Fig. 3. This effect has also been observed in the pure face-centered cubic (fcc) metals aluminum,¹⁰ copper,¹¹ and nickel.^{12,13} For irradiation temperatures below about 550°C, the concentration of faulted interstitial dislocation loops increases with

Fig. 3 Dislocation loops clustered about grown-in dislocations in annealed 304 stainless steel irradiated at 370°C to 2.0×10^{21} neutrons/cm².

TABLE 1
QUANTITATIVE CHARACTERIZATION OF THE DISLOCATION
STRUCTURE IN IRRADIATED 304 STAINLESS STEEL

Irradiation tempera- ture, °C	Fluence, neutrons/cm ² (>0.1 MeV)	Faulted loops		Dislocation density, cm/cm ³	Reference
		Concen- tration, cm ⁻³	Mean diameter, Å		
370	1.4×10^{20}	1.1×10^{15}			Bloom ⁷
483	1.4×10^{20}	3.4×10^{14}			Bloom
467	1.4×10^{20}	2.0×10^{14}			Bloom
496	1.4×10^{20}	1.6×10^{13}			Bloom
524	1.4×10^{20}	$<1 \times 10^{12}$			Bloom
460	4.0×10^{21}	2.0×10^{15}	750	$<10^9$	Brager et al. ⁸
595	3.0×10^{22}	6.0×10^{14}	350	4.5×10^{10}	Brager et al.
435	1.5×10^{22}	1×10^{16} *	150		Bloom and Stiegler ⁹
535	1.5×10^{22}	2×10^{15}	500		Bloom and Stiegler
590	3.5×10^{22}	$<1 \times 10^{12}$		2×10^{10}	Bloom and Stiegler
370	2.0×10^{21}	9.2×10^{14}			Bloom and Stiegler
590	1.75×10^{22}	2.1×10^{13}	1200*	2.4×10^9	Bloom and Stiegler
590	1.75×10^{22}	4.2×10^{13}	1200*	2.4×10^9	Bloom and Stiegler
460	2.8×10^{21}	1.3×10^{14}			Bloom and Stiegler

*Estimated.

increasing fluence. At temperatures in the range 550 to 600°C, the Frank dislocation loops unfault and form a dislocation network. A few unfaulted loops are usually visible at these temperatures. Available quantitative information describing the dislocation structure is summarized in Table 1.

Voids

Irradiation of 304 stainless steel at temperatures in the range 350 to about 650°C (0.35 to 0.55 of the absolute melting temperature) produces cavities, which have been identified as voids. The lower limit for void formation is inferred from the small void sizes found at 370°C and from results of Cawthorne and Fulton,^{1,2} in which voids were not observed in 316 stainless steel after irradiation at 300°C to 1.6×10^{22} neutrons/cm². The upper temperature limit for void formation is somewhat less certain and, as will be discussed below, appears to be a function of the neutron fluence.

Micrographs illustrating the development of the void structure as a function of temperature and fluence are shown in Fig. 4. A number of important qualitative observations are readily apparent. First, there appears to be a fluence threshold above which voids are observed, and this threshold increases with increasing irradiation temperature. Second, it is often observed that at low void

Fig. 4 Cavity structure for annealed 304 stainless steel as a function of fluence and temperature.

concentrations, whether due to low fluences at 370°C or higher fluences at higher irradiation temperatures, a significant fraction of the total void population is associated with either dislocations or precipitate particles. With increasing void concentration, such associations become more difficult to detect. Third, the shapes of the voids appear to be influenced by the neutron fluence and irradiation temperature. At low fluences and low temperatures, the smaller voids appear spherical, but many of the larger voids are quite irregular in shape or polyhedral, with no one form predominating. With increasing fluence and temperature, the large voids often develop a common shape. Voids associated with rod- or needle-shaped precipitates are often elongated in the long dimension of the particle. This is particularly obvious in Fig. 5, a micrograph of a specimen irradiated at 590°C to 2.5×10^{22} neutrons/cm². Brager et al.⁸ have identified

Fig. 5 Annealed 304 stainless steel irradiated at 580°C to 2.5×10^{22} neutrons/cm². The rod precipitates are FeCr sigma phase.

the rod-shaped precipitates as Fe—Cr sigma phase. The upper temperature limit for void formation in 304 stainless steel appears to be about 650°C for fluences of about 5×10^{22} neutrons/cm². At higher irradiation temperatures cavities are observed, but these cavities have the characteristics of helium bubbles; they are much smaller than the voids that form at just slightly lower temperatures, and they are often found in grain boundaries, whereas the voids that form at lower temperatures are not.

Irradiation temperature and fast-neutron fluence are the two most important variables that influence void formation in a given material. Other important variables that must be discussed before quantitative results on the temperature and fluence dependency of void formation can be considered are the neutron flux and energy spectrum. These two variables determine the rates that displacement damage, helium, and other reaction products are produced in the lattice. Data for the concentration of voids in specimens irradiated at constant temperature and fluence (>0.1 MeV), or to the same number of displacements per atom (DPA) but at different fluxes and in different neutron-energy spectra, are tabulated in Table 2. Displacements per atom were calculated¹⁴ with the ENDF/B version 2 nuclear data, the position-dependent neutron spectrum as reported by Edwards et al.,¹⁵ and the Kinchin and Pease¹⁶ displacement model with a displacement threshold of 25 eV. The void concentrations are estimated to be accurate to $\pm 25\%$. Within this accuracy no strong correlation exists between the concentration of voids and the neutron flux or the DPA rate. Second-order effects could exist, but if so they are masked by experimental uncertainties, effects of alloy composition, etc. In the following paragraphs data on the concentration and size distribution of voids will thus be discussed in terms of fluence and temperature and will be treated as independent of flux.

The concentration of voids is shown in Fig. 6 as a function of fluence for irradiation temperatures of 370 to 380, 460 to 470, and 590 to 600°C. The bulk of the data for irradiation temperatures in the range 370 to 470°C was obtained from EBR-II safety-rod thimble 3D1 and control-rod thimble 5C3, which were irradiated in rows 3 and 5, respectively. These two thimbles were from the same heat of 304 stainless steel. All results reported by Sandusky et al.¹⁷ and those results reported by Harkness and Li,⁶ Bloom and Stiegler,^{7,9} and Brager et al.⁸ for irradiations above 470°C were from different heats of 304 stainless steel. The concentration of voids as a function of fluence has generally been analyzed in terms of a power function of the fluence (i.e., a straight line in Fig. 6). Bloom⁷ analyzed results for samples irradiated at the same temperatures and found the void concentrations proportional to $(\phi t)^{0.7}$ at 370°C and $(\phi t)^{1.7}$ at 460°C. Brager et al.⁸ empirically fit the data for all irradiation temperatures in the range 370 to 600°C and described the void concentration as a function of temperature and fluence by the expression:

$$\rho = (\phi t)^{1.60-2.7/\theta+150/\theta^2} \exp(-0.015T + 10.253) \quad (1)$$

TABLE 2

COMPARISON OF VOID CONCENTRATIONS IN ANNEALED 304 STAINLESS STEEL
IRRADIATED AT DIFFERENT NEUTRON FLUX LEVELS TO THE SAME NEUTRON FLUENCES

Irradiation tempera- ture, °C	Irradiation time, sec	Fluence, 10^{21} neutrons/cm ²			DPA rate*		Void concentration, voids/cm ³	Reference
		>10 keV	>0.1 MeV	>1.0 MeV	10^{21} DPA/sec	DPA*		
370	4.29×10^7		6.0				2.0×10^{15}	Brager et al. ⁸
370	3.62×10^7	13.3	7.6	0.5	0.17	6.3	3.6×10^{15}	Bloom ⁷
370	5.72×10^6	9.4	8.0	1.1	1.57	9.0	2.5×10^{15}	Bloom
465	2.43×10^7	12.6	9.0	0.5	0.30	7.3	5.5×10^{14}	Bloom
472	7.50×10^6	10.6	9.0	1.2	1.35	10.1	4.0×10^{14}	Bloom
458	3.57×10^7	27.0	17.5	1.7	0.44	15.8	1.1×10^{15}	Bloom
462	3.64×10^7	18.9	12.0	0.9	0.28	10.3	7.5×10^{14}	Bloom
460	7.22×10^6	14.8	13.0	2.3	2.09	15.1	9.0×10^{14}	Bloom

*DPA = displacements per atom.

Fig. 6 Void concentration as a function of neutron fluence for annealed 304 stainless steel.

where (ϕt) = neutron fluence, 10^{22} neutrons/cm² (>0.1 MeV)

T = temperature, °K

$\theta = T - 623$

$\rho = 10^{15}$ voids/cm³

The curves on Fig. 6 were calculated with Eq. 1. It should be pointed out that the values of the constants in Eq. 1 are heavily biased toward temperatures in the range 370 to 470°C since over 80% of the data analyzed were from this range. Recent results of Sandusky et al.¹⁷ and Bloom and Stiegler⁹ indicate that, at higher irradiation temperatures, saturation in the concentration of voids may occur at a fluence of 3 to 4×10^{22} neutrons/cm². If this happens, extrapolation of available data using the equation of Brager et al. may lead to too large predictions of the void concentration. Sandusky et al.¹⁷ found that no

small voids were present in specimens of 304 stainless steel irradiated at temperatures above about 500°C . In an extreme example no voids smaller than $700 \text{ \AA}$ in diameter were present in a specimen irradiated at 646°C to 5.4×10^{22} neutrons/cm². Bloom and Stiegler⁹ examined specimens of 304 stainless steel irradiated at 590°C to fluences of 1.8, 2.3, and 3.5×10^{22} neutrons/cm². The void concentration and size-distribution data are shown in Fig. 7. A 30% increase in fluence, from 1.75 to 2.25×10^{22} neutrons/cm², caused the void concentration to increase by about a factor of 3, from 5.4×10^{13} to 1.4×10^{14} voids/cm³. With

Fig. 7 Effect of fast-neutron fluence on the void-size distribution in 304 stainless steel irradiated at 590°C .

a further increase in fluence to 3.5×10^{22} neutrons/cm², the void concentration increased slightly to 1.7×10^{14} voids/cm³, thus suggesting that the nucleation process may have been nearing completion. The reduced nucleation rate was substantiated by the lack of small voids (no voids <180 Å in diameter) in the specimen irradiated to the highest fluence.

For irradiation temperatures below about 500°C, the distribution of void sizes is strongly sensitive to the irradiation temperature but relatively insensitive to the fast-neutron fluence. Void-size-distribution curves for specimens irradiated at 370 to 380°C and 460 to 470°C are shown in Fig. 8. The primary effect of increasing the neutron fluence was to increase the void concentration. This produced only a slight increase in mean void diameter and no apparent increase in maximum void diameter. In Fig. 8 all voids with diameters less than 100 Å are counted in the smallest size interval (i.e., the data points at 75 Å in diameter). These results would indicate that at 370 to 380°C the mode of the void-size distribution occurs at the smallest observable void diameter. Results of Brager et al.⁸ for irradiation at 370°C in which the measurements were extended to smaller void sizes indicate that this is not the case and that the mode occurs at about 100 Å. Above 370 to 380°C the mode of the distribution always occurs at a void diameter considerably above the diameter of the smallest observable void. Thus, unless the void-size-distribution curve is bimodal with one mode occurring at a void diameter below the visibility cutoff, it can be assumed that only a small fraction of the total void population is not observed by transmission electron microscopy. Data for irradiation temperatures above 500°C are limited, and only a few results are available on the effect of fluence. These results would indicate, however, that at the higher irradiation temperatures the behavior is somewhat different. Bloom and Stiegler⁹ found that at 590°C and over the fluence range 1.75 to 3.5×10^{22} neutrons/cm² (see Fig. 7) both the mean and maximum void diameters increased as fluence to about the 0.5 power, significantly faster than at the lower irradiation temperatures. Mean void diameters as a function of fluence for irradiation at 370 to 380, 460 to 470, and 590 to 600°C are shown in Fig. 9. The curves were calculated with the equation of Brager et al.⁸

$$d = (\phi t)^{0.15-2.4/\theta^2} \exp(7.45 - 1700^\circ\text{K}) \quad (2)$$

where (ϕt) , θ , and T are as previously defined and d is the mean void diameter in Å. Since nearly all the data shown in Fig. 9 were used in determining the constants of Eq. 2, the agreement between the curves and data is good. The primary limitation of the present equation appears to be at temperatures above about 500°C. Equation 2 predicts $d \propto (\phi t)^{0.148}$ at 590°C, whereas the data of Bloom and Stiegler⁹ indicate that $d \propto (\phi t)^{0.5}$.

Examination of the available data for annealed 304 stainless steel reveals variations in void concentrations and sizes that are outside the experimental uncertainty. Sandusky et al.¹⁷ recently reported results for irradiations at temperatures in the range 408 to 686°C to fluences up to 5.4×10^{22}

Fig. 8 Effect of fluence on the void-size-distribution curve for annealed 304 stainless steel irradiated at (a) 370 to 380°C and (b) 460 to 470°C.

Fig. 9 Mean void diameter as a function of fast-neutron fluence for annealed 304 stainless steel.

neutrons/cm². Some of these results are summarized in Table 3. The void concentrations are significantly lower and the mean void diameters are significantly larger than those reported for the EBR-II safety-rod or control-rod thimbles or for the high-temperature (>470°C) data reported by Brager et al.⁸ or Bloom and Stiegler.^{7,9} It thus appears that significant variation in the void concentrations and void sizes occurs from one heat of 304 stainless steel to another. Also suggested in the results of Sandusky et al. is a very sharp upper temperature limit for void formation at about 650°C. At higher temperatures, only a few small cavities, believed to be helium bubbles, were observed.

The volume change resulting from void nucleation and void growth is most easily obtained by measuring the density change of a given specimen. Immersion density results for annealed 304 stainless steel irradiated at 370 to 380, 410 to 420, and 460 to 470°C are plotted in Fig. 10. Data indicating a density change of less than 0.1% have not been included unless confirmed by electron microscopy. As reported by Bloom⁷ and Brager et al.,⁸ the fluence dependency of the density decrease is a function of the irradiation temperature. A least-squares fit of the three sets of data shown in Fig. 10 gives slopes of 0.9, 1.3, and 1.6 for irradiation temperatures of 370 to 380, 410 to 420, and 460 to

TABLE 3

QUANTITATIVE ELECTRON MICROSCOPY RESULTS FOR ANNEALED
304 STAINLESS STEEL AS REPORTED BY SANDUSKY¹⁷

Temperature, °C	Fluence, 10^{22} neutrons/cm ² ($E > 0.1$ MeV)	Void-volume fraction, %	Average void diameter, Å	Void-size range, Å	Void density, voids/cm ³
408	2.58	$0.1^{+0.1}_{-0.05}$	120	20-330	1.2×10^{15}
462	4.62	$2.4^{+2.4}_{-1.2}$	460	170-1000	3.9×10^{14}
504	3.40	$1.1^{+1.1}_{-0.55}$	660	80-2000	2.9×10^{13}
556	3.71	$1.8^{+1.8}_{-0.9}$	1000	200-2200	2.1×10^{13}
581	3.79	$1.4^{+1.4}_{-0.7}$	1110	200-2600	1.3×10^{13}
603	4.42	$2.0^{+2.0}_{-1.0}$	1870	400-3800	4.0×10^{12}
633	4.94	$1.5^{+1.5}_{-0.75}$	1830	600-3700	3.4×10^{12}
644	5.08	$0.1^{+0.1}_{-0.05}$	1450	500-2350	6.5×10^{11}
646	5.39	$1.4^{+1.4}_{-0.7}$	2080	700-3800	2.2×10^{12}
656	4.81	0	~110	80-130	
682	5.26	0			0
686	5.41	0			0

470°C, respectively. Equation 3 is an empirical temperature-dependent swelling equation developed by Brager et al.⁸

$$\frac{\Delta V}{V} = 10^{-10} (\phi t)^{2.05-2.7/\theta-78/\theta^2} (T-40) \exp \left(0.015T - \frac{5100}{T} + 32.6 \right) \quad (3)$$

where $\Delta V/V$ is the volume change, and all other terms have been previously defined. Equation 3 was based on all available data for *all* temperatures in the range 370 to 600°C. Substituting 375, 415, and 465°C in Eq. 3 gives slopes of 1.1, 1.7, and 1.8, respectively. Thus the trend for increasing fluence dependency with increasing irradiation temperature (up to 500°C) is confirmed by both treatments. For irradiation temperatures below 500°C, the slopes of the void concentration-fluence curves (Fig. 6) are similar and follow the same trends as the density decrease-fluence curves, a result that is to be expected if the primary effect of increasing the fluence is to increase the void concentration, with only small changes in the distribution of void sizes. As discussed previously, the behavior at temperatures above about 500°C appears to be different: the void concentration appears to increase over a relatively narrow range of fluence and then saturates, with the voids continuing to grow. This behavior should lead

Fig. 10 Density decrease vs. neutron fluence for annealed 304 stainless steel irradiated at 370 to 380, 410 to 420, and 460 to 470°C.

to a density decrease which initially has a very high fluence dependency (while both nucleation and growth are occurring) and which then (once nucleation ceases) approaches the third power of the void-growth rate.

It is interesting to note that, although the void concentrations and size distributions reported by Sandusky et al.¹⁷ are considerably different than those reported by Brager et al.⁸ and Bloom and Stiegler,^{7,9} the bulk volume changes are similar.

EFFECT OF COMPOSITION ON VOID FORMATION

Results pertaining to the effect of composition on void formation in austenitic stainless steels are limited. Annealed 316 stainless steel has been irradiated⁸ at temperatures in the range 370 to 800°C to peak fluences of about 5×10^{22} neutrons/cm². Irradiation conditions for other alloys such as Incoloy 800, titanium-modified 304 and 316 stainless steel, and 347 stainless steel have generally been limited to one or two temperatures and fluences.

Lauritzen et al.¹⁸ have examined 304 and 347 stainless steels and Incoloy 800 after irradiation at 660°C to 3.0×10^{22} neutrons/cm². The compositions of these alloys are listed in Table 4. Results of electron microscopy and helium analyses are summarized in Table 5. The three alloys exhibited marked differences in void concentration, mean void size, and bulk volume increase. For the 304 stainless steel, the void concentration is much higher and the mean void diameter much smaller than would be expected for this temperature on the basis of the previously discussed results. It would appear that the material had been irradiated much below 660°C. It is noted, however, that the helium contents are much higher than would be predicted,¹⁹ and the presence of large amounts of helium may have increased nucleation. The differences in behavior of these three alloys were apparently not due to obvious microstructural differences (i.e., precipitate density, etc.). Bloom and Stiegler²⁰ have irradiated standard 304 and titanium-modified 304L (0.2% titanium) stainless steels at $450 \pm 50^\circ\text{C}$ to 1.75 and 1.5×10^{22} neutrons/cm², respectively. The preirradiation anneal was 1 hr at 1038°C. The density decrease in the standard alloy was about a factor of 4 larger than that of the modified alloy; 0.57% and 0.14%, respectively. For these conditions the distribution of void sizes was approximately the same, but the concentration of voids was significantly lower in the titanium-modified alloy. In specimens of titanium-modified 304 stainless steel that were annealed 1 hr at 925°C and irradiated at 590°C, a strong correlation between microstructure and void distribution was found.²¹ This heat treatment resulted in the formation of a high density of small coherent precipitate particles, as shown in Fig. 11(a). The particles tend to be aligned in rows. Figures 11(b) and 11(c) show microstructures after irradiation to 2.0 and 3.0×10^{22} neutrons/cm², respectively. A strong correlation between voids and precipitate is obvious. Nearly every void is

TABLE 4
ALLOY COMPOSITION BY WEIGHT

Alloy	Composition, %										ppM	
	C	Mn	Si	Cu	Mo	P	S	Ni	Cr	Other	B	N
304 stainless steel	0.06	1.55	0.41	0.27	0.50	0.025	0.010	9.15	18.42		16	540
347 stainless steel	0.05	1.16	0.72	0.20	0.14	0.023	0.009	9.32	18.20	0.91 Nb + Ta	4.4	540
Incoloy 800	0.05	0.99	0.25	0.33		0.007	0.007	32.0	20.44	0.51 Ti, 0.40 Al	12	930

TABLE 5
SIZE AND DENSITY OF CAVITIES IN IRRADIATED AUSTENITIC STAINLESS STEELS

Alloy	Mean diameter, Å	Average cavity density, 10^{15} cavities/cm ³	Volume fraction of cavities, %	Bulk volume increase, %	He content, at. ppm
304 stainless steel*	260	1	1.1	1.21	33.7
347 stainless steel	75	2	0.08	0.54	78.5
Incoloy 800	175	7	2	2.47	21.2

*Transmission-electron-microscopy data on 304 stainless steel represent the average of data collected from grip and gauge regions of the same tensile specimen.

Fig. 11 Effect of irradiation at 590°C on the microstructure of titanium-modified (0.2% Ti) 304 stainless steel. (a) Annealed at 925°C. (b) Irradiated at 590°C to 2.0×10^{22} neutrons/cm². (c) Irradiated at 590°C to 3.0×10^{23} neutrons/cm².

attached to a precipitate particle. Areas with a high precipitate density also have a high void density. The samples were irradiated at the same temperature for the same time but at different flux levels to produce the different fluences. It appears that the voids and the precipitate particles have grown simultaneously, and such growth indicates the existence of a binding energy between vacancies and one or more of the elements present in the precipitate.

Available results for 316 stainless steel irradiated in the annealed condition are listed in Table 6. The general trends in the concentration and size of voids appear to be similar to those observed in 304 stainless steel, namely, a decreasing concentration of voids and increasing void size with increasing irradiation temperature. Further, there appears to be considerable variation in the concentration and size of voids from one heat to another. These limited results indicate that at low fluences the concentration of voids is much less than would be found in 304 stainless steel. For example, Brager et al.⁸ found less than 10^{11} voids/cm³ after 3×10^{21} neutrons/cm² at 370°C, whereas in 304 stainless steel the concentration would be about 7×10^{14} voids/cm³. This may be an indication of an increase in the incubation period before the onset of void nucleation in 316 as compared to 304 stainless steel.

Composition may prove to be an important variable when the concentrations of the major helium-producing elements, such as Ni, Fe, Cr, N, and B, are radically changed. Ion-bombardment experiments by Nelson and Mazey²³ have shown that void concentrations and swelling were significantly greater in materials that had been injected with a uniform distribution of helium before bombardment. Bloom and Stiegler²⁴ have compared microstructures of 304 stainless-steel specimens that contained no preinjected helium to those of specimens that contained a uniform distribution of 20 at. ppm helium. The

TABLE 6
SUMMARY OF IMMERSION DENSITY AND TRANSMISSION-ELECTRON-
MICROSCOPY DATA FOR ANNEALED 316 STAINLESS STEEL

Irradiation temperature, °C	Fluence, neutrons/cm ² (>0.1 MeV)	Void density, voids/cm ³	Average void diameter, Å	Immersion density change	Reference
450	5.2×10^{22}		135		Cawthorne and Fulton ^{1,2}
510	4.5×10^{22}		252		Cawthorne and Fulton
560	3.2×10^{22}		258		Cawthorne and Fulton
430	$1.0-1.3 \times 10^{22} *$	$1.2-1.8 \times 10^{15}$	134		Barton and Higgins ^{2,1}
506	$1.0-1.3 \times 10^{22}$	$4-6 \times 10^{14}$	328		Barton and Higgins ^{2,2}
526	$1.0-1.3 \times 10^{22}$	$1-2 \times 10^{14}$	218		Barton and Higgins
565	$1.0-1.3 \times 10^{22}$		311		Barton and Higgins
647	$1.0-1.3 \times 10^{22}$	..	240		Barton and Higgins
370	3.0×10^{21}	$<1 \times 10^{11}$			Brager et al. ⁸
420	9.0×10^{21}	1.1×10^{15}	145		Brager et al.
440	2.0×10^{21}	$<1 \times 10^{11}$			Brager et al.
525	1.9×10^{22}	6×10^{14}	260		Brager et al.
565	2.7×10^{22}	5×10^{14}	290		Brager et al.
600	2.7×10^{22}	1.5×10^{14}	325		Brager et al.
700	3.0×10^{22}	$3 \times 10^{13} \dagger$	108†		Brager et al.
375	7.6×10^{21}	$5.0 \times 10^{13} \ddagger$	40		Bloom and Stiegler ^{2,0}
455	1.9×10^{22}	6.9×10^{13}	236	-0.13	Bloom and Stiegler
510	1.5×10^{22}			-0.09	Bloom and Stiegler
580	1.9×10^{22}	1.0×10^{13}	670	-0.14	Bloom and Stiegler

*Total fluence.

†Helium bubbles.

‡Based on estimated foil thickness.

specimens were neutron irradiated at 390°C to 7.4×10^{21} neutrons/cm². The smaller and more numerous voids that occurred in the specimen containing preinjected helium demonstrate that helium is an effective void-nucleating agent. It is expected that the helium which is produced during neutron irradiation would have a similar effect.

EFFECT OF MICROSTRUCTURE

Structural features such as dislocations, coherent and noncoherent precipitates, and grain boundaries provide sinks for vacancies and interstitials and traps for the precipitation of helium. It is to be expected that changes in the metallurgical structure of a given alloy will influence void nucleation and growth by altering the vacancy and interstitial concentrations and the helium distribution.

Results reported by Claudson²⁵ and Holmes and Straalsund²⁶ indicate that cold-working 316 stainless steel either 25 or 75% essentially eliminated swelling over the temperature range 370 to 650°C to fluences of 3.0×10^{22} neutrons/cm². Type 304 stainless steel in the 50% cold-worked condition was included in the same experiment and swelled about the same as annealed 316 stainless steel at all irradiation temperatures above 370°C . At 370°C no swelling was observed.

Stiegler and Bloom²⁷ have examined 304 stainless-steel samples that had been irradiated at 455°C to 2.5×10^{22} neutrons/cm². Three different preirradiation microstructures were included: annealed, 10% cold worked, and 10% cold worked followed by 24 hr at 482°C and 100 hr at 700°C . The latter treatment reduced the dislocation density to about 10^{10} cm/cm³ and resulted in the precipitation of 100-Å-diameter carbide on the dislocations. These results are summarized in Table 7. Void-size distributions are shown in Fig. 12.

The most pronounced effect of cold work was to reduce the void concentration by about an order of magnitude as compared to the annealed condition. In the material that had been cold worked and then given a recovery treatment before irradiation, the void concentration was about the same as in the annealed material; but the void distribution was shifted to larger sizes, thus resulting in a larger void volume. The reasons for the different behavior of 50% cold-worked 304 stainless steel reported by Claudson²⁵ as compared to 10% cold-worked 304 stainless steel reported by Stiegler and Bloom²⁷ are not apparent.

SUMMARY AND DISCUSSION

These experimental observations can be qualitatively compared to the predictions of various nucleation- and -growth models to establish which

TABLE 7
EFFECT OF MICROSTRUCTURE ON THE CONCENTRATION
AND SIZE OF VOIDS IN 304 STAINLESS STEEL

Material condition	Void concentration, voids/cm ³	Average void diameter, Å	Calculated void volume, %
Annealed	2×10^{15}	193	0.88
10% cold worked	2.1×10^{14}	170	0.06
10% cold worked + 24 hr at 482°C + 100 hr at 700°C	1.9×10^{15}	220	1.28

mechanisms might possibly be operative. The experimental observations for annealed 304 stainless steel are summarized as follows:

1. At low damage levels (i.e., conditions of irradiation temperature and fast-neutron fluence that produce relatively low concentrations of voids and dislocations), the spatial distribution of voids and dislocations is not homogeneous. As the fluence is increased, inhomogeneities become more difficult to detect if present.

2. Neither the concentration of voids nor the size distribution is strongly sensitive to the neutron flux over the range 2.1×10^{14} to 1.8×10^{15} neutrons/(cm²)(sec).

3. The fluence at which damage is first detected increases with increasing irradiation temperature.

4. In the range 370 to 500°C, the void concentration increases monotonically with increasing fluence up to about 7×10^{22} neutrons/cm². In this same temperature range, the void-size distribution is quite insensitive to the neutron fluence, with the mean void diameter approximately proportional to $(\phi t)^{0.15}$.

5. At higher irradiation temperatures ($>500^\circ\text{C}$), saturation in the concentration of voids has been observed. At these higher temperatures the void growth appears to have a higher fluence dependency.

6. Both ion-bombardment experiments and neutron-irradiation experiments have shown that helium significantly increases the void-nucleation rate.^{2,3,24}

7. The concentration and size distribution of voids appear to be sensitive to the concentration of minor alloying elements (there is significant heat-to-heat variation). The bulk volume change is not nearly so sensitive.

Possible nucleation mechanisms suggested to explain void formation include (1) nucleation on preexisting sites, (2) nucleation in displacement cascades or in overlapping cascades, (3) homogeneous nucleation by random fluctuations in the size of vacancy clusters, (4) nucleation in displacement cascades stabilized by

Fig. 12 Void-size distributions in 304 stainless steel irradiated at 455°C to 2.5×10^{22} neutrons/cm² (>0.1 MeV). Void concentrations were 2.5×10^{15} , 2.1×10^{14} , and 1.9×10^{15} voids/cm³ for the annealed, 10% cold worked, and 10% cold worked plus aged specimens, respectively.

transmutation-produced helium, and (5) nucleation in vacancy clusters stabilized by the presence of insoluble gases such as helium.

Nucleation on preexisting sites may be responsible for the heterogeneous void distributions that are observed at low fluences. However, if this were the predominant nucleation mechanism in stainless steel, a very early saturation in the concentration of voids would occur and the fluence at which damage is first observed would not increase with increasing irradiation temperature.

Nucleation in vacancy clusters, which are created in single or overlapping displacement spikes, would occur if the vacancy supersaturation were sufficiently high to stabilize such clusters. Under these conditions the nucleation rate should be highest at low fluences and then decrease because of the decreasing vacancy supersaturation with increasing fluence. This does not appear to be the general trend in the experimental results. Further, since the equilibrium vacancy concentrations are established in very short times (relative to the irradiation times), the incubation period that increases with increasing temperature is difficult to rationalize. Nucleation in vacancy clusters created by overlapping displacement cascades should also lead to a strong flux dependency; this is not observed. In addition, Urban^{1,2} has shown that voids are formed by electron irradiation of pure nickel. Since displacement cascades are not formed during electron irradiation, it can be assumed that they are not a prerequisite for void nucleation. If the vacancy clusters that are created in displacement cascades are below the critical size, then the distribution of void-embryo sizes may be altered from the equilibrium distribution, but the nucleation kinetics should be similar to that calculated from homogeneous-nucleation theory, either according to Harkness and Li^{6,28} or Katz and Wiedersich²⁹ if indeed homogeneous nucleation can occur.

Harkness and Li^{6,28} have examined the behavior that would be expected for homogeneous void nucleation. Standard expressions from existing nucleation theory are used to describe the nucleation of voids in the presence of a vacancy supersaturation. The steady-state vacancy and interstitial concentrations are achieved through a balance between the point-defect generation rate, the rate of migration to sinks, and the rate of recombination. The calculations predict an early saturation in the concentration of voids (at fluences of 10^{22} neutrons/cm² or less), with the saturation occurring more rapidly at higher temperatures and with the concentration of voids at saturation strongly dependent on the neutron flux. Below 470°C such saturation has not been observed for fluences to about 7×10^{22} neutrons/cm². Further, at 400°C and 2×10^{15} neutrons/(cm²)(sec), the concentration of voids is predicted to be about 4×10^{16} at 1×10^{22} neutrons/cm². This predicted value is more than an order of magnitude higher than the measured values. A flux dependency, if present, is much weaker than predicted by the model. For neutron fluxes 2×10^{14} and 2×10^{15} neutrons/(cm²)(sec) at 400°C, the predicted concentration of voids at 1×10^{22} neutrons/cm² would be 4×10^{15} and 4×10^{16} voids/cm³, respectively. Such differences could easily be detected experimentally. The data shown in Table 2

cover this range of neutron flux, and such a large effect is not present. Finally, a number of experiments have shown that, when an insoluble gas, such as helium, is injected into stainless steel before irradiation, the void nucleation rate increases significantly. Helium is also produced continuously during neutron irradiation of stainless steels. At these irradiation temperatures the helium is mobile. If the vacancy supersaturations were sufficiently high to cause homogeneous nucleation of voids, then an even lower energy site would be a vacancy cluster or void embryo that contains helium.

The exact role of helium (or other gases) in void nucleation has not been established. Shively³⁰ has proposed that nucleation might occur in displacement spikes that are stabilized by helium diffusing into them before they can dissolve. Early in the irradiation the nucleation rate, $\dot{n}$, would depend on the concentration of helium present [proportional to the fluence above the (n, α) threshold, $(\phi_1 t_1)$], and on the rate of production of displacement spikes (proportional to the flux above the primary knock-on threshold, ϕ_2) or $\dot{n} \propto \phi_2 (\phi_1 t_1)$. The voids are assumed to become increasingly effective as sinks for helium, causing the nucleation rate to diminish and eventually approach zero. This model is in agreement with many of the trends that are present in the void-concentration data for neutron-irradiated 304 stainless steel. However, there are results which demonstrate that at least in other fcc metals the combination of helium and displacement spikes is not prerequisite for void nucleation. The electron-irradiation experiments of Urban^{1,2} have demonstrated that gases but not displacements spikes are necessary for void nucleation in nickel. Also, voids form during neutron irradiation of aluminum,¹⁰ in which case the displacement spikes are very diffuse.

A second nucleation mechanism, initially suggested by Cawthorne and Fulton^{1,2} and discussed by Bullough and Perrin³¹ and Gulden and Kaae,³² would rely upon the precipitation of helium to form equilibrium gas bubbles. Such bubbles would grow by acquiring additional helium and vacancies until they reach a critical size determined by the prevailing vacancy and interstitial supersaturations. At this point they would undergo unstable expansion as a void. A modification of this mechanism might allow for the diffusion of helium into subcritical void embryos (i.e., vacancy clusters) and thus reduce the critical size for a vacancy cluster as calculated from homogeneous-nucleation theory. This modification would eliminate the requirement for an equilibrium helium bubble.

At present, none of these nucleation mechanisms have been treated analytically. They can, however, qualitatively account for a number of the experimental observations. The incubation period before void nucleation begins occurs because the helium concentration is initially zero and then increases approximately linearly with fluence. Longer incubation periods are required at higher temperatures since the amount of helium required to stabilize a void embryo is larger because of the lower vacancy supersaturations. Heterogeneous void distributions could result because such structural irregularities as precipitates and dislocations trap helium and thus become preferred nucleating

sites. Since helium is mobile at the temperatures of interest, saturation in the void concentration would be expected when it becomes significantly more probable for a newly formed helium atom to reach an existing void or other trap rather than a subcritical void embryo. Finally, the potent effect of preinjected helium in increasing the void concentration can be readily understood.

Most swelling models have assumed that void growth is limited by vacancy diffusion. For a void growing in an infinite medium, $dr/dt \propto 1/r$ or $r \propto t^{1/2}$, where r is the void radius and t is time. Experimentally at temperatures below 500°C the mean void radius is approximately proportional to $(\phi t)^{0.15}$. Brager et al.⁸ have demonstrated that the diffusion-controlled growth model is in reasonable agreement with the observed void-size-distribution curves at 370 to 470°C when the increasing density of vacant and interstitial sinks is accounted for. Limited results at high temperatures⁹ show that the mean and maximum void diameters increase as $(\phi t)^{0.5}$ over the range of fluence 1.75 to 3.5×10^{22} neutrons/cm².

Alloy composition and microstructure have been shown to be important variables in determining the details of the void structure as well as the total volume change. Changes in composition and preirradiation heat treatment are particularly important when they induce changes in precipitate structure. For example, in the titanium-modified 304 stainless steel annealed at 925°C and irradiated at 590°C , a large fraction of the voids had nucleated on a precipitate that was present before irradiation. In standard 304 stainless steel, a similar association between voids and precipitates is observed, but in this alloy the precipitate particles nucleate and grow during the irradiation. The presence of a high dislocation density, such as that resulting from cold working, is effective in reducing the irradiation-induced density decrease, primarily because the void nucleation is reduced. A dislocation structure formed by giving cold-worked material a recovery anneal ($\sim 10^{10}$ cm/cm³) does not affect nucleation (as compared to annealed material) but does enhance void growth. It is generally accepted that voids show a net growth because dislocations preferentially remove interstitials from the system because of the stronger elastic interaction between interstitial atoms and dislocations than between vacancies and dislocations.^{28,29,33} The result is that a dislocation line has a greater capture volume for interstitials than for vacancies. When the density of dislocations is extremely high, as in the cold-worked material, the dislocations may act as efficient sinks for both vacancies and interstitials and thus depress the concentration of both. In addition, the high dislocation density may trap helium atoms either individually or in small groups. Both effects will tend to reduce void nucleation. When the density of dislocations is lower, as in the recovered material, the dislocations still act as efficient sinks for the interstitial atoms but not for vacancies because of the higher mobility and volume for capture of interstitials. As a result, voids experience a greater net influx of vacancies and thus grow at a faster rate than in materials that are free of dislocations.

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DISCUSSION BY ATTENDEES

Johnston: If there is indeed an incubation period in the void formation, this is a phenomenon that should be explained by a successful theory or model. I wonder if the data do indeed indicate a real incubation period.

Bloom: The experimental data do indicate an incubation period before damage is observed by transmission electron microscopy. It appears that this incubation period increases with increasing irradiation temperature. For example, at 370°C, no damage is observed at 10^{18} neutrons/cm². Any defects that might be present are thus less than about 10 Å diameter. At the same temperature small dislocation loops are observed at about 3×10^{19} neutrons/cm², and voids are present at 2×10^{21} neutrons/cm². At 525°C no damage is observed at 1×10^{20} neutrons/cm², but at higher fluences dislocation loops and voids do form. Harkness has reported that at about 600°C no voids were present at about 1×10^{22} neutrons/cm². Again at higher fluences (about 2×10^{22} neutrons/cm²), voids and dislocations are certainly formed.

Harkness: Isn't it possible that the lower number density of voids at high temperatures is a contributing factor to the high apparent growth rate at these temperatures? For a density of 10^{14} voids/cm³ much more individual void growth must occur for a given increment in void volume than if 10^{16} voids/cm³ were present.

Bloom: The concentration of voids is an important factor in the void growth rate. The low void concentrations at high temperature give high growth rates. When the concentration of voids is higher, the voids apparently compete for the available vacancy supply leading to lower growth rates of the individual voids. This is very apparent in the (304 + 0.2 Ti) alloy shown in the paper. In regions of high void concentration, the voids are smaller, and in regions of lower void concentration, the voids tend to be much larger.

Wazzan: You stated that helium is very "potent" with regard to swelling and that this is due to helium promoting nucleation of voids. As I see it, helium can lead to increased swelling by (1) providing nucleation *sites* for voids and/or (2) stabilizing small voids. How can you from your *data* specify that it is item (1) where the influence of helium comes in and it is not item (2) or most probably both? I believe both factors contribute to enhanced swelling in the presence of helium.

Bloom: As demonstrated by both ion bombardment and neutron irradiation experiments, helium is effective in promoting void nucleation. The mechanism by which this occurs is not fully understood. As discussed in the manuscript, it is likely that helium stabilizes small-void embryos.

REPORT ON THE CEA PROGRAM OF INVESTIGATIONS OF RADIATION-INDUCED CAVITIES IN METALS: PRESENTATION OF SOME RESULTS*

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ABSTRACT

Different theoretical and experimental studies have been undertaken at the Commissariat à l'Énergie Atomique to establish the fundamental basis of void formation in irradiated metals and to correlate the damage according to the different nature of particles. These studies are essentially: computer simulation of atomic displacement cascades and their thermal annealing, theoretical calculation of the nucleation and growth of voids; experimental studies of the swelling and defect supersaturation levels obtained in pure metals under neutron irradiation, ion bombardment, etc. After an overall review of these programs, the main results are given.

Voids are formed under irradiation in the steel structural elements of fast-neutron reactors in the temperature range from 300 to 700°C for fluences greater than 10^{22} neutrons/cm² ($E > 0.1$ MeV). This constitutes a serious technological problem in the designing of power reactors, for in these reactors the steel will be exposed to neutron dose rates of 6×10^{15} neutrons/(cm²)(sec) (e.g., in the Phenix reactor) and fast fluences greater than 10^{23} neutrons/cm².

Since it is very difficult and indeed sometimes impossible to obtain such high dose rates and fluences in the existing experimental reactors, we are faced with two problems:

1. Predicting the variation of swelling G as a function of temperature T , neutron dose rate Φ , and fluence Φt , to take into account $G = f(T, \Phi, \Phi t)$ when designing the reactor.
2. Developing alloys where little swelling would take place.

*The results presented in this paper were obtained, most of them quite recently, by authors whose names are listed in the appendix. These results will eventually be published, in more detail, independently.

There are various ways to cope with these problems:

- To set up a phenomenological description of swelling based on the observation of steels irradiated in a fast-neutron reactor.
- To investigate the physics of swelling, starting from a sound knowledge of the fundamental processes involved, and to set up models that must be compared with experimental observations on irradiated steels or pure metals.
- To establish experimental and theoretical correlations between swelling caused by neutrons and swelling caused by other particles (ions, electrons) which can produce greater radiation damage in a shorter time.

These three ways are all explored by the Commissariat à l'Énergie Atomique, but we will discuss only the last two.

Since the first observations of radiation-induced voids in stainless steels,^{1,2} voids have been observed in a great number of neutron-irradiated metals between 0.3 and 0.6 Tf: nickel,³⁻⁶ aluminum,^{4,7,8} copper,⁴ molybdenum,⁹⁻¹² vanadium,^{9,13} niobium,⁹ iron,¹⁴ tungsten,¹² and platinum.¹⁵ To explain the formation of voids in metals, investigators have proposed models.¹⁶⁻²⁴ The more sophisticated of these models¹⁸⁻²⁴ make use of practically the same assumptions to account for the growth of voids, but the analysis of nucleation sometimes differs (homogeneous nucleation¹⁸ or microbubbles of gas acting as embryos).¹⁹⁻²⁴ The assumptions in most cases are the following:

- The supersaturation of defects is the driving force for the precipitation of vacancies.

- Since the nucleus of a void can grow only if it absorbs more vacancies than interstitials, we must suppose that interstitials are more strongly attracted than vacancies to sinks other than voids. Now, in metals, dislocations are the only sinks whose long-range interaction with point defects is not negligible.^{2,5,26} We are thus led to suppose that dislocations attract preferentially interstitials.^{20,27,28}

A prediction of the swelling of metals from first principles is possible only if the following parameters are accurately known:

- The number of defects of each type created by high-temperature irradiation.

- The rates of elimination to the sinks of the various defects in supersaturation. This requires knowledge of the formation and migration energies of defects, as well as the relevant interaction energies, and knowledge of the role of displacement spikes and of gas atoms on the nucleation of voids.

Obviously the present state of our knowledge precludes a purely theoretical approach. We must instead set up simple models and test them by comparison with experimental observations. Such a state of affairs accounts for the various paths that have been taken simultaneously at the CEA to improve our knowledge of the fundamental processes of the swelling of metals:

- Investigation of the formation of voids by means other than irradiation.

- Experimental investigation by transmission electron microscopy of the formation of voids by neutron or ion irradiation in a great number of pure metals.

- Experimental determination of the defect supersaturation.

- Investigation of the production of defects by neutron or ion irradiation by means of computer simulation of displacement cascades; investigation of the formation of defect clusters by a Monte Carlo method.

- Setting up of theoretical models for the swelling of metals.

INVESTIGATION OF THE FORMATION OF VOIDS BY VACANCY CLUSTERING WITHOUT IRRADIATION

To understand the formation of voids under irradiation, we must be aware of the analogies that may exist with the formation of voids when vacancies are the only defects in supersaturation.

1. We can study the formation of voids in pure metals at high temperature by applying both a temperature gradient and an electric field that create an important supersaturation and flux of vacancies.²⁹ Macroscopic voids, e.g., the Kirkendall effect, had been observed in silver.³⁰ An investigation of this phenomenon in silver, aluminum, and nickel has shown that voids are present only in silver, in the supersaturated regions, and that their presence seemed related to the oxygen content of the specimen³¹ (Fig. 1).

2. The formation of voids by quenching is probably correlated with the presence of dissolved gas in the samples.³² We have, accordingly, investigated the role of controlled gas contents (H_2 , O_2 , He) on the formation of voids.

Supersaturated vacancies in a wide range of concentrations can be retained by quenching. Accordingly some of the investigations in progress are aimed at analyzing the mechanisms responsible for the elimination of the supersaturation. We are especially trying to determine accurately the main parameters controlling the clustering of vacancies and to define the nucleation conditions of the various types of vacancy clusters (loops, tetrahedra, voids).

These investigations are conducted on aluminum, magnesium, and nickel by means of techniques of electrical-resistivity measurement and transmission electron microscopy. The first results on aluminum indicate that, probably because of their higher mobility, only divacancies take part in the nucleation of loops.^{33,34}

SWELLING OF PURE METALS UNDER FAST-NEUTRON OR ION IRRADIATION

For a good understanding of the fundamental processes involved in the formation of voids by irradiation, and to establish reliable correlations between

Fig. 1 Voids in silver subjected to an electric field and a thermal gradient; current density = 4×10^4 A/cm², VT = 1500°/cm.

the swelling induced by neutrons or ions, it is important to start from a sound experimental basis. This basis can be obtained by irradiating in well-defined conditions the same materials by neutrons or ions.

Fast-Neutron Irradiations

We have tried to deduce the influence of different factors (temperature T , dose rate Φ , dose Φt) on swelling, by irradiating a dozen metals at different temperatures in the range 0.3 to 0.6 T_m . For each metal, samples with different impurity content and different amounts of cold work have been irradiated in the same capsules. Different well-defined alloys (Cu-Al, Cu-Ge) have also been irradiated in the same conditions.

All the metals (Al, Mg, Cu, Au, Ni, Fe, V, Ti, Zr, Nb, Mo, W) have been irradiated in the Siloe pool reactor. The irradiations have been conducted under a helium atmosphere in heated capsules at dose rates between 3×10^{13} and 3×10^{14} neutrons/(cm²)(sec), ($E > 0.1$ MeV) to fluences in the range 10^{19} to 10^{21} neutrons/cm² ($E > 0.1$ MeV). Dose monitors and five thermocouples placed in the irradiation assembly were used to measure flux and temperature.

Extra irradiations were also conducted in capsules submerged in the water of the Siloe reactor (Al, Mg) and in the Rapsodie fast neutron breeder reactor (Fe, Ni, Mo, V). After irradiation the samples were examined by transmission electron microscopy (cf appendix); in some cases the swelling was also measured by density (Al, Mg, Ni, Fe, Mo, V).

As yet the results are too recent and partial for a detailed interpretation to be given. Moreover, accurate calculations of the number of defects and gas atoms (He, H₂) created by the irradiation are not finished, so that we cannot yet compare efficiently the swelling of the different metals.

Effect of Temperature

The variation of the overall swelling, void mean radius, and density as a function of temperature for metals irradiated to the same fluence with the same dose rate is shown in Table 1 and Figs. 2 to 13. We can immediately see that almost all the tested metals (Cu, Al, Ni, Mg, Mo, V) present a maximum swelling around $0.45 T_m$. On the other hand, niobium does not swell any more at $0.45 T_m$; the peak in this metal seems to be at a temperature below $0.3 T_m$. Gold, titanium, and zirconium do not seem to swell at the investigated temperatures ($T > 0.3 T_m$).

We can also note that:

- The number of voids decreases almost exponentially as temperature increases (Fig. 3).
- The mean radius of voids increases with temperature.
- The radius of the smallest voids observed at each temperature increases with temperature [e.g., Figs. 5(c) and 6(c)].

Effect of Fluence

The effect of fluence at constant dose rate on swelling will be known in a few months for all the metals. The actual data refer to aluminum, magnesium, and nickel on which the work was first started. The results (Figs. 14 to 19) give an almost linear plot between swelling and the measured fast-neutron dose, although the variation of void density and mean radius is not exactly the same for aluminum and magnesium. In both cases the void density tends to saturate.

Effect of Dose Rate

Very few results are yet available. A few experiments on aluminum and magnesium indicate that, at constant dose and temperature, an increase of dose rate by a factor of 2 or 3 reduces swelling about 20 to 30%.

Effect of Cold Work

The effect of cold work has been investigated at about $0.35 T_m$. The main observations carried out at present are given in Table 2, and Figs. 20 and 21 are

TABLE 1

INFLUENCE OF TEMPERATURE ON THE SWELLING

All metals were well annealed and irradiated at a dose rate of 2.5×10^{14} neutrons/(cm²)(sec), ($E > 0.1$ MeV), to a fluence of 5×10^{20} neutrons/cm² with the exception of nickel [dose rate, $\approx 1.3 \times 10^{14}$ neutrons/(cm²)(sec); fluence, $\approx 2.3 \times 10^{20}$ neutrons/cm²]

Metal	Temperature, °C	T/T _m	Mean diameter of voids, Å	Void density, voids/cm ³	ΔV/V, %
Face-Centered Cubic Metals					
Al (99.9999%)	55	0.35	240	2×10^{14}	0.15
	220	0.52	570	10^{13}	0.1
	250	0.56	0	0	0
Cu (99.99%)	220	0.36	≈ 50		≈ 0
	250	0.39	230	3.5×10^{14}	0.16
	335	0.45	560	2.7×10^{13}	0.32
	435	0.52	> 1500	$\approx 10^8$	0.003
	600	0.64	0	≈ 0	≈ 0
Ni (99.95%)	300	0.33	90	4×10^{15}	0.18
	400	0.39	160	8.5×10^{14}	0.2
	500	0.45	200	5.8×10^{14}	0.23
	600	0.50	270	5×10^{13}	0.07
Au (99.99%)	220	0.37	0	0	0
	250	0.39	0	0	0
	335	0.455	0	0	0
	435	0.53	0	0	0
Body-Centered Cubic Metals					
Mo (99.9%)	600	0.3	$20 < d < 30$	8×10^{16}	0.1
	800	0.37	80	10^{16}	0.2
	900	0.405	$80 < d < 200$	3×10^{15}	0.2 to 0.4
	1200	0.51	$300 < d < 600$	10^{14}	0.2
W (99.99%)	900	0.32	50 to 60	10^{16}	0.1 to 0.2
Nb (99.998%)	600	0.325	50 to 60	10^{16}	0.1 to 0.2
	900	0.435	0		0.0
V (99.5%)	335	0.304	140	3.4×10^{14}	0.05
	435	0.355	280	2×10^{14}	0.22
	600	0.44	780	1.5×10^{13}	0.38
	800	0.54	0	0	0.0
Hexagonal Compact Metals					
Mg (99.9999%)	55	0.35	390	6.5×10^{14}	1.12
	220	0.53	1370	5.6×10^{12}	0.54
	250	0.56	0	0	0
Ti (99.95%)	335	0.305	0	0	0
	435	0.355	0	0	0
	600	0.44	0	0	0
	800	0.54	0	0	0
Zr (99.95%)	435	0.33		≈ 0	0
	600	0.41	0	0	0
	800	0.5	0	0	0

Fig. 2 Variation of the overall swelling vs. temperature. †Extrapolated values for nickel.

examples. For aluminum and nickel, swelling increases with cold work. On the other hand, slightly cold-worked copper swells more than annealed or as-rolled material. In the case of magnesium, no appreciable effect of cold work can be detected. Finally, for vanadium, cold work reduces swelling.

These results reveal the impossibility of deducing a general law for the effect of cold work. Nevertheless, we must note that the cold work taken into account corresponds to a dislocation density present in the material before irradiation; in fact, there is an important change of the dislocation density during irradiation owing to annealing or loop formation; this change is very different from one metal to another, and this makes the comparison between the different metals impossible. But we could compare the experimental results for aluminum and copper with the swelling models. In both cases we have a good agreement with the calculated values of swelling (Fig. 39).

Fig. 3 Variation of the number of voids vs. temperature.

Nevertheless, some general features can be drawn from the effect of cold work on swelling for the tested metals, and these features hold true however different the global effects may be:

- The distribution of voids is more uniform in the annealed than in the cold-worked specimens; in the latter, rows of voids can be detected, often in direct relation with the dislocation network (Fig. 22).

- A spreading of the void-size distribution is observed on the cold-worked materials (Figs. 23 and 24).

Effect of Impurities and Controlled Additions

Tables 3 and 4 and Fig. 25 show that the swelling of aluminum and magnesium varies very much with the global content of impurities (for all the

Fig. 4 Variation of the mean radius of voids vs. temperature.

other metals, samples corresponding to different purities have been neutron irradiated but are not yet examined).

To understand the effect of impurities on swelling, we thought it more advisable to test metals containing specific impurities chosen so as to change a given physical parameter; particular attention was given to stacking-fault energy (Tables 5 and 6).

In all the cases investigated (nickel, copper), alloying elements that lead to a reduction of stacking-fault energy minimize swelling (Figs. 26 and 27). The most striking example is that of Cu-7% Al ($\gamma_f \approx 2$ to 3 ergs/cm²) in which no damage is observed.

The analysis of the mechanisms involved is not simple. In the case of copper, the results might be explained by the modification of strain field around dissociated dislocations, the dislocation becoming thus a neutral sink for vacancies and interstitials. One must also notice that in Cu-Al alloys the mobility of vacancies is greater than in pure copper. For this reason it is not impossible that the swelling maximum occurs at a lower temperature.

Ion and Electron Bombardment

The main interest in ion or electron bombardment is to simulate in a few hours or days the damage obtained after many years of neutron irradiation. The advantages or disadvantages of the different ions (metal or carbon ions, protons,

(a)

(b)

Fig. 5 Copper (99.99%) irradiated to $\sim 5 \times 10^{20}$ neutrons/cm² ($E > 0.1$ MeV). (a) $T = 250^\circ\text{C}$. (b) $T = 335^\circ\text{C}$. (c) void-size distribution.

Fig. 6 Magnesium (1 ppm) irradiated to 4.58×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) $T = 55^\circ\text{C}$. (b) $T = 220^\circ\text{C}$. (c) void-size distribution.

Fig. 7 Aluminum (1 ppm) irradiated to 4.58×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) $T = 55^\circ\text{C}$. (b) $T = 220^\circ\text{C}$.

Fig. 8 Gold irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) $T = 220^\circ\text{C}$. (b) $T = 400^\circ\text{C}$.

(a)

(b)

Fig. 9 Titanium irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) $T = 335^\circ\text{C}$. (b) $T = 800^\circ\text{C}$.

Fig. 10 Zirconium irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV).
 $T = 435^\circ\text{C}$.

Fig. 11 Tungsten irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV).
 $T = 900^\circ\text{C}$.

(a)

(b)

Fig. 12 Molybdenum irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV).
(a) $T = 600^\circ\text{C}$. (b) $T = 1200^\circ\text{C}$.

(a)

(b)

Fig. 13 Annealed vanadium irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) $T = 335^\circ\text{C}$. (b) $T = 600^\circ\text{C}$.

Fig. 14 Effect of fluence on the swelling of aluminum, magnesium, and nickel. Electron-microscope measurements for aluminum and magnesium; density measurements for nickel. For both magnesium and aluminum, the dose rate is 1×10^{14} neutrons/(cm 2)(sec) and T/T_m is 0.35. For nickel, the dose rates are (+) 1.3×10^{14} and ($\bullet$) 2.3×10^{14} neutrons/(cm 2)(sec) and T/T_m is 0.39.

alpha particles) have already been discussed,³⁵⁻³⁷ and we will not dwell on this problem here. The aim of these studies is

- To select materials that exhibit little swelling.
- To establish correlations between the effects of neutron irradiation and bombardment by different particles. These correlations can be established empirically at doses where results of swelling by neutron irradiation are available.

For high doses the correlation is easy if one admits that, for a given total number of defects created, neutrons and charged particles lead to the same swelling. The more convenient unit in that case is the number of displacements per atom produced by the different irradiations, as calculated by methods similar to that of Kinchin and Pease³⁸ or by computer simulation of displacement cascades.³⁹ This simple correlation is valid only if the spatial distribution of the defects created and of the sinks is almost the same in specimens irradiated with different particles. This is probably the case of high-energy ions of medium mass (C^+ of 20 MeV).

For heavy ions of low energy (a few hundred kiloelectron volts) and neutrons, the spatial distribution of defects is similar (cascades are only larger);

Fig. 15 Aluminum.

Fig. 16 Magnesium.

Fig. 17 Magnesium, 55°C.

but the annihilation of defects at the surface of the specimen cannot be neglected at high temperature. Finally, for electron irradiation in a high-voltage microscope, in addition to surface effects, the spatial distribution of defects is completely different from that due to neutrons. Thus, to establish reliable correlations between the bombardment with different particles, we must know

- The production rate of defects and the effect of their spatial distribution on the formation of void nuclei.
- The distribution of these defects after diffusion at the temperatures involved.

As we shall see, the first point is treated by computer simulation. For the second point, we are trying to estimate the defect supersaturation by experimental techniques and unsophisticated theoretical models. Figure 28 shows an example of the computed variation of the vacancy supersaturation as a function of depth in a copper foil bombarded with Cu^+ ions at different dose

(a)

(b)

(c)

Fig. 18 Aluminum (1 ppm) irradiated at 55°C.

(a) fluence, 1.8×10^{20} neutrons/cm² } (E > 0.1 MeV)
 (b) fluence, 6.7×10^{20} neutrons/cm² }
 (c) void-size distribution.

rates. These calculations are made by solving the differential equations corresponding to the balance between production and annihilation of point defects; interstitial and vacancy recombination, as well as annihilation on dislocations and surfaces, are taken into account, but the variation of the number of sinks with time is neglected.⁴⁰

TABLE 2
EFFECT OF COLD WORK ON SWELLING
OF PURE METALS

Metal	Impurity content, ppM	Tempera- ture, °C	$\Delta V/V, \%$		
			Annealed	Slightly cold worked	As rolled
Al*	60	55	0.064		0.35
Mg†	1	55	0.46	0.46	0.46
	100	55	0.16	0.18	0.20
Cu*	100	250	0.17	0.31	0.14
Ni*	500	335	0.5	0.65	1.0
V*	5000	435	0.25	0.08	<0.01

* $\sim 5 \times 10^{20}$ neutrons/cm² ($E > 0.1$ MeV).

† $\sim 1.5 \times 10^{20}$ neutrons/cm² ($E > 0.1$ MeV).

Furthermore, a difficulty arises if we bombard with foreign ions. The implantation of the foreign ions causes a composition change that may play a role in swelling. We have undertaken a systematic study of the swelling of some steels and certain pure metals by ion bombardment with different particles (Ni^+ , Cu^+ , C^+ , H^+ , He^+ , e^-), the different usual parameters being varied in those experiments (temperature, dose, dose rate, helium content, amount of cold work, etc.) (Table 7).

Nevertheless, we probably cannot directly compare the results on helium-preinjected samples with those obtained under neutron irradiation where helium is produced gradually. Work is in progress to specify the role of the helium production rate on swelling kinetics.

Our first results concern mainly nickel bombarded with Ni^+ or Ni^{2+} ions (from 100 to 500 keV) and copper bombarded with 500-keV Cu^+ ions. The samples were either thin foils (2000 to 3000 Å) directly examined by transmission electron microscopy after bombardment or thick foils back thinned after irradiation; the samples were not helium preinjected.

(a)

(b)

(c)

Fig. 19 Magnesium (1 ppm) irradiated at 55°C:

- (a) fluence, 5.5×10^{19} neutrons/cm² } (E > 0.1 MeV)
 (b) fluence, 6.7×10^{20} neutrons/cm² }
 (c) void-size distribution.

(a)

(b)

Fig. 20 Vanadium irradiated to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) annealed, (b) 10% cold worked.

Fig. 21 Aluminum irradiated to 4.5×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) annealed. (b) as rolled.

Fig. 22 As-rolled aluminum irradiated to 4.5×10^{20} neutrons/cm² ($E > 0.1$ MeV). Parts (a) and (b) represent the same grain under different contrast conditions.

Fig. 23 Effect of cold work on void-size distribution (nickel, 335°C). N = number of voids of size between R and $R + dR$; N_t = total number of voids.

Fig. 24 Effect of cold work on void-size distribution (magnesium, 1 ppm).

TABLE 3
MAGNESIUM

$\sim 70^\circ\text{C}$; 1.5×10^{20} neutrons/cm² ($E > 0.1$ MeV)

Purity, %	Void diameter, Å	Void density, voids/cm ³	$\Delta V/V$, %	Defect
99.9999	420	2×10^{14}	0.46	Faulted loops
99.99	250	3×10^{14}	0.16	Faulted loops
99.95	290	4×10^{14}	0.3	Faulted loops

TABLE 4
ALUMINUM

$\sim 70^\circ\text{C}$, 4.5×10^{20} neutrons/cm² ($E > 0.1$ MeV)

Purity, %	Void diameter, Å	Void density, voids/cm ³	$\Delta V/V$, %	Defect
99.99995	240	2×10^{14}	0.15	Loops
99.994	200	1.6×10^{14}	0.064	Loops
99.9		0	0	Loops

Some conclusions valid for both copper and nickel can already be drawn:

- Swelling appears at a higher temperature in ion-bombarded samples than in neutron-irradiated samples (Fig. 29, Table 8), although the total dose is much higher in ion-bombardment experiments. This dose of about 40 displacements/atom (dpa) is roughly 100 times higher than for neutron experiments, the dose rate being of course much higher.

- In the case of ion bombardment, a reduction of dose rate leads to a higher swelling for a given temperature (nickel) and to the start of swelling at a lower temperature (copper) (Fig. 30, Table 8).

We can conclude from these two facts that a reduction of particle dose rate shifts the swelling peak toward lower temperatures; at a given temperature swelling is very sensitive to dose rate.

We have performed ion-bombardment experiments on nickel preinjected either with helium or oxygen. In both cases the overall swelling is changed with respect to undoped specimens, but not in the same way; helium reduces swelling (Fig. 31), but oxygen increases it. Therefore we must be cautious in extrapolating to neutrons the results of ion-bombarded gas-doped samples.

We have also tested the effect of the number of sinks on the swelling of copper. We find that swelling decreases when sink density increases (Fig. 32).

Fig. 25 Effect of purity on the swelling of magnesium irradiated to 4.58×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) 1 ppm. (b) 100 ppm. (c) 500 ppm.

TABLE 5
EFFECT OF ALLOYING ELEMENTS ON
THE SWELLING OF COPPER

Metal	Temperature, °C	Mean diameter of voids, Å	Void density, voids/cm ³	$\Delta V/V$, %
Cu (99.99%)	250	230	3.5×10^{14}	0.17
Cu-O ₂	250	410	9×10^{13}	0.28
Cu-H ₂	250	610	2×10^{13}	0.31
Cu-1% Al	250			0
Cu-7% Al	220			0
	250			0
	350			0
Cu-2.5% Ge	250	465	2×10^{13}	~0.1
Cu-5% Ge	250	500	$<10^8$	~0

TABLE 6
INFLUENCE OF ADDITIONS ON THE
SWELLING OF NICKEL

Dose rate: 1.3×10^{13} neutrons/(cm²)(sec) ($E > 0.1$ MeV)
Fluence: 2.3×10^{20} cm⁻²

Addition	Content, at. %	Temperature, °C	$\Delta V/V$, %
Fe	0	400	} ≈ 0.1
	10	400	
	50	400	0.
	50	500	≈ 0.005
Mo	10	400	0.

DETERMINATION OF DEFECT SUPERSATURATION

To give a sound basis to the correlations between bombardments by various particles and to test the main conclusions of the theoretical models of swelling (pp. 70-73), we are attempting to determine the defect supersaturation in conditions where voids are formed. For this purpose we measure the enhancement of diffusion under irradiation.⁴¹⁻⁴³ In Table 9 are listed the methods and the systems used to test and improve them.

A first group refers to investigations of the kinetics of the directional ordering induced by a stress or a magnetic field.⁴⁴ A second group refers to

Fig. 26 Copper-7% aluminum ($\gamma_F \sim 2$ to 3 ergs/cm^2) irradiated to 5×10^{20} neutrons/cm² ($E > 0.1 \text{ MeV}$) at 220°C .

direct investigations of diffusion by sectioning techniques⁴⁵ or by means of the ion microprobe⁴⁶ (layers of about $20 \text{ \AA}$ may be peeled off) (Fig. 33). The investigations are in progress, but the first results have not yet been analyzed.

COMPUTER SIMULATION OF THE FORMATION AND ANNEAL OF DISPLACEMENT CASCADES

A computer program of the simulation of displacement cascades in solids has been set up to get as accurate an idea as possible of the number of defects created by neutron or ion irradiation. This enables us also to know the role of the spatial distribution of cascades on the nucleation of voids. Torrens and Robinson³⁹ started this program, and it is now being developed cooperatively by Oak Ridge, Harwell, and Saclay. It will be published elsewhere. Here are a few results recently obtained at Saclay on the creation of defects in some metals for primary knock-on atoms (PKAs) of energy lower than 150 keV . We have verified (Fig. 34) that the number of defects created depends linearly on the energy yielded to the lattice.

Other calculations for PKAs of higher energy and different metals (all the metals subjected to neutron irradiation) are in progress. Also, the cascade model has been used to study the defects created in copper, gold, and tungsten by

(a) PURE NICKEL

(b) Ni-10% Fe

(c) Ni-10% Mo

Fig. 27 Effect of alloying elements on the swelling of nickel irradiated to 2×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 400°C. (a) pure nickel. (b) Ni-10% Fe. (c) Ni-10% Mo. The 10% molybdenum in nickel lowers stacking faults and seems to inhibit swelling; the nickel with 10% iron, where stacking-fault energy is almost unchanged, swells.

Fig. 28 Calculated steady-state supersaturation of vacancies in a copper thin foil bombarded with Cu^+ ions. Temperature, 400°C ; foil thickness, $3000 \text{ \AA}$.

TABLE 7
ION-BOMBARDMENT FACILITIES

Ions	Particles	Ion sources	Accelerators	Beam intensities, $\mu\text{A}/\text{cm}^2$	Materials
Heavy	Ni^+ , Cu^+ , Au^+	R-f ion source	500 kV, Fontenay	0.1	NiCuAu steel
Heavy	Ni^{2+} , Fe^{2+}	Isotope separator	50 kV, Grenoble; 150 kV, Saclay	40	NiFe steel
Mean	C^{2+}	Reflex	Cyclotron, Saclay	1	Ni steel
Light	Protons	R-f ion source	Van de Graaff, 2 MeV, Bruyères le Châtel	>10	AlMg
Light	Helions	Reflex	Cyclotron, Saclay	10	NiCu steel

(a) 300°C; $\Delta V/V = 0$

(b) 450°C; $\Delta V/V = 4\%$

Fig. 29 Copper bombarded with 500-keV Cu^+ ions to a dose of about 40 dpa.

TABLE 8
COPPER

Temperature, °C	Copper neutron irradiated to ~0.5 dpa	$\Delta V/V$, %	
		Copper bombarded with 500-keV Cu^+ ions	
		Dose rate: 2×10^{-4} dpa/sec Dose: 4 dpa	Dose rate: 2×10^{-3} dpa/sec Dose: 40 dpa
220	0		
250	0.17		
300	~0.3		0
400		0.7	0
450	~0.02		4

(a)

(b)

Fig. 30 Effect of dose rate on the swelling of copper bombarded with 500-keV Cu^+ ions at 400°C. (a) dose rate = 2×10^{-3} dpa/sec; dose, 40 dpa; $\Delta V/V = 0$. (b) dose rate = 2×10^{-4} dpa/sec; dose, 4 dpa; $\Delta V/V \sim 0.7\%$.

(a) HELIUM-PREINJECTED NICKEL

(b) PURE NICKEL

Fig. 31 Effect of preinjected helium on the swelling of nickel bombarded with 200-keV Ni^+ ions at 500°C.

TABLE 9

RADIATION-ENHANCED DIFFUSION

Directional order in the reactor	Anelastic relaxation	Inverted torsional pendulum; elastic aftereffect	System AgZn
	Magnetic aftereffect	Magnetic permeability	System FeNi
Diffusion profiles for fast-neutron and ion irradiation	Self-diffusion	Chemical, electrochemical peeling	^{195}Au in Au
	Impurities diffusion	Ion analyzer	Au in Al; Ni^+Cu^+ in AlAuCu

(a)

(b)

(c)

Fig. 32 Effect of the sink density on the swelling of copper bombarded with 500-keV Cu⁺ ions. (a) annealed copper; $\Delta V/V \sim 4\%$. (b) as-rolled copper; $\Delta V/V \sim 0.5\%$. (c) copper preinjected with ⁸⁵Kr by glow discharge; $\Delta V/V \sim 0$.

(a)

(b)

Fig. 33 Diffusion profiles (by ion microprobe) under ion irradiation. Impurity diffusion: (a) Ni^+ (470 keV) in copper single crystal; (b) Cu^+ (500 keV) in aluminum single crystal.

TABLE 10

RESULTS OF BOMBARDMENT OF [100] AND [110] SURFACES OF
Fe, Cu, W, AND Au BY 20-keV IONS OF Fe, Cu, W, AND Au*

Bombarded surface	Temp., °K	Damage energy, eV	Number of created vacancies	Energy lost by sputtering, eV	Number of sputtered atoms
Fe [100]	15	14,779	199	165	1
	293	14,923	201	139	1
	723	15,674	217	184	2
[110]	15	14,837	187	136	1
	293	14,557	188	164	2
	723	15,457	219	142	2
Cu [100]	15	14,481	173	267	3.5
	293	15,229	212	207	2.5
	723	16,953	259	298	4
[110]	15	16,546	232	184	3
	293	16,558	248	101	2
	723	16,592	250	97	2
W [100]	15	17,931	145	500	4
	293	17,569	162	645	6
	723	17,509	232	626	6
[110]	15	17,140	238	536	6
	293	16,894	248	597	9
	723	17,496	269	521	8
Au [100]	15	15,541	214	952	9
	293	17,090	273	890	11
	723	17,760	293	696	9
[110]	15	17,697	273	475	5
	293	17,561	278	575	8
	723	18,002	297	399	7

*Obtained by Cung, Doan, and Torrens using the computer simulation program of Torrens and Robinson (proceedings of this conference). The damage energy is the primary energy less the inelastic energy loss during the cascade. The results are based on statistical analyses of sets of 21 events for each surface orientation and crystal temperature.

20-keV ions of Cu^{2+} , Au^+ , and W^+ . We will eventually compare the model to the experimental results of Beavan, Scanlan, and Seidman on tungsten.⁴⁷

We have studied the effect of crystal orientation and temperature on the shape of the cascade, the number of vacancies created, and the number of atoms channeled and ejected at the surface (Table 10).

The cascades have been processed in a program simulating the nucleation of defect clusters by annealing.⁴⁸ This program, as those of Beeler⁴⁹ and Doran,⁵⁰

Fig. 34 Variation of the number of vacancies created in displacement cascades with damage energy $[E - E(\text{inelastic})]$ in iron, nickel, and copper; E and $E(\text{inelastic})$ being the PKA energy and the total inelastic energy loss, respectively.

is based on the Monte Carlo method but is much less refined; however, this program is faster because of the introduction of simplifying assumptions:

- We consider successive time intervals Δt that may be much longer than the duration of an atomic jump. All the events occurring in Δt are considered as a whole.

- For every type of mobile defect, a relative mean path is defined. The mean path for single vacancies is taken as a unit.

- The various interactions between defects are isotropic.

- The mutual attraction of defects is taken into account in the following manner: For each type of interacting defect, we define the three radii R_0 , R_1 , R_2 as $R_0 < R_1 < R_2$. The center of the trapping defect is taken as the origin. (The trapping defect is the less mobile of the interacting defects.) When the distance between defects is less than R_0 , R_1 , or R_2 , the probability for clustering or annihilation to occur during Δt is, respectively, 1, 0.5, or 0.1, if we

do not consider purely random encounters. For $R > R_2$, the defects move independently.

To compare this model with Doran's, we considered the case of a cascade in an infinite medium. The annealing of cascades created in iron by 5- and 20-keV PKAs has been simulated using Doran's data. Figure 35 shows that our results do not differ very much from his. Also, we have ascertained that the results are rather insensitive to the interaction parameters.

Prior to investigating the problem of void nucleation, we tried to compare the efficiency of different types of irradiations in producing clusters at temperatures about $0.4 T_m$ (efficiency is defined as the ratio of the number of clusters of a given size to the total number of defects created, after an anneal for time Δt).

Fig. 35 Computer simulation of displacement-cascade annealing in iron. Comparison with Doran's results. $T = 800^\circ\text{K}$, $E = 20\text{ keV}$.

To simulate the annealing of defects created by neutrons or ions at various dose rates, we divided the irradiated solid into cells. The number of cells is equal to the number of cascades created during an arbitrary lifetime of the cascades. When we take into account the interactions between neighboring cascades, the reflection of defects on the cell boundaries is set as a boundary condition. For irradiation by 1-MeV electrons, we consider a cell where the Frenkel pairs are randomly distributed. As in the previous case, reflection boundary conditions are set.

As an example, we considered the case of copper irradiated by neutrons (2×10^{-7} dpa/sec), by 90-keV Cu^+ ions ($\sim 10^{-3}$ dpa/sec), and by 1-MeV electrons ($\sim 10^{-3}$ dpa/sec).

After a time t , corresponding to 10 single-vacancy jumps, we can notice that (Figs. 36 to 38)

- For 1-MeV electrons there remain only single vacancies and interstitial clusters of different sizes (especially $n > 6$).

Fig. 36 Variation of vacancy clustering with PKA energy from short-term annealing in copper at 800°K. The cross at 90 keV corresponds to the annealing of cascades produced by Cu^{2+} ion bombardment ($\sim 10^{-3}$ dpa/sec).

- The influence of the PKA energy (for neutrons and ions) is sensible only for clusters of more than 10 vacancies.

- The interaction between cascades appears to be negligible for the time t considered.

These results are not yet very significant. There is a calculation in progress in which larger times t are considered and new cascades are periodically injected into the cells.

Furthermore, gas atoms and dislocations will eventually be introduced into the cells.

THEORETICAL MODELS OF SWELLING

As we have mentioned, the great number of relevant parameters and our insufficient knowledge of them preclude a purely theoretical approach; the model must be gradually refined by comparison with experimental results. The only valid test is the comparison with the formation of voids in pure metals, for only then do we have an exact knowledge of the basic parameters. This is why we have devoted more energy in gathering experimental data on the formation of voids in pure metals than in setting up an original theoretical model.

We have, nevertheless, set up a model (G.B.1 Model)⁵¹ analogous to the one proposed by Harkness and Che-Yu Li.¹⁸ We assume that the concentration of interstitials and vacancies does not vary appreciably during short time intervals. We solve the equations of balance between production and elimination of

Fig. 37 Variation of interstitial clustering with PKA energy from short-term annealing in copper at 800°K. The cross at 90 keV corresponds to the annealing of cascades produced by Cu^{2+} ion bombardment ($\sim 10^{-3}$ dpa/sec).

defects for a succession of quasi-steady states, to take into account the variation in time of the sink density. We assume, of course, a homogeneous production of point defects.

We have compared the predictions of this model with experimental results on aluminum and copper, and the following conclusions are drawn:

- The homogeneous-nucleation laws that were used do not describe properly the nucleation of voids nor the nucleation of loops.
- The experimental histograms of the void sizes cannot be deduced from the underlying assumptions of the model, but there is a good agreement on the overall values of swelling.

Fig. 38 Distribution of interstitials in clusters of size n as percent of the final number of interstitials from short-term annealing of a random distribution of Frenkel pairs produced by electron irradiation ($\sim 10^{-3}$ dpa/sec; copper at 800°K).

Despite these drawbacks, the growth of voids as described by the model agrees rather well with the experimental results.

The experimental results on the influence of cold work and the predictions of the model are in good agreement, if we adopt an empirical nucleation law and if we assume a variation of the dislocation density proportional to time and fitted onto the observations (Fig. 39).

The laws for void growth proposed by Bullough and Perrin²³ are extremely sophisticated, but they are difficult to apply to neutron irradiations where the void number depends on dose, temperature, etc. For example, this model predicts that, for an equal dose, there must be a temperature T_1 that is lower than the temperature of maximum swelling and a temperature T_2 that is higher, for which the void radius is the same. Yet we have always observed on the neutron-irradiated metals that the void radius increases with temperature.

On the other hand, the analytical form of the Bullough and Perrin model is quite handy in predicting the effect of different parameters. In particular, it gives the right order of magnitude for the shift of the swelling peak as a function of dose rate²² which we have observed in copper.

To account for our experimental results, we have been led to use a model (G.B.2)⁵¹ with a nucleation law of the form $I = \alpha n^\beta \exp(-\beta T/T_m)$, α, n, β being fitted on the experimental results.

Fig. 39 Calculated effect of cold work on swelling (G.B.1 Model). $\phi = 1.8 \times 10^{14}$ neutrons/(cm²)(sec); $t = 1.8 \times 10^6$ sec; $T = 55^{\circ}\text{C}$. The two experimental points correspond to cold-worked and annealed samples.

The growth law is based on the same assumptions as the G.B.1 Model, but, to give a better description of swelling at high temperatures, we take into account the thermal-equilibrium concentration of vacancies. The void-size histograms are rigorously determined, and their shape is found to agree with the shape given by Sears.²⁴ With this model we have studied the influence on swelling of temperature, cold work, dose rate, and dose (Figs. 40 to 45). Although there is a rather good agreement with the experimental observations, the model is certainly not yet sophisticated enough. Accordingly we are attempting to set up a nucleation law where the precipitation of gas would appear explicitly.

CONCLUSIONS

A few facts seem to stand out:

1. For aluminum, magnesium, and nickel, swelling varies almost linearly as a function of dose—this is in agreement with the theoretical predictions.
2. For a given metal, if the dislocation density is reasonably well known, the theoretical models of swelling account in a rather satisfactory way for the experiments on the effect of cold work.
3. Additions that cause a decrease of stacking-fault energy also cause swelling to decrease, but the mechanism seems complex.

Fig. 40 Comparison between calculated (G.B.2 Model) and experimental values of swelling as a function of dose in aluminum. $\phi = 10^{14}$ neutrons/(cm^2)(sec); $T = 55^\circ\text{C}$; $L = 10^9 \text{ cm}^{-2}$. The nucleation rate, $2.45 \times 10^{11} \text{ t}^{-0.64}$, has been fitted on the experimental values.

4. Copper, aluminum, nickel, magnesium, molybdenum, and vanadium exhibit a peak in swelling at about $0.45 T_m$. The peak of niobium is probably located at about $0.3 T_m$. Gold, titanium, and zirconium do not swell between 0.3 and $0.6 T_m$. Experiments are in progress to check whether or not a peak exists at a lower temperature.

5. The results obtained on the pure samples, undoped with gas and bombarded with ions, seem to show that the temperature of the maximum swelling is very sensitive to dose rate. Apart from the effect of dose rate, at constant dose, on the amount of mutual recombination, there is also an effect of

Fig. 41 Comparison between calculated (G.B.2 Model) and experimental values of swelling as a function of temperature in copper. $\phi = 2 \times 10^{14}$ neutrons/(cm²)(sec); $t = 2 \times 10^6$ sec; $L = 2 \times 10^9$ cm². The nucleation rate, $1.07 \times 10^{13} \exp(-28.75 T/T_f)$, has been fitted on the experimental values.

dose rate at constant irradiation time. The lower the dose rate, the lower the peak temperature.

These results therefore tend to prove that, at a given temperature, the slower the kinetics of cluster formation, the greater the probability for voids to be formed.

Although the model proposed by Bullough and Perrin²² yields the right order of magnitude for the observed shift, we feel that there is still room for other explanations, and we may venture to formulate several nonmutually exclusive hypotheses:

- As the particle dose rate increases, clearly the proportion of divacancies created increases steeply. Now, calculations⁵² have shown that the relaxation volume of divacancies is about twice the relaxation volume of single vacancies. Divacancies are therefore certainly more attracted by the stress field of dislocations than single vacancies. This may lead to the elimination of divacancies on dislocations. This is perhaps partly responsible for the decrease in

Fig. 42 Predicted effect of cold work on swelling in aluminum (G.B.2 Model).

Fig. 43 Predicted effect of the number of cavities on swelling in aluminum (G.B. 2 Model). $\phi = 2.58 \times 10^{14}$ neutrons/(cm²)(sec); $t = 1.77 \times 10^6$ sec; $L = 10^9$ cm⁻²; $T = 100^\circ\text{C}$. The nucleation rate is assumed to be time independent and varies from $4.22 \times 10^9 \exp(-15.38 T/T_f)$ to $4.22 \times 10^{12} \exp(-15.38 T/T_f)$.

Fig. 44 Predicted effect of dose rate on swelling in aluminum (G.B. 2 Model). As the dose increases the peak of swelling shifts to the high temperatures. The nucleation rates, shown on the figure, have been assumed to be time independent. In these cases the maximum of swelling decreases as the dose rate increases. $\phi_1 = 2.58 \times 10^{14}$ neutrons/(cm²)(sec); $\phi_2 = 2.58 \times 10^{15}$ neutrons/(cm²)(sec); $t_1 = 1.77 \times 10^6$ sec; $t_2 = 1.77 \times 10^5$ sec. $L = 10^{10}$ cm⁻².

swelling when dose rate increases, if we can neglect the contribution of diinterstitials.

•On the other hand, it is reasonable to assume that a spherical void cannot be formed in the absence of gas,²⁰ and numerous experimenters have verified the influence of gas on nucleation. If the theoretical models for swelling account satisfactorily for the growth of voids, they are clearly at fault when it comes to nucleation. This is probably due to the fact that they do not take into account the role of gases in the kinetics of clustering.

It may well be that the final configuration obtained by clustering of vacancies, loops or voids, results from a competition between the clustering rate of vacancies, which depends on the supersaturation and the diffusion of gas atoms to the clusters.

Experiments and calculations are in progress to test these hypotheses.

Fig. 45 Predicted effect of dose rate in aluminum, calculated with a model similar to Bullough's model. The voids are assumed to be preexisting and their number to be temperature independent. In this case the values of the maximum of swelling are almost similar. Curve 1, $\phi_1 = 2.58 \times 10^{14}$ neutrons/(cm²)(sec); $t = 1.77 \times 10^6$ sec. Curve 2, $\phi_2 = 2.58 \times 10^{15}$ neutrons/(cm²)(sec); $t = 1.77 \times 10^5$ sec. $L = 10^{10}$ cm⁻²; void density = 2×10^{15} cm⁻³.

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APPENDIX

The following authors have contributed to the investigations:

Formation of Voids by Vacancy Clustering Without Irradiation

Electromigration	C. Monty	SRMP	Saclay
Quenching	J. Hillairet	SPSRM	Grenoble
	P. Regnier	SRMP	Saclay
	V. Levy	SRMP	Saclay

Neutron Irradiations

Irradiation Assemblies	C. Thomas de Montpreville	SRMP	Saclay
	D. Gros	Service des Piles	Grenoble

Experiments on

Al	A. Risbet	SRMP	Saclay
	V. Levy	SRMP	Saclay
Mg	R. Levy	SRMP	Saclay
	V. Levy	SRMP	Saclay
Cu	J. P. Poirier	SRMP	Saclay
	V. Levy	SRMP	Saclay
Ni and alloys	G. Silvestre	SER	Grenoble
	A. Silvent	SER	Grenoble
	G. Sainfort	SER	Grenoble
Mo	J. Pelissier	SPCC	Grenoble
Nb	C. Fisher	SPSRM	Grenoble
	A. Bourret	SPSRM	Grenoble
Ti, } Zr }	N. Azam	SMG	Saclay
	L. Le Naour	SMG	Saclay
Au	C. Kauffer	École des Mines	Nancy
	M. Gerl	Ecole des Mines	Nancy
V	G. Brun	SRMA	Saclay
W	J. Leteurtre	SM Pu A	Fontenay-aux-Roses

Ion Bombardments

Ni ⁺ ions	C. Fiche	SEPP	Fontenay-aux-Roses
	M. Lott	SEPP	Fontenay-aux-Roses
	J. Delaplace	SMG	Saclay
	N. Azam	SMG	Saclay
	A. Silvent	SER	Grenoble
Cu ⁺ ions	M. Lott	SEPP	Fontenay-aux-Roses
	C. Fiche	SEPP	Fontenay-aux-Roses
	V. Levy	SRMP	Saclay

Vacancy Supersaturation Measurements

Strain-Induced Ordering and Magnetic After- effect	E. Bisogni	SPSRM	Grenoble
	J. Hillairet	SPSRM	Grenoble
	W. Chambron	SPSRM	Grenoble
Diffusion Under Neutron Irradiation	D. Acker	SRMP	Saclay
	M. Beyeler	SRMP	Saclay
	G. Brebec	SRMP	Saclay
Diffusion Under Ion Irradiation	C. Fiche	SEPP	Fontenay-aux-Roses
	M. Lott	SEPP	Fontenay-aux-Roses
	M. Beyeler	SRMP	Saclay
	B. Blanchard	SIS	Grenoble

Formation and Annealing of Cascades

I. Torrens	SRMP	Saclay
N. V. Doan	SRMP	Saclay
D. P. Dang Dinh Cung	SRMP	Saclay
J. M. Lanore	SEPP	Fontenay-aux-Roses

Swelling Models

G. Brébec	SRMP	Saclay
M. Gomolinski	SPM	Saclay
G. Brun	SRMA	Saclay

DISCUSSION BY ATTENDEES

Kulcinski: What is your displacement rate in dpa/sec for the ion-bombardment experiments?

Adda: The displacement rates used varied between 1 and 10^{-4} dpa/sec.

Kulcinski: Do you irradiate bulk samples or thin foils, and do you see any significant difference between these (i.e., do you note any surface effects because of the short range of 200- to 500-keV ions in nickel)?

Adda: Bulk samples and thin foils have been used, and the results are the same. The experiments have been done in conditions such that the surface effects are negligible. (See calculations in the text and of Fig. 28.)

Farrell: The results for magnesium and zirconium are interesting. At Oak Ridge we have found that swelling in magnesium is less in a warm-worked specimen than in an annealed specimen and that swelling decreases with decreasing purity. We, too, have not been able to find voids in high-purity zirconium or in Zircaloy-2 at several irradiation temperatures.

Harkness: What were the ranges of your 100-keV ions, and do you feel this was sufficient to avoid surface effect?

Adda: The range of the 100-keV ions is about 400 Å, but the displacement rate is extremely high (1 dpa/sec). Most of the experiments were done with higher energies up to 500 keV. Figure 28 of my paper shows the results of a calculation of the concentration of defects in a foil, and we can see that the loss at the surface, for high dose rate, affects a very restricted part of the foil.

Harkness: An alternate explanation to your dose-rate effects may be that at high dose rate the microstructure consists of a high number density of small voids, voids too small to be observed in the electron microscope, whereas at lower dose rates the lower nucleation rates result in fewer larger voids that may be seen.

Adda: This surprising effect of dose rate has of course puzzled us; therefore we looked at the foils with special attention. The voids should have had to be less than 20 Å to escape observation, and we do not feel they were there.

Harkness: What changes in the surface energy were necessary in order to fit your model to the aluminum and to the copper data?

Adda: We found that the usual homogeneous-nucleation expression could not be used for these metals, and we used a phenomenological law adjusted to experimental values for the number of voids.

Seeger: Could you indicate which information had to be inserted into the theoretical curves for swelling (e.g., surface energies, defect migration energies, etc.), and how many parameters were fitted to the experimental data?

Adda: The nucleation rate has been fitted onto the experimental values. As to the growth part of the calculation, we used the best known values for the physical quantities, except for the interstitial-dislocation interaction parameter that is adjusted.

IMPLICATIONS OF METAL SWELLING IN FAST REACTOR DESIGN

4
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ABSTRACT

This engineering-oriented paper defines the problems in fast-reactor design which are imposed by the phenomenon of void formation in metals (especially stainless-steel alloys). The properties of fast reactors that give rise to concern over dimensional instability of structural materials are stated in general terms. The impact of swelling on the design and probable performance of selected reactor components (fuel elements, fuel-element support hardware, and core structural components) is discussed. The effect of stainless-steel swelling on some fast reactors designed before the phenomenon was discovered is conjectured, and the major modifications of design practice needed to accommodate swelling are scoped. Radiation-enhanced creep plays an important role in some design strategies to accommodate swelling; that role is defined, and the sensitivity of core behavior to creep is discussed. An empirical assessment of stainless-steel swelling and radiation-enhanced creep, from EBR-II operating experience, is made. Brief attention is given to the probable effect of swelling on fast reactor economics.

CHARACTERISTICS OF FAST REACTORS

It is advisable for scientists, working in the highly important field of fast-neutron-radiation effects, to have a general understanding of the impact of metal swelling on fast reactor design. To convey such an understanding requires first the introduction of some of the important characteristics of fast reactors.* Since this introduction assumes minimal prior exposure to the subject and the authors have strived for simplicity through liberal use of generalizations, readers

*Throughout this paper the reactor coolant is assumed to be sodium, and the reactor fuel is assumed to be (U,Pu)O₂. Fast reactors can be designed with other coolants and other fuels, but the problems of metal swelling are not avoided by these changes alone.

who already possess a general understanding of fast reactors should proceed directly to the next section.

Figure 1 shows the core and environs of a typical liquid-metal-cooled fast breeder reactor (LMFBR). In the core, fission heat is generated in long, slender, hermetically sealed fuel elements. A cross-sectional view of a typical fuel element through its fueled region would show a stainless-steel tube (cladding) of 0.25-in. outside diameter and 0.015-in. wall thickness, containing fuel in the form of close-fitting pellets. The fueled length, corresponding to the height of the reactor core, is typically 3 ft and is sandwiched between 1.5-ft-long axial-blanket sections containing natural UO_2 , all within the same cladding. The function of the axial blankets is to capture neutrons that leak from the core in the axial direction and convert ^{238}U to ^{239}Pu . The other major contributor to fuel-element length is a 3-ft storage plenum for fission gas (not shown in Fig. 1). This capacity permits the fuel element to operate to an economical level of burnup ($\sim 100,000$ MWd/metric ton) without undue risk of cladding failure from overpressurization. Thus a typical fuel-element length, including top and bottom end plugs welded to the cladding, is about 9 ft.

Fig. 1 Typical LMFBR core and environs.

Averaged over the entire core at full reactor power, fuel elements generate heat at the rate of about 8 kW/ft. This is about one-half the rate that would produce central melting, an undesirable occurrence. Assuming a core height of 3 ft and a plant thermal efficiency of 40%, a 1000-MW(e) plant requires about 100,000 fuel elements.

For convenience in handling, fuel elements are grouped into larger units called fuel assemblies. Figure 2 shows a typical fuel-assembly cross section. This assembly contains 217 fuel elements arranged in a regular triangular pattern and has a hexagonal stainless-steel housing (wrapper tube) about 5 in. wide across flats and 0.140 in. thick.

Fig. 2 Typical LMFBR fuel assembly.

Sodium flows upward through the vertically standing assembly and through the fuel-element bundle, at a velocity of about 20 ft/sec, while acquiring a temperature rise of about 300°F and a dynamic pressure loss of about 60 psi. Adequate and uniform cooling of all fuel elements in the assembly requires reliable support of the individual elements and preservation of uniform spacing between them. The fuel-element-support method (not shown in Fig. 2) may consist of a helical wire wrap on each element or a system of intermittent grids affixed to the wrapper tube.

The core of the 1000-MW(e) plant, therefore, contains about 500 fuel assemblies and generally about one-tenth as many channels (guide tubes) for control assemblies. The in-core portions of the guide tubes are externally identical to fuel assemblies but are hollow and aligned with vertical drive shafts. These drive shafts are frequently protected in above-core tubular extensions of the guide tubes, as shown in Fig. 1. The drive shafts, and affiliated mechanisms atop the reactor vessel, move control material (nuclear poison) into and out of the core, in response to operator action or automatic signal. The controlled movement of this nuclear poison, which, like fuel, is contained in assemblies for handling convenience, permits the reactor to be started up, shut down, and operated for long periods at constant power level. Surrounding the fuel and

control assemblies are, typically, two rows of radial-blanket assemblies and one row of assemblies that serve as a radial reflector and thermal shield. The radial blanket has a composition and function similar to that of the axial blanket previously described. The radial reflector, composed chiefly of stainless steel, further reduces loss of neutrons by radial leakage and protects the reactor vessel from high temperature and excessive neutron damage during its 30-year lifetime.

In total, the typical 1000-MW(e) fast reactor contains on the order of 1000 assemblies—fuel, control, radial blanket, and radial reflector. Their combined weight, on the order of 200 tons, is borne by a support structure consisting of two horizontal grid plates shown in Fig. 3. In addition to bearing the massive load, the grid plates provide the principal vertical orientation of each assembly. This is achieved by plumb alignment of upper-plate and lower-plate holes that are closely bored to the size of the tubular nozzle at the lower end of the assembly.

Fig. 3 Typical LMFBR core-support concept.

The geometric array of assemblies (typically triangular) and their center-to-center spacing are also established by the holes in the upper and lower grid plates. Some clearance between neighboring assemblies is desirable to facilitate fuel handling that is performed, one assembly at a time, with an in-reactor machine. The handling machine raises, lowers, and carries the assembly by the handling head at its upper end. A nominal clearance of 0.050 in. between 5-in.-wide assemblies is considered an adequate provision for fuel-handling convenience. Since the handling heads normally are submerged under many feet of opaque sodium, the fuel-handling operation is done blindly, and the absolute location of a given handling head must be known with good accuracy.* Obviously this task becomes more difficult with structural material that is not dimensionally stable.

The total length of the reactor assemblies, from the bottom of their nozzles to the top of their handling heads, is about 14 ft. The assemblies are supported at more places than merely the upper and lower grid plates to avoid vibration and gross distortion from the temperature, temperature gradients, and radiation effects. Figure 3 shows a typical design in which a support plane is created at the upper end of the assemblies by spacer pads affixed to the wrapper tubes, and another plane of support is accomplished near the midlength, using spacer pads. Spacer pads at these intermittent elevations may be of the full-circumference type (shown in Fig. 2), or they may be installed only at corners or at mid-flats. With these two planes of tightness, the location of the individual assemblies is much more certain than would otherwise be the case.

Positive, reliable, and reproducible fixation of the fuel relative to the reactor's geometric center is highly important because of the neutronic sensitivity of fast reactors to dimensional changes. This sensitivity can be expressed in the following relations that are typical for fast reactors:

$$\frac{\Delta k}{k} \sim -0.5 \frac{\Delta r}{r} \quad (1)$$

and

$$\frac{\Delta k}{k} \sim -0.3 \frac{\Delta h}{h} \quad (2)$$

where $\Delta k/k$ is the departure from nuclear criticality (reactivity), r is the core radius, and h is the core height.

Interpreting Eqs. 1 and 2, a 0.7% change in core radius or a 1.2% change in core height gives $\Delta k/k$ a value of 0.0035.[†] In a plutonium-fueled fast reactor,

*In existing fast reactors, the allowable radial uncertainty in handling-head location is 0.25 to 0.5 in. Improved designs are being developed to increase the allowable uncertainty to 1 in. or more.

†Core contraction causes positive reactivity; core expansion causes negative reactivity.

this amount of reactivity is defined as "1 dollar," which is the reactivity equivalent of the delayed-neutron fraction. Since the delayed-neutron fraction represents the margin of safe control of the nuclear chain reaction, anomalous reactivity effects that are a small fraction of 1 dollar are closely watched during reactor operation and must be explained. Uncertainties of stainless-steel swelling confound the predictability of reactivity trends during the life of a core (~2 years) and hinder confident operation accordingly. Further information regarding fast reactor characteristics can be found in Ref. 1.

IMPACT OF SWELLING ON SELECTED CORE COMPONENTS

Although core-metal swelling is a problem that can affect the design strategy of the entire plant, it is convenient to examine separately the effects of swelling on (1) fuel elements, (2) fuel-element support, and (3) core structure. Items 1 and 2 represent components of the fuel assembly, which has a short service life compared with that of the plant (i.e., 2 years vs. 30 years). Since fuel assemblies are expendable and have no inherent design permanence, the plant owner can capitalize on scientific breakthroughs and evolutionary advances in materials science during the plant lifetime. Item 3, however, represents or implicates core hardware or design approaches that are not easily changed during the life of a particular plant. Therefore the approach to core support and restraint and the design strategy to accommodate core-metal swelling become permanent features of the plant and are among the most important design decisions.

Fuel Element

Stainless-steel swelling was first observed on fuel-element claddings in the United Kingdom fast reactor program.² That cladding involvement, plus the fact that the United States fast reactor program was committed to fuel-element development more than to any other single endeavor, made it inevitable that fuel-element lifetime be the first subject of concern with respect to implications of swelling. Specifically, the need to discount the successful irradiations of oxide fuel elements in the Dounreay Fast Reactor (DFR) and the Experimental Breeder Reactor II (EBR-II) was widely discussed, for example, as in the Edison Electric Institute's Fast Breeder Reactor Report.³

Illustrating this point, Fig. 4 shows the effect of stainless-steel swelling on typical mixed-oxide fuel elements in three fast reactors.* Identical fuel elements,

*In Fig. 4, and throughout this paper unless otherwise noted, the basis for swelling predictions is the August 1969 BNWL-WARD expression for cold-worked 316 stainless steel.⁴ This expression is given below in equation form and in Fig. 5 in graphical form:

$$\Delta V/V = 1.01 \times 10^{-3} \phi^{0.6} \times (\phi t)^{1.69} \{ [\exp(-7808/RT)] - [5480 \exp(-25300/RT)] \} \quad (3)$$

where $\Delta V/V$ = fractional volumetric change, ϕt = fluence (neutrons/cm²) of $E > 0.1$ MeV, T = temperature in °K, and $R = 1.987$.

in terms of size, composition, power rating, and burnup, experience vastly different amounts of cladding dilation from the metal-swelling source. The ratio of cladding dilation in EBR-II, the Fast Flux Test Facility (FFTF), and a commercial LMFBF power plant is about 1 : 5 : 7.

Fig. 4 Cladding dilation from radiation-induced swelling in three fast reactors.

It is not self-evident, however, that extra cladding dilation due to radiation-induced swelling increases the probability of cladding failure. Some investigators regard this phenomenon as a potential promoter of higher burnup.⁴⁻⁷ This is derived from the thesis that dilation of the inside diameter of the cladding makes it possible to accommodate more fuel expansion. If this thesis is correct, and there is some experimental evidence that it is,⁸ cladding dilation due to swelling would permit a higher smeared density of fuel (helpful

to breeding gain and Doppler effect) and would increase the intrinsic burnup capability of fuel elements to a limit not yet defined.*

The present view of fast reactor core designers seems to be that metal swelling should not be interpreted as a cladding problem or a fuel-element problem, as was first done. It is a safer speculation that core lifetime will be limited by something other than the intrinsic burnup capability of high-quality fuel elements. If this speculation proves correct, the emphasis in fuel-element development should gradually shift toward higher smeared density and the lowering of fabrication costs by eliminating requirements that purchase burnup capability beyond the usable range.

Fuel-Element Support

The helical-wire wrap, with advantages of low cost, moderate pressure drop, and good mixing potential, was the most popular fuel-element support system in fast reactors built or committed before the discovery of metal swelling. However, several of the AEC-sponsored 1000-MW(e) LMFBR design studies¹⁰⁻¹⁴ chose intermittent grids, partly to realize a small improvement in breeding gain from the lower mass of stainless steel. Since the discovery of metal swelling, core designers have debated whether grids are required (because of metal swelling) for early cores in near-term high-flux LMFBRs [FFTF and the 300- to 500-MW(e) demonstration plants], or whether their development can be deferred to an era when major fast reactor problems are under control and research and development emphasis can focus on modest economic gains.

The potential problems of the wire wrap are (1) it offers little compliancy to accommodate planar differential swelling between the fuel-element bundle and the wrapper tube, and (2) differential swelling between cladding and wire could produce either wire breakage or slackness. Even if all the metallurgical determinants of swelling are known and held constant, differential swelling between the fuel-element bundle and its wrapper tube and between the cladding and its helical wire is inevitable because of temperature differences (see Fig. 5). Figure 6 shows typical average axial-temperature profiles for cladding, helical wire, and wrapper tube. The wire temperature is less than that of the cladding by the amount of the film ΔT plus half the cladding ΔT . The wrapper tube is still cooler owing to the characteristic excess flow area at the bundle periphery. This excess area is normally less for a wrapped bundle than for a gridded bundle.

*The limit might be imposed by a void content at which thin-walled metal tubing is no longer an acceptable pressure-vessel material capable of surviving thermal shocks and other duty indigenous to fuel-element cladding. This limiting void content has not been established empirically except that it is evidently higher than the maximum thus far seen on unfailed fuel elements ($\sim 10\% \Delta V/V$). Reference 9 derives the estimated effect of swelling on tensile properties, using an analogy with powder-metallurgy technology that may be a useful first approximation until more data are reported.

Planar differential linear expansion between a wire-wrapped bundle and its wrapper tube, perhaps 1.5% in near-term LMFBRs,⁹ can be accommodated by providing initial clearances in the assembly. Similarly, differential elongation

Fig. 5 Swelling estimates of 316 stainless steel 20% cold worked—FFTF interim design basis (August 1969).

between the cladding and its wire wrap, about 0.18% in the near term,⁹ can be allowed for by providing initial slackness in the wire. (Wire-wrapped test elements, irradiated in EBR-II to >100,000 MWd/metric ton, have been

Fig. 6 Typical axial trace of average metal temperatures in an LMFBR fuel assembly.

deformed by tight wires into helixes 180° out of phase with the wires.⁸ Although undesirable and easily avoided, this condition has not been blamed for any failures in the U. S. fuel-development program.) However, deleterious thermal and vibration effects will probably impose an upper limit on these design tactics. The grid type of support appears potentially to be better able to cope with the two types of differential growth.

If the wrapper tube, cladding, and helical wraps should follow swelling laws that differ from one another in an adverse direction, owing to differences in composition or cold work, metal swelling could impose a burnup limit on the helical-wrap concept as low as 30,000 MWd/metric ton in a high-flux LMFBR.¹⁵ For this reason, LMFBR core designers are not unanimous in their opinions about fuel-element support, although most agree that fuel-element support is unlikely to emerge as the burnup-limiting component in near-term cores. Fortunately the choice is not an irrevocable 30-year decision, but one that can be reconsidered for follow-on cores when metal swelling and other pertinent behaviors are better characterized. On the basis of such reasoning, the FFTF Project has chosen the wire wrap for initial use, but the U. S. LMFBR Program is supporting a modest development of industrially favored grid designs.

Core Structure

In fast reactor cores of conventional design, metal swelling will cause the wrapper tubes of fuel and blanket assemblies and the guide tubes for control and safety assemblies to elongate and dilate (enlarge in cross section) during service. Also, when swelling of wrapper and guide tube material is not circumferentially uniform, bowing will occur, and other forms of distortion (e.g., twist) are possible. The supporting structure for the core and blanket assemblies (grid plates) and the structure over the assemblies (instrument or hold-down plate) are generally considered permanent installations. Both components are typically exposed to temperatures in the swelling regime ($700\text{--}1100^\circ\text{F}$) and must be examined for the possibility of excessive swelling during a 30 ± 10 -year lifetime.

The Atomics International (AI) 1000-MW(e) LMFBR plant design,¹⁶ with certain simplifications, was chosen as a basis for calculations of the impact of metal swelling on the core structure in commercial fast reactors. Details of the calculations are given in Ref. 9. The residence times were taken as 2 years for the core assemblies, 5 years for the radial blankets, and 30 years each for the radial-reflector assemblies, the grid plates, and the instrument plate.

Elongation

The end-of-life elongation of opposite walls of each assembly is shown in Fig. 7. The inside walls elongate more than the outside walls owing to temperature and flux gradients.* Average elongations of the core assemblies

*Axial and radial neutron-flux profiles, in a typical fast reactor, resemble chopped cosine curves with a maximum-to-minimum ratio of about 2 from core center to core edge.

Fig. 7 Elongation of wrapper-tube walls due to swelling (end of life).

range from 0.822 to 1.673 in. from their original lengths of 142 in. The large elongation in the first row of radial blanket assemblies is due to their extended residence time.

Elongation of assemblies, and differences in elongation, will somewhat complicate the design of the fuel-handling machine. More flexibility is required than when the elevation of the handling head is unchanging. Also, in some reactors a sweep arm or similar device ensures that assemblies are properly seated in the grid plate. A 1- to 2-in. change in assembly length will make such an operation more difficult, particularly in a core containing both old (long) and new (short) assemblies. On the whole, however, elongation appears to be the least serious manifestation of swelling of wrapper and guide tubes, although it is not trivial.

Dilation

The radial dilation of each row of assemblies (assuming no restraint) is shown in Fig. 8 at end of life. The total diametral dilation would be twice the amount shown. The maximum diametral growth of any assembly during its

Fig. 8 Dilation of wrapper tubes due to swelling (end of life).

expected lifetime is about 0.230 in. The plane of maximum dilation occurs about 7 in. above the core midplane, the location of the worst combination of flux and temperature in this design. Clearly the nominal 0.050-in. gap between assemblies is insufficient to accommodate swelling-induced dilation. The necessary gap is about 0.280 in., i.e., the maximum diametral growth of any assembly plus a fuel-handling allowance of 0.050 in.

Bowing

Differential swelling of opposite sides of the wrapper tube can be expected to produce an irreversible bowing of the assembly. The elongation of opposite walls of each assembly is shown in Fig. 7, from which it is evident that significant elongation differentials exist at the end of life and that these differentials are especially large near the core edge. Differential elongations shown in Fig. 7 correspond to free-bowed shapes (neglecting mechanical interferences with neighbors) shown in Fig. 9.

If the outward free bowing were suppressed by top-end restraint, the bowing profiles would appear as shown in Fig. 10. This figure shows an inward bow of the fueled length of about 0.46 in. in the outer core assembly and more in the inner blanket assembly (0.88 in.). This inward movement of fuel represents a mechanism for slow but substantial reactivity addition (see "Characteristics of

Fig. 9 Free (unrestrained) bowing of assemblies due to differential elongation (end of life).

Fig. 10 Bowing profiles of assemblies with top-end restraint (end of life).

Fast Reactors"). For such reasons (originally to preclude positive reactivity feedback from thermal bowing), spacer pads were located in the core zone. Figure 11 shows the effect of locating the spacer pad, as was done by AI, $10\frac{3}{4}$ in. above the core midplane. Although this is effective in counteracting positive reactivity effects, relatively high bending stresses are implied by the shapes indicated in Fig. 11, and spacer pads placed along the fueled length interfere with the accommodation of dilation.

Except for the influence of creep,* a fuel assembly removed from the restraining effect of its neighbors will tend to assume the free-bowed shape depicted in Fig. 9. This could create considerable difficulty if subsequent operations (i.e., intrasite transport, cleaning, decay storage, and shipping) are designed to accommodate only straight components as was the practice before metal swelling was discovered.

Fig. 11 Bowing profiles of assemblies with top-end restraint and in-core spacer pads (end of life).

*This includes not only thermally actuated creep but also the recently discovered property called radiation-induced creep which, at typical LMFBR core temperatures, may greatly exceed thermal creep.

Grid Plate and Instrument Plate

To define the swelling problem with respect to "permanent" components at the fuel-assembly extremities (grid plates and instrument plate), Duffy et al.^{1,7} performed a number of transport-theory calculations related to the AI 1000-MW(e) design. Axial-blanket lengths were varied from 10 to 20 in. to improve the general usefulness of the study. Figure 12 shows the high-energy neutron

Fig. 12 Percent $\phi_1/\phi_{1,max.}$ for grid plate and instrument plate vs. axial blanket thickness.

fluxes at the top and bottom of the upper grid plate and the instrument plate as a function of axial-blanket thickness, with these fluxes expressed as percentages of the high-energy flux at the core midplane.

Despite higher operating temperatures it appears that swelling of the instrument plate will be less than that of the upper grid plate, using the same lengths for upper and lower blankets and current swelling estimates. The long upper plenum in the AI design causes a 10-fold reduction in instrument-plate flux relative to the upper grid plate. Figure 13 gives swelling estimates of the

Fig. 13 Volumetric expansion of upper grid plate.

upper grid plate as functions of service lifetime and axial-blanket length. The BNWL-WARD 1969 swelling estimates for solution-treated 304 stainless steel* were the basis for these calculations.⁴ (Unlike smaller core components that can be fabricated in an annealed or cold-worked condition, the massive grid plate is conventionally specified to be annealed.) It appears from Fig. 13 that a 15-in. blanket offers adequate shielding for the upper grid plate, although this conclusion is sensitive to the questions of whether swelling depends on flux as well as fluence, and whether such dependence works to the advantage or the disadvantage of long-lived components. Differential swelling can be a serious problem in grid plates,[†] and the only protection is to keep the absolute swelling of the top surface very low. The grid-plate design concept that uses a high-flux-region insert (as in the Enrico Fermi reactor) has merit in view of the prevailing uncertainties concerning long-term, low-flux swelling effects. Not only is replacement facilitated by this design, but buckling due to radial swelling variations can be avoided.

IMPACT OF SWELLING ON SOME EXISTING REACTORS

Operational fast reactors, such as EBR-II and the Enrico Fermi Atomic Power Plant in the United States, were designed with no knowledge of, or deliberate provision for, stainless-steel swelling. Fast reactors now in the latter stages of construction, such as the Prototype Fast Reactor (United Kingdom) and the BN-350 (USSR), had little forewarning of the phenomenon during their design periods. Brief comments on the impact of swelling on these reactors are offered in the following paragraphs. A more extensive discussion is given in Ref. 9.

Experimental Breeder Reactor II

Although EBR-II was designed¹⁸ 10 years before stainless-steel swelling was recognized, swelling has caused no serious problem in 7 years of operation, and plant factor has increased steadily. Low flux and low burnup combine to limit the removal fluence of driver-fuel assemblies to a value at which swelling is negligible. The use of EBR-II to irradiate ceramic fuel elements to high burnup and structural materials to high fluences has occasionally resulted in swelling-provoked deformations that hinder removal of assemblies from the core and fuel elements from assemblies. Recently removed control and safety-rod guide tubes (thimbles) have survived the highest fluences to date—nearly as high as FFTF driver assemblies at goal burnup and ~60% of the lower end of the range of

$$*\Delta V/V = 4.32 \times 10^{-49} (\phi t)^{1.71} \exp\{[(3.567 \times 10^4)/T] - [(1.379 \times 10^7)/T^2]\} \quad (4)$$

†A 1% linear variation in volume growth between opposite faces of a grid plate that is 10 ft in diameter and 4 in. thick produces a free bow of 1.5 in.

interest for commercial reactors (Fig. 14). Guide-tube temperatures, however, cover only the lower half of the range of commercial interest. Data on swelling and mechanical properties from these thimbles were expected in the second half of 1971.

Fig. 14 Fast-neutron fluence and required test time vs. program objectives.

The EBR-II assemblies employ hexagonal wrapper tubes 2.290 in. across outside flats, with a nominal cold gap between assemblies of 0.030 in. One $\frac{3}{8}$ -in.-OD spacer pad (produced by indenting the inside surface of the wrapper tube) is provided in the center of each flat, at an elevation about 1 in. above the

core midplane. Nominal height of each spacer pad is 0.014 in.; therefore the nominal cold gap between pads is 0.002 in. Because no plane of support is provided at the top ends of the assemblies, they are free to splay outward (away from the core center line) from differential thermal expansion and differential swelling.

Except at the spacer pads, dilation of the wrapper tubes can occur freely until the 0.030-in. gap between assemblies is consumed. That amounts to about 1.3% $\Delta L/L$ or 3.9% $\Delta V/V$ swelling, consistent with the response of cold-worked cladding at 10% burnup of fully enriched mixed-oxide fuel elements under test in the EBR-II neutron flux. The mechanical loads on the spacer pads are not precisely known, but they have produced sufficient creep and/or swelling suppression so that the distance across pads remains relatively unchanged while normal dilation occurs just $\frac{1}{2}$ in. away. This behavior has kept the reactor from being seriously limited by the presence of in-core spacer pads.

Enrico Fermi Fast Breeder Reactor

The Enrico Fermi Atomic Power Plant was designed¹⁹ in the same era as EBR-II but has many distinguishing features, some of which may affect how the reactor responds to stainless-steel swelling.²⁰

The fuel elements and separate upper and lower axial-blanket elements are housed within a square wrapper tube 2.646 in. across outside flats. The wrapper tube is 347 cold-worked stainless steel, nominally 0.096 in. thick. Vertical orientation of reactor assemblies is provided conventionally by a double grid plate that receives the tubular nozzles in close-fitting holes. A plane of spacer pads exists 4.5 in. above the midplane of the 30.5-in.-long core. These pads, made of Colmonoy, are welded to the corners of the wrapper tubes and machined to close tolerances.

The handling head of each core and inner-radial-blanket assembly is captured by a stiff hold-down finger projecting downward from a horizontal hold-down plate. This finger prevents lifting from hydraulic forces and also precludes radial displacement of the assembly's upper end from differential thermal expansion or differential swelling. The center-to-center spacing of hold-down fingers is slightly less than the center-to-center spacing of grid-plate holes. Accordingly, when the hold-down plate is lowered (as it always is before reactor startup) and the handling heads are captured by their respective hold-down fingers, an inward gathering of assemblies occurs, and all clearance at the spacer-pad plane is eliminated. This design strategy is commonly called the "tight-core concept," and it produces very dependable reactivity effects.

The design, based entirely on thermal-effect considerations, must be analyzed for the effects of swelling. Because of low-burnup expectations and low temperatures of the metallic core A fuel, very little swelling will be experienced until the proposed UO_2 core is installed and operated well into its life expectancy. At a peak total flux of $\sim 6.5 \times 10^{15}$ neutrons/(cm²)(sec)

($\sim 70\% > 0.1$ MeV), the oxide core will have a burnup-to-fluence (swelling) ratio similar to that of future LMFBRs.

Elongation of the wrapper tube due to swelling can be accommodated by the feature originally provided to accommodate thermal expansion, i.e., the nozzle spring. Dilation accommodation, in this reactor with in-core spacer pads, would be problematical except for the encouraging performance of EBR-II. Assuming enough assistance from radiation-enhanced creep and/or retardation of swelling by compressive stress in the spacer-pad region so that the full 0.047-in. nominal gap between assemblies can be claimed as dilation provision, a peak $\Delta V/V$ of $\sim 5.3\%$ can be permitted. In the diagram of dilation accommodation (Fig. 15), note that the corner fuel element is intentionally omitted (in the oxide core design) since the fuel-element support grids are affixed to the wrapper tube by setscrews into corner pegs. The plane of the spacer pads does not coincide with a grid.

Fig. 15 Swelling accommodation in Fermi oxide core. BOL = beginning of life; EOL = end of life.

The effects of swelling-produced bowing (differential elongation) are shown qualitatively in Fig. 15. The S-shape thermal bow should gradually become more pronounced with swelling. This is because very little swelling will occur below the spacer-pad plane ($\sim 700^\circ\text{F}$). With a higher inlet temperature, the S-shape thermal bow could reverse. The limiting factor in the ability of the Fermi design to accommodate bowing is the necessity to mate the handling head with the hold-down finger when the hold-down plate is lowered prior to startup. The nominal allowable mismatch is $\frac{1}{4}$ in., although with adverse maximum tolerances

this is reduced to about $\frac{1}{16}$ in. It can be surmised that the feasibility of high-fluence operation will be greatly assisted by radiation-enhanced creep.

Prototype Fast Reactor

The British Prototype Fast Reactor (PFR)²¹⁻²³ was under construction when the phenomenon of stainless-steel swelling was first observed. At that point, obviously, options were limited for core redesign in response to this newly discovered property. In synthesizing the reference design, however, the engineers at Risley had made certain decisions that appear fortunate in terms of giving the core a capability to accommodate some metal swelling.

The distinguishing feature of the PFR core plan (Fig. 16) is the rosette pattern of fuel and nonfuel assemblies in the core. It is intended that each fuel assembly, in groups of six, lean on a central structural member externally similar to the fuel-assembly wrapper tube. In most cases the "leaning post" also serves as a safety-rod or control-rod guide tube. Contact between a fuel assembly and its assigned leaning post is brought about by an out-of-plumb alignment of the two nozzle support points. Contact is established at a spacer-pad plane well below the bottom of the 36-in.-long core. A bending bar concentrically located in the fuel-assembly nozzle deflects elastically under the force needed to insert

Fig. 16 Prototype Fast Reactor core plan.

the nozzle into its receiving socket,* producing a contact force at the spacer pads.

Because the below-core spacer pads are the only intentional region of contact between a fuel assembly and its leaning post, the full gap between adjacent wrapper tubes is available to accommodate dilation in the fueled length. This represents a potential for accommodating swelling of up to 8.7% $\Delta V/V$ (0.16-in. gap out of a 5.7-in. lattice spacing). Clearance between the upper and lower guide tubes is ample to accommodate elongation of the latter. No other problems from swelling-induced elongation are apparent.

Swelling-induced bowing in this unrestrained design is apt to produce greater problems than either dilation or elongation. Without restraining stresses, radiation-enhanced creep cannot play a role in maintaining wrapper-tube straightness. Excessive bowing from swelling differentials will presumably be prevented by rotation that serves to equalize swelling circumferentially.

BN-350 Reactor

Like the British PFR, the Russian prototype LMFBR, BN-350, was well under construction when metal swelling was discovered, reported, and confirmed in the Western World. It is believed that no last-minute alterations were made as a result of this discovery, so the core would be expected to have only limited capability to accommodate swelling.

The BN-350 core²⁴ is essentially a hybrid between EBR-II and Fermi. The fuel assemblies are hexagonal, free to bow at the top, and radially restrained only by the surrounding fence of radial blanket and reflector assemblies. Spacer pads are located in the fueled zone—at wrapper-tube corners.

The wrapper tube is 3.780 in. across outside flats with a nominal cold gap between assemblies of 0.079 in. (see Fig. 17). The spacer pad occupies only 0.059 in. of the gap between assemblies, leaving a cold clearance in the spacer-pad plane of 0.020 in. (compared with 0.002 in. in EBR-II). Thermal expansion to operating temperatures would still leave a gap of at least 0.016 in., although this would disappear with metal swelling after a peak burnup of about 30,000 MWd/metric ton based on Fig. 5. Further burnup requires that the wrapper tube distort around the spacer pads, assisted by radiation-enhanced creep. As an upper limit, assuming the 0.079 in. gap is fully effective in accommodating dilation, the core could survive metal swelling of $\sim 6\% \Delta V/V$, equivalent to a peak burnup of about 70,000 MWd/metric ton based on the swelling relation plotted in Fig. 5.

As is evident in Fig. 17, wrapper-tube dilation will produce pad-on-wrapper contact instead of the conventional pad-on-pad contact. In addition to possibilities of damage to the stainless-steel wrapper tube, removal of a swollen assembly is made more difficult by this design approach. If, for example, a

*It is intended that this force be no more than the assembly's deadweight.

Fig. 17 The BN-350 core-assembly pattern.

wrapper tube has dilated more than 0.020 in. in any plane below the spacer pads, it becomes trapped by its six neighbors and must be forcefully extruded through the constriction formed by the adjacent assembly's spacer pads. Full core refueling, removing assemblies starting from the outside, appears to be the only way to utilize the full 0.079-in. gap and thereby to achieve a respectable burnup in this design.

STRATEGIES OF SWELLING ACCOMMODATION

Since the first reported indication of the stainless-steel swelling problem² in late 1967, fast reactor core designers have examined numerous design solutions in varying levels of details. This section reviews the progress in this area of activity.

FFTF Approach

On the FFTF Project, considerable effort was devoted to interpreting the design implications of swelling, evaluating engineering solutions to the problem, and developing specialized analytical tools for predicting the response of the core to metal swelling. Most of the early contributions to the design literature²⁵⁻²⁹ resulted from the special timeliness of this project. It is to be expected, therefore, that a current favorite among design strategies for accommodating metal swelling would be the FFTF approach, including its close variations.

The design strategy for accommodating metal swelling in the FFTF can be summarized as follows:

1. The fuel elements (217 per assembly) are housed within conventional rigid wrapper tubes. Flexible or articulated wrapper tubes were considered but were not chosen because extensive development was deemed necessary.

2. Wrapper-tube dilation is accommodated by large interassembly gaps.

3. Spacer pads are located above the core, and the interassembly gap is unobstructed over the high-fluence region of the wrapper tube.

4. Fuel-bundle swelling is accommodated by wrapper-tube dilation plus porosity within the as-fabricated fuel assembly.

5. A peripheral core clamp suppresses bowing due to differential elongation and maintains tightness at the above-core spacer-pad planes.

6. Radiation-enhanced creep is depended upon to promote reasonable assembly straightness for refueling and to relax high bending stresses effected by the core clamp.

The mechanical design of the core clamp has not been disclosed in detail. Its function is to maintain tightness at the spacer-pad planes when engaged and to provide clearances for fuel handling when disengaged.

In the FFTF or clamped-core approach, differential thermal elongation, differential swelling elongation, and radiation-enhanced creep interact in a highly complex manner as shown in Fig. 18 (taken from Ref. 29). When only thermal strains are considered, the bowing profile of all assemblies except the one at core center line is qualitatively represented by Fig. 18(a). Differential swelling alone would produce shapes such as the one in Fig. 18(b), and the additive effect of

Fig. 18 Assembly deflection patterns in the clamped-core approach.

thermal and swelling strains is shown in Fig. 18(c). In suppressing free bowing in the direction that would be produced by differential thermal elongation and differential swelling elongation, the core clamp imposes high bending stresses. The relaxation of these stresses, by radiation-enhanced creep, alters the bowing profile markedly [Fig. 18(d)]. Note that the shapes qualitatively depicted in Fig. 18 are a function of time, location in the reactor, and the design expressions used to describe swelling and creep.

When the core is unclamped for fuel handling and the above-core restraints (see Fig. 3) are removed, the assemblies assume shapes of a basically different character, as shown in Fig. 19, which is also taken from Ref. 29. Again, it is

Fig. 19 Assembly deflection following removal of restraint.

convenient to analyze separately the three factors responsible for distortion. With the reactor at zero power, the thermal strains are removed; then the assemblies would be straight [Fig. 19(a)] if no other distortion mechanisms were operative. Differential swelling is not reversible, however, and therefore the upper ends would tend to splay outward [Fig. 19(b) and (c) and also Fig. 9] when freed of restraint. But with sufficient stress relaxation at power, the profile at zero power can actually be reversed [Fig. 19(d)]. Note that the radial position of the top end, which must be known with fair precision for blind fuel handling, is a strong function of swelling and radiation-enhanced creep.

Other Approaches

Other design strategies to accommodate stainless-steel swelling or to mitigate otherwise the principal problems of swelling have been examined, although generally not in the detail of the FFTF approach. Some of these alternate methods have been documented in open literature.³⁰⁻³⁵ Reference 9 describes many alternatives and analyzes their relative effectiveness, economic penalties, and developmental requirements. This section is a compendium of the open literature in this area.

Extrapolated EBR-II

In this approach³⁰ the basic simplicity of the EBR-II design is retained to the maximum possible extent. A thick spacer pad is added at the top end of the assembly to limit free-end deflection, but no peripheral core clamp is used. Spacer buttons on the wrapper-tube flats are retained in the high-fluence region, although some design modification is suggested to facilitate their collapse under the simultaneous effects of swelling and creep. In another modified EBR-II approach, the spacer buttons are moved to the lower-axial-blanket region.⁹

Cold Wrapper Tube

This design³¹ evolves from the observations that (1) most of the problems caused by metal swelling are associated with dimensional instability of the wrapper tubes (see "Impact of Swelling on Selected Core Components"), and (2) metal below a certain threshold temperature is dimensionally stable. The swelling threshold³⁶ appears to be $\sim 660^{\circ}\text{F}$, a temperature not appreciably below typical LMFBR sodium-inlet conditions. Therefore a dimensionally stable wrapper tube is preserved by channeling reactor-inlet sodium past the inside surface of the wrapper tube. This cold bypass stream mixes with the hot main stream above the high-fluence region of the wrapper tube, and reactor outlet temperature is not degraded significantly.

Articulated Assembly

Articulating* the assembly has the desirable effect of reducing deformation and straining forces compared with rigid members that have equivalent amounts of differential swelling. Designs employing one, two, or three joints have been assessed.⁹

Circular Wrapper Tube

Since wrapper tubes will be dimensionally unstable under the influences of swelling and creep, one should consider making them in the most easily

*That is, providing joints or localized areas of increased or complete flexibility.

fabricated and structurally optimum shape, i.e., a circular tube. These tubes, oriented by a grid plate into the usual triangular array, could be held in line contact with their six neighbors by means of a simple peripheral clamp, as in SEFOR.³⁷ Space for dilation accommodation is conveniently afforded by the cuspidated areas between three tubes, provided that radiation-enhanced creep is a large and dependable effect at high fluences.

Bowing-Minimization Features

Inasmuch as most of the free radial displacement of core-assembly upper ends is caused by the portion of wrapper tube above the core region (see Fig. 9), the problems associated with suppressing bowing are decreased if this length can be reduced. Placing the fission-gas storage plenum beneath the fuel and housing the upper axial blanket in a separate assembly have been proposed as a means of accomplishing this goal.³²

The ^{233}U -Th Cycle

Among the five or six neutronic methods* that have been proposed to combat the metal-swelling problem,⁹ the use of the ^{233}U -Th cycle is the least obvious but the most interesting. Substituting ^{233}U for ^{239}Pu as the principal fissile isotope has two effects that are beneficial in terms of reducing the swelling-to-burnup ratio. First, ^{233}U has a higher fission cross section and can therefore produce the same fission rate with a lower neutron flux. Second, the ^{233}U -Th fuel system has greater spectral flexibility, i.e., swelling could be reduced by lowering the average neutron energy without a serious diminution of the breeding ratio.

Refractory Metals

In principle, the metal-swelling problem can be solved by replacing stainless steel, entirely or strategically, with material that does not swell at fast reactor conditions. Complete substitution and various schemes of partial substitution have been evaluated,³³ using molybdenum as the replacement material. Apparently molybdenum swells only at temperatures above the range of design interest.³⁸ This desirable property, along with its high-temperature strength, must be balanced against penalties in neutronic performance^{39,40} and increased fabrication costs⁴¹ inherent in most refractory-metal candidates.

Periodic Rotation of Assemblies

Rotating assemblies 180° periodically during their in-reactor residence reduces elastic bending deflection (bowing) by averaging the fluence and swelling

*Methods of decreasing high-energy neutron fluence on core and core-proximity hardware.

on the wrapper-tube circumference. This is the reference strategy in the gas-cooled fast reactor³⁴ and is compatible with a number of other partial solutions³² in evolving a composite strategy for coping with metal swelling.

Periodic Annealing

In the Calder Hall class of British gas-cooled reactors, the problem of radiation-induced swelling of graphite is solved by periodic in situ annealing. A brief high-temperature ($\geq 1400^\circ\text{F}$) annealing of irradiated 304 stainless steel has been found to sharply reduce the void content.⁴² It has been proposed,³⁵ therefore, that periodic in situ annealing be considered for future reactors as a method of coping with swelling. Obviously, considerable design and materials work would be needed to demonstrate feasibility. If the design problems associated with in situ annealing prove too formidable, periodic out-of-reactor annealing (which requires more fuel handling and a larger on-site fuel inventory) could be considered.

EMPIRICAL ASSESSMENT OF SWELLING AND RADIATION-ENHANCED CREEP FROM EBR-II CORE COMPONENTS

Contemporary LMFBR core design requires reliable expressions for swelling and creep as well as an understanding of integral swelling-creep effects. Core components removed from EBR-II, at fluences approaching near-term targets (see Fig. 14), exhibit deformations that are attributable to these irradiation effects. In many ways these components offer the best current opportunity (1) to assess the reliability of contemporary swelling and creep estimates at high fluences and (2) to gain insight into the response of stainless-steel components to the fast reactor environment.

Argonne National Laboratory (ANL) is coordinating the effort to derive maximum engineering value from the EBR-II core-component measurements. The EBR-II project provides the neutron fluxes,⁴³ temperatures,⁴⁴ and nondestructive measurements employed in the analyses. Destructive measurements are obtained from EBR-II and other projects within ANL and from other participating U. S. laboratories.

Analytical efforts to date have been directed toward understanding (1) wrapper-tube bow, (2) moat formation near wrapper-tube spacer pads, and (3) fuel-element-cladding bow. With regard to wrapper-tube bow, a number of discharged tubes have permanent convex curvature (with respect to the core vertical center line), presumably due to transverse differential swelling. Figure 20 compares measured permanent transverse displacements of the experimental assembly XA08 wrapper tube with displacements calculated by several different procedures. The XA08 assembly held a number of mixed-carbide fuel elements that achieved about 10% burnup of heavy atoms, and the wrapper tube had an exposure of about 8×10^{22} neutrons/cm² maximum total fluence.

Measured displacements (shaded area in Fig. 20) were obtained by an appraisal of positive transparencies of two photographs⁴⁵ of opposite sides of the assembly.⁹ Use of this relatively crude procedure was responsible for the wide scatter band of the measured displacements. Currently, deformations of

Fig. 20 Relative transverse displacement vs. axial distance from top of wrapper tube for EBR-II assembly XA08.

EBR-II components are being measured directly and more accurately (see below).

The other curves in Fig. 20 were calculated with various modifications of the GROW code,³² which essentially integrates the equation

$$\frac{d^2 x}{dz^2} = \frac{1}{R} = \frac{\Delta(\Delta L/L)}{D} \quad (5)$$

where x = transverse displacement

z = axial position

R = radius of curvature

$\Delta(\Delta L/L)$ = difference in "strain" from one side of wrapper to the other (a linear transverse strain distribution is assumed)

D = distance across the wrapper tube

The curve labeled Harkness-Li is based on $\Delta L/L$ values due to steel swelling alone, as found from the following empirical fit of results from the SCIM code:^{4,6}

$$\% \Delta V/V = 2.054 (10)^{-20} (\phi\tau)^{0.955} \times [-1 + 6 (10)^{-3} \tau - 1.15 (10)^{-5} \tau^2 + 7.16 (10)^{-9} \tau^3] \quad (6)$$

where $\phi\tau$ is the total EBR-II fluence and τ is the temperature in $^{\circ}\text{C}$. The curve labeled WADCO is based on a swelling correlation in Ref. 47. Data from both sources are intended to apply to solution-treated 304 stainless steel. The XA08 wrapper tube was predominantly of that material, although the corners had about 10% cold work.

The curve labeled "density data" is based on the density measurements from four sources.^{4,8-51} The data appear to be mutually consistent and indicate that the density varies about linearly from one side of the wrapper tube to the other. The maximum $\% \Delta V/V$ on the side of the wrapper tube nearest the core vertical center line was 3.65% and on the side farthest from the center line, 2.55%. The axial position of these maximum values was about 1.5 in. above the core midplane.

Tentative conclusions can be drawn from Fig. 20: First, the WADCO swelling correlation appears to give better differential swelling predictions than the SCIM-code fit, for the conditions under which the XA08 assembly was irradiated. Second, creep must have taken place to keep the wrapper tube straighter than the density data would indicate. This occurrence of creep is not surprising, for the calculated displacements of Fig. 20 produce unrestrained assembly upper-end deflections in the range of 0.3 to 0.6 in., and the initial upper-end clearance between the XA08 assembly and the relevant adjacent (never swollen) assembly was only about 0.02 in., according to calculations that considered thermal deflections and elastic interactions of the assemblies.^{5,2} Because no open-literature code exists that accounts for both creep and interactions of assemblies, the BOW-V^{5,3} and CRASIB^{5,4,5,5} codes are being combined.

Directly measured permanent displacements of safety- and control-rod thimbles 3A1, 5A3, and 5D1 were no larger than the XA08 wrapper-tube displacements,* even though the thimbles had peak fluences 1.7 to 2.1 times greater.^{5,6} Calculated maximum displacements, using the WADCO correlation, are as large as 0.8 in. This must mean that either (1) swelling saturates, or (2) even the relatively loose EBR-II core provides enough restraint, and thereby enough creep occurs, to keep the thimbles quite straight. In view of the large amounts of creep described elsewhere in this section, the latter alternative currently seems more likely. Density measurements yet to be made on the thimbles should resolve this uncertainty.

*The transverse thimble-tube dimensions are identical to those of the wrapper tubes.

With regard to moat formation near wrapper-tube spacer pads, the distances across the stamped spacer pads of the XA08 assembly wrapper tube remained essentially unchanged because of pad loads, even though nearby the tube was swelling about 20 mils across flats.^{30,45,49} In Fig. 21 the measured permanent displacements near a pad are compared with displacements calculated by the AXICRP code⁵⁷ using a centrally loaded, circular, flat-plate (disk) representation and a WADCO creep correlation for solution-treated stainless steel.⁵⁸ In the

Fig. 21 Permanent displacement vs. radial distance from spacer-pad center for EBR-II assembly XA08 wrapper tube.

calculations the disk edge was prevented from rotating by application of a suitable pressure distribution but was allowed to move radially. Other calculation conditions are given in Table 1. The added edge pressures were intended to simulate compressive stresses produced by swelling.

None of the calculated curves reproduce the localized moat formation that occurred. The 50- and 60-lb-pad-load curves do show total displacements as large as measured, but according to recent BOW-V calculations the pad loads should be less than 25 lb, rather than more.⁵³ No additional calculations of this type

TABLE 1
FIGURE 21 CALCULATION CONDITIONS

Curve letter	Pad load, lb	Added edge pressures, psi	Elapsed time, hr*
A	25†	4,600	9,580
B	50	4,200	8,460
C	50	9,000	8,480
D	50	4,200	10,700
E	60	9,000	10,600

*Effective full-load exposure time of the pads was about 10,300 hr.

†Suggested by BOW-II calculations.

are planned until either (1) AXICRP has been modified to account for local swelling effects that have been observed⁴⁹ (and that might influence moat formation), or (2) additional evidence accumulates that indicates the creep correlation employed generates low values.

With regard to fuel-element-cladding bow, almost all fuel elements discharged from experimental assembly X040A had permanent concave curvature (with respect to the assembly axial center line).⁵¹ The elements had reached about 5.8% maximum burnup of heavy atoms and 4.3×10^{22} neutrons/cm² maximum total fluence. Their curvature was probably due to creep resulting from transverse differential thermal stresses.* The explanation for these thermal stresses is as follows: Between the peripheral elements and the wrapper tube, the coolant subchannels have larger equivalent diameters and flow areas than the subchannels inside the element bundle. Therefore the exterior sides of the peripheral elements are exposed to higher unit coolant flow rates than other element sides in the bundle. Consequently the coolant temperatures in the peripheral subchannels are lower than in interior subchannels, and temperature gradients across the elements result that are believed to increase as the periphery of the bundle is approached. Restraint of the elements by the wrapper tube and element spacer wires produces axial thermal-bending stresses in the element claddings.

Figure 22 compares measured permanent transverse displacements, for several of the X040A elements, with displacements calculated by using the CRASIB code⁵⁴ in conjunction with the WADCO swelling correlation for solution-treated austenitic stainless steel⁴⁷ and the LIFE-I (NØH = 0 option) creep correlation.⁵⁹ [The element claddings are 0.290-in. outside diameter x 0.020-in.-thick wall, annealed (Rockwell B 85), 304L stainless steel.] The elements were assumed to be restrained transversely at 29 different axial

*At press time, differential swelling seems to account for much of the curvature.

Fig. 22 Permanent transverse displacement vs. distance from upstream end of element for fuel elements from EBR-II assembly X040A.

positions; i.e., an exaggerated amount of transverse restraint was imposed. One check calculation was made in which the element was restrained at only 11 axial positions. This reduced restraint, which is probably less than that actually imposed by the 6-in.-pitch helical spacer wires on the fuel elements, decreased calculated permanent displacements by only 0.1%.

The reference temperatures for the X040A assembly indicate that the gradients across the peripheral elements are substantially greater than for the elements of the second row in from the periphery (450°F/in. vs. 50°F/in. at core outlet). As a result the calculated displacements based on the reference temperatures are substantially greater for the peripheral elements than for the second-row-in elements (Fig. 22). However, the measured displacements for the peripheral elements are only modestly greater than for the second-row-in elements. Accordingly it was adjudged that the coolant mixing coefficient used to calculate the reference temperatures might have been too small. In a demonstration of this possibility, the reference temperatures were modified rather arbitrarily so that the gradients across the peripheral elements were closer to those across the second-row-in elements (135°F/in. vs. 70°F/in. at core outlet). Calculated displacements based on the modified temperatures are in reasonable agreement with the measured displacements, although interesting discrepancies still remain.

Similar calculations were also performed using the WADCO creep correlation.^{5,8} This correlation, which includes irradiation-induced creep only, gave maximum displacements of 7 to 13% less (and 0 to 5 in. farther downstream) than the LIFE-I correlation, which includes both thermal- and irradiation-induced creep.

Fuel elements^{5,6} discharged from a number of other experimental assemblies have been found to be deformed in the same manner as those from assembly X040A.

EFFECT ON FAST REACTOR ECONOMICS

The impact of metal swelling on energy costs is difficult to assess at this time, but it is reasonably clear that the phenomenon will tend to raise those costs somewhat. The design strategies described earlier (see the section entitled "Strategies of Swelling Accommodation") all contain the potential for increases in capital cost, fuel-cycle cost, or both, although not by so much as to undermine the role of the fast breeder reactor as a major future energy source for the world.

Potential design solutions have been evaluated more in terms of fuel-cycle costs than capital costs.⁹ In most solutions, including the clamped-core concept, decreases in breeding gain and specific power are virtually inevitable relative to preswelling estimates. These decreases follow directly from the decrease in fuel-volume fraction caused when core space must be assigned to accommodate metal swelling. The sensitivity of fuel-cycle costs to breeding ratio and specific power is shown in Fig. 23. Included is a thumb-shaped zone that covers the designs for large oxide cores that have been proposed in the past 8 years. The 1000-MW(e) follow-on designs are plotted specifically. None of these studies allowed for metal swelling. The leading portion of this thumb, i.e., high specific power and high breeding ratio, is achieved through sophisticated design features

such as thin nonfreestanding wrapper tubes, negligible gap between assemblies, and other promoters of high fuel fraction. It now appears that this region is tenuous because of the imperatives of accommodating metal swelling. Pending further development work, the shaded zone of the thumb must be viewed as

Fig. 23 Effects of specific power and breeding ratio on fuel-cycle costs, and potential impact of swelling.

representing combinations of breeding gain and specific power possibly unattainable in a design that allows for the amount of swelling now being projected (Fig. 5). Part of this loss is recoverable through an increase in fuel smeared density, the feasibility of which ironically capitalizes on cladding swelling to afford more space for fuel swelling (see the subsection "Fuel Element," page 89).

A cost-benefit analysis⁹ for development of new low-swelling alloys indicated that having to accommodate only 5% swelling in breeder reactors over the period 1970 to 2020 has a 1970 present worth of from \$864,000,000 to \$5,600,000,000 relative to the case of 15% swelling.

RECOMMENDATIONS FOR MATERIALS RESEARCH AND DEVELOPMENT

Confident mechanical design of the 1000-MW(e) LMFBR core, particularly when using the FFTF (clamped core) approach, requires, within the context of this conference, reliable expressions for swelling and radiation-enhanced creep over the ranges 700 to 1150°F, 10^{14} to 10^{16} neutrons/(cm²)(sec), and 0 to 4×10^{23} neutrons/cm² ($E > 0.1$ MeV). Near-term reactors (FFTF and the demonstration plants) demand such data only to one-half this fluence but over the same temperature and flux range. Behaviorisms of particular interest include: (1) saturation of either swelling or creep; (2) effects of stress on swelling; (3) effects of large (deliberate) or small (unintentional) variations in composition, temper, microstructure, etc., on swelling and creep; (4) synergistic effects of swelling and creep; and (5) effect of voids on ductility.

The highest priority activity among short-range research in this area should be to resolve whether or not saturation of swelling and radiation-induced creep occurs at high fluences. Development of a low- or no-swelling variety of stainless steel should be regarded as having the highest priority among long-range core-related research and development projects, with perhaps one-tenth as much effort devoted to an economically viable backup structural material (e.g., molybdenum).

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DISCUSSION BY ATTENDEES

Kulcinski: What do you see as the major advantages or disadvantages in using refractory metals in future LMFBRs?

Huebottter: Our calculations show that economics are a standoff between nonswelling molybdenum and swelling stainless steel, if we take account of the higher strength of the former. Dimensionally stable material, especially in the wrapper tubes, would take much of the guesswork out of the core-design business, and this would probably reflect in greater reactor reliability. We would prefer, however, to find a metallurgical solution to the steel swelling problem within the iron-chrome-nickel family of alloys because the neutronic properties are better for fast reactor application.

Che-Yu Li: If the stainless-steel swelling problem can be solved, will the swelling of the fuel still cause significant problems?

Huebottter: Fuel swelling would eventually limit core life if nothing else did first. Before stainless-steel swelling was discovered, it appeared that core life would be limited by an excessive rate of fuel-element failures caused by inexorable fuel swelling against cladding with very low ductility. We would gladly return to that situation because steel swelling threatens to reduce core lifetime as well as produce design problems.

Burchill: Although much attention has been given to reducing the exponent of the fluence dependence of swelling, little attention seems to have been given to the design implications of the temperature at which peak swelling occurs. Most fast breeder reactor designs have a core-midplane temperature of 500 to 525°C. If the swelling temperature dependence peaks at about this temperature or lower, the differential swelling across the fuel-assembly duct (which causes bowing) caused by the flux gradient will be opposed above core midplane by the swelling dependence on the temperature gradient. If, however, the swelling temperature dependence peaks at about the core outlet temperature, the differential swelling is enhanced by both the flux and temperature radial gradients at all axial locations. For example, solution-treated 316 stainless steel

with a peak swelling at about 500°C would cause less core distortion than cold-worked 316 stainless steel with a peak swelling at about 600°C if the fluence dependencies were the same.

Huebotter: I have not evaluated this specific case, but intuitively I argue with the comment.

Wechsler: Would the speaker please comment on possible consequences of swelling with regard to changes in available coolant-channel area?

Huebotter: Since the wrapper tube is expected to swell nearly as much as the fuel-element bundle, coolant area per pin is expected to change very little. Even without wrapper-tube swelling, the spacing between elements is maintained at a minimum value by the helical spacer wire. Long before any significant coolant starvation has occurred, another phenomenon imposes a limit on fuel-assembly lifetime. Namely, the wrapper tube would be overstressed by an inexorably expanding fuel-element bundle.

Zwilsky: How sensitive are the neutronic parameters to opening up of the core to accommodate swelling? For instance, what would a 5 or 10% opening of cooling channels do to power density and breeding ratio?

Huebotter: As a result of the lower fuel fraction in the core, both breeding ratio and average specific power will decrease. I would guess that the loss of breeding ratio will be about 0.05 and the loss of specific power (increase in fissile inventory) will be about 5 to 10%. These numbers are from memory, though, and I would urge you to consult USAEC Report ANL-7786 in which such calculations are given.

VOID FORMATION IN CLADDING AND STRUCTURAL MATERIALS IRRADIATED IN DFR

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ABSTRACT

Immersion density measurements and transmission-electron-microscopy studies have been carried out on specimens of four stainless steels (AISI M316 and M316L, FV548, and EN58B) and of a nickel-based precipitation-hardening alloy (Nimonic PE16) irradiated in the Dounreay Fast Reactor to fluences up to 8.5×10^{22} neutrons/cm² in the temperature range 300 to 700°C. Void formation has been shown to be very sensitive to small differences in composition and preirradiation condition. Volume changes for a given material, condition, and irradiation temperature can be adequately represented by a linear function of fluence following a threshold exposure during which essentially no swelling of technological significance occurs. Each material studied shows a characteristic temperature dependence of swelling.

Prolific void formation in neutron-irradiated materials is a comparatively recent observation, first reported by C. Cawthorne and E. J. Fulton¹ at a Harwell symposium in 1966 and publicized more widely in an article in *Nature*² in 1967. Because of its influence on the dimensional and mechanical stability of cladding and structural components of fast reactor systems, however, the phenomenon has since tended to overshadow the better known effects of exposure to fast-neutron fluxes. Previously recognized problems associated with irradiation in a fast-neutron environment, such as low-temperature hardening, high-temperature embrittlement, and the acceleration of diffusion-controlled processes, although far from completely understood, have tended to give rise to less concern as more experimental evidence has accumulated. Now, although these phenomena may necessitate the imposition of precautionary restraints on reactor component design and operation, they seem to present no insurmountable obstacles to the development of the fast reactor system. The consequences of void formation, however, being as yet uncertain, seem potentially more

formidable and are apt to dominate present-day assessments of fuel-pin and structural-material behavior in fast reactor service.

In investigating the incidence of voidage in potential cladding and structural materials, British workers, like their opposite numbers in the United States, have benefited from the availability of indigenous fast reactor irradiation facilities over a long period. British high-fluence high-temperature data have mainly been derived from examination of samples of the cladding of experimental fuel pins irradiated in the Dounreay Fast Breeder Reactor (DFR) to fluences approaching 9×10^{22} neutrons/cm² in the temperature range 230 to 700°C, although, as will be seen later, samples irradiated at temperatures less than about 350°C are rarely examined for void incidence. This work has been principally concentrated on austenitic stainless steels in the AISI 316 range with a modified nickel-concentration range, hence our designation M316. This steel has approximately 17% chromium, 13½% nickel, and 2% molybdenum, and casts with two levels of carbon, M316 with 0.05% carbon and M316L with 0.02% carbon, have been used in the irradiation program at the Dounreay Experimental Reactor Establishment (DERE). The M316L material for the work described here was drawn from two separate casts differing significantly in nitrogen, boron, and phosphorus levels, emphasizing that the principal difference between this and the M316 material lies in the carbon content. We have also examined a nickel-based precipitation-hardening alloy, Nimonic PE16, and a niobium-stabilized 17% Cr–12% Ni–1½% Mo steel, FV548. Some samples of the 18/8 titanium-stabilized steel, EN58B, widely used in the DFR for in-pile facility components, have also been examined. Two initial material conditions—solution treated (and aged where precipitation occurs) and 15 or 20% cold worked—have been introduced as fabrication variables.

The work to be described is mainly derived from examination of material taken from fuel-pin cladding, and this material is to be notionally regarded as having been irradiated while stressed to an indeterminate level. At Dounreay, about 800 pins have now been irradiated, and it should be noted that the results presented here are from only about 20 of these pins. The pins selected were not necessarily typical of the whole population, criteria such as diametral-change indications of higher-than-average swelling having in some cases influenced the choice.

Further details of this work will be found in two recent papers^{3,4} by members of the group working at Dounreay.

EXPERIMENTAL METHODS

Two experimental techniques, density measurement and transmission electron microscopy, are used in our investigations.

Our interest is mainly in density changes of technological significance, and a change of 0.1% has been arbitrarily selected as a limit of discrimination. It

should be noted that it is our general practice to express data in terms of the percentage ratio of the density change to the final density, so that the resulting figure is numerically identical to the voidage-induced volume change.

Sections of fuel pin about 0.5 cm long are cut, the fuel is removed, and the cladding is decontaminated. An electron-microscopy specimen is taken by spark machining or mechanical punching, and the remainder is electropolished as a density sample. Immersion density measurements are made using distilled water.

The electron-microscopy disks are thinned by grinding and jet electropolishing using an electrolyte of 15% perchloric acid in butylcellusolve. The majority of the specimens discussed here have been examined on a 100-keV Siemens Elmiskop I microscope, but the 1000-keV AEI EM8 instrument at Harwell has been used in cases where the presence of very large voids has necessitated the examination of too great a foil thickness for effective penetration by the 100-keV electron beam.

Void diameters are measured directly from the electron micrographs, and void concentrations are then estimated from immersion density measurements and void diameters, assuming the voids to be spherical for the purpose of deriving void volumes. In a few cases, void concentrations have been estimated via foil-thickness measurements from stereo pairs; values so obtained generally lie within $\pm 20\%$ of those derived from the more accurate density method, and this, we think, represents the uncertainty limit in estimates of swelling, $\Delta V/V$, from electron micrographs.

VOLUME CHANGES

Normalization of Data

The DFR core geometry results in each pin experiencing a temperature profile rising from about 230°C to, in a typical case, 650°C along its length, whereas the flux profile has a peak at the core (and hence the fuel-pin) center line. Thus there is a need for a method of normalization to permit comparisons of different pins. We have found that, in any temperature range, the relation between swelling and fluence (or displacement dose—the number of times each atom is displaced during the irradiation period) can adequately be represented by assuming that a threshold, below which essentially no volume change is observed, is followed by swelling at a linear rate with increasing dose. It is suggested that the dose required before the commencement of the linear regime is associated with the establishment of a dislocation structure conducive to efficient separation of interstitials and vacancies and not with the nucleation of the voids, since electron microscopy reveals voids at subthreshold doses. There is insufficient evidence as yet to indicate whether the threshold level is a function of temperature or if, at a given temperature, it varies from material to material or is dependent on material condition. For the purposes of this analysis, a threshold of six displacements per atom, corresponding to a total fast fluence of

about 1.2×10^{22} neutrons/cm², has been chosen. The displacement doses have been derived by a modified Kinchin and Pease model.^{5,6} The pins discussed did not all have the same displacement dose, so that the derived swelling rates imply varying amounts of extrapolation, and quantitative reliance on the rates given is not recommended. The qualitative conclusions reached regarding relative swelling rates are, however, insensitive to the actual threshold value used (within a factor of about 2), and some general implications concerning the factors influencing the development of voidage in different materials can be drawn.

Fig. 1 Derived swelling rates for samples of solution-treated and cold-worked M316 and M316L fuel-pin cladding. A threshold of 6 displacements per atom has been assumed.

Volume Changes in M316 and M316L Steels

Measured volume changes have been compared by determining values of the swelling rate, and results for M316 and M316L cladding from 12 pins are shown in Fig. 1. The most obvious difference between the various groups of profiles lies in the higher swelling rates of solution-treated samples as compared

with similar samples of cold-worked material. There are, however, also significant differences in the shapes of the profiles; those for M316 cladding peak at a little over 600°C and those of M316L cladding peak at about 500°C. The ascription of the different temperature dependencies of the two versions of this steel to compositional differences is suggested, first, by the factor of 2.5 in the respective carbon levels, and, second, by the similar forms of the cold-worked and solution-treated profiles for each material. This indicates that, apart from influencing the magnitude of the volume changes, variation in the amount of cold working is of secondary importance in determining the shape of the profile. There is, however, a strong implication from these results that reduction of the carbon level in austenitic steels might be an important factor in reducing susceptibility to void formation.

Fig. 2 Derived swelling rates for samples of solution-treated and aged and cold-worked FV548 and of solution-treated and aged Nimonic PE16 fuel-pin cladding. A threshold of 6 displacements per atom has been assumed.

Volume Changes in FV548, Nimonic PE16, and EN58B

A similar analysis has been made of volume-change data from samples taken from pins clad in FV548 and Nimonic PE16 (Fig. 2). The profiles here show that FV548 in both preirradiation conditions is less susceptible to void development than corresponding samples of M316 cladding (Fig. 1), although the respective carbon contents—0.06 to 0.09% in FV548 as compared with 0.05% in the

M316 steel used—seem at first sight to be contrary to the earlier view that a lower carbon level is advantageous in reducing the incidence of voidage. The FV548, however, has a niobium level that is specified as eight times the carbon content, suggesting that control of the behavior of carbon may be a more important factor. Some additional evidence in support of this view comes from measurements made on samples of EN58B steel; although this steel was irradiated in essentially unstressed conditions and data may thus not strictly be comparable with those from pin cladding samples, the swelling rates appear to be much lower than the high carbon level (0.15%) might presage, and control of carbon by preferential formation of titanium carbide would, in this case, provide an explanation of the reduced susceptibility to void formation. The presence of niobium or titanium carbide does not in itself seem to convey any distinct advantage unless care is taken to control the form of the precipitation, since solution-treated FV548 is not noticeably an improvement on solution-treated M316L steel. In this case the aging of the FV548 would have produced a relatively coarse precipitation of incoherent carbides. The presence of a finely divided coherent precipitation may, however, be advantageous; certainly the low swelling profiles shown by aged Nimonic PE16 cladding (Fig. 2) suggest that the presence of finely dispersed γ' particles may be, in this case, an effective void suppressant.

ELECTRON MICROSCOPY

Voids in M316 Stainless Steel

Samples of cladding from three pins have permitted a comparison to be made of void morphology in solution-treated and cold-worked M316 steel.

Pin A-1064 was clad in 20% cold-worked M316 steel and was irradiated to a peak (centerline) fluence of 6.1×10^{22} neutrons/cm². Figure 3 shows a group of electron micrographs of samples from this pin. The lowest temperature at which voids were seen was 380°C, when the mean void diameter was 120 Å with lattice damage on a fine scale, loops being resolvable in some fields. The voidage and lattice damage coarsen with rising irradiation temperature, and above 500°C the larger voids in the material are associated with $M_{23}C_6$ precipitates. In the 580°C sample, it can be seen that the voids attached to large $M_{23}C_6$ particles are much larger than those isolated from precipitates. At the higher irradiation temperatures, the voids show well-defined facets consistent with a truncated octahedral morphology. Void-size histograms (Fig. 4) show the size distributions to be approximately Gaussian.

Pins A-097, irradiated to a peak fluence of 6×10^{22} neutrons/cm², and A-1170, irradiated to a peak fluence of 3.6×10^{22} neutrons/cm², were clad in solution-treated M316 steel.

Void sizes and concentrations⁷ from samples of all three pins are presented in Fig. 5. A comparison of data from pins A-1170 and A-1064 shows that to

Fig. 3 Electron micrographs of samples of cold-worked M316 stainless-steel cladding from pin A-1064. (a) 630°C; 17 displacements per atom; $\Delta V/V = 0.8\%$. (b) 580°C; 24 displacements per atom; $\Delta V/V = 1.7\%$. (c) 530°C; 28 displacements per atom; $\Delta V/V = 1.65\%$. (d) 490°C; 30 displacements per atom; $\Delta V/V = 0.9\%$. (e) 440°C; 31 displacements per atom; $\Delta V/V = 1.1\%$. (f) 380°C; 29 displacements per atom; $\Delta V/V = 0.3\%$.

Fig. 4 Void-size variations in cold-worked M316 stainless steel from pin A-1064 as a function of irradiation temperature.

Fig. 5 Influence of irradiation temperature on void size and concentration in samples of solution-treated and cold-worked M316 stainless-steel fuel-pin cladding.

achieve a particular void size requires a higher fluence in cold-worked material than in solution-treated material, and a comparison of the 550°C samples of solution-treated M316 steel from pins A-097 and A-1170 shows that the higher fluence in the A-097 sample has produced a significant increase in void size with essentially no change in void concentration. It is concluded that, at these fluence levels, the void concentration is relatively insensitive to either preirradiation condition or fluence, whereas the mean void volume is strongly influenced by both. The higher swelling rates in solution-treated material noted above are thus a consequence of more-rapid growth of voids than would occur in cold-worked material, and the increase in swelling with increase in fluence is due to continued growth of the voids rather than to further nucleation.

Voids in M316L Stainless Steel

Again, a comparison has been made of cold-worked cladding from pin V-1013 and solution-treated cladding from pins A-1034 and V-051, the latter having been exposed to the higher peak fluence (8.5×10^{22} neutrons/cm²). Figure 6 shows voids in a sample from V-051, which immersion density work had shown to have swollen by 7.4%. Void-size and -concentration data again support the view that void sizes are much more dependent on fluence than are void concentrations, so that increasing swelling is again a consequence of continued void growth rather than of significant changes in void concentration.

When micrographs from M316L steel are compared with those from M316 steel, the most noticeable differences lie in the absence in the M316L steel of the large amounts of intragranular $M_{23}C_6$ which were present in the higher carbon steel at high temperatures. The stabilization of stacking faults by carbide precipitation could explain the deleterious effects in the M316 steel. The stacking fault $M_{23}C_6$ and associated dislocations could assist void nucleation and/or growth by promoting stability of the void embryo and by influencing the vacancy/interstitial separation process, so accelerating the growth of voids in close association with them. The observation of only small amounts of $M_{23}C_6$ in M316L steel supports the conclusion reached when the immersion density data are considered; that is, suppression of extensive $M_{23}C_6$ formation is an important factor in controlling the incidence of voidage.

Voids in Nimonic PE16 and FV548

A comparison has been made of two pins irradiated side by side to a peak fluence of 5.6×10^{22} neutrons/cm². Pin A-205 was clad in solution-treated and aged Nimonic PE16 and pin A-206 in solution-treated and aged FV548. Figure 7 is an electron micrograph of a sample of FV548 from pin A-206 showing voids with well-defined facets—consistent with truncated octahedra bounded by $\{111\}$ and $\{100\}$ faces—stacking-fault loops (of as-yet unidentified character), a dislocation substructure, and zones denuded of voids adjacent to grain boundaries. (Although, in our experience, voids never form actually on grain

Fig. 6 Voids in a sample of solution-treated M316L stainless-steel cladding from pin V-051 after irradiation at 510°C to 8×10^{22} neutrons/cm² (40 displacements per atom).

boundaries, the existence of denuded zones adjacent to the boundaries is not an invariable feature; in many specimens, denuded zones are absent, whereas in others zones up to 1500 Å thick have been seen.)

Void-size and -concentration data⁷ have been compared. From 400 to 550°C, the lower swelling of the Nimonic PE16 as compared to that of the aged FV548 (Fig. 2) is due to a smaller concentration of voids, the sizes being about the same in both materials. Above 550°C the void sizes in Nimonic PE16 do not increase with increasing irradiation temperature.

Electron microscopy of cold-worked FV548 is still in progress.

FACTORS INFLUENCING VOID DEVELOPMENT

On the basis of the experimental evidence presented above, it is instructive to analyze the various factors influencing the development of voidage in the cladding and structural materials examined in the Dounreay program.

Temperature

Electron-microscope studies have shown (Figs. 3 and 5) that there is a consistent increase in void diameter and a steady decrease in void concentration

Fig. 7 Faceted voids, stacking-faulted loops, and dislocations in a sample of solution-treated and aged FV548 cladding from pin A-206 after irradiation at 470°C to 5.6×10^{22} neutrons/cm² (28 displacements per atom).

as the irradiation temperature rises, suggesting that temperature is the dominant factor influencing void nucleation and growth. There is no evidence from any of our work of any maximum in the nucleation rate at an intermediate temperature.

Although our studies support the generally held view that voids are not observed in stainless steels after irradiation at temperatures below about 360°C, we have no evidence of an upper temperature limit for void development. None of our samples had been irradiated at temperatures approaching the 750 to 775°C high-temperature cutoff assumed in most swelling models.

Our work has shown that the relation between void size and temperature can be disrupted by the influence of large precipitate particles. The M316 cladding of pin A-1064 irradiated at 580°C (Fig. 3) showed that voids attached to large $M_{23}C_6$ particles were very much larger than neighboring voids isolated from precipitates. Thus accelerated swelling might occur at high temperatures if thermal or irradiation processes lead to the appearance of coarse precipitation, and the efficacy of measures aimed at inhibiting the formation of such precipitates in austenitic stainless steels has been demonstrated in this work.

Fluence

The evidence presented suggests that the void population in the steels investigated is established at a relatively low fluence and changes little thereafter, increasing swelling with increasing dose resulting principally from growth of existing voids. This is contrary to the view expressed by some American workers.^{8,9}

Materials Variables

Our work has shown that minor changes in the composition of stainless steels can materially improve resistance to swelling. This evidence, obtained, for example, by comparing our data for M316 steel and the niobium-stabilized version, FV548, supports the conclusions previously reported by Comprelli¹⁰ in a comparison of 316, 304, 347, and 321 steels and by Bloom¹¹ in relation to unstabilized and titanium-stabilized 304 steel. There is the further indication from our comparison of M316 and M316L steels that simple reduction in the carbon level may also be beneficial, and Comprelli has shown that deliberate coarsening of carbide precipitates before irradiation impairs swelling resistance. It has also been shown that the addition of aluminum and titanium to nickel-based alloys to form γ' -phase precipitates reduces void formation, and Bagley et al.¹² have presented pin-swelling evidence that Nimonic PE16 shows a minimal swelling rate over a wide fluence range.

Such modest variations in composition appear to affect not only the magnitude of the swelling but also the temperature sensitivity. Thus M316 stainless steel shows a maximum swelling rate at temperatures above 600°C, whereas the niobium-stabilized version, FV548, shows a maximum at about 450 to 500°C with a second maximum at above 600°C, and the low-carbon M316L shows a broad maximum at about 500°C. Nimonic PE16, on the other hand, shows negligible temperature sensitivity—or even a falling swelling rate with increasing temperature—in the range up to 700°C.

These deductions are supported¹² by mensuration data from a large number of fuel pins, in most of which the void contribution to diametral change was not checked, but it has been found³ that pin strain correlates well with cladding swelling so that void-development tendencies may validly be inferred from pin-swelling behavior to provide evidence confirming the conclusions reached here.

The most advantageous changes in alloy composition may be those which tend toward the development of very stable, finely dispersed coherent precipitation (e.g., TiC, NbC, γ'), although our evidence suggests that, if thermal conditions produce coarse incoherent precipitates, any improvement resulting from titanium and niobium additions may arise more from control of the role of carbon in the steel than from the presence of the carbide precipitation itself. Interaction of coherent precipitates with the matrix might, however, provide defect traps at which point defect recombination would be promoted and the

excess vacancy concentration would thus be reduced. Heat treatments which coarsen the precipitation, yielding micron-sized particles, clearly have a detrimental effect on swelling resistance, in part because of a diminution in the defect-scavenging effect and in part because of acceleration of void growth on certain precipitate particles. Thus it would appear that during irradiation the number of vacancies rejected into voids is determined primarily by material characteristics.

The volume-change data presented here and the accumulated fuel-pin experience noted above indicate unequivocally the powerful effect of cold working on void generation, maximum swelling rates in 20% cold-worked material being some two to three times lower than those in solution-treated material from the same cast at fluences up to about 8×10^{22} neutrons/cm². Electron microscopy indicates that the effect is due to a reduction in size rather than in number of the voids. Straalsund¹³ has confirmed that 316 steel subjected to various amounts of cold work before irradiation shows negligible voidage after irradiation to a fluence of 3×10^{22} neutrons/cm² in the temperature range 400 to 700°C, but Bloom,¹⁴ noting lower swelling in 10% cold-worked 304 steel than in solution-treated 304 steel after irradiation to 2.8×10^{22} neutrons/cm², attributed the effect to a reduction by a factor of 20 in the number of voids. There is a marked discrepancy between Bloom's conclusion and that reached in the present work.

Stress

The influence of stress on void development is still unclear, and the Dounreay work reported here has done little to clarify the situation. The only controlled in-pile experiment carried out by British workers was carried out in a thermal reactor at Harwell by Barton and Nutter.¹⁵ The material was pure nickel, which was irradiated at 500°C to a fluence of 3.6×10^{20} neutrons/cm². Electron-microscope evidence showed that changing the tensile stress level from 0.23 MN/m² (34 psi) to 17.24 MN/m² (2500 psi) had no significant effect on either void size or concentration.

Hypotheses on the effects of stress suggest either (1) that tensile stress should promote void growth by opposing the surface-tension forces tending to minimize void size or (2) that tensile stress should inhibit void growth by enhancing the flow of interstitials to voids.

In the first case, theory suggests that the stress levels must be very high (~ 400 MN/m² $\equiv$ $\sim 60,000$ psi) and the void diameter large (>200 Å) if stress is to exert any significant effect. Thus only at high temperatures, where void diameters can be large, is it expected that stress might significantly enhance void development. And yet, Dounreay pin data¹² show clearly that cladding strain is not insensitive to fuel type or fuel density and that the cladding shows a tendency to swell less opposite gaps in the fuel column than elsewhere, indicating that the indeterminate stress or strain levels induced by the fuel are important. The situation still has to be resolved.

CONCLUSIONS

1. Up to fluences of the order of 8×10^{22} neutrons/cm² (40 displacements per atom), the neutron-irradiation-induced swelling of a group of austenitic cladding materials can be adequately represented by a linear function of fluence, after a threshold of the order of 1.2×10^{22} neutrons/cm² (6 displacements per atom) during which no swelling of technological importance occurs.

2. Void formation in these materials has been shown to be very sensitive to small differences in composition. In particular, it has been shown that reduction of the carbon level or control of the role played by carbon in stainless steels can change both the magnitude of the swelling and its temperature dependence.

3. Cold working has been shown to have a powerful effect in reducing the rate of swelling of stainless steels.

4. Electron-microscopic evidence shows that a void population characteristic of the irradiation temperature is established relatively early in the irradiation and that subsequent swelling is a consequence of growth of those voids rather than of further nucleation.

5. At any temperature there is little significant difference between the void concentrations of solution-treated and cold-worked samples of the same steel, and different swelling rates are a reflection of different void growth rates.

6. The effect of stress on void generation is not yet clear.

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DISCUSSION BY ATTENDEES

Che-Yu Li: Could you comment on the effect of carbon level on swelling?

Bramman: Our work at Dounreay shows that reduction in the carbon level or control of the behavior of carbon by the addition of carbide-forming elements have the most significant effect with respect to M316 steel in the higher temperature region—the temperature range in which $M_{23}C_6$ precipitation begins to occur. We have attributed the higher swelling of M316 steel in this temperature range to the influence of $M_{23}C_6$ in accelerating nucleation and/or void growth rates rather than postulating that carbon in solution in the matrix has a significant effect.

Bullough: Is a continual rise at temperatures exceeding the peak swelling temperature, as in 316, ever seen in the absence of hydrostatic tensile stress? The effect of the higher carbon in 316 compared with 316L may be due to the fact that the carbon increases the yield stress and thus enables a higher elastic hydrostatic stress to prevail. At high temperatures, when the steady-state

vacancy concentration is near the equilibrium value, such hydrostatic stress should assist void growth by normal diffusion processes.

Bramman: All the data I have presented refer to fuel-pin cladding, which, as I have said, is stressed during irradiation. We have examined some samples of M316 and M316L which had been irradiated in an unstressed condition, but our data from these are, as yet, not sufficiently comprehensive to indicate whether the differences observed between M316 and M316L cladding samples are shown in the absence of stress.

Beeler: I would like to mention two features of carbon atom and precipitate behavior in the alpha iron seen in computer experiments: (1) Single-layer carbon platelets form at (110) and (100) void facets. The associated strain field inhibits the dynamic approach of interstitials to voids. (2) By virtue of a shielding effect, hard precipitates acted as heterogeneous nucleation sites for either vacancy or interstitial clusters by enhancing the purely statistical mechanism for clustering first pointed out by Luck and Sizmann.

Harkness: If carbon content is so important to swelling, what are the implications for carbon-bombardment simulation work?

Bramman: I think that the important point is that in the M316 steel, our irradiation times are sufficiently long for massive amounts of $M_{23}C_6$ to be a characteristic feature of electron micrographs of our higher temperature samples. Although Stuart Nelson's group at Harwell has loaded some of its samples with large amounts of carbon in the course of cyclotron-bombardment studies, there is no evidence of significant precipitation in their electron micrographs. Perhaps the point is that you can stuff as much carbon in as you like, provided you take steps to stop the growth of large precipitates of $M_{23}C_6$; and the ways of doing that are to keep the diffusion time short (as in the cyclotron) or to encourage the formation of other types of carbide by adding niobium or titanium (as the Dounreay work has shown).

Dutton: Is the stress present in your cladding such that you might expect significant thermal creep as measured out-reactor?

Bramman: I do not know what the stress levels were in our cladding samples, but, although voidage in the cladding is the principal cause of pin dimensional changes, there is some indication that creep does take place in the cladding.

McElroy: You have made no comment on helium and its effect. Would you care to comment?

Bramman: We have made no studies of the effect of preinjecting particular levels of helium into our samples prior to irradiation. Our view is that helium plays an essential part in stabilizing the embryo voids, and an amount of helium sufficient for this has been produced by (n,α) reactions long before technologically significant numbers of voids are detected. Therefore I do not see the point

in concerning ourselves with comparisons of samples irradiated with and without preinjected helium.

Burchill: In light of the correlation of swelling using a threshold followed by a linear dependence on fluence, please comment on the implications on separation of flux and time dependence of swelling. Is the linear dependence on fluence generally employed in fast breeder reactor design calculations in the United Kingdom?

Bramman: Our correlation of data is based on displacement dose (or fluence) rather than on dose rate (or flux). At present our data are not sufficiently discriminating to tell whether the rate at which the threshold dose is achieved has any relevance. Nor are our data—or anyone else's, for that matter—sufficiently good to justify anything but a simple threshold-plus-linear rise correlation. In view of that, why give a design engineer a power-law formula?

Appleby: I am intrigued by the large variation in high-temperature swelling of the claddings from the two solution-annealed FV548-clad pins. Were there any differences in the fuel configurations of the two pins? I am thinking of differences in fuel-pellet density or fuel-cladding gap.

Bramman: We have not investigated that possibility, and I would hesitate to make any off-the-cuff comments since I do not have the relevant data on hand.

Comprelli: Early in the presentation, it was mentioned that the cladding was stressed to some indeterminate degree. Yet, most of the pin $\Delta D/D$ data shown were consistent with the $\Delta V/V$ measurements for that position. Can one infer the effect of stress on these values? Does the indeterminate value of stress only exist in life until the swelling causes the cladding to pull away from the fuel? Is it feasible that the lattice deformation associated with radiation-enhanced creep is influencing the swelling rate? Can this effect be quantitatively inferred from the pin data?

Bramman: The pin dimensional changes are not wholly accounted for by the presence of voids in the cladding, but the correlation is generally sufficiently good for us to say that other pin deformation mechanisms are of secondary importance. Certainly, in our higher burnup pins, some creep is occurring. To what extent the creep processes influence the rates of void growth is not clear—indeed, it is not clear that there is any effect at all. I do not know of any clear evidence that the cladding pulls away from the fuel early in the radiation—the opposite is more correct: the fuel comes into intimate contact with the cladding.

EFFECTS OF COLD WORK ON VOID FORMATION IN AUSTENITIC STAINLESS STEEL

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ABSTRACT

The effects of cold work on void formation in austenitic stainless steels were investigated for fluences up to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV) at temperatures ranging from 370 to 850°C. Although bulk density measurements revealed as much as 0.7% volume change in the annealed material, no density decrease was found in any of the cold-worked irradiated specimens. Transmission electron microscopy examination of the specimens revealed that void formation had occurred in the cold-worked steels over the same temperature range as for the annealed steels. For the 27% cold-worked steels, the void sizes were comparable to those of the solution-treated steels, but the number density was reduced by a factor of about 50.

Since the phenomenon of irradiation-induced void formation was first observed, considerable effort has been expended toward both the characterization of swelling and the development of more swelling resistant metallurgical states in austenitic stainless steels. One simple treatment that has been the subject of considerable speculation is that of cold working. This paper reports the results of a series of irradiation experiments designed to determine the effects of cold work on swelling in austenitic stainless steels.

EXPERIMENTAL

The specimens investigated consisted of small right cylinders, approximately 0.5 cm in diameter by 1.25 cm long, of annealed (1065°C for $\frac{1}{2}$ hr and air cooled), 27% and 75% cold-worked 316 stainless steel, as well as 50% cold-worked 304 stainless steel. The cold work was introduced by swaging. The irradiations were carried out in three identical irradiation pins, shown schematically in Fig. 1. Each irradiation pin contained a series of small sodium-filled

Fig. 1 Schematic representation of irradiation pin.

subcapsules that contained samples representing the four material conditions. The temperature of each subcapsule was maintained by a balance between the gamma heating of the contents in the capsule and the heat transfer across the argon-gas gap between the subcapsule and the outer-pin wall. The outer pin was in contact with the reactor coolant sodium. The various combinations of gas gap and local heating resulted in a variety of irradiation temperatures for the subcapsules in a given pin. The neutron flux varied with position, as shown in Fig. 1. Thus the neutron flux for each irradiation temperature was different. The three pins were irradiated in equivalent positions of row 2 in Experimental Breeder Reactor II (EBR-II) to peak fluences of 1.25×10^{22} , 3×10^{22} , and 5.1×10^{22} neutrons/cm² ($E > 0.1$ MeV), respectively. Bulk density measurements, using the Archimedes technique, were made on all irradiated specimens as well as archive specimens. Transmission electron microscopy (TEM) examinations were carried out on selected specimens.

RESULTS

The results of the density measurements are summarized in Table 1. The target irradiation temperatures for a given subcapsule (7D, for example) was essentially the same for irradiation pins B-24, B-25, and B-27. Since the pins were exposed to irradiation for different times however, the indicated fluence for the same subcapsule designation is different for the three different pins. In general, the irradiation temperatures were calculated on the basis of estimated

TABLE 1
IMMERSION DENSITY SWELLING DATA FROM PINS B-25, B-24, AND B-27

Pin identification		B-25				B-24				B-27			
		Fluence, 10^{22} neutrons/cm ² (E > 0.1 MeV)	Temp., °C		$\Delta V/V$, %	Fluence, 10^{22} neutrons/cm ² (E > 0.1 MeV)	Temp., °C		$\Delta V/V$, %	Fluence, 10^{22} neutrons/cm ² (E > 0.1 MeV)	Temp., °C		$\Delta V/V$, %
Sub-capsule	Material*		Start	Finish			Start	Finish			Start	Finish	
7D	1	0.75	390	390	0.03	1.83	390	390	0.27	3.08	390	395	0.66
	2				0				-0.07				-0.04
	3				0.15				-0.02				0.08
	4				0				-0.07				-0.08
5D	1	0.96	435	430	0.08	2.35	430	450	0.38	3.96	430	470	0.73
	2				-0.05				-0.09				-0.02
	3				0.11				0.15				0.78
	4				0				-0.10				-0.10
3D	1	1.19	640	640	-0.2	2.9	625	650	-0.14	4.88	625	690	0.08
	2				-0.10				-0.14				-0.11
	3				-0.05				0.11				0.49
	4				-0.12				-0.10				-0.04
1D	1	1.25	780	780	-0.15	3.05	750	775	-0.14	5.14	750	810	-0.09
	2				-0.15				-0.18				-0.17
	3				-0.20				-0.09				-0.12
	4				-0.14				-0.11				-0.15
1U	1	1.25	840	840	-0.13	3.05	815	830	-0.10	5.14	815	850	-0.11
	2				-0.12				-0.08				-0.16
	3				-0.18				-0.20				-0.14
	4				-0.14				-0.14				-0.12
2U	1	1.22	715	715	-0.11	2.99	680	730	0.04	5.04	680	770	-0.03
	2				-0.15				-0.13				-0.08

	3				−0.03				0.52				0.45
	4				−0.14				−0.08				−0.08
4U	1	1.09	560	560	0.03	2.63	540	590	0.14	4.47	540	615	0.09
	2				−0.07				−0.03				−0.07
	3				−0.15				−0.08				−0.17
	4				−0.11				−0.05				−0.07
6U	1	0.85	460	460	0.03	2.07	460	470	0.26	3.5	460	515	0.48
	2				−0.08				0.08				−0.01
	3				0.04				0.20				0.26
	4				−0.06				−0.04				−0.11

*1 denotes annealed 316 stainless steel; 2 denotes 27% cold-worked 316 stainless steel; 3 denotes 50% cold-worked 304 stainless steel; and 4 denotes 75% cold-worked 316 stainless steel.

TABLE 2
IRRADIATION-INDUCED VOID FORMATION IN
SOLUTION-TREATED 316 STAINLESS STEEL

Sample No.	Fluence,* 10^{22} neutrons/cm ² (E > 0.1 MeV)	Temp., °C	Diameter, Å			Void density, 10^{15} voids/cm ³
			Min.	Av.	Max.	
25-7D-1	0.75	380	74	101	151	2.7
24-7D-1	1.8	380	89	168	257	3
27-7D-1	3.1	380	74	180	273	1.8

*Constant flux.

gamma heating and heat-transfer characteristics of the subcapsules. The calculated irradiation temperatures agree well with results from melt pellets that were included only in pin B-25. Note from Table 1 that the calculated irradiation temperatures often increased during exposure. The increases were due to the fact that irradiation-induced swelling increased the gas gap during exposure.

Inspection of the data in Table 1 reveals several trends. In general, for the solution-treated materials, the swelling behaves as expected on the basis of past studies. That is, with increasing irradiation temperatures, the swelling initially increases, passes through a maximum, and eventually goes to zero at high temperatures. The maximum appears to occur at a relatively low temperature, on the order of 425°C. In general, at the very high irradiation temperatures, increases in density on the order of about 0.1% were found. These density changes are consistent with changes found during thermal aging.¹ The variation of irradiation temperature with time for a particular subcapsule prevents the quantitative description of the variation of swelling with fluence. It is not possible, for example, to distinguish between a linear relation, $\Delta V/V = A + B \phi t$, or a power law, $\Delta V/V = A(\phi t)^n$.

The effects of cold work on swelling in 316 stainless steel are evident. Over the whole range of investigation, there was only one cold-worked 316 stainless-steel specimen (pin B-24, specimen 6U-2) which showed any swelling. For this specimen the indicated swelling was quite small; also, TEM examination of this specimen revealed no voids. It is therefore expected that the bulk density measurements reflected porosity or some other defect in that particular specimen, which may have existed before irradiation.

In contrast to the 316 stainless steel, considerable swelling was found in 50% cold-worked 304 stainless steel. In order to display the temperature dependence of swelling found in the cold-worked 304 stainless steel, the small fluence variations within a given pin were ignored, and the swelling values were plotted as a function of temperature for each pin. These approximate plots of swelling vs. irradiation temperature are shown in Fig. 2. With increasing irradiation temperature, the swelling for cold-worked 304 stainless steel first increases to a maximum at about 480°C, then decreases to essentially no swelling at about 600°C. Above 600°C the swelling again increases to another maximum at about 700°C before returning to zero at about 800°C.

Transmission-electron-microscopy examination of the specimens irradiated in this study have not yet been completed and will be the subject of a later report. The results obtained so far, however, reveal several interesting trends. For a constant flux with increasing time, the void number density in the annealed 316 stainless steel was found to increase to an approximately constant value, after which nucleation ceased and the void size continued to increase. Microstructural data obtained for irradiation, at constant flux, for fluences varying from 1 to 4×10^{22} neutrons/cm² ($E > 0.1$ MeV) at irradiation temperatures between 420 and 470°C are shown in Table 2. These data show

Fig. 2 Temperature dependence of swelling in 50% cold-worked 304 stainless steel.

that the minimum, average, and maximum void diameters increase with increasing fluence, whereas, within the experimental scatter, the number density remains essentially constant. At present, there are insufficient data to establish if the same trends occur for the cold-worked 316 stainless steel.

The primary effect of cold working in 316 stainless steel is that of a large reduction in the void number density. In Table 3 the void size and number density are compared in the annealed and 27% cold-worked material for several irradiation temperatures. The very-low number densities associated with the cold-worked material increase experimental difficulties associated with obtaining meaningful number-density and size-distribution data. However, the general experimental trends are evident. The void number densities are decreased by a factor of 10 to 100 at low irradiation temperatures and are decreased to unmeasurably low values at higher temperatures. Void size is not significantly affected.

Examination of the 50% cold-worked 304 stainless steel revealed two significant differences between this material and the cold-worked 316 stainless steel. Figure 3 shows the microstructures of 27% cold-worked 316 stainless steel and 50% cold-worked 304 stainless steel which were irradiated at 380°C to a fluence of 1.8×10^{22} neutrons/cm² ($E > 0.1$ MeV). As shown in Fig. 3, at this

TABLE 3
EFFECTS OF COLD WORK ON VOID SIZE AND NUMBER DENSITY

Specimen No.	Condition*	Temp., °C	Fluence, 10^{22} neutrons/cm ² (E > 0.1 MeV)	Av. void diameter, Å	Void density, voids/cm ³
24-7D-1	A.	380	1.8	165	3×10^{15}
24-7D-2	27% C.W.	380	1.8	160	5×10^{13} to 3×10^{14}
24-5D-1	A.	445	2.4	280	1.7×10^{14}
24-5D-2	27% C.W.	445	2.4	No voids observed	
24-2U-1	A.	740	3	304	5×10^{13}
24-2U-2	27% C.W.	740	3	No voids observed	

*A. = annealed at 1065°C; C.W. = cold worked.

relatively low irradiation temperature, the dislocation structure in the 304 stainless steel is not nearly as effective in preventing void nucleation as the 316 stainless steel. The primary difference in structure between the two steels is the more pronounced cellular structure in the cold-worked 304 stainless steel. Voids tend to form in the center of the cells, away from the cell boundaries. Even though the dislocation network within the cells does not prohibit void formation, the dislocation density appears to be as high as that in the cold-worked 316. Above about 650°C, significant recrystallization begins to occur in the cold-worked 304 stainless steel, as opposed to the cold-worked 316 stainless steel. The microstructures of the cold-worked 304 and 316 stainless steels after irradiation to 3×10^{22} neutrons/cm² at approximately 740°C are compared in Fig. 4. As shown in Fig. 4, considerable recrystallization has occurred in the cold-worked 304. Recrystallization appears to become significant at temperatures approximating those of the minimum in the swelling curve and increases with increasing temperature.

DISCUSSION

Many results of this study appear to be consistent with nucleation and growth models discussed by various investigators.²⁻⁴ The rapid rise in dislocation loop and void number densities in the early stages of irradiation and the essentially constant values over the relatively wide range of irradiation time covered in this investigation support the hypothesis that the nucleation rate is highly dependent on the supersaturation of various species. During the early stages of irradiation, the supersaturation and, hence, the nucleation rate are very high. As the number density of the various sinks (voids and loops) continues to increase, however, the supersaturation is reduced until nucleation essentially ceases. These general features may be incorporated within several nucleation

(a)

1000 Å

(b)

1000 Å

Fig. 3 TEM micrograph of (a) 27% cold-worked 316 stainless steel and (b) 50% cold-worked 304 stainless steel after irradiation to 1.8×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 380°C. (Magnification, 89,000 x.)

(a)

1000 Å

(b)

1000 Å

Fig. 4 TEM micrograph of (a) 27% cold-worked 316 stainless steel and (b) 50% cold-worked 304 stainless steel after irradiation to 3×10^{22} neutrons/cm² at 740°C. (Magnification, 50,000 x.)

mechanisms, including nucleation from spike-induced clusters, helium-assisted nucleation, heterogeneous nucleation at various impurities or defects, and homogeneous nucleation. Thus it does not appear that the results of the present study can be used to discriminate among these mechanisms.

The primary effect of cold work found in this study was a decrease in void number density, with very little change in void size. Classical growth theories, such as that of Bullough and Perrin,⁵ suggest that the growth rates of voids are reduced by increased dislocation densities, such as would be induced during cold working, as long as the voids are sufficiently far apart that they do not influence each other's growth. Initial consideration of these growth theories would therefore lead to the prediction of a reduced void growth rate for the cold-worked material. In contrast, the experimental results show essentially the same void size for the cold-worked and annealed materials. These results may be at least qualitatively rationalized if one assumes that the nucleation rate is very highly dependent upon supersaturation. Such a result has been predicted, for example, by the nucleation model of Katz and Wiedersich.⁴ The exact details of the co-nucleation of both voids and loops will be exceedingly complex. Because of such factors as different formation energies for vacancies and interstitials and the different roles to be played by helium for void and loop nucleation, the nucleation kinetics of loops and voids may be expected to be much different. However, the two nucleation processes may also be expected to be tightly coupled. That is, the instantaneous nucleation rate of voids may, in general, be expected to depend on both the void and interstitial loop concentrations and the size distributions.

The concept to be presented here may be illustrated by considering a case in which the interstitial loops nucleate much easier than the voids and, because of their higher number density, essentially control defect supersaturation. A schematic representation of the relation between nucleation rate and supersaturation is shown in Fig. 5(a). If, at the start of irradiation, the supersaturation is at some high value, the nucleation of the loops will very rapidly proceed. Neglecting recombination effects, the supersaturation will be inversely proportional to the sink density, including dislocations as well as loops. Thus, as the nucleation proceeds, the supersaturation will very rapidly drop, owing to the increased loop density, until a low enough supersaturation (say S_0) is obtained so that nucleation becomes negligible. Two resulting variations in supersaturation with time are shown in Fig. 5(b). In the first case, where a low initial dislocation density is assumed, the initial supersaturation will be very high, inducing a rapid nucleation rate and a similarly rapid decrease in supersaturation until eventually the limiting value, S_0 , is attained. In the second case, where a high original dislocation density is assumed, the nucleation rate would begin at a lower value but again decrease until S_0 is attained. In both cases the same limiting value of supersaturation would be attained. That value is attained in one case by a low dislocation density and a high loop density but is attained in the other case by a high dislocation density and a low loop density.

Fig. 5 Schematic representation of (a) variation in nucleation rate with supersaturation and (b) resultant variation of supersaturation with time.

In either case the total sink density (for both loops and voids) would approach about the same value. Since loops are expected to perform essentially the same function as dislocations insofar as void growth is concerned, the net sink density (such as that represented by dislocation density in many growth models^{2,5,6}) will approach about the same value and be essentially independent of the initial dislocation density. If the sink density saturates during an early portion of the irradiation, void growth for both the cold-worked and annealed materials may therefore be expected to occur at approximately the same rates.

Thus, if nucleation is highly supersaturation dependent, the total sink density in the two cases of high and low initial dislocation density (including both preirradiation- and irradiation-induced sinks) may be expected to approach approximately the same final value. Under these conditions the subsequent growth of the irradiation-induced defects may be very insensitive to the preirradiation structure.

The irradiation behavior of the 50% cold-worked 304 stainless steel is difficult to explain. At low irradiation temperatures, no gross differences in dislocation structure between the 304 and 316 stainless steels could be found which would explain the increased void formation in the cold-worked 304 stainless steel. Unfortunately the present study did not include solution-treated 304 stainless steel. However, swelling of solution-treated 316 stainless steel determined in this study is significantly less than that for solution-treated 304 steel reported elsewhere.^{6,7} Thus the primary differences in the low-temperature swelling behavior between these two steels may be due to basic differences in alloy composition rather than structure. Although many possible explanations, including differences in precipitation behavior, stacking-fault energy, impurity trapping, etc., can be offered, the reason for these pronounced differences in swelling behavior is presently a matter of speculation. However, these differences do serve to emphasize the pronounced impact that minor variations in alloy chemistry can have on radiation-damage-structure development.

The high-temperature irradiation behavior of the cold-worked 304 stainless steel is a clear-cut example of a problem that many investigators anticipated in the irradiation performance of cold-worked stainless steels; considerable recrystallization of the 50% cold-worked 304 stainless steel occurred at temperatures above 650°C. Increased void formation of the recrystallized regions resulted in the pronounced second hump in Fig. 2. Some evidence of recrystallization was found in the 75% cold-worked 316 stainless steels. However, this occurred at high temperatures, above the void-formation range. Selection of dimensionally stable material for fast reactors must therefore include careful considerations of a balance between cold-work stability and void-formation temperature range.

CONCLUSIONS

The following conclusions resulted from this study:

1. The general features of void formation in 316 stainless steel are similar to those which have been anticipated on the basis of classical nucleation-and-growth theories. That is, for a given flux and with increasing irradiation time, void number density rapidly increases in the early stages of irradiation, after which it remains essentially constant and void growth continues.
2. The major impact that cold working has on void formation is a drastic decrease in void number density and essentially no change in void size. These results may be interpreted in terms of nucleation and growth concepts.

3. Both the thermal stability and effectiveness of cold-work-induced dislocation structure in the prevention of void formation depend strongly on minor variations in alloy chemistry. Thus it is possible in some austenitic stainless steels to have significant amounts of recrystallization and subsequent void growth during irradiation.

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DISCUSSION BY ATTENDEES

Bullough: With regard to the observation that cold work leads to a reduction in void concentration, could you comment on the difficulties of actually observing the voids in such highly dislocated materials?

Straalsund: The observation of voids in the heavily cold-worked structure is indeed difficult, and this adds uncertainty to the determination of accurate number densities. These difficulties also occur in the observation of voids in the solution-treated material due to the heavy degree of loop formation. These uncertainties are small, however, compared to the differences observed between the annealed and cold-worked materials.

Spitznagel: Did you try to characterize or did you notice any significant differences in the nature and amount of precipitation occurring in the annealed and cold-worked materials?

Straalsund: In the solution-treated 316, there were two types of observed precipitates: coherent submicron-size cuboidal $M_{23}C_6$ and ribbon-shaped sigma. Both phases were found in the cold-worked 316 stainless steel. Considerable precipitation of these precipitates was found on cold-work-induced microtwins and dislocation tangles.

Sosin: Was any attempt made to stabilize dislocation structures by a preirradiation anneal at a suitable temperature above the irradiation temperature?

Straalsund: No. However, samples are presently under irradiation which have had stabilization treatments.

Appleby: Your solution-annealed 316 showed dramatically lower swelling at high temperatures than the annealed 316 of John Bramman reported in the previous paper. He attributed large swelling differences in M316 and M316L as due to carbon-content variation. What was the carbon content of your material?

Straalsund: The carbon content was normal, i.e., about 0.05%.

Bramman: Have you observed grain-to-grain differences in void number density in cold-worked material? If so, does this not make determination difficult?

Straalsund: Grain-to-grain differences have not been observed, but they also have not been specifically looked for. It is noteworthy that the voids were not homogeneously distributed within a grain, and this does make accurate determination difficult.

FLUENCE AND TEMPERATURE DEPENDENCE OF VOID FORMATION IN HIGHLY IRRADIATED STAINLESS STEELS

5389680
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ABSTRACT

Void formation in the 300-series austenitic stainless steels was examined by transmission electron microscopy, and bulk swelling was measured by immersion density. Specimens of 316 and 347 stainless steels were obtained from fuel-pin claddings, and the 304 stainless steel was obtained from a materials capsule. Volume increases of up to 10% were measured after fluences of up to 7.3×10^{22} neutrons/cm² ($E > 0.1$ MeV). Void size increased with irradiation temperature, but the void number density decreased. The upper temperature limit of void formation in 304 stainless steel was found to be $650 \pm 15^\circ\text{C}$. At the higher fluences it was found that void nucleation had effectively ceased and that continued swelling was primarily due to void growth. Extensive intragranular precipitation in 316 and 347 stainless steels at 525 to 550°C had provided void-nucleation sites.

The extent of irradiation-induced swelling to be expected in the core components of liquid-metal-cooled fast breeder reactors is a vital design consideration. Since the first reported measurements of stainless-steel swelling in 1967,¹ considerable effort has been devoted to characterizing and understanding the phenomenon. Numerous experimental fuel pins and materials capsules have been irradiated to high burnups and fluences in EBR-II. Recent results describing the irradiation-induced swelling of various austenitic stainless steels are described here. The volume changes in 316 and 347 stainless-steel fuel-rod claddings from the General Electric Company F2 series experiments (irradiated to burnups of over 100,000 MWd/metric ton) have been determined by immersion density measurements and transmission electron microscopy. Type 304 stainless steel irradiated in a materials test capsule to fluences of 5.4×10^{22} neutrons/cm² ($E > 0.1$ MeV) with accurately known temperatures in the range 380 to 690°C (716 to 1274°F) has been studied by electron microscopy.

TEST DESCRIPTION

The F2 series of fuel-rod irradiations consisted of (U,Pu)O₂ fueled encapsulated pins in 0.250-in.-OD by 0.220-in.-ID cladding. The principal variables were fuel density and the type of cladding alloy. The pins were irradiated in a 19-pin subassembly in row 4 of EBR-II at peak linear powers of 14 to 16 kW/ft to burnups in excess of 100,000 MWd/metric ton and fluences to 7.3×10^{22} neutrons/cm² ($E > 0.1$ MeV). Peak mid-wall cladding temperatures were calculated to average 515 to 540°C (960 to 1010°F) during the irradiation. A full description of the test design and conditions is available.²

TABLE 1
COMPOSITION OF TEST ALLOYS

	Type 304*	Type 316†	Type 347‡
Composition, wt. %			
C	0.054	0.05	0.066
Mn	1.5	1.66	1.79
P	N.D.‡	0.018	0.025
S	N.D.	0.019	0.012
Si	0.5	0.68	0.74
Cr	18.7	17.40	18.57
Ni	8.95	12.53	10.48
Mo	0.2	2.34	0.22
Cu	0.1	0.15	0.22
Co	0.2	0.08	0.245
Nb + Ta	N.D.	N.D.	0.77
N	0.056	N.D.	N.D.
Fe	Balance	Balance	Balance
Grain size (ASTM)	N.D.	7½	9

*Solution-annealed strip.

†Solution-annealed weld-drawn tubing.

‡N.D. = not determined.

Materials capsule MT3 contained a strip of annealed 304 stainless steel 0.200 in. wide by 0.010 in. thick which extended along the entire length of the capsule. The capsule was irradiated in row 4 of EBR-II, and the strip received a wide range of neutron fluences [0.7 to 5.4×10^{22} neutrons/cm² ($E > 0.1$ MeV)] over a wide range of temperatures (380 to 690°C). Calculated temperatures (estimated accuracy $\pm 15^\circ\text{C}$) are a function of position along the strip; at selected locations the calculations were confirmed by melt-alloy temperature sentinels. Compositions and metallurgical conditions of the test alloys are given in Table 1.

EXPERIMENTAL PROCEDURE

Specimens for immersion density measurement were prepared from 1-in.-long sections cut from the fuel pins. The fuel was removed by drilling, reaming, and subsequent electropolishing of the inside cladding surface.³ These operations reduced the wall thickness from a nominal value of 0.015 in. to 0.011 to 0.013 in. A minimum of six density measurements were made on each specimen, using boiled distilled water with a few drops of wetting agent added. Control data were obtained from unirradiated archive specimens of the cladding tubing and from sections taken from the plenum regions of the irradiated fuel pins.

Transmission-electron-microscopy (TEM) specimens were prepared by cutting 3-mm-diameter disks from the cladding with an electrodischarge machine (EDM); in this way the material was not deformed during the cutting operation. The resultant curved disks were thinned by twin-jet electropolishing in a special* specimen holder. The TEM specimens were punched from the 304 stainless-steel strip and thinned similarly. Large numbers of voids were counted and measured. Foil thicknesses were determined experimentally whenever possible, either by counting surface voids⁴ or by slip trace analysis. Otherwise the thickness was estimated from electron transparency. Void-size distribution, mean void size, void number density, and void volume fraction were calculated for each specimen.

RESULTS AND DISCUSSION

The immersion density measurements showed that the fuel-pin claddings with the highest exposure exhibited the greatest extent of swelling of any materials yet irradiated in-reactor. Swelling values of up to 10.0% $\Delta V/V$ in 347 stainless steel and 8.7% $\Delta V/V$ in 316 stainless steel were measured in sections irradiated at about 525°C (975°F) to fluences of $\sim 7.0 \times 10^{22}$ neutrons/cm² ($E > 0.1$ MeV). Figure 1 shows the data plotted as a function of fluence. The swelling values for 347 stainless steel are generally greater than those for 316. Two fuel pins clad with 316 stainless steel had been loaded with fuel of different densities [83.9% theoretical density (T.D.) powder fuel and 86.7% T.D. pelleted fuel] so that a qualitative comparison could be made of the effects of stress on metal swelling. The higher density fuel with its higher effective swelling rate had caused a higher stress in the cladding. Consequently the pin with the higher density fuel had undergone 0.9% plastic deformation of the cladding compared to zero deformation for the cladding of the low-density pin. It was found that the cladding from the higher density pin had increased in volume slightly more than anticipated from correlations derived from unstressed data. Table 2

*Designed and built by E. A. Fischione.

Fig. 1 Cladding-volume increase vs. neutron fluence in F2 series fuel pins.

compares the swelling values measured for the two pins with the values calculated from a correlation obtained from the available 316 stainless-steel swelling data.

The examination of the 304 stainless-steel strip established the upper temperature limit for void formation in that alloy at $650 \pm 15^\circ\text{C}$. No voids were found in any specimen irradiated in the calculated temperature range of 654 to 692°C , whereas specimens irradiated at only slightly lower temperatures (645°C ,

TABLE 2
COMPARISON OF SWELLING DATA
FROM 316 STAINLESS-STEEL-CLAD FUEL RODS

Specimen	Fluence, 10^{22} neutrons/cm ² ($E > 0.1$ MeV)	Temperature, °C (°F)	Measured $\Delta V/V$, %	Calculated $\Delta V/V$, %	Deviation (calculated minus measured $\Delta V/V$)	Relative cladding stress
F2V-F	7.32	508(946)	7.65	6.5	-1.15	High
F2X-J	6.57	512(954)	5.76	5.4	-0.36	Low
F2V-J	7.32	522(972)	8.56	6.4	-2.16	High
F2X-M	5.60	522(972)	3.28	4.0	+0.78	Low

633°C) contained voids. The average void size increased markedly with temperature (Fig. 2), indeed some very large voids were found. The only previous observation of material containing many voids greater than 1000 Å was reported in the initial work on British fuel cladding.¹ It has been speculated that these large voids resulted from stress in the cladding. In the present case, however, the stress in the 304 strip was essentially zero during irradiation. Thus the only prerequisite for large voids in 304 stainless steel appears to be a combination of high temperature (500 to 650°C) and long exposure times [11,400 hr, $\sim 5 \times 10^{22}$ neutrons/cm² ($E > 0.1$ MeV)].

It is apparent that void diameters can meaningfully be measured by thin-foil transmission electron microscopy only when most diameters are significantly smaller than the foil thickness. Many of the voids observed in the high-temperature foils were larger than the foil thickness. This raised the question of whether or not the large void sizes were real or whether they had been substantially enlarged during electrolytic foil thinning. In the resolution of this question, a plane section was cut through a specimen, and the surface was polished by ion sputtering.⁵ A two-stage carbon replica of this surface revealed many voids greater than 2000 Å in diameter. Voids observed by the transmission and replication techniques are compared in Fig. 3, showing the equivalence of the results.

Figure 2, showing the temperature dependence of void size, includes data obtained by other experimenters.⁶⁻⁸ The General Electric data are self-consistent but show larger void sizes than data from other laboratories. The General Electric data were obtained from higher fluence material than the other data, and it is proposed that the nucleation of voids in the General Electric high-temperature specimens has ceased and that the swelling is continuing by void growth only. Examination of the void size distributions supports this concept. Figure 4 shows the dependence of minimum void size on temperature;

Fig. 2 Mean void size vs. irradiation temperature for 304 stainless steel irradiated in EBR-II.

at high temperatures no small voids exist, a fact demonstrating that nucleation has essentially ceased. The total void number density in the 304 stainless-steel strip decreases as the temperature increases, as shown in Fig. 5.

Data on void size and number density from the 316 and 347 fuel-pin claddings confirm the trends observed in the 304 stainless-steel strip. A section from a 316-clad pin irradiated at 545°C to a fluence of 3.1×10^{22} neutrons/cm² ($E > 0.1$ MeV) showed 2×10^{14} voids/cm³ with a mean void diameter of 365 Å (Fig. 6). The volume increase was 0.7% as measured by immersion density. Another section irradiated to 7.1×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 525°C showed 4×10^{14} voids/cm³ and a mean void diameter of 640 Å (Fig. 7). The volume increase (immersion density) in this case was 8.7%. Thus the higher exposure specimen had much larger voids despite the slightly lower irradiation temperature, whereas the void number density was only a factor of 2 greater.

TRANSMISSION

REPLICATION

Fig. 3 Comparison of voids observed by transmission and replication techniques in 304 stainless steel irradiated at 630°C (1166°F) to 5×10^{22} neutrons/cm² ($E > 0.1 \text{ MeV}$).

Fig. 4 Minimum void size observed in 304 stainless steel vs. irradiation temperature.

There has been considerable controversy, complete with conflicting sets of data,⁶⁻⁸ over the question of whether void nucleation or void growth continues with increasing neutron fluence (at constant temperature). Because the material in the experiments reported here covered nearly the whole temperature range in which void formation occurs, some insight into this problem may be gained. After nucleation, each void acts as a vacancy sink. Vacancies in close proximity to a void have a high probability of migrating to the void and being absorbed by it. Thus a vacancy gradient is produced and results in a net flow of vacancies into the void. The volume containing the vacancy gradient may be thought of as the sphere of influence of the void. Since the size of the sphere of influence is related to vacancy mobility, the sphere will increase with increasing irradiation temperature. As irradiation continues, more and more voids are nucleated until their spheres of influence impinge on each other. At that point, void nucleation will essentially stop since newly created vacancies have a much higher probability of contributing to growth of existing voids. If this analysis of the sequence of events is correct, the conflicting data can be explained: Early during

Fig. 5 Void number density in 304 stainless steel vs. irradiation temperature.

irradiation, i.e., at low neutron fluence, nucleation will be the dominant mechanism of swelling. After the impingement of the spheres of influence, void growth only will take place. Since the size of the spheres of influence increases with temperature, it follows that, at higher irradiation temperatures, void nucleation will stop sooner (i.e., at lower neutron fluence) than at lower temperatures. Therefore an observation of continuing nucleation with increasing neutron fluence need not be inconsistent with an observation of continuing void growth at a higher irradiation temperature.

This argument can be applied qualitatively to the data from this experiment. The strongest supporting evidence is the consistent increase in minimum observed void diameter with increasing irradiation temperature found in the 304 stainless-steel specimens. Only two disks had voids as small as the resolution

Fig. 6 Type 316 stainless steel from pin F2H. Specimen irradiated at 545°C to 3.1×10^{22} neutrons/cm² ($E > 0.1$ MeV). Mean void diameter, 365 Å; void number density, 2.1×10^{14} voids/cm³; swelling, 0.7% $\Delta V/V$.

Fig. 7 Type 316 stainless steel from pin F2V. Specimen irradiated at 525°C to 7.1×10^{22} neutrons/cm² ($E > 0.1$ MeV). Mean void diameter, 640 Å; void number density, 4.4×10^{14} voids/cm³; swelling, 8.7% $\Delta V/V$.

limit of the microscope ($\sim 20 \text{ \AA}$). Both had been irradiated at relatively low temperatures ($< 410^\circ\text{C}$) for which the spheres of influence around voids would be small. Therefore nucleation was still occurring when irradiation was terminated. In all other 304 stainless-steel disks, some minimum void size substantially greater than $20 \text{ \AA}$ was observed. In these disks the spheres of influence around existing voids had overlapped and caused nucleation to cease. The higher the irradiation temperature, the earlier in life nucleation apparently had stopped, as evidenced by the ever-increasing minimum void diameters.

The 316 and 347 stainless-steel specimens show extensive intragranular precipitation. The precipitate is more abundant in 347 than in 316, and the particles show a definite orientation relation to the matrix material. Voids are frequently associated with these particles. Analysis of the nature of the precipitation by electron diffraction is incomplete, but the indications are that the precipitate is sigma phase. Much larger particles of M_{23}C_6 are randomly dispersed in the grain boundaries. Figure 8 shows the structure of 347 stainless-steel cladding from pin F2T irradiated at 540°C to 3.9×10^{22} neutrons/cm² ($E > 0.1 \text{ MeV}$). A large M_{23}C_6 particle can be seen in the grain boundary, and the extensive fine precipitation within the grains is readily apparent. Similar unidentified fine precipitation in 316 stainless steel has been observed by Bisson and Vouillon.⁹ Rod-shaped particles identified as M_{23}C_6 have also been found by Brager and Kissinger¹⁰ in 316 stainless steel irradiated to low fluences in EBR-II at 480°C (900°F).

Data on void size and number density from our fuel-pin claddings are given in Table 3 together with comparable data for 304 stainless steel obtained from the materials capsule MT3.

TABLE 3
EFFECT OF PRECIPITATION ON VOID FORMATION

Alloy	Source	Fluence, 10^{22} neutrons/cm ² ($E > 0.1 \text{ MeV}$)	Temp., $^\circ\text{C}$	Swelling, % $\Delta V/V$	Void		Intra- granular precipitation
					Number density, voids/cm ³	Mean diameter, $\text{\AA}$	
304	Materials capsule MT3	3.71	555	1.8*	2.1×10^{13}	1000	Light
316	Fuel pin F2H	3.1	545	0.7†	2.1×10^{14}	365	Heavy
	Fuel pin F2V	7.1	525	8.7†	4.4×10^{14}	640	Heavy
347	Fuel pin F2T	3.9	540	2.25†	1.5×10^{15}	250	Very heavy

*Swelling estimated from TEM void volume fraction.

†Swelling measured by immersion density.

Fig. 8 Type 347 stainless steel from pin F2T. Specimen irradiated at 540°C to 3.9×10^{22} neutrons/cm² ($E > 0.1$ MeV). Mean void diameter, 250 Å; void number density, 1.5×10^{15} voids/cm³; swelling, 2.25% $\Delta V/V$.

Fig. 9 Type 304 stainless steel from MT3. Specimen irradiated at 555°C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV). Mean void diameter 1000 Å; void number density, 2.1×10^{13} voids/cm³; swelling, 1.8% $\Delta V/V$.

Fig. 10 Type 347 stainless steel from pin F2T. Specimen irradiated at 540°C to 3.9×10^{22} neutrons/cm² ($E > 0.1$ MeV). Mean void diameter, 250 Å; void number density, 1.5×10^{15} voids/cm³; swelling, 2.3% $\Delta V/V$.

The void number density [materials irradiated to fluences of 3 to 4×10^{22} ($E > 0.1$ MeV)] increases by two orders of magnitude from 304 (Fig. 9) through 316 (Fig. 6) to 347 stainless steel (Fig. 10) (note different magnifications), whereas the average void diameter decreases by a factor of 4. The observed increase in void number density qualitatively corresponds to the degree of intragranular precipitation which was very slight in 304 stainless steel, heavy in 316, and even heavier in 347. Void nucleation is thus enhanced by the presence of small precipitate particles. However, the overall vacancy supersaturation is apparently not affected to the same extent, since the few voids in 304 stainless steel grew much larger than the greater number in the 347 and produced almost as much swelling.

CONCLUSIONS

1. The upper temperature limit of void formation in 304 stainless steel is $650 \pm 15^\circ\text{C}$.
2. Continued swelling in 304, 316, and 347 stainless steels at high fluences is due to the continued growth of existing voids rather than to further nucleation of new voids.
3. At a particular fluence, mean void diameters increase with irradiation temperature whereas the void number density decreases.
4. At 525 to 550°C , void nucleation is assisted by the presence of fine intragranular precipitation.

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DISCUSSION BY ATTENDEES

Shewmon: Could you tell me the differences between 347 and FV 548? Are they both niobium-stabilized stainless steel?

Appleby: Both 347 and FV 548 stainless steels contain niobium, but the FV 548 resembles 318 more in that it also contains molybdenum. Type 347 has no molybdenum addition.

Shewmon: Why is there a divergence between your high swelling results and the low swelling Bramman reported?

Appleby: The difference in observed swelling may or may not be attributable to the molybdenum. However, it must be remembered that significant differences in swelling have been observed from heat to heat for the same alloy, so it is not too unusual that a considerable difference exists between two similar alloys. In the 347 stainless steel, the high amount of swelling at 7×10^{22} neutrons/cm² ($E > 0.1$ MeV) is caused by the initial nucleation of a high number density of voids which subsequently grow. This appears to be related to the high density of intragranular precipitates produced during irradiation.

Bramman: Did you try annealing the 304 samples with 1800-Å voids in it? We annealed a sample of solution-treated M316L that showed after irradiation a 74% volume change with an average void diameter of 1150 Å. After 1 hr at 900°C, expecting the voids to have disappeared, we found the volume change to have fallen to 5% and the average diameter to have been reduced to 930 Å. After annealing for 1 hr at 1200°C, the mean size grew to 17,000 Å, the voids being optically visible on a polished surface.

Sandusky: No, not yet.

Carpenter: It is well known that helium bubbles can nucleate preferentially at precipitate particles when materials containing a supersaturation of helium are annealed. In this and some of the earlier papers today, there have been observations of voids nucleated at precipitate particles. This phenomenon seems to be most prevalent in materials irradiated at and above temperatures corresponding to the swelling peak. One role of precipitates may, therefore, be to trap insoluble gases (particularly helium), which can then stabilize vacancy clusters from which voids may grow. At higher irradiation temperatures one would expect the gases to become increasingly mobile, helped by irradiation-enhanced diffusion.

Appleby: The precipitate particles may well be trapping helium and then nucleating voids as suggested. However, it should be noted that these observations of voids associated with precipitates are at variance with Nelson's results for PE16, where the fine precipitation in this alloy may be inhibiting void formation. Obviously the two types of precipitates are very different with respect to size and coherence, and these factors are likely to be most important. As yet we have not investigated this point in any detail.

Bloom: May I point out one thing? If you compare your data on 304 stainless steel to those of Brager and to some of our data, you find that your void concentrations are, in general, much lower and sizes are, in general, much larger. I suggest that there may be significant heat-to-heat variations.

Appleby: Yes, we are aware of this. We did perform tests to confirm the nature of our alloy, and we could find nothing that would indicate that this was an extraordinary heat.

SUPPRESSION OF VOID FORMATION IN STAINLESS STEEL

375360

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ABSTRACT

Work is in progress at Hanford Engineering Development Laboratory with the goal of developing a cladding material which is resistant to swelling, has good elevated-temperature mechanical properties, and meets the established criteria for liquid-metal-cooled fast breeder reactor materials selection. The primary material presently under investigation is AISI 348 stainless steel, a niobium-stabilized austenitic alloy. By means of certain thermomechanical treatments, precipitation of niobium carbide can be caused to occur in association with extrinsic stacking faults. The extensive NbC precipitation that takes place not only enhances the elevated-temperature tensile and creep properties of the material but also provides a very high concentration of sinks and traps for point defects. The existence of a highly specific sink for vacancies appears to sufficiently alter the normal void-nucleation-and-growth scheme so that it may be possible to suppress void formation completely. Screening experiments utilizing high-energy heavy-ion bombardment have demonstrated the effectiveness of the microstructure of thermomechanically treated 348 stainless steel in reduction of the tendency for swelling. Neutron-irradiated specimens have been examined recently, and these results are also presented.

Volume expansion, or swelling, of nonfissile core components in liquid-metal-cooled fast breeder reactors (LMFBRs) is a potentially serious problem in the development of commercial LMFBRs for electric-power generation. At this time, adequate consideration of swelling in design can apparently circumvent most of the service problems due to swelling. In fact, some fuel designers have suggested that a certain limited amount of swelling may be beneficial in the case of stainless-steel fuel cladding. The complete elimination of swelling effects, however, is still desirable, and work is in progress at a number of AEC laboratories with the goal of identifying a cladding/structural material which is resistant to swelling and has satisfactory elevated-temperature mechanical

properties. For near-term LMFBR application, the material should be a product of current technology.

A material under investigation for this purpose at Hanford Engineering Development Laboratory (HEDL) is AISI 348 stainless steel, a niobium-stabilized austenitic alloy with typical composition as shown in Table 1. By

TABLE 1
NOMINAL COMPOSITION OF 348 STAINLESS STEEL

Element	Fe	Ni	Cr	Nb	C	Mn	Si
Concentration, wt. %	Bal.	10.5	18.0	0.60	0.04	1.1	0.5

means of certain specific thermomechanical treatments (hereafter referred to as TMT), precipitation of NbC can be caused to occur in association with extrinsic stacking faults in this alloy, by a mechanism described by Silcock and Tunstall.¹ Briefly, the process involves the dissociation of a sessile perfect dislocation into Frank and Shockley partials separated by an extrinsic stacking fault. Nucleation of NbC precipitates occurs at the Frank partial; the volume expansion due to precipitation of NbC is accommodated by vacancy emission from the Frank partial, which then climbs around the NbC particle. New NbC particles then nucleate at the Frank partial, and the process is repeated, resulting eventually in a substantial concentration of stacking faults decorated with NbC particles. Additional NbC precipitation occurs at dislocations and at isolated sites in the austenite matrix. A typical microstructure of TMT 348 stainless steel is shown in Fig. 1. The extensive NbC precipitation that takes place not only enhances the elevated-temperature tensile and creep properties of the material but also provides a very high concentration of sinks and traps for point defects. The extrinsic faults should function as surface sinks for vacancies, with a normal stacking-fault concentration providing the capacity for absorption of some 10^{20} vacancies/cm³. Although this quantity is rather small in comparison with the total number of vacancies produced during a high-fluence fast-neutron irradiation, it may still be possible to suppress void formation through alteration of the normal defect-nucleation-and-growth scheme. The precipitates at isolated sites in the matrix are also expected to play an important role. Helium bubbles have been reported² to form on matrix NbC precipitates during 600°C neutron irradiation; a high density of such precipitates should serve to trap a significant portion of the helium generated by (n,α) reactions and thereby reduce the extent of grain-boundary helium agglomeration and consequent embrittlement. This paper presents the results of irradiation experiments intended to establish the effectiveness of the TMT microstructure in the suppression of void formation.

Fig. 1 Representative microstructure of TMT 348 stainless steel.

EXPERIMENTAL

Specimens of commercial AISI 348 stainless steel were thermomechanically treated to produce various microstructures that may be generally classified as either containing a high concentration of NbC-precipitated stacking faults or

containing a high density of dislocations decorated with NbC precipitates, with few stacking faults present. The thermomechanical treatments basically involve a high-temperature solution anneal (1 hr at 1300°C) followed by water quenching. The specimen is then stress-aged at 700°C for 1 hr or less, unloaded, and then aged for several days at 700°C. The stress-aging treatment produces the desired nucleation sites for NbC precipitation, and it is through control of the stress (or, more precisely, strain) during this treatment that the final microstructure is controlled. Strains of 2 to 3% result in a maximum concentration of stacking faults, but strains in excess of 7% or so produce only NbC-decorated dislocations with no stacking-fault formation.

Two irradiation methods were employed, heavy-ion bombardment and fast-neutron irradiation. The heavy-ion irradiations were conducted with the tandem Van de Graaff accelerator at Ion Physics Corporation, using 5 MeV Ni^{2+} ions with a flux of about 10^{13} ions/(cm²)(sec). Two types of TMT microstructures were subjected to heavy-ion bombardment: (1) a high density of dislocations copiously decorated with NbC precipitates and (2) a moderately high density of NbC-precipitated stacking faults. The fast-neutron irradiations were carried out in pin B-40 in row 2 of the Experimental Breeder Reactor II (EBR-II), with a nominal peak fluence of 3×10^{22} neutrons/cm² ($E > 0.1$ MeV). The TMT 348 stainless-steel specimens irradiated in pin B-40 were prepared almost 2 years prior to the preparation of the ion-bombarded specimens and thus represent a more primitive-type TMT, with a microstructure consisting of NbC-decorated dislocations and a low density of stacking faults. After irradiation, the specimens were thinned and examined by means of conventional transmission electron microscopy.

RESULTS

The first screening experiment utilizing high-energy heavy-ion bombardment was carried out at an irradiation temperature of 375°C, with a 5-MeV Ni^{2+} ion fluence of 1×10^{16} cm⁻². The resultant microstructure is shown in Fig. 2. The stacking faults have disappeared, as evidenced by the absence of the typical stacking-fault fringes; the characteristic bands of NbC precipitates remain to mark the original location of the faults. The remaining resolvable irradiation-produced defects have agglomerated into small clusters, probably Frank-type dislocation loops. The same irradiation conditions produce somewhat larger Frank loops, both interstitial and vacancy types, in 316 stainless steel. Subsequently TMT 348 stainless-steel specimens were bombarded at 625°C to an ion fluence of 3×10^{16} cm⁻². A specimen containing no stacking faults was found to have a void concentration of about 5×10^{13} cm⁻³, with void diameters in the range 80 to 250 Å. No dislocation loops, faulted or perfect, were observed. A specimen containing stacking faults, on the other hand, had a much lower void concentration, less than 5×10^{12} cm⁻³; in this case the voids were

Fig. 2 Microstructure of TMT 348 stainless steel after bombardment at 375 °C to an ion fluence of $1 \times 10^{16} \text{ Ni}^{+2} \text{ cm}^{-2}$.

slightly larger, with diameters in the 100 to 300 Å range. The voids appear in areas approximately midway between adjacent stacking faults, as seen in Fig. 3. The faults themselves have been removed, and the NbC precipitates that formed on the faults have coarsened considerably. For comparison purposes the

Fig. 3 Voids in ion-bombarded TMT 348 stainless steel; $3 \times 10^{16} \text{ Ni}^{2+} \text{ cm}^{-2}$ at 625°C .

microstructure of a solution-annealed 316 stainless-steel specimen bombarded under the same conditions is shown in Fig. 4. The void-volume fraction in 316 stainless steel is approximately 500 times as great as that in TMT 348 stainless steel. Evidence that may clarify the mechanism by which the retardation of void

Fig. 4 Voids in ion-bombarded solution-annealed 316 stainless steel; 3×10^{16} $\text{Ni}^{2+} \text{ cm}^{-2}$ at 585°C .

formation occurs in TMT 348 stainless steel is provided by Fig. 5. The bands of NbC precipitates (i.e., original stacking-fault locations) are surrounded by dense tangles of dislocations, apparently resulting from the preferential nucleation (and subsequent growth and interaction) of dislocation loops in these regions.

Fig. 5 Dislocation tangles resulting from loop interactions in ion-bombarded TMT 348 stainless steel; $3 \times 10^{16} \text{ Ni}^{2+} \text{ cm}^{-2}$ at 585°C .

The results of the neutron-irradiation experiment are largely incomplete and certainly less than encouraging. No voids were detected in a specimen irradiated at 600°C ; however, at an irradiation temperature of 500°C , a substantial concentration of voids was observed, as shown in Fig. 6. The void-volume

Fig. 6 Microstructure of neutron-irradiated TMT 348 stainless steel; 3×10^{22} neutrons/cm² at 600°C.

fraction in this case is about 0.8%. The voids are generally associated with rather coarse NbC precipitates in the matrix. There are also needle-like (Fe, Cr) sigma-phase precipitates evident in the matrix, and the NbC precipitates at the stacking faults do not appear to have coarsened significantly. There are no dislocation loops present, and the original stacking faults have disappeared.

DISCUSSION

The results of the heavy-ion-bombardment experiments indicate great promise for TMT 348 stainless steel as a swelling-resistant alloy for LMFBR applications. The microstructure functions in the intended manner, with the NbC-precipitated stacking faults acting as vacancy sinks. The existence of a preferential sink for vacancies, at least during the critical initial stage of irradiation, is quite the opposite of such conventional fast breeder reactor materials as cold-worked 316 stainless steel, which initially contains sinks that are highly specific for self-interstitials. Current theories³ of void formation demand a biasing effect in which interstitials are preferentially absorbed at sinks; with TMT 348 stainless steel, the bias is reversed. A plausible mechanism for the irradiation behavior of TMT 348 stainless steel containing a high concentration of stacking faults and a low dislocation density would thus first involve the absorption of vacancies at stacking faults, with those interstitials escaping recombination clustering to nucleate Frank loops. At the same time, vacancies drifting to the stacking faults may be attracted to the small NbC particles and serve to relieve the compressional strain at those sites, permitting further growth of the precipitates. Interstitial Frank-type loop growth continues, with eventual interaction between loops and the formation of continuous tangles. Unfaulting of the loops may occur at some stage in the growth process. Subsequent vacancy and interstitial production may well lead to void formation, since the vacancy sinks are saturable and the microstructure develops into a type that provides biased interstitial absorption. A process of regeneration of the stacking faults would, of course, be highly desirable, and work is in progress to achieve such a system. The effect of helium such as generated in fast reactor irradiation remains an unknown in these heavy-ion-bombardment experiments; subsequent screening irradiations of TMT 348 stainless steel will be conducted with specimens containing helium.

The results of the EBR-II irradiation of TMT 348 stainless steel provide some contrary evidence on the swelling resistance of this material. However, it should be reemphasized that the results are incomplete and that the material itself does not represent the current state-of-the-art development in processing of the alloy. Failure of the material to retard void formation at the lower irradiation temperature may be attributed to three factors: (1) the stacking-fault density was too low; (2) the dislocations introduced during stress aging provided suitable sinks for interstitial atoms, thus biasing the defect nucleation scheme in favor of void formation; and (3) the initial solution-annealing temperature was too low, leaving excess niobium and carbon available for dissolution and reprecipitation during irradiation. These radiation-induced precipitates may have been influential in void nucleation.

A final critical evaluation of the usefulness of TMT 348 stainless steel as an LMFBR material must await the results of EBR-II irradiation of the optimum alloy microstructure. These specimens will not be available, however, until early

1972; meanwhile, heavy-ion-bombardment experiments will be conducted to determine whether breakaway swelling occurs at higher fluences.

CONCLUSIONS

Thermomechanically treated 348 stainless steel offers some promise as a swelling-resistant material for LMFBR applications. Heavy-ion-bombardment experiments conducted with the optimum alloy microstructure have demonstrated that the defect nucleation-and-growth scheme typical of the common austenitic steels is completely altered in this material. Fast-neutron-irradiation experiments, however, indicate that the TMT microstructure may only postpone the onset of void formation to a higher fluence level. The EBR-II irradiation results point out the importance of a high vacancy-sink (i.e., extrinsic stacking fault) density and the necessity for placing the alloy in a thermally stable state.

ACKNOWLEDGMENTS

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3. See, for example, *Irradiation Effects on Structural Alloys for Nuclear Reactor Applications*, American Society for Testing and Materials, Special Technical Publication No. 484, 1971.

DISCUSSION BY ATTENDEES

Kulcinski: Is it fair to compare ion-bombardment and neutron-irradiation results at identical temperatures when the displacement rates are some four orders of magnitude different? (That is, there is probably a shift in the "effective" irradiation temperature of the ion-bombardment results to lower temperatures, R. Bullough and R. L. Perrin, ASTM-STP-484, 1970, p. 317.)

Laidler: Of course not. I am cognizant of the "temperature-shift" effect; the observation of an absence of voids in TMT 348 steel neutron irradiated at 500°C is comparable to the heavy-ion-bombardment results obtained at an irradiation temperature of 625°C. Specimens ion bombarded at 750°C will likely be

comparable to the 600°C neutron-irradiation results, but these specimens have not yet been examined.

Russell: Did you say that stacking faults are effective vacancy sinks?

Laidler: Yes. The experimental observation of disappearance of the extrinsic stacking faults on irradiation is thought to be good evidence of their effectiveness as sinks, since unfaulting must occur by climb of the Frank partial.

Bullough: It is not clear to me why vacancies should be attracted to the stacking faults. In any case, the important thing is to enhance the recombination.

Laidler: I agree that the most desirable structure for a damage-resistant material is one in which recombination predominates; hopefully that state can be achieved in this material via the process described in the paper.

Harkness: Is it not true that any such structure that you have developed can only be a short-term answer, since to work it must be annihilated by the radiation-produced vacancies? Introduction of recombination centers might be a longer-lasting solution to the problem.

Laidler: The sinks are saturable, and their period of effectiveness is relatively short; however, the production of a microstructure that promotes recombination may indeed be a result of the action of these sinks during the initial stage of irradiation. The $\Delta V/V$ value for the TMT 348 steel neutron irradiated at 600°C is not as great as has been observed in some other stainless steels irradiated under similar conditions, so the microstructure was effective to some extent. Further improvement is expected with more advanced thermomechanical treatments. An ideal situation would be one in which the vacancy sinks are regenerative, but this is not likely to be achieved with a carbide-precipitation process.

Rowcliffe: Did you observe interstitial loops in your stacking-fault-containing steels after irradiation?

Laidler: None whatsoever.

McElroy: You emphasized precipitates (with carbon) as sites for void formation. Could local helium from carbon (n, α)'s, because of its increased concentration in precipitates, be influencing the formation of voids at these sites?

Laidler: I would expect this to be a second-order effect. At any rate, it would be almost impossible to differentiate such a mechanism from the other contributing factors.

Young: What are the findings in neutron- and ion-irradiated steels about vacancy loops? Are they found at low dose? At high dose?

Laidler: Dr. Bloom of Oak Ridge National Laboratory has identified faulted loops in neutron-irradiated 304 stainless steel as interstitial in nature. In ion-bombarded 316 stainless steel, I have observed mixed populations of vacancy- and interstitial-type Frank loops at irradiation temperatures of 425°C and below at damage levels up to 10 displacements per atom. At higher irradiation temperatures and higher damage levels, the loops are solely of the interstitial type.

HELIUM PRODUCTION IN STAINLESS STEEL AND ITS CONSTITUENTS AS RELATED TO LMFBR DEVELOPMENT PROGRAMS

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ABSTRACT

It has been well established that helium produced by various nuclear reactions can severely limit the ductility of austenitic stainless steels at certain elevated temperatures and that, in the presence of a high fast-neutron flux, helium atoms can serve as nuclei for void formation. The critical importance of void formation to the development of liquid-metal-cooled fast breeder reactors has increased the need to know rates of helium production in fast-neutron environments. This paper compares the helium concentrations measured in numerous alloys and pure elements irradiated by several laboratories in widely differing neutron spectra. It is shown that the rate of helium production and which elements contribute to this rate depend very much on the shape of the neutron spectrum. Nickel is one of the major contributors of helium in stainless steels irradiated in fast-neutron spectra. In thermal-neutron spectra, nickel and its reaction products are responsible for huge amounts of helium at fluence levels above $\sim 10^{22}$ neutrons/cm². Helium-production curves for stainless steel and its constituents are presented to provide a basis for correlating radiation-effects data.

It has been well established that helium formed by various (n,α) reactions can severely limit the ductility of austenitic stainless steels at temperatures greater than half the melting-point temperature and that, in the presence of a high fast-neutron flux, helium atoms can serve as void nuclei.¹⁻⁶ It appears, however, that hydrogen, which can be formed by (n,p) reactions, does not significantly affect mechanical properties or void formation, presumably because of its high solubility and high mobility.⁷ As a factor causing dimensional instabilities, void formation has become a critical problem that must be taken into consideration in the development of liquid-metal-cooled fast breeder reactors (LMFBRs).⁸⁻¹² Because of the importance of these effects, it is essential to know the rate of helium production in various materials irradiated in fast-neutron environments.

In thermal reactors the major sources of helium in stainless steel are thought to be (n,α) reactions with boron, nitrogen, and certain reaction products of nickel, such as ^{59}Ni and ^{58}Co .^{13-16,21,25} In fast reactors, on the other hand, depending on the shape of the neutron-flux spectrum, the production of helium and hydrogen appears to be dominated by primary (n,α) and (n,p) reactions with Ni, Fe, Cr, and such impurities as nitrogen and boron.^{14-24,26,27} Such other gases as neon and argon can be produced from various nuclear reactions with Mg, Na, Ca, and K impurities, although in amounts presumed to be small compared with helium and hydrogen.

Considerable uncertainties persist in the energy-dependent (n,α) cross sections for most of the important elements in stainless steel. Care must be exercised, therefore, in using such cross sections for predicting helium production for the neutron environments expected in the Fast Test Reactor (FTR) and in future LMFBRs.¹³⁻²⁷

Programs have been under way at the Hanford Engineering Development Laboratory (HEDL) and at Atomics International (AI) to determine both spectrum-averaged "integrated" (n,α) cross sections and energy-dependent (n,α) cross sections.^{18-24,27,31-34} This is being accomplished by irradiating alloys, compounds, and pure elements in a variety of neutron environments during dosimetry tests, which provide the necessary flux-spectral data, and by measuring the resulting helium concentrations by high-sensitivity mass spectrometer.

This paper presents preliminary results of this work. First, there is a discussion of the importance of neutron energy and how changes in neutron spectrum can be correlated with helium production and void formation. A number of evaluated data curves for calculating helium-production rates in thermal- and fast-neutron environments are then presented. The "Experimental Data" section includes the experimental results of this work and combines them with those of other laboratories to obtain the helium-generation curves, which are then used in the section entitled "Calculation of Helium Production" to obtain integral (n,α) cross sections.

HELIUM PRODUCTION AND VOID FORMATION

Neutron-Flux Spectra

A number of studies of helium-generation rates in structural and fuel-cladding materials¹⁴⁻²⁷ have shown that it is important to consider neutron-spectrum differences while analyzing irradiation test results. One of the best methods of extrapolating measured helium concentrations from materials irradiated at one reactor condition to materials in another neutron environment is by combining energy-dependent neutron fluxes with energy-dependent (n,α) cross sections, the latter having been adjusted for consistency with integral as well as monoenergetic data.³¹⁻³⁴ The problem with this method at present is

Fig. 1 Thermal and fast reactor neutron spectra, arbitrarily normalized, with spectrum mean energies in brackets.

that far too little is known of the energy-dependent (n,α) cross sections of the elements that make up the alloys considered for LMFBFR use.

A few neutron spectra of current interest to the U. S. LMFBFR program are shown in Fig. 1 along with their mean neutron energies. Spectra for the FTR driver fuel,³⁷ grid plate,³⁸ and vessel wall³⁸ (which are typical of an LMFBFR) are included along with a core center and a blanket spectrum from the metal-fueled Experimental Breeder Reactor II (EBR-II).³⁹ For comparison it should be noted that the hardest core spectrum anticipated for most LMFBFRs has a mean energy in the range of 0.4 to 0.6 MeV. Spectra from two thermal reactors, the High Flux Isotope Reactor³⁵ (HFIR) and the Engineering Test Reactor³⁶ (ETR), are included because of the desirability of using thermal-reactor test data to provide low-energy base points that are useful for interpolating data to intermediate neutron energies. The Watt fission spectrum⁴⁰ provides a reference point for this and subsequent discussions.

It is most important to have consistent methods of specifying fluxes and fluences as a function of the environment (neutron energy) so as to compare and

correlate data obtained in various thermal and fast test reactors and to extrapolate these data to other power- and test-reactor applications. The integral-flux data for EBR-II and HFIR presented in this paper are based on multiple-foil data-reduction techniques^{3,5,39,45-47} that employ the SAND-II computer code⁴¹⁻⁴⁴ combined with reactor-physics calculations. Applications of these techniques have been described for other thermal and fast reactors,^{41-44,48} and they are currently being used by the Fast Reactor Materials Dosimetry Center⁴¹ (FRMDC) which has been established at HEDL to assist fuels and materials experimenters and reactor designers in defining the neutron environment in thermal and fast test reactors. Integral-flux data for environments other than EBR-II and HFIR have been inferred from the data presented by the experimenters using conversion factors presented in their reports and later in this paper.

The total 1 σ absolute uncertainties associated with the assigned integral-flux values for this study have been estimated to be 10 to 30% or less for most of the experimental data. For data from EBR-II^{39,45} and HFIR,^{35,46,47} the uncertainties are estimated to be 10 to 15% or less, and relative uncertainties between integral-flux values within a single facility should be even lower.

There are several neutron-flux parameters used for the correlation of irradiation effects and helium-production data. Fast flux effects are often correlated with flux or fluence above 0.1 or 1.0 MeV and on occasion above 3.68 MeV, whereas thermal flux effects are usually correlated with the measured equivalent 2200 m/sec flux, Φ_0 , or the calculated thermal flux less than some cutoff energy, such as 0.4 eV, $\Phi(<0.4 \text{ eV})$. Another convenient parameter for correlating EBR-II and other fast reactor data, and which is used extensively in this paper, is the neutron mean energy $\bar{E}$. Table 1 lists the values of most of these parameters for several locations in EBR-II and FTR, for the Watt fission spectrum, and for typical locations in the ETR and HFIR cores. These values are given to facilitate data handling and to emphasize the spectral changes that are encountered by fuels and materials irradiated in EBR-II and other fast reactors.

Definitions of normalized integral flux (flux fraction) and neutron mean energy are given by Eqs. 1 and 3.

$$\text{Flux fraction} \quad \Phi(>E) \equiv \int_E^{\infty} \phi(E) \, dE \quad (1)$$

where $\phi(E)$ is the differential neutron flux [neutrons/(cm²)(sec)(MeV)]

and

$$\int_0^{\infty} \phi(E) \, dE = 1 \text{ neutron}/(\text{cm}^2)(\text{sec}) \quad (2)$$

$$\text{Neutron mean energy} \quad \bar{E} \equiv \int_0^{\infty} E \phi(E) \, dE / \int_0^{\infty} \phi(E) \, dE \quad (3)$$

Figure 2 is a side view of the EBR-II reactor, which has been utilized to obtain a large fraction of the helium-generation data discussed in this paper.

TABLE 1
MEAN NEUTRON ENERGIES AND FLUX FRACTIONS

Environment	Coordinates (r,z), cm	Measured or calculated flux fraction				$\bar{E}$ (MeV)
		<0.4 eV	>0.1 MeV	>1.0 MeV	>3.68 MeV	
EBR-II						
Core center A*	(4,2)	<10 ⁻⁸	0.88	0.26	2.9 × 10 ⁻²	0.82
Core region B	(13,2)	<10 ⁻⁸	0.86	0.26	2.9 × 10 ⁻²	0.82
Core edge C	(4,18)	~10 ⁻⁷	0.78	0.17	1.8 × 10 ⁻²	0.62
Inner blanket D	(34,2)	<10 ⁻⁸	0.77	0.12	1.5 × 10 ⁻²	0.50
Upper blanket E	(10,33)	1.4 × 10 ⁻⁵	0.61	7.2 × 10 ⁻²	5.5 × 10 ⁻³	0.35
Inner blanket F	(34,57)	1.8 × 10 ⁻⁵	0.40	1.8 × 10 ⁻²	9.1 × 10 ⁻⁴	0.16
FTR						
Driver fuel	Typical	<10 ⁻⁸	0.63	0.13	1.6 × 10 ⁻²	0.48
Grid plate	Typical	0.002	0.12	3.2 × 10 ⁻⁴	2.2 × 10 ⁻⁷	3.2 × 10 ⁻²
Core barrel	Typical	0.005	9.1 × 10 ⁻²	7.0 × 10 ⁻⁵	3.5 × 10 ⁻⁸	2.6 × 10 ⁻²
Core vessel	Typical	0.043	5.7 × 10 ⁻³	6.2 × 10 ⁻⁷	2.6 × 10 ⁻⁹	2.3 × 10 ⁻³
ETR core	Typical	0.36†	0.29	0.17	3.0 × 10 ⁻²	0.51
HFIR core	Typical	0.47†	0.24	0.13	2.2 × 10 ⁻²	0.38
Fission	Watt form ⁴⁰	0.000	0.986	0.692	1.35 × 10 ⁻¹	2.0

*Locations are identified by these letters in Fig. 2.

†The 2200 m/sec equivalent thermal-neutron flux, Φ_0 , is related to the thermal flux less than 0.4 eV by $\Phi (<0.4 \text{ eV}) = 1.2\Phi_0$ (Eq. 4).

Fig. 2 Location of pure element capsules in EBR-II during Run 31F and positions for flux-spectral data given in Table 1.

Locations of capsules containing pure elements irradiated during the Run 31F dosimetry test, and positions corresponding to the flux-spectral data presented in Table 1, are identified.

For consistency and proper correlation of thermal-reactor data, it is important to use the equivalent 2200 m/sec thermal-neutron flux, Φ_0 . If a flux monitor such as cobalt with a $1/v$ response is used, Φ_0 is obtained directly by dividing the measured value of the cadmium-difference-saturated activity by the 2200 m/sec thermal cross-section value (37.2 barns).

The thermal flux that usually results from reactor-physics calculations and from SAND-II^{4,2} code multiple-foil calculations is the flux for all neutrons less than 0.4 eV. To account for this requires that the SAND-II values therefore be corrected to the equivalent 2200 m/sec thermal value (Φ_0) by the relation

$$\Phi_0 = \frac{\sqrt{\pi}}{2} \left(\frac{T_0}{T} \right)^{1/2} \Phi(<0.4 \text{ eV}) \quad (4)$$

where T_0 equals 293°K for neutrons in thermal equilibrium at 20°C and T is the bulk temperature of the reactor moderator. A similar relation applies for fast reactor-physics calculations, but without the factor of $\sqrt{\pi}/2$. Both of these relations assume that a true Maxwellian thermal flux exists and that the

Fig. 3 Measured variation of mean neutron energy with reactor position in EBR-II for Run 31F.

absorption, of neutrons in the flux monitor or reactor moderator follows a $1/v$ law, conditions only approximately met for most test-reactor applications.

Figure 3 provides a convenient means of comparing EBR-II irradiation data from various laboratories with the data reported in this paper. Four curves showing the relation between mean energy $\bar{E}$ and reactor position coordinates (r, z) are given for approximate conversion between position and mean energy. Figure 4 presents curves that show the relations between two flux fractions and mean energy ($\bar{E}$) in EBR-II.* Using Fig. 4, we can therefore convert, for example, the EBR-II data correlated against flux (>0.1 MeV) so as to correlate against mean energy $\bar{E}$, or against flux (>3.68 MeV).

*This single set of curves will give only approximate estimates of these flux fractions, within about 10 to 30%, depending on the mean neutron energy. More precise values, which reflect the effects of asymmetry, boundaries, etc., within EBR-II, are available from the FRMDC.

Fig. 4 Curves to convert flux fractions to mean energy in EBR-II. *Values given are only approximate since a single curve does not exist for all EBR-II spectra, i.e., to within about 10 to 30%, depending on the mean energy.

Material Composition Effects

It is obvious that the rate of helium production in any alloy depends on the concentration of those elements contributing significantly to the production, whether they be major or minor constituents. Table 2 lists compositions of some austenitic stainless steels where it can be seen that considerable variations in concentration exist, especially among the rather large number of trace elements usually present. Although variations in composition will affect the absolute amounts of helium generated, inhomogeneities of elements with high (n, α) cross sections will correspondingly affect the spatial distribution of the gases. Ljungberg²⁶ and others have pointed out that very high helium concentrations may be achieved in the vicinity of inclusions and grain boundaries that contain elements with high (n, α) cross sections. Mastel⁴⁹ and Woodford et al.⁵⁰ saw this when they observed halos of helium bubbles around boron oxide particles in irradiated materials.

Because nitrogen has a relatively large (n, α) cross section for fast reactor neutron spectra, interest has centered around the behavior of this element under reactor conditions. Recently, Bagnall et al.⁵¹ found considerable enrichments of nitrogen near the surfaces of newly received 304 and 316 stainless steels. After

TABLE 2
COMPOSITION OF SOME AUSTENITIC STAINLESS STEELS

Element	Composition, wt. %		
	300 series	EBR-II control- and safety-rod thimbles	Typical FTR cladding ^{6,7}
B	<0.005	<0.0005	0.001 (max.)
C	<0.3	0.07	0.04–0.06
N	<0.05	0.029	0.01 (max.)
O	<0.02		
Al	<0.01		0.05 (max.)
Si	<1.5	0.52	0.75 (max.)
P	<0.02	0.015	0.02 (max.)
S	<0.02	0.013	0.01 (max.)
Ca	<0.1		
Ti	<0.5		0.01 (max.)
V			0.2 (max.)
Cr	16–26	18.5	17–18
Mn	<2	1.11	1.5–2
Fe	Balance	70.1	Balance
Ni	6–22	9.4	13–14
Co			0.05 (max.)
Cu	<0.2	0.16	0.1 (max.)
As			0.03 (max.)
Nb	<1.0		0.05 (max.)
Mo	2–3	0.10	2–3
Sn	<0.01		
Ta			0.02 (max.)

exposure to hot flowing sodium, however, and depending on the temperature, the surfaces could become depleted in nitrogen. Farrar^{5,2} found that milligram-size specimens of iron irradiated under vacuum for 8 days at the EBR-II core center at a temperature between 450 and 700°C lost virtually all their nitrogen, whereas higher concentrations of nitrogen in specimens of 304 stainless steel under similar conditions became depleted by approximately 20%.

In another experiment, Dudey, Harkness, and Farrar^{2,4} reported nitrogen and helium gradients along the length of a highly irradiated EBR-II stainless-steel safety-rod thimble. The helium concentrations above core midplane were up to 2.4 times those measured an equal distance below core midplane. The corresponding nitrogen gradient of 45% appeared insufficient in magnitude (at least at the time of measurement) to explain all the helium gradient. This led the authors to point out the possibility of additional trace elements with high (n, α) cross sections becoming enriched at the core center and regions above it. The important observation made, however, was that future LMFBRs will operate at

higher temperatures than those in EBR-II, so that if these enrichments were temperature-dependent they could well be enhanced.

The conclusion to be drawn is that, in any neutron spectrum where a significant fraction of the helium is produced by neutron reactions with impurity elements, it is very important, when one is calculating helium production, to consider impurity spatial variations not only before but also during the irradiation. The latter determination unfortunately can only be approximated by postirradiation examination.

Neutron Spectral Effects on Helium Production

Studies have shown that helium can significantly influence the development of voids and that their number and size depend critically on the helium content.^{6,12} Therefore it would be useful to have on hand helium concentrations expected in stainless steel after different neutron exposures. To obtain that information requires that the neutron-energy dependence of helium production be taken into account.

Effects of variation of neutron-spectrum mean energy $\bar{E}$ upon helium production are illustrated in Fig. 5. The two curves were obtained from measurements to be presented later in Table 4 of helium in Cr, Fe, Ni, and 304 stainless steel irradiated at several core and blanket locations in EBR-II (see Fig. 2). Since all the specimens were irradiated for the same period of time (Run 31F), the total neutron fluences at the different locations were not the same. Therefore, in order to study the effect of changing neutron mean energy, the helium concentrations at the outer locations have been renormalized to values for the same total fluence. Accordingly all points were recalculated for the total neutron fluence received by the row 4 center sample, 1.3×10^{21} neutrons/cm². The lower curve in Fig. 5 was determined by measurement of the helium in specimens of pure Cr, Fe, and Ni and weighting these concentrations according to the proportion of these elements in 304 stainless steel.

A comparison of this and the upper curve, which was obtained by direct measurements of helium in 304 stainless steel irradiated at the same locations, shows that for the lowest mean energies most of the helium is produced from impurities, whereas for the higher mean energies it comes principally from Cr, Fe, and Ni.

Figure 6 again illustrates the dependence of helium production on neutron energy. Here, EBR-II helium-concentration data from a number of different laboratories have been likewise renormalized to a total neutron fluence of 1.3×10^{21} neutrons/cm² for comparison with the stainless-steel curve obtained from Fig. 5. The scatter in the experimental data in Fig. 6 is attributed not to experimental uncertainties in the measurement of helium but, rather, to differences in the stainless steels and in their impurity contents and to possible migration effects. Mass transfer and differences in nitrogen content as a function of depth in stainless steel could also have affected the helium-production rates in

Fig. 5 Spectral effects of helium production for a constant total fluence ($>10^{10}$ MeV) of 1.3×10^{21} neutrons/cm². Helium concentrations in 304 stainless steel as a function of mean neutron energy obtained from measurements of helium during EBR-II dosimetry test, Run 31F. Note: For the lowest mean energies, most of the helium is produced from impurities, whereas for high mean energies, it comes principally from the major constituents of the stainless steel.

the different samples.^{24,51} Nevertheless, the one curve in Fig. 6, seems to represent reasonably well the trend in the data from the different experiments.

Neutron Spectral and Fluence Effects on Void Formation

Experiments using charged particles have shown that voids will develop in stainless steel without the presence of helium; however, their number and size depend critically on the helium content.⁶ Accelerator and reactor studies have shown^{6,12} that the influence of helium can become significant once its concentration exceeds about 1 at. ppM. In general, the studies suggest that, broadly speaking, helium will play an important, although changing, role in void nucleation and growth as its concentration increases above 0.1 at. ppM. Figures 5 and 6 show that helium concentrations of this level are typically reached in

Fig. 6 Spectral effects of helium production for a constant total fluence ($>10^{20}$ MeV) of 1.3×10^{21} neutrons/cm². Measured helium contents of stainless steels irradiated in EBR-II to total fluences up to 7×10^{22} neutrons/cm². *Composition of guide thimbles is shown in Table 2, and each data point has been renormalized to a total fluence of 1.3×10^{21} neutrons/cm² for comparison with this work (Run 31F).

stainless steels irradiated in the EBR-II core center ($\bar{E} \approx 0.8$ MeV) to total neutron fluences of $\sim 4 \times 10^{20}$ neutrons/cm². For softer neutron spectra like those anticipated for FTR and LMFBRs, with neutron mean energies less than 0.5 MeV (see Fig. 1 and Table 1), irradiation to fluences greater than $\sim 1 \times 10^{21}$ neutrons/cm² will be required to obtain the 0.1 at. ppm helium level.

In a test reactor such as EBR-II, materials will be exposed to less and less energetic neutron spectra at greater axial distances from the reactor midplane. This is demonstrated clearly in Fig. 3, where neutron mean energies drop from

Fig. 7 Estimated density change and helium content for a 304 EBR-II stainless-steel safety-rod thimble irradiated at $450 \pm 30^\circ\text{C}$ vs. fluence. Data points are from specimens taken from different axial positions. The approximate mean energies of these positions are given by the right ordinate scale.

- , PNL density data
- , ORNL density data
- △, ANL density data
- , Curve fit to density change vs. fluence data
- , Fluence vs. mean neutron energy curves to achieve different levels of helium in stainless steel

~ 0.8 to ~ 0.1 MeV over a distance of 75 cm. Figure 5 shows that such differences in spectrum will result in significantly different helium-generation rates and helium spatial heterogeneities, depending on whether the helium comes from the major constituents or the impurities. Because, at the same time, the atom displacement rate will be changing differently, the ratio of helium concentration to the number of displacements will also change with axial position. Thus significant differences in the size and distribution of voids¹¹ might be expected at different axial locations, if not differences in their macroscopic volume and in the mechanism of their development.

The change in helium content of stainless steel is illustrated in Fig. 7, which shows data from an EBR-II row 3 safety-rod thimble that exhibited neutron-induced volume changes⁵⁴ varying up to $\sim 4\%$. The data points and the solid curve relate the density change to the fast-neutron fluence (>0.1 MeV) for 10 specimens taken at different axial positions from this component. For each point the neutron mean energy was found from Fig. 3 and is shown approximately by the right ordinate scale. Also in Fig. 7 are three dashed curves showing the fluences required to generate helium concentrations of 0.1, 1, and

10 at. ppM. These three curves were obtained from Fig. 5 and are plotted in Fig. 7 as a function of neutron mean energy. The approximate helium content of a specimen for a specific density change can therefore be obtained from the intersection of the solid curve with one of the family of dashed curves. For example, the data points with mean neutron energies of ~ 0.7 MeV had ~ 10 at. ppM helium, mainly from Cr, Fe, and Ni, whereas the specimen with the lowest mean energy ($\bar{E} \approx 0.2$ MeV) had only ~ 0.3 at. ppM helium, presumably coming mainly from such impurities as nitrogen and boron. Considering the possibility of large spatial variations of nitrogen, the helium content of the latter specimen could vary from this value by more than a factor of 3 over a depth of ~ 0.3 to 1 mm (~ 10 to 40 mils) with additional variations within a surface layer of ~ 0.04 mm (1.5 mils) due to recoil effects, as will be discussed in the subsection "Helium Diffusion and Recoil," page 210. It should be pointed out that the apparent relation shown in Fig. 7 between density change and neutron fluence can be misleading. Although the specimens with the higher density changes received the higher fast fluences, they also experienced harder spectra with higher mean neutron energies. Thus, even though macroscopic swelling may be reasonably well correlated with fast-neutron fluence (>0.1 MeV, for example),⁵⁵ this parameter will not provide a satisfactory correlation with void size and density which are influenced by helium content, which in turn is dependent on neutron-spectrum shape. Figure 7 is, nevertheless, a convenient way to illustrate the interrelations of fluence, helium content, and density change.

Figure 8 shows the change, as a function of mean neutron energy, in the relation between the number of helium atoms and the number of gross displacements in EBR-II irradiated stainless steel. Displacement damage rates were calculated using Doran's gross displacement damage function,⁵⁵ and the helium-production data were obtained from the experimentally determined Fig. 5. There are significant changes in the ratio of helium-atom to displacement-atom productions within the EBR-II core and blanket regions. It is believed that the effect of this change on void development has not yet been studied, since most property-change data have been correlated with fast fluence (>0.1 MeV)—a parameter rather insensitive to such changes.

It should be noted here that hydrogen, which can be generated by (n,p) reactions, has not been considered because it is not expected to contribute significantly to mechanical- or physical-property changes in stainless steel owing to its relatively high solubility and high diffusion rate at elevated temperatures.^{7,14,26}

The conclusion that may be drawn from this discussion is that the direct correlation of irradiation-effects data with a single irradiation parameter, such as fast fluence >0.1 MeV, is not always appropriate.⁵⁵ Correlations of void density and size distribution, total volume change, or loss in ductility at elevated temperatures, without taking into account differences in neutron spectrum and differences in displacement and helium-generation rates, may lead to improper

Fig. 8 Change of helium production per gross displacements as a function of mean neutron energy in EBR-II irradiated stainless steel.

damage modeling. This in turn could lead to improper extrapolation of data from thermal and fast test reactors to LMFBR conditions.

Helium-Production Rates

This section presents some empirical equations and evaluated data curves from which helium production in stainless steels may be estimated for environments of thermal and fast reactors. These estimates should be considerably more accurate than those of earlier studies^{14-16,19,24,27} because they include the important new experimental data^{5,13,21} on the effects of secondary as well as primary reactions with nickel. The data used and the derivation of these curves are given later in the "Experimental Data" section, but it seems appropriate here to discuss the results without all the supporting evidence because of the importance of helium production to the proper understanding of void formation and growth.

The production of helium (and sometimes hydrogen) in stainless steels irradiated in thermal and fast reactors has been discussed by Alter and Weber,¹⁶ DePino,¹⁵ Ljungberg,²⁶ Birss,¹⁴ Scherrer and Moteff,²⁷ and others. In fast

reactors it has been generally assumed that helium production is controlled primarily by fast-neutron-induced (n, α) reactions with Ni, Fe, and Cr and with certain impurities, such as nitrogen. This has been confirmed by several authors^{1,8-20,24} who agree that nickel is a major contributor of helium in stainless steels irradiated in a hard neutron spectrum, contributing more than iron to the helium production.

For thermal reactors, on the other hand, it was generally assumed until recently that the helium-production rate would be proportional to the thermal-neutron flux and to the boron content until a significant fraction of the ^{10}B had burned up. At a thermal-neutron fluence of $\sim 10^{21}$ neutrons/cm², the ^{10}B would effectively have been consumed and the helium production would then cease.^{1,4,15} Recent measurements by Brager and Robbins^{5,13} and by Weitman, Daverhög, and Farvolden²¹ have, however, shown anomalously high helium-production rates in stainless steel and nickel, respectively, irradiated in thermal reactors. The nonlinear increase in the production rate suggests that this could be due to (n, α) reactions with ^{59}Ni or ^{58}Co , which are formed from ^{58}Ni by (n, γ) and (n,p) reactions, respectively.²¹ Very recently, Kangilaski and Bauer²⁵ and Bloom and Farrar⁵⁷ found very large amounts of helium in stainless steels irradiated in the thermal reactors ETR and HFIR. Both values (2000 at. ppm helium in 347 stainless steel in ETR; 1800 at. ppm helium in 316 stainless steel in HFIR) are consistent with the trends noted by Weitman.²¹ Although there is evidence to suggest both of the reactions in the two-stage process take place with thermal neutrons, the possibility that one of them requires neutrons with higher energies has not yet been ruled out. These measurements of high helium concentrations were used along with other data in the subsection "Correlation of Thermal-Neutron-Induced Helium" (page 212) to obtain the helium-production rates to be discussed later in this section.

Although much is still unknown about the exact sources and cross sections for thermal- and fast-neutron helium production, the experimental measurements described above, and others given in more detail later,^{2,3,24,30,56} have dramatically increased the knowledge of effective rates of helium generation.

The helium-production rates deduced from data and curves in the subsections entitled "Helium Concentrations" (page 208), "Correlation of Thermal-Neutron-Induced Helium" (page 212), and "Correlation of Fast-Neutron-Induced Helium" (page 213) can be represented satisfactorily by two empirical equations.

In a thermal-neutron environment, the helium production in stainless steel and nickel is proportional to the nickel content and is related to the equivalent thermal-neutron fluence (Φt) by

$$\text{He (atoms/g of nickel)} = 9.8 \times 10^{-19} (\Phi t)^{1.68} \quad (5)$$

This equation is applicable for fluences ranging between $\sim 3 \times 10^{20}$ and $\sim 1 \times 10^{23}$ neutrons/cm².

TABLE 3
DATA FOR RATE OF HELIUM PRODUCTION IN A FAST REACTOR

Material and composition	Value of K for Eq. 6	Applicable range of fluence, neutrons/cm ² (>3.68 MeV)	
		Low	High
Iron*	3.2×10^{-5}	$\sim 10^{1.7}$	$\sim 10^{2.1}$
Chromium*	3.2×10^{-5}	$\sim 10^{1.7}$	$\sim 10^{2.1}$
Nickel*	3.7×10^{-4}	$\sim 10^{1.7}$	$\sim 10^{2.1}$
Stainless steel (from Fe, Cr, and Ni only†)	6.1×10^{-5}	$\sim 10^{1.7}$	$\sim 10^{2.1}$
Stainless steel (EBR-II central core region‡)	9.1×10^{-5}	$\sim 10^{1.9}$	$\sim 3 \times 10^{2.1}$
Stainless steel (EBR-II blanket region‡)	2.0×10^{-4}	$\sim 10^{1.7}$	$\sim 10^{2.1}$

*Data used to derive these values have not been corrected for possible impurity effects which, at least for nickel, are considered negligible.

†Amount of helium in stainless steel to come from Fe, Cr, and Ni alone, determined by measurements of helium in pure elements. The weighting assumed a composition of 71.5% Fe, 20% Cr, and 8.5% Ni.

‡Assuming composition shown in Table 2, column 3.

In a fast-neutron environment, the helium production in Fe, Cr, Ni, and stainless steel is related to the fast-neutron fluence ($\Phi t > 3.68$ MeV) by

$$\text{He (atoms/g of material)} = K \Phi t \quad (6)$$

Values of K and the applicable ranges of fluence corresponding to the ranges experienced by the data used to obtain the curves are given in Table 3.

Equations 5 and 6 are useful for roughly estimating the helium content of a material irradiated in some specified neutron environment. If more reliable estimates are required, variations in flux spectra and variations in stainless-steel composition must be considered. Other factors that could possibly affect helium concentrations include temperature of irradiation, mass transfer of impurities (before or during irradiation), precipitate formations, alpha-particle recoil, and diffusion of helium.

For the convenience of those engaged in the planning of irradiation-effects programs and in the correlation of experimental data for reactor-design applications, a set of helium-production curves is shown in Fig. 9 for stainless steels exposed to several neutron spectra of current LMFBR interest (see Fig. 1). These curves are based on data shown later in Figs. 11 to 13 (and represented by Eqs. 5 and 6) assuming a nominal stainless-steel composition, column 3 of

Fig. 9 Helium production in stainless steel for different reactor spectra.
 *Major elements only. Helium produced by nuclear reactions with Fe, Ni, and Cr only, composition as specified in Table 3. †Ref. 27.

Table 2. The helium-production curves in Fig. 9 are given as a function of total neutron fluence ($>10^{-10}$ MeV) for each environment and are extrapolated to a maximum total fluence of 10^{24} neutrons/cm². Conversion of total fluence to an equivalent fluence <0.4 eV, or fluences >0.1 MeV, >1.0 MeV, or >3.68 MeV may be accomplished by the use of Table 1 and Figs. 3 and 4.

Figure 9 also shows some recent estimates by Scherrer and Moteff²⁷ of the helium content of stainless steel for irradiations in the ETR, EBR-II, and DFR

(Dounreay Fast Reactor). The error bars show the limits of their estimates for very high fluences, based on the use of available measured spectral-averaged and energy-dependent cross sections. Except for ETR their estimates are reasonably consistent with, but somewhat lower than, those of this study. Their ETR prediction is much lower because the effects of thermal-neutron (n,α) reactions with nickel reaction products were not included. Helium-production curves have also been reported by Birss¹⁴ for stainless steels and Nimonic alloys with nickel contents ranging from 13 up to 45%. His results are reasonably consistent with those of this work for fast reactors. As with Scherrer and Moteff, however, his thermal-reactor calculations result in lower values than those shown in Fig. 9.

It should be emphasized that, although the predictions in Fig. 9 are extrapolated to a total fluence of 10^{24} neutrons/cm², the available experimental data are limited to total fluences less than $\sim 10^{23}$ neutrons/cm². Burn-in or burnout effects may become important for higher fluences, and these may increase or decrease the helium content. For instance, for a total fluence of $\sim 10^{23}$ neutrons/cm² in HFIR, between 10 and 80% of some of the major constituent and impurity isotopes of stainless steel could be consumed. Although most of these atoms will convert to other isotopes of the same element, the (n,α) cross sections of the new isotopes will be different from the parent isotope, with a resulting decrease or increase in helium-production rate.

On the basis of the production curves in Fig. 9, it appears that helium concentrations in stainless steel with the composition shown in Table 2, column 3, will not exceed ~ 300 at. ppM after exposures to $\sim 10^{24}$ neutrons/cm² ($>10^{-10}$ MeV) in the hardest EBR-II core spectrum ($\bar{E} \approx 0.8$ MeV). For the hardest FTR core spectrum ($\bar{E} \approx 0.5$ MeV), the corresponding value is ~ 150 at. ppM. Secondary reactions do not now appear to be significant sources of helium because of the relatively few low-energy neutrons in fast reactors. Even for the very soft grid-plate and vessel-wall spectra for FTR and LMFBRs, the thermal component of flux will be orders of magnitude lower than the core values of total flux. It therefore appears that studies involving the effects of helium for most LMFBR materials need not consider concentrations greater than ~ 150 at. ppM. Irradiations in such high-flux thermal reactors as HFIR can generate these amounts in a few months, but the ratio of helium production to displacement damage is two orders of magnitude larger than in fast reactors, making the irradiations not completely prototypical for void-nucleation studies.

EXPERIMENTAL DATA

Irradiation of Pure Elements

Many of the data used in the previous section for calculations of helium production were obtained from the authors' experimental irradiations of alloys and pure elements in several neutron environments.^{20,29,30} Accurate measurements by high-sensitivity mass spectrometer of very low levels of helium

resulting from the (n,α) reactions were combined with neutron-flux data obtained by the multiple-foil technique³⁹ to yield spectral-averaged and energy-dependent (n,α) cross sections.³¹⁻³⁴

Elements were selected to include as many as possible that appear in the various alloys considered for fast reactor use. Reactive elements and those with melting points less than 630°C were included in the form of higher melting-point compounds (CaF_2 , NaF , PbS). Future analysis of the helium in other fluorine compounds (FeF_2 , MnF_2), when compared with the amount of helium in pure Fe and Mn, will give the fluorine (n,α) cross section which will then be subtracted from the other data. Additional elements of interest, such as C, N, and O, were represented by crystals of ZrC , TiC , TiN , HfN , Al_2O_3 , and SiO_2 which were irradiated along with pure Zr, Ti, Hf, Al, and Si. Altogether, 30 pure elements and 23 compounds containing an additional 17 elements were included. Sixteen of the elements were represented in more than one form, and such representation will be useful in estimating the uncertainties in the technique.

Five separate capsules containing duplicate specimens of all these elements and compounds were irradiated for 8.25 days at 50 MW in EBR-II during the dosimetry test, Run 31F, in November 1968. The capsules were located as shown in Fig. 2 to give significant differences in neutron-flux-spectrum shape and were adjacent to multiple-foil flux-spectral sets. Another five capsules at nearby locations (not identified in Fig. 2) contained specimens of Fe, Ni, and Al wire which were also used for helium determinations. The multiple-foil sets, coupled with reactor-physics calculations (2DB code),³⁷ provided accurate flux-spectral data at each location.^{39,45} Other irradiations similar to this are in preparation, and much longer irradiations have been in progress since 1967.

Mass Spectrometry

The mass-spectrometer system involves no new concepts, but it does have refinements over other systems⁵⁻⁸⁻⁶¹ which have led to simplicity of operation and an ability to detect very low concentrations of helium in small specimens. Figure 10 shows the major features of the sample-handling system and the mass spectrometer. Determination of the helium content is made by weighing a small piece of the material and melting it in a resistance-heated tungsten coil under vacuum. Immediately after the ^4He is released, a precisely known volume of ^3He is added. After mixing of the isotopes, the gas passes over Zr-Ti alloy getters directly into the mass-spectrometer volume, which is isolated from its vacuum pumps for "static mode" operation. A measurement of the $^4\text{He}/^3\text{He}$ ratio and a knowledge of the weight of the material then produce the helium concentration. The low-level ^3He spike is obtained by successive expansions through calibrated volumes. A nearly constant mass discrimination of the mass spectrometer is repeatedly measured during each series of runs by analyzing a known mixture of ^3He and ^4He . At least one analysis of each material is made without the addition

Fig. 10 High-sensitivity gas mass-spectrometer system.

of the ^3He spike to determine the possibility of direct formation of this isotope by nuclear reactions. In all samples so far analyzed, including a wide variety of alloys, no ^3He has been detected, which indicates that $(n, ^3\text{He})$ reactions are far less frequent than (n, α) reactions. There is the possibility, however, that some ^3He is formed but is subsequently consumed through its high thermal-neutron (n, p) cross section for thermal-neutron irradiations.

The reproducibility of helium measurements at concentration levels above 10 at. ppB (10^{-8} atom fraction) generally has a 1σ standard deviation of about 2%. The absolute accuracy, determined from uncertainties in sample mass, spike size, and isotopic ratio measurement is approximately 3%. Analyses of milligram specimens with helium concentrations of less than 50 ppT (5×10^{-11} atom fraction) have been performed routinely with uncertainties of 10%, and improvements to lower this limit are being undertaken.

Preparation of specimens for helium analysis consists of cutting the sample to a size generally in the range of 1 to 10 mg. This is followed by etching to remove the surface layer that could contain nontypical concentrations of helium due to (n, α) reactions with surface impurities, such as nitrogen, and to recoil to and from adjacent materials.

Helium Concentrations

The helium concentrations of duplicate specimens of Fe, Ni, and Al wires from the 10 capsules are shown in Table 4 along with capsule locations and neutron flux (total and >3.68 MeV flux). Also shown are the results from Fe, Ni, and Cr pieces and results from 304 stainless-steel specimens cut from the capsule and subcapsule materials.

It is readily apparent from Table 4 that, with the exception of one chromium sample, there is close agreement between the results from duplicate specimens. The helium concentrations drop by more than two orders of magnitude from the row 4 center capsules (H41 and H43) to the row 7 outer capsules (H83, H84) as might be expected from examination of the neutron flux (>3.68 MeV). Helium concentrations in the iron pieces are systematically less than in the 0.5-mm-diameter wire specimens, and the reverse is true to a smaller extent in the nickel. Both of these trends can probably be attributed to the effects of impurities. Measurement of the nitrogen contents of the unirradiated iron and nickel wires by a new high-sensitivity gas-chromatographic technique⁵³ gave values of 690 and <14 at. ppM, respectively, but after the irradiation the nitrogen content of the iron was found to be less than 7 at. ppM.

In Table 4 it is interesting to compare the two sets of data from different heats of 304 stainless steel. Significantly more helium was found in the outer capsule material than in the inner subcapsule material for irradiation near the core center, but the trend is completely reversed at the outer locations. Analyses of the preirradiated outer-capsule stainless steel gave concentrations of boron and nitrogen of 2.6 at. ppM and 5150 at. ppM, respectively. After irradiation,

TABLE 4 HELIUM-CONCENTRATION DATA FROM EBR-II RUN 31F

Capsule No.	EBR-II coordinates (r,z), cm	Neutron flux, neutrons/(cm ²)(sec)		Helium concentration, 10 ⁻⁹ atom fraction*							
				Fe		Ni		304 S.S.		Al wire	Cr piece
		Total	>3.68 MeV	Wire	Piece	Wire	Piece	Subcap.	Outer		
H41	13.1, -1.83	1.83 × 10 ¹⁵	5.26 × 10 ¹³	100.9 102.5 98.0	96.4 98.6	1358 1367	1418	293 297	344 347		77.3 126.5
H43	13.1, +3.81	1.81 × 10 ¹⁵	5.20 × 10 ¹³	113.0 115.8		1350 1348		304 304	343	181 181 173	
H56	24.7, -1.83	1.35 × 10 ¹⁵	2.99 × 10 ¹³	64.9 63.3	67.6 59.8	790 790	798	170 178 180	183 183		59.2
H58	24.7, +3.81	1.33 × 10 ¹⁵	2.95 × 10 ¹³	62.8 62.0		770 768		173.0 174.6	183	103 103	
H71	33.6, -1.86	9.04 × 10 ¹⁴	1.07 × 10 ¹³	21.5 23.8	20.3	282 283	286	67.8 67.0	65.4 65.4	32.6	17.9
H73	33.6, +3.81	8.93 × 10 ¹⁴	1.05 × 10 ¹³	22.4 22.7		272 270		65.2 67.4	65.0	38.9 39.4	
H79	33.6, +37.39	3.43 × 10 ¹⁴	9.45 × 10 ¹¹	2.40 2.54 2.30	2.28 2.39	26.6 25.5	26.6 26.8	8.54 8.31	6.03 5.98	2.88	2.36
H81	33.6, +43.10	2.70 × 10 ¹⁴	5.61 × 10 ¹¹	1.48 1.44		13.9 14.7		4.64 4.28	4.22	2.11 2.24	
H83	33.6, +55.09	1.57 × 10 ¹⁴	1.87 × 10 ¹¹	0.420 0.465 0.454		4.57 4.26 4.06	4.47 4.33	2.35 2.64	1.71 1.98 1.60		
H84	33.6, +57.78	1.37 × 10 ¹⁴	1.44 × 10 ¹¹	0.34 0.37		3.59 3.31		1.60 1.66	1.23 1.02 1.00	0.59 0.64 0.80	

*For an irradiation of 8.25 days (7.13 × 10⁵ sec) at 50 MW.

the nitrogen in the outer-capsule material ranged from 5100 at. ppM at the outermost location to 4120 at. ppM at the core center. No such measurements have yet been made on the subcapsule material. Many of the results in Table 4 have already been discussed under "Neutron Spectral Effects on Helium Production" (page 196) in connection with Fig. 5, and further comments will be made in the subsection on "Correlation of Fast-Neutron-Induced Helium" (page 213).

Helium determinations were also made on specimens of seven other elements (B, Ti, V, Mn, Co, Cu, and Zr) at the row 4 center location. It is more convenient, however, to present these data later in Table 5 where they are used to calculate spectral-averaged (n, α) cross sections.

Helium Diffusion and Recoil

In any measurements of helium concentrations, especially in thin samples, the possibility of helium loss due to diffusion or recoil must be considered. In this work, however, it was felt that far too little was known to make useful corrections for these phenomena, and, instead, measures were taken to reduce their possible effects on the results.

Birss¹⁴ considered various effects that alpha-particle recoil could have on the surfaces of stainless steels exposed to several reactor coolants. He concluded that only a very thin surface layer of material [less than ~ 0.038 mm (1.5 mils)] would be affected and that, depending on the coolant, there would be a net gain or loss. For stainless steel in sodium, he estimated that more helium would escape and thereby deplete the surface helium concentration; but for CO₂-cooled or NaK-cooled reactors (such as the DFR), the opposite effect would occur. These phenomena could become important in experiments where (n, α) reactions occur in very thin foils and should be considered whenever very thin specimens like those for transmission-electron-microscope (TEM) studies might be taken from the surface of a cladding or structural material.

The possibility of helium loss due to recoil and diffusion has been considered by Freeman et al.¹⁹ and Weitman et al.,⁶² both groups having made helium measurements in irradiated materials with mass-spectrometer systems. Freeman et al., whose Fe, Ni, and Cr specimens were placed directly in the NaK coolant of DFR, noted no difference within experimental errors between helium concentrations before and after etching the surfaces. This was consistent with their calculations and the recoil calculations of Birss.¹⁴ They also found negligible loss of helium from nickel specimens heated to approximately 400°C following an irradiation at $\sim 300^\circ\text{C}$. Weitman et al.,⁶² on the other hand, have measured a significant diffusion loss from small cylinders of irradiated iron held at 500°C.

In the present work no experiments to specifically measure helium diffusion have yet been made, mainly because there has been considerable evidence to suggest that these effects have been usually, if not always, relatively in-

significant. However, the possibility of loss by diffusion was minimized because all pure-element specimens in this experiment were wrapped in gold foil to assure good thermal contact with the capsule walls for dissipation of heat produced by various nuclear reactions. Gold is considered not to be a significant source of helium itself because of a very small (n,α) cross section.¹⁷ The relatively short length of the irradiation (8.25 days) minimized the time that the samples experienced elevated temperatures. Recoil effects were also minimized by the etching of each specimen before analysis, a procedure designed mainly to remove surface impurities along with any excess helium that had come from them.

Comparisons of helium concentrations from the numerous milligram-size samples shown in Table 4, including the stainless-steel pieces and the wires and pieces of both iron and nickel with surface-to-volume ratios differing by as much as a factor of 5, have so far indicated no obvious differences.

Another interesting observation from Table 4 is that aluminum specimens from capsules H41 and H56 melted during irradiation, whereas the aluminum wires in nearby capsules H43 and H58 were recovered and analyzed for helium content. Even though the aluminum wires in the latter two capsules were probably very close to their melting points, they appear to have retained the amount of helium that would be expected from extrapolation of the results from the other capsules. The integrated (n,α) cross section obtained later in the section entitled "Calculation of Helium Production" from these data, moreover, agrees very well with the (n,α) cross section determined during the same experiment by radiochemical means. Although there is still a possibility that each aluminum specimen lost a few percent of its helium, it nevertheless suggests that other specimens with much higher melting-point temperatures probably fared even better.

It must be realized, of course, that lack of diffusion in one experiment does not preclude its occurrence in another. Diffusion will be affected by the occurrences of inhomogeneities, inclusions, grain boundaries, and dislocations. This is further complicated in a reactor environment by transport mechanisms associated with structural defects and the appearance of voids and bubbles filled or partly filled with helium and perhaps some other gases. Ljungberg²⁶ has speculated that the diffusion distance of helium before it precipitates in bubbles is dependent on the helium-generation rate and that this distance is extremely short if the helium concentration in solution is very high. The fact that the authors have measured 2000 at. ppm quantities of helium in stainless steels irradiated for many years at elevated temperatures suggests that, at least in these alloys, helium loss is probably small. With all this in mind and until further experiments have been conducted, it seems that there are too many complicating factors to make adequate corrections for helium diffusion loss. Instead, the experiments reported here make use of etched samples with differing surface-to-volume ratios and assume negligible loss when the results agree.

Fig. 11 Helium content in stainless steel and nickel irradiated in thermal reactors. Curve can be represented by the equation $\text{He} = 9.8 \times 10^{-19} (\Phi t)^{1.68}$ atoms He/g of Ni. (Φt = thermal-neutron fluence.)

Correlation of Thermal-Neutron-Induced Helium

Figure 11 shows some experimentally determined helium concentrations^{21,25,56,57} in several types of stainless steel and in nickel irradiated in thermal reactors. Recently, Weitman et al.²¹ reported data that indicated an anomalous helium production in nickel. They attributed this to secondary

reactions in the nickel and suggested the source might be ^{58}Co , ^{59}Ni , or possibly some other primary reaction product. Kangilaski and Bauer²⁵ and Bloom and Farrar⁵⁷ confirmed Weitman's finding for high fluences with data obtained from stainless steel and nickel irradiated in the thermal reactors ETR and HFIR. Because of this dependence on nickel, the thermal-reactor data have been plotted as atoms of helium per gram of nickel vs. the 2200 m/sec equivalent thermal fluence. The straight line (log-log) in Fig. 11, which is the basis for Eq. 5 in the subsection "Helium-Production Rates" (page 201), was drawn to fit to the data of Refs. 21, 25, and 57.

It is not known at present why the data of Brager and Farrar⁵⁶ do not fall on the line, for their measurements were made by exactly the same technique used for many of the other points. It could be due to a combination of uncertainties associated with material composition (304 stainless steel), sample size, and fluence estimates. In spite of these few anomalous data, the correlation found for the thermal-reactor data is remarkably good. The additional measurement by Robbins¹³ of 237 ± 45 at. ppm helium in 304 stainless steel irradiated in ETR has not been included in Fig. 11 because the thermal fluence was not reported. A rough estimate of this fluence using data from Table 1, however, shows that his result is reasonably consistent with the curve in Fig. 11. From this curve it is apparent that secondary reactions between thermal neutrons and nickel will begin to dominate the production of helium in austenitic steels and nickel at thermal fluences ($\sim 10^{20}$ neutrons/cm²) sufficient to significantly deplete any ^{10}B present.

Correlation of Fast-Neutron-Induced Helium

The experimental data for Fe, Cr, Ni, and stainless steel from this work are plotted along with other data in Figs. 12 and 13 vs. the fast-neutron fluence (>3.68 MeV). In Fig. 12 the helium-production rate of iron was found to be the same as that of chromium within experimental uncertainties. The correlations of the data from the various laboratories are reasonably good, especially for nickel, whose relatively high (n,α) cross section will tend to overshadow the effects of possible impurities. The somewhat high helium concentrations for the two iron specimens with fluences below $\sim 10^{18}$ neutrons/cm² (EBR-II blanket capsules H79 and H81) suggest that impurities and neutrons with energies less than 3.68 MeV are contributing to the generation of helium as softer spectra are encountered, although the possibility of low-energy subthreshold reactions cannot be ruled out.

Figure 13 presents a grand compilation of available experimental data^{20,23,24,56} on different types of stainless steel irradiated in EBR-II. The atoms of helium produced per gram of stainless steel vs. fast fluence (>3.68 MeV) is plotted. A number of factors makes this more difficult to interpret than either of the previous two figures. First, the (>3.68 MeV) parameter is not appropriate for correlating all the data, because low-energy

Fig. 12 Helium content in nickel, iron, and chromium irradiated in a fast reactor.

neutron reactions become important in the lower fluence data that were obtained from materials irradiated at the higher axial EBR-II blanket positions. Second, although nickel is a major contributor of helium in the central core region of EBR-II, the effect of the variation in nickel content among the stainless steels (9 to 14%) is not taken into account. Third, the effect of migration and mass transfer of minor elements and impurities cannot be properly considered because the exact temperatures and other conditions experienced by the specimens during irradiation were not specified.

The lack of linearity of the curves fit to the EBR-II data of this work for two types of stainless steel (the large solid triangles in Fig. 13) emphasizes the changing effect of impurities and of possible subthreshold reactions. This effect was illustrated earlier in Fig. 5, where the same data were normalized to one fluence. At that time it was shown that the percentage of helium which must

Fig. 13 Helium content in stainless steel irradiated in EBR-II.

have originated from elements other than Cr, Fe, and Ni varied from ~38% at the core center (fast fluence $\sim 3 \times 10^{19}$ neutrons/cm²) to ~70% at the outer-blanket locations (fast fluence $\sim 10^{17}$ neutrons/cm²). This excess has tentatively been attributed to such impurities as nitrogen and boron rather than to low-energy primary or secondary (n,α) reactions. For each sample the estimated helium contribution from nitrogen was subtracted, and the resulting data are plotted as small solid triangles in Fig. 13. A further correction for helium produced by boron would lower some of the low-fluence data points by about the same amount but would not affect higher fluence points which experienced the harder core spectra.

Because of the complicated nature of these various effects and the need for data at total fluences exceeding 10^{23} neutrons/cm² [equivalent to a fast flux

(>3.68 MeV) of $\sim 3 \times 10^{21}$ neutrons/cm² at EBR-II core center] where changes in mechanical and physical properties of materials are of primary concern, three curves representing different bounding conditions have been fit to the data of Fig. 13.

The lowest curve represents a case of stainless steel with low nickel content (8.5%) and assumes negligible helium production from impurities. This provides a lower bound for helium production and is based on the experimental data presented in Fig. 12 and a composition of 71.5% Fe, 20% Cr, and 8.5% Ni. The middle curve represents a case of stainless steel with normal impurities, such as those specified in Table 2, columns 3 and 4, and only applies to reasonably hard spectra ($\bar{E} > 0.5$ MeV). The top curve represents an approximate upper bound for helium production in stainless steel for soft out-of-core EBR-II, FTR, and LMFBR types of spectra, where impurities and low-energy subthreshold reactions can completely dominate the production of helium.

The curves in Figs. 11 to 13 served as a basis for the helium-production curves presented earlier as a function of total neutron fluence in Fig. 9.

CALCULATION OF HELIUM PRODUCTION

Reaction-Rate Equations

The purpose here is not to consider all the equations and information needed to predict helium production accurately but rather to review briefly the basic cross-section data required for such calculations, for this is an area of major uncertainty. Until the cross-section data are improved and updated, the most direct and practical way of determining helium production will continue to be by extrapolation of direct measurements of helium content.

The total amount of helium (atom fraction) in a material from all (n, α) reactions (neglecting burnout and burn-in effects) is given by

$$\text{He} = \Phi t \sum_{i=1}^m N_i \bar{\sigma}_i \quad (7)$$

where the spectral average (n, α) cross section is defined as

$$\bar{\sigma}_i \equiv \int_0^\infty \sigma_i(E) \phi(E) dE / \int_0^\infty \phi(E) dE \quad (8)$$

and the total neutron fluence is

$$\Phi t \equiv t \int_0^\infty \phi(E) dE \quad (9)$$

In these equations, N_i is the isotopic atom fraction of the i th target atom in the material, $\sigma_i(E)$ is its energy-dependent (n, α) cross section, and $\phi(E)$ is the differential neutron flux.

Equation 7 is applicable for fluences where the burnout and burn-in of target and reaction products by all mechanisms including (n,α) and (n,p) reactions, etc., are much less than $\sim 10\%$ (i.e., $\bar{\sigma}_i' \Phi t \ll 0.1$, where $\bar{\sigma}_i'$ is the total cross section for burnout). Equation 7 would not apply, however, if secondary reaction products having high (n,α) cross sections are formed as in the case of nickel irradiated in a thermal-neutron environment (see the subsection on "Correlation of Thermal-Neutron-Induced Helium," page 212).

Spectral-Averaged and Energy-Dependent Cross Sections

There are several papers that discuss predictions based on calculations^{1,4-16,24,26,27} using Eq. 7, and some of these authors have compared their results with measurements and have found rather large discrepancies. Before these are discussed, however, the measured EBR-II spectral-averaged cross sections for this work will be presented.

The expression used to obtain measured values of spectral-averaged cross sections, $\bar{\sigma}_m$, for comparison with calculated values, Eq. 8, is

$$\bar{\sigma}_m = N_m / \Phi t \quad (10)$$

where N_m is the measured atom fraction of helium atoms per sample target atom and Φt is the SAND-II multiple-foil-derived value of total fluence.^{3,9}

Preliminary results from mass-spectrometric measurements of the helium concentration in 11 pure elements irradiated in the EBR-II row 4 center position (capsule H41) are shown in Table 5. The helium concentrations range from 220 at. ppm for boron down to 16 at. ppB for zirconium. The measured values of spectral-averaged cross sections were obtained using Eq. 10, which amounted to dividing the helium concentrations shown in Table 5, column 2, by 1.29×10^{21} neutrons/cm², the total neutron fluence at this location. Although the absolute uncertainties for the values of $\bar{\sigma}_m$ depend on the 10% (1 σ) estimated uncertainty of fluence, the relative uncertainties between the $\bar{\sigma}_m$ values for the different elements are limited only by the relative uncertainties in helium concentrations, 2 to 3% (1 σ), and the possibility of effects from impurity elements. The fourth column shows some SAND-II calculated values of spectral-averaged cross sections obtained by integrating the available energy-dependent cross sections over the multiple-foil-derived differential flux spectrum using Eq. 8.

Examination of Table 5 shows that nickel has a measured cross section 20 times larger than the calculated value, a result found by others^{1,8} which will be discussed a little later. It is also evident that nickel is the most important contributor of helium from among the major components of stainless steel. The cross sections of iron and chromium appear to be about the same and are only 7% that of nickel. In addition to boron, another major contributor of helium is expected to be nitrogen, whose spectrum-integrated (n,α) cross section is

TABLE 5
SPECTRAL-AVERAGED CROSS SECTIONS AT THE
EBR-II ROW 4 MIDPLANE

Element	Helium conc., 10 ⁻⁹ at. fraction	Spectral-averaged cross section, mb		Energy-response range*	
		Measured	Calculated	E _{lower} , MeV	E _{upper} , MeV
B	220,000	171	204†	0.016	1.6
N			23	1.6	5.6
Al	181	0.140	0.147		
Ti	<77	<0.060			
V	21	0.016			
Cr	100	0.076	0.061	5.3	12.5
Mn	110	0.085			
Fe	100	0.077	0.051	5.2	12.5
Co	50	0.039	0.032	5.8	13.0
Ni	1,350	1.05	0.053	5.5	11.6
Cu	90	0.070	0.072†	2.5	11.7
Zr	16	0.012			

*Range in which 90% of helium is produced at the EBR-II row 4 midplane.

†Quoted values represent the contributions to the elemental cross sections from only the isotopes ¹⁰B and ⁶³Cu.

estimated to be 23 mb, a value subject to verification by measurements on nitride samples.

Table 5 also shows the calculated energy range of the neutrons (for the row 4 midplane in EBR-II) which produce 90% of the helium for each element. The range for copper was calculated using a new evaluated $\sigma(E)$, which, as will be seen later in Fig. 14, has a low- as well as a high-energy response. There is also the possibility that, besides B, N, and Cu, some of the other elements have low-energy cross sections. This would result in a reduction of the lower limits from the ~5-MeV values shown in Table 5, which were calculated with existing evaluated energy-dependent cross sections that drop to zero below 4 to 5 MeV.

One of the more common ways of reporting measured fast-neutron cross sections is by converting the spectrum-averaged values $\bar{\sigma}_m$ to the equivalent fission-averaged values $\bar{\sigma}_f$, based on the Watt⁴⁰ form of the fission spectrum $\phi_f(E)$. The measured $\bar{\sigma}_m$ values from this work were therefore converted to $\bar{\sigma}_f$ values using Eq. 8. This amounted to multiplying each value in Table 5 by a ratio R, where

$$R = \frac{\int_0^\infty \sigma(E) \cdot \phi_f(E) dE}{\int_0^\infty \sigma(E) \cdot \phi_{EBR}(E) dE} \quad (11)$$

R was calculated for each reaction using existing evaluated $\sigma(E)$'s and the multiple-foil-derived energy-dependent flux for EBR-II, $\phi_{\text{EBR}}(E)$. Evaluated $\sigma(E)$'s for Ti, V, Mn, Ni, and Zr were either unavailable or were considered inadequate. Values of $\bar{\sigma}_f$ were therefore obtained from the measured $\bar{\sigma}_m$ values in Table 5 for these elements by the use of a value of R (4.55) equal to the average of the R values for Al (4.51), Cr (4.55), Fe (4.51), Co (4.58), and Cu (4.58). The resulting fission average cross sections are compared in Table 6 with other measured and calculated values from the literature.

The fourth, fifth, and sixth rows in Table 6 provide some values of $\bar{\sigma}_f$ calculated by the present authors, Alter and Weber,¹⁶ and compiled by Birss,¹⁴ respectively, for comparison with measured values. The values from the present work were obtained using Eq. 8 and the Watt⁴⁰ form of the fission spectrum. The evaluated energy-dependent cross sections used here and in Eq. 11 are those in current use by the FRMDC and are partly based on the Karlsruhe⁶⁴ evaluated $\sigma(E)$'s. Other calculated values of $\bar{\sigma}_f$ have been reported^{14,15,24,27} with differences depending on the procedures and evaluated cross-section data utilized. The final row in Table 6 gives preliminary values obtained in this work based on radiochemical measurements of reaction-product activities performed by a number of different laboratories for the EBR-II Run 31F dosimetry test and summarized by Kellogg and Zimmer.⁴⁵

The most direct comparisons in Table 6 can be made between the results of this work and the cross sections reported by Weitman et al.^{18,22} and Freeman et al.,¹⁹ both groups having used mass spectrometry to measure helium concentrations in a manner similar to that used in this work. Weitman et al. irradiated their specimens in a capsule under a boral shield in a central position of the Studsvik R2 reactor, a thermal reactor of the MTR (Materials Testing Reactor) type. The specimens of Freeman et al. were irradiated in the DFR. In general, the agreement is satisfactory.

The most significant discrepancy in Table 6 is the difference between the measured and calculated nickel cross sections. This was first noticed by Weitman and Däverhög¹⁸ and has since been confirmed by the other two measurements. There appears to be reasonably good agreement among the measured values for titanium and copper. The low value of Freeman et al. for iron, compared with the other two values, might be explained partially by their correction for helium production from nitrogen. As noted earlier (see the subsection "Material Composition Effects," page 194), iron specimens in the present work had lost virtually all their nitrogen during the irradiation. If such a phenomenon had occurred in Freeman's samples (which were in contact with the Na-K reactor coolant), his uncorrected value would be ~ 0.30 mb which is closer to the other values. The high measured value reported in the present work for chromium has not yet been confirmed and might well be the result of nitrogen and oxygen impurities which have yet to be measured.

A comparison of the first and last rows in Table 6 is particularly interesting since both experiments were conducted at the same time and under the same

TABLE 6
COMPARISON OF FISSION-SPECTRUM-AVERAGED (n, α) CROSS-SECTION VALUES

Source of data	Fission-spectrum-averaged (n, α) cross section ($\bar{\sigma}_f$), mb														
	¹⁴ N	B	¹⁰ B	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	⁶³ Cu	Zr	Mo
Measured, mass spectrometer, EBR-II (this work)*		75	380	0.63	<0.27	0.073	0.35	0.39	0.35	0.18	4.8	0.32	0.46	0.055	
Measured, ^{2,2} mass spectrometer, Studsvik R2					0.22		0.19		0.36		4.8	0.37			
Measured, ^{1,9} mass spectrometer, DFR							0.17		0.18		4.7				0.13
Calculated for Watt spectrum (this work)†	87		451	0.66			0.28		0.23	0.15	0.25		0.47		
Calculated for fission spectrum (Alter and Weber) ^{1,6}	41	126	635	0.65	0.51	0.035	0.38	0.13	0.44	0.23	0.60	0.54	0.72	0.18	0.84
Compilation of available calculated and measured values (Birss)‡	93			0.65	0.53	0.033	0.2	0.13	0.23	0.31	4.5	0.72		0.18	0.12
Measured, radiochemistry, EBR-II (this work)§				0.63					0.73¶		4.0¶		0.53		

*The data for ¹⁰B and ⁶³Cu were inferred from elemental data using current isotopic abundances. No corrections were made for helium produced from impurities, which are thought to be negligible in most cases (see text).

†Calculations used the SAND-II code and the evaluated $\sigma(E)$'s from Ref. 32 except for Cr, Fe, and Ni, where Karlsruhe^{6,4} values were used, and for ⁶³Cu, where the data shown later in Fig. 14 were used.

‡It appears that Birss^{1,4} based his values for Cr, Fe, Ni, and Mo on earlier data of Freeman et al., Ref. 19.

§Radiochemical measurements of reaction products from Run 31F converted to Watt spectrum by Eq. 11.

¶Cross sections shown are for ⁵⁴Fe and ⁵⁸Ni isotopes only. In elemental Fe and Ni, these cross sections represent 0.043 and 2.7 mb, respectively.

conditions (Run 31F). The radiochemical determination of aluminum agrees well with the value based on helium content and, as noted in the subsection "Helium Diffusion and Recoil" (page 210), this suggests little, if any, loss of helium by diffusion from the latter specimens at the irradiation temperatures encountered. A similar comparison for ^{63}Cu is not easily made because of a lack of data for ^{65}Cu . A more important comparison can again be made among the nickel cross sections. The radiochemical value of 4.0 mb for ^{58}Ni , when adjusted for isotopic abundance, will contribute 2.7 mb to the total nickel cross section. The balance of 2.1 mb, needed to make a total of 4.8 mb measured by mass spectrometry, must therefore have come from one or more of the remaining four nickel isotopes. If the data are correct, and only one other isotope is responsible, its fission-averaged (n,α) cross section would have to be 7.9 mb for ^{60}Ni , 165 mb for ^{61}Ni , 56 mb for ^{62}Ni , or 178 mb for ^{64}Ni . This problem should be resolved when the complement of separated highly enriched isotopes of nickel, now being irradiated by the authors at several locations in EBR-II, are analyzed for helium content.

The general conclusion that must be drawn from the lack of agreement between measured and calculated values in Table 6 is that the present evaluated energy-dependent cross sections, $\sigma(E)$, can sometimes be very much in error both in shape and magnitude. Before they can be used for predictions of helium concentrations therefore, many, if not all of them, should be reevaluated with the help of integral measurements using mass spectrometry and recently developed cross-section-evaluation methods.³¹⁻³⁴

Thermal-Neutron Cross Sections

Thermal-neutron (n,α) reactions with several isotopes in the atomic mass range $A = 40-65$ are energetically possible, but, because the coulomb barrier strongly inhibits alpha emission, the higher helium-production cross sections can be expected to come from the more exoergic reactions. In this respect Weitman et al.²¹ list the Q values of several isotopes including ^{54}Fe (0.9 MeV), ^{57}Fe (2.3 MeV), ^{58}Co (3.5 MeV), ^{58}Ni (3.0 MeV), ^{59}Ni (5.2 MeV), ^{61}Ni (3.1 MeV), and ^{63}Cu (1.6 MeV). Nevertheless, it was surprising when these authors recently found a rapid and accelerating helium buildup in nickel irradiated in a mixed thermal and fast flux. To explain the rate, which was many times more than could be accounted for by Münnich's⁷⁵ earlier measurements of 0.66 ± 0.35 mb and 45 ± 20 mb for the thermal (n,α) cross sections of ^{58}Ni and ^{61}Ni , respectively, the authors suggested a two-stage process whereby one or more nickel reaction products were contributing to the helium production. They calculated that if ^{58}Co , formed by the $^{58}\text{Ni}(n,p)^{58}\text{Co}$ reaction, were totally responsible it would have a thermal-neutron (n,α) cross section of $\sim 10^3$ barns.²¹ If on the other hand ^{59}Ni , formed by the $^{58}\text{Ni}(n,\gamma)^{59}\text{Ni}$ reaction, were responsible, its thermal cross section would be ~ 10 to 100 barns.⁶³ Recent measurements, mentioned in the subsections "Helium-Production Rates"

Fig. 14 SAND-II evaluated cross section for the $^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$ reaction (energy range 10^{-10} to 18 MeV). *The 90%-response-region energy limits:

1, EBR-II 31F, R33.6, Z59.2 cm	6, APFA III CORE SURF
2, ATRON4—MIDPLANE	7, EBR-II 31F, R33.6, Z0.0 cm
3, IRLPOS 3R = 52.4 cm	8, EBR-II 31F, R5.2, Z59.2 cm
4, IRLPOS 2R = 49.4 cm	9, EBR-II R5.2, Z0.0 cm
5, IRLPOS 1R = 44.8 cm	

(page 201) and "Correlation of Thermal-Neutron-Induced Helium" (page 212), have given very high helium concentrations in ETR²⁵ and HFIR⁵⁷ stainless steels, consistent with these reaction schemes.

Recent experiments have brought to light other low-energy (n,α) and (n,p) cross sections in this mass region. Figure 14 shows a SAND-II plot of the recently re-evaluated energy-dependent cross section for the $^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$ reaction.^{34,66} Both this and the cross section for the $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ reaction⁶⁵ show significant subthreshold values. The bars in Fig. 14 show the calculated 90% response range for the former reaction in nine different spectral environments. It is clear from all these findings that some of the present evaluated $\sigma(E)$ curves for Fe, Cr, Ni, etc., used to generate the results in Table 5 and the resulting energy-response ranges require a revision to include a $1/v$ thermal cross section and possibly some resonance structure.

Table 7 provides a listing of some 2200 m/sec thermal-neutron (n,α) and (n,p) cross sections σ_0 reported in the literature. The (n,p) reactions identified with an asterisk are exoergic and could have a thermal-neutron cross section either higher or lower than the (n,α) value, depending on the Γ width for proton

TABLE 7
THERMAL-NEUTRON CROSS SECTIONS FOR (n, α) AND (n,p) REACTIONS

Isotope or element*	σ_0 (n, α)		σ_0 (n,p)†	
	mb	Reference	mb	Reference
³ He			5.4×10^6	69
⁷ Be	<1000	69	5.1×10^7	69
⁶ Li	$\sim 9.5 \times 10^5$	68		
Li	$\sim 7.1 \times 10^4$	28		
¹⁰ B	$\sim 3.8 \times 10^6$	68	<200	69
B	$\sim 7.6 \times 10^5$	28	<40	69
O	~ 0.09	28		
¹⁴ N			~ 1800	69
²¹ Ne	<1500	70		
Ne	~ 4	28		
³² S	$\sim 151 \ddagger$	71		
³³ S	$\sim 52 \ddagger$	72	~ 2.3	76
S	~ 140	28	†	
³⁵ Cl	~ 3.1	73	~ 400	77
Cl	~ 2	28	†	
Ar	$\sim 2 \times 10^{-2}$	28, 74	†	
⁴⁰ K			3800	76
K	~ 4	28	†	
Ca	~ 2	28		
⁵⁴ Fe			<1.5	65
Fe	<5	69		
⁵⁸ Co	$\sim 10^6 \S$	21	†	
⁵⁹ Co	~ 0.14	73		
⁵⁸ Ni	~ 0.66	75	†	
⁵⁹ Ni	$\sim 10^4 - 10^5 \S$	63	†	
⁶¹ Ni	~ 45	75		
Ni	~ 1	28	†	
⁶³ Cu	~ 0.005	34	†	
⁶⁴ Zn	<0.015	69		
⁶⁶ Zn	<0.020	69		
⁶⁷ Zn	~ 0.006	69		
⁶⁸ Zn	<0.020	69		

*Cross-section values for elements are calculated from the isotopic values.

†The (n,p) reactions identified by a dagger are exoergic and could have high cross sections (see text).

‡Report BNL-325 (Ref. 77) lists values of 7 ± 3 mb and 190 ± 80 mb for ³²S and ³³S respectively, which do not correspond to these values (Ref. 71 and 72).

§Value based on thermal-reactor data assuming that all helium from nickel reaction products comes from this isotope.

emission. The possibility exists, therefore, that such reaction products as ^{58}Co and ^{59}Ni could dominate hydrogen as well as helium production in alloys of nickel, perhaps resulting in anomalously high rates of hydrogen and helium production in thermal reactors. As mentioned earlier, however, the hydrogen does not seem to be a problem in radiation damage owing to its high solubility and high mobility, although it could pose a problem if it were to become excessive in a power-reactor cover gas.

The cross sections in Table 7 and others as they become available will help define new evaluated $\sigma(E)$'s with appropriate low-energy responses for elements and impurities that contribute to helium production in austenitic stainless steels. Such $\sigma(E)$'s should improve the prediction of helium-generation rates and should help in the resolution of some present inconsistencies in dosimetry.^{3,4,41,44,65}

CONCLUSIONS AND SUMMARY

The mechanical and physical properties of LMFBR cladding and structural materials are affected in various ways by the presence of helium produced by nuclear reactions. Therefore knowledge of helium-production rates is important for the development and testing of suitable alloys for fast-reactor applications.

Preliminary results of programs at HEDL, AI, and other laboratories indicate that helium concentrations between ~ 0.1 and ~ 150 at. ppm will be most important for fuel cladding and structural material damage studies. Between approximately 0.1 and 20 at. ppm, the helium is expected to have its most significant effect on nucleation and on the size and density distribution of voids.^{6,12,78} Above, say 20 to 100 at. ppm, the effect of helium on nucleation is expected to diminish, but its effect on the behavior of cavities is expected to become more important.^{5,21} The ~ 150 at. ppm concentration corresponds to a total neutron exposure of $\sim 10^{24}$ neutrons/cm² in the FTR core.

Mass-spectrometric measurements of total helium produced in alloys irradiated in several available fast- and thermal-neutron spectra have been correlated with equivalent data obtained by irradiating pure elements. It is now widely believed that nickel, besides being a major source of helium in fast-neutron environments, is also the primary source of helium in alloys containing nickel irradiated to high fluences in thermal reactors. Although the proportions of the various possible nuclear reactions are not yet known, apparently one or more two-stage thermal-neutron (n,α) processes occur with nickel and nickel reaction products. These result in accelerated helium production for high total neutron fluences ($>10^{21}$ neutrons/cm²), where the effects of ^{10}B diminish due to burnout, and explain the unusually high helium concentrations in nickel-bearing steels irradiated in the thermal reactors ETR and HFIR.

Whether helium is produced in fast-neutron spectra primarily by the major constituents (and by their reaction products), or by impurities (such as nitrogen,

sulfur, and boron), depends very much on the location in the reactor and on the hardness of the flux spectrum. If impurities are a major source of helium, their initial heterogeneity and subsequent movement will be a major concern in the interpretation and correlation of irradiation-effects data.

A review of all the experimental data available indicates that both low- and high-energy primary and secondary (n,α) reactions must be considered if reliable correlation and subsequent predictions of helium production are to be achieved. For instance, it is now well established that helium generated in commercial cladding alloys in thermal and fast reactors is often roughly proportional to the nickel content of the alloy. Varying helium concentrations will be encountered, nevertheless, in connection with spectral variations, with secondary reactions, burn-in and burnout, impurities, mass transfer, inclusions, recoil effects, and surface gradients of elements with high (n,α) cross sections.

Thus in one environment the major source of helium may be from reactions with low-energy neutrons, whereas in another it is from high-energy neutrons. Consequently it is not altogether satisfactory to correlate measured helium concentrations on the basis of a single parameter, such as the total fluence, fluence for neutrons >0.1 MeV, >1 MeV, etc.; instead, flux spectral and material property differences must be considered, even if only in a rudimentary manner.

Calculation of the rate of helium generation in a material in any LMFBR neutron environment requires a knowledge of the flux spectrum and the energy-dependent or spectral-averaged (n,α) cross sections of all major and some minor constituents. At the present time, most of these cross sections are inadequately known and require extensive revision. Until this has been accomplished, it is recommended that measured rather than calculated spectral-averaged cross sections be used, and that helium-generation rates for thermal and fast reactors be obtained from production curves based on helium measurements.

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DISCUSSION BY ATTENDEES

Wazzan: Earlier today we saw that swelling data on a given material, irradiated under "similar conditions," varied quantitatively from one laboratory to another. Some authors, e.g., Dr. E. Bloom, suggested that difference in the heat of the alloy could account for this. Sandusky replied, saying this was not the case. It appears we are neglecting the effect of one important parameter on such discrepancy in data from one laboratory to the other, namely, the irradiation temperature. Since void number and mean diameter are strongly dependent on the irradiation temperature, and since temperature control in the reactor over exposure periods upwards of 1 year is rather poor, how meaningful then is a comparison of results from one laboratory to another?

McElroy: There are others here who perhaps should answer this question since it is not related directly to the subject of this paper, namely, helium production. Relative to helium production, however, we do not believe that changes in helium concentration are seriously affected by temperature differences; i.e., there is apparently little loss of helium due to diffusion at any of the temperatures encountered in existing test-reactor data.

Odette: Did you have to assume a mechanism in the two-stage helium-production process in order to place data from different irradiations on the same helium vs. fluence plot?

McElroy: No, no mechanism was assumed, and the derived curve is completely empirical.

Odette: Then can the data provide information concerning the half-life and cross section of the helium parent? Is it likely to be the ^{59}Ni ?

McElroy: Yes, the data can; however, the possibility of other two-stage reactions such as $^{58}\text{Ni}(n,p)^{58}\text{Co}$ followed by $^{58}\text{Co}(n,\alpha)$ or similar reactions with the other naturally occurring isotopes in elemental nickel complicate the analysis. Nevertheless, it is apparent that ^{59}Ni is at least one, if not the single most, important contributor to the total measured amount of helium.

Wilson: You indicated that the helium production in n-irradiated nickel was a two-stage process at high fluences. Is this also the dominant process in iron and cobalt?

McElroy: The answer is no on the basis of studies made by J. Weitman et al., which are referenced in our paper.

HELIUM MIGRATION IN METALS

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ABSTRACT

The results of helium-release measurements after 300-keV helium implantation in palladium, copper, nickel, and 304L, 309, and 316 stainless steels are presented. The implantation doses extend from 10^{12} to 10^{18} helium atoms/cm². For all doses, most of the helium release occurs above 400 to 600 °C, although at higher doses some strongly dose-dependent low-temperature release occurs. The properties of helium interstitial and substitutional defects were calculated using models of the face-centered cubic and body-centered cubic lattices. In general, helium-interstitial activation energies of motion were less than 1 eV, with the exception of palladium. Detrapping from substitutional sites results in activation energies ranging from approximately 2 to 5 eV, the higher activation energies being found mostly in body-centered cubic materials. A rate-determining step associated with substitutional detrapping is tentatively assigned to the high-temperature helium release.

The formation of voids during neutron irradiation of reactor cladding materials at elevated temperatures has been well established.¹⁻³ Both hydrogen and helium are generated as an inevitable by-product of the (n,p) and (n,α) reactions. The formation of voids has been simulated by charged-particle irradiation at elevated temperatures.⁴ The role of helium in both modes of void formation (neutron- and charged-particle irradiation) has been experimentally investigated and has been the subject of considerable speculation. Nelson and Mazey⁴ demonstrated that helium injected prior to charged-particle irradiation of 316 stainless steel at elevated temperatures increases the density and total volume occupied by voids by approximately an order of magnitude. Recently Bloom and Stiegler³ showed that helium is also a very effective agent for nucleating voids during neutron irradiation. However, the effect is not as dramatic as in charged-particle irradiation.

Theories that attempt to quantitatively explain such things as void density and size as a function of neutron fluence or particle dose at different

temperatures require, as input, the disposition of helium in the lattice and its migrational characteristics. Both the theoretical results of such calculations and experimental helium-release data presented in this paper bear directly on this question.

EXPERIMENTAL RESULTS

The experimental helium-release results reported here were obtained from two annealing programs in different experimental configurations. All implantations were carried out in the 450-keV positive-ion accelerator at Sandia Laboratories, Livermore, Calif. In the first series of measurements, samples were implanted at liquid-nitrogen temperatures and subsequently placed at room temperature in a high-temperature annealing chamber.⁵ The samples were then heated using a 20-min isochronal-annealing program. The second type of release measurements involved implantation at liquid-nitrogen temperatures in a chamber connected to a sensitive helium mass spectrometer. In this approach, the helium release was measured immediately after implantation and also during a linear heatup ($\sim 10^\circ\text{C}/\text{min}$) of the sample. The helium mass spectrometer consists essentially of an all-metal vacuum system with an EAI Quad 150 spectrometer. The helium peak is swept continuously in the integrating mode using a titanium sublimation pump to reduce the reactive gas background. The samples consisted of 1.6-cm-diameter disks, 1 mm thick with an optical polish on the implantation side. High-purity palladium, copper, and nickel were obtained from MRC Corporation (Marz Grade), and commercially available stainless steel was used. The pure metals were annealed at 800°C for 1 hr, the 316 stainless steel at 600°C for 1 hr, and the 304L and 309 stainless steels at 700°C for 15 min prior to implantation. The implantation of 300-keV helium atoms results in a layer of helium atoms centered $0.7\ \mu$ from the surface of the sample, having an approximately $0.4\text{-}\mu$ full width at half-maximum (assuming a Gaussian distribution).

Figure 1 shows the fractional helium release as a function of annealing temperature (20-min isochronal) for palladium implanted to a series of doses. A dose of 10^{12} helium atoms/ cm^2 corresponds to a helium atom fraction of approximately 4×10^{-7} in the implanted layer. Thus the range of helium atom fraction in these experiments is from $\sim 4 \times 10^{-7}$ to $\sim 4 \times 10^{-1}$. The helium release is strongly concentration dependent, in agreement with results^{5,6} of earlier implantations at 5 MeV. As the concentration first increases, successively higher annealing temperatures are required for release until, at a concentration range of 10^{-4} to 10^{-3} helium atom fraction, a reversal of this tendency occurs. Finally, at the highest atom fraction, ~ 0.4 , release occurs at room temperature. The 10^{18} helium atoms/ cm^2 data presented in Fig. 1 are discussed separately below. At 1200°C the evaporation of palladium metal results in removal of $1.4\ \mu$ in 20 min. Consequently, at the highest temperatures, the release of helium

Fig. 1 Fractional helium release in palladium as a function of temperature for a 20-min isochronal-annealing program. The samples were implanted with 300-keV helium atoms to the indicated doses at temperatures near -180°C .

cannot necessarily be attributed to migration of helium or helium bubbles to the surface of the sample.

The qualitative model advanced by Holt et al.^{5,6} to explain the concentration dependence of the helium release for doses up to 10^{17} helium atoms/cm² is consistent with these data. The agglomeration of helium atoms into bubbles has been experimentally observed by Barnes and Mazey⁷ in copper at a concentration of 10^{-3} and by Thomas⁸ in palladium at a concentration of $\sim 10^{-3}$. Helium bubbles are considerably less mobile than atomic helium, and the probability of bubble formation increases with increasing helium concentration. This explains the data qualitatively to a helium atom fraction of 10^{-3} to 10^{-4} . At higher doses an interconnected porosity forms in the implanted layer and allows helium to

Fig. 2 Fractional helium release in stainless steel (304L and 309) as a function of temperature for a 20-min isochronal-annealing program. The samples were implanted with 300-keV helium atoms to the indicated doses.

migrate to grain boundaries. The helium release cannot then be described by a diffusion process but is related to considerable surface deformation.

Assuming that the helium release from the lowest concentration sample is most closely associated with atomistic helium migration, one may estimate an effective activation energy of helium migration. Using a simple Arrhenius expression, a temperature of 700°C (appropriate for 0.5 release), a frequency factor of 10^{13} sec^{-1} , and 10^6 jumps, one gets an effective activation energy of $\sim 1.9 \text{ eV}$.

Figure 2 shows the helium release from 304L and 309 stainless-steel samples implanted to nearly the same helium concentration of $\sim 4 \times 10^{-5}$ atom fraction.

Fig. 3 Helium-release rate in 316 stainless steel as a function of annealing temperature for a linear heatup rate of $\sim 10^{\circ}\text{C}/\text{min}$. The sample was implanted at -180°C to a dose of 10^{16} 300-keV helium atoms/ cm^2 .

Relatively higher temperatures than palladium are required for helium release. Using the same arguments as above, one obtains effective activation energy of ~ 2.5 eV for helium in stainless steel. The somewhat higher release temperature and correspondingly higher effective activation energy in stainless steel, as compared to palladium, are at least in qualitative agreement with the calculations presented below for iron. Alternatively, of course, this difference may be due to the effects of alloying.

In the second type of release measurements discussed above, a linear heatup rate was used to anneal the sample from -190°C immediately after implantation. The data are summarized in Figs. 3 to 5. In each case the temperature derivative of the number of helium atoms measured in the spectrometer is plotted as a function of annealing temperature. The data in Fig. 3 correspond to a dose of 10^{16} helium atoms/ cm^2 , in Fig. 4 to a dose of 10^{17} helium atoms/ cm^2 , and in Fig. 5 to a dose of 10^{18} helium atoms/ cm^2 (note scale change). In each case the implanted area was 0.32 cm^2 . The total fractional release at the end of each run shown in Figs. 3 to 5 is 1.5×10^{-3} , 0.9×10^{-4} , and 0.22, respectively.

It seems that, in the concentration range from 10^{-5} to 10^{-2} helium atom fraction, very little mobility occurs at temperatures below 600 to 700°C in the time scale of these experiments. The substantially increased release rate of 10^{18} helium atoms/ cm^2 dose sample may be better appreciated in Fig. 6. Here the

Fig. 4 Helium-release rate in 316 stainless steel as a function of annealing temperature for a linear heatup rate of $\sim 10^{\circ}\text{C}/\text{min}$. The sample was implanted at -180°C to a dose of 10^{17} 300-keV helium atoms/ cm^2 .

Fig. 5 Helium-release rate in 316 stainless steel as a function of annealing temperature for a linear heatup rate of $\sim 10^{\circ}\text{C}/\text{min}$. The sample was implanted at -180°C to a dose of 10^{18} 300-keV helium atoms/ cm^2 .

Fig. 6 Helium-release rate in 316 stainless steel as a function of annealing temperature for a linear heatup rate of $\sim 10^\circ\text{C}/\text{min}$. The samples were implanted with 300-keV helium atoms at -180°C . The dose of sample 316-1 was 10^{16} helium atoms/ cm^2 ; of sample 316-2, 10^{17} helium atoms/ cm^2 ; and of sample 316-3, 10^{18} helium atoms/ cm^2 .

data shown in Figs. 3 to 5 are replotted on a semilog plot. One notes the more than four orders of magnitude difference in release rates for the various doses.

These very-high-dose effects have also been studied in the pure metals. Figure 7 shows the temperature derivative of the helium release as a function of annealing temperature for palladium implanted to a dose of 10^{18} helium atoms/ cm^2 . There are two well-separated regions of helium release. The lower temperature portion ($\sim 175^\circ\text{C}$) accounts for an 0.11 fraction of the total helium release, is strongly dose dependent, and is almost negligible for doses of less than 5×10^{17} helium atoms/ cm^2 . The higher temperature helium release starting at 450°C is present at lower doses and is essentially equivalent to the release shown in Fig. 1. The 10^{18} data shown in Fig. 1 are qualitatively consistent with the data in Fig. 7. The incomplete release exhibited by the isochronal-annealing data of Fig. 1 can now readily be explained since the sample evolved considerable helium while remaining at room temperature approximately a week before measurements were initiated.

Figure 8 shows the helium-release data for nickel. Here the data represented by nickel 2 are for a sample with a dose of 10^{18} helium atoms/ cm^2 ; the data represented by nickel 3 are for a sample with a dose of 7.5×10^{17} helium atoms/ cm^2 . For the higher dose sample, the release starts near -150°C with a fractional release up to 150°C of 0.08. Insignificant release occurs between 150

Fig. 7 Helium-release rate in palladium as a function of annealing temperature for a linear heatup rate of $\sim 10^\circ\text{C}/\text{min}$. The sample was implanted to a dose of 10^{18} 300-keV helium atoms/ cm^2 near -180°C .

Fig. 8 Helium-release rate in nickel as a function of annealing temperature for a linear heatup rate of $\sim 10^\circ\text{C}/\text{min}$. The samples were implanted with 300-keV helium atoms at approximately -180°C . Sample 2 was implanted to a dose of 10^{18} helium atoms/ cm^2 , and sample 3 was implanted to a dose of 7.5×10^{17} helium atoms/ cm^2 .

Fig. 9 Helium-release rate in copper as a function of annealing temperature for a linear heatup rate of $\sim 10^{\circ}\text{C}/\text{min}$. The sample was implanted to a dose of 10^{18} 300-keV helium atoms/ cm^2 .

and 375°C , forming a plateau region, whereas the release starting near 400°C is similar to that found at lower doses in previous runs. The low-temperature release of the sample implanted to the lower fluence (nickel 3) is considerably reduced compared to the higher dose sample (nickel 2). This reduction is a demonstration of the strong fluence dependence of the low-temperature release.

The high-dose helium-release data for copper are presented in Fig. 9 for an implantation dose of 10^{18} helium atoms/ cm^2 . Again a low-temperature peak appears centered between 0 and 50°C and separated from the high-temperature release. In copper, however, the separation is not as pronounced as in palladium and nickel. Also, additional experiments reveal a more-complicated situation for the low-temperature release. In copper the possibility of a flux dependence in addition to the strong fluence dependence cannot be dismissed.

One may estimate an effective activation energy associated with the low-temperature-release peaks of palladium, nickel, and copper following the previously mentioned procedure. Using center temperatures of 100, 100, and 0°C for palladium, nickel, and copper, one finds effective activation energies of approximately 0.75, 0.75, and 0.55 eV, respectively. Clearly, to obtain activation energies rigorously requires extensive isothermal-annealing data in the appropriate temperature region. Experiments are now in progress to investigate both the high- and low-temperature release via isothermal annealing.

THEORETICAL RESULTS

A helium atom introduced into a metal lattice via such energetic means as ion implantation may reside as either a substitutional or an interstitial gas atom. The above-described experiments were conducted at sufficiently low temperatures that vacancies were not mobile during implantation; therefore helium atoms can occupy substitutional sites either dynamically or through migration. On the other hand, those helium atoms which come to rest sufficiently far from vacancies or vacancy clusters will be interstitial, if they are not mobile. Clearly, more-complicated configurations, such as a divacancy with a helium atom (vacancy plus substitutional helium atom), may also be generated during implantation. However, in this paper, only the "simpler" elemental substitutional and interstitial helium-atom configurations will be considered.

The interatomic potentials for the host-atom interaction including non-central interactions are described in Ref. 10. An approximate quantum mechanical method originally due to Wedepohl¹¹ was used to obtain the helium host atom (and short-range metal-metal potentials) described in Ref. 12. The host-atom potentials are short ranged and are adjusted to fit the elastic constants, which requires noncentral forces for face-centered cubic (fcc) metals (in particular, palladium). Single vacancy formation and migration energies were used to determine a cutoff radius for the potentials for the fcc metals, which was taken as midway between the second and third neighbor distances for the body-centered cubic (bcc) metals. An example of the host-atom potentials is given in Fig. 10 for copper, iron, and palladium. Good agreement was found between the spectrum of vibrational modes predicted by these potentials and the experimental phonon-dispersion curves for copper and iron. The helium-metal interatomic potentials used for He-Fe, He-Cu, and He-Pd are shown in Fig. 11.

Two completely independent methods were used to calculate the helium defect configurations. In each case not less than 200 atoms in the vicinity of the defect are allowed to relax, which is sufficient to determine the energy to approximately 0.01 eV. In method A, used for the fcc metals (which require noncentral forces), a shell of atoms is allowed to relax to its approximate minimum energy and then held fixed while the next set is relaxed, etc. Method B (used for the bcc calculations) allows all atoms to be moved simultaneously—a physically more appealing process. In either case a sufficiently large number of atoms was allowed to relax to obviate the need for elastic continuum forces. Test-case calculations involving both methods give the same answer for central-force calculations.

As discussed above, the helium defect configurations were calculated for the interstitial and substitutional positions in the fcc and bcc lattices. These configurations are shown in Figs. 12 to 15. In Figs. 12 and 13 are shown the symmetrical interstitial positions for a helium atom in an fcc and a bcc lattice, respectively. In Figs. 14 and 15 are shown the paths of motion of the helium

Fig. 10 Central part of Cu-Cu and Pd-Pd potentials and Fe-Fe potential valid in the region of $r_n \leq r \leq r_c$, where r_n is the inner matching radius and r_c is the cutoff. The fcc potentials are sixth-power polynomials fitted to elastic constants and a short-range quantum mechanical potential. The Fe-Fe potential has fourth- (fifth-) power form for $r \leq (>) r_m$, the midpoint between the first and second neighbor distances. The Fe-Fe potential is also fitted to the Wedepohl potential determined in Ref. 10 at short range.

Fig. 11 He-Cu⁺, He-Pd, and He-Fe potentials determined by the modified Wedepohl method. The Hartree-Fock-Slater (HFS) approximation to the exchange is used in all cases. Note the deviation from Born-Mayer behavior at small internuclear separations.

Fig. 12 Symmetrical interstitial positions of an inert-gas atom in an fcc metal lattice.

Fig. 13 Symmetrical interstitial positions of an inert-gas atom in a bcc metal lattice.

atom during the substitutional detrapping process—a “pop-out” mechanism—in an fcc and a bcc lattice, respectively. Positions A and B are the nearest stable interstitial positions in which the helium atom can reside. The paths A_i, B_i are possible directions the helium atom may follow while diffusing toward positions A and B, respectively.

Fig. 14 Substitutional detrapping (pop-out) of an inert-gas atom in an fcc lattice. The various migration paths are indicated in the figure.

Fig. 15 Substitutional detrapping (pop-out) of an inert-gas atom in a bcc metal lattice.

In Table 1 are summarized the results for a variety of different fcc and bcc metals. The activation energies, with the exception of that for palladium, fall into two groups: (1) the helium-interstitial migration energies, which are less than 1 eV and somewhat smaller for the bcc than the fcc metals, and (2) the

TABLE 1
CALCULATED ACTIVATION ENERGIES
OF MOTION FOR HELIUM (eV)

Metal	Interstitial	Substitutional (pop-out)
Cu *	0.45	2.15+ (1.97)‡
Cu	0.57	(1.88)
Pd	1.74	(3.16)
Ag	0.86	(1.53)
Fe	0.17	3.98 (3.75)
V	0.13	3.20 (2.96)
W	0.24	4.75 (4.42)
Ta	~0	3.44 (3.30)
Mo	0.23	4.19 (3.87)

*From Ref. 13.

+Value derived from mapping of diffusion path.

‡Value based on relative energy of helium atoms in vacancy and interstitial position.

pop-out energies, which are considerably higher than interstitial migration energies. The bcc pop-out energies are again higher than the corresponding fcc energies. The helium-interstitial activation energy for palladium is large in comparison to the other interstitial activation energies. As discussed in Ref. 12, a number of modifications was attempted for palladium, none of which resulted in a significant lowering of the activation energy.

DISCUSSION

It would be extremely satisfying if one could now readily identify the experimentally determined effective activation energies of helium release with the calculated activation energies of helium motion. Unfortunately, and not without precedent, this is not to be the case! This is partly due to the fact that both more experiments and calculations must be performed to explore other possibilities. For example, calculations following the above-described technique were done for the divacancy and a vacancy with a neighboring helium substitutional atom in copper. The divacancy migration energy was found to be approximately 0.6 eV, and the vacancy-helium-substitutional complex activation energy was found to be 0.85 eV. This type of helium defect may exist after

implantation at -190°C at reduced concentration (compared to substitutional helium). Furthermore, the concentration could be flux dependent.

It is suggested that the high-temperature helium release characterized by an effective activation energy of approximately 1.9 eV for copper, and approximately 2.5 eV for iron, is associated with a rate-determining step of detrapping of a substitutional helium atom. This tentative assignment is consistent with the conclusions of three investigating groups. Rimmer and Cottrell¹⁴ predicted that all inert gases, including helium, will preferentially occupy substitutional sites. Russell and Hastings¹⁵ concluded that helium introduced in copper via a (n,α) reaction is initially interstitial. At higher temperatures, helium becomes substitutional via capture of two vacancies. Cost and Johnson¹⁶ suggest that helium is substitutional in aluminum at elevated temperatures. This conclusion is based on measurements of lattice parameter and electrical-resistivity change due to 46-MeV helium-implanted aluminum. They point out that the magnitude of the lattice-parameter effect is two to three times that of vacancies and could be due to captive vacancies associated with the helium atom.

The assignment of the helium interstitial migration energy with the high-dose low-temperature release, although tempting, is premature. The experimental and calculated activation energies in copper are in good agreement, but the absence of low-temperature release in low-dose implantations is not readily explained.

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DISCUSSION BY ATTENDEES

Armijo: Was it possible to measure the rate of helium release for 304 or 316 stainless steels containing 1 to 100 at. ppM—when held at temperatures of 500 to 700°C? If so, were you able to measure an activation energy for helium release for these materials over this range of temperature?

Bauer: It is certainly possible to measure the helium release isothermally in the temperature range 500 to 700°C. We intend to do so. So far we have only the isochronal data available. Our estimated value of the effective activation energy is based on those data only.

Harkness: Is it possible to determine what the rate-controlling step in your gas release is? Can you tell if it is diffusion through the matrix or from trap release?

Bauer: Purely on the basis of the experimental results, one cannot determine the rate-controlling step of the helium release. The calculations indicate that low-temperature release is possible due to helium interstitial motion and high-temperature release due to detrapping from substitutional sites. As discussed in the paper, we make the latter assignment on the tentative basis; the prior assignment is in our opinion premature.

Russell: Your calculated energies (2 eV) for the migration of a helium atom from a substitutional site to an interstitial site seem high. Did you calculate the energy to move from a substitutional position to a neighboring vacant site?

Wilson: Yes, we calculated the energy required to move a helium atom from one vacant site to an adjacent vacancy in copper. It requires only 0.2 eV for this process because of the small "size" of the helium atom. This is a factor of ~ 5 less than the vacancy migration energy in copper.

Shewmon: What evidence do you have that your release at high temperature is not due to bubble migration?

Wilson: In the lower concentration implanted samples, helium release begins at temperatures below those required to observe bubbles via transmission electron microscopy (G. J. Thomas, private communication). The amount of helium release at higher temperatures is concentration dependent and dependent on helium-bubble formation.

Young: Could the low-temperature-release peak be related to radiation damage produced by the injection?

Bauer: Most of the radiation damage is confined to a region near the implanted layer, and any vacancies (or vacancy clusters) remaining in the region between the surface and the implanted layer could only act as traps. The helium atoms must pass through the damage distribution in order to be released. If these vacancies or vacancy clusters are saturated at high doses ($\sim 10^{18}$ helium atoms/cm²), the release may more easily take place via interstitial motion.

All this is speculative at this point, but we are struck by the agreement between the calculated interstitial activation energy and the onset of low-temperature helium release.

SPECIFIC-HEAT STUDY OF HELIUM-BUBBLE FORMATION IN ALPHA-IRRADIATED ALUMINUM

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ABSTRACT

We have measured the low-temperature specific heat after various annealing treatments of aluminum that has been cyclotron irradiated to produce concentrations of about 50 and 300 ppM helium. For specimens annealed above 600°C, the presence of the characteristic helium lambda peak at 2.15°K provides definite evidence for the precipitation of helium as gas bubbles. Examination of the magnitude of the lambda peak indicates that helium precipitation is complete after 10 hr at 625°C.

In 1958 Keesom and Seidel¹ observed a pronounced peak at the helium lambda temperature in the specific heat of a boron-doped silicon crystal that had been irradiated with thermal neutrons and annealed. A similar effect in the specific heat was also reported² for beryllium oxide irradiated with neutrons. The anomaly in the specific heat at the lambda temperature was attributed^{1,2} to the formation and subsequent precipitation of irradiation-produced helium within the crystal.

Other investigators reported the formation of helium gas bubbles after annealing alpha-injected helium in copper³ and aluminum⁴ samples. In the Al-He system the electrical-resistivity and lattice-parameter measurements⁵ suggested that helium atoms were no longer in supersaturated solid solution after the samples were annealed above 400°C. Our purpose in this study was the use of the helium lambda peak, as a definite measure of the presence of condensed helium, in examining the precipitation of helium as gas bubbles in aluminum. These results are compared with electron-microscopy results on equivalently prepared samples.

EXPERIMENTAL METHOD

Heat capacities of three Al-He samples were measured. The samples were prepared from 99.9999% pure aluminum ingot* that had been rolled to final thicknesses of 0.15 and 0.005 in. Prior to injection of helium, these samples were annealed 1 hr in air at 400°C. In two samples of 0.015-in. thickness, a homogeneous distribution of roughly 50 at. ppM helium was produced by irradiating with 46-MeV alpha particles.† The third sample of 0.005-in. thickness was irradiated so that alpha particles were injected in a region with a thickness of about 0.001 in. located approximately halfway through the specimen. This sample had a locally high concentration of helium which, if homogeneously distributed, would correspond to 300 ppM. During all irradiations the samples were cooled by a flow of water at about 60 psig over the back surface. Helium additions were checked by mass-spectrographic analysis before and after annealing.

For the heat-capacity measurements, the sample, an encapsulated commercial germanium resistance thermometer, and the heater wire (Pt-9% W) were glued with GE varnish to a silicon disk (1.736 g). A small part of the metallic capsule of the thermometer was filed off so that the helium gas in the capsule could be removed. The silicon disk with its attachments was suspended by cotton thread in an evacuated metallic can. Cooling of the sample and the silicon disk down to the liquid-helium range was obtained through the electrical wires to the heater and the thermometer. The thermometer was calibrated against the helium-vapor pressure. Heat capacity was measured using the heat-pulse technique. The heat capacity of the addenda (silicon plate, thermometer, heater wire, GE varnish, and thread) was measured so that the heat capacity of the Al-He sample alone could be determined. Some variation of the heat capacity was found between different runs owing to variations in the amount of GE varnish used to glue the samples. Measurements were made in the temperature range from 1 to 4°K.

RESULTS AND DISCUSSION

The heat-capacity results for the addenda plus an aluminum sample irradiated to produce 50 ppM helium are shown in Fig. 1. The superconducting transition near 1.2°K and the first- and third-power specific heat-temperature coefficients of $\gamma = 1.354 \times 10^{-3} \text{ J}/(\text{mole})(\text{deg})^2$ and $\beta = 0.027 \times 10^{-3} \text{ J}/(\text{mole})(\text{deg})^4$ are in good agreement with the results of Phillips for pure normal-state aluminum.⁶

In Fig. 2 the results are shown both before and after heat treatment for a second aluminum sample that was irradiated to produce an inhomogeneous but

*Cominco American, Incorporated, Spokane, Wash.

†Cyclotron at Argonne National Laboratory, Argonne, Ill.

Fig. 1 Heat capacity prior to heat treatment of an aluminum sample injected with 50 ppM helium. The superconducting transition for aluminum appears near 1.2° K.

locally high helium concentration as previously described (referred to as the 300-ppM sample). When this sample was measured after irradiation with the helium present atomically, the straight line typical of pure aluminum was obtained. After the sample was annealed for 10 hr at 625°C, the specific heat showed an additional helium lambda peak. The magnitude of this peak corresponds to approximately 35 at. ppM helium. After a further anneal for 38 hr at 625°C, the magnitude of this peak was unchanged. Similar results were obtained for a sample injected with 50 ppM helium for which a lambda peak was first observed after an anneal of 10 hr at 625°C and subsequently for 10 hr at

Fig. 2 Heat capacity before and after heat treatment of an aluminum sample injected with 300 ppm helium. The difference in the straight-line portions of the two measurements is due to small differences in the amount of GE varnish used to fasten the sample to the silicon.

640°C. The interpretation of these results is that the precipitation of helium to form gas bubbles was complete after the first 10 hr of annealing at 625°C. Mass-spectrographic analyses for helium, which were made on several samples after the precipitation anneals, in all cases showed that losses of helium from the sample were less than 50%. For example, a sample injected with 50 ppm helium was analyzed at 35 ppm after being annealed for 10 hr at 550°C, a treatment we have shown by electron microscopy to produce helium bubbles.

A possible interpretation of these results is that, for the bubble-size distributions in these specimens, only a small fraction of the bubbles contribute to the heat capacity. A calculation based on gas-bubble equilibrium at 550°C, using $\gamma = 1000$ ergs/cm² as the surface energy of aluminum, shows a bubble 50 Å in diameter to contain roughly 10^3 helium atoms. If we assume the liquid helium to have a density given by helium in equilibrium with its vapor and we consider the helium to be adsorbed on the surface of the bubble, then the 1000 helium atoms in a 50-Å bubble will be present as roughly one and one-half monolayers. Frederikse⁷ has shown that helium in the surface-adsorbed state does not exhibit the lambda peak when present as three to four monolayers or less. Also, the number of helium atoms in a bubble, when calculated on the basis

Fig. 3 Annealing treatments and presence of lambda peak for two aluminum samples injected with helium.

of a van der Waals gas for bubble diameters in the range from 10 to 100 Å, increases roughly as $r^{2.8}$. Thus the number of monolayers over the surface of a bubble should increase as $r^{0.8}$. On the basis of such a rough calculation, one would predict that a bubble radius of about 200 Å is required to make the five or six monolayers necessary to produce the lambda peak.

There is interest in considering the annealing treatment that was required to produce the lambda peak. In Fig. 3 the results for isochronal annealing treatments given to two samples are shown. For the 50-ppM sample, the lambda peak did not show up until the annealing temperature reached 625°C. At that temperature a 1-hr anneal did not produce the bubbles necessary to result in the peak, but a 9-hr anneal did. Similarly, the 300-ppM sample did not show the peak at 450°C but did at 625°C.

Transmission-electron-microscope examination of samples given various anneals has been made in conjunction with the specific-heat measurements. In Fig. 4, helium bubbles that are from 200 Å to less than 50 Å in diameter may be seen in a 50-ppM sample annealed for 10 hr at 625°C. These bubbles have a polyhedral shape as has previously been observed in aluminum.⁸ From measurements of bubble density and size, calculations of the amount of helium present as bubbles were made which were in good agreement with the amount of helium injected and that determined by spectrographic analysis. It is significant that electron-microscope evidence for bubbles has been found for specimens annealed at 550°C. Bubble-size distributions are known to increase in size, but

Fig. 4 Helium bubbles in aluminum irradiated to produce 50 ppm helium as seen by transmission electron microscopy. Annealed at 625°C for 10 hr.

no lambda peak was found for this anneal; these facts support the supposition that the lambda peak does not occur until bubbles reach a critical size.

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DISCUSSION BY ATTENDEES

Wiedersich: There seems to be an appreciable difference in specific heat of the annealed sample vs. the nonannealed sample *above* the lambda peak. Would you comment on this excess in specific heat?

Katyal: The difference in specific heat is a consequence of a trivial difference in experimental conditions, i.e., the properties of the varnish, used in mounting, change from run to run. We are interested only in observing the lambda peak.

Wilson: You indicated that, for bubble sizes below 50 Å, no specific heat anomaly was observed. How did you determine this value?

Cost: Electron microscopy of specimens annealed for 10 hr at 550°C showed bubbles with an average size of roughly 50 Å and a maximum size of less than 150 Å. The specific-heat anomaly was not observed on an equivalent sample given this anneal.

TRANSMISSION ELECTRON MICROSCOPY OF RADIATION-INDUCED DEFECTS

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ABSTRACT

Radiation-induced defect clusters of sizes larger than about 10 Å can be directly observed by means of transmission electron microscopy. The shape as well as the nature of the defects (vacancy or interstitial type) can be determined by comparing the calculated electron-microscopic contrast profiles for different possible defect clusters (Frank dislocation loops, perfect dislocation loops, voids, bubbles) with the results of contrast experiments. The main emphasis in this paper is on the results of contrast calculations for voids and bubbles. The influence of the focusing mode on the size and sign of the contrast figures is calculated. The results of the calculations are compared with some experimental observations of voids and bubbles in He⁺-bombarded gold films.

In recent years, transmission electron microscopy has become a useful tool for the study of radiation damage in metals and reactor materials. Silcox and Hirsch¹ were the first to observe resolvable dislocation loops in neutron-irradiated copper. Later Makin, Whapham, and Minter² found, in addition, a high density of small unresolvable defects ("black spots"). The density and size distribution of the radiation-induced defects were determined by counting, with the assumption that the diameters of the contrast figures correspond to the actual sizes of the defects. However, besides the density and size distribution of the defects, the nature and geometrical shape of the defects are of great interest. Especially, it is important to know whether the defects resulted from the agglomeration of vacancies or interstitials.

Considerable progress has been made in the theory of electron-microscopic contrast formation from defects in crystalline materials (see Hirsch et al.,³ Amelinckx et al.⁴). Aided by the theory, it is possible to calculate the contrast for any defect model with a known geometrical shape and a known strain field.

To determine the nature of the defects in irradiated materials, we first have to calculate the contrast of various defect models. The results of the computations indicate differences in the contrast between different defect models. By exploiting these differences, we can devise experiments by which the shape and the nature of the observable defects may be ascertained.

These methods are briefly explained in the first four sections of this paper. Emphasis is on the contrast of voids and bubbles. It will also be shown that the contrast of voids and bubbles can be influenced strongly by the focusing conditions of the objective lens. In later sections some experimental details are summarized, and some experimental observations concerning the contrast of defects are described.

This paper emphasizes the methods for the analysis of radiation-induced defects. For a more detailed exposition of the theory of the contrast formation and a more complete review of the results on irradiated metals and reactor materials, the reader is referred to other articles (Rühle,⁵ Wilkens^{6,7}).

SHORT SUMMARY OF CONTRAST FORMATION IN TRANSMISSION ELECTRON MICROSCOPY

The images of lattice defects are due to a diffraction contrast. As the electron beam passes through a crystalline solid, the beam is split into the direct beam and diffracted beams. (The directions of the diffracted beams depend on the lattice spacing through the Bragg equation.) If the direct beam is used for image formation (the diffracted beams are prevented from passing through the objective aperture), the so-called "bright field" is produced. If only one of the diffracted beams is used for image formation (i.e., the direct beam and all other diffracted beams are prevented from passing through the objective aperture), then a "dark-field" image results. The variation of intensity observed on the micrograph depends on the local thickness of the foil, on the crystallographic direction of the incident beam, and on the focusing mode of the objective lens.

To obtain well-defined contrast conditions, one should perform the electron-microscopic diffraction imaging under "two-beam diffraction conditions." Under these conditions the orientation of the incoming electron beam with respect to the crystallographic axes is chosen so that the incident electron beam is reflected by one set of lattice planes only, i.e., besides the incident beam, only one diffracted beam with diffraction vector $\mathbf{g}$ is strongly excited. However, since the Ewald sphere for electrons with energies of 100 keV or more is very flat, other reflections are always slightly excited. Especially the "systematic reflections" (Bragg reflections with diffraction vectors $n\mathbf{g}$, where $\mathbf{g}$ = diffraction vector of the strong excited beam; $n = -1, \pm 2, \pm 3, \dots$) can never be avoided.

Under dynamical two-beam conditions, a strong-beam dark-field image results if the strong diffracted beam (diffraction vector $\mathbf{g}$) is used for image

formation. If the specimen is imaged with the diffraction vector $-g$ or $+2g$ ($n = -1, +2$), a weak-beam dark-field image is produced.^{8,9} In the weak-beam dark field, more details on the defect structure are observable.

A critical length that is important for describing diffraction phenomena is the "extinction length" ξ_g . The value of ξ_g depends on the substance and on the particular reflecting plane. Small deviations $\Delta\theta$ of the direction of the incident beam from the exact Bragg conditions (Bragg angle θ) are described by the normalized excitation error $w = s \cdot \xi_g = \xi_g \cdot |g| \cdot \Delta\theta$. For $w \neq 0$, the effective extinction length ξ_g^w is given by^{3,10} $\xi_g^w = \xi_g / \sqrt{1 + w^2}$. Micrographs taken under two-beam dynamical diffraction conditions (with $w \approx 0$) are called "dynamic images." Micrographs taken with a specific excitation error $|w| \gtrsim 1/\xi_g$ under two-beam conditions are called "defined kinematic" images; those taken under unspecified kinematical diffraction conditions without strong excitation of a low-order reflection are called "undefined kinematic" images.

For calculations of the contrast of the disturbed lattice, "the column approximation" introduced by Hirsch, Howie, and Whelan¹¹ is applied. In this approximation it is assumed that, because the diffraction angle 2θ of the electrons is very small, the intensity at a given point on the micrograph is determined entirely by the variation of the diffraction conditions within a column (about 10 Å diameter) above the respective point at the exit surface of the transmission foil. This approximation has been justified by comparing the results of the column approximation with those of the more exact solution of the problem¹²⁻¹⁴ for the case where the defects are imaged with a strong excited beam. However, in the case of weak diffracted beams, this approximation is applicable only in specific cases.¹⁵

If the lattice planes in the neighborhood of the defects are bent, the contrast can be calculated by solving the differential equations of the two-beam approximation numerically. In such computations, the quantity characterizing specific defects is the z derivative of the displacement field of the defect, where z denotes the directions of the bisector of the incident and the reflected electron beams (two-beam case).

There are several physically equivalent formulations of these differential equations. The scattering by the defects may be described in terms of plane waves,^{10,67} Bloch waves,^{16,17} or modified Bloch waves.¹⁸ For numerical integrations, Bloch-wave equations are preferable because a scattering between the Bloch waves takes place only where the z derivative of the displacement field is essentially different from zero. Therefore the Bloch-wave equations must be solved only in the regions close to the defect.

For small defect clusters (small compared with the effective extinction length of the operating diffraction vector), the tails of the contrast profile can be calculated analytically in first-order perturbation theory.^{7,18} From these approximations, general features of the contrast figures (i.e., symmetry relations and direction of contrast) can be obtained. The first-order perturbation theory is especially helpful in determining the expected contrast of perfect dislocation

loops that are under different orientations with respect to the incident electron beam.⁷

A very important parameter in all contrast calculations is the parameter of the anomalous absorption,¹⁰ which is assumed to be ≈ 0.1 or slightly below this value.^{19,20}

In the dynamical and kinematical theory of electron diffraction, the contrast of defects is calculated at the lower surface of the foil, and it is assumed that this plane is imaged in the electron microscope. This (ideal) imaging technique is called "in-focus" imaging. However, for certain defects (voids, bubbles) the contrast depends not only on the imaging conditions—as calculated by the dynamical theory—but also on the exact focusing mode. The observable contrast depends strongly on the focusing conditions of the objective lens, i.e., the distance ξ_1 between the lower surface of the foil and the imaging plane of the microscope. If $\xi_1 \neq 0$, an "out-of-focus" picture is produced.

DIFFRACTION CONTRAST FROM BUBBLES (WITHOUT STRAIN FIELD)

Both atomic defects (vacancies and interstitials) and clusters of these atomic defects are nucleated in irradiated materials. Only the clusters that are larger than the resolution of the electron microscope can be observed by means of transmission electron microscopy. The observable clusters will simply be called defects. There are essentially two different types of defects: defects with or without a strain field in the vicinity of the defects.

In this section the contrast of defects without a strain field in the vicinity of the defects will be discussed, and we restrict ourselves to the contrast of three-dimensional cavities. In the following section the contrast of defects with a strain field will be described.

"In-Focus" Contrast of Defects Without Surrounding Strain

For the contrast calculations of defects without surrounding strain, it is assumed that the vicinity of the cavity has the structure of the ideal crystal. For simplicity, a cavity not surrounded by a strain field will be called a bubble. This case is important for small gas-filled voids or large empty or partially empty voids since in the latter case the expected strain is negligible.*

*At this point it should be noted that, in the case of a gas-filled bubble in equilibrium with the surrounding matrix, strain will be left in the matrix. Under the conditions of thermal equilibrium, the gas pressure is $p = 2\sigma/r_0$, where σ is the surface tension of the solid and r_0 is the radius of the bubble. Shuttleworth,²¹ Herring,²² and Lidiard and Nelson²³ pointed out that the surface energy γ and the surface tension σ are not necessarily equal for solids. (By surface energy we mean those terms in the free energy of a solid which are proportional to the surface area.) These two quantities are related by $\sigma = \gamma + F \cdot d\gamma/dF$, where the differentiation indicates a change of the area F of the bubble under conditions in which the number of surface atoms remains constant. The surface tension σ can be considerably different from the surface energy in the case of copper; there are indications that σ has a value²⁴ that ranges between $-0.2 \gamma \lesssim \sigma \lesssim 0.3 \gamma$.

The contrast of bubbles was calculated by Ashby and Brown²⁵ and in detail by Van Landuyt, Gevers, and Amelinckx,²⁶ the results of Van Landuyt et al. were applied by Ingram²⁷ and Ruedl.^{28,29} The contrast of the bubbles can best be calculated by the matrix method developed by Gevers³⁰ and Amelinckx.³¹ With this method^{30,31} the amplitudes of the transmitted beam T_{z_1} and of the scattered beam S_{z_1} are calculated at the lower surface of a perfect crystal (thickness z_1) by multiplying the amplitudes of the incoming beams (T_0, S_0) by the "scattering matrix" $M(z_1)$. If a perfect crystal (thickness t) contains a bubble of thickness z_2 , the amplitudes T^b and S^b of the transmitted and reflected beam at the exit surface are (see Fig. 1)

$$\begin{pmatrix} T^b(x,y) \\ S^b(x,y) \end{pmatrix} = M(z_3; x,y) V(z_2; x,y) M(z_1; x,y) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1)$$

The column vector $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ in Eq. 1 represents the initial values of T and S at the entrance surface ($z = 0$), the matrix M_1 describes transmission through the first

portion of the crystal with thickness z_1 , and the matrix $V(z_2)$ determines the scattering by the bubble (thickness z_2). The value of the excitation error s to be used in $V(z_2)$ is that of the preceding perfect column; therefore s is constant since the crystal is perfect apart from the void. M_3 describes the scattering through the second part of the perfect crystal with thickness z_3 . The amplitudes T^b and S^b are, in general, a function of the coordinates (x,y) since the thickness z_2 of the bubble with an arbitrary shape depends on (x,y) . We restrict ourselves mainly to the case where the z_2 dimension of the cavity is constant; see Fig. 1. Clearly, a bubble of arbitrary shape can always be decomposed in a sequence of bubbles with constant thickness. The variation over the projected area of the bubble can easily be obtained by using the thickness-intensity relations that are described here. Contrast of bubbles with a spherical shape will be discussed later in some detail.

In Eq. 1 the scattering matrix $M(z_1)$ can be described as [the dependence of z_2 on the (x,y) coordinates is not noted explicitly anymore]:

$$M(z_1) = \begin{pmatrix} T_1 & S_1 \\ S_1 & T_1 \end{pmatrix} \quad (2)$$

where the explicit expressions for T_1 and S_1 are to a good approximation:^{26,30}

$$T_1 = \cos \pi \alpha z_1 - i s \frac{z_1^2}{2} \sin \pi \alpha z_1$$

$$S_1 = \frac{i}{2} \frac{\sqrt{1 + w}}{z_1} \sin \pi \alpha z_1$$

Fig. 1 Schematic representation illustrating the notation used. The case of a penny-shaped bubble is considered. A bubble with arbitrary shape must be decomposed in a sequence of bubbles as shown in this figure. The foil thickness is t , subdivided in the thickness of the bubble z_2 and in the thicknesses z_1 and z_3 of the parts above and below the bubble (perfect crystal). The wave vectors of the incoming and reflected beams are k_0 and k_g , respectively.

with

$$\alpha = \frac{1}{\xi_g^w} + i \frac{1}{\tau_g \sqrt{1+w^2}}, \quad w = s \xi_g, \quad \text{and} \quad \xi_g^w = \frac{\xi_g}{\sqrt{1+w^2}}$$

where s is the excitation error, ξ_g is the extinction length for the diffraction vector g , and τ_g is the corresponding anomalous absorption length.

The minus sign in T_i^- and S_i^- (Eq. 2) indicates that in the corresponding expressions the sign of s has to be changed.

In Eq. 1, $V(z)$ is the vacuum matrix:

$$V(z_2) = e^{-2\pi i \epsilon z_2} \begin{pmatrix} e^{-\pi i s_1 z_2} & 0 \\ 0 & e^{\pi i s_1 z_2} \end{pmatrix} \quad (3)$$

In Eq. 3 the factor $e^{-2\pi i \epsilon z_2}$ describes the phase difference between a beam passing through a bubble of thickness z_2 and a beam passing through the regions of the perfect crystal.

This phase shift is caused by the difference of the mean inner potential V_0 in the gas-filled bubble and in the perfect crystal. From the mean inner potential V_0 (<0) in a metal, ϵ can be calculated to

$$\epsilon = \frac{eV_0}{2E} k_0 \quad (4)$$

where e is the charge of an electron, E is the total energy of the electron, and k_0 is the vacuum wave vector of the electrons.

The phase factors can be neglected if we image the bubbles "in focus," i.e., if we image (with the objective lens) exactly the exit surface of the foil. However, if we image the defect "out of focus" (i.e., if we image a plane with a distance from the exit surface), the phase factor is very important (see the next subsection).

From the amplitudes T^b and S^b , the intensities can be calculated; however, normal absorption also has to be taken into account in the present case, i.e., the intensities have to be multiplied by an absorption factor

$$e^{-\mu(z_1 + z_3)}$$

where μ is the normal absorption coefficient, and absorption by the bubble is obviously neglected.

On the other hand, the amplitudes T^p and S^p in the perfect regions (columns not intersected by a bubble) can be calculated to

$$\begin{pmatrix} T^p \\ S^p \end{pmatrix} = M(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (5)$$

where $t = z_1 + z_2 + z_3$ is the thickness of the film. In this case an absorption factor $e^{-\mu t}$ has to be taken into account for the intensities I . The contrast is defined by

$$C_{T,S} = \frac{I_{T,S}^b - I_{T,S}^p}{I_{T,S}^p}$$

(superscripts b and p refer to bubble and perfect region; the subscripts T and S indicate the intensity of the transmitted or scattered beam).

It is clear from Eqs. 1, 2, and 3 that the contrast depends on the thickness t of the film, the thickness z_2 of the bubble (which may vary over the cross section of the void), the normal absorption factor μ and the anomalous absorption length τ_g , and on the excitation error w .

In our considerations we restrict ourselves to the case $w = 0$, i.e., the exact Bragg condition. In the dynamical condition ($s = 0$), the calculated contrast of the bubble is independent of the depth position z_2 of the defect since Eq. 1 simplifies to

$$\begin{pmatrix} T^b \\ S^b \end{pmatrix} = e^{-2\pi i \epsilon z_2} \cdot M_3 M_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (6)$$

Since the basic property of the M matrices is that $M(z_1) \cdot M(z_1) = M_3 \cdot M_1 = M(z_1 + z_3)$ (see Ref. 30), the relation in Eq. 6 describes transmission and scattering by a perfect crystal of thickness $(z_1 + z_3)$. The intensity of an electron beam passing through the bubble can be calculated by

$$I_{T,S}^b = I_{T,S}^p(z_1 + z_3)$$

and the contrast of the bubbles is

$$C_{T,S} = \frac{I_{T,S}^p(z_1 + z_3)}{I_{T,S}^p(t)} - 1 \quad (7)$$

The foil thickness-intensity relationships for bright field and dark field are plotted in Fig. 2 for different factors of normal absorption μ (thickness fringes of a wedge-shaped crystal, see Ref. 3). For different materials and different operating reflection vectors, different experimentally determined values of μ have to be applied. The curves for bright field plotted in Fig. 2 include the upper and lower values for different materials imaged with diffraction vectors of not too high order.

From the curves plotted in Fig. 2, the theoretical predicted contrast of voids in bright field and dark field can be calculated from Eq. 7. The expected contrast of small bubbles with constant thickness is plotted against the foil thickness in Fig. 3. It follows that the bubbles exhibit the strongest contrast in a very thin region of the crystal. The contrast depends sensitively on the exact value of the foil thickness, especially in the case of a very thin crystal region. The contrast is strongest at thicknesses slightly smaller or larger than 0.5 extinction length, i.e., at the front or the rear of the first dark thickness fringe in dark-field images or at the front of the second dark fringe in bright-field images. These results have been verified experimentally by Ruedl.^{28,29}

The calculated contrast figures of penny-shaped bubbles with different thicknesses z_2 are plotted for a constant foil thickness (4 extinction distances) in Fig. 4. The curves indicate that, for small (normal) absorption factors μ , the bubbles exhibit predominantly negative contrast in bright field and predominantly positive contrast in dark field. Figure 4 also shows that the *sign* of the contrast can be different for bubbles with different thicknesses z_2 .

Fig. 2 Intensity-thickness relation for $w = 0$ (bright field I_T and dark field I_S). Normal and anomalous absorption are taken into account. The value of the anomalous absorption coefficient was $\kappa = 0.1$; the values of the normal absorption coefficients are noted in the diagram.

So far we have calculated the electron-microscopical contrast for bubbles with a constant thickness z_2 . If the thickness of the bubble varies over the projected area of the bubble, the sign and magnitude of the contrast will also vary over the projected area. For dynamical two-beam imaging conditions ($w = 0$), the contrast can easily be obtained from Fig. 2 for each point within the projection of the bubble.

We calculated the contrast for bubbles with a spherical shape at the lower surface of the foil (in focus). For these bubbles the thickness z_2 (cf Fig. 1) depends for a bubble with radius R_b only on the distance r from the center of the bubble

$$z_2 = 2 R_b \sqrt{1 - \rho^2}$$

where ρ is the reduced distance from the center of the bubble $\rho = r/R_b$ ($0 \leq \rho \leq 1$). The dependence of the sign and magnitude of the contrast as a function of the distance ρ can be determined with Fig. 2 for bubbles with different radii R_b in foils of different thicknesses t .

Fig. 3 Dependence of contrast for bright field (C_T) and dark field (C_S) from the foil thickness. The thickness of the penny-shaped bubble is $0.1 \xi_g$, the normal absorption factor μ is $\mu = 1/\xi_g$; $w = 0$.

The magnitude of the contrast produced by a spherical bubble always varies over the range of the projection of the bubble ($0 \leq \rho \leq 1$) onto the lower foil surface. For certain ratios between the foil thicknesses and the bubble diameters also, the sign of the contrast changes over the projection of the bubble.

The contrast profiles for two examples ($R_b = 0.1 \xi_g$ and $R_b = 0.4 \xi_g$) are plotted in Fig. 5 as a function of $\rho = r/R_b$. The foil thickness is $3.75 \xi_g$. In both cases, maximum contrast is obtained for $\rho = 0$. The small bubble ($R_b = 0.1 \xi_g$) reveals for $t = 3.75 \xi_g$ a weak negative contrast; the intensity inside the projected area of the bubble (onto the image plane) is smaller than the background intensity. As expected for small bubbles, the sign of the contrast does not change over the whole range of ρ ; however, the magnitude of the contrast decreases with increasing ρ . This contrast will be barely visible since the intensity deviates less than 20% from the background intensity and since this weak contrast changes slowly over the radius of the small bubble. For the large bubble

Fig. 4 Variation of bright field (C_T) and dark field (C_S) contrast with increasing bubble thickness $z_2/\xi_g = R_0/\xi_g$. The thickness of the foil is $4\xi_g$. The different normal absorption factors μ are noted; $w = 0$.

($R_b = 0.4 \xi_g$) the calculated contrast is a bright spot surrounded by a dark ring, i.e., the sign of the contrast changes in this case. The diameter of the bright part is 0.87 of the diameter of the bubble; the outer diameter of the dark ring corresponds to the actual diameter of the bubble.

For other bubble diameters and foil thicknesses, similar or more complicated contrast figures can be calculated. However, for all in-focus contrast calculations, the outer diameter of the contrast figures is always equal to the actual size of the bubbles.

For $w \neq 0$ the in-focus contrast of large bubbles ($d \gtrsim 0.3 \xi_g^w$) may be brighter or darker than the background intensity, depending on the depth

Fig. 5 Contrast of spherical bubbles of two different sizes. Bright-field images. The change in the normalized intensity I/I_0 (I_0 = background intensity) is plotted over the reduced bubble radius $\rho = r/R_b$; R_b = bubble radius; contrast $C_T = I/I_0 - 1$; $w = 0$.

position of the bubble and on the magnitude and sign of w (see Ref. 26). The contrast of small bubbles is so weak that it is not possible to observe the defect for large values of w .

"Out-of-Focus" Contrast of Bubbles

We derived formulas in the preceding subsection which can be used to calculate the amplitudes of the transmitted and scattered wave field at each point of the exit surface of the foil. The intensity distribution can be imaged with the electron microscope by imaging the exit surface of the foil, i.e., the lower plane of the foil coincides with the image plane of the objective lens. In this way an in-focus picture is produced.

However, if we image, as sketched in Fig. 6, a plane that has a certain distance ξ_i from the lower surface of the foil, we produce an out-of-focus picture. The intensity distribution of an out-of-focus picture will be, in general,

Fig. 6 Schematic representation illustrating the notation used for out-of-focus calculations. The center of the bubble lies at $x = y = \xi = \eta = 0$. ζ_i describes the distance between the lower foil surface and the image plane.

different from the in-focus picture since the waves emerging from the exit surface of the foil interfere with each other when reaching the image plane at $\zeta_i \neq 0$.

The wave field in the image plane (at a distance ζ_i from the foil, see Fig. 6) can be calculated from the wave field at $\zeta = 0$. The coordinate system will be chosen, as shown in Fig. 6. We normalize the wave field $\Psi(r, \zeta)$ at $\zeta = 0$ outside the bubble so that $\psi(r, 0) = 1$ for $r > r_0$ [$r = r(\xi, \eta)$]. For the wave field at $r < r_0$, we can write $\psi(r, 0) = 1 + \Delta(\xi, \eta)$, where $\Delta(\xi, \eta)$ is a complex quantity.

The two-dimensional Fourier transformation of the wave field at $\zeta = 0$ is

$$\tilde{\psi}(\mathbf{p}) = \int_0^\infty \psi(r) \exp(-2\pi i \mathbf{p} \cdot \mathbf{r}) d^2 r \quad (8)$$

with $\mathbf{p} = \mathbf{p}(\mathbf{p}_\xi, \mathbf{p}_\eta)$.

The amplitude of the wave field at the point $(\xi, \eta) = \mathbf{r}$ at a distance ζ from the exit surface is then given by (for details see Ref. 32)

$$\psi(\mathbf{r}, \zeta) = \int_0^\infty \tilde{\psi}(\mathbf{p}) \exp[2\pi i (\mathbf{p} \cdot \mathbf{r} + \zeta \sqrt{k_0^2 - \mathbf{p}^2})] d^2 \mathbf{p} \quad (9)$$

This equation satisfies the necessary conditions that the modulus of the wave vectors of all partial waves is k_0 and that Eq. 9 with $\zeta = 0$ leads to the Fourier transform of Eq. 8.* Since $\mathbf{p}^2 \ll k_0^2$, we develop to the first order

*Equation 9 also can be obtained by solving the Kirchoff integral of the diffraction theory.^{3,3,4} It should be noted^{3,4} that the influence of the astigmatism of the objective lens and the finite aperture on the out-of-focus image can be neglected for defect structures larger than about 8 Å and for values of ζ larger than about 4000 Å.

$$\sqrt{k_0^2 - p^2} \approx k_0 - \frac{1}{2} \frac{p^2}{k_0} \quad (10)$$

and we obtain

$$\psi(r, \xi) = \exp(2\pi i k_0 \cdot \xi) \int_0^\infty \tilde{\psi}(p) \exp \left[2\pi i \left(p \cdot r - \frac{1}{2} \frac{p^2}{k_0} \xi \right) \right] d^2 p \quad (11)$$

where the phase factor $\exp(2\pi i k_0 \cdot \xi)$ can from now on be omitted.

We calculate the out-of-focus contrast for a bubble, and we restrict ourselves to cases where the projection of the bubble onto the (ξ, η) plane is a circle with radius r_0 . Furthermore, we assume that $\Delta(\xi, \eta)$ depends only on the distance from the center of the bubble and not on the azimuth angle φ .

With Eq. 8 we obtain from Eq. 11

$$\psi(r, \xi) = \int_{p=0}^\infty \int_{r'=0}^{r'=r_0} \psi(r') \exp \left\{ 2\pi i \left[(p, r - r') - \frac{1}{2} \frac{p^2}{k_0} \cdot \xi \right] \right\} d^2 p d^2 r \quad (12)$$

The integration over $d^2 p$ can be solved analytically. If we introduce a polar coordinate system (r, φ) , the integration over the azimuth angle φ can also be performed analytically when $\psi(r') = 1 + \Delta(|r'|)$, and we obtain

$$\psi(r, \xi) = 1 - 2i\beta \exp[i\beta\rho^2] \int_{\rho'=0}^1 \Delta(\rho') J_0(|2\beta\rho\rho'|) \exp[i\beta\rho'^2] \rho' d\rho' \quad (13)$$

with $\beta = \pi k_0 r_0^2 / \xi$, $\rho = |r'|/r_0$ and J_0 is the zero-order Bessel function. Explicit calculations of $\psi(r, \xi)$ require that $\psi(\rho') = 1 + \Delta(\rho')$ is known. $\Delta(\xi')$ is essentially different for bubbles of various sizes and shapes and can be calculated from Eqs. 1 and 5.

Small Bubbles

If the dimensions* of the bubble are very small compared to the operation extinction length, $\Delta(\rho')$ will be proportional to the actual thickness z_2 of the bubble at the distance $\rho = r'/r_0$. In this case

$$\psi(\rho') = 1 + \delta G(\rho') \quad (14)$$

In Eq. 14, δ describes the change of $\psi(\rho')$ in the center of the bubble. The quantity δ is complex and can be calculated from Eqs. 1 and 5. For small bubbles the imaginary portion of δ is most significant, i.e., the phase shift of the wave going through the center of the bubble relative to the wave field in the perfect crystals. From Eq. 3 the phase factor will be

$$e^{-2\pi i \epsilon z_2} - 1 \approx -2\pi i \epsilon z_2$$

*This approximation is valid for spherical bubbles with a diameter smaller than about $0.2 \xi_g$ independent of the excitation error w .^{3,2,3,4}

where z_2 is the thickness of the bubble at $\rho = 0$ (see Fig. 1). The real part of δ is negligibly small for the case of small bubbles.

The term $G(\rho)$ in Eq. 14 is a geometrical factor that describes the thickness of the bubble as a function of the distance $\rho = r/r_0$ from the center of the bubble. For spheres, G is $G = \sqrt{1 - \rho^2}$, and for small disks, G is $G = 1$.

For these two simple geometrical shapes, the intensity distribution was calculated with a computer from Eq. 13. For the integration it was assumed that the mean inner potential³ is -10 V.

Some results of the calculations are represented in Figs. 7(a) and 7(b). The reduced intensity I/I_0 (I_0 = background intensity) of the out-of-focus contrast is plotted as a function of the distance $\rho = r/r_0$ from the bubble center at $r = 0$.

As pointed out (in the preceding subsection) the contrast of small bubbles (radius $r \leq 0.1 \xi_g$) is weak for in-focus conditions and large foil thicknesses. The small bubbles are nearly invisible. Figures 7(a) and 7(b) indicate that the small defects reveal a stronger contrast if they are imaged under out-of-focus conditions.*

The calculated contrast is, for negative values of ζ , a bright, circular center surrounded by a sequence of dark and bright Fresnel fringes. However, only the contrast of the first dark Fresnel fringe is strong enough to be visible.

The size of the white center represents, within 10%, the real diameter of the bubble for $\beta \leq -1$. However, the diameter of the white center exceeds the actual bubble size for $\beta > 1$. This is true for small spherical bubbles and for small disks.

The calculated ratios of the inner and outer diameters of the first dark Fresnel fringe to the actual bubble diameters are plotted in Fig. 8 as a function of the actual bubble diameter for $\zeta = -8000$ Å. Figure 8 shows that, only for bubbles smaller than 20 Å, the diameter of the inner bright area (equivalent to the inner diameter of the first dark Fresnel fringe) deviates more than 10% from the actual bubble diameter.

However, the results shown in Fig. 8 clearly verify that the outer diameter of the first dark Fresnel fringe is much larger than the actual size of the bubble. Therefore this quantity should never be used to determine the size of small bubbles.

If one calculates the out-of-focus intensities for $\zeta > 0$, the contrast is reversed; a dark spot is surrounded by a series of bright and dark rings.

Large Bubbles

For large bubbles (diameter larger than about 0.2 extinction lengths) the wave field at $\zeta = 0$ must be calculated according to Eqs. 1 and 5. With the numerically obtained wave field, Eq. 13 has to be integrated. The integration was performed until now only for a few bubble sizes, and one result is plotted in

*It should be noted that for the contrast calculations the mean inner potential of -10 V was assumed. Actually this value is too low for almost all metals; a value of -20 V should be closer to the real value of V_0 .

Fig. 9. The out-of-focus contrast was calculated for a bubble with a radius of $0.4 \xi_g$, and the thickness of the film was $3.75 \xi_g$. The in-focus contrast calculations (compare Fig. 5 and the heavy solid line in Fig. 9) predict a bright circular center surrounded by a dark ring.

Fig. 7 (See facing page for caption.)

For a defocusing distance $\zeta = -6000 \text{ \AA}$, the contrast is modified when compared with the in-focus contrast. However, the general feature of the contrast remains the same since the small intensity oscillations for $\rho < 0.8$ cannot be observed experimentally. For $\zeta = -6000 \text{ \AA}$, the outer diameter of the first dark ring corresponds to the actual diameter of the bubble. This result is not correct for $\zeta = +6000 \text{ \AA}$ because, in this case, the outer diameter of the first intensive dark ring is at $\rho = 1.15$.

Fig. 7 Results of out-of-focus calculations (mean inner potential $V_0 = -10 \text{ V}$); I/I_0 (I_0 = background intensity) is plotted over the reduced radius of the defect $\rho = r/r_0$ (r_0 = radius of the defect) for different values of $\beta = \pi \kappa_0 r_0^2 / \zeta$. Note that the out-of-focus contrast extends over the actual size of the defect. κ_0 = wave vector of the electrons, ζ = defocusing distance. (a) spheres; (b) cylindrical disks. The thickness of the disks is equal to r_0 . ($w = 0$).

Some preliminary calculations for additional bubble diameters show that the results from Fig. 9 cannot be generalized for all sizes of bubbles and foil thicknesses. Detailed results of contrast calculations and a discussion of the results will be published elsewhere.³²

Fig. 8 Contrast width of the inner (d_{in}/d_b) and outer (d_{out}/d_b) reduced diameter of the first dark Fresnel fringe as a function of the actual bubble diameter (defocusing distance $\zeta = -8000 \text{ Å}$). d_b = diameter of the spherical bubble.

CONTRAST OF SMALL DEFECTS WITH SURROUNDING STRAIN FIELD

The lattice planes are bent in the vicinity of a defect if the defect possesses a strain field. Therefore a scattering between the Bloch waves existing in the lattice occurs, which changes the amplitudes at points close to the defect.

If the defects are smaller than the extinction lengths, their structure and shape are not directly resolvable on micrographs. However, as shown in different papers (for a summary see Refs. 4 to 6), information on the type and shape of the defects can be obtained by imaging the defects under well-defined dynamic and kinematic diffraction conditions. The results of the observations have to be compared with the results of contrast calculations, which will be described shortly.

Defects produced by condensation of vacancies and interstitials are distinguished by the sign of the elastic displacement in the vicinity of the defects; defects produced by interstitials have a positive sign (positive misfit parameter^{3,5}); defects produced by condensation of vacancies have a negative sign (negative misfit parameter).

Fig. 9 Out-of-focus contrast calculations for large bubbles ($R_b = 0.4\xi_g$, $\xi_g = 250 \text{ \AA}$). The foil thickness is $3.75\xi_g$ for $\zeta = +6000 \text{ \AA}$ and $\zeta = -6000 \text{ \AA}$. The reduced intensity I/I_0 ($I_0 =$ background intensity) is plotted vs. $\rho = r/R_b$. The in-focus contrast ($w = 0$) is also represented.

For dynamic and defined kinematic diffraction conditions, the results of the contrast calculations are available for several defect models, such as Frank dislocation loops, perfect dislocation loops, and strain centers with a spherically symmetrical displacement field.^{5,6,36-39} In the following subsections the important features of the contrast are summarized, additional details on the contrast for voids are represented, and the required experiments for the analysis of the defects are described.

Results of Contrast Calculations for Small Defect Clusters

1. Under two-beam dynamic diffraction conditions, a small defect within a surface layer of about 1 extinction distance ξ_g^w thickness shows a black and white (BW) contrast (see Figs. 10 and 11). A BW contrast is described by a vector l pointing from the center of the black portion to the center of the white portion.

The magnitudes of the black and white portions of the contrast (BW contrast) strongly depend on the exact value of the foil thickness, if the foil is thinner than 4 extinction distances. Highest contrast is expected from a defect in bright field in foils with a thickness of $t_1 = (2n + 1) \xi_g^w / 2$ ($n = 0, 1, 2, \dots$) and in dark field in foils with a thickness $t_2 = n \xi_g^w$ ($n = 1, 2, 3, \dots$). The defects are nearly invisible in bright field in foils with a thickness of t_2 and in dark field in foils with a thickness of t_1 .

Fig. 10 Black and white contrasts (BW contrasts) in a He^+ -bombarded gold film. The diffraction vector $g = (220)$ is noted, foil orientation $[001]$, dark-field picture.

Fig. 11 Schematic plot of the depth oscillations of the BW contrast from small defects (Frank dislocation loops, small voids) of vacancy type. The calculated contrast figures are drawn at that depth position at which the loop centers were assumed. d.f. = dark field, b.f. = bright field. g = diffraction vector, b = Burgers vector (in the case of Frank loops only). For defects of interstitial type, the black and white contrast portions must be interchanged. In the intermediate (transition) regions $l_{k,k+1}$ complicated contrast figures are calculated.

The magnitude of the BW contrast is independent of the exact value of the foil thickness t , if t is larger than ~ 5 extinction lengths and $\xi_g^w/\tau_g = 0.1$. In this case the thick foil approximation is applicable.¹⁸

2. The BW contrast of small defects shows the following characteristic features for different shapes of defects:

- a. For small dislocation loops, the direction l of the BW contrast is determined by the main component of $d(g \cdot R)/dz$ where g is the diffraction vector, $R(x,y,z)$ is the displacement field of the defect, and z is the coordinate parallel to the reflecting lattice planes. For defects with an isotropic displacement field (voids, see next subsection), l is always parallel to $+g$ or $-g$, independent of the direction of the diffraction vector. For Frank dislocation loops (the Burgers vector b of the loop is perpendicular to the loop plane), l is parallel or antiparallel to b or to the projection of b onto the image plane, independent of the diffraction vector with which the defects are imaged. However, the angle between b and the diffraction vector must be smaller than $\sim 60^\circ$.

For perfect loops³⁶⁻³⁸ (Burgers vector may not be perpendicular to the loop plane) the direction of the BW contrast l is, in general, no longer parallel or antiparallel to the Burgers vector b ; the angle between l and b depends on the loop orientation relative to the diffraction vector g . For certain orientations, complex contrast figures are calculated.^{36,37,39}

- b. The sign of $(g \cdot l)$ depends on the sign of the defect (vacancy or interstitial) as well as on the distance of the defect to the nearest foil surface. Thus for a defect with a given sign of the misfit parameter, the sign of $(g \cdot l)$ oscillates, as shown in Fig. 11, with the depth position of the defect inside the foil (depth oscillations). If a defect lies close to a boundary of the layers (transition regions), the calculated contrast figures are complex for all types of defects.³⁶

3. Contrast calculations show that the defects appear as black dots under both unspecified (many beam) and defined kinematic diffraction conditions. As shown by Maher, Perrin, and Bullough,³⁹ the contrast width under defined kinematic conditions also depends on the diffraction vector g . Preliminary many-beam calculations, when compared with experimental observations,⁴⁰ have shown that the diameter of the contrast figures (at 10% deviation from the background intensity) corresponds best to the actual size of the defect if the electron beam is close to a $\langle 100 \rangle$ or a $\langle 110 \rangle$ direction of the foil.

The largest diameter of the black dots (which, in general, do not have a circular shape) on positive prints corresponds to the diameter of the defect.

Results of Contrast Calculations for Voids

The contrast of voids with a surrounding strain field has been calculated for different void sizes, different amounts of strain in the vicinity of a void, different diffraction conditions, and different foil thicknesses. In this calculation both contrast effects, i.e., diffraction contrast by the empty space inside the foil (see the section "Diffraction Contrast from Bubbles (Without Strain Field)") and by the strain, were considered. So far, only in-focus contrast has been calculated for voids with a strain field.

The contrast due to the strain in the vicinity of the void is strongest under exact two-beam diffraction conditions. The strain is described by means of the (dimensionless) normalized misfit parameter⁴¹

$$P = \Delta V \cdot \frac{|g|}{\pi \xi_g^w{}^2}$$

where ΔV represents the volume misfit of the defect, with $\Delta V = \epsilon_m \cdot 4\pi/3 R_s^3$ for a spherical void (R_s = radius of the inclusion); ϵ_m is the relative volume misfit, which is for a gas-filled void⁴²

$$\epsilon_m = \frac{2\gamma p R_s}{4\mu R_s}$$

where p is the pressure inside the void, γ is the surface energy (see first subsection in preceding section) and μ is the shear modulus. Figure 12 shows the results of the calculations concerning the visibility and type of contrast.⁴³ The diagram is divided into three areas. In area A (small defects, large misfit parameter) BW contrasts with depth oscillations (Fig. 11) are expected. In area B, BW contrasts will occur; however, the depth oscillations of the BW contrasts are suppressed due to the relaxation at the surface of the foil.⁴³ The direction l for all BW contrasts of defects belonging to area B is the same as for small defects lying in the first layer L_1 as described in Fig. 10 (Ashby and Brown case⁴⁴). Defects in area C (large voids) reveal no BW contrast under dynamical

Fig. 12 Type of contrasts of spherical voids (inclusions) as a function of the reduced radius R_v/ξ_g (R_v = radius of the void, ξ_g = extinction length) and of the normalized misfit parameter P . Region A: black and white contrasts with depth oscillations; Region B: black and white contrasts without depth oscillations; Region C: no black and white contrasts calculated, pure thickness contrast.

diffraction conditions. The contrast of the large voids is determined mainly by the thickness contrast described in the preceding section.

For small voids (area A) the absolute value of the strain can be estimated by comparing the results of the calculations with quantitatively evaluated micrographs. It should be possible to determine at least the order of magnitude of the strain around the small voids by imaging the defects with different diffraction vectors $\mathbf{g}$, thus changing the value of the normalized misfit parameter P .

A comparison of the experimental observations with the contrast calculations will give the value of ϵ_m . However, the magnitude of the contrasts depends on the exact value of the foil thickness t , if t is smaller than 4 extinction distances. It must be noted that if the diffraction vector $\mathbf{g}$ is changed the reduced foil thickness (measured in extinction distances) may be changed. Therefore the quantitative evaluation is possible only for thick foils.

Required Experiments for the Analysis of Small Defects

1. The Burgers vector and the shape of small defects can be determined by imaging the defects under different two-beam diffraction conditions, i.e., with different $\mathbf{g}$ vectors. The defects reveal BW contrasts. From the directionality of the BW contrasts, the geometrical shape of the defect can be determined.

2. The type of small defects (vacancy or interstitial) can be determined by measuring the distance between the depth position and the nearest foil surface with the stereo technique^{4,5,6} and by comparing the results of the measurement with the calculated depth oscillations (Fig. 11).

3. The volume density and size distribution of the defects can be evaluated from micrographs taken under kinematic diffraction conditions. The thickness of the film can be determined by stereo measurements.^{5,6}

CONTRAST FROM LARGE DISLOCATION LOOPS

If the diameter of a dislocation loop is larger than about one extinction distance, the geometrical shape of the loop is resolvable with the electron microscope. The contrast of the large loop can be explained by the contrast of a single dislocation line.

Contrast of a Perfect Dislocation Loop

A perfect dislocation loop consists of a closed dislocation line; no stacking fault is present inside the loop. The Burgers vector of the dislocation line can be determined with the rule $(\mathbf{g} \cdot \mathbf{b}) = 0$ for (nearly) vanishing contrast.

From contrast calculations by Howie and Whelan^{10,11} for a single dislocation, it is known that, in the defined kinematic case ($w \gtrsim 1$), the actual position of the dislocation does not coincide with the black line (minimum of the contrast profile). The black line will always be on the side of the dislocation

where the lattice bending (caused by the dislocation) locally reduces the excitation error w ; the magnitude of the shift depends on the magnitude of w .^{*} With this property of the dislocation contrast, we can determine the type of the loop.^{4,7-50}

The analysis can be applied only unambiguously for loops that have a Burgers vector $\mathbf{b}$ perpendicular to the loop plane. The loop plane must be inclined to the image plane (the image plane is the plane perpendicular to the incident electron beam). For cases where the loop planes are parallel or perpendicular to the image plane, the observable shapes of the loops change very little with the tilting of the specimen. If the loop is inclined, the contrast from the line segments of the loop most strongly inclined to the image plane is weaker than the contrast from the other segments of the loop.[†]

The loop normal $\mathbf{n}$ may be defined so that the angle between $\mathbf{n}$ and the direction of the incident electron beam $\mathbf{k}_0$ is always acute. Then we may differentiate between two orientations of a loop plane (i) $(\mathbf{g} \cdot \mathbf{n}) > 0$ and (ii) $(\mathbf{g} \cdot \mathbf{n}) < 0$. By tilting the specimen (tilt axis perpendicular to $\mathbf{g}$) to high tilting angles and by observing the change of the projected loop width, one can determine which of the two orientations occurs for a specific loop.

From the above-mentioned fundamental property of the dislocation contrast, it follows for $w \neq 0$ that the contrast lies either outside [case (a)] or inside [case (b)] the projected loop position. A decision between the two possibilities may be reached either by changing the sign^{4,7} of w near the same diffraction vector $\mathbf{g}$, or by changing from $\mathbf{g}$ to $-\mathbf{g}$ with the fixed sign of w .[‡] The latter experiment is normally preferred since, especially in thick films, the transmissivity is low for negative values of w .

If all experiments were performed with $w > 0$, we determine the nature of the loop by combining the results of large-angle tilting experiments [case (i) and case (ii)] with the results of the $+\mathbf{g}/-\mathbf{g}$ experiments.

The following rules are valid for differentiation between vacancy and interstitial loops:

(i) + (a) or (ii) + (b) $\rightarrow$ vacancy loop

(i) + (b) or (ii) + (a) $\rightarrow$ interstitial loop

This rule works correctly only if Burgers vector $\mathbf{b}$ is perpendicular to the loop habit plane. The above rules are no longer valid if $\mathbf{b}$ contains a shear component $\mathbf{b}_s$ which lies in the plane of the loop and if $\mathbf{b}_s$ changes the sign of $(\mathbf{g} \cdot \mathbf{b})$ relative

^{*}For $w \approx 0$ the center of gravity of the contrast profile coincides with the position of the dislocation line.

[†]The line through the two weak parts is parallel to the trace of the image plane and the habit plane.

[‡]Effectively one has to change the sign of $(\mathbf{g} \cdot \mathbf{b})_s$.

to the corresponding sign of $(\mathbf{g} \cdot \mathbf{b}_e)$.^{*} This occurs for certain orientations of $\mathbf{b}_s$ relative to $\mathbf{g}$ and for certain magnitudes of $\mathbf{b}_s$. To determine the nature of the loops, we need the direction of the Burgers vector, and this direction can be evaluated by a sequence of different tilting experiments (Maher and Eyre^{51,52}).

Contrast of a Dislocation Loop with Stacking Fault (Partial Dislocation)

If a dislocation loop contains a stacking fault, the surrounding dislocation is, in general, a partial dislocation. In this case $(\mathbf{g} \cdot \mathbf{b})$ will, in general, not be an integer. Extended contrast calculations by Silcock and Tunstall⁵³ have shown that the contrast of the dislocation is much weaker for $(\mathbf{g} \cdot \mathbf{b}) = -\frac{2}{3}$ than for $(\mathbf{g} \cdot \mathbf{b}) = +\frac{2}{3}$ (in both cases $w \approx 1$). On the basis of this result and on the basis of a similar method described earlier under the heading "Contrast of a Perfect Dislocation Loop," it is possible to determine the nature of the loops.⁵⁴ The fault displacement vector $\mathbf{R}$ can be determined with the rule $\mathbf{g} \cdot \mathbf{R} = 0$, i.e., the stacking fault is invisible if $\mathbf{R}$ is perpendicular to $\mathbf{g}$.

SOME EXPERIMENTAL DETAILS

Determination of the Excitation Errors

The sign and magnitude of the excitation error w may be determined from the Kikuchi line pattern (see Hirsch et al.³). These lines usually can be observed in fairly thick crystals; however, the number of defects inside the crystal should not be too great. Kikuchi lines are due to Bragg reflections of inelastically scattered electrons, which are "incident" under all possible angles. The geometric locus of the Bragg reflected beams is a wide cone with a semiangle of $90^\circ - \theta$ (θ = Bragg angle). This cone intersects the photographic plate along parts of a hyperbola, which becomes almost a straight line because of the large opening angle and the large distance between the specimen and the plate. Two parallel Kikuchi lines always belong to one set of lattice planes; the distance f between the lines corresponds to an angle difference 2θ , which is also the distance between the corresponding diffraction spots.

Under dynamic two-beam conditions, the Kikuchi line pair passes through the spots of the incident and diffracted beams. If the foil is now rotated over a small angle $\Delta\theta$, the positions of the diffraction spots are nearly unchanged, whereas the beam producing the Kikuchi lines rotates over the same angle. Therefore the Kikuchi lines are displaced with respect to the diffraction spots over the distance

$$\Delta f = f/2\theta \cdot \Delta\theta$$

^{*}The component of the Burgers vector is $\mathbf{b}_e$ that is perpendicular to the loop plane.

From this $w = \xi_g \cdot s = \xi_g \cdot g \cdot \Delta\theta$ can be determined. The sign of w is defined such that w is negative if the displacement of the Kikuchi lines on the diffraction pattern is toward the spot of the direct beam and is positive if the displacement is away from the spot of the direct beam.

Determination of Foil Orientation and Tilting Angle in Stereo Measurements

For certain experiments the exact orientation of the foil relative to the incident electron beam must be known. As shown by Thomas⁵⁵ and coworkers, the orientation can be determined simply from Kikuchi patterns. The orientation can either be determined by indexing three independent pairs of Kikuchi lines or by comparing the observed Kikuchi pattern with an indexed Kikuchi line map. The orientation of the foil relative to the electron beam can be determined within an accuracy of $\pm 0.1^\circ$.

To determine the tilting angle in stereo experiments, we may also use the displacement of Kikuchi lines. If the specimen is tilted by an angle normal to the incident beam, the whole Kikuchi pattern shifts by a vector perpendicular to the tilting axis. From the shifting, the tilting angle may be determined with an accuracy of $\pm 0.2^\circ$.

Evaluation of Stereo Micrographs

Stereo pairs are obtained by producing two micrographs with different orientations of the specimen relative to the electron beam. If the distance of two points on the micrographs changes by the parallax p from one micrograph to another, the relative difference in height h of the two points inside the specimen is calculated from the simple parallax equation

$$h = \frac{p}{2M \sin \gamma} \quad (15)$$

where M is the overall magnification of the micrographs, and 2γ is the total tilting angle.

This equation is, as shown by Nankivell,⁴⁶ only correct under certain conditions, which often cannot be attained experimentally. Therefore corrections must be added to the simple parallax equation. The most important is the correction of the tilt error. If the optical axis and the tilt axis do not intersect (see Fig. 13), the correction term, which has to be added to Eq. 15, is

$$(\Delta h)_t = \frac{\Delta s(s_a + 2s + \Delta s) \cos \gamma}{l_0} \quad (16)$$

The distance between the first principal plane of the objective lens and the plane that is normal to the optical axis, and contains the tilt axis, is l_0 ; this distance is approximately the focal length of the objective lens of the microscope.

Fig. 13 Positions of the specimen for stereo pairs. The distance between tilt axis and optical axis = s_a , Δh is the height difference of two points inside the foil, tilt angle is $2\gamma = \gamma_+ + \gamma_-$.

This error can be kept small if Δs is small.* However, for certain experiments, Δs has a large value, and in this case the correction described through Eq. 16 is significant and must be taken into account.

The length s_a in Eq. 16 can be determined from

$$s_a = \Delta h_s \cdot \text{ctg } \gamma$$

where Δh_s is the change in the distance between the specimen and the first principal plane of the objective lens during the tilting experiment. This change is actually the change in the focal distance of the objective lens for the two

* Δs is the distance of the projection of the two points, for which the height difference has to be determined, onto the image plane.

micrographs of the stereo pairs. A calibration of the focal length l' (Fig. 3) vs. the "strength" of the objective lens yields Δh_s . The strength is represented best by the electrical current through the coils of the objective lens.

EXPERIMENTAL RESULTS

Experimental Results on Small Defect Clusters

The experimental results of the study on small defects in neutron-, ion-, and electron-bombarded materials have been summarized in Refs. 5 and 6. Since these papers were published, it has been well established that reliable experimental results for both defect-size distribution,^{5,6} and the type of small defect clusters observed in neutron-irradiated face-centered cubic^{5,7,58} materials can be obtained.

In body-centered cubic materials, the type and size distribution of the defects depend sensitively on the impurity content of the material. This was demonstrated for molybdenum in the extended studies by Eyre et al.^{5,9-62} For niobium, Loomis⁶³ showed that the defect structure depends strongly on the amount of oxygen that is in solution in the material.

The fine structure of the small defect clusters can be studied by the weak-beam method. In this technique we image the defects with a weakly excited beam, i.e., a dark-field beam with a high excitation error w . On weak-beam micrographs the defects appear as bright spots on a dark background. In this imaging technique the resolution of details of the defects is usually improved compared with the regular bright- and dark-field images since the effective extinction length is much smaller in the weak-beam micrograph.^{8,9}

In Fig. 14 the advantage of the weak-beam micrograph is demonstrated. Parts (a) and (b) of Fig. 14 represent a bright-field and a dark-field micrograph, respectively, of a foil of high-purity niobium irradiated⁶³ with 4×10^{19} neutrons/cm² ($E_n > 0.1$ MeV).

The observable large defects (with diameters between 200 and 400 Å) show a jerky structure in the regular bright-field and dark-field micrographs. If we image under weak-beam dark-field conditions [(d) of Fig. 14], we find that each defect is composed of very small clusters. The diameters of the very small clusters are just above the resolution limit of the electron microscope. However, contrast experiments by Cockayne⁸ and by Häussermann⁶⁴ indicate that in the case of heavy-ion bombarded copper foils one small defect cluster can yield more than one white spot under weak-beam conditions. The number of observable spots in (d) of Fig. 14 is not necessarily identical with the number of defects. Further theoretical and experimental work is necessary for a full evaluation of the weak-beam micrographs.

Fig. 14 Defects in neutron-irradiated niobium [oxygen content < 0.02 wt.%, neutron dose 4.10^{19} neutrons/cm² ($E_n > 0.1$ MeV)], foil orientation near $[110]$. The diffraction vector $g = (1\bar{1}2)$ is noted. (a) bright-field image; (b) dark-field image (w slightly positive); (c) $w \sim 0.5$; (d) weak-beam picture. In the weak-beam dark field a high density of small defects is resolved.

Experimental Results on the Contrast of Small Bubbles

The dependence of the contrast behavior of the small bubbles on the focusing and imaging conditions was studied, and the results of the observations were compared with the results of the out-of-focus contrast calculations. For this purpose, epitaxially grown, gold single crystals (~ 600 to $1000 \text{ \AA}$ thick) were irradiated with He^+ ions at energies between 25 and 150 keV and at temperatures between room temperature and 400°C . After an irradiation with $6 \times 10^{16} \text{ He}^+$ particles/ cm^2 at temperature above 100°C , gas-filled bubbles were formed.* The irradiated foils were investigated with a Siemens electron microscope operated at 100 kV.

The small bubbles (diameter smaller than $\sim 30 \text{ \AA}$) were only observable if we imaged the foil out of focus (see Fig. 15). The sign, size, and magnitude of the contrast depend strongly on the defocusing conditions, i.e., on the sign and magnitude of ξ ; the distance between the lower surface of the foil and the focal plane of the objective lens (cf Fig. 6).

For a quantitative comparison of the theoretically predicted out-of-focus contrast (see section entitled "Diffraction Contrast from Bubbles") and the experiments, the distance ξ between the exit surface of the film and the focal plane must be known.

We determined ξ by measuring a part of the current I_{ob} through the objective lens in the different focusing conditions. The change of I_{ob} was calibrated vs. the change in the distance of the focal plane, and it was found that a change of $\Delta I_{\text{ob}} = 1 \mu\text{A}$ corresponds to a change of $\Delta \xi = 0.0105 \mu$. The relation between ΔI_{ob} and $\Delta \xi$ was linear in the distance range of interest.

The bubbles were imaged under different focusing conditions; one example of the through-the-focus series is shown in Fig. 15. If ξ is negative the bubbles show, as predicted by the theory (see the subsection "'Out-of-Focus' Contrast of Bubbles"), a contrast that has a white inner part surrounded by a weak dark ring. For positive ξ , the contrast has a black dot surrounded by a weak white ring. Figure 15 also shows that the bubbles are invisible under in-focus conditions ($\xi = 0$).

The size of the black ($\xi > 0$) and white ($\xi < 0$) central portion of the contrast of the small bubbles is almost independent of the exact imaging conditions and of the exact value of ξ , for distances of ξ that are not too large. However, the outer diameter of the first Fresnel fringe depends strongly on ξ .

The actual bubble size can be determined from the diameter of the central portion of the contrast. Normally the outer diameter of the Fresnel fringe is at least 50% larger than the actual bubble size. The experimental results are in good

*Details on the results of the irradiation experiments and the dependence of the observable defect structure (black spots or bubbles) on the irradiation conditions are described elsewhere.^{6,5}

Fig. 15 Gold film irradiated with 6×10^{16} He^+ ions/ cm^2 at 100°C ; through-the-focus series. The differences in $\zeta = \Delta f$ are noted. The contrast of the center changes from dark (with white Fresnel ring) to bright (with dark Fresnel ring). Foil orientation (001), g close to (200).

agreement with the contrast calculations described in a preceding subsection entitled "‘Out-of-Focus’ Contrast of Bubbles." More results, especially the dependence of the contrast on the imaging condition, will be published elsewhere.

The out-of-focus contrast of bubbles with different geometrical shapes can be more complicated. Figure 16 shows the through-the-focus series of voids produced in stainless steel after irradiation with Ni^+ ions at high temperature.^{6,6} For $\zeta < 0$ the white center contains a black spot surrounded by a black ring. For $\zeta > 0$ the opposite is true. Preliminary contrast calculations show that the actual size of these voids coincides with the outer diameter of the bright portion for $\zeta < 0$.

CONCLUSIONS

The electron-microscopy contrast of defects observable in irradiated material was discussed, and emphasis was placed on the contrast of voids and bubbles. It was shown that voids and bubbles produce a phase shift of the electron wave inside the crystal. The phase difference relative to the perfect crystal can only be made visible (especially for small voids) by working out of focus.

The following important contrast features were calculated and also determined experimentally:

1. Small voids and bubbles are only observable if the defects are imaged out of focus.
2. The sign of the contrast depends on the sign of the defocusing conditions. To distinguish between voids and defects of other shapes, a through-the-focus series is required.
3. The diameter of the inner contrast ring corresponds to the actual diameter of the bubbles in the size range between 20 and 80 Å.
4. For larger bubbles the width and intensity of the out-of-focus contrast depends on the actual size of the bubble and the thickness of the film.

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Fig. 16 Voids in stainless steel irradiated with 3-MeV Ni^{2+} ions;^{6,6} through-the-focus series. The change in ζ from micrograph to micrograph (left to right) is ~ 3000 Å. The contrast reverses from underfocused to overfocused; the voids are invisible under in-focus conditions.

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DISCUSSION BY ATTENDEES

Ardell: The contrast at the defocused images you just described must depend upon the divergence of the incident illumination, yet you made no mention of this factor in your presentation. Have you estimated the effect of beam divergence in your calculations?

Rühle: In the calculations it was assumed that a beam without any divergence (parallel electron beam) is used. The influence of the beam divergence can be estimated; I think it is not important for structures with sizes larger than 10 Å.

Rosolowski: Void densities can be determined from electron micrographs if the number of voids intersecting the surfaces can be measured. Some workers identify such surface intersecting voids by their "fuzzy" outline. Others find very few such fuzzy voids in the electron micrographs they obtain. Would you care to give your opinion of this method of void-density determination?

Rühle: I do not know the method of counting the fuzzy contrast figures for the determination of the void density. I would suggest that the void density be determined by counting and by measuring the thickness of the foil with the stereo technique.

VOID FORMATION IN NEUTRON-IRRADIATED METALS

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ABSTRACT

The characteristics of void formation in high-purity metals are reviewed and summarized in terms of irradiation and material variables. Fluence, irradiation temperature, flux and spectral effects, and the role of impurities are discussed. Results are compared and contrasted with those for stainless steel and evaluated in terms of proposed mechanisms for the nucleation and growth of voids. Although general trends of behavior are established for most of the experimental variables, exceptions are invariably found. The observations indicate that details of the damage structure are purity and structure sensitive.

This symposium very nearly marks the fifth anniversary of Cawthorne and Fulton's first report¹ that voids develop in stainless steel exposed to high fast-neutron fluences at elevated temperatures. The significance of this discovery was slow to be absorbed, but, once reactor designers realized the potential seriousness of the problem, experimental and theoretical programs aimed at defining and understanding the nature, extent, and implications of this new form of radiation damage accelerated activities to a high level. For technological reasons the bulk of the effort has gone into studies of stainless steels and other engineering alloys because their use in liquid-metal-cooled fast breeder reactors (LMFBRs) will encompass the range of conditions under which voids are known to form. Although the problem is a complex one involving vacancies, interstitials, and transmutation products and their migration through the host material, comparatively little work has gone into studies of relatively pure materials. In 1968 Mastel and Brimhall² first found voids in an irradiated pure metal, nickel, and observed that their formation was greatly accelerated over that in stainless steel. Voids were found in nickel at fluences 2 to 3 orders of magnitude lower than in stainless steel. Since that time, several studies have established that voids form in a wide range of materials crystallizing in the face-centered cubic, body-centered cubic, and hexagonal close-packed crystal

systems. A summary of all observations of voids in relatively pure metals is tabulated in the Appendix to this paper.

Only the effects of irradiation and material variables on the formation of voids are examined here. The characteristics of void formation in pure metals are compared and contrasted with those in stainless steel, and the observations are also used to evaluate proposed models for the formation of voids. Neither the effects of the voids on mechanical and physical properties nor the response of the voids to annealing treatments is considered in this paper. The latter subject is the topic of another paper at this conference.³

At this point the reader should be aware that the picture is by no means complete. It is somewhat like a jigsaw puzzle at a stage where only a few isolated areas have been fitted together. There is no tendency or general trend that is not violated at one time or another. Part of the problem may arise because we do not yet recognize the full range of variables that are important. What follows then is a summary of our present-day knowledge of the formation of voids in high-purity metals.

EFFECTS OF IRRADIATION VARIABLES

Fluence

Void concentrations and sizes have generally been found to increase with increasing fast-neutron fluence. In several cases, concentrations have been observed to saturate, but no comparable reduction in the rate of growth of voids or in the swelling has been noted.

Packan⁴⁻⁶ characterized the population of voids in high-purity aluminum irradiated in the High-Flux Isotope Reactor (HFIR) at about 55°C as a function of fast-neutron fluence. The material had a nominal purity of 99.9999% with respect to metallic elements but contained about 20 at. ppm hydrogen. Below a fluence of about 10^{19} neutrons/cm², no voids were evident in the microstructure. At that and higher fluences, octahedral voids were observed with the vertexes often truncated by {100} planes. Concentrations and sizes of voids increased with increasing fluence. Typical micrographs illustrating the appearance of the voids as a function of fluence are shown in Fig. 1. At the lower fluences the voids often appeared to exist in clusters, and occasional pairs of voids were found. At a fluence of about 10^{20} neutrons/cm², Packan reported that many of the voids were elongated [see Fig. 1(b)] and suggested that these formed by coalescence of the void pairs found at lower fluences. At a fluence of 5×10^{20} neutrons/cm², the voids were generally equiaxed and apparently distributed homogeneously, although some exceptions were noted that will be described later.

The HFIR is a thermal reactor that has a thermal flux about three times greater than the flux above 0.1 MeV at the reactor center line. Aluminum has a relatively large cross section for the production of silicon by the thermal-neutron

Fig. 1 Voids in high-purity aluminum irradiated in HFIR at about 55°C.

(a) 1.5×10^{19} (b) 7.7×10^{19} (c) 1.6×10^{20} (d) 5.2×10^{20} (e) 1.6×10^{21} (f) 1.6×10^{22}

Sources: For a–e, N. H. Packan, Fluence and Flux Dependence of Void Formation in Pure Aluminum, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam. For f, K. Farrell, Oak Ridge National Laboratory, unpublished micrograph.

Fig. 2 Dislocation structure formed in high-purity aluminum irradiated in HFIR at 55°C. (a) 7.7×10^{19} neutrons/cm² ($E > 0.1$ MeV). (b) 1.6×10^{21} neutrons/cm². Source: J. O. Stiegler, unpublished micrographs.

reaction $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ followed by β^- decay to ^{28}Si . Exposure of aluminum in the HFIR to a fluence of 1.6×10^{22} neutrons/cm² (>0.1 MeV) is estimated to produce about 0.4 wt.% silicon, which is appreciably greater than the solubility limit, estimated to be only 0.05 wt.% at 250°C. During irradiation, silicon in excess of the solubility limit is precipitated as elemental silicon. The small black spots shown in Fig. 1(f) were identified by electron diffraction as silicon.⁷ In this high-purity material, many silicon particles were seen in association with voids (this is even more pronounced at higher irradiation temperatures; see below). It is likely that because of the high binding energy between silicon atoms and vacancies, 0.25 eV,⁸ the silicon atoms are dragged to the voids by vacancies. Farrell, Stiegler, and Gehlbach⁹ earlier identified silicon in some commercial aluminum alloys, but there it was dispersed on a finer scale than the voids.

Packan⁴⁻⁶ reported a complex dislocation structure that evolved along with the voids. At low fluences, it took the form of discrete loops [Fig. 2(a)], and at higher fluences it appeared as a dislocation network [Fig. 2(b)]. At the highest fluence studied by Packan, 1.6×10^{22} neutrons/cm², only a densely packed dislocation structure was evident. Interstitial loops were identified¹⁰ in the specimen irradiated to a fluence of 7×10^{19} neutrons/cm², and it is generally assumed that the interstitials are contained in the dislocation structure. In this particular case, the estimated number of interstitials contained in the loops very nearly balanced the number of vacancies stored in the voids. At higher fluences, however, a balance was not obtained;¹¹ too few loops were present to account

Fig. 3 Concentration of voids as a function of fluence in high-purity aluminum irradiated in the HFIR at 55°C. Source: N. H. Packan, Fluence and Flux Dependence of Void Formation in Pure Aluminum, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

for all the interstitials. It must be supposed that the dislocations represent dislocation loops that have grown to a size much larger than the thickness of the foils examined in the electron microscope.

Concentrations of voids determined by Packan⁴⁻⁶ as a function of fluence are plotted in Fig. 3 (the concentration for the highest fluence specimen has been revised and is slightly greater than Packan's original estimate). The error limits, $\pm 30\%$, represent the estimated accuracy of the measurements. It is clear from this plot that the rate of increase of the concentration of voids decreases sharply at a fluence of about 10^{22} neutrons/cm². The term saturation is used in this paper to describe this effect, although, as will be discussed later, this may not be entirely accurate. Between 7.7×10^{19} and 1.6×10^{21} neutrons/cm², the concentration of voids is an approximately linear function of fluence, but, below 7.7×10^{19} neutrons/cm², the void concentration appears to fall much more rapidly than linearly. There is some uncertainty as to the validity of the void-concentration measurement at very low fluences. The concentration is low, and all the voids are small. Thus it is possible that an appreciable fraction is not being counted and the concentration is higher than reported. As Packan⁴ pointed out, there currently is no adequate way to take this into account.

Fig. 4 Void size as a function of fluence for high-purity aluminum irradiated in the HFIR at 55°C. Source: N. H. Packan, Fluence and Flux Dependence of Void Formation in Pure Aluminum, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

Consequently the shape of the void concentration—fluence curve cannot be defined with certainty in the low fluence region.

Packan⁴⁻⁶ also measured the distribution of sizes of voids as a function of fluence. The results, given in Fig. 4, show that the maximum and mean void diameters vary as the $\frac{1}{6}$ power of fluence. The diameter of a void of mean volume shows the same variation up to a fluence of 1.6×10^{21} neutrons/cm². Above this point the void nucleation rate decreases, and the growth rate, as measured by the diameter of a void of mean volume, increases slightly.

Overall swelling data for high-purity aluminum are presented in Fig. 5. Two sets of immersion density results are shown, together with calculated density changes based on Packan's measurements of the void population. The curve is drawn through the results of Jostsons et al.,¹² which are believed to be most accurate because a large specimen size was employed. Over the fluence range 1.4×10^{20} to 1.4×10^{21} neutrons/cm², the density change varies as about the 1.3 power of fluence. At higher fluences this power decreases, and, between 1.4×10^{21} and 1.6×10^{22} neutrons/cm², there is a very nearly linear change of density with fluence. Not enough points are available in the high fluence region to determine whether or not the curve bends over in the manner drawn. Nevertheless, the rate of increase of the swelling is clearly a decreasing function of fluence. It is not clear whether or not any significance can be attached to the

Fig. 5 Density change, $-\Delta\rho/\rho$, in high-purity aluminum irradiated in the HFIR at 55°C. Sources: Triangular points, N. H. Packan, *Fluence and Flux Dependence of Void Formation in Pure Aluminum*, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam. Circular points, A. Jostsons, E. L. Long, Jr., J. E. Ferguson, and K. Farrell, *Swelling in Aluminum and Its Alloys* (to be published).

relatively large density decreases measured at low fluences. Holmes¹³ found similar large changes in stainless steel that he attributed to factors other than void formation.

In the intermediate fluence range, the void concentration is a linear function of fluence and the diameter of a void of mean volume varies as the $1/6$ power of fluence. This corresponds to a volume change proportional to the 1.5 power of fluence, which is reasonably close to the value of 1.3 determined on different specimens by immersion density measurements. It is not clear what significance can be attached to this slope. In Nickel-70 irradiated at 480°C, Holmes¹⁴ found that swelling varied as the 1.45 power of fluence, but, in stainless steel, Bloom¹⁵ showed that it was a variable function of irradiation temperature.

In addition to the inhomogeneities in the distribution of voids in aluminum mentioned earlier, regions adjacent to grain boundaries were denuded of defect structures. Voids were absent in bands $0.3\ \mu$ thick and loops in bands about $2\ \mu$ thick. Occasional exceptions were noted, but defects were never observed in the grain boundaries.

Stiegler and Bloom¹⁶ found similar behavior in most respects in Nickel 270 (99.98%) irradiated in the Experimental Breeder Reactor II (EBR-II). In their case, concentrations of about 1 to 3×10^{14} voids/cm³ were observed irrespective of fluence above 3.2×10^{19} neutrons/cm² ($E > 0.1$ MeV) and irradiation temperature between 370 and 525°C. Voids were clustered in patches at low fluences but were homogeneously distributed at higher fluences. Stiegler and Bloom suggested that the high concentration of voids found at low fluences formed on some sort of preexisting nuclei. They argued that saturation of concentration did not occur until higher fluences were reached. The nearly constant void concentrations were presumed to occur because the rate of nucleation of new voids nearly equaled the rate of elimination of voids by merger of closely spaced ones. As in aluminum, voids grew with increasing fluence, and, in a specimen irradiated to a fluence of 1.5×10^{22} neutrons/cm² at 470°C, voids ranging up to 1300 Å in diameter were found. The average diameter was 650 Å. No voids smaller than 250 Å were detected, suggesting that at this point nucleation had ceased.

Care must therefore be exercised in interpreting a reduced slope of void concentration vs. fluence curves as signifying a diminution of the nucleation rate. Additional tests need to be applied; in particular, loss of voids by merger must be accounted for.

At low fluences, individual dislocation loops were found by Stiegler and Bloom¹⁶ in Nickel 270. These were replaced at higher fluences by dislocation lines decorated by loops, as shown in Fig. 6(a). At very high fluences, only isolated dislocation lines were observed [Fig. 6(b)].

Straalsund¹⁷ also studied Nickel 270 irradiated in the EBR-II at 480°C to fluences between 1.3×10^{20} and 3×10^{21} neutrons/cm². He found the concentration of voids to increase in this range, but the maximum value observed was less than the saturation concentration found by Stiegler and Bloom.¹⁶ The average void diameter also increased with increasing fluence.

In summary, in the few observations made on pure metals to date, the concentration of voids increased with increasing fluence up to a point beyond which saturation apparently occurred. Void sizes also increased with increasing fluence. In the one case in which detailed measurements were made, the mean void diameter varied as the $1/6$ power of fluence. The interstitials initially formed dislocation loops that apparently grew and interacted to form a loosely defined network.

Temperature

In general, void concentrations decrease with increasing irradiation temperature and average void sizes increase. As a consequence, swelling reaches a broad maximum at some intermediate temperature. Shapes and distributions of voids vary with irradiation temperature in complex ways.

These features are illustrated in Fig. 7, which shows typical micrographs of the void structure in high-purity aluminum irradiated at 55, 125, and 150°C to a

Fig. 6 Dislocation structure in commercial-purity nickel irradiated in the EBR-II at 470°C. (a) 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV). (b) 1.5×10^{22} neutrons/cm². Source: J. O. Stiegler and E. E. Bloom, Void Formation in Irradiated Nickel 270, *Radiat. Eff.*, 8: 33 (1971). Reproduced courtesy of Gordon and Breach, Science Publishers, Inc., New York.

fluence of 2×10^{21} neutrons/cm² ($E > 0.1$ MeV). Statistical data describing the population of voids are given in Table 1. At 55°C the voids appeared as equiaxed polyhedra distributed fairly uniformly throughout the material, although, as mentioned earlier, occasional irregularities were observed. At this fluence level, there was no visible evidence of the transmutation-produced silicon. At irradiation temperatures of 125 and 150°C, Farrell, Wolfenden, and King¹⁸ found that the void population could not be characterized as simply as that. The voids displayed a variety of shapes including plates, ribbons, rods, and cylinders as well as equiaxed polyhedra. Up to one-third of the voids were elongated in the specimen irradiated at 150°C. Particles of transmutation-produced silicon were frequently associated with the voids, particularly those exhibiting nonequiaxed shapes. Elongated voids as long as 3μ were found in the specimens irradiated at 150°C. This should be compared with a maximum diameter of 0.04μ for the equiaxed voids produced at this fluence at 55°C.

The zone adjacent to grain boundaries which was denuded of voids increased in width with increasing irradiation temperature from 0.2μ (Ref. 4) at 55°C to about 1μ at 150°C (Ref. 18). The void population immediately adjacent to the denuded zone differed appreciably from that within the grains. At the lower irradiation temperatures, voids were more numerous than in the grain interiors, and, at the higher irradiation temperatures, they were larger than those in the interiors. In all cases the volume change associated with the voids in the

Fig. 7 Effect of irradiation temperature on voids formed in high-purity aluminum irradiated to a fluence of 2×10^{21} neutrons/cm² ($E > 0.1$ MeV). Note differences in magnification. (a) 55°C; (b) 125°C; (c) 150°C. Source: K. Farrell and J. O. Stiegler, unpublished micrographs.

TABLE 1
VOID CONCENTRATIONS IN HIGH-PURITY ALUMINUM
IRRADIATED TO A FLUENCE OF 2×10^{21} neutrons/cm²
($E > 0.1$ MeV)

Irradiation temperature, °C	Void concentration, voids/cm ³		References
	Grain interiors	Near grain boundaries	
55	3.2×10^{14}	3.2×10^{14}	4-6
125	2.8×10^{13}	1.4×10^{13}	18
150	1.2×10^{12}	2.4×10^{12}	18

near-grain-boundary regions was several times larger than that for voids in the grain interiors. This is not to say that the near-grain-boundary regions actually swelled more; that depends on the ultimate resting place of the atoms displaced from those sites, which may have been some distance away.

When the irradiation temperature was increased from 55 to 125°C, the concentration of voids decreased by a factor of about 5 (13 to 2.8×10^{13} voids/cm³). A further increase of temperature to 150°C resulted in a precipitous drop in the concentration, by a factor of 20, to 0.12×10^{13} voids/cm³. This is evidently very near the upper temperature limit for void formation in high-purity aluminum. This conclusion is reinforced by some observations by Farrell et al.¹⁹ on aluminum irradiated to a fluence of 1.6×10^{22} neutrons/cm² ($E > 0.1$ MeV) at a temperature estimated to be between 150 and 200°C. In that specimen, voids were virtually absent from the grain interiors, but bands of large voids existed in the near-grain-boundary region.

Brimhall and Mastel²⁰ found voids in high-purity nickel (99.997%) at irradiation temperatures ranging from 260 to 750°C (0.31 to $0.59T_m$). The concentration decreased with increasing irradiation temperature, and the average void size increased, but the calculated volume fraction of voids differed by a factor of only about 2 over the range 380 to 640°C. The occurrence of voids at 750°C is somewhat surprising. The concentration was extremely low, only about 10^{11} voids/cm³, and it was not established whether the cavities were actually voids or helium bubbles. In stainless steel, Bloom and Stiegler²¹ found that the voids were replaced by helium bubbles at an irradiation temperature of 770 to 840°C. Until this point is clarified, $0.59T_m$ should not be used as an upper temperature limit for void formation. In aluminum the limit appears to be about 200°C ($0.51T_m$) for the irradiation conditions studied to date.

An exception to the general observation that the concentration of voids decreases with increasing irradiation temperature was found by Stiegler and Bloom¹⁶ in Nickel 270 irradiated to a fluence of 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) at temperatures ranging between 375 and 525°C (0.38 to

0.46T_m). In these specimens, the concentrations varied between 2 and 3×10^{14} voids/cm³ and showed no systematic trend with respect to temperature. Void shapes varied from cubes at 385°C [Fig. 8(a)], to truncated octahedra at 470°C [Fig. 8(b)], to rods elongated in $\langle 110 \rangle$ directions at 525°C [Fig. 8(c)]. About one-third of the voids were elongated for 525°C irradiation, and the maximum length-to-diameter ratio was about 5. These voids were much smaller than the "supervoids" found in aluminum at an equivalent homologous temperature.²² No significant differences in total void volume were found as a function of irradiation temperature.¹⁶

Stiegler and Bloom¹⁶ also examined the dislocation structure in Nickel 270 as a function of irradiation temperature. At a fluence of 1.4×10^{20} neutrons/cm², it consisted of ragged dislocation lines decorated by small loops. The structure was qualitatively the same at all irradiation temperatures but coarsened as the temperature increased (Fig. 9).

In summary, the defect structure usually, but not always, coarsened with increasing irradiation temperature. Over the temperature range in which voids form, swelling was not a rapidly varying function of irradiation temperature. However, the morphology of the voids was strongly influenced by temperature.

Flux and Spectral Effects

Flux and spectral effects are difficult to separate experimentally. Variations in flux are usually obtained by varying the irradiation position in a reactor or by employing different reactors. These flux changes are invariably accompanied by changes in the neutron spectrum. Consequently the relative rates of production of damage and introduction of transmutation products are usually altered. For cases where transmutation products are a part of the damage state, both flux and spectral effects may contribute to changes in type, amount, and distribution of damage.

Packan⁴⁻⁶ investigated the effect of flux on the void population in high-purity aluminum by irradiating specimens to the same fluence in the HFIR and the Oak Ridge Research Reactor (ORR) at fluxes differing by about an order of magnitude. These are both water-moderated reactors having similar spectra. For the positions used by Packan, the ORR/HFIR ratio of fluxes greater than 8 MeV is 0.11; greater than 0.82 MeV, it is 0.10; and greater than thermal energy, it is 0.06 (Ref. 4). Specimens were irradiated in contact with the cooling water, the temperature of which was about 55°C in both cases.

Packan used flux monitors to measure the fluxes in the two cases. Fluences and fluxes for these irradiations, given in Table 2, showed that the specimens were exposed to approximately the same fluence but that the HFIR irradiation occurred at a fast-neutron flux 10 times greater than the ORR irradiation.

Micrographs illustrating the appearance of the voids in the two specimens are shown in Fig. 10, histograms depicting the void-size distributions are given in Fig. 11, and statistics describing the void population are summarized in Table 2.

The concentration of voids in the specimen irradiated at the higher flux was twice that irradiated at the lower flux, but the average void size was smaller, so that the total void volumes were nearly equal in the two specimens. Voids in the specimen irradiated at the lower flux tended to be elongated and distributed less homogeneously, often in patches or strings. In summary, lowering the flux by an order of magnitude decreased the void concentration by a factor of 2 but did not influence the overall swelling. In appearance, voids produced at the lower

TABLE 2

IRRADIATION PARAMETERS AND VOID STATISTICS FOR EXPERIMENT TO EVALUATE THE EFFECT OF FLUX ON THE VOID POPULATION⁴⁻⁶

Reactor	Flux, neutrons/(cm ²)(sec) (E > 0.1 MeV)	Fluence, neutrons/cm ² (E > 0.1 MeV)	Void concentration, voids/cm ³	Mean void diameter, Å	ΔV/V, %
ORR	1.1×10^{14}	1.3×10^{20}	1.9×10^{13}	323	0.04
HFIR	10.9×10^{14}	1.6×10^{20}	3.8×10^{13}	244	0.03

flux looked much like those formed at higher irradiation temperatures. The fluence was too low to allow location of the transmutation-produced silicon or evaluation of its part in the evolution of the microstructure.

In cases in which transmutation products play a role in the establishment of the damage structure, differences in spectra may be of vital importance. This is particularly true in comparing results of irradiations in fast and thermal reactors. For example, Weitman, Däverhög, and Farvolden²³ recently pointed out an anomalously high production rate of helium in nickel irradiated in a mixed fast-thermal spectrum. They suggested that a fast-neutron reaction produced an intermediate, short-lived product that had a high thermal-neutron (n,α) cross section. Bloom²⁴ recently measured helium-production rates in Nickel 270

Fig. 8 Effect of irradiation temperature on void shapes in Nickel 270 irradiated in the EBR-II to a fluence of 1.4×10^{20} neutrons/cm² (E > 0.1 MeV). (a) 375°C; (b) 470°C; (c) 525°C. Source: J. O. Stiegler and E. E. Bloom, Void Formation in Irradiated Nickel 270, *Radiat. Eff.*, 8: 33 (1971). Reproduced courtesy of Gordon and Breach, Science Publishers, Inc., New York.

Fig. 9 Effect of irradiation temperature on the dislocation structure formed in Nickel 270 irradiated in the EBR-II to a fluence of 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV). (a) 375°C; (b) 525°C. Source: J. O. Stiegler and E. E. Bloom, Void Formation in Irradiated Nickel 270, *Radiat. Eff.*, 8: 33 (1971). Reproduced courtesy of Gordon and Breach, Science Publishers, Inc., New York.

Fig. 10 Effect of flux on the void structure of high-purity aluminum irradiated to a fluence of about 1.5×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 55°C. (a) Exposed to a flux of 1.1×10^{14} neutrons/(cm²)(sec). (b) Exposed to a flux of 10.9×10^{14} neutrons/(cm²)(sec). Source: N. H. Packan, Fluence and Flux Dependence of Void Formation in Pure Aluminum, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

Fig. 11 Void-size distributions for the specimens shown in Fig. 10. Source: N. H. Packan, Fluence and Flux Dependence of Void Formation in Pure Aluminum, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

irradiated near the midplanes of the HFIR and the EBR-II and found over 100 times more helium produced in the HFIR (mixed spectrum) than in the EBR-II (fast spectrum) per unit flux of neutrons having energies in excess of 0.1 MeV.

Stiegler and Bloom¹⁶ recently compared the available void-concentration data for nickel,^{16,17,20} and for a fluence of about 1.5×10^{20} neutrons/cm² and a temperature in the range 475 to 500°C, they pointed out a variation of nearly 2 orders of magnitude in measured void concentrations, as

TABLE 3
VOID STATISTICS FOR NICKEL IRRADIATED TO A FLUENCE
OF ABOUT 10^{20} neutrons/cm² AT 475 TO 500°C

Nominal material purity	Reactor	Temp., °C	Fluence, neutrons/cm ²	Void concentration, voids/cm ³	Mean void diameter, Å	$\Delta V/V$, %	Reference
99.98	EBR-II	480	$1.3 \times 10^{20} *$	9×10^{12}	250	0.012	17
99.98	EBR-II	470	$1.4 \times 10^{20} *$	3.2×10^{14}	160	0.08	16
99.997	ETR	500	$5.7 \times 10^{19} \dagger$	8×10^{14}	165	0.16	20

*E > 0.1 MeV.

†E > 1 MeV.

shown in Table 3. They suggested that the differences from one experimenter to another were possibly due to impurity effects. This cannot be ruled out, but the specimen that showed the highest void concentration²⁰ was irradiated in a thermal reactor with a mixed spectrum, whereas the other specimens^{16,17} were irradiated in the EBR-II in a fast spectrum.

A spectral-related effect was found by King, Long, Stiegler, and Farrell,²⁵ who compared void populations in two specimens of an X8001 aluminum alloy (commercial-purity aluminum with a 1% nickel addition) irradiated to 10^{22} neutrons/cm² in the HFIR. One of the specimens was exposed to a thermal fluence of 3.7×10^{22} neutrons/cm² in the Savannah River C Reactor before exposure in the HFIR. The specimen developed a higher concentration of voids that were smaller on the average than in the specimen irradiated in the HFIR only. Total void volumes were estimated to be approximately equal. It was suggested²⁵ that the silicon generated by a thermal-neutron reaction in the Savannah River Reactor, which was estimated to exceed 0.5 at.%, influenced the nucleation and growth of voids during the subsequent irradiation in the HFIR.

In summary, void sizes and concentrations were shown to be more than simple functions of the fast-neutron fluence. In several cases, changes in flux and/or spectrum altered the defect structure either by modifying the rate of production of damage or by varying the relative rates of formation of damage and introduction of transmutation products.

EFFECTS OF MATERIAL VARIABLES

Impurities

Like most other variables, the role of small quantities of impurities on void formation in high-purity materials is ambiguous. Several reports have indicated that swelling is retarded by the presence of impurities,^{11,12,14} but another has

TABLE 4
EFFECTS OF GAS PREINJECTION ON THE CONCENTRATION OF VOIDS
IN HIGH-PURITY ALUMINUM IRRADIATED TO A FLUENCE
OF 2×10^{21} neutrons/cm² ($E > 0.1$ MeV) AT 125 AND 150°C (REF. 18)

Site	Void concentration, 10 ¹³ voids/cm ³			
	Grain interiors		Near grain boundaries	
	125	150	125	150
Irradiation temperature, °C				
Uninjected	2.8	0.12	1.4	0.24
Preinjected with 3 at. ppM H	2.1	0.67	1.0	0.67
Preinjected with 9 at. ppM H	2.2	1.5	1.6	1.8
Preinjected with 3 at. ppM He	2.4	2.6	1.3	2.5

shown it to be accelerated.²⁶ Clearly the quantity of impurities is not the only factor that is important. Type and distribution are other factors that may contribute to the outcome.

Farrell, Wolfenden, and King¹⁸ studied the effects of small quantities of hydrogen and helium on the population of voids formed in high-purity aluminum. They injected nearly uniformly with a cyclotron either 3 at. ppM helium or 3 or 9 at. ppM hydrogen. The specimens were annealed for 30 min at 350°C before being irradiated in the ORR to a fluence of 2×10^{21} neutrons/cm² ($E > 0.1$ MeV) at 125 and 150°C. As can be seen in Table 4, the preinjected gases had no significant effect on the concentration of voids in specimens irradiated at 125°C but did increase the concentration dramatically in the specimens irradiated at 150°C. In the latter case, void sizes decreased correspondingly, so that the total void volume was not modified appreciably. In addition, the voids tended to be more equiaxed in the specimens containing injected gases. In the specimens irradiated at 150°C, 3 at. ppM hydrogen had an easily measurable effect; 9 at. ppM hydrogen resulted in an additional increase, but 3 at. ppM helium was most effective at increasing the concentration of voids. Similar effects of the gas additions were found in both the grain interiors and the near-grain-boundary regions.

Farrell et al.¹⁸ argued that they were unable to detect an increase in the population of voids at an irradiation temperature of 125°C because the increase in void concentration found at 150°C was much less than the concentration in the uninjected materials irradiated at 125°C. It is unclear how the preirradiation heat-treatment that may have agglomerated the gases influenced the results. No gas bubbles were visible in the microstructure after this treatment.

The pronounced effect of hydrogen in increasing the concentration of voids was somewhat surprising since Packan^{4,6} found hydrogen concentrations in the

Fig. 12 Voids formed in high-purity aluminum after (a) irradiation in the HFIR to a fluence of 5.2×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 55°C and (b) irradiation as in (a) followed by annealing for 1 hr at 300°C to remove the damage and then reirradiated to an additional fluence of 5.1×10^{20} neutrons/cm². Source: N. H. Packan, Voids in Re-Irradiated Aluminum, *J. Nucl. Mater.*, 37: 251 (1970). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

starting material several times greater than the injected amounts. The form and distribution of the hydrogen must be important parameters governing its effectiveness in stimulating the nucleation of voids. Packan^{4,6} verified that the preexisting hydrogen had no effect on void formation. He irradiated specimens that had been degassed by solid-state extraction to reduce the hydrogen content to 2.2 at. ppm alongside untreated specimens containing 14.5 at. ppm hydrogen. He found no significant change in either the concentrations or sizes of voids or in the total void volume.

Packan²⁷ performed an additional experiment that may be interpreted in terms of an effect of gases on the nucleation of voids. He irradiated a rod of high-purity aluminum in the HFIR at 55°C to a fluence of 5.2×10^{20} neutrons/cm² ($E > 0.1$ MeV). He examined the void structure in part of the rod, then annealed the other part for 1 hr at 300°C to remove all visible evidence of the damage, and reirradiated the piece to an additional fluence of 5.1×10^{20} neutrons/cm². Micrographs comparing the void structure after the two irradiation treatments are shown in Fig. 12, and detailed size distributions are given in Fig. 13. The void concentration in the reirradiated specimen was over twice as large as that present after the original irradiation, $2.6 \pm 0.2 \times 10^{14}$ vs. $1.1 \pm 0.04 \times 10^{14}$ voids/cm³. The average void size in the reirradiated specimen was smaller, and the voids were distributed over a narrower range of sizes than in the original irradiation, but the most frequently observed void size and total void volumes were the same in the two cases. No significant differences were noted in the dislocation loops. Packan²⁷ suggested that remnants of voids from the

Fig. 13 Void-size distributions for the specimens shown in Fig. 12. Source: N. H. Packan, Voids in Re-Irradiated Aluminum, *J. Nucl. Mater.*, 37: 251 (1970). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

original irradiation survived the annealing treatment and served as preexisting nuclei which grew into voids during reirradiation and to which an equal number of voids were added during the second irradiation. This is a plausible explanation since the void nucleation rate is approximately linear in this fluence range. It is also possible that the void nucleation rate was influenced by dissolved solid or gaseous transmutation products. The lack of large voids, however, argues that the void concentration must have been high during the early stages of the reirradiation.

The situation with regard to substitutional impurities is even less clear because no systematic investigations of simple systems have yet been under-

Fig. 14 Effect of a purity on the microstructure of aluminum irradiated in the HFIR to a fluence of 1.6×10^{21} neutrons/cm² ($E > 0.1$ MeV) at 55°C. (a) High-purity aluminum (99.9999%). (b) Commercial-purity aluminum (99%). Source: J. O. Stiegler, unpublished micrographs.

taken. Stiegler et al.¹¹ first reported that commercial-purity aluminum (99%) did not begin to swell until fluences were achieved several orders of magnitude in excess of those required for the onset of swelling in high-purity material. Holmes¹⁴ showed that in nickel the rate of swelling decreased as the concentration of impurities increased. Levy et al.²⁶ verified that impure aluminum swelled less than the pure material but found that in magnesium the swelling first decreased with increasing amounts of impurities and then increased. Using less pure material, Jostsons and Farrell²⁸ found the swelling to decrease with decreasing purity in magnesium.

Purity level appears to affect both the type and amount of damage that is produced. This is illustrated in Fig. 14, which compares the microstructures of high-purity and commercial-purity aluminum irradiated to a fluence of 1.6×10^{21} neutrons/cm² at 55°C in the HFIR. The high-purity material, which was populated by a high concentration of voids and a complex dislocation structure, swelled almost 1%. In contrast to this, the commercial-purity material contained no voids but only the unusual dislocation-loop structure shown in Fig. 14(b). Before irradiation, this material contained a large number of inclusions surrounded by an irregular dislocation structure, evidently punched out during cooling from the final annealing temperature. The dislocations within the grains in Fig. 14(b) formed in the vicinity of the punched-out dislocation loops.

Farrell et al.¹⁸ attempted to stimulate the formation of voids in the commercial-purity material by injecting it with uniform distributions of hydrogen and helium before neutron irradiation. No neutron damage was produced in these specimens irradiated in the ORR to a fluence of 2×10^{21} neutrons/cm² ($E > 0.1$ MeV) at 125 and 150°C. However, when the neutron-irradiated specimens were subsequently irradiated with 200-kV electrons in an electron microscope²⁹ at a temperature less than 50°C, they developed a loop structure similar to the one shown in Fig. 14(b).

Levy et al.²⁶ compared the damage in copper and a Cu-7% Al alloy irradiated at 250°C to a fluence of 5×10^{20} neutrons/cm² ($E > 0.1$ MeV). The copper swelled 0.17%, but, in the alloy, there was no evidence of any visible radiation damage. In contrast to this, Wolfenden³⁰ found cavities identified as voids in a Cu-10 wt.% Al alloy irradiated at 125°C ($0.32T_m$) but only black-spot-type damage in copper irradiated at the same temperature ($0.29T_m$).

Jostsons et al.¹² measured density changes in several aluminum alloys as a function of fluence. The results are plotted in Fig. 15, along with values for high-purity aluminum. Clearly the onset of swelling is retarded, and the shape of the curve is modified in the alloys. No swelling from the formation of voids was evident in the 6061 alloy until fluences in excess of 4.5×10^{22} neutrons/cm² were reached. Measurable volume changes did occur at lower fluences due to the large quantities of transmutation-produced silicon which were present. Swelling from silicon formation has been subtracted from the density-change data shown in Fig. 15. The microstructure of the 6061 alloy was very complex, consisting of

Fig. 15 Density Change, $-\Delta\rho/\rho$, as a function of fluence in aluminum and several of its alloys irradiated at about 50°C. Source: A. Jostsons, E. L. Long, Jr., J. E. Ferguson, and K. Farrell, Swelling in Aluminum and Its Alloys (to be published).

a fine dispersion of Mg_2Si precipitate particles and a high dislocation density. The resistance of this alloy to swelling consequently may be more than a simple impurity effect.

Both the 8001 and 1100 alloys also contained precipitate particles, so at least some of the impurities were not in solution. The position of the curve for the 8001 alloy is somewhat surprising since this alloy is essentially 1100 aluminum with the addition of 1% nickel. Two factors may have contributed to enhanced swelling in it relative to the 1100 alloy: (1) the nickel addition approximately doubles²⁴ the transmutation-produced helium concentration in the alloy on account of the large effective (n,α) cross section for nickel in a mixed fast-thermal-neutron spectrum and (2) the alloy was irradiated in a recovered state containing a subgrain size of about $2\ \mu$ in diameter,²⁵ which may have selectively removed interstitials from the material, leaving a greater net vacancy concentration. In addition, the 1100 aluminum alloy was irradiated at a

flux about an order of magnitude lower than that for the other materials shown in Fig. 15. However, Packan's observations⁴⁻⁶ indicate that this is not likely to influence the swelling significantly.

In summary, we cannot be very specific about the role of impurities in void formation. Some, particularly gases, stimulate void formation but do not appear to alter the swelling appreciably. Others inhibit void formation and retard swelling in some presently unidentified manner.

Crystal Structure

The previous discussion has been largely confined to a description of void formation in face-centered cubic (fcc) metals because the systematic investigations that have been undertaken all have been made on metals in that crystal system. Nevertheless, fragmentary observations have been made establishing the occurrence of voids in the body-centered cubic (bcc) and hexagonal close-packed (hcp) crystal systems. Although these studies have been less extensive, most of the general trends described earlier are followed.

Among the bcc metals, voids have been found in iron,^{31,32} vanadium,³³⁻³⁵ niobium,^{35,36} tantalum,³⁷ molybdenum,^{35,36,38-41,43} and tungsten.³⁸ No information is available on the effect of fluence on the void structure, but void concentrations decrease and sizes increase with increasing irradiation temperature. With the exception of iron, void concentrations in the bcc metals are often up to 2 orders of magnitude higher than in fcc metals exposed to comparable irradiation conditions. Void sizes are correspondingly smaller, so that the resultant volume change is not significantly affected.

As is the case with the fcc metals, impurities play a large role in determining the makeup of the void population. Wiffen³⁴ found that increasing the concentration of interstitial impurities in vanadium from 220 to 1250 ppm resulted in an order of magnitude increase in the void concentration but had little effect on void sizes. He also found that the addition of small amounts of reactive elements changed the characteristics of the void distributions, but not in any consistent or easily understood manner.³⁶ The addition of 20% titanium to vanadium suppressed void formation completely.³⁶ Elen found the same effect with only 3% titanium.³⁵ Wiffen³⁶ observed that voids in an Nb-1% Zr alloy were fewer in number, larger in size, and more heterogeneously distributed than in niobium, but he could detect little effect of a 1/2% zirconium addition to molybdenum.

Nonhomogeneous void distributions were found in most of these materials. In addition to configurations of the type described earlier, Wiffen found ordered arrays of voids on a bcc lattice parallel to the host lattice in molybdenum,³⁶ niobium³⁶ and tantalum.³⁷ Evans⁴² also observed a void superlattice in molybdenum irradiated with 20-MeV nitrogen ions.

Radiation damage in the hcp crystal system is somewhat confusing in that voids have been observed in rhenium³² and magnesium^{26,44} but not in

Zircaloy-2 (Ref. 45) nor in reasonably high-purity zirconium^{46,47} and titanium.⁴⁶ Reasons for the differences are presently not understood.

Voids in rhenium⁴³ appear to be nearly equiaxed, but those in magnesium⁴⁴ are hexagonal cylinders compressed along $\langle 0001 \rangle$ with the basal planes forming the largest faces. Levy et al.²⁶ studied the fluence dependence of the void structure in magnesium and found that the void concentration tended to saturate at a fluence in the vicinity of 10^{21} neutrons/cm² but that the cavity growth rate accelerated so that swelling did not diminish but continued at an approximately linear rate. They noted that magnesium swelled at an appreciably faster rate than did aluminum. Jostons and Farrell⁴⁸ confirmed this difference and found that at a fluence of 10^{21} neutrons/cm² the swelling in magnesium was a factor of 2 larger than in aluminum.

Void Spatial Distributions

In addition to the gross variations in the concentrations and sizes of voids in the regions adjacent to grain boundaries mentioned earlier, a large number of other nonrandom features have been observed in void populations which can be interpreted in terms of material variables ranging from microstructural features to anisotropy of elastic properties.

Stiegler et al.¹¹ first reported the occurrence of nonrandom configurations in the void distributions formed in high-purity aluminum. They showed a three-dimensional wall of voids surrounded on either side by void-free regions (Fig. 16). Farther away from the wall, the void distribution appeared homogeneous. The explanation offered to account for this unusual feature was that the wall marked the position of a prior grain boundary that had been swept away during recrystallization before the irradiation. Stiegler et al. argued that the voids nucleated on some unspecified impurity clusters that had been present in the boundary. The denuded zones adjacent to the wall indicated that the boundary acted as a sink for the impurities that were involved.

In his survey of the effect of fluence on void formation in high-purity aluminum, Packan⁴⁻⁶ observed that at low fluences the voids often appeared in patches separated by void-free areas. He also found the void pairs noted earlier. At higher fluences, as the concentration of voids increased, the distributions appeared random, although no rigorous tests for randomness were applied.

In a study of some deformed high-purity iron that had recovered and partially recrystallized during irradiation, Farrell and Houston³² found lines, possibly walls, and also clusters of voids. The example shown in Fig. 17 illustrates the gross nonhomogeneity of void formation in this material. On the other hand, Kulcinski, Mastel, and Brimhall³¹ found an apparently homogeneous distribution of voids in iron of comparable purity that had been recrystallized by annealing at 800°C for 2 hr prior to irradiation. Farrell and Houston³² argued in favor of an impurity-aided nucleation mechanism and suggested that the impurities segregated to the dislocation structure introduced

Fig. 16 Wall of voids formed in high-purity aluminum irradiated in the HFIR to a fluence of 5.2×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 55°C. Source: J. O. Stiegler, K. Farrell, C. K. H. DuBose, and R. T. King, High-Fluence Neutron Irradiation Damage in Aluminum, in *Radiation Damage in Reactor Materials*, Symposium Proceedings, Vienna, 1969, Vol. 2, pp. 215–232, International Atomic Energy Agency, Vienna, 1969 (STI/PUB/230).

by deformation. The high-temperature annealing treatment used by Kulcinski et al.³¹ presumably destroyed any structure to the impurity distribution.

Kulcinski et al.³¹ observed but did not comment on variation of the shapes of the voids within a single grain. They observed several closely spaced voids that were nearly equiaxed and bounded by the same crystallographic faces but that had distinctively different overall shapes. It is possible that local impurities, possibly very small precipitate particles, were present in or on the voids and perturbed their shapes. Elongated voids, for example, often have precipitate particles at one end.

Fig. 17 Clusters of voids formed in high-purity iron irradiated in the HFIR to a fluence of 1.5×10^{21} neutrons/cm² ($E > 0.1$ MeV) at a temperature of 415°C. Source: K. Farrell and J. T. Houston, *Heterogeneous Distribution of Irradiation Voids in Iron*, *J. Nucl. Mater.*, 35: 352 (1970). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

Stiegler and Bloom¹⁶ used a statistical test to define clustering of voids in Nickel 270 exposed to low fluences. Clustering was not evident at higher fluences, even though the concentration of voids did not increase. It was suggested that nucleation that occurred in the void-free areas was compensated for by merger of voids in the clusters.

The most outstanding example of nonrandomness is the ordered arrays of voids found in both neutron-irradiated^{36,37} and in ion-bombarded⁴² materials. In molybdenum and niobium³⁶ the voids are arranged on a bcc superlattice parallel to the host lattice. In neutron-irradiated materials the order is far from perfect; it breaks down over long distances, and individual voids are somewhat displaced from true superlattice positions. Two suggestions^{42,49} have been offered to account for this phenomenon: (1) periodic segregation of the impurities responsible for nucleation of the voids and (2) minimization of the elastic interaction between voids in an elastically anisotropic material by the

formation of an ordered array of voids. These effects are discussed more fully in other papers at this conference.^{3,6,50}

Several examples of nonrandomness in the spatial distribution of voids have been observed and documented. The nonrandomness is most evident at low fluences and in materials not given high-temperature annealing treatments before irradiation. However, the apparent randomness observed at high fluences has not been rigorously demonstrated.

COMPARISON OF PURE METALS AND STAINLESS STEEL

Up to now, stainless steel has been the standard for comparison in discussing void formation because it has been examined under a wide range of conditions and consequently characterized more completely. Many of the general features observed in stainless steel are also found in the "pure" materials. The principal difference is that voids can be detected in pure metals at fluences over 2 orders of magnitude lower than in stainless steel. Because of this, several examples of apparent saturation of the concentration of voids have been observed in pure metals. To date, saturation of concentration has been found in stainless steel only at an irradiation temperature of about 600°C or higher.^{21,51} At lower temperatures, void concentrations have been found to increase at a constant rate even to fluences as high as 5×10^{22} neutrons/cm² (Refs. 21 and 51).

Except for nickel irradiated in a thermal reactor,²⁰ void concentrations in the pure fcc and hcp metals have been less than 10^{15} voids/cm³. In cases where saturation of the concentration of voids has been observed, concentrations are well below this value. Except for irradiation at 600°C where saturation is observed, concentrations of voids in stainless steel exceed this amount, and, for irradiation at 380°C, concentrations as high as 10^{16} voids/cm³ have been reported. Concentrations well in excess of 10^{16} voids/cm³ have been found in many of the bcc metals,^{35,36} particularly at the lower irradiation temperatures.

The apparent limitation^{15,21,51} to the maximum void size found in stainless steel irradiated at 370 and 470°C seems to be unique to that system. No evidence has been found for a limiting void size in any of the pure metals. For example, in nickel irradiated at 470°C to a fluence of 1.5×10^{22} neutrons/cm², voids as large as 1300 Å in diameter have been observed.¹⁶ In stainless steel irradiated to somewhat higher fluences, voids in excess of 300 Å in diameter have seldom been found.^{15,21,51}

An empirical equation⁵² that has been developed to describe the void population in stainless steel indicates that the mean void size varies as the fluence is raised to the 0.1 to 0.15 power. The variation occurs with radiation temperature. This range is only slightly less than the value found for high-purity aluminum, 0.16 (Refs. 4 to 6). In both stainless steel and aluminum, the void size increases greatly with increasing irradiation temperature, but the largest voids found in stainless steel^{15,21,39,52,53} are over an order of magnitude smaller than the largest ones found in aluminum.²²

In aluminum irradiated at 55°C, the total void volume or swelling varies as the 1.3 to 1.5 power of fluence over the range of fluences where the void concentration is increasing and then decreases when saturation of the concentration occurs. In stainless steel the fluence exponent in the presaturation range is a function of irradiation temperature, increasing from about 0.8 at 370°C, to 1.4 at 470°C, to a value probably in excess of 2 at 600°C (Refs. 21 and 51).

One feature common to both stainless steel and the pure metals is a strong dependence of void formation on composition. Void concentrations and sizes can be changed by as much as an order of magnitude by relatively small changes in composition.

In stainless steel the interstitials precipitate as Frank loops for irradiation temperatures below about 550 to 575°C (Refs. 21, 51, and 52). They form initially on a finer scale than the voids, grow slowly, and can be recognized as loops even at high fluences. In the pure metals the loops are unfaulted and they grow rapidly and interact to form a complex dislocation network in which the original loops cannot be recognized. This behavior is also observed in stainless steel for higher irradiation temperatures. The only pure material in which faulted loops have been observed is magnesium,^{26,44} but they have not yet been identified as interstitial in character.

COMPARISON WITH MODELS

The previous examples illustrate the complexity of the situation, for not only are several defect species involved in the formation of voids but also their environment evolves continuously during the irradiation. Several processes have been suggested to account for the nucleation of the voids, all of which depend critically on the instantaneous vacancy and interstitial concentrations. These in turn depend on the microstructure through the distribution of sites at which defects may be trapped or annihilated. To date, only Harkness and Li⁵⁴ have attempted to calculate the nucleation rate in terms of a changing microstructure. For small time increments, they compute the change in microstructure for the available vacancy and interstitial supersaturations and then use that microstructure to calculate the supersaturations for the next time increment. Harkness and Li believe that nucleation occurs in displacement spikes but use a homogeneous-nucleation approach, the validity of which has recently been questioned.⁵⁵ Nevertheless, their results show the extreme sensitivity of the nucleation rate to the microstructure and the related defect supersaturations.

Processes commonly suggested for void nucleation are:

1. Nucleation on preexisting sites.⁵⁶
2. Homogeneous nucleation.^{56,57}
3. Nucleation in displacement spikes.^{56,57}
4. Nucleation in overlapping spikes.⁵⁸
5. Nucleation in spikes stabilized by helium.⁵⁹
6. Nucleation on helium bubbles.^{1,15,60}

Of these proposals, only the case for homogeneous nucleation has been treated quantitatively,⁵⁵ but not in terms of a changing microstructure. The other possibilities have been considered only qualitatively. An attempt is made here to compare the experimental observations with the qualitative predictions in order to narrow the list of possibilities. From the variations and contradictions in behavior that have been observed, it seems highly unlikely that any single mechanism can explain *all* cases.

In all the models listed above, the nucleation rate should ultimately decrease and the concentration of voids saturate as the vacancy supersaturation decreases owing to buildup of the sink concentration in the microstructure.⁵⁴ In homogeneous nucleation and nucleation in displacement spikes and overlapping spikes, the rate should decrease continuously once the vacancy and interstitial concentrations reach their steady-state values for the initial microstructure. At the irradiation temperatures involved in void formation, this should occur in a few minutes at most. In the mechanisms involving helium, the nucleation rate should initially be low, then increase as the helium concentration increases, and finally decrease as the vacancies, interstitials, and helium atoms drain to the radiation-produced defect structure.

There are several pieces of evidence that some of the voids are nucleated on preexisting sites. The frequently observed heterogeneous void distributions^{11,16,18,32,36} support this view, as do the observations of Stiegler and Bloom¹⁶ that the concentration of voids in one lot of Nickel 270 was independent of irradiation temperature and fluence. It is not clear whether the special locations are true void nuclei or peculiar sites in the lattice that are transformed into voids during irradiation. Unless they are augmented by the irradiation, such locations should be exhausted early in the irradiation. Both in Nickel 270 and high-purity aluminum, there is evidence for an additional source of voids that is not saturated as quickly. In the case of aluminum, it is the major source of the voids; in the nickel, it is probably less important than the preexisting sites.

The homogeneous-nucleation mechanism is unlikely to be a major source of voids since it encounters problems in explaining the enhanced void concentrations in materials containing gases and in Packan's²⁷ reirradiation experiment. Clearly, if gases are present in some forms, they enhance void nucleation; and, in practice, they are always present.

The concept of the displacement spike in aluminum is nebulous. Spikes are large and diffuse, and, on account of the absence of correlated collisions, large vacancy-rich regions are not formed.⁶¹ Spikes or overlapping spikes are therefore not likely to be important factors in void formation in aluminum, although they may be important in some other systems. However, the formation of voids in the high-voltage electron microscope in copper,⁶² nickel,^{63,64} and stainless steel⁶⁵ indicates that spikes are not a necessary prerequisite for void formation. Neither experimental observations nor theoretical models are quantitative enough to allow the role of spikes to be evaluated.

In aluminum the only remaining alternative is nucleation on helium (or hydrogen) bubbles generated during the irradiation. Qualitatively, there are no arguments that can be advanced against this possibility. Because a theoretical treatment must consider the migration and precipitation of helium, in addition to the behavior of the vacancies and interstitials, no quantitative estimates of nucleation rate are available. Such a process also would be expected to be sensitive to microstructural features that may influence the trapping and precipitation of helium (and hydrogen) atoms.

In materials other than aluminum, the evidence is too scanty to allow any comparisons to be made, except to say that preexisting nuclei or nucleation sites account for at least part of the voids in some cases.

The factors that complicate theoretical treatments of the nucleation of voids also cloud the picture of void growth mechanisms. Packan⁴⁻⁶ found that in high-purity aluminum the average void size was roughly proportional to the $1/6$ power of the neutron fluence, a value far below any of the expected exponents for simple growth mechanisms for voids growing under a constant vacancy supersaturation in an infinite medium.^{5,6} Undoubtedly the vacancy supersaturation decreases with time, but in a complicated way dependent on the development of the microstructure. Until this can be taken into account and detailed calculations made for the different mechanisms, there is no basis for deciding among the possibilities, except for the case of void growth limited by absorption of vacancies onto the void surface.^{6,6} In this mechanism the rate of increase of the void radius, dr/dt , is proportional to time and independent of void size. In a given time increment, all the voids in the population increase their radii by a constant amount. In effect, the void-size distribution curve is translated bodily to larger void sizes. As the supersaturation decreases, the speed of translation decreases correspondingly. This behavior is not reflected in the void-size distribution curves that Packan obtained for high-purity aluminum as a function of fluence (Fig. 18). As the fluence increases, the curves change shape and are not merely translated to larger void sizes.

Neither the experimental models nor the theoretical predictions are advanced to the point that allows us to be specific about the mechanisms of nucleation and growth of voids that are in effect under particular circumstances. Nevertheless, it is clear that microstructure and composition are important variables influencing the state of the damage. Moreover, the damage is dependent on more than the fast-neutron fluence and the temperature of irradiation; flux and spectral effects are important in at least some cases. All the models being developed assume that average vacancy and interstitial concentrations are adequate for describing the situation. However, studies of the formation of voids in the electron microscope^{6,3,6,4} show that the local environment influences the behavior of voids; voids grow only when interstitial sinks are nearby. All these factors need to be incorporated into more realistic models for the formation of voids under neutron irradiation.

Fig. 18 Void-size distributions as a function of fluence for high-purity aluminum irradiated at 55°C. Source: N. H. Packan, Fluence and Flux Dependence of Void Formation in Pure Aluminum, *J. Nucl. Mater.*, 40: 1 (1971). Reproduced courtesy of North Holland Publishing Company, Amsterdam.

CONCLUDING REMARKS

During the past 5 years, a vigorous start has been made toward assembling the puzzling features of void formation in neutron-irradiated metals. Because of the complexity and scope of the problem, no fully satisfactory experimental or theoretical description of the situation exists. Nevertheless, some features are gradually becoming recognizable. The detailed nature and extent of the damage are purity and structure sensitive. Furthermore, it is likely that more than one void-nucleation mechanism is operative. Several examples exist of a saturation in the concentration of voids, but no limitations to void growth have yet been detected. In general, void concentrations decrease with increasing irradiation temperature and increase with increasing fluence, but exceptions to these trends have been noted. Void formation occurs in the three crystal structures common to metals. To date, zirconium and titanium are the only relatively pure metals in which voids have not been found when irradiated to high fluences in the appropriate temperature range. Some alloys (vanadium and niobium) also appear to resist the formation of voids.

Work during the past 5 years has been largely concerned with mapping the extent of the problem. More systematic studies of the effects of irradiation and material variables on the damage now are necessary. The damage must be fully characterized as a function of these variables to define the microstructure. This information is necessary to test the different theoretical proposals since there is no way a priori to calculate the development of the dislocation structure during

irradiation. The models, in turn, must be expanded to consider the effects of a continuously evolving microstructure on their predictions. Finally, attention must be paid to the characteristics of impurities in metals, particularly helium, and how they influence the development of radiation damage.

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APPENDIX

A summary of observations of voids in high-purity materials is presented in Table 5. In addition to results from the literature, the table includes some unpublished information obtained over the past 2 years at Oak Ridge National Laboratory and some revisions and additions to previously published data. The displacement-per-atom figures were obtained by D. Jenkins, ORNL, using the Kinchin-Pease model and the appropriate spectra for HFIR, ORR, and EBR-II.

The results have been obtained by several laboratories using a variety of techniques. As a consequence, experimental errors are variable. Individual papers should be consulted for estimates in uncertainties in irradiation parameters and void characteristics. The absence of entries in the table indicates that the quantity was not determined; where available, reasons for omission are given under Comments. Under Spectrum, the symbol F indicates a fast-neutron spectrum only and M indicates a mixed fast and thermal spectrum.

The table reflects the concentration of experimenters in defining the population of voids. No comparable observations exist characterizing the dislocation structure. This is the largest void in our understanding of the subject.

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TABLE 5
SUMMARY OF VOID OBSERVATIONS IN HIGH-PURITY MATERIALS

Material	Purity	Irradiation temp., °C	T/T _m	Flux, neutrons/(cm ²)(sec)	Fluence, neutrons/(cm ²)(sec)	Spectrum	Displacements per atom	Void concentration, voids/cm ³	Mean void diameter, Å	Total void volume, %	Comments	Ref.
Aluminum	99.9999%	55	0.35	~10 ¹⁵	1.5 × 10 ¹⁹ *	M	0.02	~1 × 10 ¹²	161			4-6
					8 × 10 ¹⁹ *	M	0.1	2.1 × 10 ¹³	201	0.01		4-6
					1.6 × 10 ²⁰ *	M	0.23	3.8 × 10 ¹³	244	0.03		4-6
					5.2 × 10 ²⁰ *	M	0.7	1.1 × 10 ¹⁴	299	0.19		4-6
					1.6 × 10 ²¹ *	M	2.3	3.9 × 10 ¹⁴	329	0.86		4-6
					1.6 × 10 ²² *	M	23	6.5 × 10 ¹⁴	495	7.4		4-6
					1.1 × 10 ¹⁴	M	0.2	1.9 × 10 ¹³	323	0.04		4-6
					10.9 × 10 ¹⁴	M	0.2	3.8 × 10 ¹³	244	0.03		4-6
	99.999	50	0.35		3.2 × 10 ¹⁹ †	M		Low	270			67
	99	50	0.35		2.1 × 10 ²²	M		1.8 × 10 ¹⁴	550	1.4		69
	99	50	0.35		3.2 × 10 ²³	M		1.3 × 10 ¹⁴	480	0.75		69
	99.999	55	0.35	8 × 10 ¹³ †	1.6 × 10 ²⁰ †	M		5 × 10 ¹³	300			68
	99.99995	70	0.37		4.5 × 10 ²⁰ *	M		2 × 10 ¹⁴	240	0.15		26
	99.994	70	0.37		4.5 × 10 ²⁰ *	M		1.6 × 10 ¹⁴	200	0.064		26
	99.9	70	0.37		4.5 × 10 ²⁰ *	M		0	0	0		26
	99.9999	{	125	0.43	2 × 10 ²¹ *	M		{ 2.8 × 10 ¹³ 1.4 × 10 ¹³			Grain interiors	18
											Near grain boundaries	18
			150	0.45	2 × 10 ²¹ *	M		{ 1.2 × 10 ¹² 2.4 × 10 ¹²			Grain interiors	18
											Near grain boundaries	18
	99.9999 + 3 ppM He	{	125	0.43	2 × 10 ²¹ *	M		{ 1.4 × 10 ¹³ 1.3 × 10 ¹³			Grain interiors	18
											Near grain boundaries	18
			150	0.45	2 × 10 ²¹ *	M		{ 2.6 × 10 ¹³ 2.5 × 10 ¹³			Grain interiors	18
											Near grain boundaries	18
	99.9999 + 3 ppM H	{	125	0.43	2 × 10 ²¹ *	M		{ 2.1 × 10 ¹³ 1.0 × 10 ¹³			Grain interiors	18
											Near grain boundaries	18
			150	0.45	2 × 10 ²¹ *	M		{ 6.7 × 10 ¹² 6.7 × 10 ¹²			Grain interiors	18
											Near grain boundaries	18

	99.9999 + 9 ppm H	$\begin{cases} 125 \\ 150 \end{cases}$	$\begin{cases} 0.43 \\ 0.45 \end{cases}$	$\begin{cases} 2 \times 10^{21} \text{ s} \\ 2 \times 10^{21} \text{ s} \end{cases}$	$\begin{cases} M \\ M \end{cases}$	$\begin{cases} 2.2 \times 10^{13} \\ 1.6 \times 10^{13} \\ 1.5 \times 10^{13} \\ 1.8 \times 10^{13} \end{cases}$				Grain interiors Near grain boundaries Grain interiors Near grain boundaries	18 18 18 18
Copper	99.999	260	0.39	$1.2 \times 10^{20} \text{ s}^\dagger$	M	3×10^{14}	230	0.17			67
Nickel	99.997	380	0.38	$5.2 \times 10^{19} \text{ s}^\dagger$	M	4×10^{15}	83	0.11			20
		500	0.45	$5.7 \times 10^{19} \text{ s}^\dagger$	M	8×10^{14}	165	0.16			20
		575	0.49	$6.2 \times 10^{19} \text{ s}^\dagger$	M	2.5×10^{14}	245	0.17			20
		640	0.53	$5.2 \times 10^{19} \text{ s}^\dagger$	M	8×10^{13}	270	0.07			20
		750	0.59	$5.2 \times 10^{19} \text{ s}^\dagger$	M	$\sim 10^{11}$	~ 400	<0.001			20
		260	0.31	$1.2 \times 10^{20} \text{ s}^\dagger$	M	4×10^{16}	60	0.30			20
		385	0.38	$1.4 \times 10^{20} \text{ s}^\circ$	F	0.19	2.9×10^{14}	126 $\ddagger$	0.05		16
	99.98	410	0.40	1.5×10^{15}	$1.4 \times 10^{20} \text{ s}^\circ$	F	0.19	3.2×10^{14}	133 $\ddagger$	0.07	16
		440	0.41	1.5×10^{15}	$1.4 \times 10^{20} \text{ s}^\circ$	F	0.19	2.0×10^{14}	151 $\S$	0.06	16
		470	0.43	1.5×10^{15}	$1.4 \times 10^{20} \text{ s}^\circ$	F	0.19	3.2×10^{14}	160 $\S$	0.08	16
		525	0.46	1.5×10^{15}	$1.4 \times 10^{20} \text{ s}^\circ$	F	0.19	2.4×10^{14}		Elongated voids	16
		370	0.37	0.1×10^{14}	$1.1 \times 10^{18} \text{ s}^\circ$	F	0.0011	1.2×10^{14}	<60 $\ddagger$		16
		370	0.37	3.3×10^{14}	$3.2 \times 10^{19} \text{ s}^\circ$	F	0.034	2.9×10^{14}	103		16
		470	0.43	5×10^{14}	$1.5 \times 10^{22} \text{ s}^\circ$	F	18	$\sim 1.0 \times 10^{14}$	650		16
		480	0.44		$1.3 \times 10^{20} \text{ s}^\circ$	F		9×10^{12}	250	0.012	17
		480	0.44		$1 \times 10^{21} \text{ s}^\circ$	F		9.4×10^{13}	350	0.22	17
		480	0.44		$3 \times 10^{21} \text{ s}^\circ$	F		1.8×10^{14}	360	0.51	17
Platinum	99.97	450	0.35	$3 \times 10^{21} \text{ s}^\circ$	F	8×10^{13}	500	0.7			
Iron	99.999	450	0.40	$3 \times 10^{21} \text{ s}^\circ$	F	1×10^{14}	280	0.12			31
	99.9+	415	0.38	$1.5 \times 10^{21} \text{ s}^\circ$	M	1.4×10^{14} 4.3×10^{13}				Recrystallized regions Nonrecrystallized regions	32 32

(Table continues on the next page.)

TABLE 5 (Continued)

Material	Purity	Irradiation temp., °C	T/T _m	Flux, neutrons/(cm ²)(sec)	Fluence, neutrons/(cm ²)(sec)	Spectrum	Displacements per atom	Void concentration, voids/cm ³	Mean void diameter, Å	Total void volume, %	Comments	Ref.
Molybdenum	99.99	800	0.37		$3 \times 10^{19} \dagger$			1×10^{16}	65	0.12		40
	99.99	1050	0.45		$1 \times 10^{21} *$	M		1.2×10^{14}	290	0.17		43
		1150	0.49		$1 \times 10^{21} *$	M		0.5×10^{14}	470	0.28		43
	99.9+	700	0.34		$1.4 \times 10^{20} \dagger$	M		3×10^{16}	40	0.10		38, 39
		1000	0.44		$1.3 \times 10^{20} \dagger$	M		5×10^{14}	200	0.19		38, 39
		440	0.25	6.5×10^{13}	$3.5 \times 10^{20} *$	M		5×10^{16}	25	0.04		35
		600	0.30	9.8×10^{13}	$5.2 \times 10^{20} *$	M		2×10^{16}	40	0.07		35
		760	0.36	8.3×10^{13}	$4.4 \times 10^{20} *$	M		5×10^{15}	50	0.03		35
Niobium		790	0.38		$2.5 \times 10^{22} *$	F		2.8×10^{15}	185	1.03	Ordered bcc super-structure	36, 70
Nb-1% Zr		790	0.38		$2.5 \times 10^{22} *$	F		2.2×10^{13}	507	1.46	Large local variations	36, 70
								1.9×10^{14}	500			36, 70
Niobium		470	0.27	7.2×10^{13}	$3.9 \times 10^{20} *$	M		3×10^{16}	20	0.01		35
		650	0.34	10.2×10^{13}	$5.5 \times 10^{20} *$	M		8×10^{15}	60	0.09		35
		750	0.37	7.7×10^{13}	$4.1 \times 10^{20} *$	M		5×10^{14}	125	0.05		35
Vanadium		600	0.40		1.7×10^{22}	F		$>10^{15}$	120			33
	220	385	0.30		$4.9 \times 10^{21} *$	F		1.2×10^{16}	50	0.08		34
	1250	385	0.30		$5.7 \times 10^{21} *$	F		1.2×10^{17}	45	0.56		34
	1000¶	475	0.34		$9.7 \times 10^{21} *$	F		1×10^{16}	82	0.34		34
	1000¶	550	0.38		$1.4 \times 10^{22} *$	F		5.9×10^{15}	168	1.77		34
	1000¶	575	0.39		$1.4 \times 10^{22} *$	F		3.5×10^{15}	194	1.58		34
	1000¶	600	0.40		$1.4 \times 10^{22} *$	F		2.0×10^{15}	226	1.47		34

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DISCUSSION BY ATTENDEES

Kulcinski: Have you seen any evidences for void alignment in aluminum that exhibited swelling in the 7 to 8% range?

Stiegler: We have reexamined these specimens carefully in a search for the void lattice but have not detected any order or void alignment.

Bauer: Just a comment on your suggestion that the string of voids in aluminum was due to a grain boundary, which was there prior to irradiation. Our measurements indicate that, in pure metals, helium agglomerates tend to stabilize grain boundaries, preventing their motion to temperatures well above recrystallization temperatures.

Stiegler: We fully agree with your comment. We suggest that the boundary was removed prior to the irradiation.

Wazzan: You showed a slide with two figures on it (Fig. 12). The material was high-purity aluminum irradiated to 5×10^{20} neutrons/cm², then annealed for 1 hr, then reirradiated to 5×10^{20} neutrons/cm². The voids after reirradiation to 5×10^{20} were more numerous but smaller. I have two questions: (1) Was the total void volume in the reirradiated sample different from that of the sample after being irradiated the first time? (2) Was the microstructure after annealing the sample for 1 hr different from the original microstructure before the first irradiation? If they were the same, then how do you account for the increase in the *number* of voids on reirradiation after annealing?

Stiegler: (1) The total void volumes were equivalent within the experimental accuracy.

(2) The microstructures were identical in the sense that no visible defect structures were present. Packan (Voids in Reirradiated Aluminum, *J. Nucl. Mater.*) speculated that the voids shrank to a size invisible in the electron microscope but did not dissolve completely because they may have contained gases. These entities were postulated to serve as preexisting nuclei in the reirradiation experiment.

We do not believe that the annealing treatment removed all the damage and restored the material to its starting state, even though no remnants of the damage were evident. When the specimens were damaged by irradiation in a high-voltage electron microscope, the dislocation-loop damage in the specimen that had been irradiated and annealed was distinctly different from the damage in the annealed material. We conclude that the absence of visible damage in the electron microscope cannot be taken as evidence that the microstructure is defect free.

McElroy: As you mentioned, there may be an effect due to silicon and flux-level effects (and concentration of voids on precipitates of silicon). The effect of helium produced locally in the silicon precipitates might be of concern in interpreting these swelling results. Would you comment?

Stiegler: Yes, this could be of some interest, and we would like to look in more detail at the effect of silicon in future tests where different effects can be studied.

Adamson: Have you looked for voids in zirconium? Do you have any comment on why voids have not been reported in zirconium?

Stiegler: I understand that workers at Battelle—Northwest, Chalk River, Oak Ridge, and Saclay have conducted a search for voids in zirconium. To date, their results have been negative. They have not speculated publicly on the reason, and neither will I.

Bramman: You used a log/log plot of density change vs. fluence. It is always tempting to do this, because both parameters change by orders of magnitude, but the effect of this is to crowd all the more accurate data into the top right-hand corner and to bias any trend line by the data of dubious accuracy in the bottom left-hand corner. The curve you showed looked very much like a transfer to log/log coordinates of a trend which might be better fitted by a linear dependence following a threshold. Is it?

Stiegler: Yes.

Chen: As supplemental information to explain the increase in density of cavities (voids or bubbles) after annealing at 300°C and reirradiation, it might be pertinent here to present a portion of our result at Purdue. We have studied the microstructure of high-purity aluminum injected with 50 ppm He atoms. The average size of bubbles after a 6-hr anneal at 550°C is approximately 25 Å. The concentration of helium atoms in the bubbles calculated from bubble size and density after 17 hr at the same temperature indicated that the majority of helium atoms injected remained in the specimen. Thus the annealing at 300°C done by the author is apparently not enough to anneal out at least some of the helium bubbles formed prior to second irradiation.

PREPARED DISCUSSION: SWELLING OF IN-744

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The swelling characteristics of the International Nickel Company experimental alloy IN-744* have been studied after Experimental Breeder Reactor II (EBR-II) irradiation. This alloy has a microduplex structure (Fig. 1) consisting of about equal numbers of ferritic and austenitic grains. The grain size, as measured by transmission electron microscopy (TEM), was 0.75 μ . The initial intent of irradiating the material was to assess experimentally the effectiveness of the high-angle grain boundary in reducing swelling. The austenitic phase has a

*Nominal composition: Fe-26 wt.% Cr - 6.5 wt.% Ni.

Fig. 1 As-received microstructure of IN-744.

composition near that of an 18-8 stainless steel, and the ferritic phase has a composition near Fe-30 wt.% Cr. The material was irradiated in the EBR-II core in the form of $\frac{1}{8}$ -in. disks of 20-mil sheet in subassembly X018B to a total dose of 2×10^{22} neutrons/cm² (calculated) and a temperature of 450°C (calculated). The samples were irradiated 8 in. above core center in a Row 4 position.

The irradiated microstructure is shown in Fig. 2. The austenitic grains (as determined by electron diffraction) exhibited "normal" void formation, in the sense that it was similar to the void formation that would be seen in 304 stainless steel after exposure to the same irradiation conditions. The denuded zone along the high-angle ferritic-austenitic grain boundary is very narrow (~ 50 Å), indicating that grain refinement is not a practical means of limiting swelling.

Fig. 2 EBR-II irradiated microstructure of IN-744. The F grains are face-centered cubic, and the B grains are body-centered cubic (fluence, 2×10^{22} neutrons/cm², $T = 450^\circ\text{C}$).

The ferrite grains, quite unexpectedly, formed very few if any voids. Instead, a high density ($\sim 5 \times 10^{15}$ voids/cm³) of coherent precipitate developed.

These precipitates evidently acted as point-defect recombination centers during irradiation and thus prevented void formation. The fact that the ferritic grains swelled much less than the austenitic grains must have caused the austenitic grains to attempt to push into surrounding ferritic grains. Some evidence of the deformed, irregular nature of the grain boundaries can be seen in Fig. 2. Figure 3 is a higher magnification micrograph of the precipitate structure in the ferrite grains.

The nature of the precipitates is also of some interest. It is well known that alloys of Fe-30 wt.% Cr suffer embrittlement, as reflected by Charpy testing,

Fig. 3 The coherent precipitate formed in the ferrite grains. Note lack of voids in the microstructure.

after aging at 475°C. Recently Lagneborg* attributed this embrittlement to a precipitate formed by spinodal decomposition. The diffraction contrast from the precipitates in this study is consistent with a particle having a spherically symmetric strain field and suggests a Guinier–Preston zone structure such as is found in Cu–Co and other systems. Some of the IN-744 starting material was held at 500°C for 8 days to assess the kinetics of formation of these precipitates and was then examined by TEM; small coherent precipitates were observed. On the basis of this result, it is somewhat surprising that an overaged structure was not observed in the irradiated sample since it had been at temperature (450°C) for over 6 months. It may be that some type of resolution mechanism is playing a role in the in-pile aging kinetics.

In summary, our results appear to be consistent with those recently reported by Nelson,† which indicated that the formation of a semicoherent phase limited void formation in the British Nimonic alloy PE-16.‡ The development of other materials containing high number densities of coherent precipitates may well offer one solution to the swelling problem.

*R. Lagneborg, *Acta Met.*, **15**: 1737 (1967).

†R. S. Nelson, *New Sci. Sci. J.*, **49**(744): 664-667 (Mar. 25, 1971).

‡Nominal composition in wt. %: Ni, 42.5; Fe, 34.0; Cr, 17.1; Mo, 3.15; Ti, 1.2; Al, 1.3; C, 0.08; B, 0.0003; and Zr, 0.03.

THE EFFECT OF TEMPERATURE ON VOID FORMATION IN IRRADIATED PURE AND IMPURE METALS

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ABSTRACT

Void formation has been studied in a number of irradiated high-purity metals at Battelle-Northwest, and the results are given and discussed in this paper. Particular emphasis is devoted to the temperature dependence of swelling in molybdenum, nickel, and rhenium. In general, voids occur in the temperature region approximately $0.3 T_m$ to $0.55 T_m$, where T_m is absolute melting temperature. This temperature regime is essentially determined by the relative stability of vacancy configurations at the low-temperature end and the vacancy supersaturation at the high-temperature end. The results are further discussed in terms of current theories of void formation. The effect of small variations in impurity level in molybdenum and nickel on void formation has also been studied. Large differences in the size and number density of voids occur in material of the same overall purity level but with relatively small variations in type and amount of impurity. However, the void swelling appears to depend only on the magnitude of the overall purity level. These results are compared to similar results of other investigators on other materials.

The study of voids in irradiated metals has evoked considerable interest and study in recent years. The amount of literature on voids has increased correspondingly, and no attempt will be made to review it in this paper. Here at Pacific Northwest Laboratory, emphasis has been placed on studying void formation in high-purity metals, particularly the metals molybdenum, nickel, and rhenium. Analyses have been done principally by transmission electron microscopy, small-angle X-ray scattering, and microhardness.

It is recognized that irradiation temperature, fluence, and material purity have profound influence on the irradiation-produced microstructure and especially on voids. Studies that have been particularly limited are those on the nature of radiation damage produced over a wide range of temperature and on the effect of small amounts of impurities on void formation.

In this paper, void formation in a wide variety of pure metals is discussed. The effect on void parameters and volume changes over a wide spectrum of irradiation temperatures is shown for the metals molybdenum, nickel, and rhenium. The results are discussed relative to current knowledge about microstructural defects and theories of void nucleation and growth. The limited data on other pure metals are discussed in terms of the general picture of void formation and possible reasons for apparent anomalous behavior. Some results on the effect of purity on void formation in nickel and molybdenum are presented. Although alloys would be expected to behave differently than pure metals, even very slight differences in the amount and type of impurities can result in significant differences in void behavior. These results are discussed in the light of similar results by other workers in the field.

EXPERIMENTAL TECHNIQUES

A brief mention of the experimental techniques and procedures is given here. A more detailed account can be found in previous articles.¹⁻³

All material used in the experiments was in the form of foils approximately 0.1 mm thick except for the single crystals. Single crystals approximately 3 mm in diameter were grown by zone refining. Sections 0.5 mm thick were cut from the single crystals for electron microscopy. All specimens were given preliminary vacuum anneals at 0.6 to 0.65 T_m (T_m = absolute melting temperature). A number of different reactors have been used for the irradiations, and all the fluence values refer to a neutron energy >1 MeV, except for the EBR-II irradiation in which the neutron energy is >0.1 MeV. The irradiations at elevated temperatures were monitored with a thermocouple, except for experiments in the EBR-II for which the temperature was calculated. All irradiations at the ambient temperature of 50°C were done in a helium atmosphere. The elevated-temperature irradiations in the EBR-II and Hanford reactors were done in liquid sodium or NaK. For irradiation in the Engineering Test Reactor, the samples were encapsulated in molybdenum or niobium and encased in a graphite block.

Analyses of the void parameters and resultant volume change were all done by transmission electron microscopy or small-angle X-ray scattering. The volume change at low temperatures was determined by dimensional changes in single crystals.

PURE METALS: RESULTS

Presented in this section are the results, from a variety of pure metals, on void size, density, distribution, and volume fraction. The metals are divided into body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close packed (hcp) for ease of presentation. Also given are the results of one particular

experiment in the EBR-II in which many metals were irradiated under identical fluence and temperature conditions.

Bcc Metals

The great bulk of the work at Battelle-Northwest on bcc metals has been on molybdenum. The temperature regime for void formation in molybdenum extends from 575°C to at least 1150°C (0.29 to 0.49 T_m), as determined by direct observation in the electron microscope. Typical microstructure of voids in molybdenum is shown in Fig. 1 together with those from nickel and rhenium. The total volume change after irradiation is plotted as a function of irradiation temperature in Fig. 2. The region of void formation is indicated by the bell-shaped part of the curve. Some of the high-temperature values have been normalized to a fluence of 2.5×10^{19} neutrons/cm² using a linear extrapolation. Some data from other sources have also been included, and the numbers on several of the data points refer to the references from which those data were obtained.^{4,5} The curve shows significant swelling at lower temperatures as well as at elevated temperatures, with a minimum in the swelling in the temperature range 400 to 600°C. The microstructure in this minimum-swelling range reveals large interstitial dislocation loops and small vacancy loops.² Vacancy loops have been identified by Eyre, Maher, and Bartlett after irradiating at the low temperature of 200°C.⁶ At 575°C both vacancy loops and voids are present.² A few vacancy loops persist at irradiation temperatures up to 750°C, but voids are the only type of vacancy damage at temperatures above 750°C. The void size increases and density decreases with temperature. The distribution of voids is very homogeneous in both size and number density.

Vanadium, niobium, tantalum, and iron are among 13 pure metals that have been irradiated in the EBR-II at 450°C. A summary of the data from this particular experiment is given in Table 1. A high density of very small voids is observed in vanadium, whereas a low density of large voids is formed in iron. The vanadium results agree well with those reported by Wiffen and Stiegler.⁷ As will be seen later, the results from iron are somewhat anomalous. We see from this experiment that no voids form in niobium, molybdenum, or tantalum at 450°C, which is $<0.3 T_m$ for these metals. However, workers at Oak Ridge have reported⁸ voids in niobium irradiated in the EBR-II at 450°C, but the total fluence was a factor of 10 higher than in the experiment reported here, and the higher fluence could explain the presence of voids. In addition, the temperatures in the two experiments may not have been precisely the same.

Apparently there is no consistent morphology of void shapes in the bcc structure. The voids are faceted by both $\{110\}$ planes and $\{100\}$ planes. Figure 3 shows the various shapes of voids in molybdenum. For the foil orientation $\{110\}$, void A is consistent with a cube with $\{100\}$ faces, and void B shows both $\{110\}$ and $\{100\}$ faceting. In iron most of the voids appeared to have $\{110\}$ faces.⁹ Similar morphologies have been reported by others.⁴ Since

Fig. 1 Representative micrographs of voids in irradiated molybdenum, nickel, and rhenium. The temperature corresponds to the low-temperature end of the void-formation range.

voids with different morphologies exist in the same general area, the selection of the particular planar faces may be purely random.

Fcc Metals

The temperature regime for void formation in nickel extends from about 250 to 650°C (0.30 T_m to 0.55 T_m). A few voids are present after irradiation at 750°C, but these are probably gas bubbles. Figure 4 shows the typical curve for the variation in volume fraction with temperature in which the swelling goes through a maximum. Results from nickel irradiated at low temperatures, $\leq 50^\circ\text{C}$, indicate that vacancy loops or stacking-fault tetrahedra form in this temperature range.¹⁰⁻¹³ Postirradiation annealing studies of nickel irradiated at 50°C also show that stacking-fault tetrahedra are the predominant vacancy defect.¹ The overall development of the defect structure is then very similar to molybdenum. Planar vacancy defects form at low temperatures, $\lesssim 0.3 T_m$, and three-dimensional vacancy clusters are stable and form at elevated temperatures $\gtrsim 0.3 T_m$.

The size of the voids in nickel increases continually with temperature at constant fluence (Fig. 5), but a saturation in the size is indicated in the high temperature range. The void density must increase initially with temperature (dotted line in Fig. 5) in the transition region from planar defects to

Fig. 2 Swelling in molybdenum as a function of irradiation temperature. Fluence normalized to 2.5×10^{19} neutrons/cm².

three-dimensional voids. The number density then decreases continually with temperature as shown in Fig. 5. This inverse relation between size and density produces the rather constant volume fraction of voids over a wide temperature range (Fig. 4). However, when the size reaches a saturation, the volume fraction decreases since the number density continues to decrease.

Preliminary work on pure nickel irradiated at very low fluences shows that the critical fluence level for void formation lies between 2 and 7×10^{18} neutrons/cm² at 280°C. The density increases rapidly with fluence. At the lowest fluence at which voids are observed, the size is still considerably above the resolution limit of the microscope. Analysis of the size distribution indicates that the size does not appear to extend down past the resolution limit. Once voids are nucleated, they must grow very rapidly. However, in the initial stages a small void will show a much higher growth rate merely because it is so small. No attempt has been made to determine a fluence dependency of the void volume at these low fluences because of the limited data. Holmes,¹⁴ however, has shown a linear fluence dependence for pure nickel at a slightly higher temperature and higher fluence range.

TABLE 1
SUMMARY OF VOID DATA IN METALS IRRADIATED
TO 3×10^{21} neutrons/cm² AT 450°C

Metal	Purity, %	T/T _m	Void diameter, Å	Void density, voids/cm ³	$\Delta V/V$, %
Ag	99.999	0.59			0
Au	99.94	0.54			0
Cu	99.999	0.53	1600	2×10^{12}	0.5
Ni	99.997	0.42	400	1.8×10^{14}	0.68
Ti	99.96	0.42			
Fe	99.98	0.40	280	1×10^{14}	0.12
Zr	99.9	0.39			
Pt	99.97	0.35	500	8×10^{13}	0.7
V	99.9	0.33	50	3×10^{16}	0.20
Nb	99.9	0.27			0
Mo	99.98	0.25			0
Ta	99.99	0.22			0
Re	99.97	0.21			0

Copper, aluminum, gold, silver, and platinum have also been irradiated and analyzed for void formation. Void formation in platinum, copper, and aluminum is similar to that in nickel. The upper temperature limit for copper appears to be about $0.55 T_m$ (Table 1). No voids have yet been found in silver or gold. A temperature of 450°C may be just past the upper temperature limit for void formation ($0.59 T_m$ for silver and $0.54 T_m$ for gold). However, voids also have not been observed in gold irradiated at 280°C ($0.41 T_m$) to a fluence of 2.5×10^{19} neutrons/cm². Voids do form in both copper and nickel under these latter irradiation conditions. These results suggest strongly that the low stacking-fault energy of gold may be hindering void formation.

The morphology of voids in the fcc structure can best be described as a tetrakaidecahedron with {111} and {100} faces. There is some question as to whether the basic or initial shape is the {100} cube with {111} truncation or the {111} octahedron with {100} truncation. A systematic study of the parameters affecting void morphology in fcc metals has not been made.

Hcp Metals

The temperature region for void formation in rhenium extends from about 635 to 1450°C (0.27 – $0.51 T_m$) (Fig. 6). In terms of the homologous temperature, the region of void formation appears to extend to a lower temperature range than that of molybdenum or nickel. It is now suspected, however, that the two lower temperatures, 635 and 720°C, may actually be higher because of

Fig. 3 Micrograph illustrating different void morphologies in molybdenum. Foil orientation is near $\{110\}$.

excess gamma heating; therefore the behavior of rhenium is not necessarily anomalous. The data also represent a higher fluence than that given for either nickel or molybdenum, and this could also account for the observation of voids at a lower temperature. The only distinguishing feature of the void formation in rhenium is the rather inhomogeneous distribution throughout the foil and the rather large size distribution as compared to either pure molybdenum or nickel. Compare the microstructure of rhenium in Fig. 1 with nickel or molybdenum. Rhenium also shows the minimum in the swelling in the temperature range 400 to 600°C which is quite similar to the minimum for molybdenum. Interstitial loops have been identified after irradiation in this temperature range, but the conclusion is that the vacancy defects are too small to detect.¹⁵

No voids¹⁶ form in titanium and zirconium after irradiation at 450°C to 3×10^{21} neutrons/cm² ($E > 0.1$ MeV). This temperature is $0.42 T_m$ for titanium and $0.39 T_m$ for zirconium if an extrapolated melting temperature for the alpha phase is used. The defect structure consists principally of vacancy dislocation loops and dislocation fragments (Fig. 7). Investigations of specimens irradiated at both lower temperatures and lower fluences reveal a lower density

Fig. 4 Swelling in nickel as a function of irradiation temperature. Fluence normalized to 5×10^{19} neutrons/cm².

and smaller size of dislocation loops but no basic change in microstructure. Workers at Chalk River have also failed to observe voids in zirconium alloys irradiated at 450°C to a higher fluence.¹⁷ There have been no reports of studies using a higher irradiation temperature than 450°C. It should be mentioned that voids have now been reported in magnesium,¹⁸ and it therefore appears that titanium and zirconium are truly anomalous in their behavior.

Comparison of Void Formation in Several Pure Metals

The temperature dependency of void formation in a wide variety of metals is illustrated in Fig. 8, where the void volumes from Table 1 are plotted as a function of T/T_m . The only data plotted are from this particular EBR-II experiment in which the fluence and temperature were constant; no attempt was made to extrapolate from other irradiations. With some major exceptions the typical bell-shaped curve similar to Figs. 2, 4, and 6 is evident. The homologous temperature for both the high-melting-point metals, molybdenum, rhenium,

Fig. 5 Effect of irradiation temperature on void size and number density in nickel. Fluence = 5×10^{19} neutrons/cm².

niobium, tantalum, and the low-melting-point metals, gold and silver, fall outside the range of the void-formation curve. Titanium and zirconium are anomalous as mentioned previously. The void volume fraction for iron is also significantly too low. However, the trend toward void formation and swelling in the temperature interval of approximately 0.3 to 0.5 T_m is plainly evident from the figure.

DISCUSSION

Void formation in metals has been analyzed theoretically and phenomenologically by a number of investigators.¹⁹⁻²² Harkness and Li,¹⁹ using a classical

Fig. 6 Swelling in rhenium as function of irradiation temperature. Fluence normalized to 4×10^{20} neutrons/cm².

nucleation and growth approach, predict a bell-shaped curve for the temperature dependence of the volume fraction, as is observed. Their curves for the temperature variation of the nucleation rate and growth rate have the same form as the temperature variation of the number density and size as shown in Fig. 5. In this approach it was assumed that the displacement spikes serve as the nuclei for voids. Wiedersich²² has developed a completely homogeneous nucleation theory for void formation in which a random distribution of vacancies and interstitials is assumed. Recently, Norris^{23,24} has produced voids in nickel by electron bombardment; a situation in which there are no displacement spikes. Spikes are therefore not essential. The temperature dependence of the void volume fraction in nickel calculated by Wiedersich agrees reasonably well with the results presented here. A lower temperature for maximum swelling is observed experimentally, as would be predicted since the fluxes and hence the defect generation rates are lower in our experiments than those used in the theoretical curves. Further, a decreasing sink density at higher temperatures would produce a lower temperature of maximum swelling and a sharper drop-off in the swelling with temperature than shown by the theoretical curves. One of

Fig. 7 Micrograph of titanium irradiated to 3×10^{21} neutrons/cm² ($E > 0.1$ MeV) at 450°C. Most dislocation loops are of vacancy type.

the important questions in explaining void formation is the apparent preferential drift of the interstitials to dislocation sinks, which results in an excess of vacancies available for void formation. Bullough, Eyre, and Perrin²¹ have developed a model of the void growth rate which considers explicitly the preferential migration of the interstitials to dislocations, and they predict a maximum in the growth rate as a function of temperature. Their prediction of the maximum for molybdenum agrees quite well with the temperature for maximum swelling in Fig. 2. Void swelling in molybdenum extends to a higher temperature than they predict, and this may be due to a higher value for the interstitial migration energy, E_M , than was actually used. It was stated that the diffusion parameters for molybdenum are not well established.

It is generally agreed that the reduction in swelling at high temperatures is due to a reduction in the supersaturation of vacancies. Because of the increased mobility and thermal-equilibrium concentration of vacancies at elevated temperatures, the irradiation cannot maintain a sufficient excess concentration of vacancies. At the low-temperature end, it would appear intuitively that the much-reduced vacancy mobility hinders void nucleation and growth. Bullough,

Fig. 8 Swelling in a variety of pure metals as a function of homologous temperature. All irradiations at 450°C to a fluence of 3×10^{21} neutrons/cm² ($E > 0.1$ MeV).

Eyre, and Perrin²¹ also show that an increase in the recombination of vacancies and interstitials reduces the growth rate at lower temperatures.

An equally important factor in determining the onset of void formation as the irradiation temperature increases is the stability of the three-dimensional vacancy clusters or void nuclei relative to other configurations. The energies of the various vacancy-defect configurations in fcc metals as a function of their size have been analyzed by Sigler and Wilsdorf²⁵ and by Johnson.²⁶ Only in nickel and aluminum is the void the energetically favored defect, principally because of the higher stacking-fault energy in these metals. However, it has now been shown that voids form in copper and platinum as well. Therefore the vacancy clusters can be stabilized as a three-dimensional defect and prevented from transformation into the more stable planar defect. It has yet to be demonstrated that voids form in gold or silver during irradiation. The extremely low stacking-fault energies in these metals may require the necessity of a very high fluence in order for voids to form. This is the situation in stainless steel, in which much higher fluences are required for void formation than in a similar metal such as nickel. The results in gold show the effect of stacking-fault energy alone, however, without the complicating effect of alloying in the stainless steel.

Bullough and Perrin^{2,7} have shown theoretically that gas atoms are necessary for the stabilization of a three-dimensional vacancy cluster in iron against collapse into a lower energy planar configuration. These gas atoms may be helium generated by the irradiation, or they may be such soluble gases as hydrogen or oxygen. Recent experimental evidence using electron bombardment has shown that either inert gases^{2,3,24} or dissolved gases, such as oxygen,^{2,8} appear to be necessary for the nucleation of voids. The experimental results presented here support this view. The vacancies in molybdenum irradiated at temperatures $<575^{\circ}\text{C}$ precipitate as vacancy loops; and in nickel irradiated at $<280^{\circ}\text{C}$, they precipitate as vacancy loops or stacking-fault tetrahedra. The critical lower temperature limit is then not solely dependent on vacancy mobility since, in molybdenum at least, both vacancy loops and voids form at temperatures above which vacancies are believed to be mobile. The vacancy loops also form at temperatures considerably below 575°C , and it is expected that vacancies must have some mobility in order to form loops. The increase in swelling at the very low temperatures, $\sim 50^{\circ}\text{C}$ in Fig. 2, is most likely due to isolated vacancies or small clusters since it is universally agreed that vacancies are not mobile in this range. The lower temperature limit is then not solely determined by vacancy mobility but is also dependent on the mobility and stabilizing influence of the gas atoms as a function of temperature.

The assignment of a lower temperature limit for void formation must, of course, take into account the fluence. In these experiments, void observation was limited by the resolution of the microscope, and at very low fluences the voids may be too small or too low in density to be observed. Also, in some materials it may be necessary to go to a higher fluence to attain sufficient vacancy supersaturation because of an increased recombination rate. Regardless of the fluence, there is a critical temperature region that divides the stable three-dimensional clusters from the two-dimensional clusters. Increasing the fluence should not change this fact. Inability of gas atoms to stabilize the vacancy clusters in titanium and zirconium may explain the presence of vacancy loops rather than voids in these metals.^{1,6} Voids may form in these metals upon irradiation at a higher temperature, but such irradiation has not been done to date. The role of gas atoms and other impurities will be discussed further in the next section.

It is difficult to make definitive conclusions concerning the void morphology. In nickel the $\{111\}$ planes have the lowest energy but only slightly less than the $\{100\}$ planes.^{2,6} Only a slight amount of impurity could alter the energy relation and thus allow $\{100\}$ faceting of the voids. Stiegler et al. observed $\{111\}$ octahedral voids in high-purity aluminum but observed $\{100\}$ square voids in commercial-purity aluminum.^{2,9} Dissolved gases also affect the morphology of quenched-in voids in fcc metals.^{3,0} Among the bcc metals, no consistent morphology is observed in molybdenum even within the same area of the sample (see Fig. 3). It is difficult to explain how impurities could be the sole explanation in this case unless the differentiation in surface energies may be so

slight that local impurity fluctuations throughout the matrix are affecting the surface energies. Full explanation of void morphology must await careful experiments using controlled amounts of impurities.

IMPURITY EFFECTS: RESULTS

In this section the effects of small variations in impurity level on void formation are presented. Impurity effects have been studied in nickel and molybdenum.

Nickel

Four different grades of nickel were irradiated at three different temperatures, 350, 400, and 450°C, at a constant fluence of 2.5×10^{19} neutrons/cm². The chemical analyses for each of the three grades of "high-purity" nickel are given in Table 2. The fourth grade, commercial-purity A-nickel, is listed as about 99.4% nickel. On the basis of overall purity, the A-nickel is about 2 orders of magnitude less pure.

The size, density, and volume fraction of the voids as a function of the irradiation temperature are summarized in Table 3. The micrographs in Fig. 9 show the differences in void size and number density among the various grades of nickel irradiated at 450°C. Regardless of purity, the average void size increases and the number density decreases with increase in temperature. The size distribution also varies considerably among the three materials, as shown in Fig. 9. This difference in the void parameters among the different grades of nickel extends to high fluences.³¹ The volume fraction, however, is approximately the same in the three high-purity materials within the experimental-error limits. The data from commercial-purity A-nickel are difficult to compare since voids were only positively identified in material irradiated at 450°C. However, it is conceivable that the void size could be less than the resolution limit of the microscope at 350°C if the size were extrapolated downward from a size of 90 Å at 450°C. In general, the relation between void size, void density, and temperature is also expected to hold for the commercial-purity nickel.

If one considers only the three high-purity nickels, there appears to be no consistent correlation between void parameters and overall purity. The differences in average size or density do not correlate with the differences in overall purity, although these differences in purity are extremely small. The least-pure nickel, Nickel II, shows a void size and a void density that are intermediate between those of the other two high-purity nickels. If one, however, compares the high-purity nickels with the commercial-purity A-nickel, a significant difference is noted. Both the size and density are much smaller in the A-nickel and hence the volume fraction is much reduced. In this case the amounts of impurities are so great as to affect a decrease in the total void volume. There is then a clear difference between the A-nickel and the other high-purity nickels.

TABLE 2
CHEMICAL ANALYSES OF THE THREE GRADES
OF HIGH-PURITY NICKEL

	Nickel I	Nickel II	Nickel III
Impurities Present, wt. ppm			
Mg	2	1	
Al	4		0.5
Si	5		<1
K		2	
Ca	2		1
Fe	7	10	10
Co		3	1
Cu	5	20	<0.5
Zn		40	<4
Zr			3
Ga		20	
Pb		8	
Interstitials Present, wt. ppm			
C	50	70	90
O ₂	57	<100	50
N ₂	<5	<6	<2
H ₂	6	6	1.5
Purities (Metallic Only), %			
	99.997	99.99	>99.998

*Commercial-purity A-nickel is 99.4% pure.

TABLE 3
VOID PARAMETERS AS A FUNCTION OF
IRRADIATION TEMPERATURE FOR NICKEL

	Void diameter, Å			Void density, 10 ¹⁴ voids/cm ³			Void volume fraction, %		
	350°C	400°C	450°C	350°C	400°C	450°C	350°C	400°C	450°C
Nickel I	97	120	132	16.0	9.0	5.0	0.06	0.07	0.06
Nickel II	155	192	254	3.6	1.2	0.9	0.06	0.04	0.06
Nickel III	210	280	340	1.2	0.5	0.4	0.06	0.05	0.07
A-nickel	*	<90	90	Inhomogeneous					<0.01

*Not detected.

(a) NICKEL I

(b) NICKEL II

(c) NICKEL III

(d) A-NICKEL

Fig. 9 Micrographs illustrating void formation in various purities of nickel irradiated at 450°C to 2.5×10^{19} neutrons/cm².

Even though the void size and number density varied significantly among the three high-purity nickels, the volume fraction remained essentially constant.

The microstructure resulting from interstitial damage was also much different in the high-purity nickels as compared to the commercial-purity A-nickel. Occasional dislocation loops within a complex dislocation network were observed in the high-purity nickel (Fig. 10). In the A-nickel, dislocation

loops were the only manifestation of interstitial damage (Fig. 11). The loops in Fig. 11 lie on the $\{110\}$ planes with $b = a/2 \{110\}$ and are pure edge in character. Loops marked "A" lie nearly in the plane of the foil and show only residual contrast from the small displacements perpendicular to b . The shape appears to be square with sides parallel to $\langle 001 \rangle$ and $\langle 011 \rangle$. Very rarely a loop

Fig. 10 Micrograph of the dislocation structure in Nickel I irradiated at 350°C to 2.5×10^{19} neutrons/cm².

with a stacking fault was observed, as shown by the fringes in loops "B" in Fig. 11(a). The fault contrast disappears in Fig. 11(b) when the diffraction vector g is changed to $\langle 113 \rangle$. This contrast behavior is expected from Frank-faulted loops with a Burgers vector of $a/3 \langle 111 \rangle$. Measurements of several of the unfaulted loops showed them to be interstitial in nature. The nature of the faulted loop was not determined. The distribution of loops was rather inhomogeneous since there was a greater density in some areas than in others. It was not possible to determine the relative concentration of voids in areas of high loop density since quite thick regions were observed in the analysis of the loops. It was not possible to observe the very small voids in these thick regions.

Fig. 11 Micrographs of the dislocation loops in A-nickel irradiated at 450°C to 2.5×10^{19} neutrons/cm². Foil orientation near $\{110\}$. (a) and (b) are same area imaged under different diffraction vectors g .

TABLE 4
CHEMICAL ANALYSES OF ZONE-REFINED
AND MRC MOLYBDENUM

Amount present, wt. ppm, in		
Impurity	3-pass Z.R.	MRC
W	100	300
Ni	1	2
Cu	3	10
Fe	2	70
K	40	50
Si	12	20
Mn		2
Ca		3
C	3	500
O	4	5
N	1	1
H	1	1

Molybdenum

Three different purities of molybdenum have been irradiated at elevated temperatures and the void characteristics compared. The three types are (1) triple-pass, zone-refined single crystal (Z.R.), (2) a commercial high-purity molybdenum (MRC), and (3) a commercial alloy (TZM). The chemical analyses for Z.R. and MRC are given in Table 4. The TZM molybdenum has approximately 0.5% zirconium and 0.1% titanium. The samples were irradiated at estimated temperatures of 635 and 720°C, and Fig. 12 shows the voids in the molybdenum after irradiation at 720°C. As mentioned previously, the actual temperatures may have been somewhat higher. The voids are slightly larger and their density is smaller in the Z.R. molybdenum as compared to the MRC molybdenum. Although voids did form in the TZM molybdenum irradiated at 635°C, no voids were observed after irradiation at 720°C. At 720°C, second-phase precipitation occurred in the TZM molybdenum. The precipitates are shown as black-white contrast in Fig. 12; no contrast attributed to voids was observed.

DISCUSSION OF IMPURITY EFFECTS

Previous work on quenching and irradiation has shown a relation between purity and void formation.^{29,30,32} Quenching studies on aluminum³² and on copper, silver, and gold³⁰ show that void formation is enhanced by the presence of gaseous impurities, particularly hydrogen. Farrell, King, and Wolfenden³³ found an increase in void formation in aluminum that had been preinjected with hydrogen by proton bombardment. Packan,³⁴ however, on comparing as-received with degassed aluminum found little difference in the void structure; there is therefore some question as to the effectiveness of hydrogen. Stiegler et al.²⁹ at Oak Ridge have studied the void formation in both commercial-purity aluminum (99%) and ultrahigh-purity aluminum (99.9999%) during irradiation. Voids formed at a much lower fluence in the high-purity than in the commercial-purity aluminum. The authors attributed this fact to a much higher concentration of dissolved gases, which serve as stabilizing agents for the voids in the high-purity aluminum. The impurities in the commercial-purity aluminum getter the dissolved gases and remove them from solution.

Our results on high- and commercial-purity nickels essentially agree with those mentioned above. The same conclusions as to the role played by the impurities in the nickels could be reached. The impurities affect not only the void formation but also the complete nature of the radiation damage. The presence of only a low density of loops and voids in the commercial-purity nickel represents a much less advanced state of microstructural damage than in the high-purity materials in which the dislocation loops had grown into a network with a high density of voids. Since the visible damage is due to those defects remaining after recombination, the recombination rate in the commer-

(a) ZONE REFINED

(b) MRC

(c) TZM

Fig. 12 Micrographs of various purities of molybdenum irradiated at 720°C to 5×10^{20} neutrons/cm². The black spots in the TZM molybdenum are small precipitates.

cial-purity nickel must be considerably greater than in the high-purity nickels. Therefore the vacancies precipitate neither as voids nor as two-dimensional-type defects at these temperatures. The vacancies are then free to be annihilated with interstitials or interstitial-type defects. Impurities can also trap the interstitials. The presence of square loops and faulted loops indicates the considerably

different behavior of interstitial defects. There is no evidence for the formation of these particular square and faulted loops in high-purity nickel irradiated at a lower fluence. The impurities may be more important in hindering the development of a high density of loops and a dislocation network. With fewer sinks for interstitials, a greater annihilation rate with vacancies will result. As mentioned before, it is generally agreed that dislocations act as preferential sinks for interstitials, and this factor allows for the buildup of an excess vacancy concentration.

Few conclusions can be drawn from the results comparing the three high-purity nickels. An overall chemical analysis does not truly indicate the extent of impurities in solution. The three materials had essentially the same overall purity and differed only as to the concentration of the different types of impurities. A significant difference in impurity distribution among the high-purity nickels could account for the rather significant differences in terms of void size and number density. Since the diffusivities and binding energies of the different impurities vary considerably, uneven distribution and clustering of impurities could be expected. The loss of interstitials to sinks and the recombination rate, however, were not affected significantly since the overall swelling did not vary.

An experiment involving the irradiation of deformed material illustrates the effect of this impurity distribution. Nickel I was irradiated at 350°C in the as-received condition in which the microstructure consisted of a dislocation-cell structure. Microstructural observations showed that the material recrystallized during the irradiation. The resulting void distribution was very inhomogeneous, as shown in Fig. 13. During such a low-temperature irradiation, any inhomogeneous impurity distribution would be retained because of the very low diffusion rates at these temperatures. For instance, inhomogeneous impurity distribution could result from segregation of impurities to grain boundaries. The resultant void distribution is then a reflection of this impurity distribution. Note the difference in the distribution between Fig. 13 and Fig. 9(a). Very similar observations and conclusions have been made by Farrell from results of cold-worked and irradiated iron.³⁵ Strings of voids in irradiated aluminum have also been attributed to the inhomogeneous distribution of impurities remaining after boundary migration.²⁹ It is probably fair to say that the significant differences in the number density and size distribution of voids in the high-purity nickels point to much heterogeneous nucleation of voids.

The reasoning just given on the effect of impurities could be applied to the results for Z.R. and MRC molybdenum. The significant result in the molybdenum experiment is the lack of voids in the TZM molybdenum at the higher irradiation temperature. The formation of precipitates can require vacancies that are amply supplied by the irradiation process. Further, once the precipitates are formed, the interfaces can serve as sites for interstitial-vacancy annihilation. Consequently the vacancies are not available for void formation. The only indication of interstitial damage was some dislocation fragments. It would seem

Fig. 13 Micrograph illustrating inhomogeneous void distribution in nickel irradiated at 350°C in the as-received condition to a fluence of 2.5×10^{19} neutrons/cm².

that concurrent precipitation may be an effective way to reduce swelling. Of course, obtaining the right precipitation reaction at the right temperature in the material of interest may be rather difficult.

CONCLUSIONS

The temperature regime for void formation in pure metals extends from approximately $0.3 T_m$ to $0.55 T_m$ (T_m = absolute melting temperature). The results on the temperature dependence of the swelling in nickel and molybdenum agree reasonably well with the theoretical predictions for these metals. The temperature region at which vacancy clusters can be stabilized against collapse into a planar configuration is an important criterion in defining a lower temperature limit for void formation. The upper temperature limit is due to a reduction in the supersaturation of radiation-produced vacancies. The anomalous behavior of titanium and zirconium in which no voids have been observed is believed due to the inability of the gas atoms to stabilize the vacancy clusters in

these metals. The lack of voids in gold is probably due to the very low stacking-fault energy, and a higher fluence than was used in the present experiments will be necessary before voids are found.

The complete radiation-induced microstructure must be considered in evaluating the effects of impurities. The dislocation microstructure due to interstitial atoms is considerably altered and much less developed in impure nickel than in high-purity nickel. Since there is a one-to-one correspondence between vacancies and interstitials, vacancy concentration and, hence, void formation are much reduced in the impure nickel. Small differences in the type and amount of specific impurities can have a significant effect on the size, number density, and distribution of voids but the resultant swelling depends primarily on the magnitude of the overall purity.

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DISCUSSION BY ATTENDEES

Shewmon: What are the fluences and their relation to swelling in the nickel-sample studies, and to what extent do the differences you show "wash out" at higher fluences?

Brimhall: The differences in terms of void size and density with high-purity nickel materials do appear to persist at higher fluences. Although the swelling increases with fluence, there is still no difference in the swelling among the three high-purity materials. We have no data from more highly irradiated A-nickel, but it is possible that the marked differences observed at low fluences will be less at higher fluences.

Birnbaum: Can you describe the general relation between the dislocation-loop structure formed at lower temperature irradiations and the void structure formed at higher irradiation temperatures? In molybdenum you seemed to imply that the temperature range in which the voids formed corresponded to a range in which you did not find dislocation-loop formation.

Brimhall: Interstitial dislocation loops form at all irradiation temperatures. At the higher temperatures, loop interaction occurs which will result in a dislocation network. It is only the occurrence of vacancy-type dislocation loops which is a function of temperature. On the basis of available experimental evidence, vacancy loops have been analyzed in samples irradiated in the range from 200 to 700°C. The vacancy loops are always very small, <100 Å in diameter. There is an overlap region at 575 to 700°C in which both voids and

vacancy loops can coexist. In general, however, vacancy dislocation loops form at low temperatures $< 0.3 T_m$ and voids form above $0.3 T_m$.

Bullough: Do you think it possible that the drop in swelling at low temperatures (up to 400°C in niobium) may be due to the release of interstitials from impurity traps? If such trapping does occur, then recombination will be inhibited and the free vacancies, vacancy aggregates formed within the cascades, and vacancy loops can exist; hence small swelling would be expected at low temperatures. As the interstitials become free, as the temperature is increased, the interstitials can destroy all these defects, and thus the swelling decreases. The vacancy loops are particularly vulnerable since they actually attract interstitials. At the same time the interstitials will aggregate to form interstitial loops. Thus at 600°C the stage is set for the formation and growth of the embryonic voids.

Brimhall: The mechanism suggested is certainly possible. We are suggesting that the fraction of the vacancy concentration represented by the loop is greater than the isolated vacancy concentration at 400°C , whereas isolated vacancies or small clusters are predominant at 50°C . However, we do not really know experimentally the relative populations of the various types of vacancy defects.

Harkness: It should be noted that the fact that one vacancy agglomerate has a higher energy than another (i.e., void vs. loop) does not mean it will not form, just that it has a lower probability of forming. Longtime experiments, such as neutron irradiations, could allow significant numbers of lower probability configurations which would not be seen in short-term quenching experiments. Presumably under irradiation both voids and vacancy loops are formed, but the loops do not survive because of their preferential attraction for interstitials.

Brimhall: There certainly is a finite probability that voids would nucleate without gas atoms. However, gas atoms should provide a strong bias toward nucleation in a three-dimensional defect and greatly increase the probability.

ANNEALING OF VOIDS IN ALUMINUM

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ABSTRACT

The activation energy for annealing of voids in neutron-irradiated 1100 grade aluminum was determined from measurements of density recovery in bulk specimens to be 1.7 ± 0.2 eV, which is significantly higher than 1.3 eV, the activation energy for self-diffusion. Trapping of vacancies by neighboring voids, as well as by transmutation-produced silicon, is used to explain this apparent discrepancy. In high-purity aluminum containing a large volume of voids, significant void coarsening occurred during annealing. When electrolytically thinned foils were annealed, the vacancies from the shrinking voids condensed at preferred sites at the oxide-metal interface. There was a wide variation in shrinkage rates for voids of a given size. No evidence was found for enhanced shrinkage of voids located on dislocations, nor is there any reason to believe that the voids may be hydrogen filled.

The annealing of quenched-in voids in aluminum has been reported by Shimomura¹ and in greater detail by Volin and Balluffi² and Westmacott et al.³ The number of quenched-in voids per unit volume is usually very low, and, in analyzing the shrinkage kinetics, it is considered valid to make the following simplifying assumptions: (1) the foil surfaces are perfect sinks for vacancies, (2) each void can be considered as a single noninteracting entity in an infinite medium, and (3) there are no vacancy traps that may retard the migration of vacancies to sinks. The results of these studies have been interpreted to be consistent with voids shrinking by a diffusion-controlled process with an activation energy of about 1.3 eV, which is similar to the activation energy for self-diffusion in aluminum at low temperatures.⁴

However, when the number of voids increases and when other structural defects are present, these simplifying assumptions can no longer be accepted.

This is the case for radiation-induced voids. Here the sintering behavior of the voids can be expected to be influenced by one another and by such additional features as dislocations and solid and gaseous transmutation products. Some of these defects may consume vacancies and accelerate void shrinkage; others may act as transient traps and thus retard elimination of vacancies. Nevertheless, voids produced at a low fluence of 3.2×10^{19} neutrons/cm² (>1 MeV) in aluminum, where the number of voids was small, are reported⁵ to follow the shrinkage kinetics of quenched-in voids. At higher fluences where many more voids and other defects are present, Packan and Braski⁶ have observed that voids of the same initial size have widely varying shrinkage rates, and these rates appear to be less than those reported for similar sized quench voids. For very high fluences and large total void volumes, massive Ostwald-type ripening of voids can occur prior to eventual sintering.⁷

In the present paper we describe measurements of the recovery of radiation-induced density changes in bulk specimens and further observations on annealing of voids in thin foils of irradiated aluminum.

EXPERIMENTAL METHODS

Specimens of commercial-quality 1100 grade (99.0%) aluminum for bulk annealing studies were cut from an irradiated Oak Ridge Research Reactor component, the "N_F tray."⁸ This was a 0.2-in.-thick plate initially in an annealed condition. After irradiation at 50°C to a fluence of 2.8×10^{22} neutrons/cm² (>0.1 MeV), specimens from the plate showed a volumetric swelling due to voids, allowances being made for changes due to silicon production,⁹ of 1.4%. Specimens were annealed in air within a copper block designed to minimize furnace temperature gradients. Densities were determined by the Archimedes method from weighings in air and in bromobenzene. The density of the solution was determined before and after each sample weighing by calibration against a standard quartz block. The precision of each density determination was ± 0.0004 g/cm³, which is about $\pm 0.015\%$ of the density of aluminum.

Some "bulk" specimens of high-purity aluminum (99.9999%), 0.020 in. thick by 0.125 in. in diameter, were cut from rods irradiated to 1.6×10^{21} and 1.6×10^{22} neutrons/cm² (>0.1 MeV) at 55°C and were annealed in air for 1-hr periods at various temperatures. Other samples from these rods were first thinned electrolytically to produce transmission-electron-microscopy specimens before annealing.

RESULTS

Bulk Annealing Experiments—1100 Aluminum

The isochronal recovery of the irradiation-induced density change in 1100 grade aluminum is shown in Fig. 1. The data have been corrected for the density

Fig. 1 Isochronal recovery of irradiation-induced volume swelling (1.4%) due to voids in 1100 aluminum.

change caused by transmutation-produced silicon. The 20-hr isochronal annealing measurements show that void annealing begins between 110 and 170°C and is complete at approximately 300 to 320°C ($\sim 0.6 T_m$). Annealing above 350°C results in a renewed density decrease due to growth of equilibrium gas bubbles, a phenomenon that will not be discussed in this paper. Isothermal recovery of irradiation-induced density changes is illustrated in Fig. 2. Analysis of the isothermal and isochronal annealing curves in Figs. 1 and 2 by the Meehan-Brinkman¹⁰ method yields activation energies in the range 1.57 to 1.88 eV with an average value of 1.7 eV.

Microstructural changes occurring during annealing are illustrated in Figs. 3 to 5. In accordance with the observations of Stiegler et al.,¹¹ voids in the as-irradiated 1100 grade aluminum (Fig. 3) are primarily of cubic shape and are distributed fairly randomly within the grains. There are, however, denuded zones at grain boundaries, and adjacent to these denuded zones are void-rich regions.^{11,12} A high dislocation content, not apparent under the absorption contrast employed in Fig. 3, and transmutation-produced silicon precipitates (~ 100 Å diameter) are additional features of the as-irradiated structure. After annealing treatments that induced partial recovery of density, the following microstructural changes were observed (Fig. 4).

1. The smallest voids annealed out.
2. The voids near grain boundaries disappeared, causing a widening of the grain-boundary denuded zones.
3. Simultaneously with the disappearance of voids, the transmutation-produced silicon precipitates coarsened.

Fig. 2 Isothermal recovery of irradiation-induced volume swelling due to voids in 1100 aluminum.

4. The dislocations were reduced in number, but many were retained in the form of irregular networks linking many remaining voids and silicon precipitates.

After annealing for 20 hr at 300°C (Fig. 5), the voids disappeared and the microstructure then contained a relatively coarse network of dislocations linking coarsened silicon precipitates.

More-detailed studies of the number and sizes of voids within the grains, in specimens in which the voids were not fully removed on annealing, showed that the number of voids decreased by elimination of the smallest voids, and the mean and maximum void sizes increased slightly (Fig. 6).

Bulk Annealing Experiments—High-Purity Aluminum

In specimens exposed to the lower fluence, initially displaying 0.85% swelling, little or no void annealing was noted for temperatures below about 200°C. At temperatures of 250 to 275°C, all the smaller voids (<200 Å diameter) disappeared, and at 300°C all voids were gone. The silicon precipitates coarsened over this temperature range, and the last voids to anneal out were invariably attached to silicon particles.

Fig. 3 1100 grade aluminum irradiated to 2.8×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 50°C showing voids and silicon precipitates within the grains, and heavy silicon precipitation at grain boundaries.

Fig. 4 Void denuded zones, coarse silicon precipitates, and dislocations in 1100 grade aluminum in Fig. 3 after 200-hr anneal at 230°C.

Fig. 5 Coarse transmutation silicon precipitates and absence of voids in irradiated 1100 grade aluminum after 20-hr anneal at 300°C.

Higher temperatures were required to anneal the voids in the higher fluence specimens. These specimens originally showed about 7.5% swelling by immersion density measurements, and the voids were almost twice as large (up to 1100 Å diameter) and almost twice as numerous (6.4×10^{14} voids/cm³) as those in the lower fluence specimen. No significant changes were noted until the annealing temperature reached 300°C, at which temperature the smaller voids disappeared and a few voids grew appreciably. Each growing void was always associated with a growing silicon particle. Much void coarsening occurred at 350°C, where the larger voids depleted their surroundings of smaller voids (Fig. 7). During this coarsening the overall swelling was progressively reduced. All voids were eliminated at 500°C. For a detailed description of these experiments, see Ref. 7.

Thinned-Foil Anneals

Specimens from the high-purity aluminum that had been electrolytically thinned for transmission electron microscopy were annealed in air or in situ in a high-vacuum electron microscope at temperatures close to 200°C. The detailed experiments and findings on these specimens will be published elsewhere. The general features of annealing were: (1) the smaller voids disappeared first, (2) there was a large variability in the shrinkage rates of voids of a given size, (3) voids in the thinner regions of foils annealed out much faster than those in

Fig. 6 Effect of 20-hr postirradiation anneal at 237°C on the size distribution and number of voids within the grains of 1100 grade aluminum.

thicker regions, (4) there appeared to be no significant differences in shrinkage rates between voids attached to dislocations and those not on dislocations, and (5) the escaping vacancies collected under the oxide films on the foil surfaces and formed pits at points where the surface had intersected a void during the thinning process.

No void growth was noticed in these thinned-foil anneals, not even for annealing conditions which produced void coarsening in the bulk annealed specimens. This is in agreement with the effect of foil thickness and emphasizes that the proximity of vacancy sinks has a major influence on the rate of void annealing, i.e., the specimen thickness and the grain size should be important considerations in void annealing.

One of the more intriguing of the above observations, the formation and growth of the surface pits during annealing, is illustrated in Fig. 8. Stereo microscopy confirms that these are unmistakably surface pits, not coarsened voids. They do not form in unirradiated specimens, and their frequency of occurrence is increased with increasing neutron fluence. The larger pits quite clearly caused denuding of voids in their immediate vicinity. The pits were also associated with enlarged silicon particles.

Fig. 7 Bulk specimen of 99.9999% aluminum irradiated to 1.6×10^{22} neutrons/cm² at 55°C and then annealed 1 hr at 350°C, showing coarsening of voids and silicon particles.

DISCUSSION

The major observations from our bulk annealing studies are: (1) the activation energy for void annealing is about 1.7 eV, which is significantly higher than the activation energy of 1.3 eV reported for self-diffusion and for quenched void shrinkage; (2) some void growth occurs in conjunction with net vacancy annihilation; and (3) changes in void size coincide with growth of silicon precipitates.

The shrinkage rate of an isolated void in the vicinity of perfect vacancy sinks is given by²

$$\frac{dr}{dt} = -\frac{D_v}{\epsilon r} \left[\exp\left(\frac{2\Omega\gamma}{rkT}\right) - 1 \right] \quad (1)$$

where r = void radius

t = time

D_v = self-diffusion coefficient

ϵ = correlation factor

Ω = atomic volume

γ = surface energy

k = Boltzmann constant

T = temperature

Fig. 8 99.9999% aluminum irradiated to 1.6×10^{22} neutrons/cm² at 55°C, then thinned for electron microscopy, and annealed 1 hr at 300°C in a high-vacuum electron microscope. Large crystallographic features are vacancy pits forming at the metal-oxide interface. This anneal does not produce much void coarsening in bulk specimens.

The temperature dependence of void shrinkage is determined by the temperature variation of D_v and by the term in the square brackets which represents the driving force. Substitution of typical values for Ω and γ for aluminum for $r = 200$ Å shows that in the range of temperatures used in our annealing experiments, 230 to 290°C, $[\exp(2\Omega\gamma/rkT) - 1]$ decreases by 10% with increasing temperature. Consequently, the activation energy for void annealing should be slightly less than the activation energy for self-diffusion. But in the irradiated aluminum, the effective activation energy is 1.7 eV. According to Bullough and Perrin,¹³ void shrinkage requires a thermal activation, $E_f - E_i$, to create a vacancy near the void-matrix interface and a migration energy E_m^1 to transport this vacancy away from the void. The vacancy-void interaction energy, E_i , is less than 0.1 eV for aluminum and will be neglected in this discussion. Since E_f , the vacancy formation energy, is about 0.7 eV (Ref. 4), the measured activation energy for void shrinkage in our bulk annealing suggests that E_m^1 is about 1 eV, a value considerably higher than 0.6 eV (Ref. 4), the activation for single-vacancy migration, E_m . It is assumed that the value for E_f in our irradiated 1100 grade aluminum is not changed from that of pure aluminum. The 0.4-eV difference between E_m^1 and E_m , we believe, is due to vacancies emitted by shrinking voids being delayed by trapping centers during their migration toward sinks where they are ultimately annihilated.

Damask and Dienes¹⁴ have shown for the relatively simple case of vacancy annealing following quenching in impure metals that the measured activation energy can range between E_m and $E_m + B$, where B is the impurity-vacancy binding energy. The observed growth of some voids during annealing in our experiments is unequivocal evidence that voids in themselves are effective vacancy traps. This arises because a range of void sizes exists in irradiated aluminum, and, according to the Gibbs-Thomson equation, the total energy of the system is reduced by the transfer of vacancies from a small void to a larger one. Another vacancy trap is provided by the transmutation-produced silicon.⁹ The equilibrium solubility of silicon in the range of annealing temperatures employed is small (0.05 to 0.10 at.% compared with about 1.0 at.% generated during irradiation), but the observations show that there is major silicon-precipitate growth occurring concurrently with void annealing. Consequently, a significant flux of silicon atoms must exist in the matrix during void annealing in irradiated aluminum. The vacancy-silicon atom binding energy has been estimated¹⁵ to be 0.26 ± 0.03 eV, and silicon has been shown¹⁶ to reduce strongly the rate of recovery of resistivity in quenched aluminum. Ceresara et al.¹⁷ have argued that some stages of recovery in irradiated Al-Si alloys are associated with the decomposition of strong silicon-vacancy complexes. Additional support for strong silicon-vacancy interactions in aluminum comes from the study of Ozawa and Kimura¹⁸ on the role of vacancies in nucleation and precipitation in Al-Si alloys at temperatures up to 300°C. Clearly, silicon-vacancy interactions can account for at least half of the difference between E_m^i and E_m ; for the remainder, it is proposed that more complex silicon-vacancy aggregates or vacancy-void trapping may be responsible.

Volin et al.¹⁹ have recently observed that in quenched aluminum foils dislocations act as preferred paths for rapid vacancy transport. Our observations on bulk annealing of radiation voids, however, show that the smaller voids anneal out first, irrespective of their position relative to the major sinks and whether or not they are on dislocations. Larger voids near grain-boundary sinks anneal out next, giving rise to a widening of the grain-boundary denuded zones. Finally, the larger voids within the grains disappear. Such behavior occurs despite the existence of an extensive dislocation network linking many voids to one another and to grain boundaries. Additionally, no enhanced shrinkage of voids on dislocations was noted in our studies of thinned foils, implying that rapid vacancy transport along dislocations does not contribute significantly to void annealing in irradiated aluminum.

Our thinned-foil studies confirm the previously reported⁶ variability in the shrinkage rates of voids of a given size. Some of this variation, we feel, will depend on the position of the void relative to the foil surfaces; the remainder will be determined by the presence of surrounding voids and by the influence of silicon and other defects. Similar considerations should apply to voids near grain boundaries in bulk specimens. In these regions, and in thinned foils, the vacancy

sinks are close enough to the voids to prevent significant void growth during annealing.

The formation of large crystallographic pits at the oxide-metal interface of thinned foils during void annealing is a new observation that raises the question of whether or not the nature of the foil surfaces or the oxide film imposes some limitation on the degree to which or the rate at which the surfaces can accept vacancies from the shrinking voids. There are obviously preferred sites for vacancy annihilation at surface irregularities, and it is feasible that, under conditions where a large void volume exists in thinned foils, vacancy annihilation may become the rate-controlling step in void shrinkage.

Smallman and Westmacott²⁰ have recently postulated that voids in irradiated aluminum are really hydrogen-filled bubbles, the rate-controlling step in void annealing being the dissociation of the hydrogen molecule. This conclusion was based on their observations that the voids annealed out of thinned electron microscopy foils more slowly than the calculated removal rates for isolated voids and that the void removal rate was dependent on the technique used to prepare the thinned foils and appeared to be accelerated by exposure to the electron beam. Our findings suggest that some of these observations are resolvable in terms of internal vacancy trapping and the efficiency of the metal-oxide interfaces as vacancy sinks. Although the presence of gases is conducive to void nucleation during irradiation²¹ or quenching,²² we have neither evidence nor reason to postulate that the voids are hydrogen filled. Also we have not seen any influence of the electron beam on void shrinkage. Even deliberate, prolonged exposures to the beam seem to have no effect on subsequent void shrinkage. The results of our present experiments are consistent with the view that radiation voids in aluminum are essentially three-dimensional vacancy aggregates whose shrinkage rates are reduced by their interaction with each other and by the influence of the irradiation-induced silicon on vacancy migration.

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DISCUSSION BY ATTENDEES

Krapp: In reference to your first slide, would you please elaborate on the silicon correction that you applied to those recovery data?

Jostsons: Since the silicon content was of a different density, its density contribution of 0.1% was subtracted from the data over all the annealing ranges.

Bauer: In one of your slides you showed a decrease in the number of voids and then a growth of bubbles. Can you distinguish between the two phenomena in the microscope, or do you infer this indirectly?

Jostsons: If you are referring to the reinstatement of swelling on annealing at temperatures above 300°C (Fig. 1), we know from the thermal history of the specimens, from the distribution of the cavities (preferred grain-boundary sites, etc.), and from their growth characteristics that the cavities developed at these temperatures are gas bubbles and not voids.

If you are asking, "Given a micrograph of a specimen of unknown history, can we tell whether the cavities are voids or gas bubbles?", the answer is more difficult. In the absence of such features as grain boundaries, we could not confidently distinguish a void from an equilibrium gas bubble. Detailed analyses of the strain contrast around a cavity may hold in some cases. See, for example, the paper by M. Rühle. At present, we feel it is safer to differentiate between voids and gas bubbles using the indirect methods outlined in the first part of our answer.

Chadderton: Are the silicon precipitates amorphous or crystalline?

Jostsons: The size of the silicon precipitates is a function of the thermal-neutron fluence and irradiation temperature. Under suitable conditions, electron diffraction ring patterns of beta-silicon were obtained. See also Ref. 9.

Adamson: You commented that often the voids seemed to be associated with (or physically connected to) the silicon precipitates. At least in some of your slides there seemed to be so many precipitates that it may be impossible for a void to exist anywhere without touching a precipitate, even if they didn't interact. Have you considered this?

Jostsons: During thinned-foil preparation, silicon particles frequently remain on foil surfaces giving a false picture of the true precipitate density. We have therefore used stereo microscopy to establish the correlation between silicon precipitates and voids.

EFFECTS OF STRUCTURAL IMPERFECTIONS ON VOIDS IN ALUMINUM

✓ 12

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ABSTRACT

Impurities, inclusions, dislocations, and grain boundaries are structural features that significantly influence the nature and distribution of voids in neutron-irradiated aluminum. Preinjected hydrogen and helium are shown to increase the nucleation of voids for a given fluence without changing the swelling, whereas substitutional-type impurities retard void nucleation. Accelerated void development is frequently noted in the immediate vicinity of inclusions, and, in some cases, large spherical shells of voids form around inclusions. Alongside grain boundaries are regions denuded of voids, and next to these are regions in which void formation is enhanced. At low irradiation temperatures, these near-grain-boundary regions contain more voids than the grain interiors, but, at high irradiation temperatures, they contain very much larger voids than elsewhere. A microstructure consisting of many fine precipitates and dislocations has a much-improved resistance to void formation.

Radiation voids in metals are usually developed at irradiation temperatures between 0.3 and 0.5 of their absolute melting temperatures. Aluminum has a melting point of 660°C, so its void-formation range is roughly from room temperature to 200°C. Voids can therefore be developed at ambient temperatures in aluminum components in water-cooled or -moderated reactors. Two Oak Ridge experimental reactors, the Oak Ridge Research Reactor (ORR) and the High-Flux Isotope Reactor (HFIR), have ambient water temperatures of 45 to 60°C. We have examined a number of aluminum components from these reactors^{1,2} and have also studied voids in high-purity aluminum,^{1,3-6} iron,⁷ and magnesium.⁸ In aluminum, radiation damage is manifest as loops, voids, dislocation lines, and silicon precipitates. The silicon results⁹ from the interaction of aluminum with thermal neutrons, $^{27}\text{Al}(n, \gamma)^{28}\text{Al}$, followed by a beta decay to ^{28}Si . Other transmutation products are hydrogen and helium.

This paper summarizes our major observations on the radiation-induced voids. In essence, we find that the creation, nature, and distribution of the voids are very sensitive to such structural features as impurities, inclusions, grain boundaries, and precipitates.

EFFECTS OF IMPURITIES

Two effects are noted in this category. The first is that gaseous impurities enhance void nucleation. This was demonstrated by preinjecting hydrogen and helium into pieces of nominal 99.9999% purity aluminum (6-9 aluminum) and then irradiating them to 8×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 150°C in a sealed can in the ORR.⁴ As little as 3 at. ppM hydrogen or 3 at. ppM helium significantly increased the number of voids and reduced their average size (Table 1 and Fig. 1) but did not affect the total swelling. Helium was more effective than an equal amount of hydrogen. This is considered an important observation because it implies that gases are involved (and may even be required) in the nucleation of voids, and because hydrogen and helium are produced in metals by (n,p) and (n, α) reactions during irradiation.

TABLE 1

INFLUENCE OF PREINJECTION WITH HYDROGEN
OR HELIUM ON THE NUMBER AND AVERAGE SIZE OF VOIDS
OBSERVED IN 6-9 ALUMINUM AFTER IRRADIATION TO
 8×10^{20} neutrons/cm² ($E > 0.1$ MeV) AT 150°C*

Treatment	Void concentration, 10^{13} voids/cm ³	Size, μ
Uninjected	0.12	0.17
Preinjected with 3 at. ppM H	0.67	0.10
Preinjected with 9 at. ppM H	1.5	0.08
Preinjected with 3 at. ppM He	2.6	0.07

*K. Farrell, A. Wolfenden, and R. T. King, The Effects of Irradiation Temperature and Preinjected Gases on Voids in Aluminum, *Radiat. Eff.*, 8: 107-114 (1971).

The second effect is that the presence of the common impurities Fe, Si, Cu, Zn, Mn, etc., in aluminum tends to postpone void formation to higher fluences, although permitting the formation of loops at dislocations.^{1,4} This is particularly apparent when the behavior of 6-9 aluminum is compared with that of a commercial-grade 99.0% purity aluminum,^{1,4} known as 1100 aluminum. In the former, voids are found at fast ($E > 0.1$ MeV) fluences as low as 10^{19} neutrons/cm², but, in the latter, fluences $> 10^{21}$ neutrons/cm² are required.

Fig.1 Influence of preinjected helium on voids in high-purity aluminum irradiated to 8×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 150°C. (a) No pre-injection. (b) Preinjected with 3 at. ppm helium. [K. Farrell, A. Wolfenden, and R. T. King, The Effects of Irradiation Temperature and Preinjected Gases on Voids in Aluminum, *Radiat. Eff.*, 8: 107-114 (1971).]

After irradiation to 10^{21} neutrons/cm² at 55°C, the 6-9 aluminum exhibits about 1% swelling and the 1100 aluminum none. Many of the impurities in 1100 aluminum are present as insoluble inclusions, but some will also be dissolved in the lattice. These impurities may influence void nucleation by tying up gases at inclusions and/or by affecting the diffusion and availability of vacancies. Silicon is a particularly interesting impurity because it is generated during irradiation. Its solubility is low, and frequently voids in high-purity aluminum are observed to be allied with silicon precipitates.^{3,4} Our general conclusion on the effect of impurities is that gaseous impurities appear to lower the threshold fluence for void nucleation, but substitutional-type impurities retard nucleation to higher fluences.

EFFECTS OF INCLUSIONS

In the present context, and to distinguish them from precipitates, inclusions are defined as unwanted, insoluble intruders in the aluminum. Precipitates are deliberately added and thermally responsive second phases. It is not easy to separate the influence of inclusions on void formation from that of the aforementioned metallic impurities, since many of these impurities make up the inclusions in aluminum. The solubility for most substitutional alloying elements in aluminum is low. One distinguishing feature of inclusions, however, noted in both 1100 aluminum and 8001 alloy (1100 aluminum + 1% nickel), is that, at fast fluences between 10^{21} and 10^{22} neutrons/cm² where voids are just beginning to appear in these materials, the voids tend to be located preferentially near grain boundaries and around some of the larger inclusions. With longer irradiation the matrix fills up with voids, and the affiliation of voids with internal interfaces becomes much less obvious.

Usually the voids are only loosely associated with the inclusions as, for example, at inclusions A in Fig. 2. They are simply in the vicinity of the inclusion, usually within about $0.5\ \mu$. We have also found examples of a much different situation, also illustrated in Fig. 2. Here the large halos or shells of voids are sections through true hollow spheres of voids and are clearly a result of some recoil reaction, probably one involving recoiled α particles. When specimens containing these shells of voids are annealed, the voids disappear and at high annealing temperatures are replaced by shells of small gas bubbles.¹¹ Examples of reactions of the type that could give these shells are $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ and $^6\text{Li}(\text{n},\alpha)^3\text{H}$, with alpha particle recoil distances of 4.1 and $5.7\ \mu$, respectively. There may be many more uncharted reactions, some with fast neutrons. However, our measurements of the shells indicate a maximum radius of $5.7\ \mu$. Observations such as this reinforce the thesis that gases, particularly helium, are potent void-nucleating agents. The distribution of the helium sources will no doubt influence the distribution of voids. Obviously, too, certain trace impurities can profoundly affect void formation.

Fig. 2 Association of voids with inclusions in 1100 aluminum irradiated to 1.6×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 55°C. Voids are clustered near some large inclusions at A. The two large spherical shells of voids are believed to be centered on smaller inclusions containing an impurity that transmutes to helium which is recoiled to the sites of the shell walls. The large holes are etch pits.

EFFECTS OF GRAIN BOUNDARIES

Aluminum has void-free zones on each side of grain boundaries. However, our recent studies^{4,12} of voids in specimens irradiated in the temperature range 45 to 190°C (0.34 to 0.5 T_m) up to fluences of $>1 \times 10^{22}$ neutrons/cm² ($E > 0.1$ MeV) have disclosed, in addition to variations in the widths of grain-boundary void-free zones, perturbations in the number and sizes of voids in regions parallel to, and immediately adjacent to, the denuded zones. These perturbations take the form of either more or much larger voids than those in the grain interiors. These effects are dependent on irradiation temperature, appear to be sensitive to material purity and microstructure, and vary from one grain boundary to another.

The width of the void-free zone at grain boundaries increases with irradiation temperature. Typical widths vary from about 1000 Å at 55°C [Fig. 3(a)] to about 10,000 Å for an irradiation temperature of 150°C [Fig. 3(b)].

Fig. 3 Enhanced void development near grain boundaries. (a) 8001 alloy irradiated to 1.6×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 55°C. (b) 6-9 aluminum irradiated to a similar fluence at about 150°C.

At low irradiation temperatures (45 to 60°C), clustering of voids occurs near the denuded zones. The width of the clustered band is approximately twice the width of the denuded zone on each side of the grain boundary [Fig. 3(a)]. The maximum size of the voids in these bands is about the same as that in the grain interiors, but there is a larger proportion of the bigger voids in the near-grain-boundary bands. We have observed this effect in pure and commercial-quality aluminum and in a number of aluminum alloys.

At irradiation temperatures near 150°C, the clustering of voids in the regions adjacent to the denuded zones is no longer apparent, having given way to a preferred enlargement of voids in those regions. Voids of 3000 to 4000 Å in diameter are common [Fig. 3(b)], and many elongated voids are observed. In the particular specimen shown in Fig. 3(b), the voids in the grain interiors had a maximum diameter of about 1500 Å. In general, the localized summated void volume in the near-grain-boundary regions is much larger than that within the grains. The most striking observation of this effect was noted in 6-9 aluminum irradiated at a temperature estimated to be between 150 and 200°C to a fluence of 1.6×10^{22} neutrons/cm² ($E > 0.1$ MeV). In this material, voids were almost absent from grain interiors, but bands of large voids persisted in the near-grain-boundary regions.

Explanations of these near-grain-boundary void effects have been offered^{4,12} in terms of the effectiveness and relative importance of grain boundaries as sinks for radiation-produced interstitial atoms and vacancies. Similar considerations probably apply to the clustering of voids near inclusions. Because of the greater mobility of interstitial atoms, the grain boundaries, or the inclusion-matrix interface, can absorb interstitials from a wider band on each side of the boundary than the band from which they can absorb vacancies. Where these two bands overlap, that is, close to the boundaries, both defects migrate to the boundary, leaving damage-free zones. In the regions where the interstitial diffusion band exceeds that of the vacancies, there will be an excess of vacancies that will encourage earlier nucleation and/or more rapid growth of voids, depending largely on the temperature. The role of impurities in these regions is unclear but may be important. Clearly, though, grain-size refinement is not likely to be a practical way of minimizing swelling in aluminum.

EFFECTS OF PRECIPITATES AND DISLOCATIONS

Dislocations and fine precipitates are structural features that usually have strong associated lattice strain fields. These fields should attract and annihilate irradiation-produced defects. If the density of dislocations and precipitates is small so that the interfield spacing is large, say greater than 2000 Å, judging from the near-grain-boundary effect, the interstitial component of the damage may be absorbed preferentially, leading to increased swelling. On the other hand, if the interfield spacing is very small, both interstitials and vacancies will be

Fig. 4 Voids in 6061-T6 alloy after irradiation to 8×10^{22} neutrons/cm² ($E > 0.1$ MeV).

absorbed and swelling should be avoided or, at least, delayed to much higher fluences.

With these thoughts in mind, we irradiated some 6061 and 6063 aluminum alloys. These are precipitation-hardened alloys containing up to 1.2% magnesium and 0.8% silicon. In their quenched and tempered conditions, their microstructures are characterized by a very finely divided Mg_2Si precipitate interlaced with dislocations. These alloys have proved to be much more resistant to radiation void formation than 1100 aluminum and 8001 alloy. For example, no voids were found in 6063-T6 aluminum after irradiation in the HFIR to 1.6×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 55°C, whereas a companion specimen of 6-9 aluminum displayed 7.5% swelling.^{5,6} Alloy 6061 in an overaged condition begins to show voids at fluences in excess of 4×10^{22} neutrons/cm² ($E > 0.1$ MeV), and these voids are usually associated with precipitate denuded regions around some of the larger precipitates (Fig. 4).

SUMMARY

Radiation void formation and growth in aluminum are known to be sensitive functions of neutron fluence and irradiation temperature. Swelling is also shown to be very much influenced by impurities, inclusions, dislocations, and grain boundaries. Grain refinement per se is not likely to minimize swelling, but some

resistance to swelling may be provided by alloying and by introducing fine precipitate-dislocation structures.

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DISCUSSION BY ATTENDEES

Balluffi: In discussing possible mechanisms by which dissolved impurities slow down void formation, you did not mention the possibility that such impurities could inhibit dislocation climb. Such an inhibition would, of course, increase the vacancy-interstitial recombination and hence decrease the number of vacancies available for void growth.

Farrell: I agree.

Norris: I should like to offer a different explanation for the void-enriched zones that you sometimes observe adjacent to void denuded zones at a grain

boundary. Dislocations, as well as point defects, are likely to be affected by the presence of the boundary. Thus, extending beyond the usual denuded zone, there may be a zone of different dislocation density and arrangement from those typical of the matrix. Void-growth characteristics are sensitive to dislocation behavior. Consequently, in some circumstances, a void-enriched zone could arise.

Farrell: We considered this possibility, but we find no unusual changes in the dislocation density in the void-enriched areas. There are dislocations threading the large voids produced at the higher irradiation temperatures.

Harkness: Are the precipitates in your system incoherent? Perhaps, in light of experimental results that show voids forming on incoherent carbide precipitates in stainless steels, the nature of the coherency of the precipitate is essential in determining whether it will enhance or inhibit void formation.

Farrell: That is a good point. In the 6063 alloy the precipitates were all coherent, and we have not found voids in this material, at least for fluences up to 1.6×10^{22} neutrons/cm². In the overaged 6061 alloy, we do get some large incoherent precipitates, and, at fluences $>4 \times 10^{22}$ neutrons/cm², voids form near these precipitates.

Smidt: J. O. Stiegler made a comment during his paper that residual hydrogen content in aluminum seemed to have no effect on void nucleation, whereas you have shown hydrogen injected in the material by particle accelerators does influence the void nucleation. Have you considered the possible effects of displacement spikes or enhanced vacancy concentration produced by the particle bombardment on void nucleation?

Have you tried annealing the specimens after particle bombardment to produce agglomeration of the damage into visible-size defects?

Farrell: The specimens were bombarded at temperatures less than 200°C, and no visible damage could be seen either immediately after bombardment or after annealing at 350°C, in which condition the specimens were neutron irradiated. We would say that damage from the particle bombardment did not significantly influence the reported observations.

THE EFFECT OF ALLOYING AND PURITY ON THE FORMATION AND ORDERING OF VOIDS IN BCC METALS

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ABSTRACT

The void populations in Mo, Nb, V, and one alloy of each of these were compared by electron microscopy. All three of the systems responded differently to the alloying. The void concentrations and sizes in the Mo and Mo-0.5% Ti irradiated at 790°C were identical within the measurement limits. After irradiation at 585°C the Mo-0.5% Ti contained more voids than the Mo, but the sizes were nearly identical. Alloying Nb with 1% Zr reduced the void concentration after irradiation at 790°C by more than an order of magnitude, but this was compensated by an increase in void size. High void concentrations were observed in V irradiated at 385 to 600°C, but samples of V-20% Ti irradiated in the range 475 to 600°C had no detectable voids. The V-20% Ti contained high densities of irradiation-produced dislocations in networks and tangles. Voids in Mo, Mo-0.5% Ti, Nb, and Ta were ordered on a body-centered cubic (bcc) superlattice parallel to the metal bcc lattice. Void ordering was not observable in the Nb-1% Zr or V.

Voids formed during reactor neutron irradiation at elevated temperatures have now been reported in most of the bcc metals, including at least vanadium,¹ molybdenum,^{2,3} tungsten,² iron,⁴ niobium,⁵ and tantalum.⁶ If these results are compared to the extensive data on austenitic stainless steel, the obvious difference is that void concentrations are higher and void sizes smaller in the bcc metals. The void population observed is strongly dependent on the irradiation temperature, with void concentration decreasing and void size increasing as the irradiation temperature is increased. There have not yet been any systematic attempts to determine the fluence dependence of void formation in bcc metals. The only investigations of the effect of alloying on void formation in a bcc system have been reported by Wiffen⁷ and Elen,⁸ who showed that the addition of 3 to 20% Ti suppresses void formation in vanadium.

Specimens of molybdenum, niobium, vanadium, and one alloy of each of these have been irradiated in the Experimental Breeder Reactor II (EBR-II) and examined for characterization of the void microstructure. Some results on tantalum are also included in a summary of recent data on the ordering of voids.

EXPERIMENTAL

The Mo, Mo-0.5% Ti, Nb, Nb-1% Zr, and Ta samples were all sections of typical refractory-metal sheet stock (0.020 in. thick) purchased from commercial vendors. The vanadium and V-20% Ti were laboratory-produced tubing and rod stock. All the materials were annealed for 1 hr at temperatures appropriate to produce a fully recrystallized structure.

Most of the specimens were irradiated in a static inert-gas atmosphere in a structural-materials irradiation experiment, but some of the vanadium and V-20% Ti specimens were structural components of a fuel-irradiation experiment. Irradiation temperatures were determined by design calculations and were checked by examination of the microstructure of stainless-steel internal capsule components and comparison with the available data on the microstructure of stainless steel as a function of irradiation temperature and fluence. All irradiations were in the core of the EBR-II.

All specimens except the tantalum were thinned for microscopy by the standard two-step electrolytic technique of dimpling and final polishing. The very high specific activity of the tantalum required thinning by a completely remote, one-step electrolytic technique. The specimens were examined in a Hitachi HU 200 E microscope operating at 200 kV, most commonly used at a direct magnification of 40,000 X. Foil thicknesses were determined by the stereographic method, and void-size parameters were determined by diameter classification on a Zeiss particle-size analyzer.

RESULTS AND DISCUSSION

All the samples discussed in this paper contained radiation damage in the form of loops and dislocation segments representing sections through dislocation networks. In general, the densities of loops and dislocation segments decreased as irradiation temperature was increased. Only the void component of the irradiation damage will be treated in this paper.

Effect of Purity in Vanadium

Vanadium samples with two different levels of interstitial purity, 220 and 1250 ppM C + N + O, were irradiated at a common temperature of 385°C to fluences near 5.3×10^{21} neutrons/cm² (>0.1 MeV). The data on the void

TABLE 1
THE EFFECT OF PURITY ON VOIDS IN VANADIUM
IRRADIATED AT 385°C*

Impurities, ppM			Fluence,† 10 ²¹ neutrons/cm ²	Void microstructure		
				Void concentration, 10 ¹⁵ voids/cm ³	Average diameter, Å	Volume fraction, %
C	N	O				
79	31	110	4.9	12	50 ± 10	0.08
350	230	670	5.7	120	45 ± 10	0.56

*Both samples annealed 1 hr at 900°C.

†Fluence >0.1 MeV.

microstructure of these samples are given in Table 1. Both samples contained voids with average diameters near 50 Å, but the sample with 1250 ppM C + N + O contained an order of magnitude more voids than did the sample with 220 ppM impurities. Void-denuded zones adjacent to grain boundaries were very narrow in both these samples, and the void distributions in regions away from grain boundaries appeared to be random. Elen⁸ examined vanadium with several purities irradiated at lower temperatures and lower fluences than the present samples and found that void sizes and concentrations varied in a complex manner with impurity levels. Both Elen's and the present results show that interstitial impurity level in vanadium has a very strong influence on the void population produced by irradiation, but many more data are required to determine the exact nature of this interaction of impurity with irradiation damage.

The Effect of Alloying in Vanadium, Niobium, and Molybdenum

Table 2 shows data on samples for which the effect of alloying on the void microstructure can be directly compared. The vanadium and V-20% Ti are compared on the basis of several irradiation conditions. The comparisons of molybdenum, niobium, and one alloy of each represent samples from two sample holders only. As these sample holders were nearly solid metal cylinders, only small temperature differences can exist between the samples in a single holder, even though there is some uncertainty in the absolute irradiation temperature for the holder. Similarly, the fluence value of 2.5×10^{22} neutrons/cm² may be subject to some absolute error but was constant for all the molybdenum- and niobium-alloy specimens.

The results in Table 1 and the first three entries in Table 2 show that irradiation of vanadium in the range 385 to 600°C to fluences up to 1.4×10^{22}

TABLE 2
EFFECT OF ALLOYING ON THE VOID POPULATION
OF NEUTRON-IRRADIATED REFRACTORY METALS

Composition,* wt.%	Irradiation conditions		Void parameters		
	Temperature, °C	Fluence,† 10^{22} neutrons/cm ²	Void concentration, 10^{15} voids/cm ³	Average diameter, Å	Volume fraction, %
V	475	0.97	10.6	82	0.34
V	550	1.4	5.9	170	1.77
V	600	1.4	2.0	230	1.47
V-20% Ti	475	0.97	0		
V-20% Ti	525	2.0	0		
Nb	790	2.5	2.8	186	1.04
Nb-1% Zr	790	2.5	$\begin{cases} 0.19\ddagger \\ 0.02 \end{cases}$	510	$<1.46\ddagger$
Mo	585	2.5	72	64	1.1
Mo-0.5% Ti	585	2.5	240	69	4.5
Mo	790	2.5	54	72	1.19
Mo-0.5% Ti	790	2.5	60	72	1.3

*All samples recrystallized before irradiation.

†Fluence >0.1 MeV.

‡Wide variation in void densities. Calculated swelling is thus an upper limit.

neutrons/cm² produced void concentrations in the range 10^{15} to 10^{17} voids/cm³ with average diameters in the range from below 50 to 230 Å. A comparison of the few available results shows that the void concentration decreases and average void size increases as the irradiation temperature is increased. The data are insufficient to determine the irradiation temperature at which the void volume fraction is a maximum, nor are there any data to determine the fluence dependence of the void population at any irradiation temperature. Typical void distributions in vanadium containing about 1000 ppm interstitial impurities for irradiation temperatures of 475 and 575°C are shown in Fig. 1. Narrow grain-boundary-denuded zones can be seen for both irradiation temperatures, and the void distributions are somewhat "patchy" for both conditions, with occasional zones of lower than average void density occurring randomly through the grain. The microstructure characteristic of the 575°C irradiation also shows a zone of enhanced void concentration adjacent to the grain-boundary-denuded zone, a feature often seen in the bcc metals.

Specimens of V-20% Ti irradiated under conditions similar to the unalloyed vanadium failed to show any evidence of void formation. The microstructure

Fig. 1 Typical void microstructures in vanadium irradiated to (a) 0.97×10^{22} neutrons/cm² (>0.1 MeV) at 475°C and (b) 1.4×10^{22} neutrons/cm² at 575°C.

shown in Fig. 2 for V-20% Ti irradiated to 1.4×10^{22} neutrons/cm² at 600°C shows a connected dislocation network that has resulted from the irradiation. There is no fine-scale component of the radiation damage. The density of dislocations generally decreased with increasing irradiation temperature (larger scale networks at the higher temperatures), but the scale of the damage varied considerably, even within a single specimen. There was also a considerable amount of precipitation in the irradiated specimens, with several different forms of precipitate present, but no attempt was made to identify these. Elen⁸ has also found a similar result in the comparison of irradiation damage in V, V-3% Ti, and V-5% Ti. His results, at lower temperatures and fluences than the present results, also confirmed that the only form of damage observed in the titanium-containing alloys was a dislocation structure. There were no voids in the alloy specimens. Comparison of the present results and Elen's results suggests that the damage forms first as small loops (as Elen observed), and these grow and intersect as the radiation progresses. These loops eventually form the dislocation networks observed in the present work.

Void parameters for the niobium and Nb-1% Zr samples irradiated to 2.5×10^{22} neutrons/cm² at 790°C are given in Table 2, and typical microstructures are shown in Fig. 3. Alloying niobium with 1% Zr reduced the void concentration by more than an order of magnitude, but this reduction is compensated by an increase in void size. The concentration of voids in the unalloyed niobium was approximately the same in three foils taken from the sample. Concentrations were often higher in the narrow area adjacent to the

Fig. 2 Microstructure of V-20% Ti irradiated at about 600°C to 1.4×10^{22} neutrons/cm² (>0.1 MeV). Note the absence of any fine-scale component of the irradiation damage. $\bar{g} = 110$.

Fig. 3 Void microstructure in (a) niobium and (b) Nb-1% Zr irradiated to 2.5×10^{22} neutrons/cm² (>0.1 MeV) at 790°C. The niobium sample is typical, but considerable variation existed in the void size and distribution in the alloy.

grain-boundary-denuded area, and in some cases voids were appreciably larger in this zone. Void concentrations in the Nb-1% Zr were definitely not uniform but varied by up to an order of magnitude from grain to grain, and in some cases even within a grain. Detailed measurements of void concentrations at three points within a single grain, with thickness measured at each point and all points well removed from grain boundaries, gave a 12-fold variation in void concentration. The void volume-fraction calculation for Nb-1% Zr is only approximate because the variation in void concentration has not been treated completely. The order-of-magnitude difference in concentration of voids and approximately equal total void volume in these two samples suggest that the addition of zirconium to niobium greatly reduces the void nucleation rate. The alloying has had little effect on the total number of vacancies that are present in the final observed void populations.

The final alloy comparison available is between molybdenum and Mo-0.5% Ti. The void-population data for a fluence of 2.5×10^{22} neutrons/cm² at irradiation temperatures of 585 and 790°C are collected in Table 2. Both materials at both irradiation conditions contained a high concentration of small voids, and accurate size measurements and counts were difficult. Except for the narrow grain-boundary-denuded zones, the void concentrations appeared to be uniform throughout any given sample, without the local variations seen in the vanadium and in the Nb-1% Zr. At 790°C the addition of 0.5% Ti to molybdenum did not change the population of irradiation-produced voids. The void concentration, size, and volume fraction are almost identical for the two materials. The void parameters for the molybdenum and Mo-0.5% Ti irradiated at 585°C show differences that are well beyond the expected experimental uncertainties. In this case, in contrast to the alloying effects in vanadium and niobium, the alloy has a void concentration that is more than three times as large as the concentration in the unalloyed molybdenum. The higher void concentration in this case is not compensated for in void size; in fact, the voids are slightly larger in the alloy. The net result is that after irradiation at 585°C the void volume fraction in Mo-0.5% Ti is four times that in molybdenum.

The data presented here suggest that the influence of purity and alloying on the processes of void formation and growth is complex. The observations presented differ from one system to the next. The data on the vanadium and niobium systems suggest that interstitial impurity atoms may stabilize the void-nucleation process. The comparison of niobium and Nb-1% Zr suggests that, although the nucleation stage may be affected, the total number of vacancies stored in this system is independent of the alloying. The partial suppression of void nucleation in niobium and the complete suppression in vanadium produced by alloying may result from the precipitation of the interstitial impurities on alloying. The lack of an alloying effect in molybdenum irradiated at 790°C and the "reverse" alloying effect at 585°C, where the Mo-0.5% Ti contained a higher concentration and a larger volume fraction of voids than did the molybdenum, may be related in some manner to the lower

TABLE 3
SUMMARY OF VOID ORDERING DATA FOR
NEUTRON-IRRADIATED REFRACTORY METALS*

Composition, wt. %	Irradiation temperature, °C	Calculated damage, † dpa‡	Void concentration, 10 ¹⁵ voids/ cm ³	Void superlattice		
				Lattice parameter, Å	Density points, 10 ¹⁵ cm ⁻³	Super- lattice occupancy
Mo	585	36	72	265	107	0.67
Mo-0.5% Ti	585	36	240§	215	201	1.20
Mo	790	36	54	328	57	0.95
Mo-0.5% Ti	790	36	60	315	65	0.94
Nb	790	34	2.8	665	6.8	0.41
Ta	585	20	190	205	232	0.82

*All specimens irradiated to 2.5×10^{22} neutrons/cm² (>0.1 MeV).

†Kinchin-Pease calculation for effective threshold displacement energy of 25 eV (Ref. 9).

‡dpa = displacements per atom.

§ Upper limit.

interstitial-impurity solubility and lower interstitial contents found in molybdenum than in niobium and vanadium. At present no model is available to explain quantitatively the alloying effects in these three systems.

Void Ordering in Niobium, Molybdenum, and Tantalum

The voids in several of the refractory-metal samples discussed above have been found to be nonrandomly distributed in the host metal lattice. The voids are partially ordered on a bcc superlattice that is parallel to the metal bcc lattice. All our data presently available on this void ordering are collected in Table 3, and examples of the appearance of this order are shown in Fig. 4.

This type of void ordering has also been reported by Evans¹⁰ in ion-bombarded molybdenum. The present void ordering is not as perfect as is that shown by Evans, and this may be a result of the higher damage concentration produced in his samples. The voids in samples discussed in this paper are not exactly on a true superlattice but seem to be randomly displaced small distances from superlattice points. In all the present samples, the void ordering was best seen in foils oriented so that one or more {110} planes of the void superlattice were parallel to the electron beam (as in Fig. 4). Viewed in this condition, the traces of some {110} void planes could be followed for many tens of intervoid spacings before the order of the particular plane would break down. As can also be seen in Fig. 4, regions of near-perfect void ordering are separated by regions having a much less regular void arrangement.

The lattice parameter and density of points for the void superlattice (in Table 3) were determined by measuring the average separation of $\{110\}$ void planes in regions of near-perfect order and converting this value to the parameter for a bcc superlattice. The final column in Table 3, the superlattice occupancy, is

Fig. 4 Examples of void ordering in (a) molybdenum irradiated at 585°C and (b) niobium irradiated at 790°C. The fluence for both samples is 2.5×10^{22} neutrons/cm² (>0.1 MeV). The voids in the niobium are imaged in an overfocused condition to improve visibility. Viewing at a low angle helps illustrate the lack of perfection in the void ordering.

the ratio of the observed void concentration to the calculated density of points in a perfect superlattice. The value greater than 1 for the Mo-0.5% Ti irradiated at 585°C probably reflects the inability to accurately determine foil thickness and count number of voids. This suggests that the true void concentration for this condition is not as large as reported in the tables. Table 3 shows that void ordering can occur in at least three metals and that it is found for void concentrations differing by almost two orders of magnitude (although in two different metals). The lattice parameter of the void superlattice, which is measured independently of foil thickness, confirms the effect of alloying in molybdenum that was discussed earlier. The alloying has had no influence on the superlattice at an irradiation temperature of 790°C, but, in the samples irradiated at 585°C, the Mo-0.5% Ti has a superlattice with a smaller parameter than does the unalloyed molybdenum. No void ordering was detected in the vanadium or the Nb-1% Zr samples discussed in this paper.

SUMMARY

Neutron-irradiated samples of Mo, Nb, V, and one alloy of each of these have been examined by electron microscopy for characterization and comparison of the void microstructures. The following features were noted:

1. In vanadium irradiated at 385°C, the void density was increased by an increase in the interstitial-impurity content of the material.
2. In vanadium irradiated in the range 385 to 600°C, void concentrations were high and decreased with increasing temperature, and void sizes increased with increasing temperature.
3. When irradiated in the range 475 to 600°C, V-20% Ti contained an irradiation-produced dislocation network but no voids or other fine-scale damage.
4. Samples of Nb-1% Zr irradiated at 790°C contained fewer and larger voids than niobium irradiated at the same temperature, but the void volume fraction was approximately equal in both materials.
5. Molybdenum and Mo-0.5% Ti contained identical void populations when irradiated at 790°C. After 585°C irradiation, however, the alloy contained a higher void concentration and higher void volume fraction than the unalloyed metal, but the void sizes were quite similar.
6. At least in the vanadium and niobium, the presence of free interstitial impurities may influence the void-nucleation process. Available data are insufficient to determine in detail the effect of either purity or alloying.
7. Voids in Nb, Ta, Mo, and Mo-0.5% Ti can be arranged in a nonrandom, ordered superlattice that is bcc and is parallel to the bcc host lattice. Data are too limited to identify the requirements for the formation of a void superlattice.

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DISCUSSION BY ATTENDEES

Cost: I wonder if it is possible that the array of ordered voids which you observe may be two dimensional rather than three dimensional. The array does not appear to show the voids in more than one plane. A two-dimensional array might be expected in the situation observed earlier today in which void nucleation was indicated to have occurred where grain boundaries had previously existed.

Wiffen: In a few cases stereo microscopy has shown that the void arrays are three dimensional. In other cases the dependence is on exact alignment of the void-superlattice planes with the electron beam before the order can be seen, and the reestablishment of the observed order after tilting large angles between major crystallographic orientations conclusively establishes the three-dimensional nature of the array. The observation of the same ordering in all grains of a given specimen proves the order to be a property of the material and the irradiation conditions. The effect of a previous grain-boundary site in aluminum (reference—J. O. Stiegler's paper—this conference, page 292) was only a very localized observation and is in no way similar to the void ordering shown here.

Ardell: Have you ever considered doing optical diffraction experiments on your electron micrographs to investigate the perfection of the void superlattice?

Wiffen: We have not, but the technique might prove useful in measuring average properties of the superlattice.

Ardell: Is there any correlation between the size of the denuded zone and the structure of the grain boundary? I ask this because there are special types of boundaries that would normally be ineffective as sinks for vacancies and interstitials.

Wiffen: There is considerable variation in the width of the boundary-denuded zones within any given specimen, but this has not been correlated with any grain-boundary parameters. All boundaries observed in the body-centered cubic metals have been bordered by denuded zones.

THE DEPENDENCE OF RADIATION EFFECTS ON THE PRIMARY RECOIL ENERGY

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ABSTRACT

The present status of the analytical theory of the displacement cascade is reviewed, with emphasis on the topics of importance for neutron damage in metals. These include atomic cross sections and interatomic potentials, electronic stopping cross sections, the energy lost from displacement cascades by electron excitation, the number of defects produced in a cascade, the effects of target crystallinity, and the spatial extent of cascades.

The effects of neutron irradiation on the properties of materials depend on the energy of the incident particles for two distinct reasons. First, the energy and mass spectra of target atoms and heavy reaction products recoiling from nuclear interactions depend on the neutron energy. Second, the partitioning of the energy of the primary recoils between the motion of target atoms and the excitation of target electrons depends on the recoil energy. In the case of irradiation by atomic ions, the incident particles behave similarly to the recoils and must be considered along with them. The various recoil atoms slow down through inelastic collisions with other atoms of the target, displacing some of these to slow down in their turn until the original energy of the primary recoil has been dissipated. In this way a considerable number of displaced atoms is produced, as is an equal number of vacant lattice sites, the so-called displacement cascade. Once formed, this nascent damaged state relaxes to an observable configuration that depends on the time, temperature, stress, impurity content, and other variables. The inelastic energy losses in the slowing-down process will appear in metals primarily as heat since the electrons produced have insufficient energy to displace atoms from lattice sites and ionization of the atoms in a metal does not produce damage. Thus, in metals, only a portion of the energy of a primary recoil is effective in producing damage. A principal purpose of this paper is to discuss the way in which this portion depends upon

the energy of the recoils. The topics discussed include atomic scattering cross sections, the slowing down of ions in solids by electron excitation, the effects of target crystallinity, and models for the production of the nascent damaged state. These are all areas in which recent studies of atomic collisions in solids have led to advances. The emphasis throughout will be on the analytical treatment of cascade theory, primarily in structureless solids, but much of what is said is also relevant to the construction of large computer models for the simulation of radiation damage in crystalline media.

ATOMIC SCATTERING CROSS SECTIONS AND INTERATOMIC POTENTIALS

The systematic investigation of those aspects of atomic scattering theory which are relevant to studies of radiation damage in metals begins with the well-known article of Bohr¹ and has been extended primarily by Lindhard and his coworkers.²⁻⁷ The purpose of their work was to find comprehensive approximation procedures that would permit collisions between atomic systems to be described in terms of only a small number of parameters. Although atomic collisions are inelastic except at the lowest energies, it is an excellent approximation to separate them into a quasielastic part that describes the deflection of the projectile and an electron-excitation part that contributes only to the energy loss. This separation is permissible largely because the low mass of electrons prevents them from carrying away significant momentum even though they may be quite energetic, but also partly because the inelastic energy loss in individual collisions is often small. Separating "electronic" and "atomic" (or "nuclear") interactions in this way permits considerable simplification in the application of scattering theory, especially since the quasielastic atomic scattering is described with satisfactory accuracy by classical mechanics. Although this approximation fails at sufficiently high energies,^{2,3,8} it does so only as the interatomic potential approaches its Coulomb limit, for which classical and quantal treatments of the scattering give the same results. The failure of the classical approximation at small scattering angles^{1,8} is principally of concern in channeling calculations, but even in these cases classical methods have been shown to be adequate for atomic projectiles.⁹⁻¹² The necessary interatomic potentials and the associated atomic scattering cross sections are discussed in this section. The energy lost to electrons will be considered in the next section.

The trajectories of two particles interacting according to a conservative central repulsive force are shown in Fig. 1, which defines several terms of interest. The barycentric (center-of-mass) scattering angle and time integral are given by¹³

$$\theta = \pi - 2p \int_R^{\infty} dr [r^2 f(r)]^{-1} \quad (1)$$

Fig. 1 The trajectories of two particles interacting according to a conservative central repulsive force are shown in laboratory coordinates. The positions of the particles and of the center of mass are shown at the apsis of the orbit. The laboratory (ϑ) and barycentric (θ) scattering angles, the "time integral" τ , and the impact parameter p are indicated.

$$\tau = (R^2 - p^2)^{1/2} - \int_R^\infty dr \{ [f(r)]^{-1} - (1 - p^2/r^2)^{-1/2} \} \quad (2)$$

where

$$f(r) = [1 - p^2/r^2 - V(r)/E_{\text{rel}}]^{1/2} \quad (3)$$

and where p = impact parameter

E_{rel} = relative kinetic energy

r = (variable) interatomic separation

$V(r)$ = potential of interatomic force

R = apsis of the collision, defined by $f(R) = 0$

The relative kinetic energy is

$$E_{\text{rel}} = AE/(1 + A) \quad (4)$$

where E is the initial kinetic energy of the projectile and A is the ratio of the mass of the target (scattering) atom to that of the projectile (scattered) atom.

The energy transferred to the target atom in the collision is

$$T = T_m \sin^2 \theta / 2 \quad (5)$$

where the maximum transferred energy is

$$T_m = 4E_{\text{rel}}/(1 + A) \quad (6)$$

The differential scattering cross section may be defined as

$$\sigma(\theta) = 4\pi p \, dp / \sin \theta \, d\theta \quad (7)$$

where $\sigma(\theta) \, d\theta$ describes the probability that particles in a uniform beam incident upon the scattering center will be deflected into the angular range $d\theta$ at θ . The differential scattering cross section may also be defined as

$$d\sigma = \sigma(\theta) \, dT/T_m \quad (8)$$

which describes the probability that the projectiles will lose energy in the range dT at T . The integrals in Eqs. 1 and 2 can be evaluated in closed elementary form only for a limited group of power potentials,¹³ so that recourse must be had either to numerical methods or to approximations. The numerical evaluation of the integrals is straightforward and tables of R , θ , T/T_m , τ , and $\sigma(\theta)$ for various relative energies and impact parameters are available for several commonly used interaction potentials.¹⁴ The approximation methods may take the form of modifying the potential function, as in the so-called matching potential method,^{15,16} or of simplifying the dynamical problem as in the impulse approximation.^{8,17,18} Still another procedure¹⁹ is to assume a convenient form for the dependence of the differential scattering cross section on E_{rel} and T and to evaluate the corresponding interaction potential using the inversion method of Firsov.²⁰⁻²²

When two atoms approach each other very closely, the interaction potential must approach the Coulomb repulsion between the two nuclei, but at larger separations the nuclear charges will be partially screened by the atomic electrons. The interaction potential may then be written as

$$V(r) = (Z_1 Z_2 e^2 / r) \phi(r) \quad (9)$$

where $Z_1 e$ and $Z_2 e$ are the charges on the two nuclei and where the screening function $\phi(r)$ approaches unity for close approaches between the two atoms. It is often convenient to approximate the screening function by an inverse power of r , the magnitude of the power depending on the region of separation important in the particular application. Lindhard et al.³ have introduced a particularly convenient representation of the scattering from the inverse-power potentials,

$$V_{\ell}(r) = L_{\ell}/r^{\ell} \quad 1 \leq \ell < \infty \quad (10)$$

where L_{ℓ} and ℓ are constants. By an ingenious application of the impulse approximation, they obtained the approximate differential scattering cross section

$$d\sigma = (\pi\alpha_{\ell}^2/\ell)(T_m/T)^{1+1/\ell} d(T/T_m) \quad (11)$$

where

$$\alpha_{\ell} = \{\pi^{1/2} L_{\ell} \Gamma[(\ell+1)/2] / 2E_{rel} \Gamma(\ell/2)\}^{1/\ell} \quad (12)$$

Equation 11 has been used to obtain simple analytical estimates of the ranges of energetic ions in matter.⁴ Its application to radiation-damage problems will be discussed later. The Firsov inversion procedure has been used^{1,9} to evaluate the accurate potentials corresponding to Eq. 11. They are softer than the power potentials, Eq. 10, and are significantly energy dependent, features that become more pronounced as ℓ increases.

The Thomas-Fermi model of the atom may be used to obtain a more accurate description of the interaction of two atoms. In this approximation

$$\phi(r) = \phi_0(r/a) \quad (13)$$

where $\phi_0(x)$ is the Thomas-Fermi screening function^{2,3} and a is a constant that depends upon Z_1 and Z_2 . Lindhard, Nielsen, and Scharff,³ following Bohr,¹ choose

$$a_L = (9\pi^2/128)^{1/2} a_0 [Z_1^{3/2} + Z_2^{3/2}]^{-1/2} \quad (14)$$

where a_0 is the Bohr radius; and Firsov,^{2,4} on the basis of approximate numerical solutions of the Thomas-Fermi diatomic-molecule problem, has suggested

$$a_F = (9\pi^2/128)^{1/2} a_0 [Z_1^{1/2} + Z_2^{1/2}]^{-3/2} \quad (15)$$

These two estimates do not differ sufficiently for a choice between them to be important. It is convenient to define

$$E_L = Z_1 Z_2 e^2 / a \quad (16)$$

and to introduce the dimensionless relative energy

$$\epsilon = E_{rel}/E_L \quad (17)$$

Then the scattering from the Thomas–Fermi potential may be represented by

$$d\sigma = \frac{1}{2} \pi a^2 t^{-3/2} f(t^{1/2}) dt \quad (18)$$

where $t = \epsilon^2 \sin^2 \theta/2$ and the function $f(t^{1/2})$ has been evaluated numerically by Lindhard et al.³ A satisfactory approximation to this function is²⁵

$$f(t^{1/2}) = \lambda t^{1/6} [1 + (2\lambda t^{1/2})^{2/3}]^{-3/2} \quad (19)$$

with $\lambda = 1.309$. The accurate potential corresponding to Eqs. 18 and 19 can be found by the Firsov inversion procedure: the calculation is sketched in Appendix A. The results are compared in Fig. 2 with the exact Thomas–Fermi screening function,²⁶ the Molière approximation,²⁷ and the Bohr (exponentially screened Coulomb) potential.¹ Clearly, although the Lindhard screening function is somewhat energy dependent, it is an excellent approximation to the Thomas–Fermi screening function over the range of separation shown. Since a ~ 0.1 Å, this covers the entire region of practical interest for radiation-damage calculations.

The principal objection to the Thomas–Fermi description of the interatomic interaction is that for large separations $\phi_0(x) \propto x^{-3}$, a rate of decrease that is far too small. The Molière approximation²⁷ has been used rather widely instead, since it is free of this particular failing. Recent experimental investigations of the energy losses of ions transmitted through the planar channels of thin gold, silver, and silicon crystals²⁸ have been used to deduce potential parameters²⁹ in the separation region near 1 Å. For the pairs He–Au, O–Au, I–Au, I–Ag, and H–Si, the potentials deduced are somewhat softer than the Molière or Thomas–Fermi potentials, but not drastically so. Thus the use of Eq. 18 to describe the atomic scattering is probably in reasonable agreement with reality. In some applications the estimates obtained using the more approximate Eq. 11 will be useful. With the behavior of Eq. 19 as a guide, it should be expected that $\ell = 1$ (Rutherford scattering) is a good approximation at high energies; that $\ell = 2$ is a reasonable overall choice; and that $\ell = 3$ is a good low-energy selection. At the lowest energies, however, where the Thomas–Fermi approach is inadequate, even larger values of ℓ are proper.²⁵

The direct experimental determination of interatomic potentials from scattering experiments is possible, and it was for this that Firsov originally developed his inversion procedure.²⁰ Unfortunately in practice the potentials are not especially well defined, principally because of experimental uncertainties associated with the small-angle scattering region.²¹ There are also significant problems associated with charge-changing and other inelastic collisions, which cloud the connection of the experimental scattering data with phenomena such as radiation damage.

Fig. 2 The screening function deduced from Lindhard's differential atomic scattering cross section at various energies is compared with the Thomas-Fermi, Molière, and Bohr screening functions.

ELECTRONIC STOPPING CROSS SECTIONS

Although the penetration of energetic particles through matter has been studied by nuclear physicists since the early 20th century, until recently almost all theoretical and experimental work was concerned primarily with light ions (protons and alpha particles) at high energies, i.e., at energies where the electronic stopping cross section is already a decreasing function of the projectile velocity. The theory of the electronic energy loss under these conditions has been reviewed by Fano.³⁰ In the last dozen years, however, experimental observations have been extended to many heavier ions and to much lower velocities, often much less than those at which the electronic stopping cross sections have their maxima. This low-velocity region is the one of principal interest in neutron-radiation-damage theory. A general review has been given by Northcliffe.³¹ Unfortunately, because of the very complicated nature of the problem, theoretical analysis has lagged seriously and no really satisfactory theory of low-energy electronic stopping yet exists.

Lindhard³² has studied the energy loss of a charged particle moving through a uniform electron gas, using his well-known dielectric-constant formalism, and finds that at low enough energy the stopping cross section is proportional to the velocity of the particle. The application of this result to the inelastic interaction of neutral Thomas-Fermi atoms led to the widely used electronic stopping theory of Lindhard et al.^{2,4,6,33} According to this theory the stopping cross section is given by

$$S_{e,L} = 8\pi e^2 a_0 \xi_e (Z_1 Z_2 / Z) \cdot v/v_0 \quad 0 < v < v_0 Z_1^{3/2} \quad (20)$$

where $v_0 = \alpha c$

α = fine-structure constant

c = velocity of light

v = velocity of the projectile

and

$$Z^{3/2} = Z_1^{3/2} + Z_2^{3/2} \quad (21)$$

The factor ξ_e is said to be approximately $Z_1^{1/6}$. Introducing numerical values for the various constants,

$$S_{e,L} (\text{eV} - \text{\AA}^2) = 1.216 (Z_1^{3/2} Z_2 / Z) [E(\text{eV}) / A_1 (\text{amu})]^{1/2} \quad (22)$$

$$0 < E(\text{keV}) < 24.8 Z_1^{3/2} A_1 (\text{amu})$$

where A_1 is the mass of the projectile.

An alternative theory has been proposed by Firsov³⁴ and elaborated by others.³⁵ This theory is based on the idea that the inelastic energy loss in a single collision between two atoms may be identified with the momentum possessed by the electrons of the projectile by virtue of their motion in the laboratory system. The collision time is regarded as sufficiently long that the electrons of the two colliding systems are completely mixed and the inelastic energy loss is calculated from the momentum transfer in this mixing process. In the original description of the theory,³⁴ the impulse approximation was used to describe the motion of the atoms. Consequently the energy lost was found to be proportional to the velocity of the projectile. An approximate Thomas-Fermi treatment of the electron distributions in the colliding atoms was used to obtain numerical results. The stopping cross section is given by

$$S_{e,F} = 7.51(3\pi^2 \hbar a_0 / 32)(Z_1 + Z_2)v \quad (23)$$

where the numerical coefficient derives from an approximate numerical integration performed by Firsov.³⁴ No statement has been made about the range of velocity for which Eq. 23 is applicable, but it should be similar to that for Eq. 20. When numerical values are inserted, Eq. 23 yields

$$S_{e,F}(\text{eV} - \text{\AA}^2) = 0.3362(Z_1 + Z_2)[E(\text{eV})/A_1(\text{amu})]^{1/2} \quad (24)$$

Both theories are highly approximate. The predicted velocity dependence cannot be expected to be accurate over more than a limited energy range. In both theories less stringent approximation would lead to a more complex dependence of S_e on velocity, but very little work has been done on this problem. Nor have any attempts been made to study the dependence of the stopping cross section on the ionic charge of the projectile. Recently the Firsov theory has enjoyed a considerable vogue since it allows the calculation of an inelastic energy loss that depends on the impact parameter in a single collision. The Lindhard theory, at least in its published form, does not permit this. The situation is further complicated by the observation that the electronic stopping power at constant velocity is an oscillatory function of Z_1 . The experimental observations have been summarized by Cheshire and Poate,³⁶ who present an interpretation in terms of the Firsov theory. These oscillations become less pronounced as the velocities of the ions are increased. The amount of information available is such, however, that their possible influence on radiation damage cannot yet be estimated.

In spite of their approximate nature, both theories are in tolerable accord with observations. Northcliffe and Schilling³⁷ have developed a semiempirical correlation procedure that permits the estimation of the electronic stopping cross section for any nonrelativistic ion in any medium. Their scheme employed almost all of the available experimental data. In Figs. 3 and 4 some predictions

Fig. 3 The electronic stopping power of ^{79}Br and ^{127}I ions in gold.

Fig. 4 The electronic stopping power of ^{12}C ions in carbon and of ^{90}Zr ions in zirconium.

of the Lindhard and Firsov theories are compared with those of the Northcliffe and Schilling correlation. Experimental data are also shown for ^{79}Br and ^{127}I ions in gold³⁸ and for ^{12}C ions in carbon.³⁹ The quantity plotted is the stopping power,

$$(-dE/\rho dx)_e = N_0 S_e/A_2 \quad (25)$$

where N_0 is Avogadro's number, A_2 is the mass of the target atoms, and ρ is the mass density of the target. Note that the term stopping power is also used for

$$(-dE/dx)_e = nS_e \quad (26)$$

where n is the atomic density of the target. In no instance shown in Figs. 3 and 4 is the energy dependence predicted by the two theories exactly correct. Northcliffe and Schilling³⁷ have already emphasized the inadequacy of the Z_1 dependence of the stopping power predicted by the Lindhard theory. The Firsov theory seems to be somewhat more satisfactory in this respect. However, the quantity ξ_e in Lindhard's theory, Eq. 20, is defined only vaguely, and its redefinition could substantially alter the Z_1 dependence. For instance, if $\xi_e = Z_1^{1/2}$ were replaced by $\xi_e = 1.564$, the Lindhard and Firsov theories would agree as long as $Z_1 = Z_2$. Such an alteration is consistent with the spirit of both theories.

In many applications of the electronic stopping theories outlined above, it is convenient to have them in the form

$$(-d\epsilon/du)_e = k\epsilon^{1/2} \quad (27)$$

where ϵ is the reduced energy defined in Eq. 17, u is the dimensionless distance x/R_L , and

$$R_L = (1 + A)^2 / 4\pi n A a^2 \quad (28)$$

is a unit of distance used by Lindhard.³ The constant k appearing in Eq. 27 is given by

$$k = nR_L(E_L E)^{-1/2} S_e \quad (29)$$

In the remainder of this article, only the case $Z_1 = Z_2$ will be of interest. In this case, Eq. 29 reduces to

$$\begin{aligned} k_L &= 0.1337 Z_1^{1/2} (Z_1/A_1)^{1/2} \\ k_F &= 0.2092 (Z_1/A_1)^{1/2} \end{aligned} \quad (30)$$

for the Lindhard and Firsov theories, respectively. However, over the entire periodic table (omitting hydrogen), $(Z_1/A_1)^{1/2}$ averages 0.655 ± 0.026 , so that the even simpler definitions

$$k_L = 0.0876 Z_1^{1/2}$$

and

(31)

$$k_F = 0.137$$

are quite accurate enough. Note that $k_L > k_F$ for $Z_1 \geq 15$ (P) and $k_L < k_F$ for $Z_1 \leq 14$ (Si).

THE ENERGY LOST FROM DISPLACEMENT CASCADES BY ELECTRON EXCITATION

Many years ago Seitz⁴⁰ introduced the idea of an ionization limit E_I , below which energy losses by electron excitation may be neglected and above which they come rapidly to dominate over energy losses by elastic collisions. He also provided estimates of E_I in insulators. Kinchin and Pease⁴¹ adopted the same model and provided estimates of E_I in metals. Dienes and Vineyard⁴² noticed that these estimates were roughly equivalent to setting E_I (keV) equal to A_1 (amu), a result that has now passed into the folklore of the subject. In this approximation the energy deposited in the target in the form of atomic motion by a recoil of energy E is

$$E_D = \begin{cases} E & 0 < E < E_{I,DV}(\text{keV}) = A_1(\text{amu}) \\ E_{I,DV} & E_{I,DV} < E \end{cases} \quad (32)$$

This model has been used widely in calculations of the effects of reactor neutron energy spectra on radiation damage.⁴³⁻⁴⁷ The model of Snyder and Neufeld⁴⁸ is essentially similar, but, following Bohr,¹ they choose E_I as the energy at which the recoil velocity reaches v_0 :

$$E_{I,SN}(\text{keV}) = 24.8 A_1(\text{amu}) \quad (33)$$

These limits are so high that energy losses by electron excitation could be neglected in neutron damage, except in light elements.

The calculation of E_D has also been treated by Lindhard et al.⁵ In this work the differential atomic scattering cross section of Eqs. 18 and 19 and the electronic stopping cross section of Eq. 27 were used. The result may be represented by

$$E_D = E/[1 + kg(\epsilon)] \quad (34)$$

where ϵ and k are defined by Eqs. 17 and 29, respectively, and the function $g(\epsilon)$, evaluated numerically and presented graphically by Lindhard et al.,⁵ is accurately represented by^{4,9}

$$g(\epsilon) = 3.4008 \epsilon^{1/6} + 0.40244 \epsilon^{3/4} + \epsilon \quad (35)$$

Figure 5 shows the damage efficiency, E_D/E , as a function of primary recoil energy for several elements. The curves were calculated from Eq. 34 using the Lindhard electronic stopping constant k_L , Eq. 30. The Firsov constant k_F would give slightly different results, but the accuracy of the theory does not warrant choosing between them. In addition, Fig. 5 shows the model of Thompson and Wright for graphite.^{5,0} This is based on Lindhard's electronic stopping theory, but the electronic losses are restricted to the primary recoil. The figure also shows the loci of the "traditional" ionization limits, $E_{I,DV}$, and of the Snyder-Neufeld values, $E_{I,SN}$. Evidently, neither the traditional nor the Snyder-Neufeld model is particularly accurate in its treatment of electronic losses. The Lindhard model probably overestimates these losses, at least at the lower energies. Improvement must await advances in the theory of electronic stopping cross sections or the acquisition of many more experimental data on them, particularly at very low energies.

The Lindhard theory of the partition of recoil energy between electronic excitation and atomic motion can be tested experimentally by using it to account for the so-called pulse-height defect in semiconductor particle detectors. This defect results from the fact that the part of the energy of an incident ion which is expended in "atomic" collisions does not appear as hole-electron pairs which can be detected electrically; i.e., the pulse-height defect corresponds to the energy E_D in Eq. 34. The correctness of this interpretation of the pulse-height defect has been verified by channeling experiments.^{5,1} Haines and Whitehead^{5,2} applied Lindhard's electronic stopping theory and scattering cross sections⁴ to the calculation of the pulse-height defect for several ions in silicon and germanium detectors, but they restricted the electronic losses to the incident particle. Forcinal, Siffert, and Coche^{5,3} used the energy-partition theory⁵ to calculate the defect for some ions in silicon, although it applies strictly only to the case $Z_1 = Z_2$. Although neither calculation is entirely satisfactory, both are in reasonable agreement with experiment. The uncertainties are too great to permit any choice between Lindhard's and Firsov's electronic stopping theories on the basis of pulse-height defect experiments.

THE THEORY OF THE DISPLACEMENT CASCADE

The calculation of the number of atoms displaced from their lattice sites as an energetic recoil slows down by elastic collisions will now be considered.

Fig. 5 The effect of electronic energy losses on the energy available for atomic displacements.

Seitz⁴⁰ introduced the important idea that a target atom is ejected permanently from its lattice site only if it receives a kinetic energy in excess of a sharp displacement threshold E_d , usually about 25 eV. In the model of Snyder and Neufeld⁴⁸ and the very similar one of Harrison and Seitz,^{54,55} if an energy T is transferred to a lattice atom, it commences to move with kinetic energy $(T - E_d)$ if this is positive. The recoils continue to produce displacements until their energies fall to E_d , the possibility of replacement collisions being ignored. In the model of Kinchin and Pease,^{41,56} the displacement threshold energy is not lost; a lattice atom commences moving with kinetic energy T if this exceeds E_d . Furthermore, replacement collisions are permitted; i.e., if the lattice atom receives energy $T > E_d$ and the incident particle retains $(E - T) < E_d$, the latter is deemed to replace the former on the lattice site. Thus, in this model, recoils produce no net new displacements after their energies fall below $2E_d$. In a later article,⁵⁷ Neufeld and Snyder have investigated the effect of including replacement collisions in their model. All these models^{41,48,54-57} assumed that the atomic scattering was isotropic in the center-of-mass system, i.e., the hard-core approximation was employed.

A very simple argument leads to an approximately correct evaluation of $\nu(E)$, the mean number of displacements produced by a recoil of initial energy E , according to each of these models. Let there be a binding energy B which is lost by each atom ejected from a lattice site, and let C be the energy at which multiplication of displacements ceases. Assume, consistent with the hard-core approximation, that the two particles in a collision share the original energy of the incident one equally in every collision. Then the number of displacements is

$$\nu(E) = \{E - [\nu(E) - 1] B\} / C \quad E > C \quad (36)$$

which may be rearranged into

$$\nu(E) = (E + B) / (C + B) \quad E > C \quad (37)$$

The numerator of Eq. 36 is just the initial energy of the primary recoil corrected for the binding energies of the additional displacements. The results for the various models are thus

Snyder-Neufeld^{48,54,55}

$$B = C = E_d \quad \text{and} \quad \nu(E) = (E + E_d) / 2E_d \quad E > E_d \quad (38)$$

Neufeld-Snyder⁵⁷

$$B = E_d, C = 2E_d \quad \text{and} \quad \nu(E) = (E + E_d) / 3E_d \quad E > 2E_d \quad (39)$$

Kinchin-Pease^{41,56}

$$B = 0, C = 2E_d \text{ and } \nu(E) = E/2E_d \quad E > 2E_d \quad (40)$$

In the first two cases, the results are approximate, being a few percent lower than more accurate solutions.^{48,57} Note that Eq. 38 differs little from Eq. 40: The inclusion of a binding energy and the omission of replacement collisions in the former are compensatory. Furthermore, in each of the three cases, the number of displacements is proportional to the energy of the primary recoil.

The effect on the calculated number of displacements of including atomic scattering cross sections that are more realistic than the hard-core approximation has been studied extensively.⁵⁸⁻⁶³ The integral equation that describes the dependence of $\nu(E)$ on the scattering law was introduced by Snyder and Neufeld.⁴⁸ The derivation of the appropriate form of the equation for various assumptions about the role of electron excitations and binding energy has been discussed at length by Lindhard et al.⁵ The derivation of the equation for a general displacement-probability function is given by Lehmann.⁵⁹ If the Kinchin and Pease model⁴¹ of the displacement process is used and only elastic collisions are considered, the integral equation may be solved for a restricted class of cross sections that includes the power laws of Eq. 11, using a Laplace-transform technique.^{60,61} This solution is outlined in Appendix B. It is convenient to define the displacement efficiency $\xi(E)$ so that

$$\nu(E) = \xi(E) \cdot (E/2E_d) \quad (41)$$

The hard-core-approximation result of Kinchin and Pease then corresponds to $\xi(E) = 1$. For the more realistic power cross sections of Eq. 11, an asymptotic expansion of the displacement efficiency is possible:

$$\xi(E) = \xi_0 + \sum_{k=1}^{\infty} \xi_k \cdot (2E_d/E)^{k+\kappa_k} \quad (42)$$

Expressions for the coefficients ξ_k and numerical tabulations of the ξ_k and the κ_k are given in Appendix B. A few values are displayed in Fig. 6. The dependence of $\xi(E)$ on the primary recoil energy is shown in Fig. 7 for selected values of the power-law index $n = 1 + 1/\ell$ (compare Eq. 11). It is clear from the rapid approach of $\xi(E)$ to its asymptotic value ξ_0 that, for energies greater than a few times E_d , the point depending on the value of n , the asymptotic value is a sufficiently accurate approximation. Thus it may be concluded that, except for energies close to the displacement threshold, the mean number of displacements is proportional to the energy of the primary recoil. Furthermore, as Sigmund has shown,⁶² this result will apply even when n changes slowly with energy. In this case the number of displacements is largely controlled by the scattering law prevailing in the energy region just above $2E_d$, whereas the spatial extent of a

Fig. 6 Parameters of the asymptotic expansion of the displacement efficiency for inverse-power differential atomic scattering cross sections. The coefficient ξ_0 is the asymptotic limit of the function $\xi(E)$.

nascent cascade will be determined principally by the scattering law prevailing near the primary recoil energy.^{2,5}

The calculations described here have assumed a sharp displacement threshold. Other forms of threshold have been investigated.^{5,7,59,64-67} In each case, there was an energy above which displacement was certain. Except near and below this energy, each calculation showed $\nu(E)$ to be linear in E , the numerical coefficient depending on the exact threshold model employed and on the investigator's choices with respect to binding energies and replacement collisions. Although no calculations have been performed in which complex thresholds and realistic scattering were combined, it seems entirely safe to say that even in such cases $\nu(E)$ would remain linear in E except in and near the threshold region.

In addition to the mean number of defects in the nascent cascade, it is possible to calculate higher moments and to study the possible importance of fluctuations. It has been shown that, as long as $\nu(E)$ is proportional to E , the

Fig. 7 The dependence of the displacement efficiency on the primary recoil energy for inverse-power differential atomic scattering cross sections.

fluctuations of $\nu(E)$ in structureless media are small and may be neglected.^{59,60,68} When the effects of channeling are included in an approximate manner, however, not only is $\nu(E)$ no longer proportional to the recoil energy,^{60,69,70} but its fluctuations may be large^{60,70} as well.

THE EFFECTS OF TARGET CRYSTALLINITY

The calculations described thus far have made the important assumption that the target media were structureless. Silsbee⁷¹ first pointed out that the distribution of energy and momentum among the atoms in a sequence of collisions might be influenced by the ordered arrangement of crystalline materials. Two types of crystal effects have been proposed. In focusing,⁷¹⁻⁷⁴ energy is transported, with or without the simultaneous transport of mass, along comparatively close-packed rows of atoms by a sequence of central collisions in which each projectile in turn passes on nearly all its kinetic energy to the next atom in the row. Focusing is a low-energy phenomenon that can occur only below a limiting energy of about 100 eV. Since this limit is considerably higher than typical displacement thresholds, an appreciable probability of focusing could substantially reduce the number of displacements in the nascent cascade and, at the same time, increase its volume because of the effects of long-range

transport of mass. Although focusing has been proposed⁷¹⁻⁷⁴ to account for the angular distribution of matter ejected from crystals during ion bombardment, the so-called sputtering ejection patterns, alternative theories,⁷⁵ and conflicting interpretations of the experimental data^{76,77} have been offered. Indeed, it must be said that there is presently no direct, unequivocal demonstration of the reality of focusing collision sequences in nature. In channeling,⁷⁸⁻⁸³ on the other hand, the motion of an energetic recoil is governed by a correlated sequence of glancing collisions with target atoms lying in closely packed rows or planes. The projectile is constrained to move in the channel bordered by these rows or planes and may travel very large distances, producing very few additional displacements as it slows down primarily by electron excitation. The original predictions of this effect⁷⁸ were quickly verified,^{79,80} and it is now the subject of a great many experimental and theoretical investigations, as well as being a tool of some importance in studying defects in crystals. In contrast to focusing, channeling is a high-energy phenomenon. It could also lead to a considerable reduction in the number of defects in the nascent cascade if it were of appreciable likelihood. The reduction in damage has been directly observed when the primary recoil (in these cases ions in an external beam) is channeled. Noggle et al.⁸⁴ have reported striking decreases in the black-spot damage produced in gold crystals by well-channeled iodine ions, and related observations have been made for other combinations of ion and target.⁸⁵⁻⁸⁹

The effect of channeling on the number of defects in the nascent cascade can be estimated on a simple model in which every particle in the cascade has the probability p of becoming channeled and of making no further displacements.^{60,69} Using the Kinchin and Pease displacement model and the hard-core scattering cross section, it is found that

$$\nu(E) = [(1 - p)(E/2E_d)^{1-2p} - p] / (1 - 2p) \quad E > 2E_d \quad (43)$$

This equation could be used with some data on the effect of neutron energy on radiation damage in copper⁹⁰ to estimate a channeling probability of about 0.07, rather larger than the value of about 0.01 which was deduced from machine calculations.⁷⁸ A smaller channeling probability can be deduced if a nonhard-core scattering cross section is used,⁷⁰ but the model is probably too simple to be reliable. Large-scale machine calculations^{91,92} have been used to examine the importance of channeling (and focusing) in deducing the number of defects produced in the nascent cascade. No important effect has been found when the recoil atoms are emitted from normal lattice sites.

Both channeling and focusing are reduced in effectiveness by any disruption of the crystalline order of the target material, including thermal vibrations, point defects, dislocations, grain boundaries, and the like. Furthermore, the disorder introduced by the irradiation itself will also interfere with these crystal effects. The importance of disordering during ion bombardment is well known in the

doping of semiconductors by ion implantation.⁹³ Hence, if either channeling or focusing were to be responsible for a significant decrease in the number of displacements in nascent cascades produced during neutron irradiation, it would be anticipated that prolonged irradiations would show an increase in the damage rate owing to the reduction of crystal effects. Experimental studies of the effects of neutron dose on low-temperature radiation damage in several metals^{94,95} have shown only a steady decrease in the damage rate with increasing dose, as would be expected from saturation effects due to the overlapping of successive cascades.⁹⁶ It seems unlikely, therefore, that either channeling or focusing plays a very important role in neutron-irradiation damage, especially in the dose range of interest in reactor applications.

THE SPATIAL EXTENT OF A NASCENT CASCADE

The number of defects in a nascent cascade which survive to alter the physical properties of the irradiated substance depends not only on the number originally produced but also on their spatial distribution, as well as on such macroscopic variables as time, temperature, and stress. A substantial fraction of the original interstitials will find themselves so close to vacancies as to be mechanically unstable, whereas many others will need to make only a very few jumps to reach a vacancy and annihilate. If the density of defects in a cascade depends on the energy of the primary recoil, a proper assessment of the energy dependence of radiation damage will require some discussion of the spatial structure of the nascent cascade, for it would be expected that less annihilation would occur in a large, low-density cascade than in a small dense one.

An early approach to this problem was to study the range of the primary recoils as a measure of the dimensions of a cascade⁹⁷ since it is accessible to direct observation. A number of analytical^{4,97-100} and computer¹⁰¹ studies of range distributions have been made. Reasonable agreement has been achieved between the calculations and experimental observations of low-energy ranges. The distribution of defects in nascent cascades has also been studied, both analytically¹⁰²⁻¹⁰⁶ and by machine methods,^{91,92,107-109} in most cases excluding inelastic energy losses. Recent analytical calculations^{25,110} have been concerned with the spatial distribution of the energy deposited in the target in the form of atomic motion, i.e., with the damage energy E_D of Eqs. 32 to 34. Since the number of defects initially produced is proportional to this energy under many different assumptions about displacement thresholds and scattering laws, its study avoids the complications concerned only with the threshold region and yet retains a reasonably accurate measure of the amount of damage produced by the primary. Winterbon, Sigmund, and Sanders²⁵ have made a careful study of the spatial distribution of the damage energy, using the Lindhard power cross section, Eq. 11, to describe the elastic scattering and excluding inelastic losses. With these assumptions the energy dependence of a moment of the damage

energy distribution is the same as that of the corresponding moment of the range distribution; i.e., the shape of the displacement cascade is independent of energy. Since (in this approximation) the mean dimensions of the cascade vary as $E^{2/\ell}$ (compare Eq. 10), its volume will vary as $E^{6/\ell}$ and the mean density of defects will vary as $E^{1-6/\ell}$. Thus, since ℓ can be taken as about 3, the density of defects will decrease with increasing energy, at least as long as inelastic losses can be ignored.

When inelastic-energy losses are included, as they must be at high energies, the picture changes somewhat. The displacement cascade will be extended along the trajectory of the primary recoil, whose range will still be a measure of this dimension of the cascade. The transverse dimensions of the cascade, however, will increase much less rapidly, since a decreasing fraction of the primary energy is carried by secondary recoils. The stopping of the primary recoil, dominated by electronic losses, varies as $E^{1/2}$, so that its range varies similarly. Ignoring the slow variation of the transverse dimensions, the cascade volume will vary also as $E^{1/2}$, or perhaps a little faster. Thus the mean density of defects in the cascade may be nearly independent of energy since their number certainly increases less rapidly than E . It seems reasonable, therefore, to suggest that the fraction of defects in the nascent cascade which survive to influence macroscopic properties will increase with increasing primary recoil energy in the range where inelastic energy losses can be ignored but will become nearly constant when the inelastic losses become important. An improvement in the simple picture sketched here requires additional theoretical analysis of the spatial distribution of defects in the cascade. In particular, it would be useful to have studies of the pair correlation functions giving the probability of finding point defects adjacent to one another. From these, something could be learned about (mechanical) annihilation and clustering in the nascent cascade. A beginning has been made in this direction by Westmoreland and Sigmund,¹¹¹ who have studied the correlation between the range of an incident ion and the damage energy deposited in the target by that ion.

SUMMARY OF THE ANALYTICAL MODEL OF RADIATION DAMAGE

Before closing this review with a few remarks about applications to neutron damage, it is useful to summarize the current analytical model of radiation damage as it has been outlined above. The energy of the primary recoil is partly dissipated in electron excitation at all energies, the fraction increasing as the recoil energy increases. The Lindhard and Firsov electronic stopping theories both account for the inelastic losses from the cascade, but much additional theoretical work is needed in this area. The mean number of defects created in the nascent cascade is proportional to the energy deposited as atomic motion of cascade particles. The variance of the number of defects is small. It is expected that the fraction of defects in the nascent cascade which survive to alter the

macroscopic properties of the material will decrease until electronic losses become important and will then change little with increasing energy. Several features of the analytical theory have been verified in recent machine calculations,⁹² thus suggesting that crystal effects are not of overriding importance in the development of nascent cascades. The most fruitful area for future research would seem to be that concerning defect-particle correlation functions because of their importance in the theory of defect annihilation and clustering.

The application of the analytical theory to practical neutron-damage problems is straightforward. An accurate description of the nuclear reactions responsible for producing the primary recoils is important. In fission-reactor applications, inclusion of the proper anisotropic angular distributions of elastically scattered neutrons is necessary. For the highest energy fission neutrons and for neutrons from fusion reactors, the contributions of inelastically scattered neutrons and of $(n,2n)$ and other complex reactions must be considered also. Machine programs^{112,113} are available to carry out such calculations, using the Lindhard energy-partition theory and neutron cross sections and other nuclear data from such sources as the ENDF/B files.¹¹⁴ The Lindhard theory has been applied to neutron damage in silicon and germanium¹¹⁵ and in zirconium,¹¹⁶ to predictions for fusion reactors,⁴⁹ and to swelling in stainless steel.¹¹⁷ Until improvements in the theory are available, particularly in the theory of inelastic energy losses, this approach seems to be the best available.

APPENDIX A: THE ACCURATE INTERATOMIC POTENTIAL CORRESPONDING TO LINDHARD'S DIFFERENTIAL ATOMIC SCATTERING CROSS SECTION

The procedure used to deduce the accurate interatomic potential corresponding to Lindhard's differential atomic scattering cross section³ parallels that used previously for the inverse-power scattering laws.¹⁹ Using Eqs. 18 and 19 of the main text for the differential cross section, the impact parameter is given by

$$(p/a)^2 = \beta \int_{\alpha x}^{\alpha} du [u(1 + u^{\frac{2}{3}})]^{-\frac{3}{2}} \equiv G(x) \quad (\text{A.1})$$

where

$$\alpha = 2\lambda\epsilon^{\frac{1}{3}} \quad (\text{A.2})$$

$$\beta = 3\lambda^{\frac{2}{3}}/2\sqrt{2} \quad (\text{A.3})$$

$$x = \sin^{\frac{1}{3}} \theta/2 \quad (\text{A.4})$$

Since

$$G(x) = G(x+h) + \beta \int_{\alpha x}^{\alpha(x+h)} du [u(1+u^{\frac{2}{3}})]^{-\frac{3}{2}} \quad (\text{A.5})$$

the impact parameters could be tabulated as a function of θ , starting at $\theta = \pi$, using 16-point Gauss-Legendre quadrature to evaluate the integral in Eq. A.5. The table was linear in $\ln \theta$. The inversion procedure required evaluation of

$$\pi F(\psi) = \int_{\psi}^{\infty} \theta(p) (p^2 - \psi^2)^{-\frac{1}{2}} dp \quad (\text{A.6})$$

which was accomplished by 96-point Gauss-Legendre quadrature. The required values $\theta(p)$ were found by 5-point Lagrangian interpolation in the previously constructed table. Then

$$r(\phi) = \psi \exp[F(\psi)] \quad (\text{A.7})$$

and the screening function is

$$\phi(r) = \epsilon(r - \psi^2/r) \quad (\text{A.8})$$

Some results of these calculations are shown in Fig. 2 of the main text.

APPENDIX B: THE NUMBER OF DISPLACEMENTS PRODUCED IN INVERSE-POWER SCATTERING

Consider a primary recoil atom of initial energy E slowing down entirely by elastic collisions in an infinite, isotropic, homogeneous medium composed of atoms of the same kind. The mean number of displacements produced, $\nu(E)$, is described by the integral equation⁵

$$\int_0^E K(E,T) [\nu(T) + \nu(E-T) - \nu(E)] dT = 0 \quad (\text{B.1})$$

where $K(E,T)dT$ is proportional to the differential cross section for the transfer of energy T in a single collision. Since energy is conserved in each collision, the function

$$f(T,E) = \frac{1}{2} E [K(E,T) + K(E,E-T)] \quad (\text{B.2})$$

may be introduced and Eq. B.1 rewritten as

$$\int_0^{E/2} f(T,E) \nu(T) d(T/E) + \int_{E/2}^E f(T,E) [\nu(T) - \nu(E)] d(T/E) = 0 \quad (\text{B.3})$$

Note that arbitrary functions of E can be used as necessary in manipulating Eq. B.3. The model of Kinchin and Pease^{4,1} will be adopted for the displacement process

$$\nu(E) = \begin{cases} 0 & 0 < E < E_d \\ 1 & E_d < E < 2E_d \end{cases} \quad (\text{B.4})$$

With the further restriction that $f(T, E)$ be a function of T/E alone, Eq. B.3 is then readily solved by a Laplace-transform technique.^{6,0-6,3} The result may be written as^{6,1}

$$\bar{\nu}(s) = [1 + 2\bar{h}(s)/\bar{G}(s)]/s \quad (\text{B.5})$$

where s is the transform variable

$$\bar{\nu}(s) = \int_0^\infty e^{-su} \nu(u) du \quad (\text{B.6})$$

$$\bar{h}(s) = 2s \int_{\ln 2}^\infty e^{-su} g(u) du \quad (\text{B.7})$$

$$\bar{G}(s) = 2 \left[\int_0^{\ln 2} (1 - e^{-su}) g(u) du - \int_{\ln 2}^\infty e^{-su} g(u) du \right] \quad (\text{B.8})$$

$$g(u) = e^{-su} f(u) \quad (\text{B.9})$$

$$u = \ln E/2E_d \quad (\text{B.10})$$

The Laplace transform of the displacement efficiency, defined by Eq. 41 of the main text, may be written as

$$\bar{\xi}(s) = \bar{\nu}(s+1) = [1 + 2\bar{h}(s+1)/\bar{G}(s+1)]/(s+1) \quad (\text{B.11})$$

For the specific case of inverse-power scattering, Eq. 11

$$K(E, T) \propto E^{n-1}/T^n \quad 0 \leq n < 2 \quad (\text{B.12})$$

where $n = 1 + 1/\ell$. The integrals in B.8 and B.7 may be written as

$$\bar{G}(s) = \begin{cases} \frac{s[1 - \Gamma(2-n)\Gamma(s)/\Gamma(s+1-n)]}{(1-n)(s+1-n)} & 0 \leq n < 2, n \neq 1 \\ \gamma + \psi(s) & n = 1 \end{cases} \quad (\text{B.13})$$

$$n = 1 \quad (\text{B.14})$$

TABLE B.1
ASYMPTOTIC EXPANSION OF THE DISPLACEMENT EFFICIENCY
FOR INVERSE-POWER SCATTERING LAWS

$$\xi(E/2E_d) = \xi_0 + \sum_{k=1}^{\infty} \xi_k \cdot (2E_d/E)^{k+\kappa_k}$$

n	The Coefficients (ξ_k)						
	ξ_0	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5	ξ_6
0.0	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0.1	0.99446	0.00027	0.00152	0.00111	0.00074	0.00049	0.00033
0.2	0.98735	0.00118	0.00333	0.00237	0.00157	0.00104	0.00071
0.3	0.97848	0.00292	0.00547	0.00379	0.00249	0.00166	0.00113
0.4	0.96762	0.00572	0.00797	0.00537	0.00350	0.00233	0.00160
0.5	0.95451	0.00985	0.01088	0.00713	0.00460	0.00305	0.00209
0.6	0.93884	0.01565	0.01425	0.00907	0.00579	0.00381	0.00260
0.7	0.92028	0.02353	0.01812	0.01119	0.00705	0.00461	0.00314
0.8	0.89841	0.03400	0.02253	0.01349	0.00838	0.00543	0.00367
0.9	0.87276	0.04771	0.02752	0.01596	0.00975	0.00625	0.00419
1.0	0.84277	0.06546	0.03309	0.01855	0.01113	0.00704	0.00467
1.1	0.80775	0.08831	0.03922	0.02121	0.01245	0.00776	0.00509
1.2	0.76690	0.11761	0.04583	0.02383	0.01366	0.00836	0.00540
1.3	0.71917	0.15514	0.05271	0.02624	0.01461	0.00874	0.00554
1.4	0.66329	0.20326	0.05946	0.02817	0.01516	0.00883	0.00547
1.5	0.59758	0.26516	0.06537	0.02922	0.01510	0.00849	0.00511
1.6	0.51983	0.34518	0.06915	0.02883	0.01416	0.00763	0.00442
1.7	0.42697	0.44924	0.06863	0.02625	0.01209	0.00617	0.00340
1.8	0.31457	0.58541	0.06036	0.02071	0.00880	0.00418	0.00216
1.9	0.17591	0.76440	0.03936	0.01175	0.00449	0.00194	0.00091
2.0	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000

$$2\bar{h}(s) = \begin{cases} \frac{s[2^s(s+1-n)B_{\frac{1}{2}}(s, 2-n) - 2^{n-1}]}{(1-n)(s+1-n)} & 0 \leq n < 2, n \neq 1 \quad (\text{B.15}) \\ \frac{1}{s} + 2^s B_{\frac{1}{2}}(s+1, 0) & n = 1 \quad (\text{B.16}) \end{cases}$$

where $\psi(s)$ is the digamma function, γ is Euler's constant, and $B_x(y, z)$ is the incomplete beta function. As has been pointed out by Sigmund,^{6,2} the transform B.5 has a series of poles at $s = 1$ and at the points $s_k < 0$, representing the zeros of the bracketed expression in Eq. B.13 or, respectively, those of Eq. B.14. It is then possible to write an asymptotic expansion of the displacement efficiency in the form

TABLE B.2
ASYMPTOTIC EXPANSION OF THE DISPLACEMENT EFFICIENCY
FOR INVERSE-POWER SCATTERING LAWS

$$\xi(E/2E_d) = \xi_0 + \sum_{k=1}^{\infty} \xi_k \cdot (2E_d/E)^{k+\kappa_k}$$

n	The Powers (κ_k)					
	κ_1	κ_2	κ_3	κ_4	κ_5	κ_6
0.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.1	0.9512	0.9663	0.9740	0.9786	0.9818	0.9841
0.2	0.9044	0.9320	0.9460	0.9547	0.9607	0.9652
0.3	0.8594	0.8970	0.9162	0.9284	0.9369	0.9432
0.4	0.8157	0.8613	0.8848	0.8998	0.9104	0.9184
0.5	0.7731	0.8249	0.8518	0.8691	0.8814	0.8907
0.6	0.7313	0.7878	0.8172	0.8361	0.8498	0.8602
0.7	0.6901	0.7497	0.7808	0.8010	0.8156	0.8268
0.8	0.6492	0.7106	0.7427	0.7636	0.7787	0.7904
0.9	0.6084	0.6703	0.7026	0.7237	0.7390	0.7508
1.0	0.5674	0.6285	0.6604	0.6812	0.6963	0.7079
1.1	0.5257	0.5848	0.6156	0.6357	0.6501	0.6613
1.2	0.4831	0.5391	0.5680	0.5867	0.6003	0.6107
1.3	0.4391	0.4906	0.5170	0.5340	0.5461	0.5555
1.4	0.3930	0.4389	0.4620	0.4767	0.4872	0.4951
1.5	0.3441	0.3830	0.4022	0.4142	0.4226	0.4290
1.6	0.2913	0.3220	0.3367	0.3457	0.3519	0.3565
1.7	0.2330	0.2547	0.2645	0.2703	0.2743	0.2771
1.8	0.1672	0.1794	0.1846	0.1875	0.1894	0.1908
1.9	0.0910	0.0948	0.0963	0.0971	0.0976	0.0980
2.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

$$\xi(E) = \xi_0 + \sum_{k=1}^{\infty} \xi_k \cdot (2E_d/E)^{k+\kappa_k} \quad (\text{B.17})$$

where

$$\kappa_k = -s_k + 1 - k \quad (\text{B.18})$$

$$\xi_0 = \begin{cases} 2(1 - 2^{n-1})/[\gamma + \psi(2 - n)] & 0 \leq n < 2 \quad n \neq 1 \\ (12 \ln 2)/\pi^2 & n = 1 \end{cases} \quad (\text{B.19})$$

$$(\text{B.20})$$

$$\xi_k = \begin{cases} \frac{2^{s_k} [1 - (s_k + 1 - n)B_{\frac{1}{2}}(2 - n, s_k)] - 2^{n-1}}{s_k [\psi(s_k + 1 - n) - \psi(s_k)]} & 0 \leq n < 2 \quad n \neq 1 \quad (\text{B.21}) \\ \frac{[(1 - 2^{s_k})/s_k + 2^{s_k} \ln 2 + 2^s \psi_{\frac{1}{2}}(s_k + 1)]}{s_k \psi'(s_k)} & n = 1 \quad (\text{B.22}) \end{cases}$$

where $\psi'(s)$ is the trigamma function, and the incomplete digamma function is

$$\psi_x(y) = \int_0^x [1 - (1 - u)^y] du/u \quad (\text{B.23})$$

This integral and the incomplete beta function are readily evaluated by Gaussian quadrature methods.

The techniques sketched here were used to evaluate the κ_k and ξ_k for a series of values of n . The evaluations of the gamma, digamma, and trigamma functions were made with the well-known reflection and recurrence formulas to increase the arguments to a point where asymptotic expansions could be used. The incomplete beta and digamma functions were evaluated by 96-point Gauss-Legendre quadratures. The zeros of Eqs. B.13 and B.14 were located by Newton's method. Some of the results of these calculations are plotted in Fig. 6 and shown in Tables B.1 and B.2. The series B.17 converges rather slowly for low energies, twenty terms yielding only about $2^{1/2}$ -digit accuracy at $E = 2E_d$. The convergence improves very rapidly, however, as E increases above $2E_d$.

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DISCUSSION BY ATTENDEES

Wilson: You seem to have used the Firsov-Lindhard theory in your graph, but do not those two authors admit that the theory is good only to 500 keV?

Robinson: Lindhard claims his theory is good to $V_0 Z_1^{2/3}$. For bromine or iodine on gold, for instance, one gets ~200 MeV.

Kulcinski: Will you comment on Lindhard's treatment of range straggling as it pertains to uncertainty in electronic and nuclear stopping power?

Robinson: Lindhard's treatment of range straggling applies primarily to the total path length covered by a projectile, rather than to its penetration, but I do not believe that straggling effects are of significance with respect to *measured* electronic stopping powers. Uncertainties in the *theoretical* values are due to imperfections in the models used.

Wechsler: It is consistently observed, especially for neutron-radiation damage, that the theory overestimates the number of defects observed experimentally. You have rejected channeling or focusing as major reasons for

the reduced experimentally observed damage. In your opinion, then, to what other sources can we attribute the theoretical overestimate of the damage?

Robinson: I attribute this effect entirely to the recombination of close pairs due to mechanical instability and/or zero point-vibration effects.

Shewmon: You have not commented at all on what I feel is a basic question in void formation, namely, the number of vacancies and interstitials that escape from a cascade and thus can play a role in forming voids, dislocation loops, etc. What is the status of the theory on this question?

Robinson: It is, of course, clear that most of the point defects produced in a nascent cascade will annihilate. Only those few, perhaps less than 1%, which survive for appreciable times can participate in void formation. The number of those which do survive and their histories are controlled by many-body processes that are very difficult to deal with in any accurate or realistic manner. For instance, the nature of the interstitial in fcc metals is still highly controversial. A realistic approach to these problems must include consideration of the influence of defects on the effective interaction potential between atoms—this may be altered by electron rearrangements, for instance. In my opinion, none of the many-body calculations performed so far has more than qualitative significance, whereas to neglect the many-body aspects is perhaps foolhardy. Much more research is certainly demanded in this area.

VOID FORMATION IN METALS DURING ION BOMBARDMENT

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ABSTRACT

The fact that fast-neutron damage in metals can be qualitatively simulated by irradiation with energetic ions from particle accelerators is well known. The technique will be briefly discussed, and the conditions necessary for obtaining quantitative design data will be reviewed. Results will be presented which point out the equivalence between the reactor and accelerator irradiations. Furthermore, a selection of results that illustrate the potential usefulness of the technique will be shown. For instance, the void swelling obtained as a function of dose for nickel, 316 stainless steel, and Nimonic PE16 will be compared to damage doses equivalent to well over 10^{23} neutrons/cm².

It is now generally accepted that radiation damage produced in metals during fast-neutron irradiation can be usefully simulated during irradiation with energetic ion beams from charged-particle accelerators; in particular, the study of void formation in fast reactor materials.^{1,2} Although it is relatively straightforward to produce qualitative data using beams of ions, the acquisition of quantitative results, which can be used as a guide to extrapolate reactor data, requires careful control of the experimental conditions.

In this paper we first discuss the requirements necessary for producing quantitative data that can be used together with the results from reactor irradiations to predict the behavior of structural and cladding materials during fast-neutron irradiation to high doses. Next we present a selection of results that illustrate the usefulness of the technique.

BASIC REQUIREMENTS

The basic requirement is to produce a region of uniform damage within a metal specimen while the specimen is maintained at an elevated temperature.

Furthermore, the irradiation dose must be sufficient to create a comparable number of atomic displacements within this damaged region to that produced in reactor components during fast-neutron irradiation. Also, the bombarding ion species chosen must be such that it does not produce adverse chemical or physical effects within the sample which might influence the formation of voids. An additional requirement is that the damaged region be sufficiently removed from the surface so that the results are representative of the bulk material.

Finally, trace quantities of helium must be introduced uniformly throughout the damaged region to simulate the helium that is produced within the material as a result of (n,α) reactions.

Helium Implantation

The presence of the helium produced in the reactor has led to speculation as to its possible influence on void formation. In an attempt to simulate the reactor condition, helium can conveniently be introduced uniformly throughout the samples by implanting them with He^+ ions prior to irradiation.³ In practice, it would be more realistic to introduce the helium during the damaging irradiation, but this introduces experimental difficulties. A compromise situation is to introduce helium and to carry out the damage irradiation alternatively in an attempt to build up the helium and damage concurrently.

Damage Density

On the assumption that it is the total number of displaced atoms which is important for the formation and growth of voids, a fundamental requirement for the comparison between accelerator and reactor irradiations is the normalization of results via the total number of displaced atoms. The theoretical considerations behind such a normalization have been discussed in detail previously.¹ However, it is appropriate to outline the features in this review.

The damage produced during accelerator irradiations has itself been normalized, through the voidage, to that produced by 4-MeV protons. In this case, owing to the accurately known Rutherford cross section and the fact that the average primary recoil energy is rather low, we can make reasonably accurate estimates of the total number of displaced atoms. The more difficult problem is in calculating the total number of displaced atoms produced during fast-neutron irradiation, where, because of the very high recoil energies, displaced atoms are created within complex collision cascades. The original treatment of Kinchin and Pease⁴ has paved the way for such calculations; however, some improvement is necessary. An attempt at such an improvement has been made,⁵ although it is still in the regime of an educated guess, and the use of typical fast reactor spectra gives numbers of displacements about half those calculated from the Kinchin and Pease model. More specifically, the damage produced by a total neutron flux of 4×10^{22} neutrons/(cm²)(sec) at the center of the Dounreay

Fast Reactor (DFR) is calculated at ~ 20 displacements/atom (dpa) against 32 dpa with the Kinchin and Pease model.

Choices of Ion Species and Energy

The choices of ion species and ion energy are interrelated, and to some extent conflicting requirements necessitate compromise.

Bombarding Ion

Ideally, we would like the particles, for example, high-energy protons, to pass right through the sample; however, because of their low scattering cross section, the time to accumulate sufficient damage is generally prohibitive. However, if we have no alternative but to stop the ions in the specimen, we must avoid using those gaseous ions which are insoluble in the specimen, particularly the inert gases and other gaseous elements that are thought to influence the nucleation of voids. Similarly, any other ion that is likely to cause precipitation within the sample during irradiation should be avoided.

The most obvious ion species would be "self-ions," i.e., in the case of a nickel specimen, Ni^+ ions. However, even then we must take care to consider the fate of the implanted ions since these essentially cause an imbalance between the total vacancy and interstitial content within the irradiated material. Theoretical considerations⁶ have shown that, in a typical situation where one extra interstitial is introduced for every 10^4 vacancy/interstitial pairs, provided the temperature is not so low that a very large fraction of migrating interstitials suffer mutual recombination and provided the irradiation-induced dislocation density is greater than about 10^{10} lines cm^{-2} , the addition of the extra interstitials can be neglected. If, on the other hand, at this same dislocation density, this extra interstitial corresponds to 10^2 vacancy/interstitial pairs, the total void volume can be significantly affected. But, if, as in steels, the dislocation density is greater than 10^{11} lines cm^{-2} , one extra interstitial in 10^2 produces no significant error.

Up until recently, the availability of self-ions compatible with structural steels and nickel-based alloys has been rather limited, and many data have been collected using such ions as carbon; carbon is already present to some extent in steels, and the addition of extra atoms is thought only to present problems at high doses. However, recent work using nickel and iron ions has, in general, borne out the results previously obtained using carbon.

Ion Energy

A general feature of neutron- and ion-irradiated metals is the existence of zones denuded of voids on either side of the grain boundary. Such zones are thought to be a direct consequence of the role of grain boundaries as a defect sink. Similar denudation effects are to be expected at free surfaces. Further-

Fig. 1 Calibration curve showing displacements as a function of depth treated by 20 MeV of C^{2+} ions after a programmed rocking of the target to produce uniform damage between about 5 and 7 μ .

more, free surfaces tend to modify the radiation-induced dislocation structures in their vicinity, especially during irradiation at elevated temperatures. Quantitative data must therefore be obtained from regions of the sample at least $\sim 0.5 \mu$ below the surface. Such a conclusion has also been made by experimenters using the high-voltage electron microscope to produce voids in thin foils wherein the effects of both surfaces must be included.⁷ In addition, to simulate more precisely the neutron case and to facilitate examination, experimenters find it desirable to produce a uniformly damaged region of about 1 to 2 μ beyond this 0.5- μ surface layer.

In a previous paper¹ the damage distribution in nickel resulting from irradiation with 20 MeV of C^{2+} ions from the Variable Electron Cyclotron (VEC) was shown to produce a rather sharp peak 0.5 μ wide at 6.8 μ below the surface. The actual number of atomic displacements within the peak was calibrated by reference to the Rutherford region close to the incident surface. Such a distribution is in line with the requirements outlined above. More recently, however, such a damage distribution has been used together with a programmed rocking of the target to produce a uniform damage zone over any required depth below the surface. Such rocking clearly imposes a time penalty, and a compromise was chosen which produced a uniform damage distribution from about 5 to 7 μ (Fig. 1). Similar distributions have been obtained using

Fig. 2 Transmission electron micrographs showing a comparison of voids between (a) DFR and (b) VEC irradiated nickel samples containing 10^{-5} atomic concentration of helium. Both samples were irradiated to the same calculated dose of 5 dpa.

48-MeV Ni^{6+} ions and 36-MeV Fe^{8+} ions. With such uniform damage distributions, it is a relatively simple matter to produce transmission electron microscope (TEM) specimens from the irradiated sample using a combination of vibratory polishing and electrochemical thinning, as previously described.¹

RESULTS

Comparison Between Reactor and Accelerator Irradiation

The acquisition of quantitative data depends on relating the total damage produced during ion bombardment to that produced during neutron irradiation. In other words, we must check to see that irradiations to the same calculated damage dose in the reactor and accelerator do in fact correspond. We must, of course, be careful to choose a system that will permit any dose-rate effects to be neglected or at least accounted for. In this context, it is possible to choose corresponding temperatures for nickel, which at the peak swelling temperatures show little or no effect of dose rate on the magnitude of the swelling, $\Delta V/V$. To eliminate the variability that might result from different helium concentrations, we decided to perform these check irradiations with nickel samples taken from the same parent material, each sample having been previously annealed to the same temperature and implanted uniformly with identical concentrations of helium (10^{-5} atom/atom). A selection of samples was then irradiated in either DFR or the VEC at corresponding temperatures to equal total damage doses as calculated from the latest damage models.⁵ Figure 2 shows two electron

micrographs of voids which illustrate the results of this experiment. In both cases, a computation of swelling from a knowledge of the void density, the void size, and the foil thickness gives answers that, within the expected experimental error, agree remarkably well. This result therefore gives us confidence both in the simulation technique and in the model for calculating damage.

As our understanding of void formation has grown, it has become increasingly evident that one of the most important parameters that influences void growth is the radiation-produced dislocation density. In relating the results of simulation experiments to those obtained from reactor irradiation, it is therefore essential to ensure that the dislocation structures are similar in nature and of comparable density. Owing to the limited reactor data, especially at high doses, it is not always possible to check this point. However, experiments on 316 stainless steel⁸ and the above-mentioned nickel experiment do, in fact, show good agreement. On the other hand, the results from low-energy ion irradiations, where the penetration depth is only a few thousand angstrom units, show a somewhat reduced dislocation density relative to either the reactor irradiations or the higher-energy VEC irradiations.

Effect of Helium and Other Gases

Once having established the equivalence of accelerator and reactor damage from the viewpoint of void formation, we can easily explore the influence of helium on the nucleation and growth of such voids. In this review it is not sensible to discuss all the experimental details, but we will simply outline the pertinent results.

In both nickel and 316 stainless steel, we can create voids irrespective of whether helium has been implanted or not. However, although the total swelling is only slightly affected by the addition of helium, the void density is influenced dramatically. For instance, in nickel the number of voids is increased by nearly an order of magnitude as a result of adding 10^{-5} atom/atom helium, whereas within the experimental uncertainty the total swelling is not significantly influenced.

In the 18/8/Ti stainless steel, the situation is somewhat different. With the addition of 10^{-5} atom/atom helium, the void density and total swelling are very similar to 316 stainless steel. However, with no helium the number of voids is dramatically reduced, and in most cases it is difficult to find even one void in a typical specimen area within the electron microscope.

The difference between these materials is thought to be a consequence of dissolved oxygen already present within the specimens because in 18/8/Ti stainless steel the oxygen is possibly bound up by the titanium additions where it is impotent as a gaseous nucleating agent. As a check on this hypothesis, when additional oxygen—well in excess of that normally present—is previously implanted into 18/8/Ti stainless steel, the void number and swelling are again similar to those of the helium-implanted steel. On the other hand, excess

nitrogen implanted into 18/8/Ti stainless steel apparently had no effect on the void density.

Fig. 3 Log swelling vs. log dose in nickel, 316 stainless steel and Nimonic PE16 at 525°C.

Dose Dependence of Swelling

The swelling produced in nickel, 316 stainless steel, and Nimonic PE16 foils—all containing 10^{-5} atom/atom helium—after irradiation with 20 MeV of C^{2+} ions from the VEC at 525°C is plotted as a function of dose in Fig. 3.

Nickel

Voids were first observed in nickel after about 0.1 dpa in a concentration of about 5×10^{14} voids/cm³. Up to 40 dpa the swelling was seen to rise

Fig. 4 Log void concentration vs. log dose in nickel and 316 stainless steel.

approximately linearly with dose to reach 6%. In this dose range the void concentration increased to about 3×10^{15} voids/cm³, although there was scatter among the experimental points. Above this dose the swelling rate decreased, as shown in Fig. 3, and at 350 dpa the swelling was about 15% rather than the 50% that would have resulted from an unchanged swelling rate. Above about 6% swelling, void overlap and coalescence occurred, and the overall void concentration decreased. At the highest dose studied, 350 dpa, regions of voids 2000 Å in diameter were found adjacent to voids about 700 Å in diameter; the swelling was, however, the same in both cases. The change in concentration accompanying this coalescence was omitted in the construction of Fig. 4, which shows the variation with dose of void concentration in nickel and 316 stainless steel.

316 Stainless Steel

Type 316 stainless steel exhibited marked differences in swelling behavior compared to nickel, as indicated in Figs. 3 and 4. No visible voids are present at doses below about 2 dpa. As the damage increases above this value, the swelling rises rapidly, and, up to about 40 dpa, the variation is approximately as (dose)². Above this dose, at which the swelling is about 5%, the swelling rate decreases, and, as shown in Fig. 3, the swelling curve merges with that for nickel to give about 15% swelling after 380 dpa. In Fig. 4 it can be seen that the void

concentration rises quickly with dose in 316 stainless steel in the early stages of swelling and reaches a maximum of 2 to 3×10^{16} voids/cm³ after about 20 dpa when the swelling is 1 to 2%. Above about 40 dpa the concentration falls as the voids grow together and coalesce.

Fig. 5 Typical electron micrograph of voids in Nimonic PE16 irradiated to 86 dpa at 525°C, together with the dislocation structure and γ' precipitates shown inset.

Nimonic PE16

The swelling behavior of Nimonic PE16 is markedly different from nickel and stainless steel, as shown in Fig. 3. Voids were first seen in C^{2+} irradiated specimens after about 2 dpa at a swelling of about 0.1%. However, recent observations of proton-irradiated Nimonic PE16 show voids just visible after 0.75 dpa at 0.01% swelling. Above 2 dpa the swelling rises very slowly with dose [approximately as $(\text{dose})^{1/2}$] to reach about 0.5% after 300 dpa. These results are for Nimonic PE16 solution treated and aged to give γ' precipitates of $Ni_3(Ti,Al)$ about 100 Å diameter and in a void concentration of about 2×10^{16} voids/cm³. The voids were first seen in a concentration of about 7×10^{14} voids/cm³, and subsequently the observed concentration varied between this value and 2×10^{15} voids/cm³. Figure 5 shows the void distribution in Nimonic PE16 after a dose of 86 dpa. Also visible on the electron micrograph is a zone free of voids, parallel to

a grain boundary and the dislocation structure in an adjacent grain in which "two-beam" diffraction conditions were operative. The inset in Fig. 5 is a reverse contrast print, at the same magnification, showing the γ' precipitate distribution imaged in a dark field using a superlattice reflection. The precipitate size and number were apparently unaffected by irradiation at 525°C.

20% Cold-Worked 316 Stainless Steel

Void formation in the 20% cold-worked steel was found to be extremely nonuniform, with the void numbers sometimes varying from zero to maximum over distances of several microns. Since the density of dislocations is likely to influence void formation,⁹ it is reasonable to infer that this nonuniformity in voidage is a consequence of local variations in the dislocation density introduced during cold working. Such variations are probably a consequence of the difficulty in producing uniform cold work in thin foils.

The general overall result of cold work was that the swelling was somewhat lower than in solution-treated steel, but, because of the lack of uniformity in void distribution, reliable values of swelling were difficult to obtain. Although the swelling due to void formation is less than in the solution-treated steel at low doses, it eventually reaches the solution-treated value of about 10% at a dose of approximately 200 dpa. Thus 20% cold work can be useful in inhibiting void formation up to a given dose level, but at high doses this is not so. Our results at 525°C indicate that, at maximum reactor fuel-burnup doses, the swelling expected in 20% cold-worked 316 stainless steel is about half that observed in the solution-treated steel.

Dislocation Structure

Although swelling is manifest as voids, it is, of course, physically caused by the equivalent interstitial content in the metal. This is present as radiation-induced dislocation loops, lines, and networks, in addition to those interstitials which reach the free surface. Bullough and Perrin⁹ have shown that the dislocation concentration during void growth is of paramount importance in determining the kinetics of void growth; the experimental determination of dislocation density is thus important in testing the predictions of theoretical models.

In all three face-centered cubic (fcc) metals studied, the first appearance of voids was always accompanied by the first appearance of small (<50 Å) dislocation loops, some of which could be positively identified as faulted interstitial loops lying on $\{111\}$ planes. In nickel the loops soon unfaulted as the dose increased and grew to form a dislocation network that increased to a maximum of about 5×10^{10} cm/cm³ at around 40 dpa. Above this dose, where large voids were produced by coalescence, the dislocation density was observed to decrease. In steel the dislocation density increased sharply with dose, reaching about 10^{11} cm/cm³ at 10 dpa, and then leveled off to reach about 2×10^{11}

Fig. 6 Log dislocation density vs. log dose in nickel and 316 stainless steel.

cm/cm³ at 350 dpa. Faulted loops only were observed up to about 20 dpa, after which some unfaulting occurred, and a dense network developed. No reduction in dislocation density was observed at high doses, as in the case of nickel. This variation of dislocation content with dose in nickel and 316 stainless steel is shown in Fig. 6. In Nimonic PE16, faulted loops were also observed, and their concentration quickly increased and, until their interaction, gave a very dense dislocation network. At all doses above 2 dpa, the dislocation density was greater than 10¹¹ cm/cm³. A typical distribution is seen in Fig. 5, where image overlap makes accurate determination of the exact value of the dislocation density very difficult.

Temperature Dependence of Swelling in 316 Stainless Steel and 18/8/Ti Stainless Steel

Figures 7 and 8 show the temperature dependence of swelling in two steels in the solution-treated and cold-worked states,^{10,11} and Fig. 9 shows the variation in void density with temperature for 18/8/Ti stainless-steel specimens. Although the general shape is consistent with the reactor results, it should be noted that the swelling peak is shifted toward higher temperatures. This is simply a manifestation of the increased dose rate and will be discussed later.

Fig. 7 Temperature dependence of swelling in solution-treated and 20% cold-worked 316 stainless steel irradiated to 40 dpa.

Fig. 8 Temperature dependence of swelling in solution-treated 18/8/Ti stainless steel irradiated to 60 dpa.

Fig. 9 Void density plotted as a function of temperature in solution-treated 18/8/Ti stainless steel irradiated to 60 dpa.

DISCUSSION

Nucleation

It is evident from the above results that helium is particularly important in nucleating voids, although other gaseous impurities, such as oxygen, can play a major role. Voids are thought to grow on three dimensional agglomerates of gas atoms which generally nucleate homogeneously throughout the solid; however, in some instances, heterogeneous nucleation occurs, especially in those cases where the samples have not previously been implanted with helium.

Temperature Dependence

Before we discuss the dose dependence of swelling in the various materials, let us first consider, in general terms, the temperature range over which voids form during accelerator irradiation.

In previous work,^{1,2} it was shown that the temperature dependence of swelling in nickel exhibited a reasonably flat plateau between about 375 and 600°C. Furthermore, the value of swelling at this plateau was fairly insensitive to dose rate over about two orders of magnitude, and, for this reason, we used nickel as our model material to calibrate the damage as a function of depth. However, it was noted that the high-temperature cutoff was about 100°C higher than the corresponding reactor irradiations. In the two stainless steels discussed above, we presented results showing the variation of void swelling with irradiation temperature, and in both cases, although the curves do not exhibit

the plateau found in nickel, the swelling is continuing to very much higher temperatures than that found after reactor irradiation.

The reason for the temperature shift is thought to be a consequence of the higher damage rate that prevails during accelerator irradiations; in some cases, the damage is created $\sim 10^3$ times faster than during reactor irradiation. The higher damage rate produces a larger dynamic concentration of vacancies, which is then equal to the thermal equilibrium concentration corresponding to higher temperatures. At low temperatures, where the swelling vs. temperature curve is rising, the increased damage rate produces more recombination and once again moves void formation to higher temperatures. The general result is that, for a 10^3 increase in damage rate, the whole swelling-temperature profile is moved by about 100°C to higher temperatures without significantly changing the peak swelling value; a full discussion of this point is found in the theoretical work of Bullough and Perrin.⁹

It is important to note that, although the void swelling-temperature range is moved to higher temperatures, other physical phenomena (such as the recovery of cold work, the coarsening of precipitates, and the annealing of radiation-induced dislocation structures) may not be affected by the change in dose rate. However, these phenomena may be affected differently, and, to make sensible deductions, we must be aware of all facets of the experimental conditions.

Void Growth

We have already emphasized the dependence of void growth on dislocation structure, and, for this reason, it seems most sensible to discuss the void growth and the evolution of the irradiation-produced dislocation lines simultaneously. From the results presented above, it is evident that at low doses the increase in swelling with dose results from a combination of continuous void nucleation and growth. At higher doses, where nucleation ceases and coalescence occurs, the increase with dose can only result from void growth; however, this is usually coincident with the approach to saturation.

The most significant differences between nickel and 316 stainless steel appear at low displacement doses. For instance, at doses below about 2 dpa, 316 stainless steel shows no radiation-induced dislocation structure or voids, but nickel shows that the dislocation structure and void swelling have already attained significant values. It is thought that this difference is a consequence of the different effective diffusivities of gaseous nucleating agents (e.g., helium or oxygen) in nickel and steel. Recent thermal-desorption studies¹³ have shown that, although the activation energies for diffusion of helium in nickel, 316 stainless steel, and Nimonic PE16 are basically similar, the total fraction that is available for diffusion throughout the lattice is significantly reduced by impurity trapping in 316 stainless steel. In nickel, it is thought that the implanted helium in solution becomes mobile, predominantly by irradiation-enhanced diffusion at 525°C , and agglomerates to form gas bubbles, which grow and eventually

become voids. In steel, however, besides the self-trapping of helium by other helium atoms, it is thought that a substantial fraction of the diffusing helium becomes trapped on other sites, e.g., in association with dissolved carbon, or at impurity complexes. Such trapped helium cannot then contribute to the diffusion or join other gas-atom agglomerates until it is released either by thermal activation at higher temperatures or by irradiation. In the nickel irradiations at 525°C, therefore, most of the implanted helium precipitates into small gas bubbles, which act as void nuclei, at the very early stages of irradiation. However, in steel, it is thought that large-scale agglomeration does not occur so readily but can only occur as a result of the diffusion of helium atoms released from traps during irradiation. For this reason, void nucleation is delayed until the irradiation dose has reached a sufficiently high level to have released a substantial fraction of trapped helium; furthermore, nucleation will continue progressively as the irradiation proceeds.

The delay in void nucleation in Nimonic PE16 compared to nickel is considered to result from enhanced recombination of defects at the coherent interface of the γ' precipitate. A vacancy moving in such an interface would maintain its identity and be slowed down sufficiently to significantly increase the probability of vacancy/interstitial recombination. The introduction of a constant fraction of recombination into nickel would have the effect of moving the dose dependence to higher values without necessarily changing its rate of increase.

The different rates of void-volume increases in nickel and steel are consistent with theoretical predictions⁹ based on the preferential attraction of interstitials to dislocations. Two possible causes of the suppression of void growth in Nimonic PE16 are postulated. First, the coherent interface results in enhanced recombination, and, second, the radiation-induced dislocation network becomes pinned on the γ' precipitates where it builds up to such a high density that the material behaves as if it were very heavily cold worked.

Above about 40 dpa in both nickel and 316 stainless steel, the swelling vs. dose curve exhibits a trend toward saturation. In nickel the saturation is readily explained in terms of the reduction in dislocation density, which occurs as a consequence of the voids occupying more and more space. However, in 316 stainless steel the explanation is not so obvious since the dislocation density continues to increase; it may be that saturation occurs as a consequence of this high density from image-force effects.⁹

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DISCUSSION BY ATTENDEES

Norris: You have emphasized the desirability of using a broad damage peak rather than a sharp one. A further point is that the damaged region is restrained by the relatively undamaged region around it. For the case of a sharp damage peak, would the stress be significant?

Nelson: In any simulation experiment, one has problems such as you have suggested. However, we think that the effect of stress is unimportant, except perhaps at the highest temperatures.

Torrens: The graph of void density vs. temperature seemed to show some anomaly at about 525°C. Since the swelling increases rapidly at this temperature, do you think that this is a real effect or just a consequence of experimental error?

Nelson: I think this is just an experimental error. At other dose values, this is not observed.

Che-Yu Li: When you use nickel or iron ions, do you get the same results as those when you use carbon ions?

Nelson: In general, provided one adjusts the damage rate, no serious discrepancy is seen. Harkness asked yesterday about the carbon we are putting in since there is an effect of carbon on reactor irradiation. Well, that is an important question. One does, in fact, see carbide precipitation at high doses. In our particular experiments, because they are done fairly quickly compared to the reactor, we do not seem to produce $M_{23}C_6$, even at high doses. But we do produce some of these other phases of carbide. As far as we can see, as long as we do not produce $M_{23}C_6$, the results with carbon are essentially the same as with nickel or iron bombardment.

Taylor: You say the swelling is the same. Are the number densities the same for the same fluence as well, because number densities in the C^{2+} irradiations are much higher than those observed in H^+ bombarded steel?

Nelson: If allowance is made for different displacement rates, yes.

Armijo: What is the carbon-ion flux in the 20-MeV carbon-ion experiments? How many hours does it take to obtain displacement ratios of 40 and 400?

Nelson: We generally perform our experiments such that the damage rate is 10^{-3} dpa/sec. However, we can vary this over many orders of magnitude.

Boltax: For solution-treated 316 stainless steel, you showed a significant increase in dislocation density (to $\sim 10^{11}$ cm/cm³) at a dose of ~ 10 dpa. What is the comparable effect in 20% cold-worked 316 stainless steel? Since the dislocation densities of the solution-treated 316 stainless steel and the 20% cold-worked 316 stainless steel are approaching one another, would you expect to see major differences between the materials?

Nelson: The dislocation density in 20% cold-worked 316 stainless steel is somewhat higher than 10^{11} cm/cm³. Furthermore, the irradiation-induced dislocation structure may be of a different type than the cold-worked, e.g., we know that faulted loops in copper grow three times faster than unfaulted loops. Generally the swelling is very much reduced at low dose but approaches the solution-treated value between 100 and 200 dpa.

Laidler: I would like to present some recent results obtained with 5-MeV Ni^{2+} ion bombardment of solution-annealed 316 stainless steel. Observed values of swelling ($\Delta V/V$) are plotted in Fig. 1 as a function of calculated displacements per atom. The specimens (with one exception, as noted) did not contain helium; the irradiations were conducted at 585°C. The results of the Hanford Engineering Development Laboratory (HEDL) are compared with results obtained with 20-MeV C^{2+} ion bombardment at 525°C by Dr. Nelson.

It was observed that void nucleation ceases at rather low displacements-per-atom levels, the void concentration actually decreasing (with associated increase in void size) above about 100 dpa. The form of the swelling curve closely parallels the Harwell results for helium-bearing stainless steel, suggesting that

Fig. 1 Comparison of Harwell swelling data for 316 stainless steel bombarded with 20-MeV C^{2+} at 525°C with HEDL results for 316 stainless steel bombarded with 5-MeV Ni^{2+} at 585°C.

Fig. 2 Voids in 316 stainless steel containing 3 at. ppm helium, bombarded at 585°C with 5-MeV Ni^{2+} to 45 dpa; $\Delta V/V = 4.6\%$ (1000 kV, 0701).

intercomparisons for the two bombarding species are not inappropriate. The importance of the introduction of helium is graphically demonstrated by the rather large increase in swelling at about 45 dpa with prior injection of only 3 at. ppM helium, with $\Delta V/V$ increasing from 0.95 to 4.6%.

That this particular data point falls so close to the Harwell curve is perhaps fortuitous, considering the 60°C difference in irradiation temperature. The microstructure of the Ni^{2+} bombarded specimen containing helium is shown in Fig. 2. The void concentration is $2.5 \times 10^{14} \text{ cm}^{-3}$, and the mean void diameter is about 700 Å.

PRODUCTION OF VOIDS IN PURE METALS BY HIGH-ENERGY HEAVY-ION BOMBARDMENT

— 8

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ABSTRACT

The production of voids in metals by high-temperature neutron irradiation and by bombardment with high-intensity beams of electrons, protons, carbon ions, nickel ions, and tantalum ions is compared in terms of defect production rates and spatial distribution of defects. Particular attention is paid to the use of heavy ions ($Z > 26$) in producing voids in pure metals during displacement rates of 10^{-3} to 10^{-1} sec^{-1} . Specific information is given on the use of 5- to 8-MeV beams of nickel and/or selenium ions to produce voids in pure and helium-doped nickel samples at 525°C. The effect of total displacements per atom (dpa) values of 0.47 to 400 on the void size, number density, and volume change is discussed. The effect of irradiation temperatures from 650 to 1000°C on the formation of voids in pure molybdenum and niobium is also presented.

The use of high-energy ion bombardment to simulate high-fluence, high-temperature neutron damage in metals has proven to be an unexpected and rewarding new scientific tool.¹⁻⁷ This relatively new approach to the study of radiation damage has generated considerable theoretical interest in the effects of extremely high defect production rates. The most notable achievement of this technique is the "preview" of some microstructural defects and dimensional problems⁶⁻⁸ we may expect to find in metals subjected to 20 years or more of intense radiation damage in future LMFBRs (liquid-metal fast breeder reactors) or CTRs (controlled thermonuclear reactors). On the other hand, the very feature of this technique which makes it so attractive, namely, the unusually high rate of defect production, can prove to be a pitfall to the unwary scientist. Careful analysis of the irradiation temperature and defect production rate is required before conclusive evidence can be obtained on kinetic processes in metals. The most notable example of this is the shift in "effective" irradiation temperature which can result from defect production rates of 10^{-4} or higher.⁹

The potential advantages of using an external beam of energetic ions to accelerate the radiation-damage rate by several orders of magnitude were first recognized in 1969 by Nelson and Mazey at Harwell.¹ They found that they could produce, in a matter of hours, a damage state in 316 stainless steel which normally required more than a year of fast nuclear reactor irradiation to produce. The initial work was performed with low-energy (100-keV) heavy ions on stainless steel, but these same scientists later found that 20-MeV carbon ions could produce similar results in a much larger volume of sample.² They have vigorously pursued this approach by examining the role of inert gases in the production of voids and have extended the work to include high-fluence damage in nickel.

Two other approaches were immediately taken by scientists at Battelle-Northwest (BNW) and Atomics International (AI) in the United States. The BNW group concentrated on using higher energy (5 to 10 MeV) heavy ions, such as copper,⁹ nickel,^{3,10} or selenium,^{7,10} to bombard stainless steel, nickel, molybdenum, niobium, and tantalum. These studies confirmed the work of Nelson and Mazey and revealed some rather intriguing three-dimensional defect structures and saturation effects in nickel.¹¹ The AI group chose to pursue the use of 1.4-MeV protons to produce damage in stainless steel and nickel, and they found equally interesting results.^{5,12} Other groups have now investigated the use of protons,¹³ deuterons,¹⁴ nitrogen ions,⁸ and high-intensity beams of electrons¹⁵⁻¹⁷ to simulate the high-temperature damage produced by neutrons. The results of these latter experiments are currently appearing in the open literature, and any extensive review of that work would be premature at this time.

This paper briefly reviews the mechanisms by which heavy ($Z > 28$) ions produce defects in metals and points out some of the major differences in specific damage rates between electrons, neutrons, light ions, and heavy ions. Recent experimental information on the fluence dependence of the formation of voids in nickel and the temperature dependence of void formation in molybdenum, TZM, and niobium will be given. The effect of preinjected helium on the formation of voids in nickel will also be discussed.

DISPLACEMENT OF ATOMS BY ENERGETIC HEAVY IONS

As a high-energy heavy ion passes through a metal, it loses energy by two major processes: electronic and nuclear collisions with the metallic atoms. The electronic interactions result mainly in ionization of the atoms and do not significantly contribute to the forceable ejection of atoms from their equilibrium positions. On the other hand, a large fraction of the nuclear energy transferred in interactions between the incident nucleus and the struck nucleus results in displaced atoms. Lindhard et al.^{18,19} and Schiott²⁰ have published rather comprehensive reviews of the factors that govern the rate at which energy is lost

in both nuclear and electronic collisions, and their theories have been modified to predict the number of displaced atoms produced by incident beams of energetic ions.⁴ The following is only a brief account of the calculation methods.

There are, in reality, three separate problems that must be solved before we can arrive at the final answer of the displaced-atom density; the range of the particle must be determined, the rate of nuclear energy loss must be calculated as a function of the distance into the solid, and finally, we must convert the nuclear energy loss into a displaced-atom density. The Lindhard model assumes that the nuclear and electronic collisions can be treated independently, that the electronic energy loss is proportional to the velocity of the incident ion, and that the atoms are randomly placed in the solid (i.e., the model ignores crystallographic effects).

The average range of an energetic ion can be calculated if we know the energy dependence of the nuclear and electronic stopping powers, $(dE/dX)_n$ and $(dE/dX)_e$, respectively. Calculation of these quantities involves a rather complex approximation of the interaction between incident and struck particles through a screened Thomas-Fermi type of potential. The reader is referred to Lindhard, Scharff, and Schiott^{1,8} for a more detailed discussion. Assuming that the various stopping powers can be calculated, the average range of the incident particle is then

$$\bar{R} = \int^E \frac{dE}{\left(\frac{dE}{dx}\right)_n + \left(\frac{dE}{dx}\right)_e} \quad (1)$$

Equation 1 gives the total path length of an incident ion into the solid, but we are usually more interested in the average projected range of that particle into the solid. This latter quantity, $\bar{R}_p$, is the perpendicular distance from the incident surface to the final resting place. The projected range can be calculated by

$$\frac{\bar{R} - \bar{R}_p}{\bar{R}_p} = \mu \Psi(E, k) \quad (2)$$

where μ is the mass ratio of the struck and incident particles and $\Psi(E, k)$ is a parametric function of the incident-ion energy and the atomic properties of the incident and struck ions through a constant k .

Equation 2 allows us to calculate the average projected range of the incident particle, but there is in reality a Gaussian distribution of ranges around the average value. We can calculate the distribution of ranges in the normal fashion;

$$\frac{N}{C} = \frac{1}{\alpha\sqrt{2\pi}} \exp - \left[\frac{(R - \bar{R}_p)^2}{2\alpha^2} \right] \quad (3)$$

where N = concentration of stopped ions per cm^3

C = incident fluence of ions per cm^2

$\bar{R}_p$ = average projected range

$\alpha^2 \cong \gamma(\bar{R}_p)^2 F(k, E, V)$

γ = four times the reduced mass ratio of the incident and struck atoms

The term $F(k, E, V)$ is a function that depends on the degree of electronic scattering through the constant k , the energy E of the incident ion, and the form of the scattering potential used (a screened Thomas-Fermi type for this study).¹⁸

We can now calculate the total amount of nuclear energy transferred to the metal atoms at any given distance into the solid by the formula

$$S_n(X) \cong \int_0^{\bar{R}_p} f(R_p) S_n(R_p - X) dR_p \quad (4)$$

where $f(R_p)$ is the fraction of incident ions with projected ranges between R and $R + dR$, and $S_n(R_p - X)$ is the nuclear energy transfer rate, evaluated at X for a particle with projected R_p .

The next step is to determine the displaced-atom density resulting from the nuclear energy transfer rates calculated from Eq. 4. Recently it was noted that only 60% of the energy lost in nuclear collisions results in displaced atoms.²¹ This reduction comes about because some of the struck atoms lose energy in nonproductive electronic interactions with the surrounding atoms. Therefore the productive energy used to displace atoms is really $0.6 \times \bar{S}_n(X)$.

The conversion from nuclear energy transfer to displaced-atom density can be made by using a Kinchin and Pease²² approximation that yields

$$N(X) \cong 0.6 \cdot \bar{S}_n(X) \cdot \frac{1}{2E_d} \cdot N_I \quad (5)$$

where $N(X)$ is the number of atoms displaced per cubic centimeter at a distance X into the solid, E_d is the displacement energy, and N_I is the incident-ion fluence.

The more universal term now being used is the number of times each atom is theoretically displaced during the irradiation. This unit, dpa (displacements per atom), can be obtained from Eq. 5 by simply dividing by the atomic density, N_o .

The dpa value at any distance into the solid is then

$$\text{dpa}(X) = \frac{N(X)}{N_o} \quad (6)$$

COMPARISON OF DAMAGE RATES FROM HEAVY- AND LIGHT-ION BOMBARDMENT

The rate at which defects are produced in a metal is mainly a function of three things: the displacement energy, the specific efficiency for transferring energy in collisions between the incident ions and the struck atoms, and the flux of particles which can be directed on the solid. In general, heavy ions, such as nickel or tantalum, are several orders of magnitude more efficient in producing damage than are protons and carbon ions. On the other hand, much higher beam currents of the lighter ions are available. A few examples of these generalities will illustrate the point.

Figure 1 shows the relative effectiveness of the more common particles used to produce displacements in a metal like nickel. We see that each tantalum ion is

Fig. 1 Displacement-damage effectiveness for various energetic particles in nickel.

five times more effective in displacing atoms than is a nickel ion, 100 times more effective than is a carbon ion, and more than 5000 times more effective than is a proton. This factor rises to 3×10^6 for 14-MeV neutrons, to 10^7 for 1-MeV neutrons, and to greater than 10^8 for 1-MeV electrons (the latter number is not shown in Fig. 1).

The data in Fig. 1 can be placed in more perspective by multiplying the damage efficiency by presently attainable beam currents listed in Table 1. The

TABLE 1
CURRENTLY ATTAINABLE FLUXES OF
HIGH-ENERGY PARTICLES USED TO
PRODUCE VOIDS IN METALS

Particles	Particles/(cm ²)(sec)
Electrons (1 MeV)	4×10^{19}
Neutrons (>1 MeV) (EBR-II)	6×10^{14}
Neutrons (14 MeV) (future CTR)	4×10^{14}
Protons (1 to 2 MeV)	6×10^{14}
Carbon ions (20 MeV)	1.2×10^{14}
Nickel ions (5 to 10 MeV)	6×10^{13}
Tantalum ions (5 to 10 MeV)	6×10^{12}

data here are taken from the literature and must be considered to be temporary as advances in ion-source technology will certainly increase some of the displacement rates in the future. The main limitation on beam currents of the lighter ions is the amount of heat input. For example, we have assumed that a few hundred watts per square centimeter is the upper energy-input limit for reasonable temperature control of the samples. Above this limit the temperature uncertainties would render quantitative work on nucleation and growth somewhat suspect. Figure 2 shows the range of relative displacement rates currently attainable with electrons, neutrons, protons, carbon ions, nickel ions, and tantalum ions. The larger beam currents presently attainable for high-energy nickel ions give the nickel ions a slight edge over the tantalum ions even though tantalum is more efficient in imparting useful energy to the lattice. The maximum displacement rates of 1-MeV electrons, 1-MeV protons, and 20-MeV carbon ions are roughly two orders of magnitude lower than the heavier ions, although they are still some three orders of magnitude higher than displacement rates in present fast reactors and proposed CTRs. Note that all these techniques are not confined to operate at the maximum damage rates. Scientists could, and

Fig. 2 Displacement rates currently available by energetic particle bombardment of nickel.

most often do, vary the damage rate by several orders of magnitude below the maximum possible.

Figure 1 also illustrates another important distinction between the various ions used for the simulation work, namely, the volume of material in which the displacements occur. In contrast to high-energy neutron bombardment that produces displacements uniformly throughout the solid, the energetic ions

produce damage in a nonhomogeneous fashion. Typical damage zones of high-energy bombarding particles are 5000 Å for 7.5-MeV tantalum, 1 μ for 5-MeV nickel, 7 μ for 20-MeV carbon, 10 μ for 1.3-MeV protons, and ~ 50 μ for 1-MeV electrons. The increased range of the lighter ions greatly alleviates the specimen-preparation problems, although techniques are now available^{10,23} to thin even samples bombarded with tantalum with a fair degree of accuracy.

PRECIPITATION OF VACANCIES INTO VOIDS

Thus far we have only considered how the individual vacancies and interstitial atoms are produced. How do these defects, especially the vacancies, end up in clusters? The answer to this question is the subject of considerable controversy at the present time, and a complete assessment of the situation is not the object of this paper. We will only point out here a few of the general points of agreement and disagreement between scientists as a background for future discussion.

The first point of general agreement is that there must be a supersaturation of vacancies in the metal before voids can be nucleated and grown. Second, the supersaturation of vacancies can only produce voids if the vacancies can move to nucleation sites and reduce the amount of recombination. Hence there is a minimum temperature required during irradiation to form voids. This minimum temperature is approximately 30% of the absolute melting point and is assumed to be associated with the vacancy migration temperature. There is also a maximum temperature above which the thermal production of vacancies reduces the supersaturation level below that required for void formation and growth. This upper temperature limit is approximately 50% of the melting point in most metals.

The third point of agreement is that, because vacancies and interstitials are produced in equal numbers during irradiation, there must be some sinks that preferentially remove interstitial atoms during irradiation, leaving an excess of vacancies in the lattice. The biased sinks are commonly assumed to be dislocations that are either present before irradiation or formed by the precipitation of interstitial atoms into dislocation loops.

The major disagreement in this field now centers around whether the voids are homogeneously²⁴⁻²⁷ or heterogeneously^{9,16,27-31} nucleated. The homogeneous theories are based on the assumption that voids are formed by the statistical agglomeration of vacancies or in the center of randomly distributed displacement spikes. The heterogeneous-nucleation theories assume that gas atoms (either inert elements produced by transmutation or residual elements, such as oxygen, nitrogen, or hydrogen) are required to stabilize the void embryos no matter how the latter are formed.

Ion-bombardment experiments can be tailored to give some insight into the void-nucleation mechanisms. For example, unlike neutron-irradiation studies,

the presence or absence of inert gases in the metal is strictly up to the experimenter. Scientists also have much more control over the impurity level of the samples during ion bombardment because these experiments are conducted in a vacuum. The high defect production rate and the possibility of varying it over several orders of magnitude should prove or disprove theories that are inherently defect-production-rate sensitive. Finally, by choosing the proper incident particle, such as an electron, one can eliminate displacement-spike effects and thereby determine their importance in void nucleation. The present experiments concentrate on the inert-gas and rate-sensitivity questions.

EXPERIMENTAL

Material

The chemical analysis of metal foil used for this study is shown in Table 2. Samples of 3 mm diameter were punched from the foil and annealed to the conditions also listed in Table 2. After the samples were annealed, they were electropolished to obtain the smoothest possible surface finish.

Irradiation

A detailed description of the experimental arrangement used to bombard the samples is given in Ref. 10. Briefly, the 3-mm samples were held on a heated stainless-steel or tantalum furnace while being bombarded. Each sample was bombarded individually with a maximum of 10 samples irradiated per run. The bombarding fluxes were slightly different for each species, but, in general, they varied from 1 to 10 $\mu\text{A}/\text{cm}^2$ [6×10^{12} to 6×10^{13} particles/(cm^2)(sec)].

The nickel, copper, and tantalum ions were produced from a sputtering source similar to that described by Mueller and Hortig³² (see also Ref. 10). The selenium ions were produced by a diode source.³³ Ideally, one would like to use only nickel ions to bombard nickel foil and to use refractory-metal ions, e.g., tantalum, to bombard niobium and molybdenum. However, the low concentrations of heavy ions required to produce reasonable damage (~ 10 to 50 dpa) resulted in less than 0.1% impurities at the position of examination. No second-phase particles were observed at these levels when metallic ions different from the targets were used.

Some of the well-annealed nickel samples were preinjected with approximately 3 at. ppm of helium atoms from the University of Washington cyclotron.³⁴ The helium atoms were uniformly distributed in a 25- μ thick layer by a technique described elsewhere.³⁵

TABLE 2
PREIRRADIATION PROPERTIES OF
MATERIALS FOR ION-BOMBARDMENT STUDIES

Impurity	Wt. ppm			
	Ni	Mo	TZM	Nb
Al	0.5	<5	<300	100
C	90	200	100 to 300	30
Cd		<10		
Co	1	<5		
Cr	0.5	<5		60
Cu	5	<2		
Fe	10	100	<300	60
H	<0.1	0.8	1 to 10	2
Mg	<0.1	<1	<100	0.8
Mn		<2		
Mo		Balance	Balance	
N	<2	1	4 to 15	90
Ni	Balance	<5		9
O	50	4.5	10 to 20	145
Pb		<10		
Si	<1	<10	<300	20
Sn	<10	<5		
Ta				200
Ti		10	4200 to 4700	60
V		5		5
W		150		80
Zr	3	<20	800 to 1100	60
Preirradiation anneal				
Temp., °C	700	1800	1800	1750
Time, hr	2	0.5	0.5	0.7
Vacuum, torr	2×10^{-6}	1×10^{-5}	1×10^{-5}	1×10^{-7}

Examination

The procedure for thinning the nickel samples was described earlier.^{7,23} The same general technique was used for the molybdenum and niobium samples except for different jetting and electropolishing solutions.

Electron-microscopy studies were conducted with a Hitachi 200F electron microscope. The average void size was determined from 160,000X photographs; the number density of voids was obtained by noting the thickness of the foil from stereo analysis or by the interference-fringe technique. All volume changes are calculated from the experimentally determined void size and number density.

Determination of Displacement Density

The displacement density was calculated by a method described earlier,⁴ and Figs. 3 and 4 show typical calibration curves for nickel and molybdenum, respectively. The calibration curve for niobium is similar to Fig. 4 and is not included here. Note that, although the dpa values per incident particle are much higher for tantalum than for nickel or selenium, the damage for tantalum ions

Fig. 3 Displaced-atom density for nickel and selenium ions in nickel.

occurs over a much shorter range. This shorter range makes the determination of the penetration distance more critical and results in a much higher error band for dpa estimates.

RESULTS

Nickel

Both pure and helium-doped samples were irradiated at 525°C with 5- to 6-MeV nickel ions and 6- to 11-MeV selenium ions. The displacement densities ranged from 0.4 to 480 dpa. Voids were found in all the samples, and Table 3

Fig. 4 Displaced-atom density for tantalum and nickel ions in molybdenum.

lists the average void size, number density, and calculated volume change for each sample.

Figure 5 graphically shows the effect of increasing displacement damage on the average void size. The average diameter rises from approximately 100 Å at 0.4 dpa to approximately 300 Å at 67 dpa. Above 100 dpa there appears to be a slight reduction in the average void size. It is also worth noting that there was little, if any, significant difference between samples that were preinjected with helium and those which were irradiated without helium. There also is no significant difference between samples irradiated with nickel ions and those bombarded with selenium ions. The morphology of the voids in all samples is consistent with {100} truncated {111} octahedra similar to those determined by other studies^{36,37} except at the highest damage states where they appear to be more like {100} cubes.

Figure 6 shows that the average void density rises from $\sim 3 \times 10^{14}$ voids/cm³ at 0.4 dpa to a constant value of ~ 3 to 4×10^{15} voids/cm³ over the entire 2- to 480-dpa range except for the two highest dpa points of the selenium-bombarded samples. There is no noticeable difference between pure and helium-doped samples or samples bombarded with nickel or selenium ions

TABLE 3
VOID DATA ON NICKEL BOMBARDED AT 525°C

Ion energy, MeV	Calculated dpa	Average void size, Å	Average void density, 10^{15} voids/cm ³	Calculated $\Delta V/V$, %
Ni → Ni, 3 at. ppm Helium				
5	1	90	1.1	0.07
5	4.4	150	2.0	0.19
5	6.5	145	2.9	0.46
5	10	155	3.2	0.61
5	25	210	3.5	1.7
5	58	250	3.3	2.7
6	67	305	2.7	4.0
5	360	250	4.2	3.4
5	480	260	4.0	3.7
Ni → Ni, No Preinjected Helium				
6	0.43	135	0.38	0.048
6	1.3	140	0.99	0.14
6	6	140	3.4	0.49
6	44	265	4.1	3.95
Se → Ni, No Preinjected Helium				
11	0.47	90	0.30	0.012
11	2	70	1.7	0.05
11	2.3	120	2.7	0.24
8	12	210	3.6	1.7
8.8	47	270	4.0	4.1
8.8	95	220	7.6	4.2
6	400	180	14*	4.4

*Calculated from superlattice of face-centered cubic (fcc) voids with 660-Å lattice constant.

over the majority of the damage range. This similarity is quite evident in Fig. 7, where we compare the microstructure of doped and undoped nickel-bombarded samples and an undoped selenium-bombarded sample. The average void size is about the same in all three samples, as is the number density (taking into account the different thicknesses of foils that were examined).

The calculated volume change is shown in Fig. 8. This figure reveals that the swelling ($\Delta V/V$) increases from ~0.02% at 0.4 dpa to ~4% at 50 dpa roughly as the $\frac{3}{2}$ power of the dpa values. Above 50 dpa the volume change seems to have saturated at 4 to 5% up to 480 dpa.

At 360 to 480 dpa, the voids developed into a rather interesting microstructure in both helium-doped and undoped samples. Figure 9 shows the

Fig. 5 Effect of displacement damage at 525°C on the average void size in nickel. Δ , nickel $\rightarrow$ nickel, 3 at. ppM helium; $\square$, nickel $\rightarrow$ nickel, no helium; $\circ$, selenium $\rightarrow$ nickel, no helium.

Fig. 6 Effect of displacement damage at 525°C on the number density of voids in nickel. Δ , nickel $\rightarrow$ nickel, 3 at. ppM helium; $\square$, nickel $\rightarrow$ nickel, no helium; $\circ$, selenium $\rightarrow$ nickel, no helium.

Fig. 7 Voids in nickel after 525°C bombardment.

voids viewed in a $\{111\}$ and a $\{110\}$ foil orientation after selenium bombardment, and Fig. 10 shows the voids from a $[100]$ direction in nickel-ion-bombarded, helium-doped nickel. These figures show that the voids are not randomly placed but rather that they tend to line up in rows parallel to the $\langle 100 \rangle$ directions. Further analysis of this structure reveals that the voids are actually aligned in an fcc superlattice with a lattice spacing of 660 Å. Figure 11 shows the comparison of a $\{110\}$ view to an artist's drawing of what the corresponding fcc structure would look like. The voids in the ion-bombarded sample are actually $\{100\}$ truncated $\{111\}$ octahedra, and therefore they do not have the exact appearance characteristic of perfect octahedra viewed in a $\{110\}$ foil orientation.

Molybdenum and Niobium

Pure molybdenum, TZM, and niobium samples were bombarded with 5-MeV nickel ions over the temperature range of 650 to 1000°C, and niobium was irradiated with 7.5-MeV tantalum ions at 900°C. In the nickel experiment the displacement density was held constant at approximately 5 dpa, but the temperature was varied. The results of the microstructural examination are listed in Table 4. Voids were found in all samples after 800, 900, and 1000°C irradiations, but only dislocation loops were found in molybdenum after the

Fig. 8 Swelling in nickel after 525°C heavy-ion bombardment. Δ , nickel $\rightarrow$ nickel, 3 at. ppm helium; $\square$, nickel $\rightarrow$ nickel, no helium; $\circ$, selenium $\rightarrow$ nickel, no helium.

Fig. 9 Void-alignment in nickel after selenium-ion bombardment.

Fig. 10 Void alignment in helium-doped nickel after nickel-ion bombardment.

650°C irradiation and in niobium irradiated at 650 and 700°C. Examples of the voids are shown in Figs. 12 and 13.

The general effect of increasing irradiation temperature was to increase the average void size and reduce the average void density in both samples. There was little difference in the niobium, TZM, and molybdenum after the 800°C irradiation, but the average void size in niobium was approximately three times that in molybdenum and TZM samples after the 900 and 1000°C studies. The

Fig. 11 Face-centered cubic superlattice of voids in nickel.

Fig. 12 Voids in niobium and molybdenum after heavy-ion bombardment at 900°C and 1000°C.

Fig. 13 Effect of irradiation temperature on the microstructure of TZM. Damage level, ~5 dpa.

TABLE 4
VOID DATA ON ION-BOMBARDED MOLYBDENUM,
TZM, AND NIOBIUM*

Irradiation temp., °C	Average void size, Å	Average void density, 10 ¹⁶ voids/cm ³	Calculated $\Delta V/V$, %
Molybdenum			
650†	ND‡	ND	
800	50	5.2	0.34
900	75	4.7	1.0
1000	120	0.53	0.48
Niobium			
650†	ND	ND	
700	ND	ND	
800	45	2	0.10
900	220	0.15	0.83
900§	200	0.24	1.0
1000	350	0.015	0.34
TZM			
800	60	3.2	0.36
900	80	1.6	0.43
1000	105	0.36	0.22

*Damage level of ~5 dpa was produced by 5-MeV nickel ions except where indicated.

†6 MeV nickel ions.

‡ND, none detected.

§7.5-MeV tantalum ions, ~8 dpa.

increased void sizes in niobium were accompanied by reduced number densities so that the total number of vacancies in the voids (i.e., the swelling) was not significantly different at the three temperatures. Figure 14 shows that the swelling for all three materials follows the characteristic bell-shaped curve found in other neutron-irradiated metals and alloys.

The morphology of the voids is difficult to determine in the molybdenum and TZM samples because of the small average size. The voids in niobium, especially after the 1000°C irradiation, appear to take on the morphology of a truncated {100} cube. This shape is evident in Fig. 15, which shows the voids viewed in {111} and {110} foil orientations. Apparently there is a slight amount of truncation on the {110} faces of the cubes.

Finally, a nonrandom alignment of voids was also found in niobium irradiated at 800°C. Figure 16 shows this alignment when viewed in a {111} foil orientation. The rows of voids, parallel to <112> directions, suggest a

Fig. 14 Effect of irradiation temperature on swelling in heavy-ion-bombarded molybdenum, TZM, and niobium. Damage level, ~ 5 dpa.

body-centered cubic (bcc) superlattice of voids in contrast to the fcc superlattice in nickel. The lattice constant of this array is determined to be $350 \text{ \AA}$, which would predict a void density (two voids per bcc unit cell) of $4.7 \times 10^{16} \text{ voids/cm}^3$. This agrees quite well with the value of $2 \times 10^{16} \text{ voids/cm}^3$ determined by measuring the number of voids in a random orientation. The volume calculations in the latter case were made by noting the thickness indicated from stereo measurements in an area of photograph which contained the voids. No aligned voids were found in niobium at higher temperatures, nor was there any conclusive evidence for aligned voids in molybdenum or TZM at 800°C .

DISCUSSION

It is fairly obvious from the present study that inert-gas atoms, such as helium, are not necessary for the formation of voids in heavy-ion-bombarded nickel, molybdenum, TZM, or niobium. This point is reinforced by the fact that preinjection of part of the nickel samples with 3 at. ppm of helium atoms did not significantly alter the size, number density, or volume change when compared to the undoped samples. These results are in agreement with those of Nelson and Mazey¹ on stainless steel, although the latter investigators did find a significant effect when the preinjected helium levels exceeded 10 at. ppm. The higher helium concentrations increased the number density but reduced the average size of the voids. Bloom and Stiegler^{3,8} found much the same result from neutron-irradiated stainless steel that contained preinjected helium levels of 20

Fig. 15 Morphology determination of voids in niobium after 1000°C.

at. ppm. The latter two experiments suggest that the helium level in our tests may have been too low to show a significant effect on the nucleation of voids.

The present results, and those of Nelson and Mazey,¹ do not agree with the work of Norris.¹⁵ Norris found that no voids could be produced in pure nickel during 1-MeV electron bombardment, but voids did appear when identical samples were irradiated after preinjection with approximately 70 at. ppm of argon atoms. He concluded from these experiments that (1) displacement spikes are not required for void nucleation because only monovacancies or divacancies are produced by 1-MeV electrons and (2) that gas atoms are required for nucleation of voids. The inference from this¹⁵ and later studies¹⁶ is that inert-gas atoms are essential for void nucleation, but Urban¹⁷ has recently shown that oxygen may play an important role. Urban's experiment was also conducted with high-energy electrons so as to eliminate the displacement-spike effects. He found that voids could be formed in pure nickel if the samples were allowed to oxidize before bombardment. It is logical

Fig. 16 Aligned voids in niobium after 800°C irradiation.

to conclude from this study that residual gases, such as oxygen, could act as the nucleating site for a void or in some manner stabilize void embryos. Urban's experiment also rules out the requirement that inert-gas atoms are *essential* for nucleation, although it is entirely possible that inert-gas atoms along with other impurities could nucleate voids.

There are ample numbers of gas atoms in the present samples to act as nuclei for voids even though relatively pure starting materials were used. For example, the residual gas concentration (O + N + H) ranges from 100 at. ppm in molybdenum to 200 at. ppm in nickel and to as high as 1000 at. ppm in niobium and TZM. If all the gas atoms were divided evenly among the highest number density of voids in each sample, we would still have approximately 100 per void in molybdenum, and up to 1000 per void in nickel, niobium, and TZM.

Apparently more attention must now be paid to the amount of impurity gases in metals. Future studies with extremely high-purity, degassed samples will help in establishing the true role of gas atoms in the production of voids.

It is worthwhile at this point to compare the swelling observed in the heavy-ion-bombarded nickel samples to that obtained from neutron irradiation. Figure 17 shows results from Argonne National Laboratory,^{3,9} Pacific Northwest Laboratory,^{3,7,40} WADCO Corporation,^{41,42} and Oak Ridge National Laboratory⁴³ studies in a rather wide range of temperatures (370 to 500°C). The neutron-induced swelling is shown to be in good agreement with the heavy-ion work even though the helium varies by more than a factor of 200 in the neutron-irradiated samples. No particular effort was made to control the gaseous impurity levels of neutron-irradiated samples, and therefore it is quite possible

Fig. 17 Comparison of neutron-induced swelling in nickel to that found in the present study. ■, present heavy-ion results; △, ANL; □, WADCO; ○, PNL; ◇, ORNL.

that they contained as much or more residual gas atoms than the present high-purity nickel which could provide ample nucleation sites.

The agreement in Fig. 17 is also quite significant considering that the displacement rates were approximately four orders of magnitude different. Bullough and Perrin⁹ predict that the major effect of the higher displacement rates associated with the heavy-ion work is to lower the effective irradiation temperature. They predict that a high-damage-rate experiment will produce swelling comparable to a lower temperature neutron experiment. The amount of temperature shift is

$$\Delta T = T_i^2 \frac{k}{E_v} \left(\frac{1}{1 + \frac{kT_i}{E_v} \ln \frac{K_i}{K_n}} \right) \ln \left(\frac{K_i}{K_n} \right)$$

where T_i = temperature of the ion bombardment

k = Boltzmann constant

E_v = diffusion energy for vacancies

K_i = defect production rate during ion bombardment

K_n = defect production rate during neutron irradiation

For example, a 525°C irradiation of niobium with $K_n = 10^{-6}$ gives $\Delta T = 148^\circ\text{C}$ for $K_i = 10^{-2}$ or $\Delta T = 117^\circ\text{C}$ for $K_i = 10^{-3}$. This means that the present work should be comparable to neutron-irradiation studies in the 380 to 410°C range, not too far from where most of the data in Fig. 14 are obtained. Brimhall, Kissinger, and Kulcinski⁴⁰ also show that the swelling in neutron-irradiated nickel is not too sensitive to the irradiation temperature in the 400 to 500°C range, so that it is reasonable that the shift in effective temperature will not be too serious. Such comparisons are not expected to be valid near the temperature threshold for swelling in metals because the model of Bullough and Perrin⁹ neglects recombination effects. One must be very careful about drawing conclusions from ion-bombardment experiments conducted in the temperature region where recombination is important.

The tendency for voids to form three-dimensional lattice structures in niobium and in helium-doped nickel during nickel-ion bombardment is consistent with previous work on selenium-bombarded nickel,⁷ nitrogen-bombarded molybdenum and TZM,^{8,44} and neutron-irradiated molybdenum and niobium.⁴⁵ The superlattices in all these studies are identical to the metal crystal lattice, i.e., fcc in nickel and bcc in niobium, molybdenum, and TZM.

There is no obvious reason for this behavior at the present time except the possibility that the voids are attempting to minimize the total strain energy in the solid induced by such large swelling. Kissinger⁴⁶ has found that there is an anisotropic strain field associated with voids which can be detected by measuring the X-ray line broadening. It is possible that the long-range interaction between these strain fields will determine whether or not voids shrink or grow on certain periodic positions in the samples.

It has also been suggested⁴⁴ that the anisotropy of the crystal lattice could initiate such an effect. This is in agreement with the fact that nickel, niobium, and molybdenum have rather high anisotropy factors.⁴⁷ One would expect on this basis that voids in more isotropic metals, like aluminum or tungsten, would not form superlattices. This is consistent with observations by Packan,⁴⁸ who has reported swelling in aluminum of 7.5% with no evidences of void alignment. However, the evidence for the exact mechanism of alignment is too meager to draw any definite conclusions at the present time.

The effect of bombarding temperature on swelling in pure molybdenum is in good agreement with neutron irradiation of identical stock material⁴⁰ except for the lowest temperature sample. The fact that no voids were found at 650°C in molybdenum, a temperature at which voids are found in neutron-irradiated molybdenum,⁴⁰ is expected because of the previously mentioned effective temperature shift.⁹ The calculated shift is approximately 140°C for the 650°C ion bombardment. Thus far no voids have been found in neutron irradiation of molybdenum at 510°C.

The similarity of swelling in the molybdenum and niobium samples was expected because the irradiations were conducted at roughly the same

homologous temperatures. The rather large void size in niobium after the 900 and 1000°C irradiations was rather unexpected, but there are few high-temperature neutron data with which to compare these results. It is significant that the total swelling (i.e., vacancies captured by voids) is roughly the same in the molybdenum and niobium samples.

The slightly reduced swelling in the TZM samples compared to the pure molybdenum appears to be mainly due to the factor of 2 to 3 lower void density in the TZM. This implies that the nucleation sites are not as numerous. If the total residual gas content is the controlling factor for nucleation, then one would expect more voids in TZM because it contains approximately 10 times more gas (Table 2). However, the addition of titanium and zirconium to the molybdenum could effectively getter the excess gas in solution, reduce the amount available for nucleation, and thereby reduce the swelling.

The fact that approximately the same results (in terms of voids) were obtained from nickel and tantalum bombardment of niobium at 900°C is important because it shows that a few hundred at. ppm of nickel-impurity atoms are not significantly affecting the nucleation process. Essentially no impurity effects are expected of tantalum in niobium because of their complete mutual solubility and similar chemical properties.⁴⁹ Even though it appears that we could use nickel or tantalum ions for bombardment of refractory metals, all future work will probably be conducted with the tantalum ions.

CONCLUSIONS

1. Helium gas is not required for the formation of voids in nickel, molybdenum, niobium, and TZM.

2. An increase in the displacement rate in nickel by four orders of magnitude over neutron irradiation does not significantly change the void-induced swelling when the shift of the effective temperature is taken into account.

3. Void-induced swelling saturates at approximately 4 to 5% in nickel that is bombarded with heavy ions at 525°C to more than approximately 50 dpa.

4. Voids form a three-dimensional superlattice in nickel and niobium which is consistent with the crystal structure of the lattice. Doping nickel with helium atoms does not alter the tendency for alignment.

5. There is little significant difference between void-induced swelling in molybdenum, TZM, or niobium over the 800 to 1000°C range at approximately 5 dpa.

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DISCUSSION BY ATTENDEES

Wolfenden: When the site occupancy on the void superlattice is not 100% (the usual case), one must use stereo microscopy to verify that the observed void superlattice in nickel is really fcc. Did you actually use stereo microscopy to verify the nature of your void superlattices?

Kulcinski: Yes. The void superlattices were fcc for nickel and bcc for molybdenum.

Harkness: What heat treatment did you give your samples after alpha bombardment but prior to ion irradiation? We have found that the heat-treating

procedure used after helium injection can significantly affect the resulting irradiated microstructure.

Kulcinski: We did not give the injected samples any heat treatment prior to irradiation other than that which occurred when the samples were raised to the irradiation temperature (525°C) for 1 to 2 hr prior to bombardment. We have examined the samples after helium injection but before having ion bombardment and also after 5 to 10 hr of annealing at 525°C . We find no visible evidence of damage above $30 \text{ \AA}$.

Wazzan: You stated that you irradiated nickel after preinjecting with helium to 3 at. ppM and found no helium effect on swelling. I have two questions: (1) Why did you not preinject to the levels that are more common in the reactor, such as 10 to 15 at. ppM helium? The 3 at. ppM helium at your dpa range may be too low to observe any effect. Also, is it possible that your sample prior to injection with helium contained enough gaseous impurities to overshadow any possible effect due to injected helium? (2) Did you inject with helium at room temperature? If yes, then when you irradiate at about 525°C , your helium may migrate to grain boundaries, etc., and void studies on such samples would not simulate reactor conditions where helium is being more uniformly and continuously produced during neutron irradiation and void formation in the reactor.

Kulcinski: First, we do not feel that preinjection of samples with helium is a good way to simulate the effect of gas produced by transmutations in a nuclear reactor. We feel that simultaneous injection of helium and charged particles is the proper way to conduct this type of experiment, and we are pursuing this approach. With respect to your first question, we have postponed the experiments involving higher helium concentration until simultaneous injection is possible. Yes, it is possible (see Table 1) that the amount of residual gases in the samples did override the effects of 3 at. ppM of helium. We did inject the samples with helium at room temperature, but, as I stated in my reply to Harkness, we could see no evidence of helium migration or precipitation at the bombarding temperature.

Nelson: I note that the saturation level of your nickel is somewhat lower than in our data at 525°C . I presume that this is a manifestation of your higher damage rate, inasmuch as our results correspond to the peak swelling temperature; whereas, owing to the temperature shift with damage rate, your results correspond to a region where the swelling-temperature profile is rising. Thus there is no basic discrepancy between the results.

Kulcinski: I agree that the differences between the absolute level of saturation in our experiments (4 to 5%) and yours (10 to 20%) should not be overemphasized. In addition to the fact that the defect production rates in our experiments were two to five times higher than yours, the starting materials were

different, the bombarding ions were different, and when helium doping was used, the values were significantly lower than yours. As you point out, Dr. Bullough has shown that the effective irradiation temperature is lowered with increasing displacement rate, and therefore, even though we both irradiate at 525°C, the effective temperature will be lower in our case. It is reasonable to assume that our lower saturation levels are then associated with the lower effective temperature.

Wiedersich: What method is used to determine the displacement rate and the total number of displaced atoms? With the high mass and energy of the ions, immediate recombination of defects in cascades may reduce the number of defects available for the swelling.

Kulcinski: The method that we use to calculate the displacement rate is described in our article in *Radiation Effects*, 1971. In this article we do not take into account thermal annealing of the defects, and we are essentially calculating the maximum number of atoms displaced at 0°K. Obviously the number that survives during high-temperature irradiation is considerably less, but, since we are concerned mainly with relative effects (i.e., effect of swelling on increasing displacements at a constant temperature), we feel that such a method of reporting the data is acceptable at this stage.

Ehrlich: At what displacement rates did you get the superlattice in fcc nickel? Did you change the displacement rate in your experiments?

Kulcinski: The displacement rates were 10^{-2} sec^{-1} for the samples in which the superlattice was found. We did not study the effect of displacement rates on the formation of this superlattice.

Chen: The authors did not detect an effect due to 3-ppm helium doping in nickel prior to irradiation. The early work on quenching using the electrical-resistivity technique indicated that at such a low concentration the probability of single-vacancy—single-vacancy encounter can be very small. In fact, that was approximately in the range where researchers on quenching used to obtain single-vacancy-migration energy from change-of-slope method. Now that the dimension, and hence the average sink distance, is smaller than usually used in quenching, it is possible that the majority of the helium atoms doped can be annealed out before bubbles are nucleated. A much higher dosage would be expected to enhance the effect of helium.

DEUTERON-GENERATED VOID FORMATION IN AUSTENITIC STAINLESS STEELS

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ABSTRACT

Simulation of in-reactor radiation damage in typical fast reactor core components by high-energy ion bombardment is discussed. The study was performed with several grades of austenitic stainless steel which were impregnated with helium to create an environment similar to that occurring during neutron irradiation and were subsequently bombarded with deuterons. Initial experimental conditions were selected to provide a damage state comparable to that caused by a neutron fluence of 1×10^{23} . The specimens were irradiated in target assemblies instrumented to permit constant temperature monitoring and close beam-focusing control. Results revealed the existence of voids in specimens irradiated within the temperature range 440 to 665°C. The voids were observed to be predominantly polyhedral, ranging in size from 52 to 699 Å and homogeneously distributed in any plane parallel to the bombarded surface. Void volumes as high as 10.1% were observed, this quantity having been measured in a region that experienced 20 to 40 displacements per atom (dpa).

One of the major technological problems affecting the development of a successful liquid-metal-cooled fast breeder reactor (LMFBR) is neutron-induced void formation. This type of radiation damage results in severe volume increases of fuel cladding and other critical core components. Swelling of common austenitic stainless steels (e.g., type 347) has been measured to be as high as 10% after fluences of 7 to 8×10^{22} neutrons/cm² ($E > 0.1$ MeV), at temperatures¹ of 468 to 538°C. This exposure, however, represents only one-fourth to one-third of the fluence anticipated for the cores of near-term breeder reactors.

Although the development and evaluation of materials that are more resistant to neutron-induced void formation are clearly required, this effort is hampered by the very long exposures (2 to 3 years) required to produce substantial swelling in existing reactors.

Fig. 1 Experimental flow sheet for General Electric deuteron-bombardment studies.

In recent years, various investigators have succeeded in accelerating the rates of void formation in metals and alloys by ion bombardment. These experiments have utilized both cyclotrons and heavy-ion accelerators to produce the required damage. Ions used to produce damage have included H^+ (Ref. 2), N^+ (Refs. 3 and 4), C^{2+} (Refs. 5 and 6), Ni^+ (Ref. 7), Cu^{2+} (Ref. 8), Se^{3+} (Ref. 9), and Fe^{3+} (Ref. 10). The purpose of this paper is to summarize the experimental methods and results obtained by deuteron bombardment of stainless steel in a cyclotron.

THE PRODUCTION OF DAMAGE

The various steps performed in the deuteron-bombardment experiments are summarized in Fig. 1. Details of each step will be discussed separately.

Design of the Instrumented Target

The target used for the deuteron irradiations is shown in Fig. 2. Specimens are sheets of 0.004-in.-thick stainless steel, 0.560 in. wide and 0.950 in. long.

Fig. 2 Cross section of the cyclotron target showing details of specimen and thermocouple attachment.

The target block is fabricated from OFHC copper and is machined to accept four sheath (grounded-junction) thermocouples. The Chromel-Alumel thermocouples are sheathed with 0.030-in.-diameter 304 stainless-steel tubing. Each thermocouple junction is radiographed and machined (if necessary) to a dimension equal to the thickness of the specimen foil. The specimen assembly is then brazed in vacuum at a temperature of 1550°F for 30 min.

Helium Implantation

In the present experiments, helium concentrations from 1 to 100 ppm were implanted into the stainless-steel targets. A depth of implantation of $\sim 25 \mu$ (0.001 in.) was obtained by bombarding with 24.6 ± 0.2 MeV alpha particles at an incidence angle of 13° . A schematic diagram of the experimental assembly used for helium implantation is shown in Fig. 3; the actual target assembly is shown in Fig. 4. The beam emerges from the cyclotron and passes through steering and focusing magnets. The shape of the beam is measured with a beam monitor and adjusted to the desired size and current. During this adjustment the beam stop is kept closed. When the desired beam conditions are obtained, the beam valve is opened. The beam passes through the first collimator, the rotating-wedge degrader, and the second collimator before striking the target. The ion current on the target is recorded and integrated to yield the total helium implanted.

Fig. 3 Assembly for helium implantation.

Fig. 4 Helium-implantation assembly showing instrumented target.

Fig. 5 Dimensions of aluminum-wedge degrader.

Penetration depths for the alpha particles were calculated from the equation

$$R_{\alpha}(E) = R_p(E/4)$$

and the range-energy data of Janni.¹¹

Aluminum degrader foils were fabricated in the form of individual wedges whose dimensions are shown in Fig. 5. Dimensions of each wedge were calculated to reduce the energy of the ion beam in a continuous manner. The wedges were prepared by pulling precut lengths of pure aluminum from a cylinder filled with 50% NaOH. If the pulling rate, the concentration, and the temperature of the solution are controlled, it is possible to routinely produce wedges of the required shape.

Immediately after helium implantation, an autoradiograph of the specimen surface is prepared. Subsequent survey of the autoradiograph using a microdensitometer provides the data for calculating local concentrations of helium. A typical map of densitometer data is shown in Fig. 6.

Deuteron Bombardment

After a short decay time, the helium doped targets are soldered to a water-cooled copper stage (Fig. 7). This stage consists of a flattened copper tube which in turn is attached to the internal probe of the cyclotron. The stage is formed such that the deuteron beam will strike the target at an angle of

Fig. 6 Distribution of helium over the specimen surface.

$6 \pm 1/2^\circ$. At this angle of incidence, the range of the 12.3-MeV deuterons in the stainless-steel target is 0.92 ± 0.07 mil. This angle was chosen to produce maximum damage at a reasonable depth from the surface of the specimen, to distribute the damage zone along the length of the target (thus assuring several specimens from a given irradiation), and to provide for better dissipation of the beam energy.

An example of a uniformly distributed deuteron beam is shown in the autoradiograph and densitometer traverses of Fig. 8. As shown, maximum intensity of the beam is centered along the line of thermocouples. The impingement zone of maximum intensity is approximately 1 mm wide and

Fig. 7 Assembly for internal deuteron bombardment.

25 mm long. The temperatures measured along the length of the two different targets are shown in Fig. 9. During the irradiation the thermocouple temperatures are monitored, and manual adjustments of the beam shape are made to maintain constant conditions. As shown in Fig. 9, the ion beam can be tuned to produce various temperature profiles along the specimen surface.

After bombardment for the desired length of time, the target is cooled to room temperature and removed from the cyclotron. The target is stored for a decay period of 1 to 2 days, after which an autoradiograph of the bombarded surface is made. Microdensitometer traverses across the autoradiograph are then

Fig. 8 Activity distribution on the surface of a deuteron-bombarded specimen.

used to construct a contour map (Fig. 8) showing the relative concentration of radioactivity on the surface of the specimen. This relative activity is a direct function of the number of ions per unit area which strike the target. Using activity data so collected, the local current density and deuteron flux at any location on the target can be calculated.

Depth-Displacement-Ratio Calculations

Two relations are used to calculate depth-displacement-ratio values for deuteron-bombarded specimens: (1) the relation between the remaining energy

Fig. 9 Temperature profile along typical targets during irradiation.

of an ion and the depth into the specimen and (2) the relation between the remaining energy and the displacement ratio per unit fluence. The former was calculated from the range-energy data of Janni.¹¹ The calculations of Yeh¹² were used to determine the displacement ratio vs. unit fluence relation.

Combination of the data from these relations yields the displacement ratio per unit fluence as a function of depth within the specimen (Fig. 10).

For the preliminary calculations used in this work, the absolute displacement-ratio-depth relation for a given target was obtained simply by multiplying each point in Fig. 10 by the ion fluence. The relation between the displacement ratio and ion energy is accurate only to energies >1.0 MeV. For lower energies the displacement ratio is merely an extrapolation of higher energy calculations. For these experiments the cutoff energy used for calculation of displacement ratios was arbitrarily chosen as 0.1 MeV. This relation defines the behavior of a single ion only. For many ions the straggling value must be taken into account (either analytically or experimentally) to reduce the peak damage zone and distribute the damage over a wider zone within the specimen.

THE OBSERVATION OF DAMAGE

Sample Preparation

Samples of irradiated targets were cut by electric-discharge machining of 3-mm-diameter disks at selected locations on the target. As many as six disks can be cut along the zone of peak damage. Typical sampling positions are shown in

Fig. 10 Atom displacement-depth relation in 304 stainless steel bombarded with 12.3-MeV deuterons. Fluence was 1.5×10^{19} ions/cm².

Fig. 8. These disks were removed by dissolving the Ag-Cu braze in a 50:50 solution of nitric acid at room temperature. Thinning of the specimens for electron microscopy must be carefully controlled. The technique consists of the following steps: electrolytically polishing the specimen from the bombarded side to a preselected depth below the surface, measuring the depth by X-ray absorption techniques, masking the prethinned surface, and, finally, polishing the specimen from the back to perforation. These procedures are illustrated in the schematic diagrams of Fig. 11. Details of the electrolytes used, as well as voltages and current densities, have been published previously.¹³

Examination of the Irradiated Specimen

Light microscopy, transmission electron microscopy (TEM), and small-angle X-ray scattering have been used to evaluate the type and magnitude of damage

Fig. 11 Foil-preparation technique for transmission electron microscopy.

produced by deuteron bombardment. Of the three, TEM constituted the principal mode of examination. Light optical metallography was successfully applied in delineating the depth of the damage zone (Fig. 12), thus confirming calculated penetration depths. Small-angle scattering (SAS) measurements have yielded quantitative data on void formation produced by neutron bombardment.¹⁴ Application of SAS techniques for quantitative analysis of deuteron-bombarded specimens, however, requires additional theoretical and experimental development.

The TEM specimens were examined with a JEM 6A electron microscope, an instrument with a peak potential of 100 kV. A number of electron micrographs sufficient to assure statistical coverage of the region of foil examined were prepared. These micrographs were photographically enlarged to a size convenient for optical analysis. Void counting and void-diameter measurements were performed with the aid of a Zeiss particle-size analyzer. These data were reduced using a computer program which calculated all the data required to characterize the type and magnitude of void damage produced.

Fig. 12 Cross section of deuteron-bombarded specimen of 304 stainless steel, showing the damage zone as revealed by etching and interference microscopy. Magnification, 800 $\times$.

RESULTS AND DISCUSSION

Comprehensive TEM examinations were made of 29 foils of austenitic stainless steel. The principal alloy investigated was type 304. Other alloys included type 321 and two modified grades of type 304—304Ti and 304LN. The former contains approximately 0.2 wt.% titanium; the latter, a low-carbon-base alloy, contains approximately 0.15 wt.% nitrogen. All were irradiated in the solution-annealed condition. Specimens of types 304 and 321 were irradiated for periods as long as 6 hr; the remaining specimens received 1- and 3-hr exposures.

All four grades of austenitic stainless steel tested showed evidence of extensive radiation damage, the type and magnitude dependent on the experimental conditions in the particular region chosen for examination. Voids constituted the principal type of damage. Void distributions in three of the alloys, irradiated at roughly comparable experimental conditions, are shown in Fig. 13. Vacancy clusters—the familiar “black spot” damage that is thought to precede the nucleation and growth of voids—were observed to be restricted to samples irradiated in the 300 to 400°C temperature range. Vacancy-cluster damage characteristic of that occurring in the austenitic alloys tested in this program is illustrated in Fig. 14. Only in the 304Ti specimens was there a conspicuous absence of observable voids. That this specimen did sustain

(a) TYPE 304

(b) TYPE 304LN

(c) TYPE 321

Fig. 13 Deuteron-generated voids in austenitic stainless steel: a comparative examination.

	304	304LN	321
Helium, ppm	20	20	20
Exposure, hr	3	3	3
Current, μA	198	180	205
Temperature, $^{\circ}\text{C}$	525	625	600
Depth, mils	0.85	0.92	0.87

Fig. 14 Typical vacancy-cluster damage produced in austenitic stainless steel by deuteron bombardment.

bombardment damage was evident, however, by the abundance of vacancy clusters.

The voids observed in these deuteron-bombarded specimens are qualitatively similar to those produced by fast-neutron bombardment, i.e., they are predominantly polyhedral and are homogeneously distributed in any given plane parallel to the surface of the specimen. In the long-term irradiations, denuded regions were observed to correspond to grain boundaries and matrix-precipitate interfaces. Figure 15 illustrates a denuded grain boundary in 304 stainless steel.

A semiquantitative comparison of the results obtained in this study can be made. Figure 16 presents the data of five separate investigators and relates the void volume formed by ion bombardment to the specimen temperature and the displacement ratio. The data shown in this figure have the following common features:

1. Specimens were annealed, 300-series austenitic stainless steels (including 304, 304LN, 304Ti, 321, and 316).
2. Void volume fractions were calculated from TEM data.
3. With the exception of the ANL⁷ and BNWL⁸ data, all specimens contained from 5 to 40 ppm helium.

The data represent ion-bombardment results obtained with deuterons, protons,^{2,7} carbon,⁵ and copper⁸ ions. For the sake of clarity, the data are presented for ranges of damage characterized by low (0.6 to 2.5) and high (10 to 40) displacement ratios. This method of presentation obscures subtle differences among materials and experimental methods. However, important conclusions can be obtained. For example, there is good agreement among the results of various studies with respect to the basic form of the swelling-temperature relation for these steels and with respect to the absolute magnitudes of swelling. In addition, the lower temperature limit for swelling is a function of displacement ratio and is $\sim 400^{\circ}\text{C}$ for high displacement ratios. The upper temperature limit is a function of the displacement ratio and appears to be in excess of 700°C , whereas the temperature for peak swelling is 575 to 600°C . Conclusions obtained from the General Electric data are that only one material (304Ti) failed to form voids when tested at conditions conducive to void formation. This swelling resistance is in qualitative agreement with preliminary reactor data of Bloom.¹⁵ Further tests will be made to confirm or correct this result.

In addition, two data points are shown in Fig. 16 which represent low displacement ratios but show substantial swelling and are not consistent with the balance of the low-displacement-ratio data. Both these data points were obtained from examinations of the surfaces of the bombarded specimens. They clearly suggest that the presence of an external surface favors (rather than hinders) the nucleation and growth of voids. This observation would be consistent with a higher affinity of the surface for interstitials than for vacancies. It should be noted that the datum of Kulcinski⁸ can support this conclusion. This result was

Fig. 15 Void distribution adjacent to a grain boundary in deuteron-bombarded 304 stainless steel.

obtained with 5-MeV Cu^{2+} ions having a range of 10^4 Å. The specimens did not contain helium; consequently void formations should have been suppressed. The substantial swelling observed therefore could be explained by the proximity of the surface.

A comparison of void formation by ion bombardment and by neutron irradiation is shown in Fig. 17. The reactor data¹ are normalized to a fluence of

Fig. 16 Void formation in 300-series steels by ion bombardment.

5×10^{22} neutrons/cm² ($E > 0.1$ MeV) (37.5 displacements/atom), and are therefore comparable to the high-displacement-ratio data obtained by ion bombardment. It is apparent that the ion-bombardment data are shifted to higher temperatures and higher swelling values with respect to the reactor data. Both these shifts must be accounted for analytically in order to use ion-bombardment data to predict in-reactor swelling. This comparison also serves a useful purpose in guiding ion-bombardment studies aimed at "saturation" effects. It is apparent that the maximum swelling produced by ion bombardment is three to four times that produced by neutron irradiation (for the same displacement ratio).

If the target fluence for a commercial reactor core is 3×10^{23} neutrons/cm² (225 dpa), this higher efficiency in converting vacancies into voids allows one to

Fig. 17 Void formation in 300-series steels by ion bombardment: a comparison with reactor data.

produce equivalent swelling by ion bombardment to displacement ratios of 60 to 75. The ion bombardment, however, must be performed at temperatures 50 to 100°C higher than the temperature for peak swelling in reactor.

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DISCUSSION BY ATTENDEES

McDonald: Can you explain why you obtained grain-boundary etching during deuteron bombardment? Do you credit it to sputtering, thermal etching, or some other phenomenon?

Armijo: The target material showed etched grain boundaries because it underwent sensitization (carbide precipitation) during irradiation. As a conse-

quence of this effect, the grain boundaries were etched by the nitric acid solution used to separate the target from its copper block.

Kulcinski: Do you notice any changes in the degree of void truncation with increasing amount of deuteron bombardment?

Armijo: A slight increase in the degree of void truncation with deuteron bombardment was observed, but it is somewhat difficult to distinguish this modification from that occurring with increasing irradiation temperature.

Bauer: Could you comment on the role of the D gas ($\sim 10^{19} \text{ cm}^{-2}$) in the void-formation process? Or is there evidence that the D gas migrates to the surface immediately?

Armijo: The diffusivity of hydrogen through stainless steels at the temperatures used in this work ranges from $\sim 10^{-6} \text{ cm}^2/\text{sec}$ for tritium to $\sim 10^{-5} \text{ cm}^2/\text{sec}$ for protons. Therefore the calculated quantity trapped in the target during irradiation was negligible. Tests will be made to measure the residual deuterium in the target.

Harkness: Do you have any evidence that helium content affects the void number density under deuteron bombardment?

Armijo: Although we have irradiated materials containing from 1 to 100 ppM helium, we have looked only at specimens containing 20 and 40 ppM. In these examinations the specimens with the higher helium content tend to show a higher void density.

Huebotter: General Electric has announced its choice of 321 stainless steel as the core material for its LMFBR Demonstration Reactor. With very little swelling data available on this alloy, what is the basis for expecting satisfactory performance of 321 stainless steel from a swelling standpoint?

Armijo: The selection of 321 stainless steel as the General Electric reference cladding was not based exclusively on resistance to swelling. Other important considerations are resistance to fuel-cladding reactions and resistance to decarburization and degradation of mechanical properties in sodium.

VOID FORMATION IN PROTON- AND NICKEL-IRRADIATED 304 STAINLESS STEEL

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ABSTRACT

The swelling of several samples of 304 stainless steel bombarded with 1.25-MeV protons or 3.5- to 4.0-MeV Ni^+ ions has been studied using quantitative stereo electron microscopy. The swelling of proton-bombarded samples is significantly greater than the Ni^+ -bombarded samples, and there was no indication of any saturation with dosage. Void formation occurred by sequential nucleation and growth.

As a means of expediting the study of swelling of cladding materials for fast breeder reactor applications, an ion-simulation capability has been developed at Argonne National Laboratory (ANL) using the 4-MV Dynamitron accelerator. Several samples of annealed 304 stainless steel have been irradiated with either 1.25-MeV protons or 3.5- to 4.0-MeV nickel ions to compare the influence of different bombarding ions on the swelling behavior. The structure of the damaged zone at various depths below the irradiated surface was examined using stereo electron microscopy. Some preliminary data for samples preinjected with helium ions are also presented.

EXPERIMENTAL PROCEDURE

The essential features of the beam-transport system and the target assembly used for the irradiations are illustrated in Fig. 1. The system was maintained at a vacuum of $<2 \times 10^{-6}$ torr using oil-diffusion pumps equipped with liquid-nitrogen-cooled baffles. The ion beam, which was of low divergence, was magnetically analyzed and rastered at a frequency of 10 kHz over the surface of the target using electrostatic deflector plates. Typical beam-on-sample conditions were either 100 μA of H_2^+ at 2.5 MeV or 0.5 μA of $^{58}\text{Ni}^+$ at 3.5 to 4.0 MeV. The slit aperture was 0.5 cm^2 or greater to provide at least four specimens at each

Fig. 1 Sample holder and beam-transport system used for ion bombardments.

irradiation. The target current was measured by periodically inserting the shutter into the beam. The current was checked calorimetrically and, in the case of the nickel bombardments only, is subject to a maximum correction of 12% due to particle neutralization. The average particle flux, obtained from the quotient of the shutter current and the aperture area, differs by less than 10% from the flux on each specimen. The spatial uniformity of the beam was continuously monitored by a wire-loop beam-profile scanner during the irradiation and by sweeping the beam across a narrow slit before commencing a run. The particle fluence quoted was obtained from the average of the calorimetric and beam-current measurements multiplied by the irradiation time.

Samples measuring 0.5 to 1 in. in diameter were cut from 0.015-in.-thick 304 stainless-steel sheet stock used in the ANL reactor irradiation experiments. The samples were either diffusion bonded to copper mounts 0.3 in. thick or brazed on with Ni-Ag alloy that had a melting temperature of 790°C. The sample mount and furnace block were clamped to the sample holder as illustrated. The temperature of the sample mount was controlled and measured by two Chromel K thermocouples that were clad in stainless-steel sheaths 0.025 in. in diameter and were inserted to a depth of 0.5 in. into 0.026-in.-diameter holes drilled in the side of the mount. The uniformity of the surface temperature of the sample was measured with an infrared pyrometer that had the emissivity set to equalize the surface and sample-mount temperatures with the beam off.

In the proton irradiations, spatial variation of the temperature across the surface was $\pm 10^{\circ}\text{C}$ of the mean surface temperature, the temperature gradient through the sample was $\approx 6^{\circ}\text{C}$ per mil, and the accuracy of the nominal irradiation temperature was $\pm 10^{\circ}\text{C}$. In the nickel irradiations the accuracy of the irradiation temperature was $\pm 2^{\circ}\text{C}$.

SECTIONING PROCEDURE

Electron-microscope specimens were sectioned at various depths below the irradiated surface by vibratory polishing.¹ The thickness of the layer removed in all samples, except the first proton irradiation, was established by measuring the depth of small hemispherical indentations in the surface using multiple-beam interference microscopy. Surface damage introduced by the mechanical polishing was removed by electropolishing the surface for ~ 1 sec. The accuracy of the depth determination was estimated at $\pm 1000 \text{ \AA}$. The accuracy of the depth of the foil in the initial proton experiments was $\pm 5000 \text{ \AA}$. Specimens were separated from the copper mount with nitric acid, the irradiated surface was stopped off with lacquer, and the specimen was dimpled and penetrated with a jet of electropolishing solution.

Quantitative metallographic analyses were performed to determine the distribution of the void and dislocation loop densities using stereo pairs of micrographs taken 5° apart with a Jem 200 electron microscope. The swelling is defined by $S = \Delta V/V - \Delta V$, where ΔV is the void volume.

DISTRIBUTION OF IONS AND ION DAMAGE

The rate of atomic displacement as a function of proton energy in the sample was calculated from the Rutherford scattering cross section using the Kinchin and Pease² model for defect formation. The mean proton energy at the measured depth of the electron-microscope foil was obtained from tabulations by Janni.³ The variation of the damage rate with depth in 304 stainless steel irradiated with 1.25-MeV protons is illustrated in Fig. 2.

The corresponding result for 3.5-MeV $^{58}\text{Ni}^{+}$ and 3.25-MeV $^{12}\text{C}^{+}$ calculated by Brice⁴ using the Lindhard theory is given in Fig. 3 together with the spatial distribution of the stopped ions normalized to 1. The magnitude of the Thomas-Fermi electronic stopping constant, used in these calculations (1.554), was taken from experimental determinations by Bowman et al.⁵ The result of a similar calculation by Brager, Kissinger, and Kulcinski⁶ at 5 MeV is also illustrated. An upper limit for the displacements per atom (dpa) may be obtained by dividing the energy deposition expressed in eV cm^{-3} by $0.82/2E_d$, where $E_d = 32 \text{ eV}$.⁷ Such calculations show that in the present energy range the intense damage zone is limited to about 1μ from the surface and varies by about

Fig. 2 Atomic displacement rate per unit current density vs. depth from the bombarded surface for 1.25-MeV protons on a stainless-steel target.

Fig. 3 Damage energy, and distributions of stopped ions normalized to 1, for 3.5- and 5.0-MeV $^{58}\text{Ni}^+$ and for 3.25-MeV $^{12}\text{C}^+$ on a stainless-steel target.

a factor of 3 between the surface and the peak. From the range straggling, it is found that the concentration of Ni^+ ions injected into the sample at the mean range is 1.85×10^{-2} atom fraction/(mC)(cm^2); however, at the depth of 0.5μ the concentration is reduced by an order of magnitude.

RESULTS

H_2^+ Irradiations

Data obtained from the quantitative microscopy of proton-irradiated samples at 450, 525, and 600°C are listed in Table 1. A plot showing the void number density, void diameter, and swelling vs. depth below the irradiated surface for the 525°C irradiation is given in Fig. 4, and micrographs of the voids at depths of 3.5, 5.2, and 8.2 μ are shown in Fig. 5. Void formation is confined to depths within the proton trajectory. With increasing depth, there is, in general, a progressive increase in the void number density, mean void diameters, and swelling corresponding to the four- to fivefold increase in displacement rate and total number of displacements in the extracted foils. The unexpected small value of the swelling observed in some samples between one-half and two-thirds of the range originates in a reduction of void growth that is uncompensated by an increase in number density in this region. Similar effects have been observed in proton-irradiated 316 stainless steel.⁸ The evolution of the microstructures with dosage which is apparent from the samples analyzed is as follows. At dosages ≈ 5 dpa, the structure consists of isolated Frank loops lying on (111) planes interspersed with a random array of small voids. A narrow depletion zone along a grain boundary was observed in one specimen irradiated at 450°C. The majority of the voids were not associated with any visible nucleation sites. The larger voids formed at 525°C and at 450°C were polyhedral shaped with (111) faces truncated by (100) planes. With increase in dosage (increasing foil depth), the mean void diameter increases, as does the minimum void size. Fewer faulted dislocation loops are visible, and a complex tangle of dislocations develops. The stereo micrographs indicate that above 30 dpa at 525°C the dislocation lines thread through the voids. The data for 450° irradiation show a similar trend.

Comparison of the above data with those obtained in the irradiation at $\sim 600^\circ\text{C}$ sheds some light on the temperature dependence of the swelling behavior. At 600°C a very rapid increase in swelling with depth was observed. At the 8.0- μ level, a swelling of 73% corresponding to a dosage of 35 dpa was measured. Other trends in the structure varied more slowly: dislocation structure was coarser, voids tended to be more rounded, and the mean void size increased. A rapid increase in void number density with temperature was noted in the number densities normalized to a constant dose rate. The normalization is justifiable on the basis of the linear relation between void number density and

TABLE 1
RESULTS OF QUANTITATIVE MICROSCOPY OF PROTON-IRRADIATED
304 STAINLESS STEEL

Temp., °C	Displacement rate, 10^{-4} dpa/sec	Dosage, dpa	Void diameter, Å	Void density, 10^{15} voids/cm ³	$\Delta V/V$, %	Dislocation density, 10^{15} dislocation loops/cm ²	Helium, ppM
450	3.2	16.6	102 ± 37	16	0.9		0
	4.7	24.5	127 ± 37	26	3.3		0
525	1.4	6.6	174 ± 43	0.87	0.3	2.8 (416 Å)	0
	1.8	8	237 ± 65	2.4	1.8		
	2.2	10	185 ± 55	1.5	0.6		
	3.7	20	325 ± 111	2.5	4.8		
	5.0	30	230 ± 70	7.0	4.4	1.1 (169 Å)	
600	4	14	480 ± 180	0.22	1.3		0
	4.7	16	428 ± 168	0.34	1.4		
	10	35	671 ± 238	2.7	73		
620	2.1	6	471 ± 192	0.16	0.9		0
500	3.1	5.1	263 ± 85	0.3	0.3		10
600	3.5	6	939 ± 322	0.056	2.4		10

Fig. 4 Void number density, mean void diameter, and swelling for proton-irradiated 304 stainless steel.

Fig. 5 Void structures at 3.5, 5.2, and 8.2 μ corresponding to Fig. 4.

displacement rate observed in these samples and proton-irradiated 316 stainless steel preinjected with helium.⁹

The effect of nucleation on the void number density and growth can be seen in the two samples irradiated at 500 and 600°C subsequent to a helium injection followed by an anneal at 800°C. At this temperature, helium is mobile and can

form small bubbles that subsequently grow into voids. Both samples, when compared with uninjected samples, showed reduced number densities and increased void diameter. This result is opposite to the refinement effect observed in samples preinjected with helium at room temperature prior to irradiation.¹⁰ Similar results were observed recently in Experimental Breeder Reactor II (EBR-II) irradiations of preinjected and subsequently annealed 304 stainless steels by Harkness and Kestel.¹¹

Ni⁺ Irradiations

Table 2 lists the results of the metallography of samples irradiated with Ni⁺ ions taken at depths of 0.2 to 0.4 μ . A detailed study of the damage vs. depth is still incomplete. Voids were observed in foils that received dosages of 25 dpa or more at 500 to 600°C. Compared with the proton-irradiated samples on the basis of calculated dosage, the microstructure of the Ni⁺-bombarded foils was significantly finer in scale. At 25 dpa at 500°C, black-spot damage was observed, and dislocation loops, which were mostly unfaulted, were small, as were the void diameters. The voids were randomly dispersed in the dislocation structure, many were intersected by dislocations, as previously observed, but the number density was significantly lower. With increase in temperature, coarsening of the structure, decrease in the void number density, and increase in mean void diameter were observed. The maximum swelling observed was 4.6% in a foil receiving a calculated dosage of 120 dpa at 600°C.

DISCUSSION

The similarity in the flux, fluence, and temperature dependences of void formation in 304 stainless steel under neutron irradiation¹³ to the ion-irradiation results observed in these experiments strengthens the basis of the ion-simulation technique as a tool for screening radiation-damage effects in reactor materials. However, from a comparison of the ion-bombardment swelling results published to date, it is clear that considerable effort will be required to establish reliable quantitative simulation of reactor irradiations.

The present results on 304 stainless steel are in reasonable agreement with published ion-bombardment studies carried out on 316 stainless steel by Keefer et al. using H₂⁺ bombardments,¹⁴ and by Kulcinski, Laidler, and Doran¹² using Cu⁺ ions. There is an order of magnitude larger swelling in H₂⁺ irradiations on the basis of the calculated number of displacements, compared with Ni⁺ irradiations. Results of a comprehensive study of swelling in 316 stainless steel by Hudson and coworkers¹⁵ indicate swelling magnitudes intermediate between the light- and heavy-ion irradiations up to intermediate dosages. The apparent reduction of swelling with increase in projectile mass might be due to recombination effects within the larger collision cascades. At higher dosages the data of Hudson et al. show clear evidence of a reduction in swelling rate above 40 dpa. Saturation

TABLE 2
RESULTS OF QUANTITATIVE METALLOGRAPHY OF Ni^+ -BOMBARDED
304 STAINLESS STEEL AND Cu^+ -BOMBARDED 316 STAINLESS STEEL^{1,2}

Temp., °C	Displacement rate, dpa/sec	Dosage, dpa	Void diameter, Å	Void density, 10^{15} voids/cm ³	$\Delta V/V$, %	Dislocation density, 10^{10} dislocations/cm ²
500	4×10^{-3}	20	121 ± 44	2.0	0.2	6.9
517	1.6×10^{-3}	33	270 ± 89	2.1	2.1	
	3.0×10^{-3}	60	278 ± 78	2.	2.3	
600	9×10^{-3}	120	342 ± 133	2.1	4.6	3.3
600	4.2×10^{-3}	18	145 ± 82	0.55	0.1	5.6
500*	2.7×10^{-2}	40	180	6.0	7.8	

* Cu^+ bombardment.

effects have also been reported in nickel-irradiated 316 stainless steel.¹⁶ Thus the absence of the decreased swelling rate in the H_2^+ irradiations is the most serious discrepancy in the ion-swelling data obtained to date.

Our results of swelling, void size, and number density for the H_2 irradiations at 525°C taken from foils at depths greater than one-half of the proton range agree very closely with the data of Keefer et al., whereas the 72% swelling observed at 600°C is consistent with the absence of saturation behavior. Significantly, foils taken closer to the bombarded surface showed fivefold less swelling, which suggests that the injected hydrogen affects the void growth. Further H_2^+ bombardments using a transmitted beam are required to determine the effect of hydrogen on swelling.

Although the energy of the ANL ion-bombardment system limits the range of self-ions to $\sim 1 \mu$, simulation of bulk behavior appears to be satisfactory. Within the errors of depth determination in the irradiations at 517°C, no loss of defects at the $\sim 0.2\text{-}\mu$ depth (1.6×10^{-3} dpa/1 sec) is apparent. Further, the magnitude of the swelling is comparable to that obtained with 5-MeV Cu^{2+} irradiation of 316 stainless steel, where the maximum damage occurs at a 50% greater depth than in the Ni^+ irradiation. We conclude that at high displacement rates, where the recombination of Frenkel pairs is predominant, the average diffusion distance (on a similar basis to that estimated by Li, Franklin, and Harkness¹⁷) is about 100 Å, so that vacancy loss to the surface has a minor influence on the void-formation kinetics. The unique advantage of the microampere Ni^+ beam capability is that it permits adequate sampling of the material in a single irradiation under condition where the displacement cascades are similar to a fast-neutron irradiation and where chemical contamination of the steel is avoided.

Some evidence may now be cited in support of the sequential nucleation-and-growth model for voids in H_2^+ -bombarded stainless steel. First, in 304 and 316 stainless steels, both the minimum void size and the mean size increase with dosage at constant temperature and ion flux. Second, the coarse structure observed at 6 dpa in the annealed helium-preinjected samples again suggests the observed void number density is determined in the very early stages of the bombardment. Third, since the number density can be normalized to a fixed dose rate after a finite dose where voids are resolvable in the microscope, the void number density corrected to a constant ion flux may be plotted vs. dosage. Such a correlation shows a weak dependence of number density on dosage over the range 1 to 50 dpa for both 304 and 316 stainless steels.

The average number density computed above was $3 \times 10^{15} \text{ cm}^{-3}$ for proton-irradiated 304 stainless steel and corresponds to 10^{-3} dpa/sec. This value is comparable to the void number density observed in selenium-irradiated nickel^{15,18} but contrasts strongly with the results of C^{2+} -irradiated 316 stainless steel, which show a rapid increase in the number density with dosage to a maximum of $3 \times 10^{16} \text{ cm}^{-3}$ for 25 dpa at 525°C. Number densities of this

magnitude were observed only in our H_2^+ irradiation at $450^\circ C$. The number density observed at $500^\circ C$, in Ni^+ -irradiated 304 stainless steel without helium was also approximately the same magnitude as the cited H_2^+ irradiation results. These comparisons lead us to believe that in the carbon-ion irradiation experiments the high number density of voids may be associated with carbide precipitation.

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DISCUSSION BY ATTENDEES

Wiedersich: How do you measure 75% volume increase from the electron micrograph?

Do you take into account the decreased average atom density at large swelling ($\Delta V/V$) in calculating the number of displaced atoms?

Taylor: We are emphasizing the very large swelling observed with proton irradiation as opposed to nickel-ion irradiation. The 75% value is the lower limit for the swelling for 35 dpa at 600°C if corrections implicit in your question are taken into account. Swelling was measured using stereo microscopy, and voids intersecting the surface were not counted. No account was taken of the swelling in calculating the displacement rate, and thus the dose was overestimated.

Corbett: Has anyone tried to construct a hologram from stereo images?

Taylor: We know of no attempt to construct holograms from stereo pairs. However, we think such an attempt would be a worthwhile contribution to stereo work.

SWELLING AS A FUNCTION OF DISPLACEMENT DAMAGE IN PROTON-IRRADIATED 316 STAINLESS STEEL

10-5

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ABSTRACT

Specimens of 316 stainless steel, preinjected with about 5 at. ppm helium, were proton irradiated at 500 and 600°C. Electron microscopy was used to determine volume swelling in specimens having undergone between 0.5 and 50 displacements per atom (dpa). Displacements were calculated from the Kinchin-Pease model with a threshold energy of 25 eV. Swelling at 500°C increased with damage up to about 25% for 50 dpa. No evidence of saturation of swelling with increasing fluence was observed. The minimum void size increased with damage, and the void density increased with atom displacement rate. These results imply occurrence of nucleation early in the irradiation, followed by continued void growth. A specimen having undergone 100 dpa at 500°C exhibited a void array which was so complex that a swelling determination could not be made. Ferrite, transformed from austenite during the irradiation, was detected in this specimen by electron diffraction as small crystallites within the austenite grains. Evidence of austenite-to-ferrite transformation was obtained for specimens with about 5 or more dpa. A specimen irradiated to about 20 dpa at 600°C exhibited frequent joining of voids to form a complex array. Preliminary examination indicates swelling at 600°C is greater than at 500°C. Voids are larger and less numerous at 600°C.

In order to gain information on void-induced swelling of candidate cladding alloys, we are pursuing a program of proton irradiation of several of these alloys. The objectives of this program are studies of the effects of atom displacement rate, total number of displacements, irradiation temperature, helium content, and microstructure on void formation and the resulting swelling. We also hope that the results of this program will lead to a correlation between proton and reactor irradiations. In this paper we will discuss progress achieved in several phases of the program for 316 stainless steel.

EXPERIMENTAL PROCEDURE

Specimens were irradiated at 500 and 600°C with protons having energies of either 0.75 or 1.0 MeV. The proton fluences were varied between 6×10^{17} and 1.3×10^{20} protons/cm² at a flux of about 1×10^{15} protons/(cm²)(sec). Specimen regions having undergone between 0.5 and 100 dpa were examined by electron microscopy.

The specimens used were 0.0127-mm-thick foils having cross-sectional dimensions of 1.78 × 0.88 cm. Each specimen was solution annealed at 980°C and then precipitation annealed at 760°C. Formation of M₂₃C₆ carbides at austenite grain boundaries occurs during the latter anneal.¹ The average grain size was 20 to 30 μ. After heat treatment, each specimen was diffusion bonded at 650°C to a copper support plate. During irradiation this plate served as a thermal conductor between the specimen and a temperature-control device.² Temperature control depended on proton-beam stability and was generally within ±5°C with periodic fluctuations of ±10°C.

Before irradiation, specimens were injected with helium by means of a cyclotron.³ As has been verified by mass-spectrometric analysis⁴ of sections of injected foils, these injections result in an even distribution of helium throughout the sample volume. The temperature of samples undergoing injection does not rise significantly above ambience. The helium content of samples discussed varied from 2 to 9 at. ppm.

After irradiation, each specimen was removed from its copper plate by immersion in nitric acid and cut into several sections. Electron-microscope foils were prepared from specific regions within the specimen thickness by electropolishing of a section. The thinning procedure was periodically interrupted so that X-ray absorption measurements could be made to determine the section thickness and hence the expected final foil position. Foil positions determined in this way are accurate within ±1000 Å.

The void number density and the distribution of void diameters in electron photomicrographs were determined by use of a particle-size analyzer. The void densities were calculated from estimated foil thickness. Contributions to the voidage for each size interval on the analyzer were determined and summed to give the total void volume.

The number of atom displacements for a given proton fluence and depth of proton penetration (i.e., proton energy) was calculated by using the Kinchin-Pease model.⁵ A displacement threshold energy of 25 eV was assumed. The proton energy as a function of penetration into the sample was determined from the work of Janni.⁶

DISCUSSION OF EXPERIMENTAL RESULTS

The results for all of the samples are given in Table 1, where they are arranged in order of increasing damage for each temperature. Since the damage produced

by the protons increases with penetration into the sample, several electron-microscope foils representing different degrees of damage can be extracted from the same irradiated sample.

TABLE 1

VOID FORMATION IN PROTON-IRRADIATED 316 STAINLESS STEEL

Sample No.	Temp., °C	He, at. ppm	Damage, dpa	Damage rate, 10^{-4} dpa/sec	Void density, 10^{15} voids/cm ³	Average void diameter, Å	Volume increase, %
28	500	9	0.46	7.0	1.8	52	0.018
6*	500	2	0.76	1.0	3.0	110	0.20
6*	500	2	1.1	1.5	9.6	70	0.19
36	500	4	2.3	1.7	0.85	190	0.38
6*	500	2	3.8	5.2	4.0	150	0.98
56A	500	6	4.8	3.9	4.3	230	3.4
36	500	4	9.2	7.0	3.0	240	2.7
56A	500	6	15	12	7.2	260	6.0
59	500	6	25	3.6	1.1	†	†
56B	500	6	38	8.8	4.0	360	13
56B	500	6	51	12	6.1	370	21
59	500	6	100	12	‡	‡	‡
38	600	6	16	6.8	1.6	590	20
38	600	6	21	8.6	2.0	590	24

*Data from Sample 6 are not included in Fig. 6 because of large uncertainties in proton flux.

†Results are considered invalid owing to sample distortion.

‡Gross swelling could not be measured on photomicrographs.

The increase in sample volume per unit volume (swelling) as a function of calculated number of displacements is shown in Fig. 1. The horizontal bars through the data points represent the variation in calculated atom displacements resulting from ± 1000 Å uncertainty in foil position along the proton path. The vertical bars represent the uncertainties encountered in determining the swelling from several photomicrographs of the same foil. These uncertainties are frequently well beyond the subjective error expected in operation of the particle-size analyzer and are thought to be real. Such variations in swelling may result from slight microstructural inhomogeneities within small regions of a sample. It is unlikely that significant inhomogeneities in helium content or proton density could occur over the small distances involved here.

The line through the 500°C data points in Fig. 1 was drawn according to a least-squares fit. The equation for this line is

$$\frac{\Delta V}{V} (\%) = 0.17N^{1.2} \quad (1)$$

where ΔV is the total void volume in a sample of volume V and N is the number of displacements per atom. In the region between about 1 and 50 dpa, there appears to be no change in the dependence of swelling on damage.

The data represented by the point at about 0.5 dpa in Fig. 1 were not used in the least-squares fitting. At this low damage, void formation is at an early stage, and the voids are very inhomogeneously distributed. Therefore accuracy of determining swelling is extraordinarily low, and the data were ignored in the fitting.

Fig. 1 Swelling at 500 and 600°C as a function of displacement damage for proton-irradiated 316 stainless steel containing helium.

Fig. 2 Voids in 316 stainless steel proton irradiated at 500°C to produce 50 dpa. (Sample 56B)

A photomicrograph of the void array in a specimen having undergone 50 dpa at 500°C is shown in Fig. 2. The minimum, average, and maximum void diameters are 95, 405, and 880 Å, respectively, the void density is 5×10^{15} voids/cm³, and the swelling is 24%. The morphology of these voids is typical of that obtained in other specimens irradiated to lower fluences at 500°C. As we have discussed previously,² the voids are bounded by {111} planes and frequently show truncation by {100} planes. Note that, although considerable void overlap occurs in Fig. 2, there is no evidence of voids having merged to form irregularly shaped agglomerates.

We have also irradiated a specimen at 500°C to 100 dpa. As can be seen in Fig. 3, the void array has become more complex with increasing damage, and we are as yet unable to determine an accurate swelling value for this sample. It is interesting that during this irradiation a portion of the sample was transformed from austenite to ferrite. Electron diffraction studies have shown that the ferrite occurs as small crystallites within the austenite grains. Because of the variation in displacement damage through the irradiated portion of the sample, it is difficult to determine the amount of transformation which is typical of the region that underwent 100 dpa. In this region we estimate, from X-ray diffraction measurements, that more than 10% of the austenite was transformed to ferrite.

Fig. 3 Voids in 316 stainless steel proton irradiated at 500°C to produce 100 dpa. (Sample 59)

Ferrite has not yet been positively identified by electron diffraction of samples irradiated to lower fluences. However, those samples containing regions in which roughly 5 or more dpa were created are magnetic. The degree to which the samples exhibit magnetism increases with increasing displacements. We have previously observed irradiation-induced austenite-to-ferrite transformation in 321 stainless steel, where the extent of transformation was greater than in type 316 (Ref. 7).

A specimen containing no helium has been irradiated at 500°C to approximately 5 dpa. Voids were produced, but the density was several orders of magnitude lower than that observed in samples containing helium. Void nucleation appears to be significantly enhanced by helium. Further, the hydrogen introduced during proton irradiation apparently plays no significant role in the nucleation of voids.

The voids produced by an irradiation at 600°C to 21 dpa are shown in Fig. 4a. Note that void faceting is somewhat less distinct than at 500°C and that there is considerable evidence of voids having joined to form elongated complexes. As can be seen from Fig. 1 and Table 1, the average swelling at this displacement level is about 24%, whereas at 500°C the same damage produces only about 7% swelling. Also, the voids produced at 600°C are less numerous and larger than at 500°C.

Fig. 4a Voids in 316 stainless steel proton irradiated at 600°C to produce 21 dpa. (Sample 38)

Ferrite was detected by electron diffraction of the sample irradiated at 600°C. A small region of ferrite growing from a grain boundary is indicated in Fig. 4b. Since no ferrite was observed by microscopy of samples irradiated to about 20 dpa at 500°C, this preliminary result suggests the austenite-to-ferrite transformation occurs more readily as the irradiation temperature is increased to 600°C.

In Fig. 5 we show the maximum, average, and minimum void diameters plotted as functions of the number of displacements created by irradiation at 500 and 600°C. The lines through the 500°C data are drawn according to least-squares fits. The increase in the minimum void size with increasing damage is particularly interesting. This means that void nucleation occurs relatively early in an irradiation and that further defect production merely leads to growth of already-existing voids. Such an effect is not unexpected in view of the fact that in these experiments the entire helium content is injected prior to irradiation.

In irradiation at 500°C, no dependence of void density on the number of atom displacements has been observed. However, as is shown in Fig. 6, a distinct dependence of void density on atom displacement rate has been found. From Fig. 6 it is apparent that a higher displacement rate can result in an enhancement of void nucleation rate. Note also that, from Table 1, an increase in displacement rate at 600°C leads to an increase in void density. These results are in agreement

Fig. 4b Micrograph showing a region of ferrite that transformed during irradiation.

Fig. 5 Maximum, average, and minimum void diameters as functions of displacement damage for proton-irradiated 316 stainless steel.

Fig. 6 Void density as a function of atom displacement rate in proton-irradiated 316 stainless steel.

with the observation made above that nucleation of voids occurs early in an irradiation.

SUMMARY

In proton irradiations performed at 500°C, the volume swelling increases nearly linearly with the number of atom displacements. At least up to a damage of 50 dpa, there is no evidence of a "saturation" of swelling. Even at very large values of swelling, the voids show little evidence of agglomeration. The irradiations cause a progressive transformation of austenite to ferrite with increasing number of atom displacements. An increase in the minimum void size with the number of atom displacements and an increase in void density with atom displacement rate both suggest that void nucleation occurs relatively early during the irradiation.

The swelling observed after 600°C irradiation to about 20 dpa is greater than that at 500°C. The void number density is lower, the average void size is larger, and agglomeration of voids is frequent at 600°C.

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DISCUSSION BY ATTENDEES

Gruber: Do you observe voids within the ferrite grains?

Keefer: We have not observed voids within the ferrite regions in 316 stainless steel. In 321 stainless steel the voids have apparently formed prior to ferrite transformation since regions of constant void orientation are commensurate with the original austenite grain size.

Bement: One mechanism proposed for strain-induced martensite formation in austenitic stainless steel involves, firstly, the strain-induced formation of an epsilon phase [hexagonal close packed (hcp)] which develops in a stacking-fault

sequence with the face-centered cubic gamma phase. The epsilon phase then transforms, presumably isothermally, to a ferrite, alpha, or quasi-ferrite (alpha-prime) phase. Do you believe that this type of transformation could be involved in the radiation-induced ferrite formation that you observe? If so, would you agree that hydrogen introduced by the proton beam could assist in stabilizing the stacking faults (by lowering the stacking-fault energy due to chemisorption), thereby stimulating transformation of austenite to ferrite?

Keefer: We do not believe the strain-induced formation of the epsilon phase can occur under our experimental conditions. Further, we have seen no evidence of an hcp phase in our diffraction studies. Should stacking faults occur, it seems doubtful that the quantity of hydrogen present in our samples is sufficient to significantly affect them.

Armijo: Can you describe any experiments to measure residual hydrogen in your steels? What is your conclusion with respect to residual hydrogen in the steel?

Keefer: Yes, we have measured the hydrogen content in an irradiated 316 stainless-steel sample. For a proton fluence of 5.9×10^{18} protons/cm², hydrogen content was increased by 300 at. ppM over the residual content. Thus about 0.5% of the protons remained as hydrogen in the sample. Since the void density was about 3×10^{15} voids/cm³, this amounts to about 8×10^3 hydrogen atoms per void, assuming all of the hydrogen was trapped in voids. Also, Robertson of the North American Rockwell Science Center has done hydrogen-permeation measurements on unirradiated 316 stainless-steel foils. He has calculated that during our irradiations the instantaneous hydrogen concentration in the lattice is approximately 10 at. ppM. Typical proton fluxes are about 10^{15} protons/(cm²)(sec).

Conrads: What was the primary energy of the protons?

Keefer: Two incident proton energies were used: 0.75 and 1.0 MeV. Microscope foils were extracted at proton penetration distances where the energy was about 0.61, 0.44, and 0.12 MeV.

THE OBSERVATION AND THEORY OF THE VOID LATTICE IN MOLYBDENUM

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ABSTRACT

Experimental observations of the void lattice in molybdenum irradiated with 2-MeV N^+ ions are presented together with a theoretical discussion of its formation. The observations take the form of electron micrographs and clearly show that the void lattice is body-centered cubic (bcc) and oriented precisely parallel to the underlying molybdenum atomic lattice. The theoretical discussion is based on the conjecture that its existence must be a direct consequence of the elastic interaction between pairs of voids in the (cubic) anisotropic molybdenum. This interaction has been used to show that such a stable bcc lattice can exist at a definite ratio of void-lattice parameter to void radius. This result has been obtained by both explicit summation of the noncentral void-void interaction and by a direct and accurate reciprocal lattice procedure.

Recent observations of Evans^{1,2} and Wiffen³ have demonstrated the remarkable ability of voids in irradiated molybdenum to form a regular array rather than a random distribution. Subsequently Malén and Bullough⁴ provided the basic theoretical explanation of the phenomenon and gave an approximate calculation of the energy per void in such a void lattice.

The energy per void was obtained by first calculating the explicit elastic void-void interaction and then directly summing this over the void lattice; the inaccuracies involved arose because the real space Green's function for an anisotropic (cubic) elastic body cannot be obtained in closed form and the lattice sums are only slowly convergent. Both these objections have been removed by an approach due to Stoneham⁵ who obtained the required energy per void directly by using Fourier-transform methods; the Fourier transform of the Green's function is a very simple analytic function, and the required energies can be obtained by simple finite sums over points of the first Brillouin zone of the molybdenum lattice.

In this paper we present some of the experimental observations on the void lattice in molybdenum irradiated with nitrogen ions, followed by a brief discussion of the pertinent features of the two theoretical studies referred to. Finally, the observations are compared with the theoretical predictions, and the possible technological significance of the phenomenon is discussed.

EXPERIMENTAL DETAILS AND RESULTS

The specimens, in disk form suitable for irradiation and subsequent electron microscopy, were prepared from four-pass-electron-beam zone-refined molybdenum. Annealing the disks in high vacuum for several hours near their melting point produced a well-characterized low-dislocation-density material with resistance ratios consistently in the region of 6000. For the irradiations the single-crystal disks (oriented so as to preclude channeling) were held in a high-temperature stage⁶ and bombarded with 2-MeV nitrogen ions in the Harwell Van de Graaff accelerator. The penetration of the nitrogen in molybdenum and the variation of the displacement damage with depth were calculated⁷ on the basis of the Lindhard, Scharff, and Schiott model and also investigated experimentally⁸ utilizing an electropolishing method to examine, by transmission electron microscopy, the damage at various depths in a single irradiated specimen. The following results were obtained on a specimen irradiated with N^+ ions at 870°C and with a calculated displacement dose of 100 displacements per atom (dpa) at the examined depth in the foil.

The first micrograph, Fig. 1, demonstrates convincingly the regularity of the void positions in the specimen and shows the coincidence of the lattice directions with those of the host molybdenum lattice. A point of interest is that the lattice even contains "dislocations," and two of these are indicated by the white arrows. By tilting the specimen to the remaining two perfect orientations, Figs. 2 and 3, the cubic symmetry of the lattice becomes apparent, and further consideration indicates, Fig. 4, that the lattice crystallizes in a bcc array. The measured "lattice parameter" of the array was $220 \text{ \AA} \pm 10 \text{ \AA}$ while the void radius was approximately 20 Å, giving an associated void swelling of 0.6% on the assumption of a perfect lattice. The identification of the electron microscope images as voids has been discussed previously;² furthermore Wiffen³ and Eyre⁹ have confirmed that voids produced in molybdenum by neutron irradiation can form arrays with similar characteristics to those shown in the present paper.

THEORY OF THE VOID LATTICE

Since the void lattice is observed to be oriented parallel to the underlying molybdenum atomic lattice, it is clear that its formation must be due to the nature of the void-void elastic interaction when the cubic anisotropy of the

Fig. 1 Electron micrograph showing the regularity of the void positions and the coincidence of the lattice crystal directions with those of the molybdenum. The micrograph was taken with the foil tilted to $z = [011]$ thus showing a projection of the lattice in the $[011]$ direction. The white arrows indicate "dislocations" within the void array.

molybdenum is included. In fact, Willis and Bullough¹⁰ have shown that in an isotropic medium two such voids (or gas bubbles) will always attract each other, and thus a stable void-lattice configuration would be impossible. The required effects of anisotropy can be included by two rather distinct but equally illuminating procedures. In the first approach⁴ explicit expressions for the noncentral void-void interaction are obtained and then used to examine the stability of the void lattice; this procedure has the advantage that one can clearly see the nature of the pairwise void-void interaction and its dependence on the degree of elastic anisotropy. In an alternative procedure⁵ the required lattice criteria are obtained directly and with no intermediate steps to degrade the accuracy of the final result.

The Explicit Void-Void Interaction⁴

Eshelby¹¹ has shown, in his discussion of the general ellipsoidal inclusion, that in a body with cubic anisotropy the spherical void can be exactly simulated

Fig. 2 Projection of void array in the [010] direction.

Fig. 3 Projection of void array in the [111] direction.

Fig. 4 The projection of a bcc lattice along the [010], [011], and [111] directions together with micrographs showing projections of the void lattice in the same directions.

by an appropriate effective spherical inclusion. This implies that the required elastic field around an isolated void may be generated by a uniform spherical shell of radial body force of appropriate strength P per unit area, where the radius of the shell is equal to the void radius r_v and the body is homogeneous and continuous; the magnitude of P is directly proportional to the actual surface tension force $2\gamma/r_v$ acting radially inward on the void surface.

The displacement field $u_i(\mathbf{x})$ associated with such a spherical shell of body force can be expressed directly in terms of the Green's tensor, $G_{ij}(\mathbf{x})$, of the infinite (perfect) body

$$u_i(\mathbf{x}) = r_v^2 P \int_{\Omega} n_j G_{ij}(\mathbf{x} - r_v \mathbf{n}) d\Omega \quad (1)$$

where the integral is taken of the surface of the unit sphere and n_i are the Cartesian components of the unit-radius vector. If $\mathbf{n}^1$ and $\mathbf{n}^2$ are the unit-radius vectors associated with two such voids whose centers are a distance R apart, then the interaction energy between the voids takes the form

$$E(R) = -P^2 r_v^4 \int_{\Omega^1} d\Omega^1 \int_{\Omega^2} d\Omega^2 n_i^1 G_{ij}(R + r_v \mathbf{n}^2 - r_v \mathbf{n}^1) n_j^1 \quad (2)$$

where the integrals are over the surfaces of the two-unit spheres associated with each void. If we expand the Green's function in a Taylor series and perform the repeated unit-sphere integrations, we find

$$E(R) = \left(\frac{4}{3} \pi P r_v^3 \right)^2 \left[G_{ij,ij}(R) + \frac{r_v^2}{5} G_{ij,ijkk}(R) \right] \quad (3)$$

where the comma notation indicates partial differentiation.

If the voids have a morphology that departs strongly from a sphere, then the inclusion model is no longer valid. Such a situation prevails if the voids are faceted, and then a star of forces, with appropriate cubic symmetry, is probably a better representation of the void than the above spherical shell model.

Siems¹² has given the general expression for the interaction energy between two such stars of forces in terms of the multiple moments of the forces, and it may easily be shown, for example, that if the two stars have bcc symmetry* then

$$E(R) = \left(\frac{8}{3} P' r_v \right)^2 G_{ij,ij}(R) - \left(\frac{8}{9} P' r_v^2 \right)^2 \left[2G_{ij,ij(jj)}(R) - 3G_{ij,ijkk}(R) \right] \quad (4)$$

To obtain explicit forms for the interaction energies (Eqs. 3 and 4), we have used the representation of G_{ij} obtained by Dederich and Leibfried.¹³ This is an

*That is eight equal radial forces P' acting along the $\langle 111 \rangle$ directions and disposed at points on the void surface $r = r_v$.

analytic perturbation expansion valid for moderate departures from elastic isotropy. Our final results, using the molybdenum elastic constants, are, for the spherical void interaction energy (from Eq. 3),

$$E(R) = -2.85 \times 10^{-14} P^2 r_v^3 \left[\left(\frac{r_v}{R} \right)^3 - 2.8 \left(\frac{r_v}{R} \right)^5 \right] (3 - 5S_4) \quad (5)$$

and, for the bcc faceted voids,

$$E(R) = -3.47 \times 10^{-13} \frac{P'^2}{r_v} \left[\left(\frac{r_v}{R} \right)^3 - 18.57 \left(\frac{r_v}{R} \right)^5 \right] (3 - 5S_4) \quad (6)$$

where

$$S_4 = (x_1^4 + x_2^4 + x_3^4)/R^4$$

and Eq. 6 has been obtained by omitting terms of $O(r_v/R)^7$ and certain small anisotropic correction terms;⁴ this truncation of the multipole expansion involved in Eq. 6 is certainly a source of inaccuracy in Eq. 6, and quantitative conclusions drawn from Eq. 6 can hardly be reliable; the direct treatment discussed below is much more reliable for such multipole situations. The spherical void result (Eq. 5) is, however, quite accurate, since the series expansions in Eq. 3 completely terminate when the analytic Green's function is used.

The energy per void $E_L(a)$, when the voids crystallize into a bcc lattice with a lattice spacing a , can now be written.

For the spherical void lattice,

$$E_L(a) = -2.85 \times 10^{-14} P^2 r_v^3 \left[\left(\frac{r_v}{a} \right)^3 K_3 - 2.8 \left(\frac{r_v}{a} \right)^5 K_5 \right] \quad (7)$$

where K_3 and K_5 are the lattice sums

$$K_S = \sum_l \left[3 - 5 \frac{(l_1^4 + l_2^4 + l_3^4)}{l^4} \right] l^{-S} \quad (8)$$

This lattice has an equilibrium spacing when $E_L(a)$ is a minimum, which occurs when

$$\frac{a}{r_v} = \left(\frac{14}{3} \frac{K_5}{K_3} \right)^{1/2} \quad (9)$$

The lattice sums (Eq. 8) have been evaluated out to the 25th shell ($l = \langle 400 \rangle$) to yield

$$K_3 = 5.23, \quad K_5 = 10.54$$

and thus, from Eq. 9, the lattice of spherical voids should have a lattice spacing such that

$$\frac{a}{r_v} = 3.07 \quad (10)$$

In a precisely analogous fashion, we find that this ratio for the lattice of faceted voids is larger (~ 8), although this latter result cannot be relied upon.

The Energy per Void: A Direct Evaluation⁵

Two basic physical assumptions were made in the analysis in the last section. First, it was assumed that the voids could be represented by an appropriate array of body forces. Second, the effects of the voids on the elastic properties of the host were ignored: the perfect-lattice Green's function was used rather than that for the imperfect lattice. In the present section we make these assumptions but make no further approximations. We exploit the periodicity of the void lattice to derive results that are exact for this model.

The host lattice distorts under the action of the body forces which represents the voids. The displacements can be found from the equilibrium equation, and the change in energy may be written formally:

$$\Delta E = -\frac{1}{2} \sum_{l,l'} \mathbf{F}_l^* \mathbf{G}_{l,l'} \mathbf{F}_{l'} \quad (11)$$

This is the sum of the work done by the body forces $\mathbf{F}_l$ and the lattice strain energy; $\mathbf{G}_{l,l'}$ is the perfect-lattice Green's function. The equation is written in a form appropriate to a discrete host lattice and is readily transformed into the continuum form if necessary. This equation can be rewritten in terms of the Fourier transforms $\bar{\mathbf{F}}$ of the forces $\mathbf{F}$ and $\bar{\mathbf{G}}$ of the Green's function

$$\Delta E = -\frac{1}{2N} \sum_{\mathbf{q}} \bar{\mathbf{F}}(-\mathbf{q}) \bar{\mathbf{G}}(\mathbf{q}) \bar{\mathbf{F}}(\mathbf{q}) \quad (12)$$

where the sum is over the N points in the first Brillouin zone of the host lattice; N is the number of atoms in the crystal.

Equation 12 is the key to the solution. First, we may exploit the periodicity of the void lattice: the $\bar{\mathbf{F}}(\mathbf{q})$ terms are finite only for values of $\mathbf{q}$ which are reciprocal lattice vectors of the void lattice, so the sum in Eq. 12 is a finite sum.

If there are n^3 host lattice atoms for every void, then the sum has n^3 terms, of which many are related by symmetry. Secondly, the continuum form of $\bar{G}(q)$ can be found analytically and exactly; no approximations are needed even for highly anisotropic crystals. Thus ΔE can be found exactly.

Calculations have been made for various possible force arrays F representing the voids. All have cubic symmetry. We have used simple cubic ($\langle 100 \rangle$), bcc ($\langle 111 \rangle$), fcc ($\langle 110 \rangle$), and spherically symmetric arrays to represent each void and some combinations of these. In principle the F should be chosen to give the correct faceting observed in isolated voids, but this has not proved practical so far. Of these arrays, only the simple cubic case fails to give a stable lattice. The predicted ratio of void-lattice parameter to void radius is very similar to the values given in the last section. For a bcc array the ratio is about 3.1 and is lower for the fcc or spherical arrays. However, higher values can be achieved for linear combinations of the force arrays, albeit at the expense of reducing the lattice binding energy. Thus a combination of bcc and simple cubic arrays leads to a ratio of about 4.5.

DISCUSSION

The fact that the theoretical analysis does indeed predict a finite lattice parameter for the void lattice is, we believe, a good indication that the basic theoretical explanation for the formation of the lattice is probably correct. The discrepancy in magnitude of the predicted ratio of the void-lattice parameter to the void radius (~ 3) and the observed ratio (~ 10) is unfortunate but probably arises both from our inability to precisely model a faceted void and our omission of the induced interaction between the voids. In an isotropic body the stress field outside a spherical void is a pure shear field, and thus the induced interaction (inhomogeneity interaction) is the only nonzero interaction. As we have previously remarked, this interaction is, in an isotropic body, always attractive,¹⁰ and, if it remains attractive when anisotropy is included, it would further reduce the lattice parameter. However, in an anisotropic body this interaction would certainly become noncentral and could well become repulsive in certain directions and thus perhaps actually increase the lattice parameter toward the observed ratio. Further work on this interaction is continuing.

Again the relative success of the theory certainly suggests that the voids are probably randomly nucleated on a scale that depends primarily on temperature, and then the voids grow until the critical ratio a/r_v is reached when the voids will crystallize to form the void lattice. If this is so, then the existence of the void lattice with its associated gain in lattice free energy should provide an interesting barrier for the further growth of the voids, since the ratio a/r_v could not then easily remain constant. Finally, the theory predicts that such a void lattice could occur only in materials with the appropriate anisotropy such as niobium, molybdenum, chromium, and vanadium. It will be interesting to see if indeed

such lattices are found in these materials and not in materials where the anisotropy is such that

$$C_{11} < C_{12} + 2C_{44}$$

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DISCUSSION BY ATTENDEES

Brudnoy: How do your calculated lattice spacings compare with experiments?

Bullough: Experimental spacings in molybdenum are measured to be ~ 9 , although some measurements are ~ 4 . It could be 10,000, you know, so we are in the right ball park.

Seeger: This morning we were told that nickel shows a face-centered cubic (fcc) lattice. How do you account for the fcc lattice in nickel?

Bullough: Well, the point is we have not done the lattice sums over fcc, but I have no reason to think that it would be unstable if we put in the right anisotropy for nickel.

Seeger: Why the fcc lattice in nickel and the body-centered cubic (bcc) lattice in molybdenum?

Bullough: We have checked the fcc and simple cubic here, and the energy per lattice atom is lower in bcc in this calculation. We have not done the same calculation for nickel.

Harkness: What is the interaction energy of the voids when they are ordered? Since it is of the order of thermal energy, why are not the effects swamped by Brownian motion?

Bullough: The interaction energy is certainly very small, but the lattice is nevertheless mechanically stable. For thermal stability we have to compare the free energy of the voids arranged in the lattice with the free energy of the same concentration of voids in random arrangements. The gain in elastic energy/void thus need not be large because of the large decrease in entropy.

Wiffen: Void ordering has been observed at the Oak Ridge National Laboratory in neutron-irradiated tantalum, in which the isotropy requirement of your model is not satisfied. Is there a ready explanation for this apparent conflict with your model?

Bullough: At the moment no, but the observation emphasizes the necessity for including the inhomogeneity effect in our calculation. This interaction is, for spherical voids, the only interaction when the body is isotropic. It is thus perhaps unreasonable to omit it in this anisotropic analysis. We are at present working on this problem, which is not too easy in an anisotropic body.

Kulcinski: It is interesting to note that our results on aligned voids show that the a/r_v value is approximately 7 for niobium irradiated at 800°C to 5 displacements per atom (dpa) and ~ 3 for nickel irradiated at 520°C to 400 dpa. (See the paper by Kulcinski, Brimhall, and Kissinger, this conference, page 449.)

Bullough: These ratios are certainly pleasantly close to our theoretical values. We intend to apply the theory to the fcc superlattice in nickel to see if it remains consistent.

THE APPLICATION OF HIGH-VOLTAGE ELECTRON MICROSCOPY TO VOID STUDIES

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ABSTRACT

Electron irradiation in a high-voltage electron microscope is employed to study factors affecting void nucleation and growth in nickel, stainless steel, and nickel alloys. It is found that the number of voids nucleated depends on the implanted gas concentration, irrespective of whether it is introduced by ion bombardment or by transmutation reactions during neutron irradiation. In stainless steel, nucleation can occur without implanted gas. An analysis is given of the effects of electron irradiation on neutron-induced voids. Void growth is shown to depend on the number and behavior of dislocations, both those preexisting and those developed during irradiation. Swelling rates in nickel indicate that maximum void growth occurs for an intermediate dislocation density. It is suggested that swelling is reduced by cold work and by precipitates because they restrict dislocation climb and by impurities because they reduce interstitial migration rates and thus increase the recombination rate.

Studies of radiation-induced voids employing reactor irradiations are time-consuming, expensive, and sometimes difficult to interpret because of the complex effects produced by neutrons. Hence there are strong incentives to develop simpler techniques for investigating the nucleation and growth of voids. One such technique is electron irradiation with the beam of a high-voltage electron microscope (HVEM).¹ Advantages of the technique are the direct, continuous observation of microscopic behavior during irradiation and the continuous production of single point defects in a well-controlled manner, without transmutation effects, without the introduction of impurities, and without collision cascades. A typical atomic displacement rate obtainable in a 1-MV microscope is 10^{-3} sec^{-1} , and this factor converts irradiation times into dose, the units being displacements per atom (dpa). The dose scale used here in

Fig. 1 Examples of voids grown by electron irradiation in the HVEM: (a) truncated cuboids in nickel and (b) truncated octahedra in stainless steel. The projection is $\langle 110 \rangle$ in each case.

reporting the results is based on a displacement cross section of 41 barns for 1-MeV electron irradiation of nickel.

The general characteristics of void growth, as observed during electron irradiation in the HVEM, have been described in a number of papers.²⁻⁷ Typical examples of voids grown in this way are shown in Fig. 1. It has been found that a void grows during irradiation only when one or more dislocations are adjacent to it and that individual voids consequently show widely differing growth rates, occasionally even shrinking, and that coalescences occur. With increasing irradiation temperature, void size increases and void concentration decreases, as for neutron irradiation. Because specimens are thin foils, surface effects are important and must be taken into account in any experiment. It has been established that dislocations more readily absorb interstitials than vacancies and thus create excess vacancies that produce void growth.

A difficulty with experimental investigation of void nucleation is that the nuclei are submicroscopic. The HVEM technique provides a means of growing invisible void nuclei to a size such that they can be observed, without, in nickel, creating fresh nuclei in the process.¹

This paper discusses some features of recent HVEM work at Berkeley Nuclear Laboratories on the nucleation and growth of voids.

NUCLEATION STUDIES

Ion-Bombarded Nickel

Electron irradiation produces voids in nickel previously given an energetic gas-ion bombardment. The ions He^+ , Ne^+ , and Ar^+ at 50 to 150 keV have been

TABLE 1

EFFECT OF IMPLANTED GAS CONTENT ON THE VOID CONCENTRATION
PRODUCED BY ELECTRON IRRADIATION

Material	Method of gas injection	Injected gas concentration, ppM	Electron irradiation temp., °C	Void concentration, 10^{14} voids/cm ³
Stainless steel		0	450	0.69
Stainless steel	He ⁺ bombardment at 20°C	0.1	450	0.86
Stainless steel	He ⁺ bombardment at 20°C	10	450	15
Nickel	Ne ⁺ bombardment at 20°C	1	420	1.8
Nickel	Ne ⁺ bombardment at 20°C	100	420	25
Nickel	Neutron irradiation at 50°C	1	400	1
Nickel	Neutron irradiation at 400°C	2	400	0.1
Nickel	Neutron irradiation at 400°C	25	400	2.5
Nickel	Neutron irradiation at 400°C	50	400	3

used with success, even if the specimen was then annealed before electron irradiation.³ On the other hand, specimens bombarded with 120-keV Ni⁺ ions to a similar dose produced a drastically reduced void density on electron irradiation.⁴ It must be concluded that void nucleation is controlled by the concentration of implanted gas atoms and that collision cascades are much less important. The gaseous impurities present in 99.995% pure nickel do not produce observable nucleation. Table 1 shows how the number of voids produced increases with the concentration of implanted gas. It should be emphasized that voids grow to sizes several orders of magnitude larger than could be explained if they were equilibrium gas bubbles. The gas atoms therefore play a role at the nucleation stage, but not subsequently except indirectly.

Ion-Bombarded Stainless Steel

The nucleation of voids in EN58A and EN58B stainless steels has been investigated⁵ using helium-ion bombardment prior to electron irradiation. Increasing the helium content increases the frequency of occurrence of voids (Table 1) but does not have a significant effect on the mean void size. Also, voids are produced in steels that have not been preinjected with helium. This indicates that commercial materials contain a sufficient residual gas content, or other heterogeneities, capable of acting as nuclei. For example, a residual gas content of 1 ppM could, in principle, produce 10^{15} bubbles/cm³ of approximately 20 Å diameter each.

Neutron-Irradiated Nickel

Studies have been made of voids nucleated by fast neutrons in thick foils (50 μ), which are subsequently thinned down for further irradiation by 1-MeV

Fig. 2 A comparison of void densities produced by electron irradiation of nickel containing 1 ppM of implanted gas, produced by (a) neutron irradiation and (b) Ne^+ ion bombardment.

electrons. Figure 2 compares the results of electron-irradiating two nickel specimens, both injected with gas to a concentration of approximately 1 ppM. The first specimen (Fig. 2a) was neutron irradiated to a dose of $2 \times 10^{18} \text{ cm}^{-2}$ at 50°C in vacuo prior to electron irradiation, and the other specimen (Fig. 2b) was implanted with Ne^+ at room temperature. Table 1 shows that the number of voids nucleated is the same, within the experimental uncertainties, in the two cases. Where neutron irradiation was at 400°C , the void concentrations were found to be characteristic of the neutron irradiation and little affected by the subsequent electron irradiation. Electron irradiation at 400°C produces lower void concentrations than neutron irradiation at 400°C . The increased displacement rate, $1.2 \times 10^{-3} \text{ sec}^{-1}$ for electrons as opposed to $3 \times 10^{-8} \text{ sec}^{-1}$ for neutrons, is expected to produce effects characteristic of a lower temperature⁸ and may be an explanation of the observations.

STRAIN FIELDS AROUND VOIDS

Voids in stainless steel are often first revealed by the imaging of strain fields (Fig. 3). Voids are resolved within the strain-field image when they have a side length $\geq 50 \text{ \AA}$. With increasing size, the image of the void is progressively enhanced and that of its strain field is diminished. The gas content in these cases is between 10 and 100 times less than that required to stabilize a gas bubble of the size at which the voids are first resolved.

THE EFFECTS OF ELECTRON IRRADIATION ON NEUTRON-INDUCED VOIDS

Pure nickel foils, previously irradiated by fast neutrons to doses between 2×10^{18} and 1×10^{20} neutrons/ cm^2 at temperatures of 50, 400, and 450°C ,

Fig. 3 Strain fields around voids in stainless steel (multibeam conditions).

have been electron irradiated in the HVEM between 400 and 450°C. In this way the subsequent growth and shrinkage of voids under the influence of electron irradiation have been studied in situ.⁶ For neutron doses $\geq 5 \times 10^{19}$ neutrons/cm², where observable voids are produced, the initially uniform distribution throughout the foil is modified by electron irradiation due to the surface denuded layers (Fig. 4). Void growth occurs in a central region, of thickness given by the ratio of the void concentrations, and is correlated with their morphology as a function of electron dose. Initially, {111} octahedral voids convert by progressive {100} truncations to a cubic shape, the transition coinciding with the onset of linear growth (Fig. 5). The reduced void volume fraction increases linearly with displacement dose up to 9% at 45 dpa.

Voids receiving a large prior neutron dose appear to be more stable, as they have a higher gas content and a greater resistance to shrinking. This would explain the much smaller denuded layer observed in the higher dose specimens (1×10^{20} neutrons/cm²) than would be expected purely from temperature considerations alone. A similar resistance to shrinking in higher gas content voids has been observed⁹ in thermal annealing of voids in neutron-irradiated nickel.

IRRADIATION-INDUCED DISLOCATION STRUCTURES

Nickel

Void growth depends on the number and arrangement of dislocations. It is therefore important to investigate how dislocation structures develop during

Fig. 4 Total void volume fraction, $\Delta V/V$, and concentration, N/V , as functions of electron dose at 400°C. Voids were initially produced by neutron irradiation at 400°C.

irradiation. Figure 6 shows how dislocations can be temporarily pinned at voids. Some examples of the variation in visible dislocation density with electron dose are shown in Fig. 7. Curve A was obtained for pure, annealed nickel at 320°C. Dislocation density increases linearly with dose up to 1 dpa, this relation resulting from the linear loop growth law.¹⁰ Then loops interact with each other and with the foil surfaces, and loop loss becomes comparable with loop growth. At a higher irradiation temperature, most dislocations disappear from a thin foil because of such interactions. Curve B of Fig. 7 is for a thin foil that was ion bombarded before electron irradiation. In this case, voids are grown, and the increase in dislocation density at doses ≥ 15 dpa is associated with increased dislocation pinning at the voids.⁴ A similar increase occurs, curve C of Fig. 7, where voids are initially produced by neutron irradiation (prior to electron irradiation) at 400°C.

Void growth behavior has been shown to vary according to the dislocation structure. In one series of experiments⁷ with thin foils of nickel, a drastic loss of dislocation line length occurred as loops interacted. Correspondingly, the void

Fig. 5 The change in void morphology during electron irradiation coincides with the onset of linear swelling.

Fig. 6 Dislocations pinned by voids in nickel.

Fig. 7 The variation of visible dislocation density with electron dose in nickel: (A) untreated, (B) with previous ion bombardment, and (C) with previous neutron irradiation.

growth rate was observed to decrease. Figure 8 shows several stages in dislocation development in a different series of experiments in nickel.⁴ The loop growth phase is over by a dose of 0.4 dpa, much too low for any significant void growth to have occurred. The loops have interacted to become an array of relatively straight dislocations, climbing as they absorb point defects and terminating at the foil surfaces (Fig. 8b). In this situation, swelling is proportional to the square of the electron dose. At higher doses, dislocations tend to intersect the voids (Fig. 8c), and the dislocation density increases. In this situation, swelling is linearly proportional to dose. It is argued that this behavior is likely to be typical of bulk material.

Stainless Steel

Loops grow, interact, and produce a dislocation network in solution-treated stainless steel as in nickel. Continued irradiation produces a general decrease in the dislocation density. The dislocations are mobile, and the network constantly changes. In the dose range 0 to 4 dpa, voids do not present serious obstacles to dislocation movement. The higher the temperature, the lower the dislocation density and the more rapidly is the network established. The dislocation

Fig. 8 Irradiation-induced dislocation structures in nickel at different stages of electron irradiation at 420°C: (a) 0.2, (b) 2.7, (c) 11, and (d) 30 dpa.

structures are similar to those reported after 20-MeV C^{2+} ion bombardment of stainless steel.¹¹ Electron irradiation also induces the precipitation of small carbide particles within the grains. This effect is less marked in solution-treated and aged material, which otherwise behaves similarly.

ELECTRON-DOSE DEPENDENCE

In HVEM experiments, it has been found that swelling, $\Delta V/V$, is due mostly to increases in size rather than in number of voids. Individual voids grow at widely varying rates, depending on the proximity of dislocations. At low doses in the HVEM, the relation $\Delta V/V \propto (\phi t)^2$ has been found^{2,5} (stage 1 behavior). Examples are shown in Fig. 9. At higher doses a linear dose dependence has been found^{3,6} (stage 2 behavior), and examples are shown in Fig. 10. Stage 1 appears

Fig. 9 Log-log plots of swelling vs. electron dose for stage 1 in nickel at 450°C and EN58B stainless steel at 500°C.

to be typical of thin-foil irradiations and is absent in the case where voids formed by neutron irradiation are subsequently grown by electron irradiation.⁶ The swelling rate is defined as the increase in $\Delta V/V$ for a dose increment of 1 dpa and is the net flow of vacancies to voids as a fraction of all vacancies created. In stage 2 the swelling rate is constant, but the dislocation density is observed to be increasing with dose. Table 2 compares some experimental values found for different conditions in nickel. There is a trend toward a lower swelling rate with a higher dislocation density. On the other hand, a very low dislocation density reduces void growth.^{2,7} Thus there is an optimum condition for void growth at an intermediate dislocation density.

Differences between the electron and heavy-ion¹² results can be understood in terms of surface effects and different dislocation densities. This also applies to a comparison with neutron results, although accurate comparisons are difficult because of uncertainties in calculating the number of displacements. It may be

Fig. 10 Log-log plots of swelling vs. electron dose less a threshold value in (A) EN58B stainless steel at 500°C, threshold 3.2 dpa; (B) nickel at 450°C, previously argon-ion bombarded, threshold 5.5 dpa; and (C) nickel at 400°C, previously neutron irradiated, threshold zero.

TABLE 2
SWELLING RATES IN NICKEL

Type of irradiation	Dislocation density, 10^{10} dislocations/cm ²		Temp., °C	Swelling rate, %	Ref.
	At 3 dpa	At 30 dpa			
HVEM	0.5	1.6	450	0.34	3
HVEM	0.9	3.2	400	0.24	6
20-MeV C ²⁺	2.0	5.0	525	0.15	12

concluded that the presence of displacement cascades does not have a large effect on void growth.

The two characteristic dose dependences found in HVEM experiments arise naturally from a simple model. Initially the dislocation density rises as loops grow. The loops then interact to create an equilibrium dislocation density, when loop loss through interaction is balanced by increase through irradiation. These two situations lead to the following dose dependences. In the first, the net flow of interstitials to loops is equal to the net flow of vacancies to voids, if there are

no other point defect sinks. We assume the number of interstitials aggregating in loops to be proportional to the dislocation line length. Thus the swelling at time τ is given by:

$$\Delta V/V \propto \int_0^\tau r \, dt$$

where r is the loop radius. Since, experimentally,¹⁰ $r = At$ at time t , where A is constant, we have:

$$\Delta V/V \propto \tau^2$$

In the second situation, when the dislocation density is constant, a similar argument produces the result:

$$\Delta V/V \propto \tau - \tau_0$$

where τ_0 is a constant. Thus the model predicts the observed dose dependences in HVEM experiments, although dislocation structures are not always those assumed.

POSSIBLE METHODS FOR CONTROL OF VOID SWELLING

Void growth occurs if the following conditions are satisfied:

1. Dislocations are present to absorb interstitials preferentially.
2. Dislocations are free to climb, and only in so doing can they absorb interstitials.
3. Interstitials must be able to migrate rapidly to dislocations, otherwise the probability of recombination with vacancies increases.

These factors suggest methods for swelling control which do not rely on the introduction of vacancy sinks.

Dislocations

Experiments with cold-worked nickel⁷ have shown that a high dislocation density produces an inhomogeneous and low void density. No interstitial loop growth is observed, and void growth rates are erratic. Thus cold work reduces the swelling, and one reason is that dislocations are prevented from climbing.

Precipitates

Dislocation movement may also be restricted by introducing a fine precipitate dispersion. Figure 11 shows such a case in Nimonic 80A, electron irradiated after a preliminary ion bombardment.

Fig. 11 Nimonic 80A following ion bombardment and electron irradiation. Interstitial loop growth is restricted by the γ' particles.

On reaching a diameter comparable with the interparticle spacing, loops were observed to cease to grow, which was clearly due to interaction with precipitates. Prolonged irradiation failed to promote further loop growth, and no void formation was observed in the time during which voids would grow in annealed nickel.

If precipitates are to influence the void characteristics, they should be distributed on a scale similar to that of the voids. Preferably they should be coherent with the lattice in order that the precipitate/lattice interface is not a ready sink for the annihilation of interstitials. The coherency should be maintained by the precipitates being resistant to overaging, remaining small, and maintaining the fine distribution. These are severe requirements, particularly under irradiation conditions where the "effective temperature" of the material is raised. The influence of precipitation on void growth is likely to result from a pinning of the dislocation network and a consequent decrease in the number of interstitial sinks.

Impurities

A reduction in interstitial velocity and thus in void growth can be achieved through the introduction of impurities, which bind with the interstitial. Figure 12(a) shows an example of the effect in Nimonic PE16, which was heat-treated to produce a coarse precipitate dispersion so that no loop-precipitate interaction occurred. Electron irradiation after preliminary ion

Fig. 12 Interstitial loop growth and interactions in (a) Nimonic PE16, which was heat-treated to produce a coarse precipitate dispersion and then ion bombarded and electron irradiated, and (b) pure nickel given the same irradiation treatment.

bombardment produced little growth of loops compared with pure nickel under the same condition [Fig. 12(b)], even for extensive periods of irradiation. No voidage was observed at the irradiation temperature chosen, $\sim 450^{\circ}\text{C}$.

CONCLUSIONS

"In situ" electron irradiation of thin foils in an HVEM provides a rapid method of simulating irradiation damage produced in materials exposed to the fast reactor environment. However, in drawing conclusions relevant to bulk conditions, allowance must be made for the effects of the proximity of the specimen surfaces in thin foil experiments and the high damage rate during electron irradiation.

Voids have been grown in pure nickel and in stainless-steel alloys in the temperature range 0.3 to 0.5 T_m ($^{\circ}\text{K}$).

In pure nickel the presence of gas—by injection or by (n,α) , (n,p) reactions—is essential for the nucleation of voids. In stainless steel, there is a sufficient residual gas content, or other heterogeneities, to nucleate voids. In both materials, an increase in the gas content increases the number of voids nucleated but decreases their mean size.

The relation between the dislocation concentration, and its distribution, and the formation and the growth rate of voids is predicted and observed.

Experiments on alloys indicate that void growth can be controlled by a limitation of the density of interstitial sinks, by the pinning of dislocations at precipitates, and by decreasing the mobility of interstitials, by solute/impurity-point defect interactions.

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Part of the presentation of this paper consisted of the showing of a film made from a sequence of micrographs. Some extracts are shown in Fig. 13.

Fig. 13 Voids growing in a nickel specimen at 450°C and seen at dose increments of 1.4 dpa.

DISCUSSION BY ATTENDEES

Kulcinski: Can you unambiguously state that nucleation is solely governed by inert-gas atoms without performing similar preinjection studies with other gas atoms such as oxygen or nitrogen?

Norris: Our experiments with He^+ , Ne^+ , and A^+ ion bombardment indicate that void nucleation in nickel is controlled by the concentration of implanted gas atoms. We do not find gaseous impurities dissolved in nickel to be effective as nucleating agents during electron irradiation. We suppose that these dissolved gas atoms are trapped in some way and are unable to move rapidly to avoid embryo, which therefore fails to become stabilized. We have not yet carried out preinjection studies with oxygen or nitrogen ions.

Balluffi: There must be a large number of significant subthreshold energy exchanges between the incident fast electrons and lattice atoms in your experiments. Conceivably, these could affect the kinetics of many of the processes involved. Have you considered such an effect in your work?

Norris: No.

Young: In one of your micrographs, there was a denuded zone around the grain boundary, and this zone had a width $\sim 0.1 \mu$. How thick was your sample?

Norris: The sample was about 0.5μ , and, obviously, when the denuded layers become comparable with this, one can get misleading impressions about what the denuded layer looks like.

Sandusky: It was demonstrated by the time-lapse photography that the dislocations were constantly in motion in the foil during irradiation. Was the specimen subjected to thermal stresses due to the electron beam? If this was not the case, what was causing the dislocation motion?

Norris: We calculate that the temperature rise due to beam heating is $\sim 10^\circ\text{C}$. Dislocation motion does not occur with a 100-kV beam in which the beam heating effect is greater than at 1 MV. This shows that the thermal stresses are not sufficient to move dislocations in our experiments. Dislocations move because a larger number of interstitials than vacancies are annihilated at them.

APPLICATION OF HIGH-VOLTAGE ELECTRON MICROSCOPY TO THE STUDY OF VOIDS AND OTHER POINT-DEFECT AGGLOMERATES

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ABSTRACT

The paper surveys the principal features of the study of defect agglomerates, in particular, voids, in high-voltage electron microscopes, in which the defects may be simultaneously generated and observed. The possibilities offered by this approach are contrasted with the requirements of reactor development. The calculation of the stationary defect distribution in the thin foils used in electron-microscope experiments is briefly reviewed. Theoretical considerations about the nucleation and growth of defect agglomerates in such foils are developed and compared with experiments on pure and oxygen-contaminated nickel foils. The majority of the theoretical conclusions were verified by the observations in a 650-keV high-voltage electron microscope.

In modern high-voltage electron microscopes, operating typically with accelerating voltages between 500 kV and 1.5 MV, the electron beam generates permanent displacements of atoms in a wide variety of metals.¹ To problems arising in connection with the development of large-scale fast breeder reactors, high-voltage electron microscopes may be applied in either one of two ways:

1. Fundamental studies of the nucleation and growth of voids and other defect clusters may be performed. Here the irradiation of foils in high-voltage microscopes has the following advantages: (a) The basic radiation-damage pattern is very simple, consisting essentially of isolated vacancies and self-interstitials. The damage rates are uniform across the specimen thickness and may be calculated from collision theory. (b) The sink geometry is simple. Conditions may be arranged so that the stationary state is mainly maintained by vacancy-interstitial recombination, with the foil surfaces being the next important sinks. Additional sinks (voids and dislocation loops) may be observed in the electron microscope, provided they exceed a minimum size. (c) The growth of voids and other defect clusters, such as dislocation loops, may be followed directly in the electron microscope. (d) Temperature, damage rates,

stationary defect concentrations, etc., may be easily varied between wide limits. (e) In contrast to bombardment by foreign ions (implantation!) and reactor experiments (transmutations, spallation, and fission products!), impurity effects may be avoided or controlled. (f) In contrast to bombardment by self-ions, equal numbers of self-interstitials and vacancies are generated, as in reactor irradiation.

2. Because the electron beam can be focused on areas with diameters of 3 to 5 μ , electron-flux densities of the order of magnitude 10^{20} electrons/(cm²)(sec) may be achieved. In the 650-keV Hitachi microscope used in our experiments, the displacement rate in nickel may be as high as 1 displacement per atom (dpa) in 10^3 sec. This is several orders of magnitude more than in reactor experiments. It is therefore possible to observe void growth up to extremely high doses in a relatively short time.

However, when a realistic simulation of reactor conditions is intended, high-voltage electron microscopy has a number of weaknesses: (1) Displacement cascades may have an effect on void nucleation. Thus heavy-ion bombardment is better suited for simulating reactor conditions at high doses. (2) In contrast to reactor experiments, impurities are not introduced during the electron irradiation. (3) Because of the high defect production rates, the steady-state defect concentrations at a given temperature are much higher than in a reactor, resulting in increased void growth. (As noted previously, the relations connecting defect concentration, defect production rate, diffusion coefficients, etc., are nonlinear and, in general, quite involved.) (4) Foils and bulk specimens respond differently to dislocation movement (i.e., plastic deformation). The dislocation densities reached after a high dose are therefore likely to be quite different in bulk material and in foils. In view of what will be said later, this may lead to different growth rates and saturation values for the total void volume.

STATIONARY DISTRIBUTION OF DEFECTS IN IRRADIATED FOILS

The simultaneous irradiation and observation in the electron microscope require the use of rather thin specimens, with thicknesses of the order of magnitude of a thousand angstroms. Since the foil surfaces may act as one of the principal sinks for the point defects generated, the foil thickness must be taken into account as one of the physical parameters, and its influence on the stationary point-defect concentration must be discussed.

We describe the diffusion of vacant sites by an effective diffusion coefficient, $D_V(C_V)$, that is a function of the total vacancy concentration, C_V (per atom), with the corresponding assumption $D_I = D_I(C_I)$ for the self-interstitials. The stationary distributions in a foil $-d/2 \leq z \leq d/2$ is governed by

$$\frac{d}{dz} \left[D_V(C_V) \frac{d}{dz} C_V(z) \right] - \alpha C_V(z) C_I(z) + \Phi = 0 \quad (1a)$$

$$\frac{d}{dz} \left[D_I(C_I) \frac{d}{dz} C_I(z) \right] - \alpha C_V(z) C_I(z) + \Phi = 0 \quad (1b)$$

with the boundary conditions

$$C_V(\pm d/2) = C_I(\pm d/2) = 0 \quad (2)$$

The recombination of vacancies and interstitials is characterized by

$$\alpha = \frac{4\pi r_0}{\Omega} [D_V(C_V) + D_I(C_I)] \quad (3)$$

where r_0 is an effective capture radius, Ω is the atomic volume, and Φ is the defect production rate per atomic volume.

Seeger² has derived the following general solution of Eqs. 1 and 2:

The intermediate integral

$$\int_0^{C_V} D_V(C'_V) dC'_V = \int_0^{C_I} D_I(C'_I) dC'_I \quad (4)$$

furnishes a relation $C_I = C_I(C_V)$, which may be used to eliminate C_I from Eq. 1a. The solution of Eqs. 1a and 2 is then

$$z = \pm \int_{C'_V=C_V}^{C'_V=C_V^{\max}} \frac{D_V(C'_V) dC'_V}{\sqrt{c_1 - 2I(C'_V)}} \quad (5a)$$

where

$$I(C_V) = \int_{C'_V=0}^{C'_V=C_V} D_V(C'_V) [\Phi - \alpha(C'_V)C_I(C'_V)C'_V] dC'_V \quad (5b)$$

The constant of integration, c_1 , is determined by Eq. 2.

For sufficiently thick foils, the concentration in the middle of the foils may be estimated by neglecting the diffusion terms in Eq. 1 (bulk conditions); the $C^{\max}$ values are then obtained from Eq. 4 and

$$C_V^{\max} \times C_I^{\max} = \Phi/\alpha \quad (6)$$

Note that α increases rapidly with increasing temperature.

We have applied the general theory to the following model involving local equilibrium between monovacancies (diffusion coefficient D_{1V}) and divacancies (diffusion coefficient D_{2V}):

$$D_I = \frac{2}{3} \times a^2 \times 2 \times 10^{13} \text{ sec}^{-1} \exp(-0.99 \text{ eV}/kT)$$

(concentration independent)

$$D_V = D_{2V} - \frac{D_{2V} - D_{1V}}{\sqrt{1 + \beta C_V}}$$

$$D_{1V} = a^2 \times 5 \times 10^{13} \text{ sec}^{-1} \exp(-1.38 \text{ eV}/kT)$$

$$D_{2V} = \frac{a^2}{6} \times 2 \times 10^{13} \text{ sec}^{-1} \exp(-0.80 \text{ eV}/kT)$$

$$\beta = 48 \exp(\Delta S/k) \exp(E_{2V}^B/kT)$$

$$\Delta S = 1.8k = \text{divacancy association entropy}$$

$$E_{2V}^B = 0.30 \text{ eV} = \text{divacancy binding energy} \quad (7)$$

Here a denotes the length of the elementary cube edge. The numerical parameters have been chosen appropriate for nickel.³⁻⁵

Evaluation of Eq. 4 for this model gives

$$D_1 C_I = D_{2V} C_V - \frac{2}{\beta} (D_{2V} - D_{1V}) (\sqrt{1 + \beta C_V} - 1) \quad (8)$$

Fig. 1 Point-defect distribution in nickel foils of various thicknesses at 700° K. Φ = the defect production rate per atomic volume.

Equation 5b may be evaluated in closed form too. Examples for the profile resulting from the numerical integration (with $r_0 = 3a/2$) of Eq. 5a are shown in Fig. 1. Figure 2 gives the widths of the "denuded" boundary layers for different temperatures.

For sufficiently high temperatures, T ($\beta \ll 1$), one may disregard the divacancies. Equation 4 takes the well-known form

$$C_I D_I = C_V D_V \quad (9)$$

Fig. 2 Width w of the "denuded layers" at the surfaces of nickel foils. (w is defined by a 1% deviation from the concentrations $C^{\max}$ at the center of the foil.) Φ = the defect production rate per atomic volume.

$C_I(z)$ and $C_V(z)$ may then be expressed in closed form in terms of elliptic functions.²

The preceding calculations may also be applied to grain boundaries acting as perfect sinks.

THEORETICAL CONSIDERATIONS ON THE NUCLEATION AND GROWTH OF DEFECT AGGLOMERATES

If a stationary distribution of point defects (see above) has been established, then the rates at which interstitials and vacancies anneal out must be the same. If voids were the only sinks, they could thus not grow to observable sizes. Void growth can only occur in the presence of another type of sink that is distinctly more effective for interstitials than for vacancies and is capable of taking up the excess interstitials. Surfaces are unlikely to provide this asymmetry to a sufficient extent. Dislocation loops form sinks for both interstitials and vacancies; because of their stronger elastic interaction with interstitials, the dislocation loops attract on the average more interstitials than vacancies and are thus capable of providing the required asymmetry. Thus, once an interstitial-

type dislocation loop has been nucleated, it may grow. In a thin foil the balance of the vacancies may anneal out at the surfaces. However, nuclei for vacancy agglomerates will, in general, shrink again since they will capture more interstitials than vacancies, except when the nuclei have formed on the compressional side of an edge dislocation. The elastic interaction forces the interstitial atoms to flow preferentially through the dilation side, whereas on the compressional side the vacancy concentration is somewhat enhanced compared with the stationary bulk value. This mechanism for the stabilization and growth of nuclei of vacancy agglomerates (voids or dislocation loops) is effective as long as the vacancy agglomerates remain in the compressional strain fields of the dislocation loops that cause the local unbalance between vacancy and interstitial flow.

There is a critical void size above which the collapse to dislocation loops is energetically favorable. The presence of gaseous impurities with low solubility counteracts this tendency, either by setting up an internal pressure in the void⁶ or by forming a chemisorbed layer on the void surface. The collapse is prevented if the available impurities stabilize the voids near their critical size; once the voids have grown much larger than the critical size, the energy barrier for collapse is so large that the voids are metastable even without stabilization by impurities or by dislocation strain fields.

The absorption of the excess interstitials causes the dislocation density to increase substantially during void growth. This increase is expected to limit eventually the further growth of voids since the increasing dislocation density will capture a larger and larger fraction of the vacancies generated and since the efficiency of a dislocation for capturing more interstitials than vacancies decreases as the separation between dislocation and void decreases (see Ref. 7 for the effects of competing sinks for the capture efficiency of dislocations).

EXPERIMENTAL RESULTS

The following experiments, carried out on (001)-nickel foils (purity 99.995%), illustrate and verify the preceding conclusions.

Formation and growth of interstitial-type loops during irradiation were observed between 20 and 570°C. In addition, vacancy-type loops were observed^{8,10} from about 200 to about 420°C. The vacancy-type loops were indeed found to grow only in the compressional strain field of edge dislocations, as shown in Fig. 3. Here large interstitial loops had been formed during irradiation at 420°C. Further irradiation at 250°C led to the formation of small vacancy-type dislocation loops inside the periphery of the interstitial-type loops, i.e., on the compressional side of the edge dislocations.

The principle that a vacancy loop can grow only as long as the compressional strain at its location is sufficiently large is illustrated by Fig. 4, which shows a large interstitial loop with a small vacancy loop at its center. As the interstitial

Fig. 3 Vacancy-type loops formed on the compressional side of interstitial-type loops.

(a)

(b)

(c)

Fig. 4 Shrinking of a vacancy loop located inside an interstitial loop during irradiation at 250°C.

loop grows during further irradiation, the strain at its center decreases and the vacancy loop shrinks.

Impurity effects have been studied by comparing foils that were irradiated immediately after preparation with foils that had been stored in air for 2 weeks or more before irradiation. In the first kind of specimens only dislocation loops were observed, whereas in the second kind stacking-fault tetrahedra (during irradiation with moderate dose rate) and voids (at high dose rates) were also found.^{9,10} We presume that during the storage in air, impurities (mainly oxygen) entered into these samples and lowered the stacking-fault energy. Since samples from which the oxide layers formed during the storage had been carefully removed by electropolishing showed void formation in much the same way as those for which this measure had not been taken, we conclude that void stabilization may be achieved by gaseous impurities present in (at best) their equilibrium concentration and that a supersaturation of practically unsolvable impurities (e.g., inert gases) is not necessary.

Since in our experiments voids were observed without prebombardment by high-energy heavy particles,^{11,12} we may conclude that displacement cascades are not necessary for void formation. The prediction that (in the absence of displacement cascades) *gaseous impurities* are required for void formation has been confirmed. The observation of vacancy-type loops and of stacking-fault tetrahedra (presumably also of vacancy type) during irradiation of contaminated samples demonstrates that at sufficiently low dose rates the presence of gaseous impurities does not ensure that small vacancy clusters grow to large voids.

In specimens that were thick enough for the surface effects to be negligible, void growth was observed at irradiation temperatures between 280 and about 600°C. Figure 5 illustrates the influence of the irradiation temperature*) for a given irradiation dose. At the three lower temperatures, the majority of the voids appear to be cubes with edges parallel to $\langle 100 \rangle$. A fraction that rises with temperature and size has truncated corners. At 500°C the observed contrast is consistent with octahedra bounded by $\{111\}$ planes. The void density decreases and the void diameter increases with increasing temperature. For a given dose the void volume increases up to 400 to 500°C and then levels off.

Figures 6 and 7 show the results of long-time experiments (see also Ref. 13). At low doses a dislocation network develops out of growing dislocation loops. (The dislocation network is visible where an extinction contour crosses the area of observation.) Here the number of voids grows with irradiation time t as $t^{1/2}$, the total void volume as t^n with $1.5 \lesssim n \lesssim 2$. In the next stage the volume growth rate is constant. This means that the distribution of the generated point defects between the various types of sinks remains constant. As the dislocation

*A high beam current density of $\sim 5 \times 10^{19}$ electrons/cm² was used. This may have caused the temperature in the irradiation spot (diameter $\sim 5 \mu$) to have risen up to 60°C above that of the sample holder. The temperatures given are those of the sample holder.

Fig. 5 Voids after 120-min irradiation with 5×10^{19} electrons/(cm²)(sec) (650 keV, defect production rate $\Phi \approx 10^{-3}$). Irradiation temperatures: (a) 280°C, (b) 380°C, (c) 420°C, and (d) 550°C.

Fig. 6 Voids during irradiation with 5×10^{19} electrons/cm² (650 keV) at 380°C after (a) 180 min, (b) 487 min, (c) 667 min, and (d) 900 min. Foil thickness $d \approx 5000$ Å.

Fig. 7 Growth of total void volume at 380°C during irradiation with 5×10^{19} electrons/(cm²)(sec) (650 keV). Foil thickness $d \approx 5000$ Å.

network becomes denser and denser, its interaction with vacancies and interstitials becomes so strong that the partition between the various sinks is changed, and the volume growth rate of the voids begins to decrease.

At 730°C, the highest achievable temperature, the voids disappeared within 3 to 4 hr. This is in accord with the result of Mastel and Brimhall¹⁴ that voids formed by neutron irradiation anneal out within 2 hr near 800°C.

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DISCUSSION BY ATTENDEES

Harkness: At saturation, were the dislocations interconnected with voids?

Seeger: Yes, thick bundles of dislocations came out of the voids.

Chadderton: Was there any indication in the dependence of void volume on time of a $t^{1/2}$ function before your later linear dependence?

Seeger: In the initial stage, Urban observed the total void volume to increase as t^n where $1.5 \leq n \leq 2$. It was the number of voids, not their total volume, that was found to increase as $t^{1/2}$.

Adda: This is just a comment. We have made a calculation of the diffusion of point defects in a thin foil bombarded with self-ions; it is similar to the one you have presented, and we agree with your conclusions. There is no difficulty in using thin foil as long as one makes sure that the displacement rate is sufficiently high for a given thickness so as to keep a zone where the concentration of defects is constant.

Seeger: Right.

Boltax: At saturation, you said the dislocations were ineffective in absorbing interstitials. Why?

Seeger: The point is, we have done a calculation, which I was unable to report here, which studies how the dislocations manage to attract more

interstitials than vacancies. They do it through their strain field. How much more they do depends on the presence of other sinks. If other sinks are small, i.e., their strain field is small, then their effectiveness in absorbing more interstitials than vacancies is reduced. So there will be a definite limit to what the dislocations can do because, when the solid is all filled with voids, then the voids become effective sinks for interstitials, and the whole thing will stop.

Boltax: At what dose (displacements per atom) did saturation occur?

Seeger: The absolute numbers should not be emphasized because it depends on the dislocation density and the thickness of the foil.

Wiedersich: Do voids intersect the surfaces at higher volume increases, or is the defect-depleted layer near the surface sufficient to prevent the growth of voids into the surface?

Seeger: Even during irradiation to very high total dose, we could not observe voids intersecting the foil surfaces. In the surface layers, where the defect concentrations and dislocation densities are low, void growth goes on very slowly. Thus, to observe void growth near the surfaces, one should apply much higher irradiation times.

VOID FORMATION IN QUENCHED OR IRRADIATED METALS

236 1700

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ABSTRACT

The detailed mechanisms responsible for the formation of voids in both quenched and irradiated metals were discussed critically. Attempts were made to correlate void-formation phenomena under quenching and irradiation conditions whenever possible. Particular attention was given to the void-nucleation problem and to the question of whether the nucleation occurs by the homogeneous or heterogeneous aggregation of vacancies under quenching or irradiation conditions. The importance of paying increased attention to the conditions for interstitial dislocation loop formation in the irradiation case was emphasized. The void growth problem was then considered, and the effectiveness of voids (and dislocations) as point-defect sinks under quenching or irradiation conditions was discussed.

On the experimental side, newly developed field ion microscope (FIM) techniques were shown to be capable of yielding direct experimental information, on the atomic level, about various defect behavior and mechanisms of interest in the void-formation problem. These techniques involve essentially the atom-by-atom dissection of specimens by pulsed field evaporation and the corresponding recording on film of the extensive number of FIM images produced at each stage of the process. Methods have been developed which allow the analysis of as many as $\sim 5 \times 10^5$ frames of 35-mm cinefilm for a single investigation. The application of these techniques to the following problems was discussed: (1) the mobility of the interstitial; (2) binding energies between point defects; and (3) the atomic structure of depleted zones.

In the present paper we begin with a general critical review of the nucleation and growth mechanisms which may be expected to lead to the formation of voids* by either quenching or by neutron irradiation at temperatures near 0.5 of the melting point T_m (°K). We then describe a number of experimental programs

*In the present paper we define voids to be cavities in the bulk of the material irrespective of whether or not they contain gas atoms.

that are in progress in our laboratory which are directly relevant to the general void-formation problem. Special emphasis is given to the use of newly developed field ion microscope (FIM) techniques as a means of revealing some of the important mechanisms on an atomic level.

Voids are generally produced when the supersaturated vacancies (v 's) produced by quenching or irradiation aggregate in the form of three-dimensional clusters and somehow avoid destruction by other mechanisms which include: (1) destruction at point-defect sinks such as network dislocations, grain boundaries, and free surfaces; (2) aggregation and collapse into dislocation configurations such as loops; and (3) encounters with migrating interstitials (i 's) (in the irradiation case).

The void-formation processes under either quenching or irradiation conditions are, therefore, complementary in many respects, and it is useful to consider them together. In general, we are forced to face two major questions:

1. The nucleation question: Under what conditions will supersaturated v 's aggregate to form supercritical nuclei in the form of three-dimensional voids rather than collapse into other configurations?

2. The growth question: Under what conditions do sufficient numbers of supersaturated v 's reach and join growing voids to produce voids of significant size?

VOID FORMATION IN QUENCHED METALS

General

In order to discuss certain general aspects of typical quenching and irradiation phenomena in a semiquantitative manner, we adopt the defect model of a metal which was employed by Harkness and Li¹⁻⁴ to simulate experimentally observed void formation in stainless steel subjected to reactor irradiation. This procedure has the advantage that these workers have carried out extensive and rather complex computer calculations of point-defect concentrations during irradiation in their model and have chosen parameters which correspond to experimental data wherever possible. Their results, therefore, provide quantitative information about point-defect concentrations which is useful for present purposes. In this model we have

$$D_v = \exp(-1.30 \text{ eV}/kT) \quad (1a)$$

$$D_i = \exp(-0.13 \text{ eV}/kT) \quad (1b)$$

$$c_v^0 = \exp(-1.65 \text{ eV}/kT) \quad (1c)$$

$$c_i^0 = \exp(-4.35 \text{ eV}/kT) \quad (1d)$$

where D_v and D_i are the v and i diffusion coefficients (cm^2/sec), and c_v^0 and c_i^0 are the equilibrium v and i concentrations.*

We begin by emphasizing that relatively large v supersaturations are achieved in typical quenching experiments. Under these conditions the driving force for v annihilation is large. If the above model metal is quenched at an infinite rate from a quenching temperature $T_q = 1400^\circ\text{C}$ to an annealing temperature $T_a = 320^\circ\text{C}$,† a supersaturation ratio $S = c_v^0(T_q)/c_v^0(T_a) \approx 10^9$ is obtained, and a v chemical potential

$$\mu_v = kT \ln\{c_v/c_v^0(T_a)\} \approx 1.06 \text{ eV}$$

is developed. During subsequent isothermal annealing at T_a , the v chemical potential remains high during virtually the entire anneal as seen in Fig. 1.

Fig. 1 Vacancy chemical potential, μ_v , as a function of f , the fraction of v defects annealed, during isothermal annealing at $T_a = 320^\circ\text{C}$ after a quench from $T_q = 1400^\circ\text{C}$ (see text).

Void Nucleation

There is considerable evidence in the literature that, even under these high supersaturation conditions, the precipitation of v 's into observable clusters

*It might be argued that the preexponential factor in Eq. 1a and the formation enthalpy in Eq. 1c are somewhat large, but these effects should not affect our major conclusions.

†The temperature T_a was chosen so that the v annealing would be complete in a typical specimen in $\sim 10^3$ sec.

TABLE 1
INVESTIGATIONS INDICATING HETEROGENEOUS
NUCLEATION OF VACANCY PRECIPITATES BY
IMPURITIES IN QUENCHED METALS

Metal	Impurities present*	Type of vacancy precipitates†	Investigator
Au	Ag, Cu, Fe, Si, Zn, Pb, Ni	Black-spot defects, s.f. tetrahedra	Cotterill and Segall ⁵
Au	? (Spec. pure material)	S.f. tetrahedra	Segall and Clarebrough ⁶
Au	Ag, Cu, Fe, Ni, Pd, Si	Black-spot defects	Ytterhus and Balluffi ⁷
Au	Ni, Fe, Cu, Ag, Si	Black-spot defects, s.f. tetrahedra	Siegel ⁸
Au	?	S.f. tetrahedra	Meshii et al. ⁹
Au	Cd, Zn	S.f. tetrahedra, dislocation loops	Quader and Dodd ¹⁰
Au	Cu, Mg, Al, H	S.f. tetrahedra	Johnston et al. ¹¹
Al	Cu, Fe, Mg	Dislocation loops	Cotterill and Segall ⁵
Al	?	Dislocation loops	DiMelfi and Siegel ¹²
Mg	H	Voids	Lally and Partridge ¹³
Al	H	Voids	Shimomura et al. ¹⁴
Cu	H	Voids	Clarebrough et al. ¹⁵
Cu	Dissolved gases	Voids	Bowden and Balluffi ¹⁶
Au	H	Voids	Johnston et al. ¹¹
Ag	H, O	Voids	Clarebrough et al. ¹⁵
S.S.‡	Gaseous P	Voids	Rowcliffe ¹⁷

*In many cases a listed impurity was present in the material but may not have been responsible for the nucleation indicated (see references for details).

†Evidence has been given¹⁸ that the so-called black-spot defects are actually small stacking fault (s.f.) tetrahedra.

‡Stainless steel containing 18 Cr, 10 Ni, 0.01 C, and 0.3 P (wt.%).

(either voids or collapsed defects) at T_a is usually heterogeneously nucleated by impurity atoms. Apparently, homogeneous nucleation by the diffusional aggregation of mobile v 's is sufficiently difficult and slow so that other more rapid annealing processes involving the heterogeneous nucleation of clusters at impurity atoms or annealing to inexhaustible sinks (e.g., already existing dislocations) predominate. In Table 1 we list a number of investigations⁵⁻¹⁷ in which it was demonstrated that impurities acted as effective agents for heterogeneous nucleation. In the majority of these experiments, the impurity content was altered in some manner, and large corresponding changes in the density of v precipitates were observed.

To our knowledge it has not yet been demonstrated satisfactorily that any significant amount of homogeneous precipitation in the form of either voids or collapsed clusters has occurred in any quenching experiment. Evidence for heterogeneous nucleation has been obtained even in materials possessing purities in the 0.99999 to 0.999999 at. fraction range. The question naturally remains as to whether or not small densities of homogeneously nucleated precipitates have been present in the highest purity materials used. Unfortunately this question cannot be answered at the present time, since low concentrations of v precipitates become difficult to measure* and since measurements of the small concentrations of impurities actually in solution have not been carried out. For example, Siegel⁸ measured a continuous decrease in the density of stacking fault tetrahedra in quenched and annealed gold as the overall specimen purity increased (as measured by a decreased residual electrical resistivity at 4.2°K). On the other hand, Meshii et al.⁹ measured a constant tetrahedron density under conditions where it was thought that the specimen was becoming increasingly pure. However, the concentrations of dissolved impurities causing the nucleation were not measured either directly or indirectly. (For example, measurements of the 4.2°K resistivity as a function of the prequench annealing time were not performed.) Chik¹⁹ has recently employed a model calculation which suggests that there should be a transition from heterogeneous to homogeneous nucleation of stacking fault tetrahedra in quenched gold when the impurity content falls below 10^{-5} at. fraction. However, this result appears to be in conflict with Siegel's⁸ experimental observations.

The nucleation of collapsed precipitates is explained in general by the use of models involving an attractive binding energy between the v defects. For example, Johnson²⁰ has estimated that in nickel a platelet of ~ 180 v 's on a $\{111\}$ plane will spontaneously collapse into a dislocation loop and that this loop might have a lower energy than a spherical void also containing v 's. Bullough and Perrin²¹ have calculated that in body-centered cubic (bcc) iron a dislocation loop will be more stable than a platelet of vacancies on a $\{100\}$ plane when the number of v 's is ≥ 22 and that it will have a lower energy than a spherical void when the latter has adsorbed ≥ 2140 v 's. The heterogeneous nucleation of collapsed precipitates by impurity atoms is then readily explained by postulating an attractive binding energy between the v defects and impurities in small clusters. Since the density of v precipitates has rarely exceeded $\sim 10^{16}$ cm^{-3} , there has always been a sufficient number of impurity atoms available in even spectroscopically pure grade materials to account for the observed precipitate densities with such a model. Johnston et al.¹¹ recently carried out systematic experiments with impurity nucleated stacking fault tetrahedra in

*Point-defect precipitates at a density $\gtrsim 10^{12}$ cm^{-3} are difficult to detect and measure by transmission electron microscopy.

quenched gold which indicated that trivalent impurities had a greater heterogeneous nucleating effect than divalent impurities and that monovalent impurities had very little effect at low concentrations. In addition, interstitial hydrogen impurities apparently acted as strong nucleating centers. All of these results were qualitatively explained on the basis of the expected strength of the electrostatic interaction between the v 's and impurities in small clusters.

In the special case of the nucleation of voids, it appears that the nucleation has always been caused heterogeneously in a number of metals by dissolved hydrogen and perhaps other gaseous impurity atoms (see Table 1). In the absence of these impurities, void formation is generally below the level of detection by electron microscopy. Hydrogen generally dissolves as an interstitial proton with an exceedingly high mobility and a decreasing solubility with temperature. Presumably the supersaturated mobile protons interact strongly with small v clusters and cause them to become supercritical and grow as voids rather than as collapsed precipitates. Apparently the gaseous impurities act to prevent the normal collapse of the v clusters into two-dimensional aggregates. Conceivable models for void nuclei consisting of vacancy defects and gaseous impurity atoms have been suggested, for example, by Shimomura and Yoshida.¹⁴

Void Growth

Once a void has been successfully nucleated, further growth occurs by the incorporation of additional supersaturated mobile v defects. Under these conditions the void may be regarded as a relatively stationary sink which attempts to set up an approximately spherically symmetric v diffusion field around it. The question that immediately arises is whether or not voids are capable of acting as nearly perfect sinks.* Under perfect sink conditions, v absorption at the void is easy, and the growth rate should depend upon the rate at which v 's are able to diffuse to the void. On the other hand, if v absorption is difficult, the growth rate may become limited by kinetic processes at the void surface. The absorption of v 's undoubtedly occurs at crystal ledges on the void surface, and voids should therefore tend to become polyhedra with faceted faces as shown schematically in Fig. 2. Continued growth then requires the continual production of surface ledges which must nucleate in the form of platelets of adsorbed vacancies on the faces of the polyhedra as shown in Fig. 2. We expect nucleation to occur on the faces, since the corners and edges are not preferential sites for the formation of v growth nuclei as they are for v shrinkage nuclei. (A similar nonsymmetry exists in the case of single-crystal evaporation and

*We define a perfect sink as a sink that operates rapidly enough to maintain the concentrations of point defects essentially at local equilibrium in its direct vicinity.

condensation.*²²) As-grown voids in quenched metals invariably appear as polyhedra in a manner consistent with the above discussion.†^{11,23-28} Under these conditions the void can only act as a perfect sink if ledge nucleation is relatively rapid and if a reasonable number of surface ledges is maintained on the void faces in the quasi-steady state.‡

Fig. 2 Schematic diagram showing atomic ledges on void surface during growth and during shrinkage. During growth the void tends to become polyhedral, and continued growth occurs by the nucleation of v platelets on its surface. During shrinkage the void tends to become spherical owing to easy formation of shrinkage ledges at its edges and corners.

To our knowledge the sink efficiency of growing voids has never been tested directly. In general, we would expect the efficiency to increase with the v chemical potential since this would tend to increase the rate of nucleation of growth ledges on the void surface. There is experimental evidence³¹⁻³³ that large voids are capable of growing at the expense of small voids during annealing under the influence of the relatively weak v chemical potentials present due to capillarity. However, the data are not always clear-cut. For example, in the work of Brimhall and Mastel,³² the void-size distributions were not measured directly,

*The problem of calculating the void sink efficiencies for v 's should be quite similar to that of calculating the "sticking coefficient" of a growing crystal for supersaturated atoms during crystal growth from the vapor as discussed, for example, by Hirth and Pound.²²

†We note, however, that observations of the final shapes of voids after growth is completed may be somewhat misleading in this respect, since the void will tend to adopt an equilibrium shape which is dependent upon minimum energy rather than kinetic factors.

‡If the ledges act as efficient line sinks, we would expect that a steady-state concentration of only a few ledges per void would be required to allow the void to act as an efficient sink. This is a result of the fact that the electrical capacitance of a loop of radius r is almost the same as the capacitance of a sphere of the same radius (see Refs. 29 and 30).

and it is not entirely clear whether the larger voids actually grew. The growth of voids under capillarity forces would indicate that void growth is easy because of the relatively small magnitudes of the driving forces involved. For example, the chemical potential corresponding to a 100 Å radius void is only

$$\mu_v = \frac{2\gamma\Omega}{r} \approx 10^{-2} \text{ eV}$$

where γ is the specific surface energy, Ω is the atomic volume, and r is the void radius. This value is far below the chemical potentials present in usual quenching and irradiation experiments (see Figs. 1 and 3). There is also evidence for void

Fig. 3 Vacancy and interstitial chemical potentials as a function of fluence (time) during irradiation. Data obtained from Harkness and Li¹⁻⁴ who calculated the quantities given using their model for reactor irradiated stainless steel subjected to a flux of 2×10^{15} neutrons/(cm²)(sec) at 500°C (see text).

growth in Kirkendall diffusion specimens under the influence of small μ_v chemical potentials. In these cases the μ_v supersaturations were almost certainly of the order of a few percent, or less,^{34,35} and therefore μ_v was typically $<10^{-2}$ eV. On the basis of these observations, we might therefore expect voids to grow easily and to act as highly efficient sinks in quenching experiments.

It is of interest to note that quantitative measurements of the sink efficiency of stacking fault tetrahedra in quenched gold³⁶ under conditions of high supersaturation have been carried out and that the efficiency is in the range ~ 0.7 that of a perfect sink. Apparently in this case the nucleation of jog lines on the stacking fault surfaces is relatively easy.

In the opposite case of void shrinkage, there is appreciable evidence that voids act as nearly perfect vacancy sources. Quantitative measurements of the shrinking of voids in thin foils of aluminum^{27,28} and copper^{16,37} have shown that the shrinkage is essentially diffusion controlled. Furthermore, voids, which were polyhedral before shrinkage, became approximately spherical during shrinkage.^{15,25,27,28,37} In this case the corners and edges do act as preferential sites for ledge nucleation as mentioned above (see Fig. 2), and v emission and shrinkage are easy.

VOID FORMATION IN IRRADIATED METALS

General

Void formation in the case of irradiation at elevated temperatures near $0.5 T_m$ is considerably more complicated than in the case of quenching because of the presence of i 's which are generated at the same rate as the v 's.

In the quasi-steady state "chemical reaction rate" formalism, the relations governing the v and i concentrations are

$$G - D_v c_v \sum_n \alpha_{nv} - \beta D_i c_v c_i = \frac{dc_v}{dt} = 0 \quad (2a)$$

$$G - D_i c_i \sum_n \alpha_{ni} - \beta D_i c_v c_i = \frac{dc_i}{dt} = 0 \quad (2b)$$

where in each equation the first term, G , is the generation rate due to irradiation, the second term represents the losses to all sinks (of which there may be n types), and the third term is the loss rate due to recombination. The α_{nv} , α_{ni} , and β are taken to be constants representing various parameters of the sinks and the recombination process. In these equations the equilibrium v and i concentrations have been neglected (i.e., $c_v \gg c_v^0$ and $c_i \gg c_i^0$), and it has been assumed that $D_i \gg D_v$. From Eq. 2 we must have

$$D_v c_v \sum_n \alpha_{nv} = D_i c_i \sum_n \alpha_{ni} \quad (3)$$

Therefore the total loss of v 's to sinks must equal the total loss of i 's to sinks. If only one type of sink is present (e.g., voids or dislocations), no void growth can

occur, since c_v and c_i will adjust themselves so that Eq. 3 is obeyed, and the v and i currents exactly cancel at the sink. On the other hand, if two or more types of sinks develop (e.g., voids and dislocations), and if for some reason the currents of v 's and i 's into a particular type of sink differ, then void growth is possible. It has been widely suggested in the past^{4,38} that dislocations should preferentially attract i 's because of their strong mutual interaction and that a relatively small excess current of i 's will therefore annihilate at the dislocations, leaving behind a slight excess number of v 's which then become available for void growth. Recently, Norris³⁹ has found direct experimental evidence in support of this model while observing void growth in nickel foils during in situ electron irradiation in a high-voltage electron microscope. Preferential void formation and growth were observed in the direct vicinity of dislocations as predicted.

In the present paper we therefore adopt this model as basic for void formation. Many detailed questions, however, remain. For example, it is of importance to understand how voids nucleate and start to grow in the first place in the presence of both v 's and i 's. Considerable information about the properties of small defect clusters is therefore required. There is clear experimental evidence that excess i 's precipitate out in the form of dislocation loops during irradiation and that this phenomenon generally accompanies void formation. Since these loops absorb i 's and make v 's available for the voids, the formation of the i loops is of great importance and requires elucidation. The overall growth kinetics of the entire process should depend upon the ability of the voids and dislocations to act as point-defect sinks, and this point, therefore, also demands attention. Furthermore, the entire process obviously depends directly upon the concentrations (chemical potentials) of the various point defects that are present. These concentrations depend in turn upon the defect mobilities which therefore should be known. Discussion of a number of these points is therefore given in the following with particular emphasis on void formation under reactor conditions at $0.5 T_m$.

Void Nucleation

Conceivable models for void nucleation during reactor neutron irradiation involve:

1. Homogeneous nucleation assuming that voids may grow by the diffusional aggregation of mobile v 's in the absence of perturbing effects due to impurity atoms or displacement cascades.
2. Heterogeneous nucleation aided by impurity gas atoms.
3. Heterogeneous nucleation aided by the high instantaneous v concentrations present in depleted zones originating at displacement cascades in the absence of any impurity atoms.
4. Heterogeneous nucleation aided by both the high v concentrations in depleted zones and the presence of impurity gas atoms.

We first demonstrate that, since homogeneous void nucleation apparently does not occur during quenching, it most certainly will not occur under typical reactor irradiation conditions. Harkness and Li have calculated the v and i concentrations expected in their model¹⁻⁴ for stainless steel (Eq. 1) irradiated at $T = 500^\circ\text{C}$ with a flux of 2×10^{15} neutrons/(cm^2)(sec). The corresponding chemical potentials are shown in Fig. 3. The values of both μ_i and μ_v are relatively large initially and decrease with increasing time as the sink density (voids and dislocation loops) increases. Note particularly that μ_v is appreciably lower than in the quenching case described on page 565 (Fig. 1).

It is noted that these results were obtained on the assumption that the i which is involved is the so-called "fast" i with a small migration energy of 0.13 eV (see Eq. 1) which migrates in Stage I of the usual recovery spectrum of face-centered cubic (fcc) metals. However, it has been suggested that a second type of "slow" i with a considerably higher enthalpy of migration exists which migrates in Stage III of the recovery spectrum (see, for example, the discussion in Refs. 40 to 42). It is therefore possible that it is this i which should be assumed to exist under irradiation conditions near $T = 0.5 T_m$. A discussion of this question along with some recent experimental information is given later on page 580. We wish to note at this point the interesting result that many aspects of the present quasi-steady-state model are independent of the choice of the diffusivity of the i (i.e., independent of whether we choose a fast or a slow i). Equation 2 may be solved for c_v and c_i as follows:

$$c_v = \frac{A_i}{2\beta} \left[\left(\frac{4\beta G}{A_v A_i D_v} + 1 \right)^{1/2} - 1 \right] \quad (4)$$

and

$$c_i = \frac{A_v D_v}{2D_i \beta} \left[\left(\frac{4\beta G}{A_v A_i D_v} + 1 \right)^{1/2} - 1 \right] \quad (5)$$

where

$$A_v \equiv \sum_n \alpha n_v \quad (6)$$

and

$$A_i \equiv \sum_n \alpha n_i \quad (7)$$

It may be seen immediately that c_v is independent of D_i and that c_i is inversely proportional to D_i . This result means that the impingement rates of the i 's upon sinks (which are proportional to the product $D_i c_i$) are independent of D_i . Accordingly the growth rates of both v and i type precipitates are independent of D_i in the simple quasi-steady-state first-order model represented by Eq. 2. The

only quantity of direct interest which is dependent upon D_i is the i chemical potential, μ_i . (We shall stress the fact later that the rate of any process which depends upon the aggregation of i 's, such as i -dislocation loop nucleation or the double jog nucleation associated with i -induced dislocation climb, should increase with an increase in μ_i .) The dependence of μ_i upon the choice of a fast or slow i is easily obtained. Since

$$\mu_i = kT \ln \frac{c_i}{c_i^0} \quad (8)$$

we have from Eq. 5

$$\mu_i = kT \ln \frac{A}{D_i c_i^0} \quad (9)$$

where $A = \text{constant}$. Since

$$D_i = D_i^0 \exp(-H_i^m/kT)$$

where D_i^0 is the usual constant pre-exponential factor, and H_i^m is the enthalpy of migration, the change in μ_i due to the choice of a slow i is then

$$\Delta\mu_i = \mu_i(\text{slow}) - \mu_i(\text{fast}) \approx H_i^m(\text{slow}) - H_i^m(\text{fast})$$

Current ideas about the slow i indicate that $\mu_i \approx 1 \text{ eV}$. As seen in Fig. 3 the choice of a slow i would then raise μ_i by about 50%, and presumably this would have an influence on the kinetics of the aggregation processes mentioned above. Keeping these results in mind, we therefore proceed on the assumption that we have a fast i present.

We now calculate the homogeneous void nucleation rate using classical nucleation theory for the present model for both the quenching case and for the irradiation case described above and show that the predicted rate in the irradiation case must be vanishingly small.

According to standard nucleation theory,⁴³ the steady-state nucleation rate should be given by

$$I \approx \frac{\beta_v(n_c)}{\Omega} \exp[-\Delta G^0(n_c)/kT] \quad (10)$$

where $\beta_v(n_c)$ is the rate at which v 's join critical nuclei of size $n = n_c$, and $\Delta G^0(n_c)$ is the free energy of formation of a critical nucleus given by

$$\Delta G^0(n_c) = -n_c kT \ln \frac{c_v}{c_v^0} + E(n_c) \quad (11)$$

where $E(n_c)$ is the free energy of the critical nucleus. (We omit the relatively unimportant Zeldovich factor⁴³ in the present treatment.) Values of $E(n)$ were

estimated so that the function $E(n)$ asymptotically approached the curve expected on the basis of macroscopic surface energy at large n (i.e., $n > 100$) as seen in Fig. 4. We, of course, ignore the probability mentioned earlier that void nuclei spontaneously collapse into lower energy collapsed configurations unless

Fig. 4 Estimated free energy of cluster $E(n)$ as a function of cluster size, n . Reasonable v defect binding energies were assumed for small n , and the curve was adjusted so that it asymptotically approached the curve expected on the basis of macroscopic surface energy at large n (see text).

blocked by impurity (gas) atoms. The $\Delta G^\circ(n)$ curve for a specimen quenched from 1400°C is shown in Fig. 5 and yields a critical size $n = n_c = 3$ and a critical nucleus energy $\Delta G^\circ(n_c) = 1.17$ eV. Assuming a sticking coefficient of unity, we estimate $\beta_v(n_c) \approx 20 \text{ sec}^{-1}$, and, therefore, $I \approx 10^{14}$ nucleations/(sec)(cm^3). This value is within a few orders of magnitude of predicting a negligible homogeneous nucleation rate upon quenching, and, in view of the crudeness of the calculation, is therefore not inconsistent with the experimental evidence cited on page 565.

The calculation of the nucleation rate in the irradiation case with i 's present is more complicated, since it is obvious that the i 's will tend to shrink the vacancy nuclei and make nucleation more difficult. We may obtain an upper limit to the nucleation rate in this case by calculating the rate as if the i 's were not present at all. According to Fig. 3 we expect the maximum nucleation rate

Fig. 5 Energy barrier to nucleation as a function of v cluster size, n , under quenching or irradiation conditions. The quantity $\Delta G'(n)$ in the irradiation case is an effective energy that involves kinetic as well as thermodynamic factors (see text).

to occur at early times in the presence of a large v chemical potential, and, using $\mu_v = 0.4$ eV, we obtain $n = n_c = 18$, $\Delta G^\circ(n_c) = 6.1$ eV (see Fig. 5), $\beta_v(n_c) \approx 10 \text{ sec}^{-1}$, and $I \approx 10^{-15} \text{ nucleations}/(\text{sec})(\text{cm}^3)$. This result clearly predicts negligible homogeneous void nucleation even though the irradiation time is long (i.e., $\sim 10^8 \text{ sec}$). This conclusion is strongly reinforced by a more realistic calculation which includes the effects of the i 's. Russell⁴⁴ has recently analyzed this problem within the framework of classical nucleation theory and finds that the effective barrier to nucleation is now given by the maximum in the curve of $\Delta G'(n)$ vs. n , where

$$\Delta G'(n) = kT \sum_0^n \ln \left\{ \frac{\beta_i(n+1)}{\beta_v(n)} + \exp \left[\frac{\Delta G^\circ(n+1) - \Delta G^\circ(n)}{kT} \right] \right\} \quad (12)$$

Here, $\Delta G^\circ(n)$ is given by Eq. 11, and $\beta_i(n)$ is the rate at which i 's join a cluster of size n . (Note that both β_v and β_i are independent of the choice of a fast or slow i as explained above.) The critical nucleation barrier $\Delta G'(n_c)$ is unfortunately difficult to calculate in this case without a detailed kinetic model giving exceedingly accurate values of the $\beta_i(n)$ and $\beta_v(n)$. However, in the present case where $\beta_i(n+1)/\beta_v(n) \sim 1$, it is clear that $\Delta G'(n)$ will coincide with $\Delta G^\circ(n)$ for small n but that $\Delta G'(n)$ will lie above $\Delta G^\circ(n)$ at the larger n . Eventually, at some value of n , $\beta_v(n)$ will be larger than $\beta_i(n+1)$, the logarithmic terms in the sum for $\Delta G'(n)$ will become negative, and the curve of $\Delta G'(n)$ vs. n will turn downward. We make no attempt in the present work to calculate $\Delta G'(n)$ completely. The beginning part of the curve is shown in Fig. 5 assuming $\beta_i(n+1) \approx \beta_v(n)$. Obviously $\Delta G'(n)$ rises higher and has a considerably flatter maximum than $\Delta G^\circ(n)$. The net effect of this is to decrease the rate of

TABLE 2
INVESTIGATIONS INDICATING HETEROGENEOUS NUCLEATION
OF VOIDS AND INTERSTITIAL DISLOCATION LOOPS BY IMPURITIES
IN IRRADIATED METALS

Metal	Impurities present	Type of point-defect clusters	Irradiation	Investigator
S.S.*	He	Voids	Protons	Keefer et al. ^{4,5}
V	Interstitial impurities	Voids	Neutrons	Wiffen ^{4,6}
Al	Impurities	Voids	Neutrons	Stiegler et al. ^{4,7}
Al	He or H	Voids	Neutrons	Farrell and King ^{4,8}
Fe	Impurities	Voids	Neutrons	Farrell and Houston ^{4,9}
S.S.*	He	Voids	Neutrons	Bloom and Stiegler ^{5,10}
Ni	He, or O?, or N?	Voids	Carbon and nickel ions	Hudson ^{5,1}
S.S.*	He	Voids	Protons, carbon ions, oxygen ions, iron ions	Nelson and Mazey ^{5,2}
S.S.*	He	Voids	Carbon ions	Nelson et al. ^{5,3}
Ni	He, Ne, A	Voids	Electrons	Norris ^{5,4}
Ni	O	Voids	Electrons	Urban ^{5,5}
Mo	N	Interstitial loops	Electrons	Evans ^{6,9}
Mo	Si, Fe(?)	Interstitial loops	Neutrons	Eyre et al. ^{7,10}
Mo	C	Interstitial loops	Neutrons	Mastel and Brimhall ^{7,1}
Cu	H	Interstitial loops	Protons	Mazey and Barnes ^{7,2}
Au	C, H, O, A	Interstitial loops	Gold ions	Thomas and Balluffi ^{7,3}

*Stainless steel.

nucleation in the presence of i's by both increasing the effective energy of the critical nucleus and decreasing the Zeldovich factor which depends upon the curvature of the free energy curve at the maximum. We conclude from this that, by any argument, homogeneous nucleation is far too slow to account for observed void formation during reactor irradiation.

Considerable evidence has been accumulated recently^{4,5-5,5} that void formation during reactor, ion, and electron irradiation is greatly enhanced by the presence of impurities, notably He and other gases (see Table 2). In many of these experiments the gaseous impurities were introduced by injection or other means, and a large increase in the rate of void formation was observed.

In the case of electron irradiation, it appears that voids do not nucleate in observable concentrations in the absence of gaseous impurities,^{54,55} and we may conclude that in this type of irradiation, where displacement cascades are absent, voids at observable concentrations are nucleated heterogeneously by impurity gas atoms. It should be pointed out that the vacancy chemical potentials in the electron irradiation experiments cited above were undoubtedly relatively large (i.e., larger than those given in Fig. 3), and that these results are therefore consistent with our conclusion regarding the impossibility of homogeneous nucleation in the reactor irradiation case.

In the case of both reactor and fast ion irradiation, void formation is also greatly enhanced by gaseous impurities (Table 2). In this type of irradiation in certain metals, the question is complicated by the existence of displacement cascades that produce large instantaneous concentrations in depleted zones which could conceivably survive in the form of small supercritical voids. A number of experiments⁵⁶⁻⁶⁴ using fast ion irradiation at lower temperatures have shown that such regions undergo spontaneous in situ collapse into stable v-type dislocation loops which may be identified by transmission electron microscopy. Recently, the FIM has been used to obtain detailed information about the atomic structure of depleted zones at low temperatures where the v's and i's are both immobile. These results, which are discussed in more detail on page 587, clearly reveal a rather spongy v-rich core region (i.e., depleted zone) surrounded by a distribution of i's. No systematic studies have been made of the temperature dependence of the formation of these regions and the stability of the depleted zones at elevated reactor temperatures. However, on the basis of all of the information available, it seems highly unlikely that void nuclei could be produced at displacement cascades in the absence of stabilizing gaseous impurities. Unfortunately it has not been possible to prove experimentally whether or not observed void nucleation under all conditions of neutron or fast ion irradiation has required the presence of gaseous impurities. Here again, as in the quenching experiments, sufficient concentrations of impurity atoms have invariably been present in all experiments to account for heterogeneous nucleation. We note that voids have been produced in nominally pure nickel and stainless steel by irradiation with fast nickel and iron ions in the absence of any specially introduced gases.^{51,52} Comparison of these results with the electron irradiation results cited above,^{54,55} which indicate an absence of voids in nominally pure material in the absence of injected gaseous impurities, suggests that depleted zones may be of help in the nucleation of voids. It seems conceivable that in certain metals such as nickel a significant number of voids could be nucleated at a small portion of the large number of cascades produced if a number of gaseous impurity atoms were also present in the neighborhood of some of the cascades. The survival rate would depend sensitively on the average v concentration in the vicinity of the cascade, and this mechanism is therefore not inconsistent with the frequent observation of zones depleted of voids at grain

boundaries.^{4,6-48,54,65-67} The formation of voids in neutron-irradiated aluminum where depleted zone effects are expected to be extremely weak^{6,8} may, of course, be due primarily to heterogeneous nucleation at gaseous impurities. We note that the fact that depleted zones may not be required for the nucleation of voids in aluminum does not necessarily imply that this mechanism is unimportant in the heavier metals where strongly developed depleted zones are generally produced.

It is worth mentioning that small collapsed *v* aggregates are never observed even though it seems conceivable that they might be nucleated by nongaseous impurities, which would allow them to adopt a collapsed form rather than a void-like form, or by the collapse of depleted zones. Such collapsed defects, if they ever formed, would, of course, be eventually eliminated by a current of preferentially attracted excess *i*'s.

Interstitial Dislocation Loop Nucleation

Relatively little attention has been paid to the mechanisms of the formation of *i* dislocation loops even though, as stressed previously, these loops play an important role in controlling void growth. The relatively large *i* chemical potentials (Fig. 3) suggest that the homogeneous nucleation of *i* loops might be important. Nevertheless, there is appreciable evidence^{6,9-73} that *i* loops are heterogeneously nucleated under many conditions by impurity atoms as seen in Table 2. For example, Thomas and Balluffi⁷³ found that *i* loops were nucleated in ion-irradiated gold at temperatures above -30°C only when impurities were introduced. The nucleating effect of impurities is easily understood on the basis of the expected strong interaction between *i*'s and various impurities.

Void Growth

Since void growth is expected to be a nucleation and growth process that involves the nucleation of surface ledges as described on page 568, we would expect void growth during neutron irradiation to be more difficult than in the quenching case because of the lower *v* chemical potential and the presence of *i*'s which make the nucleation of vacancy platelets (page 568) more difficult. Presumably, an analysis of this nucleation problem could be carried out by using the approach of Russell.⁴⁴

Both growing and as-grown voids are polyhedral in irradiated specimens in agreement with the discussion on page 568. This observation indicates that the assumption of Bullough and Perrin²¹ of a surface ledge density of $\frac{1}{2}$ is considerably too high since this assumption would correspond to an essentially spherical shape. Again, no direct tests of the void growth efficiency have been made. Norris³⁹ has reported a few measurements of isothermal void growth in electron irradiated nickel in which the void volume, *V*, increased with time according to

$$V \propto \tau^3$$

This result implies that $dV/dt \propto V^{2/3}$, i.e., a growth rate proportional to the void area. This result suggests that the ledge nucleation rate, which should be proportional to the surface area, may have been rate-limiting and that the growth efficiency was therefore low. This result should be compared with the evidence for very easy growth in a pure v system described on page 568. More work is clearly needed to clarify this problem.

Dislocation Climb and Interstitial Dislocation Loop Growth

The large-scale climb of dislocations induced by a current of excess i 's is undoubtedly also a nucleation and growth process involving the nucleation of jog pairs by i 's in the dislocation core.⁷⁴⁻⁷⁶ There is considerable evidence, reviewed recently by the writers,⁷⁶⁻⁷⁸ that dislocation climb occurs with a high efficiency in quenching experiments in the presence of large v chemical potentials. However, in the case of climb induced by excess i 's during irradiation, we expect that the process may be made more difficult by the simultaneous presence of the v 's, since, under these conditions, the v 's tend to shrink the jog nuclei and slow down the nucleation. No quantitative information is available regarding the climb efficiency in this situation.

SOME EXPERIMENTAL WORK IN PROGRESS

In this section we describe some experimental work that is in progress in our laboratory which is relevant to the previous discussion. We give special emphasis to newly developed FIM techniques that involve essentially the atom-by-atom dissection of specimens by pulsed field evaporation and the corresponding recording on film of the extensive number of FIM images produced at each stage of the process. A further aspect of the technique is the scanning and analysis of the very large number of FIM images that is generated. These methods are yielding, for the first time, an extensive amount of direct experimental information, on the atomic level, about various defects and mechanisms of interest.

Mobility of the Interstitial

In the previous discussion (page 572), we have adopted a model which assumes that the i 's produced during irradiation are highly mobile and migrate in three dimensions with a migration energy near 0.1 eV (i.e., we have assumed a so-called Stage I i). This assumption has been widely used in attempting to analyze high-temperature void formation (see, for example, Harkness and Li¹⁻⁴ and Bullough, Eyre, and Perrin^{3,8}). However, as mentioned on page 572, the existence of a second less mobile i has been proposed in the literature, and the

possible existence of such an i is a matter of considerable current controversy.⁴⁰⁻⁴² A recent explanation⁷⁹⁻⁸¹ of the recovery spectra of irradiated fcc metals includes the possibility of the thermal conversion of the fast "low-temperature i " into a less mobile "high-temperature i ."

In this section we therefore cite some recent direct FIM observations which prove the existence of the fast i in tungsten and platinum at low temperatures, and we also describe a feasible FIM experiment, which is already in progress, that is aimed at testing for the possible existence of the slower high-temperature i which is a result of a thermal conversion process.

The experiments on tungsten (Scanlan, Styris, and Seidman⁸²⁻⁸³ and Seidman and Scanlan⁸⁴) consisted of the irradiation of high-purity ($\leq 1.5 \times 10^{-6}$ at. fraction impurity level) tungsten specimens under ultrahigh vacuum conditions ($\sim 10^{-10}$ torr) with 20 keV W^+ ions at temperatures between 8 and 18°K (Seidman et al.⁸⁵). An examination of the interior of the specimens at the irradiation temperature by the pulse field evaporation technique* revealed the existence of immobile i 's distributed throughout the bulk of the specimens.

*In the pulse field evaporation technique (see Robertson and Seidman⁸⁶), a large number of small successive voltage pulses is applied to the specimen in order to remove a large number of successive atomic layers from the surface by field evaporation. The width and height of each pulse are adjusted so that only one or two atoms are removed per atomic plane by each pulse (e.g., see Balluffi, Lie, Seidman, and Siegel⁸⁷). The specimen FIM image is photographed between each pulse with the aid of an external image intensification system and a semiautomated 35-mm cinecamera. The cinefilm is then scanned with a Vanguard motion analyzer (see Scanlan, Styris, Seidman, and Ast⁸⁸ for details concerning the data recording and analysis system). All observations and measurements are therefore obtained from enlarged negatives. We emphasize that the detailed information concerning structure reported here could not have been determined if the field evaporation increments were as coarse as one atomic layer. Recently, Buswell⁸⁹ has suggested that the extra "bright spots" he observed in heavy ion or neutron-irradiated tungsten were "due to the decoration of vacancy damage, in the low field regions, by an unidentified surface contaminant migrating from the shank of the specimen." It has been shown (Seidman, unpublished work) that Buswell reached this conclusion as a result of his coarse method of field evaporation in combination with an improper analysis of the FIM micrographs, and that his sweeping judgment regarding the visibility of i 's by field ion microscopy is incorrect. Buswell employed an evaporation increment ranging between 1 and $\frac{1}{8}$ of an (011) plane, and then counted extra spots which appeared on the terraces between (011) planes in the crystallographic areas (011)-(112)-(121) and (011)-($\bar{1}12$)-($\bar{1}21$). In our laboratory the field evaporation increment corresponds to (4×10^2 to 5×10^2) of an (011) plane per pulse (frame of film). Thus it has been possible to follow the evaporation of many individual (011) planes in a sequence of 400 to 500 frames of film per plane. Several thousand feet of film of both irradiated and unirradiated tungsten specimens were analyzed for "Buswell type" extra bright spots (see Fig. 1 of his paper), and indeed they were found. A careful examination of the sequences showed that these extra bright spots were atoms which were initially at the edges of (011) planar ledges and which, as field evaporation proceeded, moved in to the terrace and gave the appearance of being extra bright spots. Buswell's work and conclusions illustrate the absolute necessity of the atom-by-atom dissection of high index planes and the simultaneous recording of the corresponding structures.

Direct observation of the unperturbed surfaces of FIM specimens during subsequent annealing experiments in the absence of field evaporation between 15 and 120°K showed that these *i*'s diffused to the specimen surface and emerged there after undergoing long-range migration (i.e., distances of ~ 200 Å) in Stage I. These *i*'s were mobile at temperatures as low as $\sim 28^\circ$ K. From a diffusion analysis of the recovery spectrum, an *i* diffusion coefficient [$D_i \simeq 0.22 \exp(-0.085 \text{ eV/kT}) \text{ cm}^2/\text{sec}$] was calculated. It was also shown by means of control experiments that the volume change of migration of the fast *i* must have been < 0.1 at. volume. An example of the appearance of *i*'s in tungsten emerging near the surface of a specimen during the course of a warming experiment is shown in Fig. 6. The arrows in the figure point to either the positions where the *i*'s have almost emerged, or to the *i*'s which have emerged. At the present time it is impossible to distinguish between these possibilities. The time interval between the two frames in both the upper (A) and lower (B) sets of photographs is 1 sec, which corresponds to a temperature interval of 0.03° C. After the annealing experiments in Stage I were completed, the specimens were warmed to $\sim 298^\circ$ K (middle of Stage II) and then recooled to 18° K for a postanneal field evaporation examination of the specimen bulk. These experiments showed that the bulk concentration of *i*'s decreased as a result of annealing through Stage I to the middle of Stage II by at least a factor of 10. Thus these experiments showed that two different types of *i*'s did not exist simultaneously in Stage I. The possibility that there is a thermal conversion of the Stage I *i* into a slower Stage III *i* will be considered shortly.

Similar experiments on platinum irradiated with 20 keV and 30 keV Pt^+ at 10° K (Petroff and Seidman⁹⁰) have demonstrated the existence of long-range migration of an *i* in Stage I between 13 and 25° K. Application of the diffusion model to the data yielded $D_i \simeq (0.08-0.8) \exp(-0.04 \text{ eV/kT}) \text{ cm}^2/\text{sec}$. It has also been shown, by a comparison of the FIM results with resistivity recovery experiments on Stage I, that the volume change of migration of the fast *i* must be $\lesssim (0.02 \text{ to } 0.03)$ at. volume. Detailed experiments concerning Stage III recovery in this metal are in progress.

Consider now the possibility that the fast *i* converts thermally* into a slow *i* with an activation enthalpy H_i^c . It is readily shown that the distance which the fast *i* travels before it thermally converts is then

$$\bar{x}_i = \left(\frac{6D_i^0}{\nu} \right)^{1/2} \exp [(H_i^c - H_i^m)/2kT] \quad (13)$$

*In this discussion it is assumed that the thermal conversion of the *i* is governed by the standard Boltzmann expression independent of its geometric configuration (i.e., whether it is an *i* which is capable of migration in one or three dimensions). The possibility that the one-dimensional *i* (the crowdion) can only be converted in the stress field of a dislocation was excluded (see Seeger⁹¹ and Schilling, Schroeder, and Wollenberger⁹² for some of the controversial aspects of this problem).

Fig. 6 Two different examples (A and B) of the appearance of i 's as they diffused to an unperturbed surface of a tungsten FIM specimen during a warming experiment between 15 and 120°K. The specimen was maintained at the best image field characteristic of 15°K throughout the entire anneal. The temperature interval between frames 1 and 2 in both A and B was 0.03°K.

where $\nu \approx 10^{13} \text{ sec}^{-1}$, and H_i^m is the enthalpy of migration of the fast i . A necessary condition for the slow i to be of importance physically at any temperature is that $\bar{x}_i$ be shorter than the typical distance to an interstitial sink. Since H_i^c must be greater than H_i^m for this model to have any interest, we see that $\bar{x}_i$ decreases as T increases. Our results on tungsten so far indicate that $\bar{x}_i$ must be greater than $\sim 250 \text{ \AA}$ at 120°K, since the fast i 's have been observed to migrate out of the FIM specimen without converting. These data yield the condition $H_i^c - H_i^m > 0.037 \text{ eV}$ in tungsten. By carrying out further FIM

experiments at successively higher temperatures, it should be possible to find the slow i if it exists.

Of particular importance in the present context is the possibility that conversion does occur and that $\bar{x}_i$ becomes exceedingly short at temperatures near $0.5 T_m$. In such a case it will be a good approximation simply to replace the fast i with a slow i in models for void formation (see page 572).

Binding Enthalpies Between Point Defects

A program aimed at determining the binding enthalpies of small defect clusters involving v 's, i 's, and impurity atoms is under way using direct observation in the FIM. The clusters are being produced by either quenching or by irradiation and are being observed by the techniques described in the previous section.

We are currently completing a study* of the divacancy binding enthalpy, H_{2v}^b , in quenched platinum (Berger, Seidman, and Balluffi^{9,3}). In this work high-purity platinum wires were resistively heated and brine quenched from 1700°C , and the quenched-in electrical resistivity increment was measured at 4.2°K . FIM specimens were then prepared from these same wires and were examined in the FIM using the pulse field evaporation technique previously described. With this technique, 151 monovacancies and 1 possible divacancy among 387,000 atoms were found on $\{315\}$, $\{203\}$, $\{421\}$, $\{321\}$, and $\{671\}$ planes in six different specimens. An example of the appearance of a monovacancy, as revealed by the dissection of successive $\{315\}$ planes, is shown in Fig. 7.

In order to verify that the observed v defects were actually quenched-in v 's, and not artifact v 's induced on the specimen surface by the field ion microscopy, a considerable number of well-annealed specimens was field evaporated and searched for artifact v 's in exactly the same manner. About 350,000 atomic sites were scanned for this purpose, and it was found that relatively high artifact v concentrations were produced on $\{210\}$ and $\{317\}$ net planes but that negligible concentrations were produced on $\{315\}$, $\{203\}$, $\{671\}$, $\{421\}$, and $\{321\}$ planes. Therefore only v defects on the latter planes were counted in the quenched specimens.

These results indicate a monovacancy concentration quenched in of 3.6×10^{-4} at. fraction and an upper limit to the monovacancy resistivity of $2.9 \times 10^{-6} \Omega\text{-cm (at.\%)}^{-1}$.

An upper limit of the divacancy binding enthalpy was readily obtained from the observation that only one questionable divacancy was found among the 151

*The data quoted in this section are to be regarded as tentative since we have not analyzed completely all the FIM cinefilm recorded.

Fig. 7 A v revealed in the FIM by the atom-by-atom dissection of successive (315) planes in platinum. Field evaporation of the plane directly above the v, the plane containing the v, and the plane directly below the v is shown in frames 1 to 3, 4 to 9, and 10 to 12, respectively.

monovacancies. The total population of vacancy-type defects in thermal equilibrium at T_q may be expressed as

$$c_t = c_{1v} + 2c_{2v} + \dots + nc_{nv} \quad (14)$$

where n indicates the size of the cluster. For the present discussion we need only consider monovacancies and divacancies. If a specimen equilibrated at T_q is quenched rapidly, so that the total v concentration is essentially constant, then the monovacancy and divacancy populations will attempt to adjust themselves during the quench to follow the thermodynamic relation

$$C_{2v} = 6C_{1v}^2 \exp(H_{2v}^b/kT) \quad (15)$$

This change in the relative populations will continue during the quench until a temperature is reached where the diffusivities of the various defects become sufficiently small so that the defect distribution is "frozen-in." The fraction of divacancies frozen-in is then largely determined by H_{2v}^b and to a lesser extent by the quenching rate (see Fig. 1 in Balluffi, Lie, Seidman, and Siegel^{8,7}). Thus a measurement of the partition between monovacancies and divacancies after quenching at a known rate may be used to obtain H_{2v}^b . Application of these considerations to the experimental results yielded $H_{2v}^b < 0.1$ eV. The present experiment therefore constitutes the first absolute limiting value of H_{2v}^b for any metal.

The application of the above technique to vacancy defects in quenched tungsten is in progress in our laboratory, and initial imaging experiments on nickel indicate that it might also be possible to study v 's in this metal. Hence the FIM is proving itself to be a useful instrument for the quantitative study of the smallest possible vacancy cluster, the divacancy. In principle, it should be possible to investigate higher order clusters, i.e., trivacancies, quadrivacancies, etc. However, considerable difficulties may be encountered in locating such defects under typical conditions because of the very small volume (10^{-18} cm³ to 10^{-16} cm³) of material which can be sampled by the FIM technique.

We would also like to point out that it appears entirely feasible to study point defect-impurity atom interactions through the use of the recently developed atom-probe FIM.⁹⁴⁻⁹⁶ This instrument has the capability of measuring the charge-to-mass ratio of a single preselected atom on the surface of the specimen, and hence is ideally suited for the task of identifying impurity atoms that bind to v 's or i 's. In a typical situation it should be possible to probe the atoms in the nearest neighbor sites around a given point defect (or point defect cluster) in order to ascertain their chemical compositions. Such a technique would provide a powerful means of investigating the heterogeneous processes responsible for void nucleation which we have discussed earlier. Such an instrument is currently being constructed in our laboratory, and experiments along these lines are being planned.

Atomic Structure of Depleted Zones

In this section we describe some recent results on the detailed atomic structure of depleted zones at low temperatures that have been obtained with the FIM using the pulsed field evaporation technique described previously. In addition, further FIM experiments are described which are under way and which are designed to elucidate the possible role depleted zones play in the nucleation of voids at $0.5 T_m$.

The zones were produced (Beavan, Scanlan, and Seidman^{9,7}) in high-purity tungsten by irradiation with 20 keV W^+ ions at 18°K and were then examined at the same temperature. The three-dimensional structure of the positions of individual v's and i's in the zones was derived from measurements made on the FIM films on our Vanguard motion analyzer.^{8,8} The detailed geometrical methods used to reconstruct the zones are described elsewhere.^{9,7} The zone that we now consider was detected on a sequence of successive (111) planes located $\sim 33 \text{ \AA}$ below the original surface of the specimen surface which was exposed to the ion beam. Figure 8 shows 20 different micrographs of this zone taken at various stages of the dissection process which involved the recording and analysis of 4.4×10^3 frames of film. The positions of the atoms, v's, and i's found in this plane are illustrated schematically below each micrograph. In no case was any v attributed to an apparent missing atom, unless the v was certified visually in the FIM micrograph. The depleted zone appeared to be contained completely within the bounds of this stack of successive (111) planes, since no v's were found on any of the planes directly adjacent to it. In the entire volume of the specimen examined ($\sim 10^{-17} \text{ cm}^3$) this was the only depleted zone detected; hence we conclude that it was caused by a single incident ion.

There were 172 v's within the region (consisting of 1850 at. volumes) which contained the zone. In addition, 17 i's were found in, or immediately adjacent to, the zone. This result yields an average i concentration of $\sim 0.92 \text{ at.}\%$. It has been shown in this laboratory (Seidman, unpublished work) that a possible contrast effect accompanying the appearance of an i is the observation of an artifact v immediately prior to the detection of the i. Making this correction, the average concentration of v's in this zone was determined to be $\sim 8.7 \text{ at.}\%$. Thus the depleted zone had a rather spongy character, and there was a large local imbalance between the v's and i's.

Figure 9 shows a (111) projection of the v and i positions. The v's are denoted by open circles, the i's by solid triangles, and the multiple concentric circles imply that more than one v projected to the same atom position. This mode of projection reveals the three distinct main branches of the zone. The direction of elongation of the three branches was along the three different $\langle 011 \rangle$ directions lying in the (111) plane. An isometric drawing of this zone is shown in Fig. 10, where the thickness of each slab* is $4.56 \text{ \AA}$ (5 at. layers), and the

*With the exception of the third slab from the bottom, which is 10 at. layers thick.

Fig. 8 Twenty FIM micrographs, out of a sequence of 4.4×10^3 recorded frames, showing a depleted zone in tungsten detected in the (111) plane at various stages of the atom-by-atom dissection process. The larger solid black circles in frames 4, 7, 9, and 16 indicate i's, the open circles indicate v's, and the smaller solid black circles indicate lattice atoms.

boundary of each slab was determined by connecting the outer point defects on its periphery by straight line segments. It is clear from Figs. 8 to 10 that the geometry of this zone is not sufficiently regular to allow it to be approximated by a sphere or a right circular cylinder or, for that matter, any simple geometric form.

Twenty-five additional i's were found in the surrounding lattice at appreciable distances from the zone. The positions of these i's are shown in Fig. 11. It was possible to show that 23 of these 25 i's could have been propagated away from the zone along $\langle 011 \rangle$ and $\langle 111 \rangle$ directions as focused replacement sequences. The measured distances of these i's from the zone along $\langle 011 \rangle$ and $\langle 111 \rangle$ directions were between 45 Å to 150 Å and 45 Å to 85 Å, respectively. Unfortunately the upper and lower limits of these distances were determined by a geometric sampling problem and not by the intrinsic range of focused replacement sequences (Beavan et al.⁹⁷).

We note that the features of the depleted zone reported in the previous section are in general qualitative agreement with many of the details of Beeler's computer simulated model.⁹⁸ In particular, the elongation along $\langle 011 \rangle$ directions arose in Beeler's model because of quasi-channeling events. The 160 displaced atomic sites which were detected are fewer than the 200 predicted by the Kinchin-Pease model but are greater than the average of 106 displaced atoms per depleted zone calculated by Beeler. The fact that the number observed is less than the number predicted by the Kinchin-Pease model is most likely due to the recombination of i's and v's which originated from different displacement events within the cascade. It is clear that the depleted zone described here may not be characteristic of the average zone produced by a 20-keV primary and that it would be possible, and desirable, to analyze a number of such zones in order to obtain a better average representation.

The structure of depleted zones at low temperatures is also being investigated in a similar manner with the FIM in platinum irradiated with Pt^+ ions (Petroff and Seidman, research in progress). An example of an i is shown in Fig. 12 which was found in a depleted zone located in the (531) and (321) planes of a platinum specimen. The 12 frames shown in this figure were selected from an extended sequence of ~503 frames. The v's that precede the i (see frames 2 to 4) may be a contrast effect caused by the displacement field of the i. Experiments have also been initiated (Dury and Seidman, research in progress) in which tungsten specimens injected with helium are being bombarded with self-ions at higher temperatures approaching $0.5 T_m$. These specimens will then be examined in the FIM at low temperatures by pulsed field evaporation, and the structure of any depleted zones or void-like regions will be determined. Special efforts, involving perhaps the use of the atom probe FIM (see page 584), will be made to detect the role of helium in producing and stabilizing the observed structures.

Fig. 9 Four (111) projection maps of the v's and i's found in the depleted zone shown in Fig. 8. The v's are indicated by open circles, the i's by solid

black triangles, and the multiple concentric circles imply that more than one v projected to the same atomic position. Note the elongation of the depleted zone along the three different $\langle 011 \rangle$ directions in the $\langle 111 \rangle$ plane.

Fig. 10 An isometric drawing of the depleted zone detected in the (111) plane constructed from the projection maps shown in Fig. 9. S.I.A. indicates a self-interstitial atom (i.e., an i).

SUMMARY AND CONCLUSIONS

1. Void formation under reactor conditions at $T = 0.5 T_m$ involves the nucleation and growth of voids and interstitial (i) dislocation loops. Preferential attraction of the i's to the dislocations produces an excess of vacancies (v's) which cause void growth. An understanding of void formation therefore requires knowledge of at least the following: (1) mobilities and concentrations of the various v and i defects present during irradiation, (2) nucleation mechanisms for both voids and dislocation loops, and (3) growth mechanisms and kinetics of both voids and dislocation loops.

2. Useful information about several aspects of void formation under reactor irradiation conditions may be obtained by considering void formation under quenching conditions in the absence of i's.

3. The driving force (i.e., v chemical potential) for void formation under typical quenching conditions is larger than that for void formation under reactor irradiation at $T = 0.5 T_m$.

4. The nucleation of v precipitates in quenching experiments, both in the form of collapsed defects and in the form of voids, appears to occur heterogeneously at impurities. There is no experimental evidence that proves the existence of significant amounts of homogeneous nucleation even in nominally high-purity metals.

Fig. 11 An isometric drawing showing the relation of the i 's in the lattice to the position of the depleted zone detected in the (111) plane (Figs. 8 to 10). The direction of the incident ion beam $\{\sim[21\bar{1}]\}$ is almost normal to the plane of the page. The arrows from the depleted zone to the i 's indicate the most probable propagation directions.

5. Voids in quenching experiments appear to be nucleated heterogeneously by gaseous impurities that interact strongly with small v clusters and prevent their normal collapse into two-dimensional aggregates.

6. Growing voids tend to be polyhedral in quenching experiments, since growth occurs by the nucleation of platelets of absorbed v 's on their surfaces.

7. Experimental evidence indicates that void growth in quenching experiments is an easy process and that voids should act as highly efficient v sinks.

8. In the case of void shrinkage during annealing, there is evidence that the process is easy and is diffusion (rather than interface) controlled, and that voids tend to become spherical because of the easy formation of shrinkage surface ledges at void corners and edges.

9. The homogeneous nucleation of voids during reactor irradiation at $0.5 T_m$ is more difficult than in quenching experiments because of the lower v chemical

Fig. 12 The uncovering and appearance of an *i* during field evaporation in the (531) plane of a FIM platinum specimen irradiated with Pt^+ ions at 10°K . This *i* was found inside a depleted zone with a *v* concentration of $\sim 2 \text{ at.}\%$. Each heavy dark arrow in the schematic drawing below each FIM pattern indicates the completion of the field evaporation of one complete (531) planar layer. Note that the *i* begins to show weak contrast in frame 6, and that its contrast becomes stronger as the electric field becomes stronger due to the removal of the atoms in the atomic plane above it. [Pétroff and Seidman, unpublished work.]

potential and the presence of *i*'s which tend to shrink *v* nuclei. Calculations of expected homogeneous void nucleation rates under quenching conditions (using classical nucleation theory) and irradiation conditions (using Russell's recent treatment of nucleation in the presence of both *v*'s and *i*'s) show that homogeneous nucleation is much too slow to occur under reactor irradiation conditions.

10. Considerable experimental evidence is available which indicates that void formation during reactor, fast ion, and electron irradiation is considerably enhanced by the presence of impurities, notably helium and other gases. It is concluded that void nucleation during irradiation is heterogeneous and that it requires the presence of impurities (apparently gaseous) which prevent nuclei from collapsing into two-dimensional aggregates. Void nucleation in quenching and irradiation experiments are therefore quite similar in this respect.

11. There is some evidence that the high *v* concentrations achieved in depleted zones during reactor irradiation may aid void nucleation in certain materials.

12. Relatively little attention has been paid to mechanisms of the formation of i-dislocation loops under irradiation conditions even though, as stressed in item 1, these loops play an important role in controlling void growth.

13. There is considerable experimental evidence that i-dislocation loops are heterogeneously nucleated at impurities under irradiation conditions.

14. Void growth during irradiation is expected to be more difficult than under quenching conditions because of the lower v chemical potential and the presence of the i 's which make the formation of growth nuclei on the void surfaces more difficult.

15. Dislocation climb induced by a current of excess i 's under irradiation conditions is a nucleation and growth process involving the formation of jog pairs by i 's in the core. The presence of v 's may hinder this process.

16. Newly developed FIM techniques have been shown to be capable of yielding direct experimental information, on the atomic level, about various defect behavior and mechanisms of interest in the void-formation problem. These techniques involve essentially the atom-by-atom dissection of specimens by pulsed field evaporation and the corresponding recording on film of the extensive number of FIM images produced at each stage of the process. (It has been possible to record and analyze $\sim 5 \times 10^5$ frames of 35-mm cinefilm for each of the investigations described in items 17 to 19. Thus we have been able to gather sufficient data to make the experiments statistically significant.)

17. The application of FIM techniques to the problem of the mobility of the i has yielded direct evidence for the existence of a fast i which undergoes long-range migration at low temperatures in Stage I of both tungsten and platinum.

18. The FIM technique has been applied to the problem of the measurement of the divacancy binding enthalpy, and a limiting absolute value of 0.1 eV has been determined for this quantity for platinum.

19. A study of the defect structures of depleted zones in tungsten irradiated with 20 keV W^+ ions has provided direct evidence for a high local v concentration (~ 8.7 at.%) and a low local i concentration of ~ 0.92 at.% in the zones. Direct evidence was also found for focused replacement sequences along $\langle 111 \rangle$ and $\langle 110 \rangle$ directions.

20. Further applications of the FIM technique to problems including (1) the possible existence of a slow i in Stage III; (2) binding enthalpies between v defects, i defects, and impurity atoms; and (3) the effect of temperature on the defect structure of depleted zones are in progress in our laboratory.

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DISCUSSION BY ATTENDEES

Russell: I would like to emphasize that my void-nucleation equation applies only to the very restricted case considered by the authors, namely, homogeneous nucleation in the presence of vacancies and solvent interstitials. The effects of active and inert-gas atoms and of interfaces were ignored, not because they were felt to be unimportant but because they made the problem very difficult. A more realistic rate equation that reflects the influence of these defects is in preparation.

Wiedersich: Do you have positive evidence for heterogeneous nucleation as contrasted to the calculated nucleation rates that are extremely dependent on the free surface energy taken? (On what surface energy and at what temperature do you base the estimates of homogeneous-nucleation rates?)

Balluffi: The only positive evidence is that all the experiments which are listed in our tables involved looking at nominally high-purity material and then either putting in or taking out impurities, and, when the impurity concentrations were changed in this way, changes in the concentrations of vacancy precipitates in the form of either collapsed precipitates or voids were found. The conclusion would be that the impurities which were put in or taken out were responsible for the changes in the vacancy precipitate density. Unfortunately, obtaining absolutely positive information through the use of a known perfectly clean system has been impossible, so that all the evidence is based on differences and the fact that these differences exist. (The data which we used in our calculations are given in the paper.)

[Note submitted after the meeting: It should also be added that it has apparently not been possible to reduce the vacancy precipitate density to either zero or to a small fixed value by continuously reducing the impurity level in metals that have been studied systematically. This lack of a final saturation value of the precipitate density implies that impurities must be involved. Some of the experimental evidence for aluminum and gold is shown in Fig. 1. Here we use the residual resistivity $\rho(4.2^\circ\text{K})$ as a measure of the impurity concentration. In the case of gold, the precipitate density, N_s , decreased continuously as the resistivity, i.e., impurity concentration, decreased. There

Fig. 1 Data for aluminum and gold: vacancy precipitate density as a function of residual resistivity.

does not seem to be any reason to believe that a further decrease in impurity concentration would not cause a further decrease in N_s . Appreciable changes in N_s for gold are seen to occur when ρ (4.2°K) changes by $\sim 2 \times 10^{-10} \Omega\text{-cm}$. Taking the average resistivity per 1% of impurity as $\sim 1.5 \times 10^{-6} \Omega\text{-cm}$, we find that these changes correspond to a concentration change $\sim 10^{-6}$ (the change in the concentration of the active nucleating impurity may, of course, be much smaller than this.) For aluminum, appreciable changes in N_s occurred for even smaller changes in the base resistance, suggesting again that extremely small impurity concentration changes caused significant changes in N_s .]

Since essentially all metals that have been used in experiments have contained impurities at these levels, it is hard to escape the conclusion that they must have influenced the precipitation of vacancies, i.e., heterogeneous nucleation occurred. Chik and Seeger would not agree with me. They would argue that in the 99.999% pure range, or better, nucleation becomes homogeneous. I would certainly question this.

Seeger: I want to say two things on the question of heterogeneous vs. homogeneous nucleation. With regard to the irradiation case, I would accept your conclusion that one has heterogeneous nucleation if you include in this meaning the strain field of a dislocation; if it means only nucleation at impurities, I would have to disagree.

Balluffi: I would regard the negative stress field of a dislocation as a heterogeneous-nucleation site. It is also conceivable that heterogeneous nucleation at impurities trapped near dislocations is particularly easy.

Seeger: With regard to the quenching case, this has been an old bone of contention between Cornell and Stuttgart. We would argue as follows. We have investigated very pure gold. We tried to explain the results on the basis of homogeneous nucleation. From this treatment you get a set of parameters. At that time we could not check these parameters. Since that time the work on platinum has come out, and essentially the same parameters come out if you interpret it in the correct way. The conclusions that we draw from the hypothesis of homogeneous nucleation agree with later work where you follow kinetics. I think this says that homogeneous nucleation may occur. I am far from saying it is the rule.

Balluffi. My argument would simply be that there is experimental evidence for heterogeneous nucleation even in nominally 99.999% pure material. There is no evidence of a saturation of the number of defects with changes in impurity concentration. On the other hand, Professor Seeger is saying that, if you use reasonable parameters for the binding energies, etc., you can explain the amount of nucleation that is observed in this system homogeneously; therefore it might be reasonable to regard it as homogeneous. Clearly the result that the precipitation data can be fit by a rather complex point-defect homogeneous-precipitation model containing a large number of undetermined parameters is not very conclusive. It would be interesting, for example, to attempt to fit the data with a similar heterogeneous model!

Seeger: On the basis of the finding that the density and size of the defects observed in the electron microscope vary strongly with the addition of impurities, the authors argue that void formation in quenched metals is always nucleated heterogeneously. While I recognize that it is not easy to distinguish in a definite way between homogeneous and heterogeneous nucleation of vacancy agglomerates in "pure" metals, I should like to point out that the criterion used by the authors is not entirely satisfactory and that I think that a better criterion is available. The unsatisfactory aspect of the criterion used by Balluffi and his associates is that addition of impurities is bound to lead eventually to heterogeneous nucleation. It is feasible that, in some of the cases investigated in this manner, the smallest additions used were large enough to cause the homogeneous nucleation of the pure specimens to be changed into the

heterogeneous nucleation of the "impure" specimens. A more satisfactory approach to the problem appears to me to be the following: develop a model for homogeneous nucleation, compare its predictions with the experimental results on the purest specimens available, and deduce from such a comparison migration and binding energies, frequency factors, etc., of divacancies, trivacancies, etc., appearing as parameters of the model. These deductions may then be compared with the results of other techniques, e.g., kinetic studies. Satisfactory agreement may then be taken as an argument for the applicability of the model and hence for homogeneous nucleation.

A number of years ago, K. P. Chik [*Phys. Status Solidi*, **10**: 659, 675 (1965)] carried out observations on the nucleation of tetrahedra in quenched gold and deduced from them, by means of a homogeneous-nucleation model, parameters characterizing divacancies, trivacancies, etc. At that time the interpretation of the electrical-resistivity studies on quenched gold was sufficiently unclear to preclude a definite comparison between the two methods. In the meantime the work of J. J. Burton and D. Lazarus [*Phys. Rev., B*, **2**: 787 (1970)] has clarified to a considerable extent the annealing kinetics. In unpublished work I have been able to convince myself that, within experimental errors, the deductions from the work of Chik and of Burton and Lazarus agree with each other. I conclude from this that Chik was indeed dealing with a case of homogeneous nucleation.

Chen: There is no denying that impurities could induce nucleation of voids. However, in the case of quenched aluminum, we found that it is not necessary to invoke the presence of impurities for the nucleation of vacancy clusters, particularly at the lower temperatures where nucleation is more favorable. We also found that the results of calculations based on classical nucleation theory were not consistent with our data. Moreover, until the formation energies of small vacancy clusters are known, any result based upon classical nucleation theory should be taken with caution, as pointed out by McComb and Meshii.

Balluffi: In reply to Professor Seeger, I keep an open mind about the situation, but I am definitely biased toward the viewpoint that the nucleation is usually heterogeneous. Hopefully, when purer and purer materials become available, the question will be settled experimentally.

I agree with Chen that the results of classical nucleation theory must be taken with caution. As seen in our paper, we use classical nucleation theory only to look at differences in the nucleation rate under quenching and irradiation conditions while holding the other parameters of the vacancy system constant. We believe that the results of such a procedure are instructive.

VOID FORMATION IN QUENCHED STAINLESS STEEL

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ABSTRACT

Disk-shaped specimens of five austenitic stainless steels were solution treated at temperatures of 1300 and 1100°C and directly quenched into salt or lead baths held at aging temperatures between 400 and 700°C. In one of the steels, which contained an unusually high phosphorus concentration (18 Cr-10 Ni-0.31 P), vacancy loops and voids were produced; the nature of the defects formed depended upon the solution-treatment temperature and on the aging temperature. It was found that there was a critical temperature below which it was necessary to quench in order to nucleate voids. Following solution treatment at 1300°C, the critical temperature was between 650 and 700°C; quenching to lower temperatures increased the concentration and decreased the average size of the voids. After solution treatment at 1100°C, it was necessary to quench to below 500°C in order to nucleate voids. The observation of voids in quenched stainless steels has not been reported previously. The phenomenon is believed to be the result of a strong phosphorus atom-vacancy interaction which increases the equilibrium vacancy concentration at the solution-treatment temperature and greatly modifies vacancy-clustering behavior at the aging temperature.

A supersaturated concentration of vacancies, of the order of 10^{-4} , may be introduced into face-centered cubic (fcc) metals by quenching from high temperatures. During the quench and during subsequent annealing, the supersaturated vacancy concentration decays by migration to preexisting sinks, such as grain boundaries, dislocations, and incoherent precipitate-matrix interfaces, and also by clustering to form stable vacancy defects. The nature of the defects formed is influenced by such variables as composition, solution-treatment temperature and atmosphere, quenching rate, and aging temperatures. In recent years, many workers have observed voids in quenched and aged fcc metals of fairly high purity. Void concentrations of the order of $5 \times 10^{15} \text{ cm}^{-3}$ may be produced in aluminum,¹ but nucleation appears to occur less readily in copper,

silver,² gold,³ and nickel.⁴ It is believed that the nucleation of voids is closely associated with the presence of dissolved gases, although the precise role of gas atoms is not clearly understood. For example, it has been clearly shown by Shimomura and Yoshida⁵ that hydrogen, dissolved from the solution-treatment furnace atmosphere, is essential for the nucleation of voids in aluminum. On the other hand, Clareborough et al.² showed that oxygen and hydrogen were equally effective in silver and that, if neither gas was present, the rate of void nucleation was very low. Increasing metallic impurity content appears to suppress void nucleation in aluminum, and, although vacancy clustering occurs readily in many aluminum alloys, resulting in the formation of perfect and imperfect (111) loops, voids are only occasionally observed.

In general, quenched and aged austenitic alloys do not exhibit any evidence of vacancy clustering, although Vingsbo⁶ reported the formation of a very small number of prismatic loops in an 18 Cr–13 Ni steel quenched from 1170°C into iced brine and aged at 350°C. It appears that, for some reason, vacancy clusters rarely achieve the critical size for stability in quenched austenite. Also mitigating against defect formation is the fact that high dislocation densities are frequently developed as a result of stresses set up around undissolved carbide and intermetallic compounds. The work described here was undertaken as a study of carbide and intermetallic compound precipitation in commercial austenitic stainless steels. The experiments were not designed to provide information on vacancy-clustering behavior, and the observation of quenching defects was an entirely unexpected phenomenon.

TABLE 1
COMPOSITION OF STEELS IN WEIGHT PERCENT

Steel design- nation	Cr	Ni	C	P	Ta	Nb
A	18.18	10.25	0.01	0.31		
B	18.11	10.4	0.10	0.03		
C	20.1	25.1	0.01	0.02		0.62
D	19.9	24.8	0.98	0.02		0.86
E	18.3	12.2	0.10	0.04	1.83	

EXPERIMENTAL PROCEDURE

The compositions of the steels used are given in Table 1. The specimens used were in the form of disks 3 mm in diameter and 0.8 mm thick. They were solution treated in a vertical furnace and then quenched directly to the aging temperature by allowing them to fall into a lead or salt bath situated below the solution-treatment furnace. Aging temperatures between 400 and 750°C were

used, and quenching rates were of the order of $500^{\circ}\text{C}/\text{sec}$. After quenching and aging, the disks were ground to $250\ \mu$, electropolished, and examined by transmission electron microscopy.

RESULTS

Three different solution treatments were used: 30 min at 1100°C ; 15 min at 1300°C ; or a double treatment of 15 min at 1300°C , after which specimens were cooled to 1100°C and held there for 30 min before quenching. Of the five steels listed in Table 1, only steel A showed quenching defects. This steel has a basic 18 Cr–10 Ni composition, with a low carbon content and an exceptionally high phosphorus content. The major precipitating phase in this steel is the tetragonal phosphide Cr_3P ; small amounts of M_{23}C_6 were also observed.

The type of vacancy defect produced varied with solution treatment and aging temperature, as shown in Table 2. The nature of the various types of

TABLE 2
THE EFFECT OF SOLUTION-TREATMENT TEMPERATURE
ON DEFECT NUCLEATION

Aging temp., $^{\circ}\text{C}$	Solution treatment		
	1100°C for $\frac{1}{2}$ hr	1300°C for $\frac{1}{4}$ hr	1300°C for $\frac{1}{4}$ hr and slow cooled to 1100°C for $\frac{1}{2}$ hr
700	No defects	Planar defects	No defects
650	(110) loops	Voids	(110) loops
600	(110) loops	Voids	(110) loops and (110) defects
500	(100) loops	Voids	(110) loops and (100) defects
450	(110) loops		
400	Voids		

planar defects observed and their influence on the precipitation of Cr_3P are described elsewhere.^{7,8}

It was found that there was a critical temperature below which it was necessary to quench in order to nucleate voids. Following a solution treatment of 15 min at 1300°C , the critical temperature was somewhere between 650 and 700°C . As the aging temperature was decreased, the concentration of voids increased and their average size decreased, as shown in Table 3. Figure 1 shows the voids formed at 600°C . The contrast at the dislocation is associated with the precipitation of Cr_3P . Figure 2 is a dark-field micrograph in which the contrast from the voids is below background where the diffracted beam intensity is

TABLE 3
VOID SIZES AND CONCENTRATIONS AFTER
QUENCHING FROM 1300°C

Heat treatment	Void concentration, cm ⁻³	Average diameter, Å
650°C for 48 hr	5×10^{14}	100
600°C for 95 hr	1.7×10^{15}	70
500°C for 48 hr	5×10^{15}	50

strong and above background where the diffracted beam intensity is weak. Confirmation that the voids were distributed throughout the foil and were not surface defects was obtained by stereo microscopy.

It was found that the void size and distribution produced by quenching to 500°C and aging for 48 hr were unaffected by subsequent annealing at 700°C for 100 hr or 750°C for 10 hr. Annealing at 800°C, however, resulted in the formation of fewer, larger voids.

Throughout this study, specimens were solution treated in a 99.99% argon atmosphere. The furnace design was unsuitable for carrying out direct quenching experiments using either a vacuum or a hydrogen atmosphere in the solution-treatment stage. It was possible, however, to carry out a solution treatment in either hydrogen or argon and to allow the specimens to fall to the bottom of the furnace and cool to room temperature before removing them from the furnace atmosphere and aging them. Following this procedure, specimens solution treated for 15 min at 1300°C in either argon or hydrogen and then aged at 500°C had identical structures. Both treatments produced $\sim 10^{14}$ voids/cm³ with a much wider range of sizes than that produced by direct quenching to 500°C.

When a solution treatment of 30 min at 1100°C was used, the critical temperature for void nucleation was reduced to between 400 and 450°C. Decreasing the solution-treatment temperature from 1300 to 1100°C had the effect of not only decreasing the vacancy supersaturation at a given aging temperature but also of decreasing the supersaturation of phosphorus. The double solution treatment was used to separate these effects in order to give a combination of a solute supersaturation typical of the 1300°C treatment and a vacancy supersaturation typical of the 1100°C treatment. Precipitation of chromium phosphide did not occur on cooling from 1300 to 1100°C since the Cr₃P solvus temperature, determined by re-solution experiments, was around 850°C. Following the double solution treatment, it was found that the sequence of vacancy defect nucleation was similar to that following the single treatment at 1100°C and that the critical temperature for void nucleation was below 450°C.

Fig. 1 Voids in steel A solution treated for 15 min at 1300°C and direct quenched to 600°C for 95 hr. Magnification, 40,000x.

Fig. 2 Voids in steel A solution treated for 15 min at 1300°C and direct quenched to 500°C for 48 hr. Magnification, 110,000x.

DISCUSSION

The quenching defects observed in steel A were not observed in any of the other steels listed in Table 1 when subjected to the same heat treatments. The most significant feature of the composition of steel A is the presence of 0.3 wt.% phosphorus, and it is believed that this factor is mainly responsible for the completely different vacancy-clustering behavior in this steel.

Quader and Dodd⁹ and Johnston¹⁰ et al. demonstrated that the concentration and nature of quenching defects in gold are strongly influenced by the addition of certain elements. The stimulation of defect nucleation is believed to be due to an interaction between vacancies and solute atoms which may arise from either electrostatic fields or strain fields associated with the solute atom. The magnitude of the electrostatic binding energy is proportional to the valency of the impurity atom, and Johnston et al. showed that, in gold, multivalent additions were more effective than monovalent atoms in enhancing the nucleation of vacancy defects. In the present case, it is suggested that the formation of stable vacancy defects arises from an electrostatic interaction between phosphorus atoms and vacancies. The existence of a phosphorus atom-vacancy binding energy would have several consequences. The vacancy concentration at the solution-treatment temperature would be increased, and the rate of vacancy migration during quenching and aging would be reduced. It is likely, however, that the most important result of a phosphorus atom-vacancy interaction is the formation of stable phosphorus atom-vacancy clusters that subsequently grow into visible defects by absorbing vacancies, the geometry of the defect formed being strongly dependent on the vacancy supersaturation.

A comparison of the results obtained using the double solution treatment with those obtained using the single treatment at 1300°C indicates that the critical temperature for void nucleation is mainly determined by the quenched-in vacancy supersaturation. When the initial vacancy concentration is high, as in the 1300°C treatment, the critical temperature is between 650 and 700°C. If the vacancy concentration is lowered by cooling to 1100°C, then loops are formed at 650°C, and the critical temperature for void nucleation is depressed to below 450°C.

It is difficult to draw any firm conclusions regarding the effects of dissolved gases on void nucleation in these experiments. Identical void distributions were produced in specimens furnace cooled to room temperature in hydrogen or argon and subsequently aged. This insensitivity to furnace atmosphere may indicate that the presence of bound phosphorus atoms stabilizes vacancy clusters in a three-dimensional form and that dissolved gases are not required to prevent collapse into a planar form.

There is no reason to suppose that phosphorus is unique in its influence on vacancy-clustering behavior. Other elements that, from strain energy or electrostatic considerations, may be considered to possess a significant vacancy binding energy should produce effects similar to those observed in the

phosphorus steel. If certain solute elements are able to modify vacancy-clustering behavior during quenching, then it is conceivable that the same elements could modify vacancy-clustering behavior under irradiation. In quenching experiments, void nucleation at 500°C occurs at vacancy supersaturations of the order of 10^6 . Under fast-neutron irradiation at say 500°C, the vacancy supersaturation is many orders of magnitude less than this, and void formation almost certainly occurs via the nucleation of stable gas bubbles. It seems unlikely that the addition of elements of high vacancy binding energy would affect the nucleation process, but they could conceivably affect the rate of growth of voids by delaying vacancies during their migration to voids and other sinks and thus increasing the probability of recombination with interstitials. For such a process to be permanently effective, encounters would be required between interstitials and vacancy-solute pairs in which the interstitial is annihilated, thereby releasing the solute atom to combine with another vacancy and so repeat the process.

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DISCUSSION BY ATTENDEES

Harkness: Could you expand on your discussion of why voids instead of loops should nucleate in austenitic stainless steels when loops are much the lower energy form?

Rowcliffe: It is not clear that loops are indeed the lowest energy form of the vacancy defect in stainless steel, e.g., Buswell (CEGB Report RD/B/N/1584)

calculates that voids are the lowest energy form of cluster at 500°C if the surface energy is taken as $<1800 \text{ ergs/cm}^2$.

Calculations of the relative energies of loops, voids, and tetrahedra based on elastic continuum methods should not be taken as a literal guide to the type of quenching defect expected in any given system.

In practice, it has been demonstrated that the type of defect formed in, e.g., aluminum, copper, gold, and now in stainless steel, is determined by such variables as quench rate, vacancy supersaturation, solute type, and concentration. Depending upon these variables, more than one type of vacancy defect may be observed in any given metal.

It could be argued that compositional changes affect macroscopic properties, such as surface and stacking-fault energy, but it seems more probable that the nature of the defect observed is governed by solute-vacancy interactions that alter the shape and stability of small vacancy clusters.

It is believed that, in the work described here, phosphorus stabilizes small vacancy clusters. When the vacancy supersaturation is high, a three-dimensional phosphorus-vacancy cluster is stable, and voids are nucleated. At lower vacancy supersaturations, clusters collapse into a planar form, and loops are nucleated.

Michel: What other impurity elements in stainless steel, besides phosphorus, would you expect to contribute to void formation upon quenching and at what concentration? What is the magnitude of the electrostatic phosphorus atom-vacancy binding energy?

Rowcliffe: This is something that would have to be determined experimentally but elements such as titanium, zirconium, and aluminum, for example, might have some effect on vacancy clustering behavior.

The experiments described do not yield a value for the binding energy. The vacancy formation energy in this steel, based on estimates of the vacancy concentration quenched in from 1300 and 1100°C, is $\sim 1.1 \text{ eV}$. We do not know what the vacancy formation energy is in this type of steel without the phosphorus addition.

Russell: What was your maximum void density?

Rowcliffe: The maximum density observed was $5 \times 10^{15} \text{ voids/cm}^3$, following solution treatment at 1300°C and direct quenching to 500°C.

PRODUCTION OF VACANCY CONDENSATES BY LASER BOMBARDMENT

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ABSTRACT

Bombardment of thin foils by a laser pulse of 3.5×10^{-8} sec duration and 1.5 cal/cm^2 total energy input has been found to produce high concentrations of vacancies in 99.98% pure nickel and vanadium. The vacancies condense upon annealing the foils at $0.31 T_m$ to form voids in nickel and faulted loops and a few isolated tetrahedra in vanadium.

Although it was initially believed that the vacancies were formed as a result of quenching, concentrations as high as 1% or 10^2 times that expected at the melting point have been observed. Also, the generation of vacancies by nonconservative motion of jogs does not appear feasible because the dislocation density is too low. Interaction of shock waves generated by the laser pulse is suggested as a possible alternative explanation. The technique offers a supplementary approach to the study of vacancy condensates and the factors that affect their nucleation.

Among the more vexing aspects of the study of voids in irradiated materials is the number of variable parameters which must be considered in an irradiation experiment. The present experiments were undertaken to reduce the parameters to one type of defect, the vacancy, and a defect concentration controlled only by the loss rate to sinks. Specific aspects of the problem of void nucleation and growth could then be examined under controlled annealing conditions.

Laser bombardment was examined as a potentially useful technique for producing a large number of microscopy samples from thin sheet specimens with a relatively simple experimental setup. As the following report will show, vacancy condensates have been observed in a variety of materials but with the unexpected result that the vacancy concentrations observed exceeded those anticipated for quenches from the melting point.¹ Although this technique opens up many fascinating new aspects to the study of vacancies in metals, it adds the uncertainties of a new phenomenon yet to be fully understood. The results presented are therefore of the nature of a survey of initial observations of laser-bombarded materials.

EXPERIMENTAL TECHNIQUE

Laser bombardment was accomplished with a ruby laser (6934-Å wavelength) operated in the "Q-switched" mode. The beam intensity was approximately 1.5×10^8 W/cm² which, with a pulse length of 3.5×10^{-8} sec, supplied a total energy of 1.25 cal/cm² to the foil surface. The samples were masked to expose a 3-mm-diameter spot to the beam so that 0.088 cal was received by the sample, and, assuming a reflectivity of 60%, approximately 0.035 cal was actually absorbed by the sample.

The impact of the laser beam did not cause crater formation at these energy densities, although a slight depression in the foil associated with surface damage was produced. Under these conditions the principal macroscopic damage consists of surface melting and vaporization of a few atomic layers.² Heat flow into the foil is relatively small, and the calculated temperature rise for nickel drops from the melting point at the front face to about 500°C within 3 μ into the sample.³ Relative distances between these features and the observation plane are shown schematically in Fig. 1.

All samples were in the form of thin sheet rolled to 0.001 to 0.002 in. thick and annealed at approximately $0.75 T_m$ for 1 hr in a vacuum ($>10^{-6}$ torr). The samples were bombarded in air (the short pulse length precludes contamination of any but a thin layer on the front face). Microscopy specimens were punched from the foil, annealed in vacuum at the desired temperature, thinned to transparency with a double-jet electropolisher, and examined in a Philips EM 200 electron microscope operated at 100 kV.

EXPERIMENTAL RESULTS

Nickel

Nickel of 99.98% purity was rolled to a thickness of 0.002 in., annealed at 1050°C for 1 hr in a vacuum ($>1 \times 10^{-6}$ torr), and laser bombarded. Anneals at 210°C ($0.28 T_m$) produced a few spots showing black-white contrast, but an anneal at a temperature at which vacancies become mobile, 245°C ($0.30 T_m$), produced the large rectangular voids shown in Fig. 2. Voids such as those shown in Fig. 2 were typical of the entire electron-transparent region of the foil. The orientation of the voids changed from grain to grain, indicating the existence of a unique orientation for the void facets. Attempts to identify the planes did not yield an unequivocal answer because of the poor definition of the void surfaces, but the closest low index planes appeared to be {100}. Figure 2 was taken of a thin, bent section of the foil with many extinction contours to show the increase in contrast predicted for voids⁴ near $w = 0$. Estimates of the vacancy concentration for this sample, even by conservative allowances for the effective volume sampled, lead to values of 0.01 atom fraction.

Fig. 1 Schematic of laser-bombardment specimen showing primary damage zone and microscopy-specimen plane.

Reproducibility of the results in nickel appears to be more troublesome than for other materials examined to date. Only one sample showed the gigantic 750-Å-wide by 5000-Å-long voids shown in Fig. 2. Some voids were visible in almost all samples though, and Fig. 3 shows an example of a void population with much smaller, 120-Å-diameter, voids. The vacancy concentration in this sample was estimated to be 1×10^{-3} atom fraction. One possible cause of the variable results in nickel is the oxygen content. Annealed material stored in air was observed to harden, and subsequent laser bombardment and annealing produced no visible voids. Annealing the same material in a vacuum restored ductility, and voids were again observed after laser bombardment.

Vanadium

Vanadium of Marz grade purity (99.98%) obtained from the Materials Research Corporation in the form of 0.002-in. foil was annealed at 1350°C and

Fig. 2 Transmission electron micrograph of voids in laser-bombarded nickel annealed at 245°C (0.30 T_m).

laser bombarded. After annealing at 400°C (0.30 T_m) for 1 hr, the faulted-loop structure shown in Fig. 4 was observed. The grain in contrast was near a (001) orientation with $g = \langle 110 \rangle$. Assuming the faults to be on {112} planes, as was found for the tetrahedron (discussed with Fig. 5), there should be 12 different orientations possible. One-sixth of these would have both dislocations and fringes out of contrast, and one-third would have dislocations visible but fringes invisible (i.e., four-tenths of those visible should not have fringes). This appears to be about the distribution observed in Fig. 4, so it can be concluded that the

Fig. 3 Transmission electron micrograph of small voids in laser-bombarded nickel annealed at 245°C (0.30 T_m). The variation in size and density between Fig. 2 and Fig. 3 is believed to be related to oxygen content.

Fig. 4 Transmission electron micrograph of laser-bombarded vanadium annealed at 400°C (0.30 T_m). Orientation near (001).

loops have not become unfaulted but are merely out of contrast. Estimates of the vacancy concentration are about 1×10^{-3} atom fraction, assuming a single layer of vacancies is absorbed to form the loop.

Another specimen of vanadium showed a few isolated areas where such tetrahedra as those shown in Fig. 5 had formed. The foil is near (001), with the diagonals of the tetrahedra along the two $\langle 110 \rangle$ directions in the plane of the

Fig. 5 Transmission electron micrograph of laser-bombarded vanadium showing large tetrahedra with faults on $\{112\}$ planes. Orientation is (001), and diagonals of tetrahedra lie along $\langle 110 \rangle$ directions in foil plane.

foil. Lothe and Hirth⁵ have predicted that intrinsic faults with a displacement vector $\mathbf{R} = \frac{1}{3} \langle 112 \rangle$ could form on $\{112\}$ planes in body-centered cubic (bcc) metals. Such a fault is consistent with the geometry in Fig. 5. The reversal of fringe contrast across the tetrahedron is also consistent with such a fault because, under $\mathbf{g} = [\bar{1}10]$ illumination, the top two surfaces of the tetrahedron would give opposite signs for $\mathbf{g} \cdot \mathbf{R}$, and the bottom surfaces would give $\mathbf{g} \cdot \mathbf{R} = 0$. The fringes apparently arise from depth changes between the faulted planes because a one-half-thickness fringe outlines the edge of the tetrahedron. Lowering of the stacking-fault energy by impurity segregation to the fault is

most likely responsible for stabilizing so large a fault in a bcc metal, although vendor's analysis showed only 112 ppM oxygen and 57 ppM carbon as the major impurities.

Iron

Zone-refined iron samples of 99.98% purity were rolled to foil, annealed at 750°C, hydrogen purified, laser bombarded, and annealed at 290°C (0.30 T_m) for 1 hr. Figure 6 shows an area of the foil containing loops and helical dislocations formed as a result of vacancy condensation.

Stainless Steel

The 316 stainless-steel samples were taken from a lot of tubing fabricated by Westinghouse Advanced Reactors Division (WARD) from high-purity consumable-electrode vacuum-remelted material. The tubing was slit, flattened, rolled to 0.002-in. foil, and annealed at 1250°C for 1 hr in a vacuum prior to laser bombardment. Figure 7 shows an area containing voids which formed after laser bombardment and a 1-hr anneal at 232°C (0.30 T_m). The micrograph is atypical of the structure in general, in that voids are not uniformly distributed through the samples as they were in the case of nickel.

Nickel-30% Copper

A series of experiments is in progress to determine the importance of stacking-fault energy on the type of vacancy defect found in both laser-bombarded and neutron-irradiated samples. On the basis of mechanical-energy calculations, Sigler and Kuhlmann-Wilsdorf⁶ have shown that voids should form in pure nickel and stacking-fault tetrahedra in copper. Voids have been observed in nickel in both the present experiments and after neutron irradiation. Addition of 30% copper to nickel should lower the stacking-fault energy of the alloy. As shown in Fig. 8, stacking-fault tetrahedra are observed in laser-bombarded samples annealed for 1 hr at 212°C. Duplicate samples are currently under irradiation in the Experimental Breeder Reactor II (EBR-II). It should be noted parenthetically that, although stacking-fault tetrahedra have been predicted for stainless steel, voids are observed after both laser bombardment and neutron irradiation. In the case of vanadium, voids have been predicted and are observed after neutron irradiation, but faulted loops and tetrahedra are observed after laser bombardment. Apparently factors other than the mechanical energy influence the type of defect which forms.

Helium Injection

The 316 stainless steel, nickel, and vanadium samples of the same materials studied above were bombarded with 15-MeV alpha particles in the Naval Research Laboratory (NRL) cyclotron to determine the effect of helium on

Fig. 6 Transmission electron micrograph of laser-bombarded iron annealed at 290°C (0.30 T_m) showing loops and helical dislocations resulting from vacancy condensation.

nucleation of voids in these materials. The goal exposure was calculated to provide 10- and 3-ppm concentrations of helium in samples placed at two radii from the beam center. The flux for the 10-ppm level was 1.3×10^{11} particles/cm². Five passes with different settings of an energy-degrading wedge were used to distribute the helium uniformly through the sample thickness. No results from laser bombardment of the helium-injected samples are available at

Fig. 7 Transmission electron micrograph of laser-bombarded 316 stainless steel annealed at 232°C (0.30 T_m) showing area with a few large voids.

this time, but a control sample of 316 stainless steel annealed at 400°C for 1 hr after helium injection shows indications of ion damage. Figure 9 shows an area with several large voids (or bubbles, since they are presumably helium filled), some small resolvable loops, and a very high density of small black spots. The bubbles are not homogeneously distributed through the sample, but the resolvable loops and black spots are characteristic features of the microstructure.

Fig. 8 Transmission electron micrograph of laser-bombarded Ni-30% Cu alloy annealed at 212°C showing stacking-fault tetrahedra and some other unresolvable defect aggregates.

Fig. 9 Transmission electron micrograph of 316 stainless steel with 10 ppm helium injected by alpha-particle bombardment in the cyclotron and an anneal at 400°C. Resolvable loops and high concentration of black spots were characteristic of the microstructure, whereas bubbles shown in the micrograph were observed only in isolated areas.

In previous cyclotron-bombardment experiments using alpha particles to simulate the production of helium by (n,α) reactions during neutron irradiations, either it was indicated that the bombardment did not produce any detectable damage⁷ or no check was made for possible alpha damage.⁸ In this work the extent of the ion damage following cyclotron bombardment did not become visible until after annealing induced agglomeration of the defects into visible aggregates. It is suggested that damage produced during cyclotron bombardment interjects an additional variable into the interpretation of the role of helium in void nucleation. At the very least, the number of vacancies and potential nuclei present during subsequent fast-neutron or ion-bombardment experiments would be underestimated.

MECHANISM OF VACANCY PRODUCTION

The preceding observations of vacancy aggregates in a variety of metals show clearly that vacancy generation is an important consequence of laser bombardment. The mechanism by which they are formed, however, is not immediately obvious. Very high quenching rates can be attained by laser-pulse heating because heat transfer away from the exposed area during the 35-nsec pulse is very minor. The surrounding material serves as a very efficient heat sink since there is no interface resistance to heat flow such as exists in other methods. Figure 10 shows a comparison between the cooling rate for laser quenching of a foil specimen and that measured for a 0.1-mm-diameter iron wire quenched into liquid helium.⁹ The minimum rate necessary to retain vacancies is included as a reference and illustrates the increase in effective quench temperature and vacancy concentration which can be obtained by the laser technique.

Quenching in the conventional sense, however, cannot account for the high vacancy concentrations observed in some of the samples, for they exceed the anticipated 10^{-5} to 10^{-4} vacancy concentration at the melting point by two orders of magnitude. In addition, the temperature rise produced by the laser pulse decreases rapidly with distance from the front face so that the section observed ($25\ \mu$ from the front face) experiences negligible temperature rise. Yet, in one series of experiments, comparable concentrations of voids were found in nickel specimens polished to depths $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the sample thickness relative to the front face.

Another potential mechanism for the generation of vacancies is the nonconservative motion of jogs on screw dislocations. Kressel and Brown¹⁰ observed enhanced vacancy production in nickel shock loaded to pressures of 70 to 330 kbars. Dislocation densities of the order of 2×10^{10} cm/cm³ were observed, although the vacancy concentration did not exceed 6×10^{-5} .

Shock waves are generated by laser bombardment as a consequence of the rapid thermal expansion of the front face,¹¹ but the peak stress is estimated to be only of the order of 10 kbars for the power density used in these

Fig. 10 Comparison of quenching rate attainable by laser-pulse heating, quench of 0.1-mm-diameter iron wire into liquid helium,⁹ and the minimum rate to retain vacancies. ---, calculated cooling rate of 3.0-mm-diameter spot in iron sheet pulse heated by laser to 1800°K. -.-, measured cooling rate of 0.1-mm-diameter iron wire heated to 1800°K and quenched in liquid helium. —, calculated minimum cooling rate to retain vacancies.

experiments.^{1,2} Pressures of this magnitude (100 kg/mm^2 , 145 ksi) could generate dislocations, and dislocations were found in some instances. Vacancy concentrations, however, were highest in the samples with the lowest dislocation density, thus indicating that dislocations serve as sinks for vacancies and limit the number available for voids. In specimens with the highest vacancy concentrations, the dislocation density was about 10^7 cm/cm^3 . If it is assumed that the equilibrium concentration of jogs is 100 jogs/cm at room temperature, jog motion of 10^9 atomic distances ($\sim 25 \text{ cm}$) would be required to produce the vacancy concentrations observed. It is therefore concluded that nonconservative motion of jogs is not the mechanism responsible for vacancy generation in these samples.

The energy input to the specimen and several energy-absorption processes are compared in Table 1. It can be seen that the energy available in the laser

TABLE 1
PROCESS ENERGETICS FOR 3-mm-DIAMETER,
50- μ -THICK NICKEL SPECIMENS

Process	Energy, cal
Laser-pulse available energy	0.088
Energy absorbed (40% eff.)	0.035
Used in sample heating	0.002
Remaining energy	0.033
Heat sample from 20° C to melting point	0.606
Create 1% vacancies	0.015

pulse is appreciably less than that required to heat the entire specimen to the melting point. There is, however, enough energy available, even after allowing for 60% reflectivity and front-face heating, to create about 0.02 atom fraction of vacancies, as is observed in the laser-bombarded nickel. This concentration obviously is not created by a thermal-equilibrium process. A mechanism associated with the passage of a pressure wave or perhaps with recurring interference between waves reflected from the free surfaces is more plausible since at any one time the energy in the pulse is concentrated in a much smaller region of the crystal.

APPLICATIONS

Laser bombardment offers many intriguing possibilities for the study of vacancy behavior in materials. Even though the mechanism of vacancy

production is not yet established, studies of vacancy condensates will yield valuable information about the type of defect formed from high vacancy supersaturations, stability, and the kinetics of coarsening and annealing. Vacancy condensates can now be studied in many materials that could not be quenched either because of allotropic transformations, thermodynamic instability of phases, or impurity contents in excess of the vacancy concentration. Comparison of vacancy condensates formed from a supersaturation of vacancies produced by laser bombardment and those formed during irradiation should provide valuable insight into the importance of such factors as the displacement cascade and helium production, especially in those materials where the void is not the form of defect aggregate observed after laser bombardment and annealing. Establishment of reproducible experimental conditions will provide additional valuable information on the nucleation and growth of vacancy condensates, absorption of vacancies at various types of sinks, and ultimately perhaps provide a quality-control device for monitoring the swelling resistance of production runs of nuclear fuel-cladding materials.

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DISCUSSION BY ATTENDEES

Michel: You mentioned that the pressure pulse generated in the specimen due to the laser-beam impingement was of the order of 10 kbars and that this pulse may be responsible for the vacancy generation from the rapid thermal expansion. Do you know whether voids have ever been observed in explosively deformed metals subjected to an energy input equivalent to that in your laser experiments, and, if so, in what metals? If not, under what conditions would you expect voids to form in explosively deformed metals, if at all?

Smidt: To the best of my knowledge, voids have not been found in shock-loading experiments probably because the higher pressure pulses (70 to 400 kbars) are much in excess of the stress to generate dislocations, and the dislocations act as sinks to reduce the vacancy concentration below levels required for formation of a high density of visible voids.

There was some evidence in Kressel and Brown's work¹⁰ that vacancy production was high at low strains but dropped off rapidly as the dislocation density increased at high strains. This might be a good method to determine if the vacancies are indeed being produced by the pressure wave. I would guess the wave should be about 10 kbars, of short pulse length, and followed by an anneal at $0.3 T_m$ to reveal vacancy condensates.

Brimhall: What type of defect structure was present in the bombarded state? In particular, were voids present?

Smidt: No voids were present in the as-bombarded condition. In the case of nickel, we annealed at temperatures of $0.28 T_m$ for 1 hr and observed small defects with black-white contrast; after an anneal at $0.3 T_m$, we saw the large voids.

Bullough: Do you see any sign of interstitials produced by the laser irradiation?

Smidt: No.

Kulcinski: Have you performed any experiments to determine the maximum extent of damage from your laser bombardment (i.e., have you used samples thicker than 50μ)?

Smidt: No, not yet, but we plan to do such experiments.

SOLUTE SEGREGATION AND STRESSES GENERATED AROUND GROWING VOIDS IN METALS

336 (11/77)

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ABSTRACT

A quantitative description of the solute segregation generated by vacancy currents around growing voids is given. Predictions of this theory are compared with direct measurements of vacancy currents, impurity currents, and solute segregation around voids in various metal alloys. From these experiments and theory, the atomic jump frequencies of vacancies around solute atoms in these alloys are obtained. Segregation around other vacancy sinks, such as dislocations and grain boundaries, is also considered. The effects of solute segregation on the surface energy of voids and the vacancy diffusion coefficient around voids are shown to lead in many cases to an increase in the total number of voids and a decrease in their average size. The stresses generated by solute segregation around voids are calculated. These stresses are shown to be capable of preventing void growth when solute segregation is excessive. Finally, it is suggested that long-range stresses generated by solute segregation around voids can lead to an ordering of voids on spatial arrays to minimize the elastic energy of a material.

During the irradiation of a metal, vacancy precipitation will commence when a critical vacancy supersaturation is reached in the metal-vacancy solution. The resulting voids will continue to form and grow in pure metals as long as the vacancy supersaturation in the solution is maintained by irradiation.

In alloys, the vacancy currents feeding the growing voids generate sympathetic solute currents that in turn cause either solute enrichment or solute depletion around the voids. Such solute segregation may affect the growth rate of a void since the segregation can change both the vacancy diffusion coefficient and the vacancy chemical potential in the zone around the void.

In this article, the diffusion process generating solute segregation is examined, and the criteria for predicting whether solute enrichment or depletion will occur around growing voids are given. Experimental measurements of solute segregation around growing voids in metals are described and compared with

predictions of diffusion theory. Finally, the secondary effects of segregation on the vacancy mobility and chemical potential in the void zone are explored.

THE SOLUTE-SEGREGATION PROCESS

When a vacancy enters the region around a growing void, an atom by necessity is expelled from this zone. If the countercurrents of solute and solvent atoms out of the void zone are in exact proportion to their atomic fractions in the alloy, then the alloy concentration around the growing void will not change.

On the other hand, if the solute current away from the growing void is proportionately greater than the solute concentration in the alloy, solute depletion will occur around the void. Intuitively, one would anticipate solute depletion when the substitutional diffusion coefficient of the solute was much larger than the solvent diffusion coefficient. In this situation, the vacancies might be expected to interchange preferentially with the solute as the vacancies flowed toward the growing voids. By means of this selective interchange, the solute would be "etched" away from the zone around the growing void.

In contrast, when the solute current away from a void is proportionately less than the solute concentration in this region, then the zone around the growing void will become enriched in solute. The latter situation might be expected when the solute diffusion coefficient is much smaller than the solvent diffusion coefficient. In this case, the *solvent* atoms would be selectively etched away from the region around the void, leaving behind a solute enriched zone.

From what has been said to this point, one might anticipate that whether a solute became enriched or depleted around a growing void could be determined from the relative diffusion coefficients of the solute and solvent in the alloy. However, the discussion above has taken into consideration only one part of the reason for differing solute and solvent diffusion coefficients. Another factor to consider is the average vacancy concentration around an impurity atom. As an example, consider the case of a strong attractive interaction between a vacancy and a solute atom. In this situation, the effective vacancy concentration near a solute atom and thus the solute diffusion coefficient in the alloy will be greatly enhanced. Because of the tight binding between vacancy-solute pairs, fast diffusing solutes in this case would tend to be dragged toward growing voids by impinging vacancy currents, causing solute enrichment around the voids. Thus this line of reasoning would predict an enrichment instead of a depletion of a fast diffusing solute around a growing void. These conflicting conclusions emphasize the need for the following quantitative statement of the problem in which all factors are simultaneously considered.

In a dilute alloy containing solvent atoms A, solute atoms B, and vacancies V, the currents J_A , J_B , and J_V of atoms A and B and vacancies V under isothermal conditions are

$$\begin{aligned}
 J_A &= L_{AA}X_A + L_{AB}X_B + L_{AV}X_V \\
 J_B &= L_{BA}X_A + L_{BB}X_B + L_{BV}X_V \\
 J_V &= L_{VA}X_A + L_{VB}X_B + L_{VV}X_V
 \end{aligned} \quad (1)$$

where the thermodynamic driving forces, X_A , X_B , and X_V , are the chemical potential gradients of solvent, solute, and vacancies in the solution and the L 's are phenomenological coefficients related to atomic mobilities. The various cross coefficients that are commonly ignored in a simple diffusion analysis are of particular interest to the present problem since they indicate that a vacancy potential gradient X_V can generate a current of solute atoms B.

For a vacancy mechanism of diffusion, one knows that the countercurrent of atoms, $-(J_A + J_B)$, must equal the vacancy current J_V in order to conserve lattice sites in the solution. Using the Gibbs-Duhem equation, which, in short, shows that the chemical potential gradients of solvent, solute, and vacancies are not independent, one can reduce Eq. 1 to a simpler form:

$$\begin{aligned}
 J_A &= L_{AA}(X_A - X_V) + L_{AB}(X_B - X_V) \\
 J_B &= L_{AB}(X_A - X_V) + L_{BB}(X_B - X_V) \\
 J_V &= -(J_A + J_B)
 \end{aligned} \quad (2)$$

If one assumes an initially homogeneous alloy ($\nabla C_B = 0$) and a solute content C_B much larger than the vacancy concentration C_V , then the ratio of the solute current J_B to the vacancy current J_V is found to be¹⁻³

$$\frac{J_B}{J_V} = -\frac{C_B D_B}{D_A/f + C_B D_B} \left(\frac{L_{BA} + L_{BB}}{L_{BB}} \right) \quad (3)$$

where D_B and D_A are the diffusion coefficients of solute B and solvent A, respectively, and f is the correlation factor. All the parameters on the right-hand side of Eq. 3 are experimentally measurable. Consequently, in alloy systems where these parameters are known, the solute current J_B generated by a vacancy current J_V can be calculated.²⁻⁵ Moreover, from the resulting ratio of J_B/J_V and the total vacancy flux directly determined from the void volume, the total quantity of solute that has either left or entered the zone around the void during void growth can also be calculated. In this manner, the degree of solute segregation around a void can be determined.

MEASUREMENT OF SOLUTE SEGREGATION AROUND VOIDS

Vacancy-Condensation Cavities in Aluminum

In electropolished aluminum, a zone 200 to 300 μ thick adjacent to the sample surface has relatively few vacancy sinks because of a low dislocation

density.⁷ Since the metal-oxide interface at the surface is a totally ineffective vacancy sink,^{8,9} cooling an aluminum sample from a high-temperature anneal will cause the vacancy concentration in this near-surface zone to reach a critical supersaturation (approximately 1%) at which vacancies begin to precipitate on the metal-oxide interface.¹⁰⁻²⁴ The resulting vacancy-condensation cavities contain about 10^{13} vacancies each (Figs. 1 and 2). The appearance of these large accessible voids in aluminum and other alloys¹¹ provides an opportunity to measure directly both vacancy and vacancy-generated solute currents in metals.

Fig. 1 A schematic diagram of a vacancy-condensation cavity on the metal-oxide interface of aluminum formed by cooling from a high-temperature anneal.

The Vacancy Current

Because only the *ratio* of the vacancy current and the vacancy-generated solute current is characteristic of a particular alloy, it is important that any quantitative experiment measure *both* the vacancy and the solute currents. The total vacancy current J_V^T that formed a vacancy cavity is directly determined from the cavity volume V_C ,

$$J_V^T = V_C \quad (4)$$

In aluminum the cavity volume is accurately determined from the displacement of interference fringes, as seen through the thin transparent Al_2O_3 film covering the condensation cavity in an interference microscope.^{2,6}

The Solute Current Generated by the Vacancy Current

Solute segregation around the cavity is measured with an electron microprobe. The total solute current J_B^T induced by the vacancy current J_V^T can be

Fig. 2 Vacancy-condensation cavities on the surface of a polycrystalline aluminum (zinc) alloy. Because the grain boundaries have acted as vacancy sinks during cooling, the zones adjacent to the grain boundaries show no vacancy-condensation cavities.

computed from the cavity volume V_C , the analyzed zone volume V_Z , the initial solute concentration C_B , and the change in solute concentration ΔC_B in the analyzed zone surrounding the cavity after cavity growth.^{2,6,25}

$$-J_B^T = C_B V_C + \Delta C_B V_Z \quad (5)$$

ΔC_B is the initial minus the final solute concentration in the zone around the cavity. Note that J_B^T is positive and negative, respectively, for solute currents toward and away from the cavity with respect to the local crystalline lattice.

Vacancy Jump Frequencies Around Solute Atoms

From Eqs. 4 and 5, we have

$$\left(\frac{J_B}{J_V}\right)/C_B = - \left[1 + \Delta C_B \left(\frac{V_Z}{V_C}\right) \right] \quad (6)$$

TABLE 1
RATIO OF VACANCY CURRENT AND IMPURITY CURRENT GENERATED
BY A VACANCY CURRENT IN ALLOY SYSTEMS*

Alloy-system solvent (solute)	$\left(\frac{J_B}{J_V}\right)/C_V$	Remarks	Impurity redistribution at a vacancy sink†	L_{BA}/L_{BB}	W_3/W_1	Ref.
Al(Zn)	-0.92	Directly observed	E	<0.79	<0.20	6
Al(Cu)	-1.0	Directly observed	None	-0.40	0.36	3
Al(Ge)	-1.92	Directly observed	D	>-0.77	>0.22	25
Al(Mg)	>-1	Directly observed	E			49
Ag(Cu)	<-1	Directly observed	D			50
Cu(In)	<-1	Directly observed	D			50
Cu(Ag)	<-1	Directly observed	D			50
Cu(Mn)	>-1	Directly observed	E			51
Cu(Zn)	<-1	Directly observed	D			51
Cu(Zn)	-2.80	Calculated	D		0.90	2
Ag(Zn)	-1.88	Calculated	D		0.37	2

*The currents are expressed with respect to the local crystal lattice and are positive and negative toward and away from a vacancy sink, respectively. All data were measured at temperatures ranging between 0.8 and 0.9 times the alloy melting point.

†D = depletion of solute at vacancy sink; E = enrichment of solute at vacancy sink.

Table 1 gives the ratio of $(J_B/J_V)/C_B$ found in various aluminum alloys along with this same parameter for other alloy systems. From Eq. 3 and the definition of ϕ as

$$\phi = \frac{J_B}{J_V} \frac{D_A/f + C_B D_B}{C_B D_B} \quad (7)$$

the ratio of the phenomenological coefficients L_{AB}/L_{BB} is given by²

$$\frac{L_{AB}}{L_{BB}} = -(1 + \phi) \quad (8)$$

From Eqs. 7 and 8, one can see that measurements of the solvent self-diffusion coefficient D_A , the solute diffusion coefficient D_B , and the solute current J_B

Fig. 3 The vacancy jump frequencies away from W_3 and around W_1 impurity atoms in a dilute alloy.

generated by a vacancy current J_V determine the phenomenological coefficient ratio L_{AB}/L_{BB} . The ratio L_{AB}/L_{BB} is important not only to experiments concerned with vacancy-generated solute segregation but also in studies of thermal migration and electromigration in metals.

For the special case of a face-centered cubic (fcc) alloy, the phenomenological coefficients have been expressed in terms of the various vacancy jump frequencies in the solution.²⁶ If W_1 is the jump frequency of a vacancy from one nearest neighbor position of a solute atom to another (Fig. 3) and W_3 is the jump frequency of a vacancy away from the solute atom (thereby breaking up the solute-vacancy pair), then the ratio of W_3/W_1 is

$$\frac{W_3}{W_1} = \frac{1 - \phi}{13/2 + 7/2\phi} \quad (9)$$

Values of this ratio are shown in Table 1. The inequality signs on the L_{AB}/L_{BB} and W_3/W_1 parameters for the Al(Zn) and Al(Ge) alloys arise from the fact that

Eq. 3 does not take into consideration the flow of solute atoms induced by a developing solute-segregation gradient. Thus Eq. 3 will predict either a greater solute enrichment or greater solute depletion than actually occurs because of the neglect of the "buffering" effect of the developing solute gradient.

The fact that W_3/W_1 is close to unity for the five alloy systems investigated to date indicates that solutes neither strongly attract vacancies nor greatly disrupt their own local environments in these alloys. The small solute-vacancy binding energies implied by these results are in agreement with both diffusion measurements,^{27,28} direct measurements of solute-vacancy binding by simultaneous length, and lattice-parameter measurements²⁹⁻³¹ and theory.^{32,33}

Solute Segregation at Grain Boundaries During Irradiation

Solute segregation can be generated by vacancy currents not only around growing voids but at other vacancy sinks, such as grain boundaries,^{34,35} free surfaces,³⁶ and dislocations. The resulting solute enrichment or depletion around these zones may contribute to such phenomena as general bulk hardening, grain-boundary embrittlement, and intergranular corrosion. Let us consider solute segregation at a grain boundary.

The values of $(J_B/J_V)/C_B$ in Table 1 are given in terms of currents expressed with respect to the local crystal lattice. For consideration of segregation at grain boundaries, it is more convenient to express $(J_B/J_V)/C_B$ with respect to the grain-boundary plane. Since the grain boundary is acting as lattice plane sink (i.e., a vacancy sink), the local lattice on both sides of the boundary is moving toward the boundary plane at a rate proportional to the vacancy current. Thus, to convert $(J_B/J_V)/C_B$ with respect to the local lattice to $(J_B/J_V)^*/C_B$ with respect to the boundary plane, one must add⁶ $J_V/J_V = 1$ to $(J_B/J_V)/C_B$. Positive values of $(J_B/J_V)^*/C_B$ imply enrichment, whereas negative values indicate a depletion of solute at the grain boundary. The change in grain-boundary solute concentration ΔC_B after a flow J_V^T of vacancies to the grain-boundary sink is given by

$$\Delta C_B = J_B^T = \left(\frac{J_B}{J_V} \right)^* J_V^T \quad (10)$$

From Eq. 10, it can be seen that a knowledge of the total vacancy flow to a grain boundary will allow us to calculate the degree of solute segregation at a grain boundary generated by irradiation. In some irradiated materials a zone denuded of vacancy cavities is present around grain boundaries^{37,38} (see Fig. 2 for a similar phenomenon in air-quenched aluminum). To calculate the total vacancy current J_V^T that impinges on a grain boundary during irradiation, the simplifying assumption will be made that all vacancies created in such denuded zones disappeared at grain-boundary sinks. Consider a material with a cross section of 3×10^{-24} cm² in a fast-neutron reactor with an average neutron flux

of 2.5×10^{15} neutrons/(cm²)(sec). If L is the width of the denuded zone, a is the nearest-neighbor separation of atoms in the metal, and 300 net vacancies are produced by each primary neutron-atom collision, then

$$J_V^T = 1.8 \times 10^{17} L a^2 t' \quad (11)$$

where J_V^T is the total vacancy current in vacancies per boundary site, L and a are in centimeters, and the irradiation time t' is in seconds. If we assume a typical denuded-zone width of 4×10^{-5} cm and an irradiation time of 6 months, the total vacancy flow to the boundary is 5400 vacancies per boundary site. From Table 1 and Eq. 10, it can be seen that either a large amount of solute enrichment or almost total solute depletion at the grain boundary should be expected under such conditions.⁶ For commercial reactor alloys, where solutes are added to prevent corrosion, a similar depletion of solutes from the grain-boundary region during irradiation could make these materials susceptible to intergranular corrosion or cracking.

SECONDARY EFFECTS OF SOLUTE SEGREGATION AROUND VOIDS

Change in the Surface Energy of a Void

Solute segregation at the surface of a growing void will change the surface energy of a void. This change in surface energy will in turn alter the vacancy concentration in equilibrium with the void. If we define the chemical potential of a vacancy in equilibrium with a flat surface to be zero, then the chemical potential $\mu_v(r)$ of a vacancy in equilibrium with a void of radius r and surface energy γ is $(2\gamma\Omega/r)$, where Ω is the volume per atom in the surrounding matrix. If the surface energy of the void is changed by $\Delta\gamma$ because of solute segregation, then the relative change in vacancy concentration $\Delta C_V/C_V$ is given by

$$\frac{\Delta C_V}{C_V} \approx \frac{\Delta\mu_v}{kT} = \frac{2\Delta\gamma\Omega}{rkT} \quad (12)$$

where k is the Boltzmann constant and T is the absolute temperature. Substituting in values of $\Delta\gamma = +70$ ergs/cm², $\Omega = 24 \times 10^{-24}$ cm³, $r = 200 \times 10^{-8}$ cm, $T = 800^\circ\text{K}$, and $k = 1.38 \times 10^{-16}$ erg/^oK, one finds that $(\Delta C_V/C_V = 1.5\%)$. Because the critical vacancy supersaturation necessary to nucleate vacancy-condensation cavities in our aluminum experiments¹⁹ is 1%, a change in the vacancy concentration in equilibrium with the cavity by the 1.5% calculated above would be enough to prevent further cavity growth since new cavities would nucleate before the supersaturation reached the 1.5% level. Thus the net effect of the solute in the alloy would be to increase the void density and decrease the average void size.

Change in the Vacancy Diffusion Constant Near a Void

Solute segregation around a void can change the vacancy diffusion constant in the region around a void. The vacancy diffusion coefficient D_V is an exponential function of temperature, $D_V = D_0 \exp(-Q/kT)$, where D_0 is the preexponential constant and Q is the activation energy for vacancy migration. In most metals and alloys, Q is proportional to the melting point T_m of the metal or alloy— $Q = \alpha T_m$, where α is approximately 7.5×10^{-4} eV/°K. Consequently, if the melting point of the metal around the void is changed by ΔT_m because of solute segregation, the vacancy diffusion coefficient will change by ΔD_V :

$$\frac{\Delta D_V}{D_V} = -\frac{\alpha \Delta T_m}{kT} \quad (13)$$

If one assumes an irradiation temperature of 800°K and a ΔT_m of +20°K caused by solute segregation around the void, then $(\Delta D/D) = -22\%$. Thus any solute segregation that increases the melting point of the material around the void will decrease the vacancy diffusivity in this region. Whether this decrease will affect the growth rate of the void depends of course on the thickness of the segregated zone³⁹ as well as on the decrease in the vacancy diffusion coefficient in the zone. Segregated solutes that tend to decrease the melting point of the material around the void will probably have no effect on the arrival rate of vacancies at the void since the process controlling the rate of growth of the void will continue to be the diffusion velocity of vacancies through the bulk.

STRESSES GENERATED BY SOLUTE SEGREGATION AROUND VOIDS

Consider the shell of segregation around the growing void depicted in Fig. 4. Since this shell is inherently coherent with the matrix material, stresses will be generated both in the shell and in the matrix if the segregating solute atoms do not have the same size as solvent atoms. For example, if large solute atoms are enriched or small solute atoms are depleted around the void, one would anticipate some state of compression in the shell. Conversely, if large solute atoms are depleted or small solute atoms enriched around the void, some state of tension would be expected in the shell of segregation.

The existence of stresses in both the shell of segregation and the matrix may play an important role in void growth in at least two ways:

1. A radial pressure gradient in the shell of segregation would directly influence the magnitude of vacancy currents impinging on the void.
2. Interaction between stresses in the matrix generated by a family of voids may lead to an ordering of voids on spatial arrays in order to minimize the elastic energy of the material.

To calculate the stresses in the shell of segregation and in the surrounding matrix, we will make an analogy with the problem of a homogeneous misfitted

Fig. 4 Solute enrichment around a growing void. The shell of segregation has an approximate thickness of t and a radius of R .

particle embedded in a matrix. This latter problem has been investigated extensively in the literature.⁴⁰⁻⁴⁷ A main conclusion of these investigations is that there are only shear stresses in the surrounding matrix and only hydrostatic stresses in the particle. Consequently only the shear modulus G of the matrix and the bulk modulus K of the particle enter into the final equations. With this knowledge, our line of attack on the stress problem in the shell and matrix will be as follows:

1. Replace the segregation shell (bulk modulus of K)-and-void combination with a homogeneous pseudoparticle with a bulk modulus K' .
2. Calculate the stresses in the surrounding matrix produced by this homogeneous, misfitting pseudoparticle.
3. Calculate the hydrostatic stress developed in the homogeneous pseudoparticle.
4. Calculate an approximate radial pressure gradient in the shell of segregation by dividing the hydrostatic stress in the pseudoparticle by the thickness of the shell of segregation.

From the definition of the bulk modulus $V (dP/dV)$, the effective bulk modulus K' of a spherical shell of material having a bulk modulus of K can be shown to be⁴⁸

$$K' = \frac{2t}{R_p} K \quad (14)$$

where t is the thickness of the spherical shell and R_p is the radius of the spherical shell. If G is the shear modulus of the matrix, then the three principal stresses in the surrounding matrix caused by such a misfitting pseudoparticle are

$$\left. \begin{aligned} \sigma_{RR} &= \frac{-12GK'}{3K' + 4G} \epsilon \frac{R_p^3}{R^3} \\ \sigma_{\theta\theta} = \sigma_{\phi\phi} &= + \frac{6GK'}{3K' + 4G} \epsilon \frac{R_p^3}{R^3} \\ P &= \frac{1}{3} (\sigma_{RR} + \sigma_{\theta\theta} + \sigma_{\phi\phi}) = 0 \end{aligned} \right\} \text{in the surrounding matrix} \quad (15)$$

Here R is the radius from the center of the void, P is the hydrostatic stress in the matrix, and ϵ is the stress-free strain between the matrix and the particle. Note the somewhat surprising result that there is no hydrostatic stress P in the surrounding matrix. Instead, all the misfit strain is carried by pure shear stresses in the matrix.

In the pseudoparticle, however,

$$\left. \begin{aligned} \sigma_{RR} = \sigma_{\theta\theta} = \sigma_{\phi\phi} &= - \frac{12K'G}{3K' + 4G} \epsilon \\ P &= \frac{1}{3} (\sigma_{RR} + \sigma_{\theta\theta} + \sigma_{\phi\phi}) = - \frac{12K'G}{3K' + 4G} \epsilon \end{aligned} \right\} \text{in the pseudoparticle} \quad (16)$$

there is only pure hydrostatic stress.

The misfit parameter ϵ is given by the change in average concentration ΔC_B in the shell of segregation relative to the matrix composition times the logarithmic change ($d \ln a / dC_B$) of the lattice parameter of the alloy with solute composition C_B : [$\epsilon = (d \ln a / dC_B) \Delta C_B$].

In Fig. 4, we note that there is actually a steep solute-concentration gradient in the shell of segregation. Consequently we expect an analogous radial pressure gradient in the shell of segregation. To obtain a rough estimate of this radial pressure gradient, we divide the pressure P calculated for our imaginary pseudoparticle by the thickness t of the shell of segregation. This approximation gives a lower limit to the actual pressure gradient.

$$\nabla P = \frac{P}{t} = - \frac{1}{t} \left(\frac{12KG}{3K + 2GR_p/t} \Delta C_B \frac{d \ln a}{dC_B} \right) \quad (17)$$

Since $GR_p/t \gg K$,

$$\nabla P = - \frac{6K}{R_p} \Delta C_B \frac{d \ln a}{dC_B} \quad (18)$$

where again K is the bulk modulus of the alloy with the composition of the shell of segregation, R_p is the radius of the shell of segregation, $(d \ln a/dC_B)$ is the logarithmic change of the lattice parameter of the alloy with solute concentration, and ΔC_B is the average difference in solute concentration (see Eq. 10 and Fig. 4) between the shell of segregation around the void and the surrounding matrix.

Effect of Stress Gradients on Vacancy Flux to Growing Void

From Eq. 2 the vacancy flux J_V is

$$J_V = L_{AA}(X_V - X_A) + L_{AB}(2X_V - X_A - X_B) + L_{BB}(X_V - X_B) \quad (19)$$

To take into consideration a variation of stress over the diffusion paths, we must add $\bar{V}_B P$, $\bar{V}_A P$, and $\bar{V}_V P$ to the equations for the chemical potentials of the solute, solvent, and vacancies, respectively. Here P is the hydrostatic stress, and $\bar{V}_B$, $\bar{V}_A$, and $\bar{V}_V$ are the volumes per solute, solvent, and vacancy, respectively. The thermodynamic forces X_A , X_B , and X_V are obtained by taking the first derivative of the chemical potentials with respect to distance. If we define $J_V(\nabla P)$ as that part of the vacancy flux generated by a stress gradient, then

$$J_V(\nabla P) = L_{AA}(\bar{V}_A - \bar{V}_V)\nabla P + L_{AB}(\bar{V}_A + \bar{V}_B - 2\bar{V}_V)\nabla P + L_{BB}(\bar{V}_B - \bar{V}_V)\nabla P \quad (20)$$

The vacancy flux will only be affected by misfit stresses in the shell of segregation since only here is there a hydrostatic stress or pressure gradient. Although a steep gradient in shear stresses exists in the surrounding matrix, the lack of a pressure gradient precludes any direct effect on the vacancy flux there.

To simplify further, we will only consider the case where there is not strong binding between a solute and a vacancy. Then²⁶ $L_{AA} \gg L_{AB}, L_{BB}$ and Eq. 20 becomes

$$J_V(\nabla P) = L_{AA}(\bar{V}_A - \bar{V}_V)\nabla P \quad (21)$$

Introducing the pressure gradient in the spherical shell from Eq. 18, one finds that the vacancy flux generated by the pressure gradient in the shell of segregation is

$$J_V(\nabla P) = -6L_{AA}(\bar{V}_A - \bar{V}_V) \frac{K}{R_p} \Delta C_B \frac{d \ln a}{dC_B} \quad (22)$$

For a better physical insight into the magnitude of this effect, it is appropriate to compare the vacancy flux generated by this pressure gradient with the

vacancy flux generated by a vacancy concentration gradient. Under the same conditions (lack of strong vacancy-solute binding), the vacancy flux generated by a concentration gradient $\nabla \ln C_V$ of vacancies is

$$J_V(\nabla \ln C_V) = -L_{AA} kT \nabla \ln C_V \quad (23)$$

Thus the pressure-gradient effect in Eq. 22 is equivalent to a logarithmic vacancy-concentration gradient of

$$\nabla \ln C_V = \frac{6(\bar{V}_A - \bar{V}_V) K}{kT} \frac{\Delta C_B}{R_p} \frac{d \ln a}{d C_B} \quad (24)$$

Assuming a fractional atomic-volume relaxation around a vacancy of $1/4$, a value of $\bar{V}_A = 27 \times 10^{-24} \text{ cm}^3$, $K = 10^{12} \text{ dynes/cm}^2$, $R_p = 200 \times 10^{-8} \text{ cm}$, $T = 800^\circ \text{K}$, a misfit of 1% between the shell of segregation and the surrounding matrix, and a shell thickness of $60 \times 10^{-8} \text{ cm}$, one finds that the vacancy concentration changes by a factor of 4 across the shell of segregation. If the direction of this vacancy concentration gradient opposes vacancy currents impinging on the void, then growth of the void may cease. The net effect of such segregation stresses would then be to decrease the average void size and increase the void density in the material.

Stress-Induced Ordering of Voids in Spatial Arrays

The shear stresses in the matrix (see Eq. 15) surrounding the void and shell of segregation give rise to stored energy in the bulk of the specimen. Similar to the ordered arrays of various precipitates and dislocations, which minimize such elastic energy, it is anticipated that an ordering of vacancy precipitates (i.e., voids) into particular spatial arrays may also lower the elastic energy of a specimen, especially if there are segregation stresses associated with the voids. Because voids are relatively immobile, such spatial arrays would have to arise during void nucleation and growth. Conditions of slow void growth at minimal supersaturations would be favorable to the production of such arrays. In such a situation, those appropriately situated voids would feel fully the favorable influence of assisting stress fields over a prolonged time span. These growth conditions are more in consonance with conditions in irradiated material, as compared to rapidly quenched metals in which large supersaturations force an unorganized, rapid type of void nucleation and growth.

SUMMARY

The theoretical basis for and the experimental measurement of solute segregation around growing voids in metals have been described. Secondary

effects of such segregation on the growth rate and location of voids in a material have been considered.

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DISCUSSION BY ATTENDEES

Balluffi: It does not seem possible that void growth could be stopped in a quenched material by changing the surface energy of a void as a result of solute segregation to the void surface. The driving chemical potential of supersaturated vacancies is simply too large.

Anthony: In the experiments that I have described, voids nucleate in aluminum cooled from near its melting point at a supersaturation of approximately 1% on the metal-oxide interface. At these small supersaturations, a change in the surface energy of the void caused by solute segregation can raise the supersaturation necessary for void growth by 1.5%. Thus voids, in this case, would not continue to grow, but new voids would be nucleated instead. In the more general case of internal void nucleation in quenched metals, I would agree with your comments.

Bement: Could gases permeate through the Al_2O_3 layer to an extent that would influence the shape or size of the voids you observe?

Anthony: The Al_2O_3 film on aluminum is several hundred angstroms thick. Gases such as oxygen and nitrogen are not able to penetrate this film during the cooling of the sample. If they were, the film, in the case of oxygen, would have simply grown that much thicker as the oxygen diffused through the oxide layer to react with the underlying metal at the anneal temperature. Hydrogen because of its relatively high diffusivity in Al_2O_3 could be a problem. Thus one should

not carry out the experiments that I have described in the presence of hydrogen. If hydrogen were present, its main effect would probably be to reduce the supercooling required for void nucleation by stabilizing small voids during the initial nucleation process. However, hydrogen should not affect the amount of segregation around the void since such segregation is a function of the atomistic process of diffusion in the bulk metal and is not a function of the gas content of the void. The size of the voids would be decreased with hydrogen present since the number of voids should increase because of the nucleation assist provided by hydrogen. The shape of the voids now delineated by particular crystallographic planes of the aluminum should not change since these planes appear because of kinetic factors rather than surface-energy minimization considerations.

Corbett: You showed voids preferentially nucleating on sites previously occupied by a grain boundary. Is there firm evidence why, e.g., electron-microprobe evidence?

Anthony: There is no firm evidence why this phenomenon occurs. It may arise from the fact that, although the underlying grain boundary in the metal has migrated away, there is still a grain boundary left in the overlying oxide film. An alternative explanation is that impurities segregating to the grain boundary were left behind at the former grain-boundary site and that these impurities caused preferential nucleation there.

ANNEALING OF LOOPS AND TETRAHEDRA

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ABSTRACT

A discussion of the mechanisms for annealing of dislocation loops and tetrahedra is presented. The growth of vacancy defects in metals is reviewed with emphasis on vacancy supersaturation. The role of dislocation climb in the shrinkage of loops and tetrahedra is discussed together with the effect of stacking-fault energy. Dislocation-loop migration by diffusion along the dislocation core is shown to be a possible mechanism for coarsening of small dislocation loops at temperatures just below that required for ordinary self-diffusion.

It is the continuous climb of dislocations caused by their stronger attraction for interstitial atoms than for vacancies which is the underlying cause for void growth and the consequent swelling of metals during high-fluence irradiation at intermediate temperatures. Therefore all factors that affect the climb rate of dislocations are potentially of importance in understanding the different swelling behavior observed in different metals and alloys.

During all but the early stages of swelling, the dislocations form a network that is interconnected with the voids. Therefore the pipe diffusion of vacancies and interstitial atoms along the cores of the dislocations may be one of the factors that significantly affect the swelling rate. As an example, two extreme cases can be imagined:

1. The dislocation acts as a perfect pipe; interstitials and vacancies that arrive at the core diffuse along it until they reach a void or recombine with an opposite defect. In this case, if all dislocations were to lead to a void, there would be no swelling in spite of continued preferential drift of interstitials to dislocations.
2. The dislocation acts as a perfect sink; each vacancy or interstitial that arrives at the dislocation is frozen in place at its point of arrival and thus contributes to the dislocation climb.

The real situation is certainly somewhere between these extremes and probably depends on stacking-fault energy, presence or absence of certain impurity atoms along the dislocation core, radius of curvature of the dislocation, the driving force that acts to cause the climb, and the temperature.

Up to the present time, dislocation-climb phenomena have mostly been studied by observing the shrinkage of vacancy loops in thin foils by transmission electron microscopy.

An experiment that has proved to be particularly useful for studying annealing processes is repeated observation of the same set of areas in an electron-microscope thin-foil specimen with intermediate heating in a furnace under well-controlled atmosphere and temperature. Quantitative measurements can be made in this way of defect size, shape, and position relative to reference points in the foil. A necessary condition for consistent results is the nearly exact repetition of foil orientation relative to the electron-beam axis each time the foil is returned to the microscope for observation. This is made possible by the use of the Kikuchi line pattern as suggested by Thomas.¹ Experiments of this type have been used to study annealing of stacking-fault loops and perfect loops in aluminum,^{2,3} stacking-fault tetrahedra and triangular faulted loops in gold,⁴ and perfect dislocation loops in magnesium oxide.⁵ The results illustrate some of the factors that affect the absorption and emission of vacancies at dislocation lines.

GROWTH OF VACANCY DEFECTS

Vacancy defects formed by quenching and aging in aluminum and gold are shown in Fig. 1. The initial vacancy supersaturation in a quenched metal can be very large, $(C_v/C_{ve}) > 10^4$. However, as vacancies gradually disappear at the dislocation loops or tetrahedra that have been nucleated, the supersaturation falls, so that the final form of the secondary defect is characteristic of small supersaturation. In most cases, dislocation loops develop polygonal shapes with sides that lie parallel to a close-packed atom row. This is consistent with the mechanism of dislocation climb recently reviewed by Balluffi.⁶ A vacancy is assumed to arrive at the dislocation line and be bound to the core strongly enough to make many jumps along the length of the line before reentering the lattice. Only if it encounters a jog is the vacancy assumed to have been annihilated, and the jog has then been moved one interatomic distance. The development of polygonal shapes requires that jog nucleation be a far less frequent process than capture of a vacancy at an already existing jog. The situation is analogous to growth from the vapor of an atomically smooth perfect-crystal face on which two-dimensional nucleation is needed to start each successive new atomic layer. The growth forms assumed by dislocation loops suggest that the dislocations are dissociated: $\frac{1}{3} [111] \rightarrow \frac{1}{6} [211] + \frac{1}{6} [011]$ or $\frac{1}{2} [1\bar{1}0] \rightarrow \frac{1}{6} [2\bar{1}\bar{1}] + \frac{1}{6} [1\bar{2}1]$. Even in aluminum where the width of splitting is expected to be small, the defect shapes approached at low supersaturation

(a)

(b)

(c)

Fig. 1 Growth forms of vacancy defects in aluminum and gold: (a) $\frac{1}{3}$ $\langle 111 \rangle$ loops in aluminum, (b) $\frac{1}{2}$ $\langle 110 \rangle$ loops in aluminum, (c) $\frac{1}{3}$ $\langle 111 \rangle$ loops (A) and stacking-fault tetrahedra (B,C) in gold.

suggest that jog nucleation is more difficult on those sides which can split into partials. In aluminum a Frank loop that converts to a perfect $\frac{1}{2}$ $\langle 110 \rangle$ loop during growth changes from hexagonal to rhombus shape during further growth. The two sides that do not lie on a glide plane for the new Burgers vector climb faster than the other four sides. For most metals and alloys in which dislocations split, the stacking-fault ribbon has a width of several Burgers vectors. In this case the growth of a loop may be analogous to the growth of a stacking-fault tetrahedron, the critical growth step being the nucleation of new ledges in the stacking-fault ribbons or on the main fault according to the mechanism

suggested by De Jong and Koehler.⁷ Because the nuclei are of core dimensions, estimates of the critical supersaturations for growth by this mechanism can only be considered semiquantitative. However, it seems likely on the basis of calculations made by Kuhlmann-Wilsdorf⁸ that growth of tetrahedra or triangular stacking-fault loops in metals or alloys of low stacking-fault energy should take place only in the presence of strong vacancy supersaturation, e.g., $(C_v/C_{ve}) > 10^2$. Bullough and Perrin⁹ have come to similar conclusions for small voids.

SHRINKAGE OF LOOPS AND TETRAHEDRA

Reliable quantitative experimental measurements of dislocation-climb rates are still meager. It is not even possible in many particular cases to be sure of the detailed mechanism of climb or to predict what will be the rate-controlling step. A start has been made toward answering some basic questions about climb by detailed observations on shrinkage of various kinds of vacancy defects in metals of different stacking-fault energy.

Shrinkage of stacking-fault loops in aluminum is shown in Fig. 2. During shrinkage the loops quickly become circular. This shows that formation of a new jog at a loop corner is an easy process. The local climb rate is a function of the stacking-fault and line-tension climb forces acting on the dislocation. At first the line-tension force is greater near the corners, which probably explains their initially faster climb rate. After the circular shape is reached, emission of vacancies proceeds at an equal rate everywhere. Since jog concentration varies from 1 to zero every 30° around the loop, the maintenance of circular shape shows that jog concentration does not significantly influence climb rate. One possibility is that the local climb force results in enough bound vacancies being emitted from the jogs onto the straight segments of dislocation line so that their concentration is equal everywhere along the dislocation core, and the climb rate is then determined by their emission from the dislocation core into the lattice. Alternatively the local climb force results everywhere in sufficient vacancies being emitted into the lattice so that the chemical force $(kT/b^2) \ln(c/c_0)$ almost exactly balances the climb force due to line tension and stacking fault. The latter could be achieved either by direct emission from jogs or by emission into the dislocation core and then into the lattice. However, the climb rate for either of the last two possibilities is then controlled by the rate at which vacancies diffuse away to the surfaces of the foil rather than by their rate of emission from the dislocation line. Dobson and Smallman² and Tartour and Washburn³ showed that shrinkage rate of Frank loops in aluminum is a function of their distance from the surface of the foil. In the latter set of experiments, $\{112\}$ foils were used, so that the climb component of the surface image force was small. Therefore the results provide strong evidence that the climb rate of $\frac{1}{3} \langle 111 \rangle$ dislocations in aluminum is diffusion controlled.

Fig. 2 Shrinkage of $\frac{1}{3}$ $\langle 111 \rangle$ loops in aluminum at 100°C . (a) After growth. (b) 213-min annealing time. (c) 793-min annealing time. (d) 1304-min annealing time.

Very different results are obtained for metals or alloys of lower stacking-fault energy. In gold, shrinkage rates appear to be dependent on the rate of jog nucleation. Figure 3 shows a field of stacking-fault tetrahedra, many of which collapse to triangular faulted loops during annealing at 300°C . Some of the triangular loops shrink on further holding at 300°C , as illustrated by the enlarged outlines shown in Fig. 4. The following is a brief summary of the observed complex behavior:

1. Loops close to the foil surface, and even those cut by the surface, shrink no faster than those near the center of the foil.
2. One or all three sides of some triangular loops did not climb at all during 10 hr at 300°C .
3. Sides of all loops remained straight and parallel to a $\langle 110 \rangle$ direction.

Fig. 3 Collapse of stacking-fault tetrahedra (6, 7, 10) and shrinkage of $\frac{1}{3}\langle 111 \rangle$ loops in gold.

4. Those sides which obviously terminated at 120° corners always were among the ones that did climb.

5. Tetrahedra did not shrink as tetrahedra but always collapsed first into triangular Frank loops.

The observations show that the rate-controlling step in the climb of a $\frac{1}{3} \langle 111 \rangle$ dislocation in gold is nucleation of a jog at a corner. Because the sides always

Fig. 4 Outlines of loops identified by the corresponding number in Fig. 3 measured at indicated times (hours) of holding at 300°C .

remain parallel to $\langle 110 \rangle$, as is the case during growth, a jog once formed at a corner must migrate a distance much greater than a lattice spacing before another jog is nucleated. Escaig¹⁰ has shown that the elastic strain energy plus stacking-fault energy at the corner of a complete tetrahedron or a dissociated triangular Frank loop is always reduced by emission of the first few vacancies. This corresponds to a slight blunting of the sharp corner. It can be described as formation of a short length of Frank dislocation on one of the three $\{111\}$ planes and short segments of Shockley partials on the other two planes, as shown at PQR in Fig. 5. Whether or not the length of the Frank segment can

Fig. 5 Conservative (corner B) and nonconservative (corner A) collapse mechanisms for a stacking-fault tetrahedron.

then continue to grow, resulting in concomitant further unzipping of the opposite stair rod into Shockley partials, depends on the stacking-fault energy. If the equilibrium spacing of Shockley partial and stair rod for a dissociated Frank dislocation is less than $7b$, then there is a continuous decrease in energy, as shown in Fig. 6. For gold, $d \approx 6b$, and therefore metastable tetrahedra should collapse to Frank loops as soon as the temperature permits vacancy formation and migration because, at a critical length of the Frank segment, the Shockley partials will be pulled apart by the force of the stacking fault and sweep over three faces of the tetrahedron. Likewise, Frank loops should always shrink because they should have no true 60° corners. Loops that appear to be triangles should actually have six sides, three of which are just too short to be resolved by electron microscopy. The apparent stability at 300°C of some tetrahedra and some Frank "triangles" in gold probably represents impurity pinning. Sharp

Fig. 6 Effect of stacking-fault energy on the energy barrier for growth of a blunt corner on a triangular stacking-fault loop. Here d_0 is the equilibrium spacing of Shockley partial and stair-rod dislocation for a split $\frac{1}{3}$ $\langle 111 \rangle$ dislocation for stacking-fault energies of 45, 38, and 30 ergs/cm²; x is $1 - PQ/AC$ (see Fig. 5); μ is the elastic shear modulus; and b is the Burgers vector.

corners where three stair-rod dislocations meet might be stabilized by one or a few impurity atoms. An example of this unexpected stability for a triangular loop is shown in Fig. 8. In Fig. 3, there are also many tetrahedra that survive 10 hr of annealing at 300°C without collapse.

A schematic view of a Frank triangle with one blunted corner is shown in Fig. 8. The contracted node, such as at C, is apparently the only site at which jogs can be easily nucleated. It is of interest to consider what should be the relative climb rates for the short side CC compared to the longer sides CB and CA. Unless a short side climbs at least twice as fast as the neighboring longer sides, it will soon disappear during shrinkage. There are two reasons why very short segments may indeed be expected to climb at least twice as fast as long sides: (1) Jogs nucleated at a corner, such as C, probably have a more than equal probability of moving off along the short side because the Frank dislocation should not be able to fully dissociate when the side is only a few times the

Fig. 7 The $\frac{1}{2}$ $\langle 111 \rangle$ triangular loop which is probably stabilized by impurity pinning at all corners. Note rapid shrinkage of second loop during holding at 350°C.

Burgers vector in length, thus making emission of the second vacancy easier. (2) On a long side, there is less chance that a jog nucleated at one end of the side will reach the other end before the next jog is nucleated there. The climb rate will depend on the average spacing between jogs and will be independent of whether they are being nucleated at one or both ends. For a short side, of length less than the average jog spacing, an entire row of atoms will be added every time

a jog is nucleated at either end. If the probability of a jog moving off from a corner in either direction is assumed equal, then very short sides would climb exactly twice as fast as long sides, neither growing nor shrinking in length. This could account for the cases like 8 and 9 of Fig. 4, where a triangular loop shrinks continuously but appears to retain sharp 60° corners.

Fig. 8 The $\frac{1}{3}$ $\langle 111 \rangle$ loop with one blunted corner.

SELF-CLIMB OF DISLOCATION LOOPS BY CORE DIFFUSION

A mechanism of coarsening for small dislocation loops which becomes important in some materials at temperatures just below that required for ordinary self-diffusion is loop migration by diffusion along the dislocation core. Recent experiments⁵ have shown that this is the primary mechanism of loop coarsening in magnesium oxide at temperatures below 1300°C . Figure 9 is a series of pictures showing migration and coalescence of several pairs of loops. From measurements of the rate of migration as a function of loop diameter, separation, and temperature, it is possible to obtain reliable values of the pipe-diffusion coefficient and of the activation energy for pipe diffusion. In an ionic crystal, both positive and negative ions must diffuse during climb of a dislocation. The rate of climb should be determined by the slower diffusing ion, which in this case is oxygen.

When two coplanar dislocation loops of areas A_1 and A_2 , and having the same Burgers vector, $\mathbf{b}$, are separated by a distance of closest approach which is at least equal to the diameter of the largest of the two loops, then the loop-loop

Fig. 9 Migration of $\frac{1}{2} \langle 110 \rangle$ loops in magnesium oxide by core diffusion (self-climb). Note coalescence of pairs 1 and 2 to form single larger loops.

interaction energy, E_{int} , is given to a good approximation by Eshelby's¹¹ formula:

$$E_{\text{int}} = -\frac{\mu A_1 A_2 b^2}{4\pi(1-\sigma)} \times \frac{1}{S^3} \quad (1)$$

where S is the distance between loop centers, μ is the elastic shear modulus, and σ is Poisson's ratio. Following Kroupa¹² and Turnbull,¹³ we assume that the change in interaction energy due to formation of a vacancy which shifts the center of gravity of the loop is reflected as a change in the energy of formation of the vacancy. The concentration of vacancies within the core of the dislocation then varies around the loop. For a pair of vacancy-type loops, it is maximum at the far sides and minimum at the points of closest approach (for interstitial-type loops, just the opposite is true).

The axial component of the shift in center of gravity due to the formation of one vacancy on a loop of radius r , at any point P along its circumference, is approximately

$$\Delta S = \frac{b^2 \cos \theta}{\pi r_1} \quad (2)$$

where θ is the angle between the axis joining the loop centers and a radius of the loop passing through the point P .

The change in vacancy-formation energy within the dislocation core, $\Delta U'_{\text{fv}}$, is then

$$\Delta U'_{\text{fv}} = \frac{dE_{\text{int}}}{dS} \Delta S = \frac{3\mu A_1 A_2 b^4 \cos \theta}{4\pi^2 S^4 (1-\sigma)r_1} \quad (3)$$

Vacancy concentration, C' , varies along the dislocation core according to

$$C' = C'_0 e^{-\Delta U'_{\text{fv}}/kT} \quad (4)$$

C'_0 is the equilibrium vacancy concentration within the dislocation pipe in the absence of a climb force. It is given approximately by

$$C'_0 = e^{-U'_{\text{fv}}/kT}$$

For $\Delta U'_{\text{fv}} \ll kT$,

$$C' \approx C'_0 \left(1 + \frac{\Delta U'_{\text{fv}}}{kT} \right) \quad (5)$$

The migration rate of the loop will be determined by the flux of vacancies passing from the far to the near half of the loop. Assuming that the loops remain circular and the vacancy concentrations given by Eq. 5 are maintained everywhere, this flux is*

$$J_1 = 2D'A \frac{1}{r_1} \left(\frac{dC'}{d\theta} \right)_{(\theta = \pi/2)}$$

where D' is the core diffusion coefficient and A is the core cross section.

From Eqs. 3 and 5,

$$J_1 = \frac{3D'AC'_0\mu A_1 A_2 b^4}{2\pi^2 kTS^4(1-\sigma)r_1^2} \quad (6)$$

The corresponding migration rate (Fig. 10) for a loop of radius r_1 is then

$$\left(\frac{dS}{dT} \right)_1 = \dot{S}_1 = J_1 \frac{b^2}{2r_1} \quad (7)$$

If both loops of the pair are migrating, the total rate of change of S is:

$$\dot{S} = \dot{S}_1 + \dot{S}_2 = \frac{3D'AC'_0\mu A_1 A_2 b^6}{4\pi^2 kTS^4(1-\sigma)} \times \left[\left(\frac{1}{r_1} \right)^3 + \left(\frac{1}{r_2} \right)^3 \right] \quad (8)$$

Fig. 10 Experimentally measured quantities, S and r .

*Direct interaction between vacancies and the loop stress field^{1,2,3} has been neglected.

By evaluating the change in S caused by a sudden small change in the annealing temperature, one can measure the activation energy for the core self-diffusion of oxygen along a dislocation pipe:

$$\dot{S} = \text{const.} \frac{1}{T} e^{-\frac{U'_{fv} + U'_{mv}}{kT}} \quad (9)$$

Neglecting the $(1/T)$ in the preexponential gives

$$U'_{fv} + U'_{mv} = \frac{(\ln \dot{S})_{T_1} - (\ln \dot{S})_{T_2}}{\frac{1}{k} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (10)$$

The product $D'_0 A$ can then be evaluated from Eq. 8.

Measurements on six pairs of loops like those shown in Fig. 9 have given $64,500 \pm 5000$ cal/mole as the activation energy for pipe diffusion of oxygen. This compares with $110,000 \pm 5000$ cal/mole obtained for shrinkage of loops above 1400°C . The rate of shrinkage is almost certainly controlled by diffusion of oxygen vacancies from the vicinity of the loop to the foil surface; the temperature dependence is a measure of the activation energy for bulk diffusion of oxygen.

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DISCUSSION BY ATTENDEES

Balluffi: Could you check to see if the migration rate corresponds to that expected theoretically?

Washburn: We are in the process of making enough measurements to be able to do that.

Adda: What factors might affect pipe diffusion along a dislocation core?

Washburn: Stacking-fault energy and impurity concentration within the core region are two likely possibilities.

Wazzan: You have presented a model for swelling in which dislocations are attached to the growing voids. I have not seen a structure like that in any of the slides that have been shown on void growth.

Washburn: In most cases, pictures are taken of voids under conditions such that dislocations are out of contrast. However, they are there. The pictures shown by Dr. Norris earlier today were clear examples of this association of dislocations with the voids.

Harkness: Observations at Argonne National Laboratory on high-dose irradiations by both neutrons and charged particles at temperatures over 500°C usually show the dislocation structure interconnected with the void structure.

Balluffi: In your measurements of the conservative migration of loops in MgO, do you have any direct experimental evidence that the rate is actually controlled by the rate of dislocation pipe diffusion, i.e., mobility as a function of size, etc.?

Washburn: Measurements on migration rate as a function of loop size and separation distance are in progress.

THEORETICAL CONSIDERATIONS OF MIGRATION AND COALESCENCE OF PORES IN SOLIDS BY SURFACE DIFFUSION

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ABSTRACT

The problem of random migration and coalescence of pores in a perfect crystal by surface diffusion is reconsidered with emphasis on the relation corresponding to coalescence in which the migrating distance is small relative to the bubble radius. This term was omitted as an approximation in earlier analyses in which the swelling during postirradiation annealing was predicted to be proportional to the $1/5$ power of time. The results of the present analysis show that after sufficient time the swelling should be proportional to the $1/4$ power of time and that this time corresponds to a particular value of swelling (found here to be about 7%). A complete understanding of the swelling behavior requires a more comprehensive analysis that considers the effects of both terms simultaneously.

The first analysis of swelling due to random migration and coalescence of gas-filled pores in solids by surface diffusion was carried out by Greenwood and Speight.¹ The time rate of change of the mean radius, and hence the volume change or swelling, was calculated by considering the mean time required for all bubbles to coalesce to form the next larger bubble size. The conclusion of their argument was that swelling should be proportional to the $2/5$ power of time for the case of in-pile swelling. The case of postirradiation annealing was later treated by Speight,² who predicted that the mean radius and swelling should vary in this case as the $1/5$ power of time.

A more detailed approach to the postirradiation annealing problem was included in a subsequent analysis by Gruber³; finite-difference techniques were adapted to calculate the complete bubble size distribution as a function of time using a digital computer. This treatment was based on a relation given by Chandrasekhar⁴ in a discussion of colloid coagulation. The results confirmed those obtained by Speight,² except for a relatively small difference in the numerical coefficient. The results further showed that the distribution approached a limiting "self-preserving" shape and that the shape of the distribution

was such that the volume change was about 15% larger than that calculated from the mean radius.

These results were confirmed by analytical computations by Baroody,⁵ who also pointed out a numerical error in the example given for swelling by random migration. The predicted values for swelling and mean radius should have been 6% and 1340 Å for the case of a 1-month, 1000°K postirradiation anneal of copper containing 10^{20} helium atoms/cm³. This example was considered at that time to be an extreme case; the purpose of the example was to illustrate the conclusion that swelling due to random migration should be small relative to other possible mechanisms. However, in more recent discussions of swelling, particularly in the case of fast breeder reactors, the projected irradiation conditions make this formerly "extreme" example appear much less severe by comparison. A more complete treatment of the random-migration problem is therefore appropriate.

ANALYSIS

The same assumptions and approximations will be used here as in the previous case³; we consider the problem of random migration of bubbles in a perfect, infinite crystal containing a constant concentration m of gas atoms per unit initial volume. The gas is assumed for convenience to behave ideally, and vacancy diffusion in the solid is assumed to equilibrate the pressure in the bubbles with the surface tension of the solid. Coalescence and equilibration are assumed to occur "instantaneously" when two bubbles collide; that is, the collision process is considered to be the rate-controlling step.

Consider a function $F(n,t)$, which represents the frequency distribution of bubbles containing n atoms as a function of time t . Let F_i denote the (time-dependent) value of this function at $n = n_i$. The appropriate solution to the diffusion equation was given by Chandrasekhar in a discussion of the analogous problem of colloid coagulation⁴; the number of collisions ΔF_{ij} between bubbles containing n_i gas atoms and those containing n_j gas atoms in a time increment Δt is

$$\Delta F_{ij} = 4\pi D_{ij} R_{ij} F_i F_j \left\{ 1 + [R_{ij}/(\pi D_{ij} t)]^{1/2} \right\} \Delta t \quad (1)$$

The diffusion coefficient D_{ij} is given by $D_i + D_j$, and the interaction radius R_{ij} is taken as the sum $r_i + r_j$. The approximation was made in the earlier analysis, following Chandrasekhar, that the interaction radius would be small relative to the mean distance traveled by the two coalescing bubbles. On this basis the second term in brackets in Eq. 1 was neglected, and the distribution function $F(n,t)$ was calculated on the basis of the simplified equation. The purpose of the present work is to investigate the validity of this approximation.

First, we note several useful relations from the previous work. The diffusion coefficient of a pore is given by

$$D_p = 3\Omega^{1/2} D_s / 2\pi r^4 \quad (2)$$

or, for the particular case of a face-centered cubic (fcc) lattice,

$$D_p = 0.301 D_s (a_0 / r)^4 \quad (2a)$$

where Ω = the atomic volume

D_s = the surface diffusion coefficient

r = the pore radius

a_0 = the interatomic distance

For an ideal-gas bubble, in equilibrium so that $p = 2\gamma/r$, where p is the gas pressure and γ is the surface tension of the solid, we have

$$r_i^2 = (3kT/8\pi\gamma)n_i \quad (3)$$

where, as before, n_i is the number of gas atoms contained in the bubble. Finally, the results of the analysis showed that the mean radius varied as the $1/5$ power of time. Thus, if we consider only the mean bubble size and calculate the time dependence of the second term in Eq. 1, we find that the magnitude of this term should increase as $t^{1/5}$. Thus, after "sufficiently long" time, this term should dominate the collision kinetics.

Since there is no simple way to quantitatively determine this time, two approaches are available; either calculate the complete solution, using Eq. 1, or calculate the "long-time" approximation, using only the second term, and compare the result to the first treatment to determine the regimes of applicability of the two solutions. The second approach is used here, both because the solution can be given in general terms, so that one relation applies to all cases, and because the calculations are simpler. The limitations of this approach will be discussed later.

As in the previous treatment, the distribution function $F(n,t)$ can be normalized by dividing by the total number of gas atoms per unit volume. The resulting equation for collisions can be written, ignoring the first term, as

$$\Delta f_{ij} = f_i f_j (n_i^{-2} + n_j^{-2})^{1/2} (n_i^{1/2} + n_j^{1/2})^2 \Delta\tau / \tau^{1/2} \quad (4)$$

where $\tau = 24\Omega^{1/2} D_s m^2 t$ and f_i represents the normalized distribution function.

As discussed in the earlier work, finite-difference techniques were applied to determine the solution $f(n,\tau)$ that satisfies Eq. 4. In these calculations a value of $\Delta\tau$ was chosen for each time step such that the largest fractional decrease in any

value f_i was 10%. The sum τ was formed from the calculated values, and the mean value of τ during the time step was used in Eq. 4.

As in the previous case, the necessary moments of the calculated distribution were computed for each value of τ to determine the variation of the mean radius and swelling with time. Figure 1 shows the results on a logarithmic plot for the $\frac{3}{2}$ moment (which determines swelling) and the ratio of the $\frac{1}{2}$ moment to the

Fig. 1 Calculated variation of mean radius and swelling parameters as a function of τ .

zero moment (which determines the average radius). The curves approach linearity very quickly (near $\tau = 1$). This corresponds to a very short time for large m (for our usual example, copper with $m = 10^{20}$, $\tau \sim 6 \times 10^4$ at $t = 1$ sec). The calculated slope for both curves was 0.25 ± 0.01 after $\tau \approx 6$.

The results can be presented very concisely in terms of the self-preserving distribution shown in Fig. 2. This figure shows the function $f(n, \tau)$ normalized so that the resulting curve is independent of time. The normalizing procedure was described in the previous work; basically it results from a separation-of-variables approach to the integrodifferential equation corresponding to the finite-difference equation, Eq. 4. The result is that the distribution can be expressed as

$$F(n, t) = m\tau^{-2k} Z(u) \quad (5)$$

where $u = n\tau^{-k}$ and k is determined either from the integrodifferential equation or from the finite-difference solution. The mean radius and volume change or

swelling are proportional to $\tau^{k/2}$. In the present case, k was found to be $\frac{1}{2}$; this value was used to calculate the self-preserving distribution shown in Fig. 2. This distribution was rather well-established at $\tau = 35$ and remained practically unchanged for higher values (up to about 800).

Fig. 2 Standardized or self-preserving distribution function.

DISCUSSION OF RESULTS

The purpose of these calculations has been to determine whether the approximation used in the earlier treatment was justified, or if the second term or both terms in Eq. 1 should be used in the analysis. A partial solution to this problem is attempted here by comparing the results of separate treatments of the two terms.

A simple comparison can be made by forming the ratio of the swelling rates predicted by the two calculations. The first analysis gave the result

$$\Delta V_1 = 0.82 A^{\frac{2}{3}} B^{\frac{1}{3}} t^{\frac{1}{6}} \quad (6)$$

and the present result is, substituting for τ ,

$$\Delta V_2 = 1.5 A^{\frac{2}{3}} B^{\frac{1}{3}} t^{\frac{1}{6}} \quad (7)$$

In both equations we have substituted, for notational convenience,

$$A = mkT/\gamma$$

and

$$B = \Omega^{\frac{1}{2}} D_s$$

The swelling rates due to these terms can be shown to be equal when

$$t_r = 6.6 \times 10^{-8} A^{-6} B^{-1} \quad (8)$$

This equation can be applied directly to determine the relative importance in a particular case. For example, in the case considered earlier, the time is approximately 1 day. It is also apparent from this result that the parameters defining A influence this time more strongly than those defining B .

Another interesting quantitative result can be determined by considering the swelling ΔV_c at which $\Delta V_1 = \Delta V_2 = \Delta V_c$. From Eqs. 6 and 7,

$$\Delta V_c = 0.82 A^{\frac{1}{6}} B^{\frac{1}{6}} t_c^{\frac{1}{6}} = 1.5 A^{\frac{1}{6}} B^{\frac{1}{6}} t_c^{\frac{1}{6}} \quad (9)$$

from which we obtain

$$A = 1.8^{-10} B^{-\frac{1}{6}} t_c^{-\frac{1}{6}} \quad (10)$$

Substituting for A in Eq. 9 and simplifying, we obtain

$$\Delta V_c = 0.07 = 7\% \quad (11)$$

This result is interesting; it shows simply and quantitatively that, independently of the parameters involved, the second term begins to dominate the swelling kinetics at about the time swelling becomes significant. This result remains true whether swelling is due to a few large bubbles or to many smaller ones.

The swelling predicted by Eqs. 6 and 7 is shown as a function of time in Fig. 3 for two cases, $m = 10^{19}$ and $m = 10^{20}$, again for copper postirradiation annealed at 1000°K . The dashed lines indicate for comparison the results predicted in the earlier work for the case of biased migration; the cases shown correspond to the presence of a thermal gradient of $100^\circ\text{C}/\text{cm}$ and a surface-diffusion heat of transport of 10 kcal/mole.

These results confirm the earlier conclusion that "swelling is not likely to be significant if it occurs only as a result of random migration of bubbles in large-grained material,"³ except for rather extreme cases.

Fig. 3 Time dependence of swelling computed for copper postirradiation annealed at 1000°K for the indicated time. The upper curves correspond to a dose $m = 10^{20}$, and the lower ones to $m = 10^{19}$, helium atoms/cm³. The dashed lines show the results for biased migration corresponding to a thermal gradient of 100°C/cm for a heat of transport of 10 kcal/mole.

CONCLUSIONS

This analysis has shown that, when swelling by random surface-diffusion migration does become significant, the mean radius and swelling should increase as $t^{1/2}$ rather than $t^{1/3}$ as predicted by the earlier analyses. Approximate values of swelling and time at which the second term becomes important have been calculated; however, these values are based on rather crude approximations. Calculation of the time corresponding to equal swelling rates assumes that the bubble-size distributions predicted by the two separate analyses are identical; this is not true. Similarly, calculation of the swelling at which the two terms contribute equally is unrealistic since it assumes that the two terms apply to independent systems. Work is therefore continuing to determine the swelling predicted by the complete equation.

ACKNOWLEDGMENT

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DISCUSSION BY ATTENDEES

Anthony: It has been recently shown for helium-gas-bubble migration in copper that there are effects of interface kinetics. This would change the size dependence of the bubble mobility from $1/R$ to a mobility less dependent on size (since interface kinetics effects increase with decreasing bubble size—lower mobilities at lower bubble sizes). What effect will such interface kinetics have on the time dependence of collision probabilities and thus swelling?

Gruber: Since swelling is dominated by the migration and coalescence of the smaller bubbles, slowing down their migration in general would slow down the swelling kinetics; but, since the mobility does not drop off as quickly as the bubbles grow, the time exponent may increase.

Cost: How do experimentally measured distributions of pores agree with your theoretical predictions? Do you care to comment as to what the distributions will be like if, say, nucleation rather than a surface diffusion dominates the kinetics?

Gruber: I am not aware of any experimental data that can be compared directly with these predictions, at least in a definitive way. The problem of nucleation is omitted in this treatment by simply extrapolating back to "single-atom bubbles." However, the fact that all small bubbles disappear in a very short time implies that the effect of nucleation should be very small, unless, of course, it results in bubbles on dislocations and/or grain boundaries, which cases are now being studied. Another possibility is that nucleation could occur at a site that would trap a bubble and prevent its further migration. This effect could limit the swelling.

Marlowe: Cornell* has followed the growth of fission-gas bubbles in UO_2 on annealing and has described that growth by diffusion of gas into the bubbles. Markworth and Baroody† have recently analyzed the bubble size distribution that arrives from such growth and have applied it to Cornell's data. Have you used your analysis for bubbles growing by collisional coalescence via a

*R. M. Cornell, *Phil. Mag.*, **19**: 539 (1969).

†A. J. Markworth and E. M. Baroody, *J. Mater. Sci.*, **5**: 55 (1971).

surface-diffusion mechanism to treat the data of Cornell, and, if so, what were the results?

Gruber: I am not familiar with that work.

Adda: I assume that you did not take the elastic interaction between voids into account in your calculation. Is this correct?

Gruber: That is correct; the interaction radius was taken as the direct sum of the bubble radii, which implies no interaction unless the bubbles contact one another.

EFFECT OF IRRADIATION TEMPERATURE ON SIZE OF DEFECT AGGREGATES IN COPPER

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ABSTRACT

We have used anomalous X-ray transmission to study the effect of irradiation temperature on the size of defect aggregates produced by fast-neutron irradiation. Nearly perfect copper crystals have been irradiated with 10^{18} fast neutrons/cm² ($E > 0.6$ MeV) at temperatures varying from 43 to 400°C, and the resulting decrease in the integrated anomalously transmitted intensities has been measured for CuK α , MoK α , and AgK α X rays. These data indicate little change in the defect structure for irradiation temperatures from 43 to 200°C; however, for temperatures above 200° the absorption coefficients rapidly increased by a factor of about 40 at 300°C, indicating a rather large increase in the sizes of the defect aggregates. This conclusion is supported by the wavelength dependence of the coefficients, line broadening of the Bragg profiles, electron microscopy, and X-ray topography. The maximum effect occurred at 300°C, whereas at 400°C (which is above the onset of stage V annealing) there was no damage detectable for these neutron doses. Similar measurements made on nearly perfect aluminum crystals that had been irradiated at 43 and 127°C for doses up to 7×10^{18} neutrons/cm² indicated no such effect in aluminum for these temperatures.

It is well known that vacancy and interstitial loops and clusters result from the irradiation of copper and many other metals with fast neutrons at reactor ambient temperatures.¹ It is not well established whether these defect aggregates are formed as a direct result of the neutron-displacement cascade or whether subsequent point-defect motion and clustering play a significant role, since no detailed study at temperatures below stage I annealing has yet been possible. The observation of defect aggregates after electron irradiation at low temperature and subsequent warming to room temperature² indicates that such aggregation may result from diffusion of the point defects. More recently, defect regions, large ($\sim 10^{-3}$ cm) clusters of interstitial and vacancy loops, were observed³ in copper after irradiation with 10^{18} neutrons at 300 to 400°C, the temperature

range of the final annealing stage for copper. And voids have been found⁴ in copper irradiated with $\geq 10^{20}$ neutrons/cm² in the temperature range 200 to 400°C. Voids and loops have been observed in many metals irradiated at comparable temperatures, but the defect regions only in copper. For each case, only a small fraction of the vacancies and interstitials produced by the irradiation are stored in the loops and clusters. Since all the aggregates result from clustering of the point defects produced by the irradiation, an understanding of the parameters that determine the particular forms the aggregate may take would coincidentally help clarify the details of void formation. Such is the intent of the work reported here.

It has been demonstrated that measurements of the intensities of dynamically diffracted X-ray transmission and diffuse scattering near the Bragg reflection peak are valuable in determining the nature, number, and size of defect aggregates in a crystal.^{5,6} Since these X-ray measurements are easier than electron microscopy, they may provide a valuable supplement to the usual tedious procedures for electron-microscopic investigations. In the present study, we have made such X-ray measurements at room temperature on copper and aluminum crystals neutron irradiated in the temperature range 43 to 400°C.

EXPERIMENTAL PROCEDURE

Nearly perfect crystals of 99.999% copper were irradiated in the CP-15 facility of the Bulk Shielding Reactor (BSR) at the Oak Ridge National Laboratory with neutron doses varying from 0.5 to 7.2×10^{18} neutrons/cm² ($E > 0.6$ MeV), flux of 6×10^{12} neutrons/(cm²)(sec). The irradiations were made in a helium atmosphere at temperatures varying from 43 to 400°C as measured by thermocouples included in the irradiation capsules. The crystals had densities of $\sim 10^2$ to 10^3 dislocations/cm² and were lamellae of dimensions $1 \times 1 \times t$ cm, $0.024 < t < 0.1$, for irradiation temperatures up to 255°C, whereas the higher temperature irradiations were carried out on parallelepipeds of dimensions $1 \times 1 \times 1$ cm. Thin lamellae of thickness less than 0.1 cm with (111) faces were prepared from the parallelepipeds after irradiation by acid sawing and polishing. These lamellae were attached to wire supports with Salol and examined by Borrmann X-ray topography to ensure that no mechanical deformation had occurred due to handling and to determine if topographical-size defects had been produced. Integrated anomalous transmission measurements of the 111 reflection using CuK α , MoK α , and AgK α X rays were then made at room temperature using a double-crystal spectrometer. Also, integrated intensity measurements were made after annealing some of the irradiated lamellae. Diffuse scattering intensities were measured in the vicinity of the 111 Bragg reflection using CuK α X rays, and Bragg line-width measurements were made of the MoK α 444 reflection using a double-crystal spectrometer. Some of these specimens were thinned and studied by electron microscopy and Lang X-ray topography.

High-purity, low-dislocation-density aluminum crystals, grown by recrystallization by Nøst,⁷ having an area of about 1 cm² and a thickness of 0.1 cm were included in the capsules for the irradiations at 43 and 127°C.

RESULTS

The decreases in the integrated anomalous transmission intensities are tabulated in terms of effective absorption coefficient, μ^* , for the neutron doses and individual irradiation temperatures in Table 1. The dose was not held

TABLE 1
EFFECTIVE ABSORPTION COEFFICIENTS

Irradiation temperature, °C	Neutron dose, 10 ¹⁸ neutrons/cm ² (E > 0.6 MeV)	μ^*_{111} , cm ⁻¹		
		CuK α	MoK α	AgK α
43 ± 1	3.6	23	15	8
127 ± 3	7.2	50	30	16
160 ± 5	1.0	7	4	2.2
210	1.0	13	6	3.3
255	1.0	93	75	49
300 ± 10	1.3	160	215	90
350	0.6	6	17	21
400	0.7	<1	<1	<1

constant for all irradiation temperatures; thus these data have been scaled linearly to a constant dose of 1×10^{18} neutrons/cm², and μ^* has been plotted logarithmically as a function of temperature in Fig. 1 in order to show the effect of temperature and the wavelength dependence more clearly. There was no indication of a significant change in the defect character for temperatures from 43 to 160°C, but at about 200°C the absorption coefficients increased sharply such that at 300°C they were 20 to 40 times larger than at the lower temperatures. The high-temperature side of the peak was also very sharp, and, at an irradiation temperature of 400°C, there was no damage detectable in terms of μ^* for these doses. In the temperature range of the peak, the wavelength sensitivity of μ^* has been completely inverted such that, for the 350°C irradiation, the shortest wavelength (AgK α) suffered the largest absorption and the longest wavelength (CuK α) was least affected, the reverse of that noted for the lower temperatures.

X-ray measurements of diffuse scattering around the Bragg peak for 111 reflections showed that the broad band (20 to 30-min angular range) of diffuse scattering characteristic of ambient-temperature irradiations⁷ persisted up to the

Fig. 1 Effective absorption coefficients for a neutron dose of 10^{18} neutrons/cm² vs. irradiation temperature.

160°C irradiation; however, at 255 and 300°C, these bands were more intense and were concentrated in a much smaller region (2 to 3 min) close to the Bragg peak so that it became difficult to separate the Bragg and diffuse scattering. For the 444 reflection, this effect resulted in an increase in the half-widths of the reflection to 5 and 8 sec for the 255 and 300°C irradiations, respectively; the

observed halfwidths for all other irradiation temperatures were equal to the theoretical value of 2 sec.

The X-ray topography and electron-microscopy studies are somewhat less complete at this time, but both methods indicate that very large defect regions were formed in the irradiations from 255 to 350°C. The sizes of these regions varied from an average diameter of about 1 μ at 255°C to about 17 μ at 350°C. The electron microscopy showed these defect regions to be of irregular shapes and composed of a rather dense array of vacancy and interstitial loops and dislocation-line segments. In the 255°C irradiation, these micron-size defect regions were separated by $\sim 10 \mu$ with few defects in the space between, as shown in Fig. 2. An electron micrograph from a crystal irradiated at 210°C is shown in Fig. 3. The defect regions are evident but much less clearly defined. Although the average diameter and number density of the defect regions in this sample can only be approximated, values for them are included with those for the other irradiation temperatures in Table 2. These findings are similar to those of Hulett et al.³ in earlier studies and are in marked contrast to the findings of rather detailed electron-microscopy studies of ambient-temperature neutron-irradiated copper, which showed⁸ a homogeneous distribution of small loops (mean radius $\sim 40 \text{ \AA}$).

One of the crystals irradiated at 127°C was annealed in hydrogen at 250°C for 66 hr, and the effective absorption coefficient was decreased about 10% by this treatment. Another crystal irradiated at 255°C was annealed at 400°C for 1 hr, and μ^* was found to decrease about 50%.

Lang X-ray topography and anomalous transmission measurements were made on the aluminum crystals irradiated with 3.6×10^{18} neutrons/cm² ($E > 0.6 \text{ MeV}$) at 43°C and with 7.2×10^{18} neutrons/cm² at 127°C. For these crystals, there was no detectable change resulting from these irradiations in the dislocation structure in the Lang topographs nor in the intensity of anomalous transmission using CuK α X rays.

DISCUSSION

Dederichs⁹ has considered the effects of clustering of point defects on anomalous transmission, and good agreement between theory and experiment has been shown for ambient-temperature neutron irradiation of copper.¹⁰ This theory treats the attenuation of the X-ray wave field in terms of effective absorption coefficients that are a result of the presence of defect aggregates. The observed intensity transmitted through an irradiated crystal (R_{obs}) is related to the intensity calculated for a perfect crystal (R_{calc}) by

$$R_{\text{obs}} = R_{\text{calc}} e^{-\mu^* t} \quad (1)$$

where t is the sample thickness and the effective absorption coefficient μ^* is composed of a photoelectric part (μ_{PE}) related to the static distortions around a

Fig. 2 Electron micrographs of defect regions formed during 255°C irradiation.

Fig. 3 Electron micrograph of defect regions formed during 210°C irradiation.

TABLE 2
PARAMETERS OF THE DEFECT REGIONS

Irradiation temperature, °C	Average diameter, 10^{-4} cm	Number per cm^3	Volume fraction of defect regions	Fraction of pairs retained
43				$\sim 1 \times 10^{-1}$
210	~ 0.7	$\sim 2 \times 10^{11}$	$\sim 3 \times 10^{-1}$	3×10^{-2}
255	1	1×10^{10}	5×10^{-3}	5×10^{-4}
300	2.5	4×10^8	3×10^{-3}	3×10^{-4}
350	17	10^6	3×10^{-3}	3×10^{-4}

defect and a diffuse-scattering part (μ_{DS}) related to the diffuse scattering from the correlations of the static displacements. For dislocation loops, these additive components are given in terms of the X-ray and crystal parameters for low-order (i.e., low Bragg angle) reflections as

$$\mu_{PE} \approx cR_0\mu_0 \left(\frac{2\pi b}{d^3}\right)^{\frac{1}{2}} = C_L \frac{R_0^3\mu_0}{2V_c} \left(\frac{2\pi b}{d}\right)^{\frac{1}{2}} \quad (2)$$

and

$$\mu_{DS} \approx 0.68cR_0^2b \left(\frac{\pi r_c F \lambda}{V_c d}\right)^2 \ln\left(\frac{D}{R_0}\right) = 0.68C_L R_0^4 \frac{\pi}{V_c} \left(\frac{b\pi r_c F \lambda}{V_c d}\right)^2 \ln\left(\frac{D}{R_0}\right) \quad (3)$$

where c = fractional point-defect concentration in the sample

C_L = concentration of loops

R_0 = radius of the loops

μ_0 = photoelectric absorption coefficient

b = magnitude of the Burgers vector of the loops

d = interplanar spacing of the diffracting planes

r_c = classical electron radius

F = X-ray structure factor

λ = X-ray wavelength

V_c = volume of a unit cell in the lattice

The term $D = (2r_c F d / V_c)$ is a cutoff parameter of the order of an extinction length and is $\sim 6000 \text{ \AA}$ for the 111 reflection used here.

In the present study the absorption coefficients plotted in Fig. 1 gave no indication of a change in the defect structure for irradiation temperatures from 43 to 160°C. For the 210°C irradiation, there was not only an increase in μ^* for all wavelengths but also a change in the ratio of the μ^* values for CuK α and MoK α . Since the μ_{PE} 's happen to be equal for these wavelengths, this change is an indication that μ_{DS} for CuK α has increased significantly more than for MoK α , and therefore R_0 or the defect configuration must have changed. This observation is consistent with the electron microscopy, which indicates a departure from the homogeneous distribution of loops found after lower temperature irradiations. This nonhomogeneity was more pronounced for the 255 and 300°C irradiations where well-defined defect regions were formed, which apparently give rise to the much larger μ^* values. It appears that there is considerable strain around the defect regions since the wavelength sensitivity is reversed above 300°C; this reversal is known to occur for large defect regions and is predicted qualitatively by Dederichs for defects with sizes of the order of an extinction length. That this is necessary to account for the X-ray results can be demonstrated by considering the possible absorption from the fractional volume occupied by defect regions from the 255°C irradiation (Table 2). If the

region of the defects was considered to be essentially amorphous to the X-ray beam and the surrounding volume unstrained, a μ^* value of 0.5% of μ_0 or $\sim 2 \text{ cm}^{-1}$ for $\text{CuK}\alpha$ would be predicted. The observed μ^* is 50 times larger. The 100- to 200-Å loops typically found inside these regions would not be capable of producing the necessary strain individually. However, the necessary magnitude of strain field might be produced by such loops if a coherent effect similar to that produced by the clustering of point defects were present here also, since this effect enhances the total strain remarkably.

From Eqs. 2 and 3, if the observed concentration of defect regions present after the 255°C irradiation acted as if they were loops of radii $R_0 \sim 0.5$ micron, the observed μ^* values could be accounted for. Since these regions are comprised of an array of much smaller loops, a somewhat more realistic calculation can be made using the Dederichs formula for clusters of point defects by adapting it to consider clusters of loops. For example, assuming 4×10^3 loops of 100-Å radius in each of the defect regions, $\mu_{\text{DS}} \sim 100 \text{ cm}^{-1}$ for $\text{CuK}\alpha$ radiation. This value is of the same magnitude as that observed, although these calculations can only be considered semiquantitative since the theory was derived for strain fields that are small compared to the X-ray extinction lengths, which is not the case here. Such long-range strain fields would also account for the change in the diffuse scattering near the Bragg peak from the extended angular range observed for ambient-temperature irradiations to the much narrower range for the 255 and 300°C irradiated crystals. Also, the broadening of the 444 $\text{MoK}\alpha$ line widths for these irradiations would be expected with such strain fields since the diffuse scattering close to the Bragg peak can become large enough that it cannot be clearly separated from the Bragg scattering.

The electron microscopy and X-ray topography, consistent with the intensity measurements, show that damage resulting from the irradiations at temperatures from 210 to 400°C consists of clusters of vacancy and interstitial loops, defect regions, separated by regions of the crystal containing few apparent defects. As can be seen in Table 2, the size of the defect regions increases and the number/cm³ decreases with increasing irradiation temperature. From the annealing results reported here and elsewhere,³ it is clear that defect regions are not produced by subsequent annealing of the randomly distributed loops and clusters resulting from irradiation at lower temperatures. The approximate volume fraction of crystal occupied by defect regions is also shown in Table 2. The concentration of point defects (computed from the loops) within defect regions was approximately equal to that found after the lower temperature irradiations. The approximate fraction of the pairs produced by the irradiation ($\approx 2 \times 10^{19}$ pairs/cm³) which remained in the crystal can be estimated and is also given in Table 2. For irradiation temperatures from 255 to 350°C, it is noteworthy that this small fraction was approximately constant within the accuracy of these values. No voids were observed in these crystals, but it is possible they were present in very low concentration.

It is clear that the peak at 300°C in Fig. 1 results from the fact that, at irradiation temperatures beginning at about 200°C, some of the damage produced by the irradiation clustered to form defect regions. Essentially no additional damage was retained in the crystal, but the form of the defect regions leads to a higher absorption. The principal question is what causes this type of damage structure. From the lack of a long tail on the low-temperature side of the peak and from the sharp change in the defect structure already apparent for the 210°C irradiation, we conclude that a nucleation type of phenomenon must be involved. Had the onset of vacancy migration alone been responsible, the peak would have been expected to rise more slowly (for $E_M^{IV} = 1$ eV, the diffusion distance is $\sim 10^{-4}$ cm at 150°C for these irradiation times) and the type of damage structure to change gradually from the randomly distributed loops produced by lower temperature irradiations. The decay of the peak probably results from the increasing equilibrium concentration of vacancies with temperature since the production rate (vacancies/sec) is an order of magnitude lower than the equilibrium vacancy concentration at 400°C. And this is the temperature range of annealing of dislocation loops in copper. However, it was found that defect regions produced in another reactor at 400°C under somewhat different conditions annealed at $\sim 500^\circ\text{C}$. The decrease in number density and increase in size of the defect regions with increasing irradiation temperature do not appear to be consistent with any impurity effects in these high-purity crystals. Also, although these are rather special crystals for starting material, defect regions have been produced by irradiation of polycrystalline copper of the same purity. At present, we are unable to account for the formation of the defect regions, but further investigations of the parameters that may affect their nucleation are planned.

The relation, if any, of these defect regions to the voids formed by irradiation of copper in the same temperature range⁴ for neutron doses of $\geq 10^{20}$ neutrons/cm² is obscure. Specifically, we do not wish to imply that the defect regions are incipient voids, but rather that they are yet another manifestation of the defect structure that can form when defects are produced in a crystal at temperatures at which they are mobile.

The absence of similar defect regions in the aluminum irradiated here is not understood. Although the lack of large numbers of dislocation loops after room-temperature irradiation is often cited as evidence for the diffuseness of the displacement cascade in aluminum, it does not seem to be indicated that the cascade is significant in the formation of the defect regions in copper. Also, voids are formed in aluminum by irradiation¹¹ in the temperature range of these studies at somewhat higher doses.

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DISCUSSION BY ATTENDEES

Brimhall: Were the clusters of loops three dimensional or two dimensional in nature?

Larson: The clusters are three dimensional as observed by the use of stereo pairs. Since the sample thickness in the micrographs varied from 500 to 3000 Å, we see only a thin slice of these micron-sized regions, however.

Spitznagel: The dislocation density in the samples appears to be quite low. What was the actual dislocation density, and have you tried bombarding samples with higher initial dislocation densities?

Larson: The density was of the order of 10^2 to 10^3 dislocations/cm². This structure has also been observed in polycrystalline samples that had much higher densities, of the order of 10^5 to 10^6 dislocations/cm².

COMPUTER SIMULATION OF RADIATION-INDUCED VOID NUCLEATION AND GROWTH IN METALS

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ABSTRACT

Computer simulation of crystal-lattice defects produced by atomic collision cascades and by isolated collision events has been used to generate primary damage states in cubic metals. Both unsaturated and saturated damage states have been generated in this manner. Thermal annealing of these damage states was also simulated. The influence of preexisting dislocations and of grain-boundary sinks was not included in the annealing simulations. The development of embryo void nuclei turned out to be an inevitable consequence of approaching a saturated damage state, regardless of whether the defects were produced by cascades or by isolated collision events. Both homogeneous and heterogeneous nucleation of voids were observed. Long-term stability of a void against both thermal dissociation and radiation attrition required impurity-atom stabilization of the edges and corners of a faceted void. This is called external stabilization. Internal stabilization by the containment of rare-gas atoms was not treated explicitly. Thermal decomposition of faceted voids began via an unzipping process at the corners.

This paper attempts to draw together the results of computer experiments from six different laboratories on (1) point-defect-cluster properties, (2) radiation-damage production, and (3) displacement-spike annealing, which bear on void nucleation, growth, and dissociation. Nearly all of the work discussed concerns alpha iron. The reason for this is as follows: Since 1963, investigators at six different laboratories have used the same atomic interaction function^{1,2} for alpha iron and, just as importantly, similar adaptations of two prototype computer programs. One of the prototypes is a dynamical-method program,³ and the other is a variational-method program.^{4,5} Since 1967, two different groups have used the same collision-cascade⁶ and displacement-spike-annealing⁷ simulation programs. As a result, a large accumulation of internally self-consistent computer-experiment results has developed for alpha iron. These data from different laboratories fit together smoothly with a refreshing minimum of ambiguity due to the use of unmatched potentials and techniques. A detailed listing of the

particular laboratories, program methods, and contributing investigators concerned is given in the appendix to this paper. Computer experiments on face-centered cubic (fcc) and hexagonal close-packed (hcp) metals which are pertinent to the void problem are also referenced in the appendix.

Connections among the types of different computer-experiment investigations which have been performed are described by the flow chart in Fig. 1, as

Fig. 1 Organization of a mechanical-properties-effects computer-experiment system for neutron-irradiated material.

they pertain to an explanation of irradiation-induced mechanical-property changes. As is well-known, void production is associated with the occurrence of undesirable mechanical properties and with dimensional instability in irradiated metals and alloys. As indicated by Fig. 1, a variety of different coordinated computer experiments is required to execute the simulation of radiation-damage production and annealing. Alpha iron is presently the only metal for which a sufficiently comprehensive set of computer experiments has been made to serve as the basis for a discussion of void nucleation, growth, and dissociation.

Figure 2 illustrates the two extremes in a computer-experiment approach to void nucleation via the properties of the primary damage state* per se. The top

*The primary damage state¹¹ is defined as that produced directly at 0°K. It includes defect configurations produced by dynamic interference among defects when more than one Frenkel pair is produced but no defect configurations that require thermally activated processes.

Fig. 2 Two extreme models for simulating the development of a saturated damage state and ensuing high-fluence damage states. (a) Random production of independent single defects. (b) Random production of locally saturated groups of defects. New defects are denoted by open circles and old defects by filled circles. (Ref. 13, Fig. 4).

row of defect-production frames shows the accumulation of individual, independently produced defects, such as Frenkel pairs in an electron-irradiated specimen. The bottom row of frames shows the accumulation of high-density groups of defects. In each of these groups, the defect positions are highly correlated, such as are the vacancy and interstitial positions in a displacement spike. The ultimate outcome of each mode of defect accumulation is, of course, a saturated damage state. However, the limiting-case damage state for Frenkel-pair accumulation is not necessarily the same as that for displacement-spike accumulation.

Computer experiments on damage production at 0°K (primary damage-state production) indicate that the occurrence of void nucleus embryos is an inevitable consequence of attaining a saturated damage state, regardless of the mode approach to this saturated state. The production of visible voids, however, is another story, involving defect coalescence prompted by mechanical- and thermal-driving forces *ab initio*, but it is still fundamentally a saturation phenomenon. Displacement-spike-annealing computer experiments constitute a basis for explaining the temperature dependence of visible void production. Computer experiments on impurity-atom effects bear on void stabilization either by internal stabilizing agents, such as helium atoms contained within a void, or by external stabilizing agents, such as impurity-atom aggregation near void surfaces.

ACCUMULATION OF INDIVIDUAL FRENKEL PAIRS

The first computer experiments on the accumulation of independently produced Frenkel pairs were done by Luck and Sizmann.⁸ Their primary

interest was to estimate the recombination-region size. In the course of their computer experiments, they also demonstrated that the defect clustering could occur, purely on the basis of fluctuation effects, without any need for thermally activated processes. These findings prompted us to examine the spatial distribution of defects in such computer experiments from the standpoint of void nucleation.

In this endeavor a SIZMANN Program⁹ was written for two small crystallite sizes, a 1000-atom crystallite and an 8000-atom crystallite. The simple cubic structure was chosen for convenience in the original calculations, which we will describe here. Since then, a body-centered cubic (bcc) version has been written for a 14,859-atom crystallite. In the simple cubic case, a recombination region encompassing 27 sites was chosen so as to closely approximate the size of the 31-site Erginsoy-Vineyard recombination region² for alpha iron. The 27-site recombination region is a cube with three atom sites on a side centered upon the defect in question.

As shown by Lehmann,¹⁰ the time average number of defects in a saturated damage state is

$$N_{av} = V/V_R \quad (1)$$

where V is the crystal volume and V_R is the volume of the recombination region. In the present case, $N_{av} = 37.3$. Up to 100,000 Frenkel pairs were produced, one by one, in the 1000-atom crystallite on a purely random basis.

Each new vacancy and interstitial was checked against the extant defect distribution for possible participation in an annihilation event. This was done by seeing if the new defect was contained in this recombination region centered about any extant defect of the opposite type. Each different run was distinguished by the random number generator used to initiate the random sampling process. The number of stable defects, N_F , is plotted as a function of the number of Frenkel pairs produced, N_{FP} , in Figs. 3 and 4 for the particular run SIZ049. If one assumes a constant Frenkel-pair production rate, then N_{FP} is proportional to the irradiation time and the fluence. The time average defect population for the saturated damage was reached after about 170 Frenkel pairs had been produced. This amounts to 0.17 displacement per crystallite atom. The fluctuation of the defect population above and below N_{av} is about 20% for the segment of the defect population vs. irradiation time curve plotted in Fig. 4.

The fluctuation of the instantaneous defect population about N_{av} is a significant feature in connection with void nucleation. We observed fluctuations downward from N_{av} of 38% and fluctuations upward from N_{av} of 83%. This feature is of interest because it provides a basis for void nucleation, which is a particular, transient event needing only some locking or stabilizing influence to complete its operation. One immediately thinks of impurity atoms as being one class of agents for this influence.

Fig. 3 Accumulation of stable Frenkel pairs randomly produced in a 1000-atom crystallite. Part 1.

Fig. 4 Accumulation of stable Frenkel pairs randomly produced in a 1000-atom crystallite. Part 2.

Another fluctuation of interest is that in the irradiation time (fluence) required to establish a saturated damage state. Ten or more different random number generators were used to initiate each type of computer-experiment saturated-damage-state run. Inspection of the results for these various runs immediately showed that the fluence needed to establish a given number of stable defects, N_F , varied widely for $N_F > 5$. The ratio of the maximum fluence observed to the minimum fluence observed for the first occurrence of each N_F value is plotted in Fig. 5. Results for both the 1000- and 8000-atom crystallite

Fig. 5 Variation in the number of Frenkel pairs which must be generated to give a specified number of stable Frenkel pairs for the first time.

are shown. In both cases, this ratio increases with N_F and is about 3.5 at $N_F = N_{av}$ for the saturated damage state. These curves show that a sizable difference exists among the radiation exposures required to saturate different crystal subvolumes of sizes 10^3 to 10^4 atomic volumes. This is the size range for the vacancy-source regions immediately associated with void nucleation and the early stage of void growth (see Table 6).

Let us now direct attention to the spatial distribution of defects in the crystallite, as the damage state develops into a saturated damage state, and the time behavior of the defect spatial distribution in a saturated damage state. Defect-distribution maps from run SIZ031 will be used to illustrate these features. In this run, maps were printed each time the defect population increased by five defects. The data for $N_F = 5, 20, 40$, and 60 are considered.

Figure 6 shows vacancies (open squares) and interstitials (open circles) for a very low defect population (five defects). The recombination-region coverage

centered about each vacancy is marked out in the z plane containing the vacancy and in the $z+1$ and $z-1$ planes above and below the vacancy. The unit of distance is the half-lattice constant (hlc), hence successive atom planes are labeled $z=1$, $z=3$, etc. The letter b in the $z=3$ map, for example, indicates that a vacancy exists immediately below it in the $z=1$ plane. Similarly, the letter a in the $z=5$ map indicates that a vacancy exists immediately above it in the $z=7$ plane. Maps for planes $z=13$, 15, 17, and 19 are not shown here in order to save space. The next two figures describe the defect distribution when

RUN SIZO31: $N_F = 5$, $N_{FP} = 5$

Fig. 6 Vacancy and interstitial distribution for five Frenkel pairs in the 1000-atom crystallite.

the defect population is 20, about half of N_{av} , and when it is 40, slightly larger than N_{av} .

The restriction on the placement of new stable defects tightens rapidly as the defect density increases. This becomes evident in Fig. 7. In this figure a new vacancy could be placed anywhere within the squared regions without inducing an annihilation event, provided it was set in further than one square from the boundary. A new interstitial could be placed anywhere in the open areas without inducing an annihilation event. Reference to Fig. 8 shows that, for $N_F = 20$, the

Fig. 7 Vacancy and interstitial distribution for 20 Frenkel pairs in the 1000-atom crystallite.

fraction of free sites in the crystallite is about 40%. In this context a free site is one not covered either by a recombination region centered on a vacancy or by a recombination region centered on an interstitial. The overlap region consists of sites which are covered both by recombination regions centered on vacancies and by those centered on interstitials, simultaneously. When $N_F = 20$, the fraction of sites in the overlap region is only about 0.05. Note that in order to obtain 20 stable defect pairs (20 vacancies and 20 interstitials), 39 Frenkel pairs had to be generated.

Figure 9 shows the defect distribution in a saturated damage state with 40 defects, a positive fluctuation of 7%. It may seem as if lots of open region were available in which to put new defects, but it must be remembered that the recombination-region coverage centered on interstitials is not shown here. In fact, only 20% of the sites are in the free region (see Fig. 8). The shape of the free-site region is not generally compact at this stage, and it is difficult to find a locally compact part of the free-site region sufficiently large to encompass the compact 27-site unit of free volume required to admit a new defect without causing an annihilation event.

At this saturation stage, 10% of the sites are in the overlap region. By inspection, one immediately sees pair configurations in planes $z = 3, 7, 9$, and 11. An interstitial triplet appears in plane $z = 7$. By taking time to read the a and

Fig. 8 Fraction of atom sites in the free-site region and in the overlap region as a function of defect content.

b notation, one can see a trivacancy threading planes $z = 5, 7$, and 9 . At least two other trivacancies exist in planes $z = 7$ and 9 , together. This is a damage state made up of small clusters.

When N_F far exceeds N_{av} , in a large positive fluctuation transient state, the occurrence of compact defect-cluster forms is mandatory. These random-placement compact cluster forms are produced at an enormous cost in terms of disappointed Frenkel-pair candidates. Recall that 39 Frenkel-pair placements had to be generated in order to produce a field of 20 stable Frenkel pairs (Fig. 7) and that 256 Frenkel-pair placements had to be generated in order to produce a field of 40 stable Frenkel pairs (Fig. 9). The largest defect population recorded in the SIZ031 run was 60 defects. It was necessary to generate 62,697 Frenkel-pair placements to produce this field of stable defects. This corresponds to 63 displacements per crystallite atom.

A saturated damage state containing 68 vacancies and 68 interstitials was monitored in run SIZT07. This defect population is a positive fluctuation of 83% and is the most dense random-placement saturated damage state we have observed to date. Defect-spatial-distribution maps for this damage state appear in Fig. 10. Only 5% of the sites are in the free-site region, which consists of scattered individual sites and pairs of sites. The fraction of sites in the overlap region is 20%. The vacancy- and interstitial-cluster forms are far more compact than those shown in the 40-defect saturation state maps. The degree of

RUN SIZ031: $N_F = 40$, $N_{FP} = 256$

Fig. 9 Vacancy and interstitial distribution for a saturated damage state in the 1000-atom crystallite. This damage state contains 40 Frenkel pairs.

vacancy-cluster compactness is comparable to that in the center of a large displacement spike in alpha iron or copper (20 keV). Surprisingly the Frenkel-pair generation level required to obtain this highly saturated damage state was only 17,000 Frenkel pairs, i.e., 17 displacements per crystallite atom. The 17,000 level is in sharp contrast to the 62,969 production level required to produce a 60-defect saturated state in run SIZ031. This comparison helps to emphasize the vast differences that exist in "required" fluence to attain a specific local density. Fluence dependence, relative to damage-state characteristics at the submicroscopic level, is not a well-defined concept. With respect to void nucleation, differences of a factor of 3 to 4 in fluence are within the realm of normal fluctuation effects in a damage state either near to or at a saturated-state level.

The fraction of sites in the free-site region decreases rapidly, at first, with increasing irradiation time. A straight line through the first three points in Fig. 8, for example, extrapolates to zero free-region sites at $N_F = N_{av}$. The size of the overlap region increases monotonically with irradiation time. This circumstance leads to a more gently sloped high-fluence branch of the free-site-region fraction for $N_F > N_{av}$. The high-fluence branch appears to extrapolate to a zero free-site

RUN SIZTO7: $N_F = 68$, $N_{FP} = 17,000$

Fig. 10 A saturated damage state in the 1000-atom crystallite containing 68 Frenkel pairs.

region at $N_F = 2N_{av}$, thus allowing a positive fluctuation of 100%, in principle. In the limiting positive fluctuation case, the overlap region should comprise between 0.33 to 0.50 of the sites as N_F approaches $2N_{av}$.

A fundamental characteristic of a saturated primary damage state in a pure metal is that the defect spatial distribution for this state is not stationary in time. When we first paged through the chronological sequence of defect-distribution maps printed by the SIZMANN Program, we were surprised to note that significant changes occurred in the defect positions and defect-cluster positions. It seemed as if defect diffusion were taking place. These changes were caused, however, purely by the normal, routine random occurrences of defect-annihilation and defect-reconstruction events in a saturated primary damage state. The local regions of high defect density and of undefected crystal were observed to "move" about in a sinuous way, from map to map for a sequence of successive time increments. The movement image impression was similar to that given by the pattern of bright and dark patches in the light reflections from a body of water at night. The completely transient saturated-damage-state defect spatial distribution scans the entire crystal continually. In effect, therefore, it can seek out any heterogeneity that may be required to stabilize a fraction of the

compact vacancy clusters present in large positive fluctuation saturation damage states, and thus provide void nuclei on a purely fluctuation-effect basis.

This athermal mode for defect-spatial-distribution change operates in a saturated damage state at all temperatures. Its effect becomes superposed on truly thermally activated defect-spatial-distribution changes. Hence it is important to emphasize that the spatial distribution of defects in a saturated damage state or in a damage state in which the overlap region exceeds 5% of the crystal volume is not stationary in time, even at 0° K.

A hard precipitate particle can enhance void-nucleation contributions by the fluctuation mechanism by providing shielding-effect benefits. This was demonstrated by putting precipitate particles larger than the recombination-region volume in the 8000-atom crystallite and observing preferential formation of large, compact vacancy clusters (or interstitial clusters) at the precipitate-host interface. Although not explicitly simulated in the SIZMANN Program runs, the immediate presence of free metalloid atoms, which are ejected from the precipitate by neutron collisions, would furnish an external stabilizing agent. Precipitates containing boron, for example, would also furnish helium atoms to serve as internal stabilizing agents.

The SIZMANN Program runs were also made using a 57-site recombination-region volume in the 8000-atom crystallite, in addition to the 27-site recombination-region volume runs in this same crystallite. As expected, one result of increasing the recombination-region volume size was to increase the average separation distance between vacancy-concentration centers and interstitial-concentration centers. In addition, for a given irradiation time (fluence), the defect clusters produced were less compact in the 57-site recombination-region runs than those in the 27-site recombination-region runs.

ACCUMULATION OF DISPLACEMENT SPIKES

A displacement spike is the most simple defect entity produced by a collision cascade. The vacancy and interstitial defects that comprise the displacement spike generally experience significant interactions with one another and cannot be considered as being independent defects or simple defects in the initial stages of vacancy- and interstitial-cluster growth. The displacement spikes of interest here are those which can contain sizable vacancy clusters, i.e., displacement spikes produced by collision cascades which were initiated by primary knock-on atoms (PKA's) with energies in the keV range.

Simulation of collision cascades initiated by PKA's with energies above 100 to 200 eV is done using the branching sequence of binary collision-chains approximation rather than the fully dynamic, many-body method. The reason is entirely one of practicability; that is, the requirements for the iterative solution of over 30,000 simultaneous differential equations, which are needed to describe

a large cascade using the dynamic method, exceed the capability of current computers.

Cascade simulation proceeds by ejecting an atom from a normal lattice site and then following its sequence of collisions with other atoms in the crystal. The ejected atom is the cascade-initiating PKA. The collision sequence of the PKA is followed until its kinetic energy falls below the level that allows collisional mobility in the crystal. Concurrently the collision sequence of each secondary knock-on atom produced by the PKA collision sequence is also followed, as are the collision sequences of third, fourth, and higher order knock-on atoms. Any atom receiving a collisional transfer of kinetic energy larger than the cohesive energy per atom is given the chance to escape from the cage of neighboring atoms surrounding it. This provision allows the influence of the extant damage state on the production of new defects to be incorporated into the simulation. The extant damage-state record is continually revised to reflect the production of new defects and the annihilation of old defects. After its energy is exhausted, an energetic atom usually terminates its collision trajectory by becoming a "temporary" interstitial atom. In this status, it is examined for stability with respect to all vacancies in the extant damage state. If it is stable, a new interstitial is added to the record of interstitial defects in the extant damage state. Otherwise the "temporary" interstitial is removed from the defect record along with the vacancy with which it recombined. Each vacancy candidate is treated in a similar fashion. In these instances, defect stability is determined on the basis of a recombination region derived from a fully dynamic, many-body simulation of vacancy-interstitial recombination processes.

A complete description of the branching sequence of binary collision-chains approximation and the spatial distribution of defects produced in gamma iron, tungsten, and copper, on the basis of this approximation, has been published.¹¹

During the past year, Seidman et al.¹² have reported the results of an ion bombardment-field ion microscope study on the structure of displacement spikes in tungsten. Their results for 20-keV displacement spikes in tungsten can be compared with the computer-experiment-simulation results for 20-keV displacement spikes in tungsten which were published in 1966. The agreement is good. This agreement, in the case of tungsten, can be regarded as a basis for assuming that the computer-experiment results for alpha iron also are physically realistic. We now turn to an account of the primary damage state resulting from the accumulation of displacement spikes on the basis of collision-cascade simulations.

As suggested by the lower row of frames in Fig. 2, simulation of displacement-spike accumulation follows the same general pattern as the simulation of Frenkel-pair accumulation. A position r for PKA ejection would be selected at random, and a collision cascade would then be initiated by starting an atom on a collision trajectory from r along a random direction d . This would be done for several PKA's, one at a time. The energy of each PKA would be

selected from the PKA energy distribution determined by the particular type and energy spectrum of primary radiation concerned. The time interval between the initiation of successive cascades would be selected at random on the basis of the PKA production rate. In general, the PKA production rate will depend on the size of the irradiated specimen, the primary radiation energy distribution, and the primary radiation flux as a function of energy.

In the case of neutron primary radiation, displacement spikes in alpha iron should begin to overlap at a fluence of about 10^{21} neutrons/cm² ($E > 0.1$ MeV). The term "displacement-spike overlap" needs to be accurately defined in this context. What is meant, specifically, is that more than one collision cascade is initiated inside a region of 10^4 atomic volumes. The region size, 10^4 atomic volumes, is the average displacement-spike volume produced by 20-keV cascades in alpha iron. Below a fluence of 10^{21} neutrons/cm², the damage structure produced by each successive cascade will be nearly the same as that produced by an isolated cascade. Above this fluence, however, each successive cascade will probably overlap a region previously altered by one or more cascades, and it can produce a different damage structure than it would produce as an isolated cascade.

Cascade-Overlap Simulation Procedure

The structure of an isolated cascade and the way in which successive cascades were superposed are perhaps best described by an example. A map of the knock-on atom trajectories in a simulated 5-keV collision cascade appears in Fig. 11. The lines shown are the projections of three-dimensional trajectories onto a (001) plane. The short heavy line with the kink in the middle is the trajectory of the 5-keV PKA that initiated the cascade. Secondary knock-on atom trajectories are represented by heavy dotted lines emanating from the PKA trajectory line. Thereafter, alternately dashed and solid lines represent the trajectories of successively higher-order knock-on atoms.

Cascade overlap was simulated by first running an isolated cascade, as in Fig. 11, and then starting other cascades within the region traversed by the first cascade.¹³ This procedure is illustrated by Fig. 12, wherein a set of primary and secondary knock-on atom trajectories is shown for each of two different cascades. Third- and higher-order knock-on atom trajectories were omitted from the drawing to avoid confusion. The first (lower-lying) set of trajectories belongs to the cascade appearing in full development in Fig. 11. The second set of trajectories belongs to a cascade initiated by a second PKA with the same initial energy and direction as the first PKA but started from a lattice site displaced three lattice constants along the [010] direction from the first PKA starting position. Damage produced by the first cascade caused the difference between the first and second set of trajectories.

Fig. 11 Collision-cascade trajectory structure in alpha iron. The lines shown are projections of all knock-on atom trajectories in a 5-keV cascade onto a (001) plane. The marked (110) structure is typical of cascades in alpha iron. (Ref. 11, Fig. 1).

General Effects of Cascade Overlap

The effects of cascade overlap were studied by overlapping as many as four cascades. This was done for copper as well as for alpha iron. The cascade energies used ranged from 2.5 to 20 keV. The distance between starting points of successive initiating PKA's varied from zero to seven lattice constants, and the angular difference between their initial directions ranged from 0 to 90° in 30° steps. In addition to studying the overlap of cascades upon each other, the degree of overlap among the component branches of individual, isolated cascades was also studied.

Let $g(E)$ represent the number of displacements produced by a cascade initiated by a PKA with energy E . The average number of displacements produced per unit of PKA energy is

$$K(E) = g(E)/E \quad (2)$$

and is called the displacement efficiency of a cascade. The general effect of running a particular cascade C through a region already containing defects produced by previous cascades was to decrease the displacement efficiency of

Fig. 12 Interaction between two 5-keV cascades. Projections of the primary (heavy solid line) and secondary (dotted and dashed lines) knock-on atom trajectories in two interacting cascades are shown. The cascade associated with the lower-lying set of trajectories was run first and is shown in complete detail in Fig. 11. (Ref. 13, Fig. 3).

cascade C relative to that which it would exhibit in an initially perfect crystal. In addition, the size distribution of vacancy clusters appeared to be changed, relative to that for an isolated cascade, but the interstitial-atom-cluster distribution in the overlap runs did not differ significantly from that found in an isolated displacement spike produced by an isolated cascade.

Table 1 lists the displacement-production and displacement-efficiency results for each instance of threefold overlap of 2.5-keV cascades in alpha iron. The initiating PKA's were started off in the same direction from points one lattice constant apart along the [010] direction. In this particular set of runs, the displacement efficiency fell off by about a factor of 6 during the course of the three passes. On the average, for all 2.5-keV overlap cases simulated, the displacement efficiency of the second cascade was reduced by 30% and that of the third cascade by 70%. A maximum reduction of 90% was observed for the third cascade. Maps of the vacancy deployment in a (001)-slab section two lattice constants thick, after the first, second, and third passes of the 2.5-keV cascades concerned in Table 1, appear in Figs. 13 to 15. Although it may appear that the vacancy density increased with each pass, the vacancy density was

TABLE 1
DAMAGE PRODUCTIVITY OF OVERLAPPING
2.5-keV CASCADES IN GAMMA IRON

No. of cascades	Cumulative vacancies	Displacement efficiency	Displacement efficiency decrease, %
1	30	12.0	0
2	56	10.4	13
3	62	2.4	80

Fig. 13 Vacancy map for the first of three successive 2.5-keV cascades in alpha iron. (Ref. 13, Fig. 9a).

Fig. 14 Vacancy map for the second of three successive 2.5-keV cascades in alpha iron. Note the beginning of large cluster formation. (Ref. 13, Fig. 9b).

Fig. 15 Vacancy map for the final cascade in the three-pass sequence. A 20-vacancy cluster is formed. (Ref. 13, Fig. 9c).

actually constant because of a compensating increase in the cumulative-collided-atom volume¹¹ (the collective volume of atoms participating in collisions). Interstitials were omitted from these figures since their cluster-size distribution is not changed significantly by overlap activity. This sequence of maps illustrates the rearrangement of defects by cascade overlap. The trend occurring in this particular sequence is the formation of larger vacancy clusters than can be produced by an individual isolated 2.5-keV cascade. From the standpoint of visible void production, this overlap effect constitutes a mechanism for the creation of embryo void nuclei. Figure 16 shows a slab region two lattice constants thick through the central region of a three-pass overlap sequence of 5-keV cascades in copper. Interstitials are shown in this instance, being represented by the open circles.

Cascade overlap does not always lead to the formation of larger vacancy clusters.¹³ Rather, the frequency of instances in which a cascade passing through a previously damaged region will break up large clusters is the same as that of instances in which it produces large clusters. Cascade overlap disturbs the isolated displacement-spike cluster-size distribution by suppressing the relative numbers of vacancies contained in middle-sized clusters. Hence, at any given time of observation in a given local region, an overlap event will be observed to have either increased the relative number of single vacancies or the relative number of vacancies contained in large clusters, within that local region. A large cluster contains 10 or more vacancies.

The size of the largest vacancy cluster which is produced by cascade-overlap processes appears to be limited.¹³ The largest observed vacancy-cluster sizes observed in the overlap computer experiments for all PKA energies were comparable to those produced by the highest-energy isolated cascades, i.e., 20-keV cascades in alpha iron and copper. Normally the largest cluster produced

Fig. 16 Production of a 25-vacancy embryo void nucleus by the overlap of three 5-keV cascades in copper.

by a 20-keV cascade contained 20 to 25 vacancies. However, as many as three large clusters can occur in a single 20-keV displacement spike.

All other factors being constant, the displacement efficiency of the second of two overlapping cascades could usually be minimized either by making the energy of the second cascade-initiating PKA less than that of the first cascade-initiating PKA or by making the initial direction of the second PKA the same as that for the first PKA. The first effect is a containment effect; that is, the smaller cascade initiated by the lower-energy PKA will usually be contained within the damage region of a previous, larger cascade, initiated by a higher-energy PKA, whenever the lower-energy PKA is ejected from a site well

inside the larger cascade region. This containment effect is what causes the third cascade in an overlap sequence to suffer a much larger depression in displacement efficiency than the second cascade in the sequence.

The opportunities for destructive interference of damage in the first cascade displacement spike on damage production by the second cascade appear to be maximized when the second PKA is ejected in the same direction as the first PKA. A complete explanation of this effect is complicated, but the major factor is truncation of the replacement collision chains that normally carry interstitials away from the displacement collision site. This truncation is enhanced when the second PKA is ejected in the same direction as the first PKA.

Structure of the Displacement-Spike Accumulation in a Saturated Primary Damage State

As mentioned before, a displacement spike is the most simple independent defect produced by an isolated elastic collision cascade. Within a displacement spike, the defect density is saturated, at least this is the case in the computer-experiment results for alpha iron, copper, and tungsten. Field ion-microscope observations for tungsten also indicate that the defect density in a displacement spike is saturated.¹² This being the case, the average macroscopic defect density is increased only by a gradual enlargement of the specimen volume in which collision cascades have been initiated. Cascade overlap does not contribute to an increased local defect density, on the average, because the defect density produced by any isolated cascade is saturated. Rather, in the region of cascade overlap, the old damage distribution is partially annihilated, partially rearranged, and partially augmented by the production of new defects, by each successive cascade, but the local defect density remains unchanged at the saturated density level.

Cascade overlap does not change the interstitial-cluster-size distribution, relative to that produced by an isolated cascade. It also does not greatly increase the size of the largest possible vacancy cluster in the primary damage state produced by collision cascades. In a given local region, cascade overlap tends either to produce large vacancy clusters where the vacancy distribution previously consisted mainly of mono-, di-, and trivacancies or to produce a distribution of mono-, di-, and trivacancies where the vacancy distribution previously contained large clusters. Therefore the saturated primary damage state should consist of three qualitatively different types of local defect-structure regions:

1. An interstitial-chaff region populated predominantly with single interstitials.
2. A vacancy-chaff region populated predominantly with mono-, di-, and trivacancies.
3. A vacancy-cluster region populated predominantly with large vacancy clusters.

At finite temperatures, this structure is amended by the collection of interstitials from the interstitial-chaff regions into dislocation loops. If the temperature is sufficiently high, faceted void nuclei will form in the vacancy-cluster regions. At still higher temperatures, the void nuclei will grow by absorbing vacancies from the vacancy-chaff regions. The detailed quantitative aspects of the defect microstructure, such as void size, void-separation distances, dislocation-loop size, dislocation-loop-separation distances, and the formation of a defect-state lattice structure, depend on the temperature history, PKA energy spectrum, PKA production rates, defect sink structure, stress distributions, and impurity-atom stabilization activity. Computer experiments on these aspects of defect-state structure are discussed in the next section.

VOID NUCLEATION AND GROWTH IN A DISPLACEMENT-SPIKE DEFECT-DISTRIBUTION ENVIRONMENT

This section describes void nucleation in a displacement-spike defect distribution and the initial void-growth stage via the absorption of mobile vacancy configurations from this particular type of local defect-distribution environment. Void nucleation is described by the results of high-temperature displacement-spike-annealing simulations together with the results of vacancy-cluster-property simulations. Vacancy-cluster-property simulation results are considered first. After the discussion of high-temperature displacement-spike annealing, the computer-experiment results on void growth are described.

Vacancy-Cluster Properties

Johnson^{1,15} and Beeler^{14,15} made a systematic study of vacancy clusters in alpha iron which covered both the stable equilibrium configurations and the migratory behavior of vacancy clusters. All of the important low-energy metastable-cluster configuration states were covered as well. From this work, one can construct the complete relative stability hierarchy of vacancy-cluster shapes and sizes. One can also use their results to describe the small cluster forms which serve as dissociation units and those which serve as building modules both for large vacancy clusters and for faceted voids.

The lowest-energy divacancy configuration was found to be two vacancies at second-neighbor sites. The binding energy of this configuration is 0.20 eV. The lowest-energy trivacancy configuration is the isosceles-triangle arrangement shown in Fig. 17a. Its binding energy is 0.49 eV. This particular trivacancy configuration, denoted as $V_3(112)$, is especially important in the theory of void nucleation and growth because all tightly bound vacancy clusters are those which maximize the occurrence frequency of this module in their surface facets. In the notation $V_3(112)$, the numbers in parentheses are the three vacancy-vacancy neighbor distances concerned in the trivacancy structure. The most

Fig. 17 The most stable V_3 – V_6 configurations in alpha iron.

Fig. 18 The compact V_{15} void in alpha iron.

stable configurations for V_4 , V_5 , and V_6 are shown in Figs. 17b to 17d, respectively. The progression from V_2 to V_6 is important in void nucleation from an environment comprised mostly of monovacancies.

The most stable V_6 form is the octahedral void shown in Fig. 17d. The next largest octahedral void is V_{19} . Except for V_{15} , the most stable form for vacancy clusters containing 7 to 18 vacancies is a double-layer (110) platelet. The stable V_{15} configuration in Fig. 18 exhibits 12 equilateral parallelogram (110) facets. The binding energy and binding energy per added vacancy are given in Fig. 19 for each stable vacancy-cluster form in alpha iron. The compact void and the double-layer (110) platelet possess nearly the same stability. The dissociation energies for the most stable vacancy-cluster configurations are listed in Table 2.

The migration energies for the monovacancy, divacancy, and trivacancy were found to be 0.68, 0.66, and 0.66 eV, respectively. In effect, therefore, all of these mobile forms have the same migration energy. All vacancy clusters larger than V_3 can be regarded as being immobile in alpha iron.

Fig. 19 Binding energies of the most stable vacancy-cluster shapes in alpha iron as a function of the number of vacancies in the cluster.

Collision cascades produce irregularly shaped vacancy clusters, as is illustrated in Figs. 13 to 16. Activation-energy calculations for the rearrangement of individual vacancies in the type of irregular cluster directly produced by a collision cascade showed a range of low activation energies. Activation energies for a vacancy movement which immediately increased the number of $V_3(112)$ triads ranged from 0.23 to 0.53 eV. Activation energies less than 0.34 eV were not observed, however, until extensive (110) faceting had developed, i.e., until a void of size V_{15} or larger was involved. Expressed as a fraction of the monovacancy-migration energy, E_{1V}^M , in bulk material, one has $0.23 \text{ eV} = 0.34E_{1V}^M$ and $0.53 \text{ eV} = 0.7E_{1V}^M$. The activation-energy range for vacancy rearrangement in an irregular cluster lies below the vacancy-migration energy of 0.58 eV in a flat (110) free surface (see Fig. 27).

TABLE 2
VACANCY-CLUSTER DISSOCIATION
ENERGIES IN ALPHA IRON

Process	Dissociation energy, eV
$V_2(2)$ to $(V_1 + V_1)$	0.88
$V_3(112)$ to $(V_2(2) + V_1)$	0.97
$V_4(111122)$ to $(V_3(112) + V_1)$	1.21
$V_6(\text{compact})$ to $V_5(\text{compact}) + V_1$	1.46
$V_n(\text{compact})$ to $V_{n-1}(\text{compact}) + V_1$	1.47

In combination, the vacancy-cluster binding-energy results in Fig. 19 and the vacancy-cluster dissociation-energy results in Table 2 indicate that the octahedral V_6 vacancy cluster is the smallest void nucleus from the standpoint of thermal stability. The low range of activation energies, pertinent to the conversion of an irregular cluster form into a stable (110)-faceted void nucleus, indicates that faceted void nucleation depends only on the prior production of irregular vacancy clusters containing six or more vacancies and a sufficiently high temperature to activate vacancy-rearrangement activity. At temperatures between $0.25T_m$ and $0.40T_m$, the vacancy-jump frequencies in the irregular clusters produced by cascades are comparable to the monovacancy-jump frequency in bulk alpha iron at a temperature of $T_m/2$. This indicates that void nucleation should occur at a temperature in the neighborhood of $T_m/3$. Here, T_m is the melting temperature.

Displacement-Spike Annealing

Short-term annealing of displacement spikes was simulated initially by Beeler¹¹ and Besco⁷ using the low-temperature version of the ANNEAL Program described by the flow chart in Fig. 20. In this work, only the effects of interstitial migration were simulated. Doran¹⁶ subsequently extended the capability of the ANNEAL Program and did simulations of high-temperature displacement-spike annealing wherein both vacancies and interstitials migrated during the annealing process. Doran also did low-temperature-annealing simulations (immobile vacancies) for longer annealing times than were used in the earlier work. We will therefore base the discussion of displacement-spike annealing on Doran's results.

Doran's high-temperature simulations were performed at 800°K and his low-temperature simulations at 300°K . The 31-site Erginsoy-Vineyard recombination region was used at 300°K . In the high-temperature-annealing simulations, Doran adopted a 63-site recombination region. This augmentation of the Erginsoy-Vineyard recombination region was suggested by Beeler's¹¹ dynami-

Fig. 20 Schematic flow diagram for the ANNEAL Program used to simulate displacement-spike annealing.

cal-method simulations of thermally activated Frenkel-pair recombination in alpha iron. The 32 sites added to the low-temperature recombination region consisted of the 24 fourth neighbors of the central site and the eight seventeenth neighbors lying on $\langle 111 \rangle$ lines through the central site.

The central portion of a 20-keV displacement spike in alpha iron, as produced by the associated collision cascade, appears in Fig. 21. The defect distribution in the same region after short-term annealing at 800°K is shown in Fig. 22. The defect distribution in the same region which resulted when the same initial displacement-spike defect distribution was annealed at 300°K is shown in Fig. 23. These visual representations of high-temperature-annealing and low-temperature-annealing results are supplemented by the tabulated data of average results over nine 20-keV displacement spikes and eight 5-keV displacement spikes in Table 3 for interstitials, and in Table 4 for vacancies.

Comparison of Doran's low- and high-temperature displacement-spike-annealing results contributes to the explanation of the temperature dependence of visible void production during neutron irradiation, i.e., the absence of visible voids during low-temperature irradiation. According to Table 4, there are an order of magnitude more irregular vacancy clusters in the size range necessary

Fig. 21 Vacancies and interstitials in the central 11 (001) planes of a 20-keV displacement spike in alpha iron. This is the initial defect distribution prior to annealing. (Ref. 16, Fig. 9).

for conversion into faceted-void nuclei after high-temperature annealing than after low-temperature annealing. During low-temperature annealing, any large vacancy cluster initially present is subjected to attrition by the impingement of mobile interstitials during the entire annealing process. Since there is no vacancy migration, this attrition cannot be compensated for by the impingement of mobile vacancies. The fraction of mobile interstitials remaining after short-term annealing is sufficient to reduce the remaining vacancy clusters to a size insufficient to serve as void nuclei. Hence the picture for low-temperature annealing is continual attrition of any large vacancy clusters, initially present in the primary damage state, by impingement of mobile interstitials.

In contrast, an increase in the number of large vacancy clusters actually occurs during high-temperature annealing, even though the total vacancy population is reduced by a factor of 5 by annihilation events. Large clusters suffer attrition during high-temperature annealing, and it is possible for some of them to be removed. However, because vacancy migration occurs during high-temperature annealing, it is possible for the attrition of large clusters to be repaired by the impingement of mobile vacancies and this does, in fact, occur. However, this is not the only factor that leads to the presence of large vacancy

Fig. 22 Defect distribution formed by high-temperature annealing of the distribution in Fig. 21. Annealing time consisted of 6000 interstitial and 1260 vacancy time steps. (Ref. 16, Fig. 12).

clusters after high-temperature annealing. In addition, *new* large vacancy clusters were observed to be built up during high-temperature annealing via homogeneous nucleation within the displacement spike. This occurrence of homogeneous nucleation of new large vacancy clusters is an important point. As Doran points out, "... of the four $V_{\geq 10}$ clusters originally present in the 20-keV spikes, two survived annealing as $V_{\geq 10}$ clusters and two as $V_{\geq 7}$ clusters. Three other $V_{\geq 10}$ clusters were produced by agglomeration of small clusters."

The nature of this homogeneous component of void nucleation in a displacement-spike defect distribution is the agglomeration of small vacancy cluster units, which usually experience significant strain-field interactions among themselves, rather than the agglomeration of independent monovacancy units. Figure 24 is a schematic description of the "before" (top part) and "after" (bottom part) vacancy-cluster arrangements in the type of nucleation concerned here. (For the moment, ignore the three parallel dashed lines in the lower part of the figure.) The ordinary homogeneous nucleation theory developed to describe the aggregation of independent single atoms or point defects to a central cluster cannot be applied to the present case without extensive modification. Void nucleation within a spike is, to a significant degree, a mechanical snap-in process, and it is not clear that a diffusion model for void nucleation is a good basis for describing nucleation events that evince this strong mechanical attribute.

Fig. 23 Defect distribution formed by low-temperature annealing of the distribution in Fig. 21. (Ref. 16, Fig. 23).

Doran¹⁷ has also demonstrated that void nucleation is more easily accomplished when a displacement-spike defect distribution is annealed than when a distribution of randomly positioned defects with the same average density is annealed. This important result clearly shows that the displacement-spike defect distribution is the naturally occurring damage distribution in which homogeneous nucleation of voids occurs at the greatest rate.

Void Growth

As demonstrated in the preceding sections, the fluctuation effect provides a mechanism for transient void growth in an irradiated material. In this subsection, void growth by correlated defect migration mechanisms is discussed. The physical point of interest is the collection of small mobile vacancy clusters by a faceted void nucleus in such a way that more vacancies are collected than interstitials.

The three mobile vacancy configurations in alpha iron are V_1 , V_2 , and V_3 . Divacancy and trivacancy migration rivals monovacancy migration as a means for vacancy transport to a growing void. This follows immediately from the fact that they are stable clusters and that their migration energy is slightly lower than that

TABLE 3

DISTRIBUTION OF INTERSTITIALS IN CLUSTERS AFTER HIGH- AND LOW-TEMPERATURE-SIMULATED IRRADIATIONS

n	Average number of I _n clusters per spike			Number of interstitials in I _n as fraction of:				
	0° K	High temp.	Low temp.	Initial total number†			Final total number	
				0° K	High temp.	Low temp.	High temp.	Low temp.
20 keV								
1	184	13.2	17.0	0.93	0.065	0.087	0.31	0.18
2	6.56	2.9	1.3	0.066	0.029	0.013	0.14	0.027
3	0.22	4.1	9.1	0.003	0.061	0.14	0.29	0.28
4	0	1.7	6.7	0	0.034	0.14	0.16	0.28
5	0.11	0.56	2.3	0.003	0.014	0.058	0.066	0.12
6	0	0.22	1.3	0	0.007	0.040	0.032	0.081
7	0	0	0.44	0	0	0.016	0	0.032
≥3	0.33	6.6‡	19.8	0.006	0.12‡	0.39	0.55	0.79
5 keV								
1	52.5	5.4	6.8	0.93	0.090	0.12	0.43	0.27
2	2.1	0.62	0.62	0.074	0.021	0.022	0.10	0.050
3	0	1.5	2.8	0	0.076	0.12	0.36	0.33
4	0	0.4	1.0	0	0.025	0.071	0.12	0.16
5	0	0	0.25	0	0	0.022	0	0.050
6	0	0	0.38	0	0	0.040	0	0.091
7	0	0	0	0	0	0	0	0
8	0	0	0.12	0	0	0.018	0	0.040
≥3	0	1.9	4.6	0	0.10	0.30	0.48	0.67

†Initial number of interstitials was 198 and 57 for 20- and 5-keV spikes, respectively.

‡Presumably somewhat low; estimate that better values are 7, 0.13, and 0.60.

for the monovacancy. Figure 25 shows the activation energies associated with changes in divacancy configurations pertinent to divacancy transport. Table 5 gives similar information for trivacancies. The first stage in void growth is characterized by these activation energies as well as that for monovacancy migration. When divacancies and trivacancies encounter the third interior plane from a (110) void facet, their binding energies begin to diminish. This diminution continues in a progressively enhanced manner all the way to the void surface. As a consequence, these clusters tend to become somewhat like weakly bound single vacancy collections as they start to be absorbed into the void. This affords a structural flexibility which aids in rapid assimilation of vacancies by the void and in the avoidance of awkward high-energy peripheral vacancy configurations that might act as barriers to void growth. The three dashed lines in the lower part of Fig. 24 are intended to represent the extent of this influence

TABLE 4
DISTRIBUTION OF VACANCIES IN CLUSTERS AFTER HIGH- AND
LOW-TEMPERATURE-SIMULATED IRRADIATIONS

n	Average number of V_n clusters per spike			Beeler‡	Number of vacancies in V_n as fraction of:				
	0° K	High temp.	Low temp.		Initial total number†		Final total number		
					0° K	High temp.	Low temp.	High temp.	Low temp.
20 keV									
1	71	14.8	40.9	0.351	0.36	0.076	0.21	0.36	0.43
2	19	0.22	11.9	0.203	0.19	0.002	0.12	0.01	0.25
3	8.4	0	5.6	0.131	0.13	0	0.083	0	0.17
4-6	9.3	1.9	2.8	0.203	0.22	0.046	0.063	0.22	0.13
7-9	1.9	1.1	0	0.070	0.075	0.044	0	0.21	0
≥10	0.4	0.7	0.11	0.042	0.037	0.042	0.01	0.20	0.02
≥7	2.3	1.8	0.11	0.112	0.112	0.086	0.01	0.41	0.02
≥4	11.6	3.7	2.91	0.315	0.332	0.132	0.073	0.63	0.15
5 keV									
1	18.0	5.0	9.9	0.336	0.32	0.089	0.18	0.43	0.41
2	5.1	0.12	2.9	0.191	0.19	0.004	0.10	0.02	0.24
3	3.0	0	1.2	0.145	0.16	0	0.067	0	0.16
4-6	2.6	0.50	0.88	0.244	0.22	0.047	0.081	0.22	0.19
7-9	0.50	0.38	0	0.057	0.071	0.049	0	0.23	0
≥10	0.12	0.12	0	0.055	0.033	0.022	0	0.11	0
≥7	0.62	0.50	0	0.112	0.104	0.071	0	0.34	0
≥4	3.22	1.00	0.88	0.356	0.324	0.118	0.081	0.56	0.19

†Initial number of vacancies was 198 and 57 for 20- and 5-keV spikes, respectively.

‡See Ref. 1.

beyond one of the void facets appearing in the schematic representation of void growth. A detailed description of vacancy-migration energies during the approach to a (110) facet along $\langle 111 \rangle$ directions¹⁸ is given in Fig. 26. Interplane and intraplane migration energies near a (110) facet¹⁸ are shown in Fig. 27. Similar data have been computed for (100), (112), and (111) void facets for use in simulating void growth.¹⁹

Full utilization of the detailed, self-consistent set of data for vacancy migration in the immediate vicinity of a void has not yet been possible. In addition to the treatment of vacancy transport to void nuclei, a full-scale simulation of void growth must also treat the transport of vacancies to interstitial clusters, in the point defect form, and to interstitial dislocation loops. Migration-energy data for these cases is not yet available. In addition to this, data are also needed on the details of interstitial migration in the vicinity of

Fig. 24 Schematic representation of vacancy distribution before (top part) and after (bottom part) void nucleation.

interstitial point defect clusters and in the vicinity of interstitial dislocation loops. For the above reasons, all void-growth simulations have concerned vacancy-vacancy interactions only and are therefore restricted to the early stage of void growth. The method used to simulate void growth will be discussed later.

Split interstitials were not strongly attracted to faceted voids in computer experiments on interstitial-void interactions.¹⁸ In fact, a $[110]$ split interstitial was able to reside closer to a void facet, without spontaneous recombination occurring, than to a monovacancy. Figure 28 shows a $[110]$ split-interstitial sitting two interatomic distances from a (110) void facet, measuring along a $\langle 111 \rangle$ line from the interstitial center to the void surface. Stability occurs because of a sizable relaxation adjustment at the surface atom plane. The two surface bumps that arise from this type of positioning are believed to give rise to a portion of the double spot contrast seen in the field ion microscope. The interstitial will not necessarily move into the void from the position shown in Fig. 28. Rather, it can rotate into an orientation parallel to the void surface in

Fig. 26 Migration-energy profile for vacancy migration between a (110) free surface and interior (110) planes inside the crystal for alpha iron.

Fig. 27 Vacancy-migration energies near a (110) free surface in alpha iron.

void facet (see Figs. 25 and 24). The probability that any vacancy moving into this volume will be captured by the void is greater than 0.5. The capture volume for interstitials includes all sites contained locally on interior planes 1 and 2 at each (110) void facet (see Figs. 28 and 24). Voids grow initially in a displacement-spike defect-distribution environment because: (1) The vacancy concentration near a void nucleus is larger than the interstitial concentration.

Fig. 28 Accommodation of the (110) split-interstitial strain field by a (110) free surface in alpha iron.

This is due, fundamentally, to the dynamic separation of interstitials from vacancy-concentration centers via collision chains during displacement-spike production. (2) The vacancy-capture volume is larger than the interstitial-capture volume. (3) Interstitial clusters transform to a dislocation-loop configuration early in the annealing process. Discussion of this point follows in the next subsection.

Interstitial Clusters and Loops

The most stable self-interstitial configuration in alpha iron is the [110] split-interstitial configuration.¹ The bow-tie-shaped arrangement of the 10 core atoms (filled circles) in the strain field of the [110] split interstitial¹⁴ appears in Fig. 29. The [110] line joining the two center atoms in the core defines the orientation of the split interstitial. It is said to be positioned on the lattice site (open circle) which these two center atoms straddle. This core involves 10 atoms and the immediately nearby *nine* lattice sites. As long as this core structure can retain its identity, the [110] split interstitial is defined. The strains along the (111) dashed lines of atoms are very large, and hence two interstitials do not attract or approach each other with their cores situated in the same (110) plane.

TABLE 6

VOLUMES, BASE DIMENSIONS, AND APPROXIMATE VACANCY- AND INTERSTITIAL-CAPTURE VOLUMES OF SMALL OCTAHEDRAL VOIDS IN A BCC CRYSTAL

No. of vacancies	Base dimension, Å	Volume, at. vol. units			Vacancy-capture volume/octahedral-capture volume	Vacancy-capture volume/interstitial-capture volume
		Octahedral	Vacancy capture	Interstitial capture		
2	2.87	6	127	66	21.2	1.92
3	5.73	19	187	102	9.84	1.83
4	8.60	44	259	146	5.89	1.77
5	11.46	85	343	198	4.04	1.73
6	14.33	146	439	258	3.01	1.70
7	17.20	231	547	326	2.37	1.68
8	20.06	344	667	402	1.94	1.66
9	22.93	489	799	486	1.63	1.64
10	25.79	670	943	578	1.41	1.63
11	28.66	891	1099		1.23	
12	31.53	1156	1267		1.10	
13	34.39	1469	1447		0.98

INTERSTITIAL CONFIGURATION

Fig. 29 The 10-atom core of a $\langle 110 \rangle$ split interstitial in alpha iron (filled circles). Open circles denote normal lattice sites.

They can approach each other easily, however, in a sidewise posture wherein their core-structure planes adopt a parallel but not coplanar stance, with their centers situated on neighboring sites in $\langle 111 \rangle$ lines. The binding energy of such clusters is 1.08 eV per interstitial. Platelet clusters form from the juxtaposition of alternate $\langle 111 \rangle$ cluster lines.

Perrin and Bullough²⁰ showed that clusters of $[110]$ interstitials, in the form of aggregated, identifiable point defects, transform to a dislocation-loop form when the cluster population reaches 16 interstitials. The loop lies in a $\{111\}$ plane. Hence simulations of interstitial-cluster properties indicate that the cluster forms are planar and that they transform to a dislocation-loop nature very early in their growth history, i.e., at a population of 16 interstitials.

IMPURITY-ATOM EFFECTS

Interstitial Impurities

The first computer experiments on impurity-atom effects pertinent to this discussion were performed by Johnson²¹⁻²³ for carbon in alpha iron and martensite. He found that carbon formed bound complexes with both vacancies and interstitials in alpha iron. The carbon-vacancy and carbon-interstitial complexes are described in Figs. 30 and 31, respectively. In an extension²⁴ of Johnson's work, we have found that the most strongly bound carbon-point

Fig. 30 The most stable carbon-vacancy configuration in alpha iron.

Fig. 31 The most stable carbon-split interstitial configuration in alpha iron.

TABLE 7
BINDING ENERGIES FOR THE FUNDAMENTAL
CARBON-POINT DEFECT COMPLEXES IN
ALPHA IRON

Complex	Binding energy, eV
C-V ₁	0.42
C-V ₂ (2)	0.62
nC-V ₂ (2)	n(0.62)*
C-I ₁	0.56
2C-I ₁	0.76

*n = 1, 2, . . . , 10.

defect binary complex in alpha iron is the C-V₂ complex. The binding energies found for the fundamental carbon-point defect complexes in alpha iron are listed in Table 7. The large capacity of V₂(2) for carbon-atom attachments, indicated in Table 7, constitutes a possibly important trapping mode not previously reported. In addition, we found that C-V₂(1) was the most strongly bound carbon-point defect binary complex in nickel. It was possible for V₂(1) to capture two carbon atoms in nickel, but attachment of more than two carbon atoms was not possible. The [100] split interstitial in nickel could collect as many as four carbon atoms without any decrease in the binding energy per carbon atom. Thus multiple carbon attachment occurs at the [100] split interstitial in an fcc metal but at the V₂(2) in a bcc metal.

As is well known, impurity-atom complexes tend to inhibit vacancy migration²⁵ and hence void growth. A related feature of carbon-vacancy and

carbon–interstitial complexes is their effect of depressing the vacancy–interstitial annihilation rate. In cubic metals, vacancy–interstitial annihilation proceeds by the split interstitial dissociating and inducing a relaxation of the close-packed atom line segment between the interstitial center and the vacancy, into a perfect crystal configuration. This relaxation process is strongly inhibited for those particular close-packed lines which approach the V_1 –C complex from the carbon side of the configuration. This effect has been demonstrated in fully dynamic computer-experiment simulations.^{2,6} Interstitial–carbon complex for-

Fig. 32 The most stable carbon–atom position near a (110) free surface in alpha iron.

mation at least raises the activation energy required for thermally induced defect annihilation. In fcc metals, multiple carbon attachment to an interstitial would preclude interstitial motion.

These features of impurity atom–point defect complexes indicate qualitatively different trapping effect consequences in bcc and fcc metals. If multiple carbon attachment to $V_2(2)$ occurs in real bcc metals, then the presence of an interstitial impurity could impede void growth. On the other hand, multiple attachment to interstitials in fcc metals would enhance void growth.

Computer experiments indicate that a carbon atom near a free surface (void facet) seeks to position itself between the free-surface atom plane and the immediately interior atom plane parallel to the free surface. The most stable carbon position near a (110)-void facet is shown in Fig. 32. It turns out that the natural starting point for explaining the behavior of carbon at a free surface in alpha iron is a look at the salient features of the octahedral carbon defect in bulk alpha iron. This is true because only short-range interactions are involved in the model and because the carbon–metal interaction dominates the metal–metal

interaction. Consequently adjustments of the positions of the six metal atoms nearest the carbon atom, in response to the free-surface perturbation, principally determine the character of stable carbon-cluster configurations near free surfaces. Table 8 contains the pertinent information required. The tetragonal distance, D_T , and the ring distance, D_R , are defined in Fig. 33. The ring distance in bulk alpha iron is 1.94 Å. This separation distance gives maximum bonding between a carbon atom and an iron atom. The tetragonal distance in bulk alpha iron is 1.75 Å.

TABLE 8
CHARACTERISTICS OF THE
OCTAHEDRAL CARBON DEFECT IN
ALPHA IRON*

Energy of the carbon atom, eV	-1.842
Configuration energy of the defect, eV	-1.31
Tetragonal distance, Å	1.75
Ring distance, Å	1.94
Tetragonal strain, hlc†	0.22
Ring strain, hlc	0.06

*Johnson's^{1,2,1} potential functions were used in computing these results.

†Half-lattice constant.

For both (110) and (100) free surfaces, the lowest-energy carbon-cluster configuration was observed to be one in which the ring distance was least disturbed while, at the same time, the tetragonal distance was lengthened toward 1.94 Å. In addition, the lowest-energy configuration also tended to be that for which the displacement vectors of the surface atoms concerned were normal to the free surface. The most stable carbon-cluster configurations were lineal strings with a binding energy of 0.42 eV per carbon atom and single-layer platelets with a binding energy of 0.48 eV per carbon atom. These binding energies apply to clusters containing four or more carbon atoms. In the model used,^{2,1} the carbon-atom migration energy in bulk alpha iron is 0.86 eV. Hence the dissociation energy for the stable carbon-cluster forms at a free surface is about 1.35 eV.

Each stable n -atom cluster of carbon atoms at a free surface (void facet) projects a compression strain field into the host crystal. This strain field opposes the migration of split interstitials toward a void. This serves to inhibit void-nucleus attrition due to impingement of mobile interstitials. The binding energy per carbon atom in a platelet at a (110) void facet exceeds that for the most stable carbon-cluster configuration in bulk alpha iron. Johnson^{2,3} found a binding energy of 0.31 eV per carbon atom for carbon clusters in bulk alpha iron.

Fig. 33 Strain-field geometry for octahedral carbon in bulk alpha iron. D_T and D_R are the tetragonal and ring distances, respectively.

Substitutional Impurities

Preliminary work has been done on vacancy interactions with substitutional impurities on a strictly size-effect basis. Artificial impurity metals were constructed with the same elastic constants and cohesive energy as alpha iron but with a different lattice constant. A 10%-oversize and a 10%-undersize impurity were considered. Both impurities impeded vacancy migration because the migration energy associated with simple migration jump-sequence patterns was as much as 0.2 eV larger than the vacancy-migration energy. The binding energies for the impurity atom-vacancy complex were both about 0.1 eV. The large impurity formed a first-neighbor complex with the vacancy, and the small impurity formed a second-neighbor complex with the vacancy.

A result from our computer experiments on alloy properties is of interest regarding void attrition. One class of substitutional metallic impurity was found

which preferred to situate itself *inside* the void rather than at the void surface. This class of substitutional impurity was one which formed a weak intermetallic compound with the host metal wherein the first-neighbor ordering energy was positive (ordering tendency) but the second-neighbor ordering energy was negative (segregation tendency).

VOID DISSOCIATION

As mentioned previously, there are not yet sufficient migration-energy data on vacancy migration in the vicinity of interstitial-cluster forms to simulate vacancy migration properly near these particular sinks. Thus void-growth and -dissociation simulations were performed on the basis of vacancy-vacancy interactions only.

When a vacancy cluster is not a regular faceted void, there are complications in specifying the vacancy-migration energy in the irregular regions. These complications arise because the number of possible defect states is too large to handle in a precomputed migration-energy scheme such as that used in the ANNEAL Program. We found that a modification of the DIFFUSION Program,^{2,7} developed for nucleation and growth studies in binary alloys, provided a solution to this problem. In this program, an unrelaxed crystal-migration energy for an atom positioned near (first neighbor) a vacancy is computed by counting the number of bonds broken when the atom is extracted from its prejump position and the number of saddle point bonds formed when this atom is relocated at the saddle point for motion into the adjacent vacancy. This unrelaxed model activation energy is then corrected for relaxation effects by using a precomputed relaxation factor that is a slowly varying function of defect-arrangement geometry. A detailed description of this method, for alloy computations, has been published elsewhere.^{2,7}

Void Growth

The ANNEAL Program does not contain a sufficiently detailed vacancy-clustering model to simulate all details of conversion from irregular vacancy clusters to faceted vacancy-cluster forms. Hence a separate simulation of this process was needed. The description of void growth given earlier was, in part, based on simulations performed using the modified DIFFUSION Program model described above.

Void Dissociation

The void-dissociation simulations were restricted to two dimensions, but the two sublattice aspect of the bcc crystal was retained. These two-dimensional simulations are preliminary studies.

In these simulations, voids tended to dissociate by way of unzipping activity at their corners. Single vacancy excursions usually were retracted and did not serve as major contributors to void disintegration. Correlated jumps of two or more vacancies at corners, however, started irreversible dissociation of a void. The following brief example is interesting in this regard.

The initial organization of a perfect faceted void is shown in Fig. 34. Each vacancy is numbered to aid in following the local vacancy movements involved in the dissociation process. The notation $TS = 0$ indicates time step zero in the simulation. The only vacancies that are eligible for migration jumps in this configuration are the corner vacancies V1, V11, V15, and V25. Each has a jump probability of 0.07 per time step.

Unzipping started with the correlated movement of two vacancies V24 and V25 along the lower right side of the void, as shown in Fig. 35. This event established a notch in the side of the void. Prior to notch formation, only four vacancies, as specified above, were eligible for migration jumps. After notch formation, V22 and V24 also become eligible for migration jumps. During $TS = 17$, the notch turned the corner and moved to the lower left side of the void (Fig. 36), and V23 replaced V25 as the "outside" vacancy. During $TS = 18$ (Fig. 37), V16 moved outside the void and set up a double notch. At a lower temperature, both V16 and V23 would be pulled back into the void as the result of a highly anisotropic jump-direction distribution, biased in favor of jumps toward the void. But, as it stands in this figure, V16 is nearly free of void influence on its jump-direction distribution at the dissociation temperature.

After $TS = 27$, three of the void sides contained notches, as illustrated in Fig. 38. What is happening as time passes is a progressive sloughing of vacancies from each side of the void. This occurs by one or two atoms running up and down each void wall as a consequence of notch formation. The dashed lines show where the old perfect void walls were positioned. This figure, together with Fig. 39, shows that the void is being converted into elongated clusters by the mechanism described above. These elongated clusters, in turn, break up into stringy clusters. By $TS = 68$ the void had disintegrated into a relatively compact V_9 , in the upper left region of the field, a V_5 string, two V_3 strings, and five monovacancies. The remaining compact remnant will also dissociate via the notch process. An examination of the numbers in Fig. 40, for $TS = 68$, shows that an extensive reorganization of vacancy-neighbor relations has occurred during dissociation.

RADIATION ATTRITION OF VOID NUCLEI

In the section titled "Vacancy-Cluster Properties," the octahedral V_6 vacancy-cluster configuration was specified as the smallest faceted void nucleus from the standpoint of thermal stability.

Fig. 34 Initial organization of a perfect 25-vacancy void.

Fig. 35 Beginning of the unzipping process via correlated movement of V24 and V25. Notch formation.

Fig. 36 Notch movement.

Fig. 37 Double notch formation.

A void nucleus in a radiation environment must also be stable against radiation attrition. This effect, wherein stray defects or collision events degrade a void nucleus, is analogous to the resolution of fission-gas atoms by radiation mechanisms from a gas bubble in fuel material. One extreme form of radiation attrition comes about from the random generation of Frenkel pairs. The opposite extreme form is, of course, cascade overlap. In the case of cascade overlap, the void nucleus must be comparable in size to the largest vacancy cluster the cascade can produce. In alpha iron, this size is about V_{25} (see section titled "General Effects of Cascade Overlap").

Fig. 38 Extensive notch formation. Vacancies are being sloughed from each side of the void.

Fig. 39 Notch mechanism converts the void into elongated clusters.

If the neutron-energy spectrum contains a sizable low-energy component, it is possible for the total production of vacancy and interstitial chaff to rival the displacement production of displacement spikes containing large vacancy clusters. When this is the case, the immunity of faceted-void nuclei to chaff radiation attrition must be considered in visible void-production estimates.

Our initial simulations of faceted-void radiation attrition by chaff damage in alpha iron indicate that V_6 nuclei would be removed by a chaff-damage accumulation of less than 25% of that required to give a saturated damage state. A V_{19} void nucleus would be reduced to a linear V_8 cluster by a chaff-damage accumulation of 38% of that required to give a saturated damage state.

Fig. 40 Disintegrated void.

Doran's high-temperature-annealing results¹⁶ show that, in many respects, displacement spikes produced by PKA with energies less than 5 keV can be regarded as sources of chaff defects. This feature, coupled with the radiation-attrition-simulation results, provides another strong indication that the standard flux- and fluence-dependence models for the production of visible voids may be oversimplified. In this regard, the recent excellent reviews on void production by Bloom,²⁸ for austenitic stainless steel, and by Packan,²⁹ for aluminum, contain highly pertinent material.

SEGREGATION OF VACANCIES AND INTERSTITIALS

Computer-experiment results which are pertinent to the question of how vacancies and interstitials segregate in a radiation environment and remain segregated are collected in this section.

Initially, the segregation of vacancies and interstitials in a primary damage state is a direct consequence of the fact that focused collision chains can occur in a crystal. This was demonstrated in the classic computer experiments of Gibson et al.³ The persistence of vacancy and interstitial segregation in a primary damage state is a consequence of the fact that a minimal finite region exists at 0°K within which a vacancy and an interstitial cannot coexist. This minimal region is called the spontaneous recombination region, or spontaneous annihilation region.

Persistent vacancy-interstitial segregation at finite temperatures can be explained on the basis of the two types of defects exhibiting (1) different clustering behavior, (2) different migration behavior, (3) different homogeneous and heterogeneous interaction ranges, and (4) different terminal-state behavior when absorbed at sinks.

According to the computer experiments of Perrin and Bullough,²⁰ interstitial clustering in alpha iron occurs in a platelet form, and these platelets transform into a dislocation-loop configuration when 16 interstitials have been collected. Thus interstitials in alpha iron do not form clusters of *identifiable* point defects larger than I_{16} , according to their results. Interstitial clusters of this size are produced directly in individual Frenkel-pair-accumulation primary damage states, and hence interstitial loops should form spontaneously in such damage states. In contrast, no interstitial cluster larger than I_3 is formed directly in most displacement spikes. Hence interstitial migration is required to form interstitial loops in a displacement-spike-defect distribution.

Large vacancy clusters are formed directly in both the individual Frenkel-pair-accumulation and displacement-spike primary damage states. Computer-experiment simulations for alpha iron indicate that vacancy clusters do not collapse into dislocation loops.¹⁵ Rather, they adopt either a double-layer (110) platelet or a compact faceted-void configuration. These forms are not produced in the primary damage state but evolve from the conversion of irregular large clusters, via correlated vacancy-rearrangement jump sequences, at temperatures above $T_m/3$.

Vacancy transport always proceeds via three-dimensional diffusion of V_1 , V_2 , and V_3 configurations. Void growth occurs on this basis during the later stages.

Interstitial transport, in the aggregation process, can proceed according to either of two distinctly different mechanisms. Accumulation of I_1 and I_2 configurations at interstitial point defect-type clusters and at interstitial dislocation loops occurs by three-dimensional diffusion. Aggregation of intersti-

tial dislocation loops, however, would tend to follow a one-dimensional glide-transport mode and to involve mechanical-driving forces.

Interstitials, as point defects, are not strongly attracted to a faceted void. This contributes to the result that the capture volume for interstitials around a (110)-faceted void is significantly smaller than the vacancy capture volume around the void. On the basis of strain-field extent and shape, one would expect that the interstitial-cluster capture volume for vacancies would be smaller than its capture volume for interstitials. To the best of our knowledge, however, this has not been explicitly demonstrated. Thus the homogeneous capture volume probably is larger than the heterogeneous capture volume, also in the case of interstitial clusters.

Perrin and Bullough²⁰ also showed that an interstitial loses its point defect identity when absorbed on the tension side of an edge dislocation in alpha iron. It therefore cannot be transmitted along a dislocation core to another position in the crystal or be reemitted. In fact, no interstitial absorbed at a structural irregularity can be thermally reemitted. In the case of vacancies, transport along dislocations is possible, and thermal reemission from sinks is also possible. In this regard, the normal thermal vacancy concentration constitutes a statistical bias in favor of void growth.

Doran's^{1,6,17} high-temperature-annealing simulations show a strong homogeneous nucleation of both interstitial and vacancy clusters which results primarily from the intrinsic attributes of the initial vacancy-interstitial segregation in the displacement-spike-defect distribution. Associated defect-cluster-property computer experiments^{1,14,15,19} show that the correlated movements involved are sufficiently strong as to exhibit a significant mechanical-driving-force attribute.

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APPENDIX

The results collected in this review were developed at the six laboratories listed below. The investigators and computer programs concerned are listed as well.

Brookhaven National Laboratory (BNL)

Investigators: C. Erginsoy, J. B. Gibson, A. N. Goland, R. A. Johnson, and G. H. Vineyard
Programs: GRAPE and JOHNSON

General Electric Company, Nuclear Materials and Propulsion Operation (GE-NMPO)

Investigators: N. R. Baumgardt, J. R. Beeler, Jr., and D. G. Besco
Programs: GRAPE, JOHNSON, SPECTRA, CASCADE, ANNEAL, and DEFECT

Pacific Northwest Laboratory (PNL)

Investigators: R. G. Bourquin, R. E. Dahl, Jr., A. DePino, D. G. Doran, and G. E. Russcher
Programs: SPECTRA, CASCADE, ANNEAL, DEFECT, and GRAINS

WADCO Corporation (WADCO)

Investigators: R. A. Burnett, R. E. Dahl, Jr., and D. G. Doran
Programs: SPECTRA, CASCADE, ANNEAL, DEFECT, and GRAINS

Atomic Energy Research Establishment (AERE), Harwell

Investigators: R. Bullough and R. Perrin
Program: HARWELL

North Carolina State University (NCSU)

Investigators: J. R. Beeler, Jr.
Programs: DYNAM, ANNEAL, DEFECT, and SIZMANN

Brief descriptions of the computer programs used are as follows:

The GRAPE Program simulates atom motion in a crystal on a fully dynamic, many-body interaction basis. This is done by solving the 3N simultaneous differential equations of motion, in classical mechanics, for an N-atom system, numerically. The interatomic forces are derived from an assumed potential-energy-interaction function. This description constitutes the definition of a dynamical-method-simulation program. GRAPE is used to study low-energy damage events ($E < 1000$ eV). In the quasidynamic mode, it can be used to determine static mechanical-equilibrium atomic configurations. This program

was developed at BNL. Computer experiments in radiation damage start with the GRAPE Program. The programs listed below are based on the GRAPE Program:

HARWELL, a dynamical-simulation program developed at AERE to study dislocations, interactions between point defects and dislocations, and dislocation-loop nucleation.

DYNAM, a dynamical-simulation program developed at NCSU to simulate impurity-atom effects in radiation-induced defect production and annealing.

GRAINS, a dynamical-simulation program developed at PNL and NCSU to study grain boundaries and defect interactions with grain boundaries.

The JOHNSON Program generates lowest-energy configurations for an array of atoms. Given an initial atomic configuration, this program systematically moves each atom, one at a time, to a position of zero net force. This process is repeated several times until the magnitude of the net force on each atom falls below a prescribed cutoff value. This is the definition of a variational-method simulation program. The JOHNSON Program is used to compute the configuration, formation, and migration energies of a defect. It can be used to study free-surface configurations and impurity-atom-defect states as well. This program was developed, in its present form, at BNL. The program listed below is based on the JOHNSON Program:

DEFECT, a variational-method program developed at GE-NMPO. Its uses are the same as those for the JOHNSON Program.

The SPECTRA Program is a Monte Carlo Program which simulates PKA production by fast neutrons. Given a particular finite specimen and incident neutron-energy spectrum, SPECTRA computes the number of PKA produced per unit volume per neutron and the energy spectrum for these PKA. This program was developed at GE-NMPO.

The CASCADE Program simulates an atomic collision cascade on the basis of the branching sequence of binary collision-chains approximation (see section titled "Accumulation of Displacement Spikes"). This program was developed at GE-NMPO.

The ANNEAL Program is a Monte Carlo Program which simulates thermally activated migration of interacting vacancies and interstitials in a crystal. As input, it requires precomputed activation energies from a dynamical- or variational-method simulation. This program was developed at GE-NMPO and PNL.

The SIZMANN Program is a Monte Carlo Program which overlays defect distributions obtained from CASCADE, ANNEAL, or field ion-microscope micrographs. The SIZMANN Program was developed at NCSU.

In all of the work for iron, the Erginsoy-Vineyard potential-energy-interaction function was used in the simulation of damage events, and Johnson's

potential was used for defect configuration, formation, and migration-energy computations. These two potential functions coincide over the atom-atom separation distance range pertinent to defect characteristic calculations.

DISCUSSION BY ATTENDEES

Torrens: To compare the results of any computer simulation with experiment, one must investigate thoroughly the sensitivity of the results to the assumptions of the model. You have described the model very briefly and have not discussed the effect of model variation on your results. Can you please indicate how model-sensitive your principal results may be?

Beeler: The results I have described pertain to alpha iron and have accumulated over the past 8 years. All of the simulation models used have been described in the journals by their authors in complete detail.

As was emphasized at the beginning, the intent of this talk was to draw together computer-experiment results directly related to void nucleation, growth, and dissociation. These results came from six different laboratories, and several different types of computer experiments were used. Hence, in my opinion, it would require an almost supernatural omniscience to describe properly, at this time, the model-sensitivity of the principal results I have described.

The system of simulation work concerned rests principally on results from the dynamical simulations of Erginsoy and Vineyard and results from the variational-method defect-property simulations of Johnson. Any meaningful assessment of model-sensitivity of the system concerned would have to begin with a critique of these fundamental investigations. In particular, the role of replacement collision chains in damage production, the question of what is the true interstitial configuration, and the question of what is the shape and size of the recombination region would have to be reevaluated on the basis of other interaction potentials for alpha iron. To the best of my knowledge, no person has yet performed a sufficiently complete set of parallel simulations to accomplish this assessment.

Seidman: Do you not think that the final defect structure of the depleted zone will depend on the "path" that you use to produce it, i.e., the defect structure of the depleted zone might be different if it is created in a lattice at a temperature $T > 0$, vs. the situation where it is created at 0°K and then annealed at temperature T ?

Beeler: I certainly agree with you in principle, but I have few ideas on what specific qualitative or quantitative differences are involved. Dynamical-method computer experiments, such as those done by Gibson et al. and by Erginsoy et al. for an initially perfect static lattice at 0°K , are needed for a "warm" and a

"hot" lattice. In these latter cases, the initial atom coordinates and momenta would be perturbed so as to represent the state of a crystal at a finite temperature. Preliminary work along this line has already been initiated.

Seeger: Could you give the physical reason why, according to your views, voids have a larger capture volume for vacancies than for interstitials?

Beeler: The capture volume is defined in the written text such that the probability for immediate capture of a defect entering a capture volume, by the void, is 0.5 or greater. Said in another way, a defect entering the capture volume adopts an anisotropic jump-direction distribution that is strongly biased in favor of jumps directed toward the void.

In the computer simulations, an interstitial could come very close to a (110) void facet. This feature occurred because interstitial strain-field relaxation along close-packed lines was easily accommodated by localized distortion of the (110) facet, as shown in Fig. 28. This precluded the need for a complete relaxation of the close-packed-line strain field to reduce the strain energy, as is the case when an interstitial meets with a monovacancy. In fact, the interstitial could come closer to the (110)-faceted void than it could come to a monovacancy without participating in an annihilation event. One side result of this basic physical feature was that the capture volume for an interstitial turned out to be smaller than that for a vacancy.

Balluffi: Your result that the interstitial may experience some difficulty in joining a void when it gets very close to the void surface may not really influence the rate at which interstitials join the void by long-range diffusion. When the interstitial typically has to make a large number of jumps to reach the void, a slight difficulty (barrier) at the void surface may not have much of an effect.

Beeler: I agree with you. Let me clarify a point raised by the wording of your question, however, on interstitials entering a void.

The computer experiments on interstitial-void interactions did not indicate that an interstitial should experience any difficulty in entering a void. The result was much more mild than this, namely, that an interstitial was not pulled into a void from afar, but only over a very short range.

An interstitial was pulled into a (110)-faceted void only when it came to within two interatomic distances of a void facet. A vacancy was pulled into the same type of void when it came to within three interatomic distances of a void facet. It is interesting to note that an interstitial was pulled into a monovacancy when it came to within four interatomic distances of the vacancy.

These details of comparative behavior are important during short-term annealing, i.e., during the first few microseconds, but not during long-term annealing, in agreement with your comment.

Norris: Voids are sometimes observed to shrink during irradiation. Preferential absorption of interstitials at voids may be a reason, but this is a matter for discussion.

Beeler: Again I emphasize what was mentioned in response to comments by Professor Seeger and Professor Balluffi, the computer experiments do not indicate that interstitials should have difficulty in joining voids. They simply indicate that interstitials are pulled into voids only over a very short interaction range. Void shrinkage during irradiation could also occur, in part, due to the statistical radiation-attrition process described in my paper (see the section titled "Radiation Attrition of Void Nuclei").

Bullough: I do think you should guard against making blanket statements about the properties and interactions from the results of the simulation of very particular situations. Thus, for example, Perrin and I found that the interstitial in alpha iron was very tightly bound to the cube-edge dislocation. This is a very particular dislocation, and the result should not be used to infer that interstitials will be tightly bound to all dislocations.

Beeler: I do think that you should guard against not listening carefully to what was said before making blanket comments about how your work was quoted. In fact, I did not mention anything about strong binding of an interstitial to a dislocation. What I did mention was that an interstitial loses its identity as a point defect upon being absorbed by a dislocation. I referred to your work because you were the first, I believe, to point out this aspect. Subsequently, other work done using more-advanced simulation procedures than yours confirms my point. In the written text, all statements bearing on this point are carefully qualified.

Bullough: You referred to the vacancy clusters formed during the anneal as void embryos. Since I believe you have not included the surface energy in the model, I cannot understand how you can make any assertions concerning the stability of such clusters.

Beeler: Actually, your belief is incorrect, surface-energy effects were accounted for. Details of these stability calculations have been published by Johnson, for example, and by Beeler and Johnson.

Blewitt: I do not understand your picture of void formation by overlap of cascades. Were your cascades formed at absolute zero? The voids are formed at high temperatures, and it is not clear what connection this (0°K cascade overlap) has with the formation of voids.

Beeler: The cascade-overlap simulations were performed at 0°K. The intent of describing the result that large vacancy clusters can be formed by cascade overlap at 0°K, without diffusion, was to show that embryo void nuclei can be formed by this process. It is not claimed that cascade overlap by itself will directly produce visible voids. However, it is claimed that cascade overlap can produce embryo void nuclei.

The mechanism by which void nuclei are formed by cascade overlap is purely statistical in nature and will operate at any temperature below the void-

dissociation temperature. According to computer experiments, cascade overlap can only produce nuclei, not visible voids, because there appears to be an upper limit on the size of the vacancy clusters that can be produced via cascade overlap, without the aid of diffusion transport. Details are given in the written version of the paper.

Blewitt: What defect concentrations do you get at saturation (in cascade-overlap damage states)?

Beeler: At 0°K the Frenkel-pair density we have associated with a displacement spike in alpha iron is 3 at.%. This estimate is based on the assumption that the collided atom volume is the appropriate volume for use in estimating the defect density. The details are given in *Phys. Rev.*, 150: 470 (1966).

This density is equal to the theoretical average Frenkel-pair density for a saturated damage state, i.e., to the reciprocal of the recombination-region volume expressed in atomic volumes. Cascade overlap did not increase this density, hence the average density at saturation via cascade overlap at 0°K is also 3 at.%.

According to Doran's high-temperature-annealing simulations, short-term annealing reduces the defect population by a factor of 5. However, it is not known what is the appropriate crystal subvolume to use in estimating the defect density associated with a single displacement spike after short-term annealing. Saturation computer experiments have not been run at a high temperature.

Doran: The degree of annihilation is, of course, sensitive to the size of the annihilation region. For a 62-site region, the high-temperature short-term simulation of alpha iron gave ~80% annihilation.

Wiedersich: A saturation density of 3 at.% of surviving defect density corresponds to a supersaturation of 10^3 for temperatures not far from the melting point of a typical metal. The supersaturation at the low temperatures simulated by the calculation is so much higher that I am not surprised that you get only clustering but no breakup of clusters.

Beeler: Yes, this view of clustering-driving forces was not explicitly utilized in describing and interpreting the simulation results. I wish to thank you for bringing it to the attention of the conference. It should be mentioned that some cluster breakup does occur in Doran's annealing simulations. However, this tends to be offset by production of new clusters.

Arsenault: What is the density of single, di-, and trivacancies in relation to the density of large vacancy clusters?

Beeler: These densities are listed in Doran's article, *Radiat. Eff.*, 2: 249 (1970). Both the preanneal and postanneal cluster-size distributions are listed. He found some dependence upon PKA energy.

Ho: Did you investigate the effects of gas atoms on the stability and energetics of vacancy clusters?

Beeler: Wilson has done calculations for helium and vacancy combinations, I believe. Our size-effect simulations for substitutional impurity atoms show that a significant role of large gas atoms in vacancy configurations is the inhibition of interstitial-vacancy recombination. I know of no systematic computer-experiment investigation, however, on the internal stabilization of voids by gas atoms.

COMPUTER SIMULATION OF ATOMIC DISPLACEMENT CASCADES IN METALS

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ABSTRACT

Atomic displacement cascades originating from primary atoms displaced with energy up to 100 keV have been investigated by computer simulation. The model includes inelastic energy loss and finite temperature effects. Results obtained for crystals of copper, iron, and gold indicate that long-range channeling and focusing are rare. The numbers of vacancies created and of those remaining are both directly proportional to the primary energy corrected for inelastic loss over the energy range up to 100 keV. The number of clusters of i vacancies is in constant ratio to the number of clusters of $(i - 1)$ vacancies, this ratio being independent of primary energy. It is thus possible to predict the frequency of large clusters, which may play a part in void nucleation.

An atom of a metallic solid under irradiation by fast neutrons of energy ~ 2 MeV could receive kinetic energy exceeding 100 keV, depending on its atomic weight and on various factors involved in the collision with the neutron. When this primary knock-on atom (PKA) leaves its lattice site, it interacts in the solid with its neighbors, which are, in turn, displaced if they receive sufficient kinetic energy. In this way a *displacement cascade* of energetic atoms builds up in the solid. The energy dissipation in the cascade takes place by a combination of elastic and inelastic processes. The latter result in electron excitation and ionization and are important for high-energy primaries but do not contribute to damage production in metals. At the end of the cascade, the vacancies and interstitials created will relax to a stable damage state under the influence of various factors, such as thermal vibrations, elastic constraints, and background defect concentrations. The main problem in the study of void nucleation in irradiated metals is the separation of different factors influencing cascade creation and annealing, and the interaction of the two processes in a high-flux situation.

The development of a displacement cascade is a many-body problem, and analytical theories have so far been confined to cascades in amorphous solids.¹ The analytical treatment predicts that the number of vacancies (or interstitials) created in a cascade originating from a PKA of energy E is

$$\nu(E) = \kappa \cdot \frac{E - E_{in}}{2E_d} \quad (1)$$

where E_d is a sharp isotropic displacement threshold energy for an atom in the solid (usually ~ 25 eV) and E_{in} is the total inelastic energy loss in the cascade. The factor κ is termed the *displacement efficiency*. In the simple theory of Kinchin and Pease,² κ is unity, and more complicated analytical treatments predict that it will vary according to the scattering law but will remain constant with varying PKA energy.¹

Using computer simulation techniques, it is possible to follow the development of displacement cascades in crystalline solids, through a series of two-body collisions in which the atoms interact according to a given central potential. Such a project was initiated by Beeler and Besco³ for PKA energies up to 30 keV in crystals of BeO, Fe, and Cu using several different interatomic potentials. Their model does not include inelastic energy losses, which could be significant in metals even at 10 keV (see section titled Results and Discussion).

We have developed a computer code capable of simulating atomic displacement cascades originating from PKA's of energy up to a limit of perhaps 1 MeV (with present machine capacity) in any crystal lattice except monoclinic or triclinic. As many as five different species of atoms may be present in the crystal. Inelastic energy losses and the effects of finite temperature are also included. Some early results of cascades in face-centered cubic (fcc) copper and gold and body-centered cubic (bcc) iron, with primary energy ranging from 10 to 100 keV, are reported here.

THE SIMULATION MODEL

The simulation model will be described in detail elsewhere; here we emphasize only those aspects which differ from earlier simulations or are relevant to the interpretation of the results.

The only crystal lattice stored in the computer is a list of 15 to 20 near-neighbor sites for one atom of each type. A cascade atom possesses, in addition to its actual position, a *reference origin*, which is a nearby lattice site. Then, before each collision, the neighbor list with respect to the reference origin is scanned in order to find the next target atom. This procedure removes any upper limit on the dimensions of a cascade.

The interatomic potential $V(r)$ used for two-body collisions is a screened Coulomb potential with the screening function given by the Molière approximation⁴ to the Thomas-Fermi function:

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \times \left\{ 0.35 \exp \left(-0.3 \frac{r}{a} \right) + 0.55 \exp \left(-1.2 \frac{r}{a} \right) + 0.10 \exp \left(-6.0 \frac{r}{a} \right) \right\} \quad (2)$$

where Z_1 and Z_2 are the atomic numbers of the colliding atoms and a is a screening radius, originally defined in the Firsov treatment⁵ by

$$a = \frac{0.885 a_0}{(Z_1^{1/2} + Z_2^{1/2})^{3/2}} \quad (3)$$

For the present work the value of a has been determined by modifying the Molière potential to coincide with Born-Mayer potentials, whose parameters were determined from elastic-constant data at the nearest-neighbor separation in the crystal. This screening radius is compared with that of Eq. 3 in Table 1, and the resulting potentials are shown in Fig. 1.

TABLE 1
COMPARISON OF MODIFIED SCREENING
RADIUS a WITH THE FIRSOV VALUE
FOR COPPER, IRON, AND GOLD

	Copper	Iron	Gold
Firsov a , Å	0.0960	0.0996	0.0688
Modified a , Å	0.0738	0.0781	0.0752

Fig. 1 Interatomic potential $V(r)$ used in the simulation (modified Molière) compared with the Firsov and Born-Mayer forms for copper, iron, and gold.

The classical equations for two-body scattering under a purely repulsive potential are well known.¹ For the above potential, as in all but a small group of power potentials, the scattering integrals must be solved by numerical methods when the energy transfer and deflection in an atomic collision during the cascade are being computed. A moving cascade atom, particularly in an ordered lattice, frequently passes almost directly between two or more lattice atoms. Then the two-body approximation is unsatisfactory because it tends to overestimate the energy loss and net deflection. We allow for the possibility of such nearly simultaneous collisions in the simulation by computing the results of a collision with each target separately, then summing the projectile energy losses, and vectorially adding the deflections.

The computation proceeds by selecting as projectile for each collision the most energetic atom in the cascade. The low-energy aspects are the most difficult since, at energies below ~ 100 eV, many-body effects supervene. In our model, a sharp isotropic displacement threshold E_d (25 eV for copper and iron and 35 eV for gold) is assumed. Atoms that receive energy greater than E_d join the cascade but make no further collisions unless their energy is above $2E_d$. A cascade atom is considered as stopped when its energy drops below $2E_d$ but may only replace a displaced target if its energy drops below E_d in the collision. Stopped atoms remain where they are, and a site once vacated, even in a replacement collision, remains vacant until the end of the cascade. Thus "redisplacement" of a stopped cascade atom, whether substitutional or interstitial, is not permitted, since such an atom will not have sufficient time to settle into a stable configuration during the cascade lifetime ($\sim 10^{-14}$ sec). No interaction between cascade atoms of *any* energy is allowed, and the only interstitials that may become collision targets are those inserted in the crystal before the beginning of the cascade. At the end of the cascade, any atom not already in a lattice site that is within a specified recombination radius of a vacancy (typically ~ 1.5 lattice parameters) is put into this vacancy. This recombination procedure may be separated completely from the cascade creation for more detailed analysis.

Inelastic energy losses are calculated on the basis of the Firsov theory.⁶ The electron-excitation energy in a single collision of impact parameter s is of the form

$$\Delta E_{\text{ex}} = \frac{\alpha}{(1 + \beta s)^5} \quad (4)$$

where α and β depend on the mass and charge of the colliding particles and α is proportional to the projectile velocity. The inelastic loss so calculated is subtracted from the kinetic energy of the projectile after the elastic collision.

The finite temperature effect is simulated in an adiabatic approximation, where the target atom is given a small thermal displacement from its lattice site and considered stationary for the duration of the collision. The root-mean-

square (rms) vibration amplitude is calculated using the Debye model,⁷ and the thermal displacement is selected randomly from a Gaussian distribution of this amplitude.

The computation is carried out in double precision on IBM System/360, Model 75 or 91 machine. Results are based on statistical analysis of samples of 10 cascades. Within each set, only the initial PKA direction is varied, being chosen at random within a solid angle of $\frac{1}{4}\pi$ of the total sphere. Typical computation times on the Model 91 are 2 sec for a 10-keV cascade and 70 sec for a 100-keV cascade in copper.

The point-defect distribution at the end of a cascade has been analyzed by a separate program⁸ that determines the number and characteristics of clusters of vacancies or interstitials. A simulation of thermal annealing of displacement cascades different conditions has been developed,⁹ and the results of this will be reported separately.

RESULTS AND DISCUSSION

Cascades have been run in a static lattice and in one with thermal vibrations included (mainly at 600°K). No detailed analysis of spatial characteristics has yet been made. In general, the higher-energy cascades result in a column of defects (with perhaps some subsidiary branches) ending in one or more vacancy-rich zones with most of the interstitials scattered around the outside. Branching of cascades following a close collision of a high-energy atom is quite common.

In Fig. 2 the damage energy $E - E_{in}$ (E_{in} is the total inelastic loss in the cascade) and the damage efficiency $\xi(E)$ (percentage of PKA energy available for damage) are plotted against the PKA energy E for cascades in copper. The introduction of thermal vibrations tends to lower $\xi(E)$ slightly. The damage energy is comparable with an analytical estimate¹ based on the Lindhard theory of inelastic losses.¹⁰ Figure 3 compares the number of vacancies created [$\nu(E)$], before any recombination, with that predicted by the Kinchin-Pease theory for the same damage energy.

The displacement efficiency κ (Eq. 1) is plotted against E in Fig. 4 for copper and iron. Contrary to the effect reported by Beeler,¹¹ no evidence has been found in any of the three metals for a decrease of κ with increasing energy, at least below 100 keV. The value of κ at 600°K is some 7% lower than for a static lattice (Table 2). Preliminary results at 0°K indicate a further decrease, but the energy invariance is retained, as is the case also when the interatomic potential is varied. Changes in the value of E_d and removal of the inelastic-energy losses produce no noticeable effect on κ . The precise reason for this sensitivity of κ to the presence of thermal vibrations is not yet fully understood. The energy invariance of κ seems nonetheless well established, in agreement with the conclusions of analytical cascade theory. This would suggest that the crystal lattice is not highly important in the development of most cascades.

Fig. 2 Variation of damage energy $E - E_{in}$ and damage efficiency $\xi(E)$ (%) with PKA energy E for cascades in copper; (a) static lattice, (b) thermal vibrations included, $T = 600^\circ\text{K}$. The dashed line is an analytical estimate based on the Lindhard theory. Error bars in this figure and in Figs. 3 and 4 indicate the statistical spread over samples of 10 cascades.

After close-pair recombination, the fraction F_s (see Table 2) of the $\nu(E)$ vacancies which survive shows the same sensitivity as κ to the presence of thermal vibrations, as well as the same energy invariance. The fraction F_s is a measure of the spatial extent of the cascade, and a decrease of F_s with increasing E (κ remaining constant) would indicate an interference between different branches of higher-energy cascades. This was the main reason suggested by Beeler for the decrease of the product $F_s\kappa$ with increasing energy in his simulations. We find no such effect over a reasonable range of recombination radius and conclude that the amount of interference between different parts of the cascade is negligible.

Fig. 2 (Continued)

Clusters of up to 15 vacancies have been observed, but so far only one cluster of four interstitials has been seen in over 1000 cascades, and even tri-interstitials are rare. The condition used to define a cluster is that adjacent point defects must be separated by a distance not greater than the nearest-neighbor separation in the lattice. A cluster analysis revealed that, to a good approximation, there exists a constant cluster factor (f_c) that gives the probability of clustering, such that

$$N_i = f_c^{i-1} N_1 \quad (5)$$

where N_i is the number of clusters of i vacancies in the cascade. This empirical rule is very well obeyed in copper and iron but less well in gold owing to the presence of more large clusters than the rule predicts. Table 2 gives the numerical values of f_c for the three metals. The cluster factor is again independent of PKA energy within the range studied here, but, since the

Fig. 3 Variation of $\nu(E)$ with E for cascades in copper, compared with that predicted by the Kinchin-Pease ratio based on the same damage energy. (a) Static lattice. (b) $T = 600^\circ \text{K}$.

statistics are necessarily worse for clusters than for single defects, we cannot say with certainty whether the introduction of thermal vibrations changes f_c . No satisfactory explanation for the existence of a cluster factor is immediately obvious. However, it provides evidence for a marked correlation in the vacancy creation during the cascade, supported by the asymmetry between vacancy and interstitial clustering.

The rule is interesting from the point of view of being able to predict the number of vacancy clusters of a given size which will be created under given irradiation conditions. Large clusters could play a part in void nucleation. Suppose that, in an irradiated material where voids are present, the ratio of

Fig. 3 (Continued)

cascade density to void density is of the order of 1000. From Eq. 5 the value of i such that a cluster of size i occurs once every 1000 cascades is given by

$$f_i^{-1} N_1 = 10^{-3} \quad (6)$$

Since i appears in the exponent, it varies little with N_1 and consequently with energy. Using cascade results after close-pair recombination, the corresponding cluster size is about 9 for copper, 8 for iron, and 11 for gold. Thus, if a single cascade may be responsible for nucleation of a void (which is by no means

(a)

(b)

Fig. 4 Displacement efficiency κ plotted against PKA energy for (a) copper and (b) iron with and without thermal vibrations.

certain), this equation might be used in connection with the ratio of cascade density to void density to predict the minimum-size cluster that can form a stable growth nucleus. It is difficult to proceed further in this hypothesis before

TABLE 2
RESULTS OF ATOMIC DISPLACEMENT CASCADES IN
COPPER, IRON, AND GOLD OVER THE PKA ENERGY
RANGE 10 TO 100 keV FOR A STATIC LATTICE WITH
THERMAL VIBRATIONS

	Copper	Iron	Gold
Displacement efficiency κ			
Static lattice	0.869 ± 0.004	0.882 ± 0.007	0.860 ± 0.006
Crystal temperature 600°K	0.809 ± 0.004	0.817 ± 0.004	0.812 ± 0.004
Survival* fraction F_s			
Static lattice	0.251 ± 0.006	0.267 ± 0.005	0.208 ± 0.005
Crystal temperature 600°K	0.228 ± 0.003	0.249 ± 0.003	0.187 ± 0.003
Cluster* factor f_c			
Static lattice	0.276 ± 0.018	0.207 ± 0.013	0.424 ± 0.010
Crystal temperature 600°K	0.262 ± 0.010	0.181 ± 0.010	0.408 ± 0.003

* The recombination radius is 1.5 lattice parameters.

investigating in some detail the effect of thermal annealing on these large clusters.⁹

Long-range channeling is relatively rare, occurring most frequently in iron and almost never in gold. Its incidence is slightly greater when thermal vibrations are present than in a static lattice, probably because small thermal displacements tend to decrease the blocking effect for an atom displaced from its lattice site. Short-range channeling is more frequent, causing a high inelastic loss and a consequent drop in $\nu(E)$ compared with the average for that energy. The effect of this is simply to worsen the statistics without altering significantly the value of κ . By contrast, if long-range channeling were common, it would tend to reduce κ owing to the large number of subthreshold collisions suffered by the channeled atom.

In future work, we intend to study such other materials as hexagonal metals and to extend the simulation to higher energies and previously damaged crystals. The recombination of close pairs at the end of the cascade will be investigated in greater detail. Thermal annealing of cascades under different conditions of temperature and background defect concentration will be studied by simulation. The program will also be used to simulate ion bombardment of solids and the influence of the crystal surface on displacement cascades.

CONCLUSION

Although the numerical results are to some extent model dependent, there is convincing evidence for some qualitative tendencies. Long-range channeling and focusing seem to play an unimportant part in cascade development in these cubic metals. The displacement efficiency and the survival fraction have not been observed to vary with PKA energy with any of the model variations that we have tried. This seems to be a real effect. Finally, an empirical rule governing the numbers of vacancy clusters of various sizes has been observed. This empirical rule could be useful in predicting the frequency of large clusters that might be nucleation centers for radiation-induced voids.

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DISCUSSION BY ATTENDEES

Bement: Why is the survival fraction for gold low relative to copper and iron? How is this difference in survival fraction related to differences in the interatomic potentials?

Torrens: The lower survival fraction for gold is related to the more compact nature of cascades in gold, mainly a consequence of the greater size and mass of the gold atom compared to the lattice dimensions. This difference is, of course, expressed in terms of the interatomic potential.

Wazzan: You say that your program may be used to treat pure metals, alloys, and compounds. You use a Molière (or Thomas–Fermi) potential. How do you modify your potential for alloy calculation?

Also, for calculations such as in aluminum, would it not be appropriate to use other types of potentials for calculating core–core interaction, such as pseudopotential?

Torrens: Up to the present, we have limited ourselves to pure metals. For alloys, we would have to use different $V_{ij}(r)$ potentials for collisions between atoms of types i and j . Since we are only concerned with dynamic collisions of energy greater than ~ 10 eV, crystal binding forces, such as those described by pseudopotentials, are not necessary to the description of the collision.

Arsenault: Sheely has published a paper showing the experimental result that, as the PKA energy increased, the displacement efficiency decreased.

Torrens: Sheely's results show that the product of the displacement efficiency and the damage efficiency (see the definitions in our paper) decrease with increasing PKA energy. We find that the *displacement* efficiency is independent of PKA energy. However, the *damage* efficiency decreases strongly with increasing PKA energy because of the increasing importance of inelastic-energy losses.

Wilson: You stated that your calculations included varying the potentials chosen. Could you give some numerical limits on the values of displacement efficiency and survival fraction calculated and state the potential used in each case?

Torrens: Variation of the hardness of the potential by changing the screening radius produced little change in the displacement efficiency, in agreement with analytical theory of cascades. The spatial distribution of the defects created is more sensitive to potential variation. This, of course, influences the survival fraction after close-pair recombination. We do not have sufficient data as yet to give any quantitative estimates, but a systematic study of the effect of model variation on the numerical results will be undertaken.

Fig. 1 Preanneal configuration of a 100-keV cascade. (The right-hand portion of this figure is on the next page.)

Fig. 1 (Continued)

PREPARED DISCUSSION

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Drs. Torrens and Robinson have kindly furnished us several of their copper cascades to run through our short-term-annealing simulation program. In this program, similar in principle to one previously described,* the cascade is "temperature corrected" by permitting interstitials and vacancies to perform correlated random walks on a face-centered cubic lattice, resulting in clustering and mutual annihilation. Defect mobilities correspond to the model of gamma-iron developed by Johnson.† (The inconsistency of using a gamma-iron model for "copper" cascades is considered unimportant for present purposes.) The simulations correspond to a real time of the order of $1 \mu\text{sec}$ at a nominal temperature of 800°K .

The preanneal configuration of a 100-keV cascade is shown in Fig. 1. This is a projection of all defects onto the x - z plane. The arrow indicates both the takeoff point (100, 100, 100) and direction (direction cosines: 0.558, 0.0094, 0.830). The main body of the cascade extends in the positive y direction (not

*D. G. Doran, *Radiat. Eff.*, **2**: 249 (1970).

†R. A. Johnson, *Phys. Rev.*, **145**: 423; **152**: 629 (1966).

shown) to ~ 270 half-lattice units, the isolated concentration of defects at large x and z is located at $y \sim 65$.

The result of a short-term anneal of this *isolated* cascade with a 32-site annihilation region (those sites found by Johnson to be unstable against recombination at 0°K) is shown in Fig. 2. The jump frequencies of the mobile interstitials (size 3 or smaller) are several orders of magnitude higher than the jump frequencies of the mobile vacancies (size 4 or smaller, but the single vacancy is very sluggish); therefore essentially all the residual mobile interstitials have escaped from the cascade. If this run were continued, the remaining mobile vacancies would eventually escape also.

Performing the annealing simulation with a 104-site annihilation region (determined by moving one interstitial jump away from the 32-site region) produced the configuration in Fig. 3.

These results are, of course, qualitative since more runs must be made before one knows how typical this run is. However, several runs made with two 20-keV cascades behaved similarly to the 100-keV cascade, in that the defect densities were lower and there was less clustering than found* in processing the cascades simulated by Beeler.†

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†J. R. Beeler, Jr., *Phys. Rev.*, **150**: 470 (1966).

Fig. 2 Short-term-annealing simulation with a 32-site annihilation region.

Fig. 3 Annealing simulation with a 104-site annihilation region.

EXPERIMENTS TO DETERMINE THE NUMBER OF "FREE VACANCIES" IN A FISSION-NEUTRON DISPLACEMENT CASCADE

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ABSTRACT

This paper addresses itself to the problem of determining the number of vacancies, called "free vacancies," that can escape from a fast-neutron cascade and freely wander in the lattice. Since these free vacancies result in diffusion, the measurement of radiation-enhanced diffusion is the technique used. Experimentally, disordered Cu_3Au was used since the migratory vacancy will usually jump to cause order and leave its path marked by a trail of high order. The resistivity change, which is a good criterion of order, was measured as a function of both fission-neutron and thermal-neutron bombardment at a temperature (of the order of 100°C) high enough to allow the migrating vacancies to move and low enough for thermal-induced ordering not to occur. The number of migratory vacancies was then determined from these data by (1) assuming the vacancy lifetime was of the order of distance between primary knock-ons and (2) comparing the ordering rate of the thermal- and fast-neutron bombardment cases and then estimating the vacancies liberated in the thermal case. Both methods indicated of the order of five vacancies per cascade, i.e., about 1% of the Kinchin and Pease number, or about 4% of the stable defects formed.

It is clear from the size and distribution of the voids formed in fast-neutron bombarded metals that long-range migration of vacancies occurs.¹ Although the number of vacant lattice sites in a displacement cascade can be estimated to within a factor of 2, the high defect density within the cascade makes it difficult to estimate the number of vacant lattice sites that escape from the cascade and are free to migrate. These migrating or free vacancies are the only ones that can contribute to void formation and therefore are of some importance to an understanding of the formation of voids.

This paper describes an experiment designed to determine the number of free vacancies in a cascade. Since vacancy migration causes diffusion, it is the

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study of this property that is used to determine the number of free vacancies arising from fast-neutron bombardment.

The diffusion can be followed easily in a disordered alloy whose stable state is in the ordered condition since the vacancy will then jump in such a way to induce order. The electrical resistivity can be used to measure the number of ordered atoms, and the number of vacancies can then be deduced. In this experiment Cu_3Au was chosen since copper and gold are of considerably different atomic size, which makes it difficult to envisage order arising from interstitial migration. The basic plan of the experiment is to bombard disordered Cu_3Au with fast neutrons at a temperature where vacancies are mobile and to measure the decrease in resistivity because of the order caused by migrating vacant lattice sites.

EXPERIMENTAL PROCEDURE

The Cu_3Au samples in the form of wires 0.015 in. (0.38 mm) in diameter were heat-treated to produce a large domain size. The large domain size is necessary if the resistivity is to be a single-valued function of the long-range order parameter S .² The heat treatment was as follows: Samples were heated to 900°C and held for 10 hr to remove the work hardening introduced by the drawing operation. Lead wires were silver soldered to the samples, which were then heated to 450°C and slowly cooled to 380°C (6° below the critical temperature for order). The samples were held for 24 hr to allow for domain growth and then air quenched to room temperature. In effect, these samples—called “disordered”—have very large domain size with a degree of order corresponding to the equilibrium order at 380°C. Higher-ordered samples were also prepared by substituting for the quench a slow cool to 250°C and holding at this temperature for 24 hr.

Three different irradiations were made at a temperature of about 150°C. This temperature was chosen because the vacancies created by bombardment are mobile, but it is not high enough for significant order from thermally created vacancies. Thus the ordering produced will only be that due to radiation-induced vacancies. Samples of ordered and disordered Cu_3Au were bombarded: (1) in a thermal flux, (2) in a fast flux, and (3) in a combination of a fast flux and a thermal flux. The fast-flux location in the Argonne CP-5 reactor is described elsewhere³; however, it is worth noting that the thermal flux is less than 10^8 neutrons/(cm²)(sec), whereas the fast flux is $1 \times 10^{12} > 0.1$ MeV neutrons/(cm²)(sec) with an average energy of 0.65 MeV. In the thermal-flux location, there are 2×10^{12} neutrons/(cm²)(sec) with a cadmium ratio of between 10^3 and 10^4 .

The electrical resistivity was measured with the I-R drop method. The system was automated and triggered to read every 10 min of full reactor power; data were recorded by a digital voltmeter and an IBM keypunch. The

temperature was measured with a copper-constantan thermocouple and controlled to $\pm 2^\circ\text{C}$ by a heater.

Finally, something should be said about the displacement cascades formed by the fast and by the thermal neutrons. In the fast-neutron case, the average primary knock-on had an energy of 20 keV. It is assumed that the spectrum of neutron energies is symmetrical about 0.6 MeV so that on the average all neutrons counted, i.e., > 0.1 MeV, had a knock-on energy of 20 keV. According to Kinchin and Pease,³ there will be 400 displacements on the average per cascade. Experimentally, based on the resistivity change at 4°K and a resistivity of $2.5 \times 10^6 \Omega\text{-cm/at.}\%$, only 100 displacements were made per cascade. In the thermal-neutron case, displacements were produced by capture-gamma recoils, with the number of displacements depending on the atomic mass and the spectrum of the capture gammas. In the case of copper, the capture cross section is 4.4 barns with an average recoil energy of about 350 barns, whereas in the case of gold the capture cross section is 98 barns with an average recoil energy of 68 barns.

Therefore, from Kinchin and Pease, it would be expected that six displacements per capture in copper and one displacement per capture in gold would be produced. Liquid-helium measurements, using the same parameters as for the fast-neutron case, indicated only three displacements for the copper per capture and only one-half displacement per capture for the gold. In the case of Cu_3Au , with consideration of different capture cross sections, about half of the displacements were caused by the copper and about half were caused by the gold.

RESULTS AND DISCUSSION

The results of these irradiations are shown in Figs. 1 to 4. In each case, there were temperature fluctuations of ± 2 from the normal temperatures. The resistivity changes that resulted from these temperature deviations were corrected.

In Figs. 1 and 2, the effects of fast- and thermal-neutron bombardment on ordered and disordered Cu_3Au can be compared readily. Obviously, from the differences between the thermal- and fast-neutron bombardment, the knock-on energy plays a very large role in the ordering process and therefore in the vacancy migration. Primarily, it should be noted that in both cases, although it is not apparent from Fig. 2, disordering is occurring as well as ordering. The disordering process occurs spontaneously with the formation of a cascade, probably as the result of replacement collisions. By measuring the resistance change at liquid-helium temperature where the vacancy is frozen and ordering cannot occur,⁴ one can determine the amount of disorder. In the thermal-neutron case, the resistivity change in highly ordered Cu_3Au at 4.2°K shows an increase of $2.6 \times 10^{-12} \Omega\text{-cm/min}$, which indicates about 80 atoms disordered

Fig. 1 The effect of fast-neutron bombardment on the resistivity of Cu_3Au . Two samples with different degrees of order are shown. The upper two curves are those of the sample with a low degree of order. The lower of these curves has the disordering component subtracted out. The lower two curves are of highly ordered Cu_3Au , and, again, in the lower of these two, the disordering component is removed. The bombardment temperature was 150°C . The decrease in resistivity is due to ordering from radiation-induced diffusion.

per displacement. On the other hand, in the fast-neutron case, there is an increase of $7.7 \times 10^{-11} \Omega\text{-cm/min}$ in the highly ordered Cu_3Au , which indicates a disordered region of 160 atoms disordered per displacement.

These results make it apparent that the different behavior shown in Figs. 1 and 2 cannot be attributed solely to the disordering reaction. It appears that in the fast-neutron case, which is typical of all high-energy knock-on events, the lifetime of the vacancy is inhibited by that part of the cascades remaining at 150°C . Earlier work at Oak Ridge⁵ offers substantial evidence that this is the case. In the Oak Ridge work shown in Fig. 5, the results of three samples are shown. Sample 15B was bombarded at 150°C in a reactor neutron spectrum, whereas sample 18A was bombarded in the center of a natural-uranium cylinder, which modified the reactor spectrum by converting approximately 10% of the thermal neutrons to fission neutrons.

Fig. 2 The effect of thermal-neutron bombardment on the resistivity of a partially ordered Cu_3Au sample. The bombardment temperature was 134°C .

The net effect was a reduction in the amount of order despite an increase in the number of displacements. Since the greater amount of disorder produced by the enhanced neutron flux will only be a percent or so of the net decrease observed in sample 15B, it was postulated that the fast cascades act as sinks or traps for the vacancies and thus decrease their mean free path. To verify this, Oak Ridge workers bombarded sample 16A at 160°C to an equivalent dose and in a comparable neutron spectrum used for sample 15B in order to build up a network of cascades before allowing the vacancies to move. In comparison to the sample bombarded at the elevated temperature, little ordering was observed. This verifies the fact that fast cascades reduce the vacancy lifetime.

The minimum observed in Fig. 1 is explainable then by the fact that at low doses the migrating vacant lattice sites have a long lifetime. That is, they make many jumps, and the order far exceeds the disordering. As the bombardment proceeds, sinks or traps are created that reduce the mean free path and reduce the ordering. At the minimum the number of atoms ordered by vacancy

Fig. 3 A comparison of the ordering of Cu_3Au by fast and thermal neutrons. The partially ordered sample was bombarded at 150°C in a fast-neutron spectrum for 240 min. It was removed from the reactor and rebombarded in a thermal-neutron spectrum. The change in slope occurring at 240 min is a measure of the relative vacancy migration in each case.

migration is just balanced by those disordered by replacement collisions in the cascade. At higher doses the mean free path of the vacancy continues to decrease, and the disordering reaction dominates. In thermal-neutron bombardment, it is clear from the low-temperature-irradiation studies that sinks are not created by the low-energy cascade of the type created by fast-neutron bombardment, which explains the absence of a minimum in thermal-neutron bombardment. The annealing spectrum of low-temperature-irradiated copper,⁶ which has a close resemblance to that of Cu_3Au , is illustrated in Fig. 6. Obviously, important differences exist between thermal- and fast-neutron irradiations in the high-temperature region. Complete recovery of electrical resistivity is observed with 5-min temperature pulses in the thermal-neutron case

Fig. 4 The effect of fast- and thermal-neutron bombardment on the ordering rate of Cu_3Au . The region in the vicinity of the change from fast- to thermal-neutron bombardment of Fig. 3 is shown in detail.

below 200°C , whereas in the fast-neutron case complete recovery is not observed until about 400°C . This annealing peak at 400°C is called "stage V" recovery. Clearly the defects recovered in stage V are responsible for radiation-induced hardness since the major portion of radiation hardness is recovered in stage V. Experiments verify that thermal-neutron irradiation does not produce radiation hardness, and, indeed, actually produces a decrease in samples hardened by fast-neutron irradiation. Therefore the assembly of defects causes the hardness, which will be called "hardness centers," and these act as sinks or traps for vacant lattice sites in fast-neutron bombardment but are absent in thermal-neutron bombardment.

From the disordered sample shown in Fig. 1 and the above analysis of the minimum, we can estimate the number of vacancies that escape from a cascade. The minimum occurs at a dose of 3000 min. As previously stated, at the minimum the number of atoms ordered by vacancies is equal to those disordered

Fig. 5 The effect of fast-neutron flux on the rate of radiation ordering. Sample 15B was bombarded in a flux of 2.5×10^{11} fast neutrons/(cm²)(sec) and 1×10^{12} thermal neutrons/(cm²)(sec) at +150°C. Sample 16A was bombarded in a flux of 2×10^{11} fast neutrons/(cm²)(sec) and 1×10^{12} thermal neutrons/(cm²)(sec) at -160°C. The sample was annealed at 148°C to cause the degree of ordering indicative of the point at 2×10^{17} and 1×10^{12} fast neutrons/(cm²)(sec) and 1×10^{12} slow neutrons/(cm²)(sec) at 150°C. Sample 18A was bombarded in a natural-uranium (about 10%) cylinder that converted some of the thermal neutrons to fission neutrons. Note that, although the number of defects was enhanced, the diffusion decreased.

by cascades. The total disordered volume based on low-temperature bombardment shows about 2×10^4 atoms are disordered per cascade or about 5×10^3 gold atoms have been moved to wrong sites. Thus the vacancies liberated from a cascade must move about the same number of atoms. With a cross section of 3 barns and a flux of 10^{12} neutrons/(cm²)(sec), there are 6×10^{16} cascades/cm³ with an average distance between primary knock-ons of 100 atom distances. In a random walk process, the number of jumps is given by the square of the distance; thus each vacancy could be expected to make 10^4 jumps. It is assumed that a vacancy would require between 2 and 10 jumps to move a gold atom for the existing degree of order; therefore it can be concluded that between one and five vacancies escape from each cascade at 150°C.

The number can also be estimated from the results in Figs. 3 and 4. The Cu₃Au was bombarded at 150°C for 250 min by fast neutrons and then removed from the reactor and bombarded by thermal neutrons at 150°C. In this experiment the change in slope induced in going from fast to thermal neutrons will be a direct comparison of the number of migration vacancies in each case

Fig. 6 The annealing curve for copper bombarded at $<5^\circ\text{K}$ by thermal and fast neutrons. At 420°K , complete recovery has occurred for thermal neutrons. Stage V recovery remains in the fast-neutron bombardments. In the lower curve the beginning of stage V can be seen.

because the sink density and the order parameter are the same. Since the slope decreases by a factor of 2, it can be concluded that twice as many vacancies per bombardment minute are migrating in the fast-neutron bombardment than in the thermal-neutron bombardment. The number of vacancies can be estimated from the thermal case.

For thermal-neutron bombardments, it is assumed that Cu_3Au corresponds to copper, and the annealing spectra of the two would seem to verify this.* Then the number of migrating vacancies can be estimated from the recovery peak in copper corresponding to the ordering peak in Cu_3Au . For copper, it is observed that 20% of the resistivity change of $7 \times 10^{-14} \Omega\text{-cm}/\text{min}$ of dose is associated with the annealing stage where ordering occurs. Since complete recovery is

*Unpublished work of the authors shows that, with the exception of stage I recovery, which occurs about 30°K higher for Cu_3Au , there is a one-to-one correspondence in the recovery of thermal-neutron-bombarded copper and Cu_3Au .

observed during this annealing stage, and it is clear that vacancies are migrating, it is reasonable to assume that they are being annihilated. Assuming that all of the vacancies present are migrating and are being annihilated at dislocation loops or in void-nucleation sites, the number of migrating vacancies can be estimated from the magnitude of resistivity change since the annihilation of 1 at.% of vacancies will reduce the resistivity by $1 \times 10^{-6} \Omega\text{-cm}$. In this case, which should be considered a maximum, there are 7×10^{13} migrating vacancies per dose minute. On the other hand, if it is assumed that the vacancies are annihilated at small interstitial clusters, since an I-V is being annihilated, the resistivity will be reduced by $2.5 \times 10^{-6} \Omega\text{-cm}$ for each atomic percent annihilated. This results in 3×10^{13} migrating vacancies per dose minute.

In a dose minute, there are 2×10^{13} cascades formed (counting those neutrons with an energy greater than 0.1 MeV). Therefore, since there are twice the vacancies liberated per dose minute for the fast-neutron-bombardment case, between three and seven migrating vacancies are liberated in a cascade in Cu_3Au . There is reasonable agreement between the two methods. Therefore, on the basis of estimates by Kinchin and Pease of the number of defects formed, less than 2% escape. On the basis of the best experimental evidence for the defects formed in a cascade, about 8% escape.

It should be noted that, if any vacancies were liberated in the dissolution of the hardness source, they would be additional to those indicated by these experiments. Evidence suggests, however, that these centers act as sinks rather than sources for vacancies. Recent results, mentioned earlier,⁴ taken at Argonne show samples hardened by fast-neutron irradiation, at 50°C , of 5×10^{17} neutrons/ cm^2 (>0.1 MeV) to a yield stress of 3 kg/mm^2 at room temperature, which is a significant increase following a bombardment of 3×10^{18} thermal neutrons.

It would be very difficult to associate this decrease with anything other than mutual annihilation of vacancies and the hardness centers. It appears that few vacancies escape from this hardness center. Clearly, further work is required in this area; the significance of the obvious attraction of the vacancies to the hardness centers has been overlooked in void studies. This concept might well play an important role in the formation of voids, and, in particular, might be the explanation for the absence of voids in low-temperature bombardments.

CONCLUSIONS

1. The number of vacancies escaping from a fast neutron is very small. Less than 10% of the vacancies created migrate long distances (less than 2% of the number estimated by Kinchin and Pease).

2. At low temperatures, i.e., below stage V recovery or $T_m/2$, there are radiation-induced sites associated with high-energy cascades which trap or annihilate vacancies. It is suggested that these sites are associated with the defect

agglomeration, which causes hardness, and are spontaneously formed in the cascade to recover with an activation energy, in many cases, close to that of the self-diffusion activation energy.

ACKNOWLEDGMENT

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DISCUSSION BY ATTENDEES

Nelson: Voids have been produced in nickel, for example, under a variety of irradiation conditions—e.g., neutrons, heavy ions, protons, and electrons. In the former two cases, cascades dominate, whereas, in the latter cases, displacements occur in ones and twos. If we compare swellings using calculated numbers of displacements before recombination, even using simple Kinchin-Pease models, the answers agree within about a factor of 2. This suggests that, if cascades are created in a "hot" lattice, then a large fraction of vacancies evaporate into the lattice rather than recombine within the cascades.

Blewitt: The remarks of Dr. Nelson are well taken. A consideration of the displacements per atom in our experiments indicates, however, that there is no large disagreement with Nelson's data. The number of displacements per atom is a rather nebulous concept since it depends on a rather arbitrary selection of displacement criteria. When he compared our data with his, it is assumed that Nelson used the so-called Half-Nelson criteria. Consider the number of displacements per dose minute for the fast cases in Cu_3Au . There are (as noted in the body of the paper) 2×10^{13} cascades per dose minute. The knock-on energy, assuming an average energy of 6×10^5 eV (which rather overestimates the number of displacements), is about 20 keV for the copper atoms and about 7 keV for the gold atoms, yielding a weighted average of 17 keV. With the

Half-Nelson model, this will produce 170 I-V pairs per knock-on or a total of 3.4×10^{15} defects per dose minute.

In the thermal case, copper has a cross section of 4.4 barns with a 300-eV capture-gamma recoil per capture. There will then be 4×10^{13} neutrons captured by the copper and 2.4×10^{14} defects created per dose minute. On the other hand, gold has a cross section of 100 barns and a capture-gamma recoil of 50 $\times$ 5 eV, so that there are 3×10^{14} I-V pairs found by the gold per dose minute. Thus, in the thermal case, there are 5.4×10^{14} defects produced per dose minute.

Since our data show that there are twice as many migrating vacancies per dose minute for fast-neutron bombardment as there are for thermal neutrons, it will be necessary to measure the defect concentration to 1.1×10^{15} per dose minute if the same void concentration is to exist (assuming all the migrating vacancies are trapped by helium and nucleated to voids). The defect concentrations or atomic displacements are thus within a factor of 3. This is hardly a big deal and in point of fact would seem to substantiate our counting methods.

Bement: What are your expectations for the effects of the degree of order in Cu_3Au on the efficiency of vacancy trapping at "hardened" sites?

Blewitt: On the basis of the fact that impurity atoms seem to have little effect on radiation hardening, I would guess that the degree of order has little effect on the hardness centers.

Seeger: With regard to the apparent disagreement between Blewitt and Nelson, I think it is very much a matter of the temperature at which you work. At high temperatures the vacancy clusters may disperse, as is evident, for example, from the radiation-hardening experiments of D. Ast and J. Diehl, *Phys. Status Solidi*, 17: 269 (1966), but also from other radiation-hardening work. What Blewitt said referred to temperatures below the annealing out of radiation hardening, i.e., below stage V. A small but important difference in temperatures between his work and that of Nelson exists. I do not feel there is any discrepancy between their experiments.

THEORY OF VOID FORMATION AND GROWTH IN IRRADIATED MATERIALS

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ABSTRACT

A detailed theory of void formation and growth is presented and correlated to the appropriate accelerator measurements in nickel and steel. The complex dependence of the swelling phenomenon on the various physical and structural properties of the irradiated materials is discussed with particular emphasis on the various mechanisms that can prevent, slow down, or completely stop the swelling process.

Since the first observation of voids in neutron-irradiated stainless steel by Cawthorne and Fulton,¹ a great deal of effort has been directed toward understanding the various ways in which the physical and structural properties of irradiated solids can influence the formation and growth of such voids. Several theories of the consequent swelling phenomenon have been developed, both by ourselves^{2,3} and by other workers,⁴⁻⁶ and used to provide correlations with, and extrapolation of, existing experimental data. Although the theories differ from one another in detail, their basic explanation of the void-growth process is the same. It is that void embryos (be they tiny gas bubbles² or simply three-dimensional aggregates of vacancies created within the individual cascades⁴) will grow under conditions of continuous neutron irradiation if the temperature is appropriate and if another sink exists in the material, such as a dislocation, with a slight preference for interstitials. The original suggestion that such a bias could yield void growth was made, in a different context, by Foreman, Greenwood, and Rimmer,⁷ but was first specifically and quantitatively applied to the void-growth problem by Bullough, Eyre, and Perrin.² The purpose of this paper is both to present the results of our theoretical investigations and to relate our results specifically to the available accelerator observations on nickel and stainless steel. These results, together with a description of the general theoretical framework, are described in the next

section, and the comparison between theory and observations is made in the section titled "General Results and Comparison with Nickel and Steels." The final section is a general discussion in which attention is particularly focused on the various ways in which the swelling phenomenon can be controlled or inhibited.

THE THEORETICAL MODEL

The neutron irradiation ensures a constant production rate of vacancies and interstitials, say K fractional concentration, or displacements per atom (dpa) per second. For the quantity K to be relevant to the void-formation and -growth problem, it is essential that it represent the number of created point defects that can contribute to the mean steady-state point-defect concentration; that is to say, it does not include those point defects that have recombined during the formation of the cascade. The precise variation of the defect production per cascade as a function of the primary recoil energy is not yet known, and reliable estimates must await the development of acceptable damage-simulation programs.* In the absence of such reliable estimates, it is usual to obtain a crude estimate by a simple proportionate reduction of the Kinchin-Pease value; a typical value of K for the fast reactor is about 10^{-6} dpa/sec. Much higher dose rates—approximately 10^{-3} dpa/sec—may be achieved by simulating the neutron damage with accelerated ions; the effects of variations in dose rate on the damage processes and swelling are, of course, of considerable importance when we wish to relate the accelerator data to the reactor situation and are discussed below.

The first stage of the swelling process involves the nucleation and growth of interstitial dislocation loops. Once any such interstitial loop has formed, it has a characteristic dislocation strain field that causes a slight preferential drift⁹ of free interstitials to it and thus ensures its further probable growth. The vacancies may also aggregate, but, if the aggregate is platelike (a vacancy dislocation loop), it also will preferentially attract interstitials; the growth of such loops should therefore be inhibited. On the other hand, if, for some reason, the vacancies can form a three-dimensional aggregate, then the elastic field around such a tiny voidlike object will probably not be sufficient (see the final section) to cause any preferential drift effects. In this situation, since the average steady-state vacancy flux will be slightly greater than the interstitial flux (by virtue of the slight preferential loss of interstitials to the growing interstitial loops), any such tiny voids can receive a net flux of vacancies and thus possibly

*Such a program has recently been developed by Torrens⁸ and will be further refined in collaboration with the theoretical groups at Harwell and Oak Ridge.

grow into larger voids.* In practice, we believe that such a three-dimensional vacancy aggregate will only nucleate in the simultaneous presence of an adequate number of gas atoms.† If no gas atoms are present in the vacancy aggregate, it should always energetically collapse to form a small dislocation loop¹⁰; in fact, Bullough and Perrin¹⁰ have shown that the voidlike embryo must contain several thousand vacancies before the three-dimensional morphology is energetically favored. Furthermore, even if one ignores this energy argument, it is clear that, although such three-dimensional vacancy aggregates could possibly nucleate homogeneously from the background vacancy supersaturation, they would be far too small to grow and would rapidly disappear; this is because of the large surface tension force present (when the void is a few angstroms in radius) in the term defining the probability of vacancy emission from the void.

In discussing the void-growth process, we therefore begin with a concentration ρ_v of tiny embryonic voids that are probably gas bubbles of say 10 Å radius or slightly less. For mathematical simplicity, we divide the total body into spherical cells, each initially of radius R_0 , where

$$R_0 = 0.68\rho_v^{-1/3} \quad (1)$$

and each with a void of radius $r_v(0)$ at its center. The dislocation density ρ_d in the body arises both from the aggregation into dislocation loops of the irradiation-produced interstitials and from any dislocations either grown in or introduced by deliberate cold working. The actual spatial configuration of these dislocations will be extremely complex and can only be sensibly represented in any general sense as a continuous distribution of equivalent "point" sinks. The presence of the preferred drift between the dislocations and the interstitials may be included by giving the dislocation elements a slightly larger capture cross section for interstitials than for vacancies. The subsequent swelling may then be studied by following the growth of one such void when diffusion processes are permitted in the cellular region around it.

The Governing Equations

The coupled governing diffusion equations for the steady-state fractional vacancy and interstitial concentrations $C_v(r)$ and $C_i(r)$ in the spherical region around each void are

*It should be emphasized that swelling requires the formation of voids; if the vacancy aggregates were only in the form of vacancy dislocation loops, there would be negligible swelling.

†Certain other structural defects, such as small incoherent precipitates, will probably suffice as void-nucleation centers.

$$D_v \left(\frac{d^2 C_v}{dr^2} + \frac{2}{r} \frac{dC_v}{dr} \right) + K - \alpha_R C_v C_i - D_v Z_v \rho_d C_v = 0 \quad (2)$$

$$D_i \left(\frac{d^2 C_i}{dr^2} + \frac{2}{r} \frac{dC_i}{dr} \right) + K - \alpha_R C_v C_i - D_i Z_i \rho_d C_i = 0$$

where $r_v < r < R$ and the outer radius of the domain R strictly increases with time (dose) as r_v increases such that

$$R = R(t) = [R_0^3 + r_v^3(t)]^{1/3} \quad (3)$$

D_v and D_i are the vacancy and interstitial diffusion constants, respectively; α_R is the recombination coefficient; and Z_v and Z_i are numbers, the order of unity ($Z_i > Z_v$), which, respectively, characterize the vacancy and interstitial capture volumes associated with unit lengths of the dislocation lines. The outer boundary $r = R$ represents the interface midway between each void, and therefore simple zero-flow boundary conditions are appropriate:

$$\frac{dC_v}{dr} = 0 \quad \text{at } r = R \quad (4)$$

$$\frac{dC_i}{dr} = 0 \quad \text{at } r = R \quad (5)$$

At the void surface, we must have continuity of flux of both vacancies and interstitials; thus at $r = r_v$

$$D_v \frac{dC_v}{dr} = K_v [C_v - C_v^e \exp(F_m b^3/kT)] \quad (6)$$

$$D_i \frac{dC_i}{dr} = K_i C_i \quad (7)$$

where K_v and K_i are, respectively, the velocities of transfer of vacancies and interstitials across the void-matrix interface, C_v^e is the thermal equilibrium vacancy concentration, and b is a distance the order of the atomic lattice spacing; the quantity F_m is the mechanical force tending to shrink the void and has the explicit form

$$F_m = P + \frac{2\gamma}{r_v} - \frac{3NkT}{4\pi r_v^3} \quad (8)$$

where P is the applied hydrostatic compressive stress, γ is the surface energy, and N is the number of gas atoms present in the void. The term involving F_m in

Eq. 6 arises from the probability of vacancy emission from the void; the analogous term in Eq. 7, corresponding to the emission of interstitials from the void, may be neglected (interstitial formation energies are characteristically very large in metals of technological interest). The matrix at the void surface should not be very disturbed,* and therefore

$$K_v = D_v/b \quad (9)$$

and

$$K_i = D_i/b \quad (10)$$

The rate of change of the void radius is given by the net vacancy flux into the void; thus

$$\frac{dr_v}{dt} = \left(D_v \frac{dC_v}{dr} - D_i \frac{dC_i}{dr} \right)_{r=r_v} \quad (11)$$

which from Eqs. 6 and 7 may be written as

$$\frac{dr_v}{dt} = \frac{1}{b} [(D_v C_v - D_i C_i) - D_v C_v^e \exp(F_m b^3/kT)] \quad (12)$$

The general procedure is thus to solve the nonlinear pair of differential equations (Eq. 2) for $C_v(r)$ and $C_i(r)$ at some initial value of $r_v(0)$ and R_0 subject to the boundary conditions (Eqs. 4 to 7) and then to use these values of $C_v(r)$ and $C_i(r)$ in Eq. 12 to give the increase in r_v . The cycle is then repeated with the boundary conditions applied at the new values of r_v and R and with the updated value of F_m . A suitable numerical method has been developed which enables this iterative procedure to be followed accurately, and thus we have been able to calculate the variation of volume swelling ($\Delta V/V$) from the relation

$$\frac{\Delta V}{V} \equiv \frac{r_v^3}{R_0^3} \quad (13)$$

This definition of volume swelling is a consequence of the assumption that the change in volume is due entirely to the growth of existing voids and that void nucleation has finished. This rather restrictive assumption can be formally circumvented by superimposing an additional transient variation on $R(t)$. Such a

*The elastic strains are very small at the interface; however, the existence of an adsorbed impurity surface layer is not impossible, and in this case the values of K_v and K_i would have to be reduced below the ideal bulk values of Eqs. 9 and 10.

procedure is supported by the observation that, when the void density does show an increase with dose, the distribution of void radii is not large.* Before we present any of the numerical results and relate them to the observed swelling in various materials (see the next section), it is useful to first highlight the immediate conclusions we can draw from this model and to present an analytic solution that is valid for conditions of considerable physical interest. It is clear from Eq. 3 and the definition of volume swelling given by Eq. 13 that the transient variation of R may be safely ignored for swelling values less than 15%; the error is only 1.4% when $r_v = 0.5R_0$. We will therefore neglect the variation in the analytic treatment but always include it in the direct numerical solutions.

An Analytic Solution

To obtain an analytic solution of Eq. 2 requires that the nonlinear recombination term (set $\alpha_R = 0$) be dropped. Fortunately, as will be seen when we discuss the general numerical solutions, recombination effects are not usually important† at and beyond the temperature when maximum void growth occurs, and therefore the analytic solution can provide useful insight in a regime of direct technical interest. When $\alpha_R = 0$, the two governing equations completely decouple and can be solved independently. We find

$$\frac{dr_v}{dt} = \frac{(K - D_v Z_v \rho_d \bar{C})}{r_v Z_v \rho_d} L(\beta_v) - \frac{K}{r_v Z_i \rho_d} L(\beta_i) \quad (14)$$

where

$$L(\beta) = [(R - r_v)\beta \cosh \beta(R - r_v) + (r_v R \beta^2 - 1) \sinh \beta(R - r_v)] \\ [R\beta \cosh \beta(R - r_v) - \sinh \beta(R - r_v)] \quad (15)$$

$\beta = (Z\rho_d)^{1/2}$, and, for simplicity, we have replaced Eqs. 6 and 7 by their equivalent ideal sink forms

$$C_v = C_v^e \exp(F_m b^3/kT) = \bar{C} \quad (16)$$

$$C_i = 0 \quad (17)$$

These simple boundary conditions are quite accurate because K_v/D_v and K_i/D_i are very large ($\sim 10^7$ cm), and the concentration gradients must remain finite.

*We shall see later, particularly when the dislocation density is low (solution treated), that the kinetics are not very sensitive to changes in the void density.

†The kinetics are sensitive to recombination when the dislocation density is very low (see the next section).

Certain Limiting Dose Dependences

The differential equation (Eq. 14) for $r(Kt)$ has been previously integrated by elementary quadrature³; however, in view of our recent success in integrating the general nonlinear equations ($\alpha_R \neq 0$), we will not present the earlier results in detail but only insofar as they relate to certain explicit limiting solutions of Eq. 14, which, although valid only over a restricted dose range, do, nevertheless, clearly illustrate the dependence of the swelling on various important parameters. When the void radius r_v is much less than R , the void growth will be unaffected by the presence of the neighboring voids; if, also, the dislocation and void densities are such that

$$\rho_d R^2 \geq 1 \quad (18)$$

then Eq. 14 can be replaced by the simpler differential equation

$$\frac{dr_v}{dt} = \frac{(K - D_v Z_v \rho_d \bar{C})}{r_v Z_v \rho_d} \left(1 + r_v \beta_v \right) - \frac{K}{r_v Z_i \rho_d} \left(1 + r_i \beta_i \right) \quad (19)$$

At the peak swelling temperatures, where the self-diffusion term $D_v \bar{C}$ can be usually neglected, we find two useful limits that yield simple analytic expressions for the swelling:

One useful limit is

$$\rho_d r_v^2 < 1 \quad (20)$$

This is appropriate when the dislocation density is low [but not too low to violate (Eq. 18)] and when the total dose is not too large; Eq. 19 then yields

$$\frac{\Delta V}{V} = \left[\frac{2}{\rho_d} \left(\frac{1}{Z_v} - \frac{1}{Z_i} \right) \right]^{\frac{1}{2}} \frac{(Kt)^{\frac{1}{2}}}{R^3} \quad (21)$$

where we have omitted the explicit contribution to the volume change from the distribution of "small" voids at " $t = 0$ ".

The other limit of physical interest is

$$\rho_d r_v^2 > 1 \quad (22)$$

and is appropriate only when the dislocation density is very high; in this case, Eq. 19 can again be integrated to yield

$$\frac{\Delta V}{V} = \left[\frac{1}{\rho_d^{\frac{1}{2}}} \left(\frac{1}{Z_v^{\frac{1}{2}}} - \frac{1}{Z_i^{\frac{1}{2}}} \right) \right]^3 \frac{(Kt)^3}{R^3} \quad (23)$$

where again we have omitted the "initial" swelling.

To give an idea of the specific validity of these expressions, we see that, when the void density $\rho_v = 10^{15}$ voids/cm³, the dislocation density ρ_d must be greater than or equal to 10^{10} lines/cm². When $\rho_d > 10^{10}$ lines/cm², Eq. 21 is valid over most of the total swelling range, and Eq. 23 can only describe a significant part of the total swelling if ρ_d approaches 10^{12} lines/cm². We thus expect that, for moderate dislocation densities, the swelling will usually increase proportional to (dose)^{1.5}.

When the dislocation density is low, so that

$$\rho_d R^2 \ll 1 \quad (24)$$

(in the above example with $\rho_v = 10^{15}$ voids/cm³, ρ_d must be $< 10^{10}$ lines/cm²), we can expand the right-hand side of Eq. 18 for small arguments in the hyperbolic functions, and we find, when r_v is much less than R , that

$$\frac{\Delta V}{V} = \left[\frac{4}{9} \rho_d R^2 (Z_i - Z_v) \right]^{3/4} (Kt)^{3/4} \quad (25)$$

where we have again omitted the initial swelling and the self-diffusion term has been dropped.

Thus we conclude that, in the vicinity of the peak swelling temperature, the dose dependence of the swelling will be a rather sensitive function of the dislocation density and void density. The analytic power law will be a minimum of (dose)^{0.75} for low dislocation density rising to (dose)^{1.5} for moderate dislocation density up to the fastest variation of (dose)³ for very high dislocation density.

Dose Dependence of Swelling at Peak Temperature

The accurate dose dependence of the swelling, obtained by numerically integrating Eq. 14 for the peak swelling temperature,* is shown in Fig. 1 for void densities of $\rho_v = 10^{15}$ voids/cm³ and 5×10^{15} voids/cm³ and various dislocation densities; Z_v and Z_i have been set equal to 1.00 and 1.01, respectively. This 1% difference between Z_i and Z_v may be justified by relating the present model to an earlier discussion of the problem² which included the drift interaction between the interstitials and the dislocations in an explicit spatial fashion. By comparison with the "drift" parameters of that work, we find it necessary to take $Z_i - Z_v \simeq 0.016$; we therefore shall always restrict $Z_i - Z_v$ to the range

*The self-diffusion terms have been omitted, and in consequence, with them, the temperature dependence of the swelling. The full numerical solution is discussed in the next section when such features are included.

Fig. 1 The kinetics of void swelling when $Z_v = 1.00$, $Z_i = 1.01$ for various void and dislocation densities. —, void density $\rho_v = 10^{15}$ voids/cm³. ---, void density $\rho_v = 5 \times 10^{15}$ voids/cm³. ρ_d is the dislocation density in lines per square centimeter. Experimental void-growth kinetics for nickel for various high dose rates are also shown. x, $K = 6 \times 10^{-5}$ dpa/sec. +, $K = 2 \times 10^{-4}$ dpa/sec. ●, $K = 2 \times 10^{-3}$ dpa/sec.

$$0.01 \leq Z_i - Z_v \leq 0.02 \quad (26)$$

and take Z_v to be unity.

Several general features of the dose dependence of the swelling which are clearly indicated in Fig. 1 are given below.

1. All the kinetics are independent of dose rate—a fact which is evident from Eq. 14 (with $\bar{C} = 0$).

2. The dose dependence does indeed vary between $(\text{dose})^{0.75}$ to almost $(\text{dose})^3$ in accord with the analytic results (Eqs. 21, 23, and 25). Furthermore, if we compare the low ρ_d curves ($\rho_d = 10^{10}$ lines/cm²) with the higher ρ_d curves ($\rho_d = 5 \times 10^{11}$ lines/cm²), the relative behavior is precisely as expected from Eqs. 21 and 25. The low ρ_d curves have a lower slope (on a log-log plot) than the higher ρ_d curves, and increasing the void density ρ_v in the former case causes a small decrease (for doses greater than 1 dpa) in the swelling, in agreement with Eq. 25 (note $R = 0.68\rho_v^{-1/3}$), whereas an increase in ρ_v in the latter case

($\rho_d = 5 \times 10^{11}$ lines/cm²) causes a linear increase in the swelling, in perfect agreement with Eqs. 21 and 23.

3. Cold work causes a substantial reduction in the swelling at low doses but eventually causes the swelling to increase with a higher power of dose. At very high dose the advantages of cold work are substantially lost.

4. We have also included some experimental swelling kinetics¹¹ observed in nickel irradiated with C^{2+} ions in the Harwell Variable Energy Cyclotron (VEC) at 525°C. These results and their detailed relation to the theory will be discussed in detail in the next section. We have included them in Fig. 1 to demonstrate that the simple result (Eq. 14) does predict a dose dependence that is really quite close to the observed variation and has a minimum of adjustable parameters; the curves depend only on ρ_v, ρ_d and Z_i, Z_v but not on K or the point defect mobilities, etc. We now turn to the general results, including the temperature and dose-rate dependence of the various solutions of the governing nonlinear equations (Eq. 2).

GENERAL RESULTS OF VOID GROWTH AND COMPARISON WITH NICKEL AND STEELS

To illustrate the general features of void growth and at the same time to give our discussion specific validity, we will first employ the physical parameters appropriate to nickel, which are given in Table 1. The parameters we consider to

TABLE 1
ASSUMED PHYSICAL PARAMETERS FOR NICKEL AND STAINLESS STEEL

Conditions: $D_v = D_v^0 \exp(-E_v^m/kT)$, $D_i = D_i^0 \exp(-E_i^m/kT)$, $C_v^e = \exp(-E_v^f/kT)$

	D_v^0 , cm ² /sec	E_v^m , eV	D_i^0 , cm ² /sec	E_i^m , eV	E_v^f , eV	$\alpha R/D_i$	Z_v	Z_i
Nickel	0.19	1.00	0.008	0.15	1.77	10^{17}	1.00	1.01
Stainless steel	0.58	1.40	0.001	0.20	1.60	10^{17}	1.00	1.02

be appropriate to stainless steel are also given in the table and will be used later to discuss some of the rather puzzling swelling features observed in the steels. Our initial emphasis on nickel is made solely because in that metal we do have sufficient reliable VEC observations¹¹ to enable the theory to be rigorously tested; it is basically a simpler material than the steels. A match between theory and measurement can be made in nickel without having to guess the effects of precipitates (coherent or incoherent) on the overall recombination or on the ability of dislocations to accept point defects, etc. We shall see that an

explanation of the swelling behavior of steel must involve such "arbitrary" processes.

Our general numerical method for integrating the governing nonlinear equations (Eqs. 2) enables us to include, if we wish, the actual observed variations of ρ_v and ρ_d with dose and temperature. However, these variations will only be included when we wish to make a specific comparison with experiment; they are often so complex that they only obscure the basic physical processes prevailing during the void-growth regime, and it is the significance of just these processes that we wish to highlight. The temperature variation and the kinetics of the volume swelling $\Delta V/V$ have all been obtained by starting the integration of Eq. 2 with a certain ρ_v and ρ_d (which then may or may not remain constant) and with an average void radius $r_v = 10 \text{ \AA}$. Neither the nucleation regime nor the restraint due to the surface tension forces or the gas pressure in Eq. 8 have been explicitly included. If further nucleation of the voids does occur, it is included in our integration analysis by directly changing R but leaving the average void radius invariant; thus any new void is supposed to grow very rapidly up to the size of the average void radius before it appeared. Conversely, if ρ_v decreases because of void coalescence at very high doses, then in this case we adjust both R and r_v to conform with the drop in ρ_v and to maintain the swelling at its value just prior to the coalescence.

In Fig. 2 we show the theoretical temperature dependence of swelling in nickel for three different dose rates; $2 \times 10^{-3} \text{ dpa/sec}$ corresponds to the highest VEC dose rate and the lowest one of $6 \times 10^{-5} \text{ dpa/sec}$ most nearly to the reactor situation. For consistency with the VEC observations in nickel,¹¹ ρ_v has been maintained constant at $10^{15} \text{ voids/cm}^3$, and ρ_d has been varied with dose. The observed ρ_d variation with dose is rather complex, with a maximum at a dose of 60 dpa of $5.4 \times 10^{10} \text{ lines/cm}^2$; the overall temperature variation is, however, very similar to a constant ρ_d of $10^{10} \text{ lines/cm}^2$. The three curves shown are all for a total dose of 100 dpa. Several interesting features that may be noted are given below.

1. All the curves have a definite maximum, and, with increasing dose rate K , the curves are simply shifted to higher temperatures. Thus, there is exactly a 100°C temperature shift in going from the low $K = 6 \times 10^{-5}$ to the high $K = 2 \times 10^{-3} \text{ dpa/sec}$. It follows that the VEC experiments, with their relatively high dose rate, must be performed at appropriately higher temperatures than the reactor environment they are intended to simulate.

2. The reduction in swelling at the low temperatures is entirely due to the presence of recombination, and the reduction in swelling at a given temperature with increasing dose rate indicates that the equilibrium concentrations of vacancies and interstitials also increase with dose rate with a consequent increase in the proportionate loss of defects by recombination. The actual variation of the steady-state vacancy and interstitial concentration is shown in Fig. 3, where the very rapid rise of C_v at low temperatures is apparent.

Fig. 2 The theoretical temperature dependence of swelling in nickel for dose rates of 6×10^{-5} , 2×10^{-4} , and 2×10^{-3} dpa/sec. The curves shown are all for a total dose of 100 dpa, a void concentration of 10^{15} voids/cm³, and a dose-dependent dislocation density as observed in the irradiated nickel which increases from 0.5×10^9 lines/cm² at a dose of 0.2 dpa to 5.4×10^{10} lines/cm² at a dose of 60 dpa and then decreases very rapidly back to 0.5×10^9 lines/cm² at a dose of >200 dpa.

3. The reduction in swelling at high temperatures is caused by the eventual dominance of the self-diffusion term $D_v C_v^e$ in Eq. 12. As we increase the temperature, the steady-state vacancy concentration arising from the irradiation will decrease and eventually become comparable with, and then less than, the increasing equilibrium vacancy concentration; in this final situation, at temperatures beyond the peak swelling temperature, void growth is thus impossible. Clearly, when the dose rate is high, the vacancy and interstitial concentrations are relatively high, and the eventual dominance of the self-diffusion term is moved to a higher temperature.

To demonstrate the effect of cold work on the temperature variation of swelling, we show in Fig. 4 the corresponding theoretical dose-rate curves for a constant dislocation density of 5×10^{11} lines/cm². The dislocation density is assumed constant purely for reasons of simplicity—there are no observations on cold-worked nickel. Again the void density is 10^{15} voids/cm³, and the total dose is 100 dpa.

Fig. 3 The initial steady-state vacancy (C_v) and interstitial (C_i) concentrations in nickel for two constant dislocation densities ($\rho_d = 10^{10}$ and 5×10^{11} lines/cm²). The equilibrium vacancy concentration C_v^e is also shown.

The temperature shift caused by the variation in dose rate is again apparent and is very similar to the lower dislocation-density situation in Fig. 2. However, cold work has caused almost a 60°C shift of all the curves to lower temperatures and has reduced the peak swelling from about 16 to 5% at this fairly high dose. It has also considerably broadened the temperature range of maximum swelling by reducing the effect of recombination; this reduction has occurred simply because the overall swelling has dropped—the dislocations are not only biasing the system but are also removing a large proportion of the total point defects, and in this situation swelling is reduced and the relative loss by recombination must be reduced.

The theoretical swelling kinetics for nickel at 525°C are given in Fig. 5, where we have included the observed dose dependence of ρ_d in the numerical integration and a constant value of $\rho_v = 3 \times 10^{15}$ voids/cm³*; this variation is described in the caption to Fig. 2. The experimental points for the highest dose rate of 2×10^{-3} dpa/sec (as previously given in Fig. 1) are again given for comparison. The rather sudden reduction in the swelling at about 100 dpa is certainly due to the corresponding drop in the dislocation density ρ_d at this dose. The physical reason for this drop and other saturation mechanisms will be discussed in the next section.

*There was no clear change in the void density with dose in nickel, apart from a slight drop due to void coalescence at very high doses; the constancy of ρ_v may be due to the predoping procedure used to get gas into the accelerator specimens.¹¹

Fig. 4 The theoretical temperature dependence of swelling in nickel for dose rates of 6×10^{-5} , 2×10^{-4} , and 2×10^{-3} dpa/sec. The total dose is 100 dpa, and the dislocation density is constant at 5×10^{11} lines/cm²; the void concentration is 10^{15} voids/cm³.

The situation in the steels appears to be quite different. In solution-treated 316 stainless steel, the void density is very low (2×10^{14} voids/cm³) at a dose of 5 dpa, rises to a maximum value of about 2×10^{16} voids/cm³ at 40 dpa, and then falls to 5×10^{14} voids/cm³ at 500 dpa.¹² The rise is presumably due to the continuous nucleation of voids, and the subsequent fall must be due to void-void coalescence. The dislocation-density variation with dose in steel is also quite different from the variation in nickel. The observed dislocation density begins to rise rapidly at a dose of 5 dpa up to a maximum density of 2×10^{11} lines/cm² at 40 dpa. However, in contrast to the nickel behavior, the density then remains at this high value, and the rapid decrease observed in nickel is not seen. The dislocations in steel appear to be very strongly pinned (probably by carbon); however, we have, nevertheless, used our general numerical procedure to include the observed variations of ρ_v and ρ_d in our theory, and the resulting kinetics are shown in Fig. 6; the parameters for steel given in Table 1 have been used, the dose rate is 2×10^{-3} dpa/sec, and the temperature is 525°C.

The experimental points¹² for solution-treated 316 stainless steel irradiated with 20-MeV C²⁺ ions at the same dose rate are also given. The agreement between the theoretical curve and the observation is reasonable until the

Fig. 5 The theoretical kinetics of swelling for nickel (Table 1) at a temperature of 525°C for a dose-dependent dislocation density, a void concentration of 3×10^{15} voids/cm³, and a dose rate of 2×10^{-3} dpa/sec. The corresponding VEC experimental points for nickel obtained at the same dose rate are also shown.

experimental points show a strong saturation in the swelling (at a dose ~ 100 dpa). The theoretical curve certainly shows a decreasing rate of swelling, due to the drop in the void concentration, but does not explain the almost complete saturation observed. There are several possible saturation mechanisms that could explain this observation, and, in the next section, we will highlight some of these and discuss their possible role in the different materials.

GENERAL DISCUSSION

Clearly, because so many different and often ill-defined factors contribute to the phenomenon of void growth, it is unlikely an all-embracing theoretical model can usefully be constructed. However, we do believe that a theoretical study is, nevertheless, useful. Furthermore, particularly by closely associating its contents and assumptions with the quantitative VEC or similar work, the study has proved possible to at least identify the physical parameters that must be playing a significant role in any particular material. Thus, although it is not really possible to confidently predict the quantitative swelling behavior of

Fig. 6 The theoretical kinetics of swelling for solution-treated steel (Table 1) at 525°C. The dose rate is 2×10^{-3} dpa/sec. The observed dose dependence of the dislocation density and the void density has been included in the theoretical curve. The corresponding VEC experimental points for steel obtained at the same dose rate are also shown.

“new” reactor materials without some observational guidance, it is possible to highlight some of the factors that could prevent, stop, or retard void growth.

The Effects of Stress

The effect of stress on swelling is of considerable technological importance. When an external hydrostatic compression is applied to a perfect body, the equilibrium vacancy* concentration is reduced to

$$C_V^e(P) = C_V^e(0) \exp(-Pb^3/kT) \quad (27)$$

where b^3 represents the vacancy activation volume. Thus the boundary condition in Eq. 6 is not affected when P is nonzero; the positive P term in F_m (Eq. 8) cancels the negative P term in $C_V^e(P)$. In other words, because the void

*The equilibrium interstitial concentration is usually increased since the interstitial activation energy is usually negative. However, for most technologically significant materials, the stress-free equilibrium interstitial concentration is negligible, and its variation with stress is irrelevant.

surface is stress free, the equilibrium vacancy concentration at the void interface will be the stress-free equilibrium value. In the irradiation situation the concentration midway between the voids is *not* the equilibrium value (Eq. 27), it is defined by the irradiation dose rate and the various loss processes via the zero flow conditions (Eqs. 4 and 5). It follows, if the point defect production rate is not significantly affected by stress, that an external hydrostatic stress will not affect void growth; it will, of course, affect any postirradiation annealing of voids since in that situation the average vacancy concentration away from the voids would be given by Eq. 27 and thus a compressive stress would cause void shrinkage.

To complete our brief discussion of the significance of hydrostatic pressure on swelling it is clear that, if the migration volumes of the point defects are appreciable, the application of pressure could modify the void-growth kinetics. However, these kinetics are only sensitive to the defect diffusion constants away from the peak swelling temperature; that is, when recombination is important. Since the migration volumes are completely unknown (the interstitial-migration volumes are probably negligible) and since the effect of pressure at the peak swelling temperature is probably the most important technological consideration, we will not discuss this effect further. We now turn to consider what is probably a more important effect, namely, the effect on swelling of a uniaxial stress.

Let us consider a void of radius r_v with its center at the origin of the spherical polar coordinate system (r, θ, ψ) and subject to a uniaxial compression T , as shown in Fig. 7; it is convenient to take $T > 0$ as a compressive stress. It is easily shown that such an applied stress creates the hydrostatic field p_h in the neighborhood of the void¹³

$$p_h = -\frac{T}{3} - \frac{5Tr_v^3(1+\nu)}{3(7-5\nu)} \frac{(1-3\cos^2\theta)}{r^3} \quad (r \geq r_v) \quad (28)$$

This spatially varying hydrostatic field will interact preferentially with the interstitials and thus tend to negate the analogous preferential effect of the hydrostatic field of the dislocations. In fact, the elastic field given by Eq. 28 (excluding the irrelevant constant term $-T/3$) has exactly the same spatial form as the elastic field around a circular pure edge dislocation loop⁹ and therefore can cause the void growth to terminate, when the void density, radii, and magnitude of T are appropriate.

If the interstitial has an associated dilation ϵ , the interaction energy between the stress field (Eq. 28) and an interstitial is¹⁴

$$E = -\epsilon p_h \frac{4}{3} \pi r_0^3 \quad (29)$$

where r_0 is the "effective radius" of the interstitial. With Poisson's ratio equal to $\frac{1}{3}$, this has the explicit form

$$E = 1.396r_0^3\epsilon T + 1.745Tr_v^3r_0^3\epsilon(1 - 3\cos^2\theta)/r^3 \quad (30)$$

Note, when $r = r_v$,

$$E = Tr_0^3\epsilon[1.396 + 1.745(1 - 3\cos^2\theta)] \quad (31)$$

Fig. 7 The various coordinates associated with the spherical void of radius r_v .

This is negative over the two "polar regions" shown in Fig. 8; that is, interstitials are attracted into the void over these regions and repelled from the remaining surface of the void. This situation may be compared to the interaction energy between a positive straight edge dislocation and an interstitial; in that case the interstitials are attracted to the region below the slip plane (tensile region) and repelled from the region above the slip plane (compressive region).

When $E(r, \theta)$ is the interaction energy between the void and an interstitial, the drift velocity of the interstitial will be¹⁵

Fig. 8 The two "polar" zones of interstitial attraction associated with a void under axial compression.

$$v = \frac{D_i}{kT} \text{grad } E \quad (32)$$

and therefore

$$\begin{aligned} \text{div } C_i v = \frac{D_i}{kT} \left[C_i \left(\frac{\partial^2 E}{\partial r^2} + \frac{2}{r} \frac{\partial E}{\partial r} + \frac{\cot \theta}{r^2} \frac{\partial E}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2 E}{\partial \theta^2} \right) \right. \\ \left. + \frac{\partial C_i}{\partial r} \frac{\partial E}{\partial r} + \frac{1}{r^2} \frac{\partial C_i}{\partial \theta} \frac{\partial E}{\partial \theta} \right] \end{aligned} \quad (33)$$

If

$$E = A + B(1 - 3 \cos^2 \theta)/r^3 \quad (34)$$

where A and B are given by Eq. 30, then

$$\text{div } C_i v = \frac{3D_i B}{kTr^4} \left[-\frac{\partial C_i}{\partial r} (1 - 3 \cos^2 \theta) + \frac{1}{r} \frac{\partial C_i}{\partial \theta} \sin 2 \theta \right] \quad (35)$$

We can now include this further interstitial-loss term in the general form of the void-swelling differential equations given in Eq. 2.

The interstitial equation becomes

$$D_i \nabla^2 C_i - \alpha_R C_v C_i - D_i Z_i \rho_d C_i + K - \frac{3D_i B}{kTr^4} \left[-\frac{\partial C_i}{\partial r} (1 - 3 \cos^2 \theta) + \frac{1}{r} \frac{\partial C_i}{\partial \theta} \sin 2 \theta \right] = 0 \quad (36)$$

The vacancy equation is, as before,

$$D_v \nabla^2 C_v - \alpha_R C_v C_i - D_v Z_v \rho_d C_v + K = 0 \quad (37)$$

The appropriate boundary conditions on $r = r_v$ are, from Eqs. 16 and 17,

$$C_v(r_v, \theta) = C_v^e(0) \exp (2\gamma \Omega_v / r_v kT) \quad (38)$$

and

$$C_i(r_v, \theta) = 0 \quad (39)$$

with zero flow conditions midway (at $r = R$) between the voids

$$\frac{\partial C_v}{\partial r}(R, \theta) = 0 \quad (40)$$

and

$$\frac{\partial C_i}{\partial r}(R, \theta) + \frac{3B}{kT} C_i(R, \theta) \frac{(1 - 3 \cos^2 \theta)}{R^4} = 0 \quad (41)$$

This two dimensional nonlinear flow problem is at present under investigation.

It is probably legitimate¹⁵ to simplify this problem by dropping the θ dependence in the interaction energy (Eq. 34) and replacing it by an effective—purely radial—attractive energy

$$E = A - G/r^3 \quad (42)$$

where the relative values of G and B can be found by ensuring an identical loss to the void by *drift* alone. We find that

$$G \simeq B/10 \quad (43)$$

With the purely radial interaction given by Eq. 42, the governing equations revert to their previous one-dimensional form with a simple additional term in the interstitial equation:

$$D_v \left(\frac{d^2 C_v}{dr^2} + \frac{2}{r} \frac{dC_v}{dr} \right) + K - \alpha_R C_v C_i - D_v Z_v \rho_d C_v = 0 \quad (44)$$

$$D_i \left(\frac{d^2 C_i}{dr^2} + \frac{2}{r} \frac{dC_i}{dr} \right) + K - \alpha_R C_v C_i - D_i Z_i \rho_d C_i - \frac{3D_i G}{kTr^4} \left(-\frac{dC_i}{dr} + \frac{2C_i}{r} \right) = 0 \quad (45)$$

with the boundary conditions, at $r = r_v$,

$$\left. \begin{aligned} C_v &= C_v^e(0) \exp(2\gamma\Omega_v/r_vkT) \\ C_i &= 0 \end{aligned} \right\} \quad (46)$$

and, at $r = R$,

$$\left. \begin{aligned} \frac{dC_v}{dr} &= 0 \\ \frac{dC_i}{dr} + \frac{3C_i G}{kTR^4} &= 0 \end{aligned} \right\} \quad (47)$$

The problem is thus to solve Eqs. 44 and 45 subject to Eqs. 46 and 47 and thus to obtain the steady-state concentrations $C_v(r)$ and $C_i(r)$ in the region $r_v \leq r \leq R$. This simpler problem is also under detailed investigation. A crude estimate of the significance of this effect can be obtained by ignoring diffusion flow and using a pure drift analysis to estimate the stress magnitude needed to stop void growth. We find that void growth will cease when

$$T/\mu \geq 2.4(\rho_L/\rho_v)^{2/3} br_L^2/r_v^2 \quad (48)$$

where ρ_L is the dislocation-loop density and r_L is the average dislocation-loop radius. This result indicates, for example, that, if $\rho_d = 10^{10}$ lines/cm² and $\rho_v = 5 \times 10^{15}$ voids/cm³, then T need only exceed $\mu \times 10^{-4}$ to stop the growth

of 200-Å-radius voids which corresponds to a maximum swelling of about 12%. A higher stress would, of course, curtail the swelling at a lower value.

Thus we conclude:

1. Hydrostatic pressure will not affect swelling during irradiation but will certainly influence any postradiation-annealing kinetics. At temperatures higher than the peak temperature, such stresses will be important, even during irradiation, since the steady-state vacancy concentration will not deviate appreciably from its equilibrium value.

2. Uniaxial stress will cause a drift flow of interstitials to the voids which could, under appropriate conditions, compensate for the preferential loss of interstitials to the dislocations. To quantitatively study this effect, one must include the diffusion flow (in addition to the drift flow), and the problem is at present under investigation.

The Effect of Precipitates

It is clear from Fig. 1 that cold work (high ρ_d) causes a substantial reduction in the swelling at a given dose; the effect is caused by the total loss of point defects to the dislocations dominating the increased bias effect. As the swelling increases, so does the net loss to the voids, and the greater the net loss of point defects to the voids, the greater will be the bias effect; the high ρ_d causes a relatively high excess of vacancies. Thus at high doses we expect the voids in cold-worked materials to grow more rapidly than in the corresponding low ρ_d situation. However, the lower dose advantage of the cold-worked material can obviously be retained to higher dose if we introduce a high concentration of neutral sinks (like the voids but without their unfortunate consequences) such as coherent precipitates. If the precipitates are incoherent, the point defects identity will be lost when they get to the precipitate-matrix interface, and thus such precipitates could obviously provide very good void nuclei—to no good advantage. On the other hand, a coherent precipitate might enable the arriving point defects to be merely trapped at the interface but yet retain their point defect identity; in other words, they are then "sitting ducks" for recombination. A large increase in recombination would certainly greatly reduce swelling. Such neutral (recombination) sinks can easily be introduced into the general field equations (Eq. 2), and an analytic condition for the complete cessation of void growth can be deduced. We find that, if C_p is the concentration of such precipitates per cubic centimeter, Z_p is the number of sites on the surface of each precipitate, and b is the jump distance, the solution given in Eq. 14 can be generalized to

$$\frac{dr_v}{dt} = \frac{(K - D_v \bar{\beta}_v \bar{C})}{r_v \bar{\beta}_v^2} L(\bar{\beta}_v) - \frac{K}{r_v \bar{\beta}_1^2} L(\bar{\beta}_1) \quad (49)$$

where

$$\begin{aligned}\bar{\beta}_v &= (Z_v \rho_d + b Z_p C_p)^{1/2} \\ \bar{\beta}_i &= (Z_i \rho_d + b Z_p C_p)^{1/2}\end{aligned}\quad (50)$$

It is clear, since Z_v and Z_i are approximately unity, that swelling will not be possible if

$$b Z_p C_p \gtrsim 10 \rho_d \quad (51)$$

the dominant loss process will then be to the neutral precipitate sinks. This simple argument is only meaningful when ρ_d is reasonably large ($\gtrsim 10^{10}$ lines/cm²) since the analytic solution has neglected recombination, which can certainly dominate when ρ_d is low. If the precipitates are roughly spherical with an average radius r_p , then the condition given by Eq. 51 can be written as

$$r_p^2 C_p \gtrsim b \rho_d \quad (52)$$

In PE16 steel (solution treated, aged, and irradiated at 525°C to a dose of 60 dpa) electron-microscope examination indicates that $r_v \sim 60$ Å, $C_p \sim 2 \times 10^{16}$ precipitates/cm³, and $\rho_d \sim 5 \times 10^{11}$ lines/cm². It is clear from Eq. 52 that the observed very low swelling in such steels could certainly be due to the nonbiased loss of point defects at the precipitates. In addition, of course, the presence of such a high concentration of precipitates could also pin the dislocations and perhaps inhibit their ability to accept the point defects, thus further emphasizing the significance of the precipitates.

Dislocation-Depletion Effect

We have commented in the previous section that saturation almost certainly occurs in nickel because the dislocation density suddenly falls at a dose of about 100 dpa. This drop in ρ_d occurs at the high dose because the voids have grown to a sufficient size to present an appreciable free surface to the surrounding dislocations. Dislocations suffer an attractive "image" interaction with a free surface, and therefore, if the dislocations are free to climb and glide, each void should have a denuded zone around it. Clearly, as the voids grow, the denuded zones will eventually begin to appreciably overlap, and the effective dislocation density will then suddenly drop (as observed) with a consequent saturation in the swelling. This image interaction has been discussed in detail by Willis and Bullough¹⁶ who have an exact solution for the climb and glide force on a dislocation loop adjacent to a spherical void. They concluded that the annular denuded zone should increase with void radius and should reach the plane surface value of about 200 Å when the void radius exceeds about 400 Å. In fact, with reasonable values for the critical glide stress, the shear modulus, and for

$\rho_v = 5 \times 10^{15}$ voids/cm³, the presence of such a depleted zone should cause the swelling in nickel to saturate at about 12%, which is reasonably consistent with the available accelerator data on nickel.¹¹

The Void-Interstitial Interaction

It has been suggested by Makin¹⁷ that a weak intrinsic attractive force exists between an interstitial and a void which, although small, is sufficiently large to be the cause of eventual saturation when the voids have grown and are the dominant point-defect sinks. Makin has also invoked this idea to explain the filling in* of voids near the foil surfaces in the high-voltage electron microscope.

The magnitude of this interaction has been effectively discussed by Willis and Bullough¹⁸ in their general treatment of the bubble-bubble interaction in an isotropic body. The point defect can be quite well simulated by a set of three equal orthogonal double forces (see, for example, the work of Bullough and Hardy¹⁹ and Bullough, Norgett, and Webb²⁰); the resulting displacement field is purely radial with the form:

$$u = -\frac{P_d(1-2\nu)}{8\pi\mu(1-\nu)} \frac{1}{r^2} \quad (53)$$

where P_d is the strength of the double forces appropriate to the point defect. An estimate of the magnitude of P_d for a point defect can be obtained using the lattice-statics method of Kanzaki²¹ which was developed by Bullough and Hardy¹⁹; for example, for a vacancy in copper,¹⁹ $P_d = 7.5 \times 10^{-12}$ dyne/cm.

When the point defect gets close to the void surface, it will eventually interact with the void in the same manner as it would with a plane free surface. This short-range interaction has the explicit form²²

$$E_{\text{int}} = -\frac{(5\nu-1)(1-2\nu)^2}{48\pi\mu(1-\nu)^2} \frac{P_d^2}{\ell^3} \quad (54)$$

where ℓ is the distance from the point defect to the void surface. This expression is only valid when $a_0 < \ell < r_v$, where a_0 is a distance of the order of the lattice parameter. The resulting force F attracting the point defect to the free surface is

$$F = -\frac{dE_{\text{int}}}{d\ell} = \frac{(5\nu-1)(1-2\nu)^2}{16\pi\mu(1-\nu)^2} \frac{P_d^2}{\ell^4} \quad (55)$$

*This effect could be due to contamination of the foil surface, preventing the loss of interstitials there.

For $\mu = 5 \times 10^{11}$ dynes/cm², $\nu = 1/3$, and $P_d = 7.5 \times 10^{-12}$ dyne/cm, we find

$$E_{\text{int}} = -\frac{7.74 \times 10^{-26}}{\ell^3} \text{ eV}, \quad F = \frac{3.72 \times 10^{-37}}{\ell^4} \text{ dyne} \quad (56)$$

and in the range of validity of Eq. 54 the interaction energy and the attractive force are extremely small and only significant at all when $\ell = a_0 \approx 2.5 \times 10^{-8}$ cm.* Even though the appropriate strength factor P_d may be slightly larger for the interstitial than for the vacancy, it still seems somewhat unlikely that this *very* weak attraction could play a significant role in the saturation phenomenon.

A more likely interstitial-void interaction† and one which is conceivably responsible for the saturation in the steels, when the dislocation density does not fall adjacent to the voids, arises because the dislocations near a void will induce a dislocation image field inside the void, and this image field will then exert a force on the nearby interstitials and cause them to drift into the voids. The important point is that this force will clearly be comparable with the relatively large force between the actual dislocations and the interstitials and thus should certainly be significant.

Saturation by Forming a Void Lattice

The formation of a regular body-centered cubic (bcc) void lattice has been observed in molybdenum after nitrogen-ion or neutron irradiation. This void lattice, which is orientated precisely parallel to the underlying molybdenum atomic lattice, must have formed as a direct consequence of the noncentral elastic interaction energy between pairs of voids in such an anisotropic (cubic) body. In fact, Malén and Bullough²³ have recently discussed the stability and dimensions of this lattice and have provided a satisfactory explanation of its existence. It is clear that, once such a lattice has "crystallized" into existence, further incorporation of vacancies into the voids will be restrained by the (theoretical) demand that a constant ratio of void lattice spacing to void radius must be maintained to minimize the total lattice energy. In molybdenum, this ratio is approximately 10, which corresponds to an overall swelling of less than 1%; thus the presence of such a restraint could usefully enhance the potential viability of molybdenum as a reactor material. It should be emphasized that such a lattice phenomenon can only occur in metals whose elastic anisotropy is appropriate; the refractory metals Mo, Nb, Cr, and V are all peculiarly satisfactory in this respect.

*In any case the elastic continuum treatment clearly fails when the separation is down to these "atomic dimensions."

†Suggested to the authors by Dr. J. R. Willis.

Note Added in Proof

Recent calculations by Tewary and Bullough [*J. Phys., F (London)*, to appear] indicate that, when the voids are faceted, this anisotropy condition is not a necessary prerequisite for the existence of a void lattice. They have also given an explanation of its observed high thermal stability.

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DISCUSSION BY ATTENDEES

Brudnoy: Do you discount entirely the results of the simulation studies with regard to the growth of voids from cascades? On what do you base your physical model? Where do you get your physical parameters?

Bullough: No, I think they are valuable insofar as they provide an estimate of the available point defects. However, I doubt if many voids actually nucleate within the cascades, and thus the detailed structure of the cascade may not be too relevant at these high temperatures. The basis of the physical model was really the point of my entire paper, so I can hardly respond to this question!

Seeger: I am quite concerned about the values that you used to characterize vacancies in nickel. The vacancy-formation energy you use (1.77 eV) would lead to a melting-point concentration of vacant sites in nickel which is at least an order of magnitude lower than has been established in any other metal. As a consequence, the vacancy-migration energy that you have been using (1.0 eV) is much too low, and the monovacancy diffusivity that you used is too high. There is strong evidence that monovacancies in nickel diffuse by an order of magnitude slower than you assumed. The reason this does not have disastrous effects for the comparison between experiment and theory is, in my opinion, that this error is partially compensated by a second one, namely, the neglect of divacancies. At the vacancy concentrations and supersaturations you consider, the divacancies make a quite large contribution to the diffusivity of vacant sites. It appears feasible that they bring up the diffusivity to something of the order of magnitude you used in your computation, but its concentration dependence will be quite different from the concentration independence you assumed.

Bullough: I agree with Dr. Seeger that a vacancy-formation energy of 1.77 eV implied a rather low equilibrium vacancy concentration at the melting point for nickel. However, it is certainly not lower than "any other metal"; several of the refractory metals have a similar high formation energy. The choice

of value for the vacancy-migration energy of 1.0 eV arose from the assumption that stage III in nickel involves the motion of monovacancies. The interpretation of this stage is, of course, controversial; it is either a monovacancy stage or the second interstitial stage; it cannot be a divacancy stage since the stage is found under conditions when the divacancy concentration is negligible. In aluminum, platinum, and gold, stage III is definitely a monovacancy stage, whereas in copper, silver, and nickel, it must be admitted there is considerable doubt. However, there is evidence for vacancy clustering at temperatures just above stage III in copper, and the work of Bournet and Dautreppe indicates the presence of vacancy clusters in nickel at such temperatures. Thus, in view of the present uncertainty, we choose to adopt the simple view that monovacancies are mobile in stage III. To refer to this assumption as an error is, we believe, a rather extreme attitude.

Wiedersich: The steep and defect-production-rate (atom fraction of displaced atoms per unit time) -dependent increase in the swelling rate (relative volume increase divided by atom fraction of displaced atoms) obtained at the high-temperature side is in part a consequence of the neglect of the thermal vacancy concentration in the diffusion equation used. The thermal vacancy concentration becomes important at high temperature not only in the boundary condition (where you include it) but also in the recombination term (where you neglect it). If properly taken into account, it is found that the growth rate becomes defect-production-rate independent at high temperature. (See H. Wiedersich, in *Second International Conference on the Strength of Metals and Alloys*, Conference Proceedings, Vol. 2, p. 784, American Society for Metals, 1970.)

Bullough: The quantity c_v in our pair of field equations is the total vacancy concentration and includes the equilibrium thermal fraction; this is ensured by the boundary condition that fixes c_v to the equilibrium value c_v^e at the void surface. There is thus no necessity to further include c_v^e explicitly in the differential equations. Thus, provided the damage rate, K , is high enough and the temperature, T , is low enough so that the steady-state radiation-produced vacancy concentration is greater than c_v^e , we do not need to concern ourselves with thermal vacancies except for the boundary condition at the voids ($c_v = c_v^e$). If K is low enough and/or T is high enough so that the radiation by itself is unable to maintain a steady-state concentration greater than the equilibrium vacancy value, then the vacancies required to maintain the concentration, i.e., c_v^e , are obtained elsewhere (mainly from the voids if they already exist).

Carpenter: Perhaps the role of incoherent precipitate particles is that the interfaces act as traps for gases. Without gas atoms to stabilize a three-dimensional vacancy cluster, prismatic punching of dislocation loops should occur in a large vacancy supersaturation. The conditions for this have been discussed by M. F. Ashby (*Scr. Met.*, 1969 or 1970).

Bullough: I regret I have not read the work of Ashby referred to. However, I do agree that incoherent precipitate particles could act as traps for gases.

Spitznagel: It has become apparent from our (Westinghouse Research Laboratory) numerical calculations with your model and as has recently been pointed out by Foreman, the swelling kinetics are very dependent on the effective vacancy concentration used. In particular, Foreman has pointed out (Report AERE-R-6358) that a local denuded region around the void results in a factor of $1/r$ reduction in the growth rate. Could you comment on this criticism of the model?

Bullough: The present model includes diffusion flow in the neighborhood of the voids, and, to that extent, there is no significant difference between our calculation and Foreman's. The reference to $1/r$ implies a confusion between the solution and the boundary conditions.

Corbett: What is the proportion of gas atoms to vacancies in your embryo? Will *one* gas atom do it? How big is the embryo?

Bullough: The growth regime is taken to begin with the void embryos as gas bubbles about $10 \text{ \AA}$ in radius. This size was chosen because it is about the minimum size for which gas laws and surface-tension effects are appropriate. If the gas pressure completely balances the surface tension, such bubbles should contain about 2000 gas atoms (surface tension $\sim 1000 \text{ ergs/cm}^2$). We think the void nuclei (the above gas-bubble nuclei) probably need very few gas atoms to stabilize the vacancy aggregate in the three-dimensional morphology. A rigorous atomic calculation is needed to ascertain the precise form and stability of these point defect aggregates.

THEORETICAL STUDY OF THE SWELLING OF FAST-NEUTRON-IRRADIATED MATERIALS

663900

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ABSTRACT

Possible mechanisms for limiting void growth under fast-neutron irradiation are analyzed. It is found that the void volume at which saturation should occur is dependent on the void number density. Higher void number densities lead to lower void volumes at saturation. The importance of knowing the generation rate of Frenkel pairs that can participate in diffusional processes rather than the total number of displaced atoms is discussed. It is stressed that this could be especially important in translating results gained by proton bombardment. The relation between the development of voids under heavy-ion and neutron bombardment is considered, using a theoretically based computer model. In this model, void nucleation is taken as the sum of a homogeneous nucleation rate and a heterogeneous term. (The homogeneous nucleation rate is taken as that recently derived by Russell and by Katz and Wiedersich.) The heterogeneous nucleation rate is an empirically fitted term based on the form expected for nucleation by helium. It is found that homogeneous nucleation can adequately explain the results from heavy-ion bombardments where the target was not previously injected with helium. Homogeneous nucleation in EBR-II irradiations is found to be important only for short exposures (fluence $<10^{22}$ neutrons/cm²) at irradiation temperatures below 400°C.

The formation of voids and dislocation loops in austenitic stainless steel during fast reactor operation has delayed the design of an economic fast breeder reactor. Much effort has been expended to characterize experimentally this form of radiation damage. Unfortunately workers are hampered by the wide range of variables that affect the phenomenon. Irradiation temperature, neutron flux, time, alloy composition, degree of cold work, and microstructural features (i.e., precipitates and grain size) have all been demonstrated to affect the void-dislocation loop microstructure developed under neutron irradiation. The

large number of variables important to the void-formation process makes the implementation of a complete test matrix an expensive and time-consuming undertaking. This realization was one of the main motivations for the development of a physically based model that could serve to suggest productive areas for experiments. It was also felt that the development of such a model would allow a more confident extrapolation of existing swelling results to reactor conditions of design interest.

More recently, a large experimental effort has been put into the simulation of fast reactor conditions by bombardment with charged particles. The translation of results obtained by ion bombardment where atomic displacement rates are from 3 to 4 orders of magnitude higher than in the reactor case is difficult at best and seemingly impossible without the use of a physically consistent model. The work presented in this paper represents the current stage of development of our understanding of the complicated phenomenon of void formation in metals during ion and neutron bombardment. The development of such a model is, by necessity, a dynamic process that continually incorporates new ideas and concepts and measures their implications against an ever-increasing body of experimental data.

BASIC CONCEPTS

The physical concept that has been modeled is the clustering of point defects from a supersaturated matrix. The level of point-defect concentration is regarded as a dynamic balance between the rate at which point defects are being pumped into the matrix from displacement spikes, the rate at which they are annihilated at sinks, and the rate at which they undergo mutual annihilation by recombination.

Since voids and dislocation loops are expected to serve as good point-defect sinks, the steady-state concentrations of vacancies are expected to decrease with time in reactor as more and more voids and loops are formed. This reduction in the concentration of point defects with time means that any process which is the function of the vacancy or interstitial concentration must also vary with time in reactor. Current estimates of the vacancy concentration present in the matrix as a function of temperature and time are given in Fig. 1. The values presented in this figure are calculated for quasi-steady-state conditions by solution of the equations

$$G_v - K_{v,sink} D_v C_v - 12 C_v C_i D_i N_0 / a^2 = 0 \quad (1a)$$

and

$$G_i - K_{i,sink} D_i C_i - 12 C_v C_i D_i N_0 / a^2 = 0 \quad (1b)$$

Fig. 1 Steady-state and thermal-equilibrium vacancy concentrations as functions of dose and irradiation temperature.

where G_v, G_i = effective generation rate of vacancies; interstitials into the matrix

$K_{v,sink}, K_{i,sink}$ = efficiency of sinks for vacancies; interstitials

D_v, D_i = diffusivity of vacancies; interstitials

C_v, C_i = concentration of vacancies; interstitials present during quasi-steady-state conditions

a = lattice parameter

N_0 = number of atoms/cm³

The details of this calculation are presented elsewhere.¹ It is of interest, however, to consider each term of the above relations separately to analyze what affects them and how they affect the final microstructure.

FRENKEL-PAIR GENERATION RATE

The Frenkel-pair generation rate of interest in the present discussion is concerned with those Frenkel pairs which can play a role in diffusive processes outside the displacement spike. This number is far less than the total number of displaced atoms one would calculate with a Kinchin-Pease-type² approach since most of these displacements will be annealed by close pair recombinations between interstitials and vacancies within the spike. Blewitt et al.³ have recently measured experimentally the number of vacancies produced per displacement spike during fast-neutron bombardment of Cu_3Au . These vacancies affect diffusive processes and can be monitored by the order-disorder transformation in this system. They found that fewer than 10 vacancies per spike instead of the 1000 calculated by a Kinchin-Pease approach were affecting diffusion. The estimation of the effective Frenkel-pair generation rate is an extremely difficult task as it is sensitive to both the nature of the bombardment and the state of the metal being irradiated. For example, it would be expected for a given density of vacancies and interstitials within a displacement spike that the larger the spike volume the lower the fraction of Frenkel pairs which will escape recombination within the spike. This is particularly important to keep in mind when comparing microstructures developed during bombardment by light charged particles, such as protons or deuterons, where only a few vacancies and interstitials are created per collision with those microstructures formed from neutron or heavy-ion bombardments where thousands of Frenkel pairs are created in each collision. If it is assumed that the density of point defects in the spike is the same in the two cases, it would be expected that the fractions of the total number of Frenkel pairs created during the bombardment, which play a role in void formation, would be much higher for the proton irradiation than for the nickel bombardment or the neutron irradiation. Therefore for a given total number of atomic displacements, one may expect a higher void volume for proton irradiation than for nickel bombardment.

A less obvious effect that might be expected concerns the trapping of self-interstitial atoms by substitutional solute atoms. Materials containing solute atoms that could strongly trap interstitials would be expected to have greater in-spike recombination due to the nature of the spike, as deduced theoretically by Beeler⁴ and experimentally by Beavan, Scanlan, and Seidman.⁵ These workers showed that the vacancies in a spike generally cluster toward the center, whereas the interstitials are found in a shell around the outside of the spike. If interstitials are trapped by solute atoms, they would be perfectly situated to recombine with vacancies as they move from the center of the spike into the matrix of the material. Experimental evidence that significant interaction can exist between the substitutional solute and the interstitial has been presented by Blewitt.⁶ He found that additions of only 0.1% of beryllium or silicon to copper

raised the stage-1 annealing peak from 50 to 200°K for the beryllium addition and to 115°K for the silicon addition. Blewitt's interpretation of these results was that, since stage-1 annealing is generally attributed to close-pair recombination and vacancies are immobile in copper at these temperatures, a large fraction of the interstitials are trapped by the solute additions. Since beryllium causes the copper lattice to contract and silicon causes it to expand, apparently atoms both smaller and larger than the host can have a significant binding energy to a self-interstitial atom.

RECOMBINATION WITHIN THE MATRIX

The trapping of point defects by substitutional solute would also be expected to increase the fraction of vacancies and interstitials mutually annihilated by recombination in the matrix of the material by effectively raising the concentration of interstitials and vacancies present.

Trapping of interstitials could lead to an additional recombination term of

$$R_T = Z_t C_{i,T} C_v D_v N_0 / a^2 \quad (2)$$

where Z_t = a geometrical factor

$C_{i,T}$ = number of interstitials trapped by substitutional solute atoms; for a strong binding energy, this number could approach that of the solute concentration

C_v = vacancy concentration

D_v = vacancy diffusivity

Assuming a low solute concentration of 10^{-3} that has a high binding energy with the interstitial, an irradiation temperature of 500°C, and a vacancy concentration of 10^{-9} , the ratio of recombination at trapped interstitials to that with free interstitials (Eq. 1) is

$$\frac{C_{i,T} D_v}{C_i D_i} \approx \frac{10^{-3} \times 10^{-9}}{10^{-16} \times 10^{-1}} \approx 10^5 \quad (3)$$

Thus a major effect on point-defect recombination is possible if strong interstitial trapping occurs. This would mean that lower fluxes of vacancies and interstitials to voids and dislocation loops would exist and the void and loop growth rates would thereby be reduced. This point has also recently been discussed by Fisher and Williams.⁷ Figure 2 shows the role of increased recombination in limiting the amount of void volume formed. Clearly, increasing the amount of recombination by solute trapping would also limit the void volume.

A particularly intriguing application is the effect of small amounts of impurity atoms on the void volume formed in pure metals. Stiegler et al.⁸ found

a much lower amount of void formation in commercially pure (1100) aluminum than in the high-purity (99.9999%) variety for a given dose after irradiation at 50°C. Two of the most common impurities in aluminum are copper and magnesium. Both of these solutes has a larger difference in size⁹ from the host than does beryllium from copper, as used in Blewitt's experiments.⁶ This implies that a greater amount of interstitial trapping might be expected in

Fig. 2 Effect of increased vacancy-interstitial recombination on void volume.

aluminum-based systems than in copper alloys. Similar results on the influence of purity have been obtained for nickel by Holmes¹⁰ for irradiations at 425°C. High-purity Nickel 270 showed both a larger amount and a higher rate of swelling than did the commercially pure Nickel 200. Both these results suggest the possibility of solute trapping of self-interstitials. It would be of interest to determine whether or not this effect can be optimized in stainless steel or other more complicated alloys.

MIGRATION TO SINKS

When the migration of point defects to sinks is being discussed, it is well to realize that these sinks are really recombination centers inasmuch as they receive nearly equal fluxes of vacancies and interstitials. Calculations indicate that only from $1/10$ to 1% of the vacancies formed result in voids; all the others are recombined with interstitials.

Equation 1 shows that the total flux of vacancies to sinks must equal the total flux of interstitials, i.e.,

$$(K_{v,GB} + K_{v,ppt} + K_{v,dis} + K_{v,void} + K_{v,loop})D_v C_v = (K_{i,GB} + K_{i,ppt} + K_{i,dis} + K_{i,void} + K_{i,loop})D_i C_i$$

where $K_{v,GB}$; $K_{i,GB}$ = efficiency of grain boundaries as sinks for vacancies; interstitials

$K_{v,ppt}$; $K_{i,ppt}$ = efficiency of precipitates as sinks for vacancies; interstitials

$K_{v,dis}$; $K_{i,dis}$ = efficiency of dislocations as sinks for vacancies; interstitials

$K_{v,void}$; $K_{i,void}$ = efficiency of void as sinks for vacancies; interstitials

$K_{v,loop}$; $K_{i,loop}$ = efficiency of loop as sinks for vacancies; interstitials

The details of each of these terms are discussed elsewhere.¹

It is evident that the importance of any sink in the system will be proportional to the magnitude of the flux of point defects to the sink. The ideal conditions for the partitioning of vacancies into voids and interstitials to dislocations are when dislocations and voids are the only important sinks and have nearly equal fluxes of point defects to them. Under these circumstances the slightly increased capture radius of the dislocation for the interstitial can be most effective in causing an excess vacancy flux to the void. That this is so can be realized by writing the accumulation rate dv/dt of excess vacancies at voids as

$$\frac{dv}{dt} = K_{v,void}(D_v C_v - D_i C_i)$$

This can be rewritten, using Eq. 1 for the case where recombination is unimportant, as

$$\frac{dv}{dt} = \frac{K_{v,void} \epsilon K_{v,loop}}{(K_{v,void} + K_{v,loop})^2} \quad (4)$$

where ϵ is a measure of the increased capture radius of dislocations for interstitials relative to vacancies and is $\ll 1$. If it is assumed that the voids and loops are the principal sinks in the system, then the sum of $K_{v,void}$ and $K_{v,loop}$

must be constant. Therefore the accumulation rate is maximized when the sink efficiencies are equal.

One of the most obvious means of limiting swelling is by raising the efficiency of other types of sinks in the system through grain refinement, precipitate dispersion, or cold work. In general, the effectiveness of adding additional sinks to the system is expected to increase with an increase in irradiation temperature inasmuch as it is much easier to limit the point-defect supersaturation ratios at higher temperatures. A major effect of adding sinks to the material is expected to be a reduction in the number density of voids. However, as will be discussed, the addition of different types of sinks can have different effects on the irradiated microstructure.

When the relative effectiveness of each type of sink is assessed, it is interesting to compare how much sink surface area may be introduced into the material by conventional fabrication techniques. We find that a $1\text{-}\mu$ grain size should be equivalent to a precipitate dispersion of 10^{15} particles/cm³ of 200 Å diameter (1 vol.%) or equivalent to a dislocation density of about 10^{11} (~5% cold work). Since it is not, at present, practical to produce an austenitic stainless steel with grain sizes smaller than $1\text{ }\mu$ while higher precipitate volume fractions or higher percentages of cold work are conceivable, further attention will be directed toward these two possibilities.

Incoherent precipitates are expected to show no preferential attraction for interstitials or vacancies. Thus, if they are the only major type of sink present, they should limit swelling. However, if dislocations are present either through interstitial loop formation or prior cold work then the precipitates would be expected¹ to have voids formed on them owing to the partitioning of the point-defect fluxes by the two types of sinks.

The role of the coherent precipitate is more difficult to assess. This will be discussed in a later section of this paper.

The most effective means of introducing sinks into a material is by means of cold work. Dislocation densities approaching 10^{12} cm/cm³ are easily introduced by a 20% deformation of 316 stainless steel.¹¹ The effect of the dislocation is complex since it is also the source of the biased attraction that makes void growth possible. Thus the situation becomes one where, at higher temperatures (>500°C), cold work is expected to be completely effective by preventing void nucleation.

At lower temperatures, void nucleation might still occur. If voids do nucleate, the overall swelling rate would be expected to increase with time as they become more and more important as point-defect sinks (Eq. 4). It is doubtful that the rate would ever exceed that of a solution-annealed material, however, whether this will occur or not will be a function of the relative effectiveness as sinks of the voids and dislocations loops developed in the two materials. One should note that it is extremely easy to be misled in this respect by log-log plots of swelling vs. dose data.

VOID AND DISLOCATION-LOOP NUCLEATION

The precise interaction of vacancies, interstitials, displacement-spike clusters, and helium-gas atoms that leads to void and interstitial-loop nucleation is an extremely complicated phenomenon. Several authors¹²⁻¹⁴ have derived an expression for homogeneous nucleation of voids, which takes the form

$$I_{\text{homo}} = N_0 \exp \left[\frac{16\pi\gamma^3}{3(KT)^3 (\ln[(B_v - B_i)/B_{ve}])^2} \right] (B_v - B_i)$$

where γ = surface energy

B_v = vacancy flux to the cavity

B_{ve} = vacancy flux to the cavity when vacancy concentration is the thermal-equilibrium value

B_i = interstitial flux to the cavity

Fig. 3 Comparison of the fraction of voids nucleated homogeneously as a function of dose and irradiation temperature. Flux, 3×10^{15} neutrons/(cm²)(sec).

The incorporation of this expression into a previously described computer routine¹ allows an assessment of the role of homogeneous nucleation in fast reactor irradiation conditions. As shown in Fig. 3, homogeneous nucleation is most important early in the irradiation. At low irradiation temperatures and longer periods of irradiation, heterogeneous nucleation, most likely on gas

atoms, probably controls void formation. Unfortunately any expression for gas-atom nucleation of voids can only be empirical at this time. However, if gas-atom nucleation is important, it must depend on the concentration of helium in the material. Thus it would be expected that, at low doses ($<10^{21}$ neutrons/cm²), samples irradiated at low temperatures ($<450^{\circ}\text{C}$), where homogeneous nucleation is expected to be important, should show observable void and loop formation, whereas at higher temperatures ($>500^{\circ}\text{C}$), where all nucleation is heterogeneous, no voids and loops would have formed. Bloom¹⁵ et al. have made such an observation experimentally.

It is of interest to consider the role of flux on the void- and loop-formation process in light of the possible nucleation mechanisms. As will be discussed later, over a limited temperature range for a given number density of voids and loops, differences in flux levels should not lead to any differences in void volume at a given total dose. However, if one assumes that the nucleation of voids and loops will depend differently on the levels of vacancy and interstitial supersaturation in the system, then it follows that different generation rates of point defects that produce different levels of supersaturation should result in different relative numbers of voids and dislocation loops. As discussed in the section on sinks, the point-defect flux to the voids and to the dislocation loops must be nearly equal if the swelling rate is to be a maximum. Thus the changing of the relative numbers of voids and dislocation loops will affect the overall void growth rate. Therefore the void growth rate would be expected to be an indirect function of flux level. The effect of flux on nucleation rate will be much greater at higher irradiation temperatures where the supersaturation ratio is much more sensitive to the steady-state concentration of vacancies and interstitials (see Fig. 1).

SATURATION MECHANISMS

Recent results from ion-bombardment experiments^{16,17} have shown that stainless-steel and nickel swelling rates decrease at high fluences, indicating a tendency for saturation to occur. These results are encouraging since the magnitude of the observed swelling at high fluences ($>2 \times 10^{23}$ neutrons/cm² equivalent) is lower than that predicted, based on the present design equations (e.g., the WADCO equation). In this section some of our preliminary thoughts on swelling saturation will be discussed. This work is in progress to provide a physical model for translating the results from ion-bombardment experiments to liquid-metal cooled fast breeder reactor (LMFBR) conditions and to investigate the possibility of lowering the magnitude of the swelling limit. In a previous paper,¹⁸ we suggested various mechanisms that may decrease the swelling rate. Recently Bullough and coworkers^{19,20} proposed that, near void surfaces, dislocation loops are attracted to the voids by image forces and are annihilated. Saturation occurs when the denuded zones around the voids overlap. Experimentally, electron microscopy reveals that, at least under some circumstances, at

high doses the voids are interconnected by dislocations.²¹ At higher irradiation temperatures, loops would be expected to unfault, glide, and tangle. In any case, it is unlikely that all the dislocations near the void surfaces will be annihilated. If these remaining dislocations can continue to climb and bias the point-defect flow, swelling by void growth will not cease. When we consider the circumstances under which a microstructure consisting of voids interconnected with dislocations would cease to accumulate excess vacancies, we must first examine whether a dislocation line is capable of being pinned by a void. In Appendix A it is shown that the climb force on an edge dislocation due to the supersaturation of interstitials is sufficiently large to climb the dislocation out of a void unless the spacing between voids is less than 50 Å. For a void density of 10^{15} to 10^{16} voids/cm³, this spacing between the voids corresponds to a rather high total swelling. However, before deciding whether a dislocation line may be pulled from a void, one must recognize that vacancies will flow out of the void and tend to bow the dislocation line in an opposite sense from the interstitial flux.

In the absence of irradiation, the equilibrium curvature of the dislocation is determined by the balance of the decrease in the surface energy of the void and the increase in dislocation energy from both the length and the curvature change. In Appendix B it is shown that, for the interests of the present discussion, the equilibrium curvature of the dislocation is several void radii. Under fast-neutron irradiation, a steady-state dislocation-void configuration will be maintained that depends on the balance between the net interstitial arrival rate at the dislocation and the rate at which vacancies can flow out of the void. In Appendix C, it is shown that under irradiation the steady-state configuration will be close to the equilibrium configuration in the absence of irradiation because the rate of vacancy flow out of the void is large relative to the incoming interstitial flux. For the void size and number density of interest to the present discussion, only a slight dislocation curvature is expected at the steady-state or equilibrium condition. The most important consequence of this type of void-dislocation interaction is that it will prevent the climb of the dislocation out of the void, although in itself, it will not necessarily prevent further void growth.

As the irradiated microstructure evolves at high doses, two types of microstructures are foreseen. In the first, a portion of the dislocations is connected with the voids whereas a fraction remains tangled but not in contact with voids. If there are dislocations near the void that are free to climb by absorbing interstitials preferentially, the excess vacancy will contribute to the void growth. As the void grows, the dislocation intersecting the voids will adjust its curvature by climbing to give a new steady-state configuration, as specified in Appendixes B and C, consistent with the void size. Thus it appears that complete saturation is not possible as long as free dislocations exist in the microstructure.

At still higher doses it would be expected that all the dislocations would be in communication with the voids. However, even in this case, void growth may

still be possible. It is shown in Appendix B that the equilibrium curvature of the dislocation increases as the void size increases. This relation provides the possibility for continued void growth. In this case the dislocation connected to the void acts as a biasing sink to allow excess vacancies to the void. Thus, if the voids are widely spaced, such that excess interstitials deposited on the dislocation are not immediately recombined with vacancies from the void, continued void growth will be possible. The total excess vacancies obtained in this situation will depend on the number of dislocations intersecting the voids and the spacing between the voids. When the spacing between the voids becomes small, the area change in the dislocation plane resulting from the increase in curvature only corresponds to a very small amount of excess vacancies, which produces a very low growth rate.

When we estimate at what void spacings we should expect rapid recombination along the dislocation, it is interesting to consider the probability of the recombination of an interstitial impinging on the dislocation line with a vacancy emitted from the void. First, it should be noted that two factors control how far a point defect will move along a dislocation core. One is the rate at which point defects will be trapped as they move along the dislocation core and the other is the rate at which they will boil off the core and reenter the matrix of the material. For the interstitial, the trapping probability is expected to be very high since by previous arguments the dislocation curvature is maintained far from what would be demanded by the interstitial supersaturation. Therefore the interstitial should be trapped almost immediately upon impingement. The trapping rate for vacancies along the dislocation core, on the other hand, is expected to be quite low since the dislocation curvature is nearly in equilibrium with the void. The distance that a vacancy could move rapidly to recombine with an impinging interstitial will be determined by its rate of boiling off into

the matrix. This distance, Z , can be estimated from $Z = \sqrt{2}a \exp\left(\frac{\Delta W_v + \Delta W'_v}{2kT}\right)$ (Ref. 22), where a is the lattice parameter, and ΔW_v and $\Delta W'_v$ are the difference in formation energy and motion energy, respectively, between the bulb value and the value along the dislocation. For $\Delta W_v + \Delta W'_v = 0.8$ eV, the value of Z is approximately 2000 Å at 500°C. Within a distance Z from the void, the vacancy on the dislocation can be considered to be at equilibrium with the void. Any interstitial arriving at the dislocation within this distance will be assured of immediate recombination with the vacancy from the void. If there is no other biasing sink in the system when the line length of the dislocation between the voids is less than twice Z , the void growth will be completely inhibited by this recombination process.

From the preceding discussion, it may be summarized that the conditions for swelling saturation are

1. All the dislocations are connected to the voids.
2. The rate of vacancy flow out of the void is sufficiently large to maintain a steady-state void-dislocation configuration.

3. The spacing between the voids is small enough to ensure recombination through the dislocation, or to limit the extent that a dislocation can climb, or both. The mechanisms suggested previously¹⁸ and the dislocation-void annihilation proposed by Bullough and coworkers¹⁹ will, of course, contribute to the decrease in swelling rate and influence the manner in which a system approaches swelling saturation.

The condition at which all the dislocations are connected to the voids depends on many variables, e.g., the number density of the voids, the density of the dislocations, the interactions among the dislocations, the interactions between the dislocations and the void, and, of course, the growth rate of the voids and the climb rate of the dislocations.

One factor of key importance in determining the exact nature of the final dislocation-void microstructure is whether the loops are faulted or unfaulted. Unfaulting of loops is expected at about an 800-Å diameter, based on a stacking fault energy of 15 ergs/cm² for 304 stainless steel. These loops will then be able to glide, thereby increasing the probabilities of void-dislocation and dislocation-dislocation interactions.

Various tangle and network structures can be produced owing to these interactions resulting in a complicated dislocation-void configuration. Experimentally the results of EBR-II irradiation generally show dense dislocation tangles at low temperatures and a loose network-type structure at higher temperatures.²³ These dislocation structures will not only influence the condition for the dislocation-void intersection, but will also affect the condition (3) for void growth described previously. The mean critical spacing L_c between the voids at which swelling saturation occurs will be the spacing that meets both conditions 1 and 3 described above. For a given critical spacing, it is easy to see that, with a higher void number density, swelling will saturate at a lower level of total volume change. It is likely that the saturation level and the manner in which the system approaches saturation will depend on the microstructure of interest and the irradiation conditions (e.g., nickel vs. stainless steel and neutron vs. ion bombardment may approach saturation differently). We illustrate these possibilities with the following three variables chosen in the model calculations. These variables are the mean critical spacing between the voids, the number density of the voids, and the effective dislocation density. The factors that will influence the mean critical spacing between the voids have been discussed. The number density of the voids depends on their nucleation rate and also on possible ripening and coalescing processes that will be considered in more detail later. The effective dislocation density depends on the consequences of several processes, such as dislocation-void and dislocation-dislocation annihilation, dislocation tangling, and point-defect recombination through the dislocation tangle when dislocations are connected to the voids. In the calculation the effective dislocation density D_E is expressed as

$$D_E = D_0 \left[1 - \left(\frac{L_c}{L} \right) \right]^n$$

where D_0 is the dislocation density calculated from the nucleation and the growth of the loops. L is the mean spacing between the voids and the exponent represents the effectiveness of the various processes described in the preceding paragraphs that will reduce the effective dislocation density and control the manner in which the system approaches saturation. For example, to fit the results on nickel by Hudson and coworkers,¹⁶ where the void number density was 3×10^{15} voids/cm³, $L_c = 2100$ Å and $n = 2$. In Fig. 4 the volume change at

Fig. 4 Effect of void number density and critical spacing on void volume at saturation.

saturation is plotted as a function of mean critical spacing between the voids for various number densities of the voids. For a given critical spacing, the saturation volume change decreases as the number density increases. This is consistent with the results by Hudson and coworkers¹⁶ and by Kulcinski and coworkers.¹⁷ The former observed saturation at 12% volume at a void number density of 2×10^{15} voids/cm³, and the latter observed saturation at 4% volume at a void number density of 2×10^{16} voids/cm³. The parameter n may depend on the system of interest and the irradiation conditions (e.g., temperature and flux). In the calculations presented here, the number density of the voids is assumed constant at high fluences because the nucleation of the new voids probably becomes insignificant owing to reduced point-defect supersaturations. However, there are possible ripening and coalescing processes that will lead to a decrease in void number density. A realistic model calculation should include this possibility.

From the preceding discussion, it is seen that the number density of the voids is an important parameter that governs the swelling saturation. At the initial stage of the irradiation, the number density of the void is controlled by the rate of void nucleation. As irradiation dose increases, ripening and coalescing

processes among the voids become possible, which will reduce the void number density. The ripening processes are caused by capillarity. The small voids are unstable relative to the large voids owing to the difference in the radius of curvature, such that the small ones will dissolve and the large ones will grow. Usually in the bulk crystal, the supersaturation of vacancies is high during irradiation to suppress this ripening process. However, at high fluences an increasing number of the voids will be connected by dislocations. The dislocation will provide an efficient path for the vacancy transport. Recently, Volin and Balluffi²⁴ measured the rate of pipe diffusion of the vacancy along a dislocation. Translating their measured values to stainless steel or nickel, by means of the homologous temperatures, the estimated ripening rate could be used to account partly for the decrease in void number density at high doses observed by Hudson and coworkers.¹⁶

One rationalization of these interesting results is that the decrease in void number density observed by Hudson et al. for 316 stainless steel is partly due to ripening of dislocation-connected voids. This effectively increased the spacing between voids, thereby postponing saturation until higher void volumes are reached. Since the peak number density was observed to occur at a void volume of only 1 to 2%, whereas saturation occurred at about 14%, it appears that this trade off between ripening and change in the saturation limit is substantial.

Results by Hudson and coworkers on nickel again indicate a peak in the void number density before reaching saturation although much less marked than in stainless steel. Since the peak number density of voids in nickel is about an order of magnitude less than that in stainless steel, ripening processes would be expected to proceed at a slower rate. Some numerical estimations of the ripening rate are given in Appendix C. The ripening processes will slow down, of course, as the void size becomes larger and more uniform. However, it must be noted that irradiation in an LMFBR usually involves long durations, which will allow considerably more ripening compared with short-time irradiation in an ion-bombardment experiment. The full consequences of this phenomenon require further evaluation.

The concept of point-defect recombination through the dislocation when the dislocation is connected to the voids can be used also to rationalize partially the low swelling observed in materials of high densities of coherent precipitates.^{25,26} Low swelling in the British Nimonic alloy* PE16 and the ferritic phase of the International Nickel Company, Inc., experimental alloy IN-744† are recent examples of this phenomenon. It has been suggested¹⁹ that both interstitials and vacancies are trapped at the precipitate-matrix interface, thereby enhancing the recombination process. The lattice misfit between the precipitate and the matrix

*Nominal composition in wt. %: Ni, 42.5; Fe, 34.0; Cr, 17.1; Mo, 3.15; Ti, 1.2; Al, 1.3; C, 0.08; B, 0.0003; and Zr, 0.03.

†Nominal composition: Fe-26 wt. % Cr-6.5 wt. % Ni.

in PE16 will produce compressive stress at the interface²⁷ that could discourage interstitial trapping at the interface. On the other hand, a significant portion of the dislocation in the system probably will intersect the precipitates owing to the high precipitate density. Recombination will then be possible between the stress-biased interstitials absorbed by the dislocations intersecting the precipitate and the vacancies trapped at the precipitate-matrix interface in a manner similar to that for the void-dislocation case. Of course, for this process to be effective, the system must include a high density of precipitates.

RELATION OF HEAVY-ION BOMBARDMENT TO NEUTRON IRRADIATION

Recent efforts to simulate the evolution of the void-dislocation loop microstructure produced during neutron irradiation by heavy-ion bombardment have been quite successful in producing similar microstructures. However, the relation of the temperature and dose dependence of swelling gained by the two techniques must be established before ion bombardment can be used confidently in establishing design data and in guiding material development for fast breeder reactor application. For the present we will restrict discussion to bombardments of stainless steel that contain no helium with heavy ions (nickel, copper, and selenium have been used by different workers).^{17,21,28} Presumably little gas is available in these materials to act as void or loop nuclei since helium is not injected or generated during the bombardment. The microstructures developed during these bombardments can be reasonably simulated in the Argonne National Laboratory computer program when the nucleation rate is based on the homogeneous expression previously described. In Table 1 the predicted and observed void sizes and number densities are compared along with probable error on the exact bombardment conditions. The effective neutron flux for each case was derived, using the following assumptions:

1. The primary knock-on energy spectrum is about the same in heavy-ion and fast-neutron irradiations.

TABLE 1
COMPARISON OF VOID SIZES AND NUMBER DENSITIES
WITH RESULTS OF ION-BOMBARDMENT EXPERIMENTS

Irra- diation temp., °C	Beam current, μA/cm ²	Length of irra- diation, hr	Void density, 10 ¹⁵ voids/ cm ³	Predicted void density, 10 ¹⁵ voids/ cm ³	Average void diameter, Å	Predicted average void diameter, Å	Ref.
500 ± 10	2.4	0.43	6 ± 3	28 ± 10	180 ± 20	111 ± 20	28
517 ± 10	0.35	5.6	2 ± 1	0.9 ^{+0.9} _{-0.5}	278 ± 78	434 ± 130	21

2. About 50 keV of energy is deposited per displacement spike in both cases.

3. The number of Frenkel pairs escaping in-spike recombination is about the same. This is tantamount to assuming that the spikes have the same spatial arrangement whether formed from heavy-ion or neutron bombardment.

On the basis of these assumptions, the number of displacement spikes created per second as a function of the fraction of range could be estimated from the energy-deposition curve for creating point defects calculated by Brice.²⁹ Roughly these assumptions led to the relation that at the end of range $1 \mu\text{A}/\text{cm}^2$ of heavy ion was equivalent to a neutron flux of 5×10^{18} neutrons/ $(\text{cm}^2)(\text{sec})$. The results presented in Table 1 imply that homogeneous nucleation is predominant during heavy-ion bombardment of targets that have not been previously injected with gas. Thus, in comparing results with the neutron case where nucleation is heterogeneously controlled, one must take great care. For example, the temperature dependencies of void formation as deduced from the two techniques are compared in Fig. 5. On the basis of the assumption that the homogeneous process predominates in heavy-ion bombardment, whereas heterogeneous nucleation is the controlling factor in the neutron case, one finds that the expected temperature of maximum swelling can be either above or below the neutron case depending on the flux level used during the ion bombardment. Similarly in Figs. 5(b) and 5(c), void number density and size are compared. As can be noted, it is possible to obtain quite close agreement with neutron results by the proper selection of flux level because the ion results bracket the neutron case. Thus the observance of similar microstructure between neutron and ion bombardment does not necessarily imply similar nucleation mechanisms.

Since many simulation experiments are aimed at determining total amounts of swelling, and since nucleation is expected to cease early in the bombardment, it is important to analyze possible flux effects on the void growth rate.

When analyzing the effect of different flux levels on the void growth rate, we must consider three different temperature regimes. At lower temperatures, reduced point-defect mobility produces high steady-state concentration of vacancies and interstitials (Fig. 1), and thereby (Eq. 1) increases the probability of mutual recombination. As discussed earlier, increased recombination leads to lower fluxes of point defects to sinks (voids and loops) and thus a lowered void growth rate. As has been discussed by Bullough,¹⁹ the temperature range over which recombination is important increases with the flux level. Our calculation has shown that, for a microstructure consisting of 10^{15} voids/ cm^3 and 10^{15} loops/ cm^3 , recombination is important up to 375°C in the neutron case [$\phi = 3 \times 10^{15}$ neutrons/ $(\text{cm}^2)(\text{sec})$] and up to 500°C [$\phi_{\text{eff}} = 1 \times 10^{18}$ neutrons/ $(\text{cm}^2)(\text{sec})$] in the nickel-bombardment case.

At higher temperatures the growth rate of voids becomes flux dependent for another reason. The void growth rate is proportional to a first approximation to

$$[D_v(C_v - C_{ve}) - D_i C_i]$$

Fig. 5 Expected temperature dependencies of void formation as deduced from neutron- and ion-bombardment experiments. (a) void volume, (b) void number density, and (c) void size.

where C_v , C_i are the steady-state vacancy and interstitial concentrations due to the bombardment and C_{ve} is the vacancy concentration to thermal equilibrium at void surface, taken as $\exp(-42,000/RT)$. Since C_{ve} increases rapidly with temperature, at some temperature it should approach C_v . The temperature at which this occurs is a function of the value of C_v and thus of the flux level. For the neutron case, $C_{ve} = 0.1 C_v$ at 580°C , and for the ion case, $C_{ve} = 0.1 C_v$ at 675°C .

Between the two temperatures defined by recombination and the thermal-vacancy concentration, i.e., 375 to 580°C for neutrons and 500 to 675°C for ion bombardment, the amount of void growth is expected to depend only on the total dose, not to a first approximation of the flux level or irradiation temperature. Of course, second-order effects such as the amount of time a dislocation loop has to glide after unfauling, which may affect the final dislocation configuration, will depend on dose level.

In the light of this discussion it is suggested, in simulating neutron irradiations in the region where growth rates are not neutron-flux dependent with heavy-ion bombardment, that ion flux level-temperature combinations be chosen to give the number density of voids and loops expected under neutron irradiation at a temperature where the growth rates of the voids and loops are expected to be independent of ion dose rate. Simulation of neutron-irradiation conditions where growth rates are expected to be flux dependent requires that results be translated through model calculations.

Another area of potential difficulty in the use of ion bombardment lies in the prediction of saturation effects. As pointed out in the previous section, the void number density may strongly affect the level of swelling saturation. Since the nucleation mechanisms appear to be different between the neutron-irradiation case and the ion-bombardment case, caution must be taken as to the direct use of the saturation level obtained from ion bombardment for LMFBR applications. The situation is further complicated by the fact that, as mentioned earlier, the ripening process may occur among the voids, reducing their number density. Since more ripening is expected in reactor, care must be exercised in assessing ion-bombardment saturation results.

Along lines of similar reasoning, the aging of the precipitate may be more important in the case of neutron irradiation because the duration of irradiation is longer. For a system such as PE16 steel, which depends on a high density of small coherent precipitates to suppress void formation, aging effects could be important. If aging occurs, the precipitate number density will decrease, and, at the same time, the precipitate may lose its coherency with the matrix. Both these possibilities may reduce the effectiveness of these precipitates. Therefore the advantage observed in short-term ion-bombardment experiments may not be applicable for the neutron case. The aging of the precipitate phase during the irradiation will be affected by both the vacancy supersaturation and the possibility of resolution due to displacement damage. This area of research will

become more important in the development of low-swelling alloys that depend strongly on the size and the number density of the second phase.

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APPENDIX A: CLIMB FORCE ON THE DISLOCATION

Force on an edge dislocation F_d due to the supersaturation of interstitials per unit length is

$$F_d \cong \frac{1}{b^2} k T \ln \frac{C_i}{C_{i,0}}$$

where b is the Burgers vector, C_i is the bulk interstitial concentration, and $C_{i,0}$ is the thermal-equilibrium interstitial concentration.

The force required to cut a void by a dislocation F_v can be estimated by³⁰

$$F_v = \frac{E_{\max}}{r}$$

where $E_{\max}$ is the maximum interaction energy between an edge dislocation and a void and can be approximated as

$$-\frac{Gb^2r}{2\pi} \left[\left(\frac{1.25}{1-\nu} \right) \left(\ln \frac{2r}{b} - 1 \right) + 0.4\pi \right]$$

where G is shear modulus, ν is Poisson's ratio, and r is void radius.

If the dislocation line length between the voids is $\mathcal{L}$, the minimum line length required to cut the void can be found by the equation

$$F_d \mathcal{L} = F_v$$

For $G = 6 \times 10^{11}$ dyne/cm², $T = 500^\circ\text{C}$, $b = 1.8 \times 10^{-8}$ cm, $r = 250$ Å, $\nu = 0.3$, and $C_i/C_{i,0} = 10^8$, the minimum $\mathcal{L}$ is found to be less than 10 Å.

The calculation given here is a rough estimate. It shows, however, that the force on the dislocation due to interstitial supersaturation is large.

APPENDIX B: EQUILIBRIUM DISLOCATION-VOID CONFIGURATION

Figure 6 shows an edge dislocation intersecting two voids. Vacancies will flow out of the voids to eliminate a portion of the dislocation plane if R , the dislocation curvature, is greater than the equilibrium value. The equilibrium curvature of the dislocation can be found by the balance between the change in surface energy of the void and the change in dislocation energy.

Fig. 6 The dislocation-void configuration expected at steady-state conditions.

The energy of the dislocation W_d is²²

$$W_d = \pi R \frac{\theta}{180} \frac{Gb^2}{4(1-\nu)} \left(\ln \frac{4R}{\rho} - 1 \right)$$

where ρ is the dislocation core radius.

The change in W_d due to absorbing dN vacancies can be approximated by

$$\frac{dW_d}{dN} \cong \frac{\partial W}{\partial R} \frac{\partial R}{\partial N} = \frac{\Omega Gb}{4\pi(1-\nu)} \frac{1}{R} \left[1 + \left(\ln \frac{4R}{\rho} - 1 \right) \right] \quad (B.1)$$

The change in surface energy of the voids due to the release of dN vacancies is

$$\frac{dW_s}{dN} = \frac{2\gamma\Omega}{r} \quad (B.2)$$

where γ is the surface energy, Ω is the atomic volume, and r is the void radius.

The equilibrium dislocation curvature R_e is given by equating Eqs. B.1 and B.2.

APPENDIX C: TRANSPORT OF VACANCIES ALONG THE DISLOCATION

For the void-dislocation configuration shown in Fig. 6, if the radius of curvature of the dislocation is greater than the equilibrium value given in Appendix B, vacancies will flow out of the void to reduce the dislocation radius of curvature. Also, if the distance between the voids is sufficiently small, such that diffusion along the dislocation is predominant, from Eqs. B.1 and B.2, the flux of vacancy arriving at point B can be written as

$$J_{v,\perp} = A_{\perp} \frac{D_{\perp}}{\Omega kT} \frac{2}{\mathcal{L}} \left\{ \frac{2\Omega\gamma}{r} - \frac{\Omega Gb}{4\pi(1-\nu)} \frac{1}{R} \left[1 + \left(\ln \frac{4R}{\rho} - 1 \right) \right] \right\}$$

where $A_{\perp}$ is the effective area of the dislocation diffusion pipe, $D_{\perp}$ is the diffusivity of the atoms along the dislocation, and $\mathcal{L}$ is the dislocation length between the voids. The net flux of the interstitial arriving at this section of the dislocation due to the supersaturation caused by irradiation is given in Ref. 1.

If the value of $A_{\perp}D_{\perp}$ is applicable, as measured by Balluffi and coworkers²⁴ and corrected to stainless steel by means of the homologous temperature, it is

seen that $J_{v,\perp}$ is greater than $J_{i,\perp}$ for a radius of curvature of the dislocation that deviates from the equilibrium value by a small amount. Therefore the assumption seems to be justified that, at steady state, the radius of curvature of the dislocation is close to the equilibrium value.

Similarly, the flux of vacancies between two voids connected by a dislocation can be calculated for the case where pipe diffusion along the dislocation is predominant. The rate of shrinkage of the smaller voids (r_1) is

$$-\frac{dr_1}{dt} = \frac{1}{4\pi} \frac{A_1 D_1}{kT} \frac{2\Omega\gamma}{\mathcal{L}} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \frac{1}{r_1^2}$$

Extrapolating the $A_1 D_1$ values of Balluffi et al. for aluminum by means of homologous temperatures, it indicates that, when a void of 200 Å radius is connected to a void of 500 Å by a dislocation 1000 Å long, the smaller voids will disappear at 500°C in minutes.

DISCUSSION BY ATTENDEES

Norris: Some of my experimental observations on the shrinkage of voids during irradiation support the idea that pipe diffusion along dislocations is an important mechanism. Figure 1 shows an irradiation sequence in nickel at 450°C. Shrinkage of the void is associated with the dislocations running into it.

Fig. 1 Part of an irradiation sequence at 450°C in nickel. The electron doses are (a) 18, (b) 20, and (c) 21 dpa. A void, to which several dislocations are connected, is observed to shrink, the interpretation being that vacancies diffuse from the void along the dislocations to a free surface.

Appleby: Referring to your comments on the usefulness of high dislocation densities arising from cold work in limiting swelling, I see some apparent contradictions here. First, there are some data to show that at high temperatures cold-worked 316 and 304 stainless steels can swell more than solution-annealed 316 and 304. Second, I think that both you and Bullough consider that dislocations contribute to the overall vacancy supersaturation and thus void formation by the preferential attraction of interstitials. Perhaps you could clarify these points.

Spitznagel: You have advocated the use of cold work to suppress swelling by dropping the effective point-defect supersaturations at large values of T/T_M . Our numerical calculations with your nucleation-and-growth model indicate a transition to rapid-swelling kinetics at higher dislocation densities similar to the result predicted by the Bullough and Perrin model. In your opinion is it likely that one of the proposed saturation mechanisms will terminate swelling before the rapid-swelling regime is reached?

Harkness [answers to Appleby and Spitznagel]: First of all, I think it is agreed that dislocations serve as good sinks for both vacancies and interstitials. Thus introducing dislocations into a system decreases the vacancy supersaturation. What Bullough and I agree on is that the slight preferential attraction of a dislocation for an interstitial makes possible a partitioning of the point-defect population so as to allow void (and interstitial loop) growth to occur.

Second, I am not aware of any data which show that the overall magnitude of swelling in unrecovered cold-worked material is higher than solution-annealed values. Certainly recent WADCO data do not indicate this.

Third, I am somewhat at a loss to explain Dr. Spitznagel's results on the swelling rate of cold-worked material being faster at high doses using our nucleation and growth expressions since our own work does not indicate this. One would expect the swelling rate of cold-worked material to increase with time as the voids become more efficient sinks in comparison with the dislocation population (see Eq. 4 in text). It is doubtful that the rate would ever exceed that of a solution-annealed material; however, whether this will occur or not will be a function of the relative effectiveness as sinks of the voids and dislocation structure developed in the two materials. One should note that it is extremely easy to be misled as to relative swelling rates by log-log plots of swelling vs. dose results.

Sosin: The work of Blewitt (shown in your slide) and others are probably the best direct evidence for the trapping of interstitials by impurities. Those experiments do show trapping, but they also, in every case I can recall, show detrapping at temperatures that are low compared to temperatures in void consideration, indicating a short time of stay of interstitials at impurities at elevated temperatures.

Harkness: As discussed in the text, one means of estimating possible binding energies between substitutional solute atoms and self-interstitials is from the size difference between the solute and the host atom. If one uses the change in lattice parameter of aluminum, nickel, and gamma iron with solute additions as a guide, much greater binding energies would be expected than Blewitt found in beryllium-doped copper.

Seidman: In treating the homogeneous-nucleation model, did you attempt to prove uniqueness by trying some other model and showing it was very, very difficult to fit the data?

Harkness: The homogeneous-nucleation model was applied to the case of heavy-ion bombardment of a material containing no known gas. The only other heterogeneous site that could act to nucleate voids is the small cluster formed at cavity spike sites. These would be expected to alter the nucleation kinetics only if they were larger or close to the critical void size. For the present, we have assumed they are smaller than the critical void size.

Li: I think it important to emphasize that during ion bombardment there is a very limited amount of time for a ripening process. During a neutron bombardment in a real reactor, the voids grow slowly and you have much more time available for ripening. Therefore there is the possibility that the swelling limit observed in the ion-bombardment case may not be applicable to the reactor situation.

Wechsler: You mentioned that there is some evidence that at low temperatures and at short time that homogeneous nucleation may occur, and that your theory predicts reasonable values in those cases. But, as I understand your theory, when you set up the kinetic equations for the generation and the removal of vacancies and interstitials, you assume a dynamic equilibrium for voids and interstitials. But at low temperatures and at short times is precisely when the dynamic equilibrium may not be established. Have you looked at that at all?

Harkness: The conditions under which the quasi-steady-state assumptions hold were detailed in a recent paper (Ref. 18 of this paper). Calculations have indicated that these conditions are met for the full range of expected reactor conditions.

Nelson: Just one small comment about the saturation of number density. I think some of our results really do not suggest that that is happening. It goes the other way, if anything.

Harkness: Your point may well emphasize that one must expect different saturation behavior depending on whether or not the dislocation loops have unfaulted. As mentioned in the text of the paper, the unfaulting of loops is expected at about 800 Å in 304 stainless steel. These loops will then be able to

glide and thus increase the probability of void-dislocation and dislocation-dislocation interactions. At higher temperatures, individual loops grow faster, thus unfault at lower dose and tend to interact with the void microstructure earlier. I should have emphasized that our result, which showed that one should expect a lower void volume at saturation with a higher void number density, assumed the same dislocation structure in each case.

NUCLEATION OF VOIDS IN MATERIALS DURING HIGH-ENERGY IRRADIATION

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ABSTRACT

High-energy radiation simultaneously produces vacancies and interstitials in crystalline materials, and, therefore, both types of defects are supersaturated during irradiation. The nucleation of defect precipitates under this circumstance is fundamentally different from the usual nucleation problem because of the competing effects of interstitials and vacancies on the size distribution of precipitate embryos. The rate of homogeneous nucleation of voids in such a material, in which interstitials as well as vacancies are supersaturated, is derived in this paper.

A useful parameter to characterize the effect of excess interstitials on the nucleation of voids is the ratio of the rates at which interstitials and vacancies arrive at and are incorporated into void embryos. At a constant vacancy supersaturation, as this arrival-rate ratio increases from essentially zero (i.e., interstitials in equilibrium with vacancies), the nucleation rate decreases and the size of the critical nucleus increases. Thus, to obtain a given rate of nucleation, increasingly larger supersaturations are required as the arrival-rate ratio increases. The calculated changes are gradual at low values of this ratio but become so drastic as the ratio approaches unity that no nucleation of voids is then possible. As in classical nucleation theory, the rate of nucleation increases very rapidly with increases in supersaturation. This rapid increase of rate is obtained for all arrival-rate ratios.

We find that the supersaturation of defects that occur during irradiation in a high flux of energetic neutrons or ions is sufficient for readily observable nucleation rates of voids at intermediate temperatures but insufficient at high temperatures.

A few years ago, Cawthorne and Fulton¹ discovered that voids form in a material during its exposure to fast neutrons. Void formation is connected with swelling of structural materials and is a considerable design problem for fast breeder reactors. Similar voids form during bombardment with energetic ions or electrons. A number of experimental²⁻²² and theoretical studies^{9,10,23-26} of the phenomenon have been conducted since its discovery. The *growth* of existing void nuclei is reasonably well understood by now. This paper treats their *nucleation*.^{27,28}

The conditions for nucleation of defect clusters during irradiation with fast particles are fundamentally different from those in other types of nucleation, such as occur in precipitation or condensation. The radiation produces defects in the material. Since most of the atoms knocked off their regular sites will come to rest interstitially in the crystal between occupied sites, the two predominant and most important defects, vacancies and interstitials, are produced in essentially the same numbers. At sufficiently high temperatures, both types of defects are mobile and will diffuse until they cease to exist owing to annihilation at such sinks as grain boundaries and dislocations, recombination with the opposite type of defect, or formation of defect clusters of various types. These defect clusters can be considered as embryos for "defect precipitates." The basic difference between this and other nucleation phenomena is that a void can grow by *adding* a vacancy or by *emitting* an interstitial, and it can shrink by *adding* an interstitial or *emitting* a vacancy; a normal precipitate can grow only by *adding* and shrink only by *emitting* molecules.

Irradiation produces the defects continuously. Hence the concentrations of both vacancies and interstitials are maintained in excess of their respective thermal-equilibrium concentration, i.e., both types of defects are supersaturated. Since the rate of destruction of the defects at surfaces, grain boundaries, and dislocations, will, in general, be different, one needs a theory of their nucleation for arbitrary and probably different supersaturations. For simplicity and to demonstrate the basic method, we have chosen to consider voids rather than other defect precipitates, such as dislocation loops. Furthermore, to keep the treatment as simple as possible, we shall not consider in this paper the complications that may be present in practical cases, such as mechanical stresses and insoluble gases stemming from (n,α) reactions.

In the following section, using equilibrium thermodynamics, we shall derive the constrained equilibrium distribution of void embryos for a given vacancy supersaturation *when* the concentration of interstitials is in equilibrium with the concentration of vacancies. As will be apparent in the section titled "Effect of Interstitials on the Void Nucleation Rate," such a distribution is needed to obtain the distribution of void embryos when both types of defects, interstitials and vacancies, are supersaturated. The steady-state nucleation rate is then derived along the lines of classical nucleation theory. In the section headed "Evaluation of the Nucleation Equations," general implications and some numerical results are discussed.

THERMODYNAMICS: THE CONSTRAINED EQUILIBRIUM DISTRIBUTION OF VOIDS

Consider a system that contains vacancies and clusters of vacancies, called voids. The free energy of the system can be written as

$$F = F_0 + \sum_x n_x W(x) - kT \sum_x \ln \frac{(x)^{n_x} (N/x)!}{(N/x - n_x)! n_x!} \quad (1)$$

where F_0 is the free energy of the system with neither vacancies nor voids, $n^0(x) \equiv n_x$ is the number of voids containing x vacancies, and $W(x)$ is the reversible work required to form a void of size x . The last term in Eq. 1 is the configurational entropy due to the presence of the voids and is obtained by calculating the number of distinguishable ways in which voids can be distributed in a crystal containing N lattice sites.

The change in free energy of the system upon adding one void of size x , i.e., the chemical potential of voids of size x , is

$$\begin{aligned} \mu_x &\equiv \frac{\partial F}{\partial n_x} = W(x) - kT \left[\ln x + \ln \left(\frac{N}{x} - n_x \right) - \ln n_x \right] \\ &= W(x) - kT \ln \frac{N - xn_x}{n_x} \end{aligned} \quad (2)$$

or, since $x n_x \ll N$,

$$\mu_x = W(x) + kT \ln \frac{n_1}{N} \quad (3)$$

For the special case of vacancies, i.e., $x = 1$, Eq. 3 becomes

$$\mu_1 = W(1) + kT \ln \frac{n_1}{N} \quad (4)$$

Applying Eq. 4 to vacancies in *thermal* equilibrium, which we denote by the subscript e , and choosing the thermal-equilibrium state as the reference state, i.e.,

$$\mu_{1e} = W(1) + kT \ln \frac{n_{1e}}{N_e} \equiv 0 \quad (5)$$

permits us to eliminate $W(1)$, the formation energy of the vacancies, from Eq. 4. The chemical potential of vacancies, Eq. 4, at any concentration $C_v \equiv n_1/N$ can then be expressed in terms of the supersaturation

$$S = C_v/C_{ve} \equiv (n_1/N)/(n_{1e}/N_e) \quad (6)$$

as

$$\mu_1 = kT \ln S \quad (7)$$

For the system to be in equilibrium requires that the formation of a void of size x from x vacancies occur without change in total free energy; thus

$$0 = \mu_x - x\mu_1 = W(x) + kT \ln n_x/N - x kT \ln S \quad (8)$$

with the use of Eqs. 3 and 7. Solving Eq. 8 for the void-size distribution n_x in equilibrium with a vacancy concentration, n_1 , yields

$$n^0(x) \equiv n_x = N \exp \{ - [W(x) - xkT \ln S] / kT \} \quad (9)$$

(In our recent paper,²⁷ we showed that the presence of interstitials, when they are in equilibrium with the vacancies, does not alter the void distribution given in Eq. 9.)

To continue further one needs $W(x)$, the reversible work required to form a void of size x . This cannot be obtained from rigorous thermodynamics, so we adapt the usual model used in nucleation theory to this problem. We therefore assume that

$$W(x) = s(x) \cdot \sigma \quad (10)$$

where $s(x)$ is the surface area and σ is the surface free energy per unit area. For simplicity the void will be considered spherical; thus its surface area

$$s(x) = 4\pi(3v/4\pi)^{2/3} x^{2/3} \equiv s^0 x^{2/3} \quad (11)$$

where v is the volume per vacancy. Combining Eqs. 9, 10, and 11, one finally obtains for the equilibrium distribution of voids

$$n^0(x) = N \exp (x \ln S - \xi x^{2/3}) \quad (12)$$

where $S \equiv C_1/C_{1e}$ and $\xi \equiv s^0 \sigma / kT = 4\pi(3v/4\pi)^{2/3} \sigma / kT$.

EFFECT OF INTERSTITIALS ON THE VOID NUCLEATION RATE

In nucleation theory one usually assumes that embryos increase or decrease in size by adding or losing one molecule at a time. In the nucleation of voids, however, a major complication arises from the presence of interstitials; not only can a void grow by adding vacancies and decay by emitting them, it also can grow by emitting interstitials and decay by adding them.

Let us write down the *net* flow of void embryos, $J(x,t)$; i.e., the rate at which voids containing x vacancies grow to voids containing $x+1$ vacancies minus the rate for the inverse process:

$$J(x,t) = \beta_v s(x) f(x,t) - \gamma_v(x+1) s(x+1) f(x+1,t) - \beta_i s(x+1) f(x+1,t) + \gamma_i(x) s(x) f(x,t) \quad (13)$$

where β_v and β_i are the rates at which vacancies and interstitials, respectively, arrive at and are incorporated into a void, per unit area, per unit time; $\gamma_v(x)$ and $\gamma_i(x)$ are the rates at which vacancies and interstitials, respectively, leave a void of size x per unit area, per unit time; $s(x)$ is the void surface area; and $f(x,t)$ is the concentration of voids of size x at time t . [The term in $\gamma_i(x)$ is very small in materials with a high energy of formation for interstitials and can be neglected.²⁹]

A standard difficulty in nucleation theory now faces us; we do not know γ_v , nor do we know the distribution of concentrations $f(x,t)$. The assumption is therefore made (although it is not usually explicitly stated) that the rates at which vacancies leave a void depend on the size of the void but not on the actual concentrations of vacancies and interstitials nor on the details of the dynamics.

We are interested in nucleation in systems in which both the vacancies and the interstitials are supersaturated to independent, arbitrary extents. First, we will consider a system in which only the vacancies are supersaturated and in which the concentration of interstitials is constrained to be in equilibrium with the vacancy concentration (a superscript zero will be used in such cases). Since, for such a system, both the vacancies and the interstitials are in equilibrium with the voids, one is able to invoke detailed balance, i.e., if one requires the net flow of embryos J to be zero, then both the flow of embryos due to the addition and emission of vacancies J_v^0 and due to addition and emission of interstitials J_i^0 will be zero separately. Thus, from Eq. 13,

$$J_v^0 = \beta_v s(x) n^0(x) - \gamma_v(x+1) s(x+1) n^0(x+1) = 0 \quad (14)$$

$$J_i^0 = -\beta_i s(x+1) n^0(x+1) + \gamma_i(x) s(x) n^0(x) = 0 \quad (15)$$

where $n^0(x)$ is the constrained *equilibrium* distribution of concentrations of voids derived in the preceding section. By rearranging Eqs. 14 and 15, one readily obtains γ_v and γ_i , the rates at which voids emit vacancies and interstitials.

As shall be shown below, one will need the constrained distribution of void concentrations $n(x)$ for arbitrary vacancy and interstitial concentrations, obtained by requiring that the net flow of embryos equal zero. Setting $J = 0$ in Eq. 13, neglecting $\gamma_i(x)$, and replacing the distribution $f(x,t)$ by the corresponding constrained distribution $n(x)$, one obtains

$$\beta_i + \gamma_v(x+1) = \frac{\beta_v s(x) n(x)}{s(x+1) n(x+1)} \quad (16)$$

Since the vacancy and interstitial concentrations are independent and therefore cannot be in equilibrium simultaneously with any void distribution, one cannot obtain $n(x)$ from thermodynamics. However, Eq. 16 can be viewed as determining the distribution $n(x)$, all other quantities in this equation being physically well defined. Eliminating the γ_v by substituting Eq. 14 into Eq. 16, we are able to relate $n(x)$ to $n^0(x)$, i.e., to the constrained *equilibrium* distribution of void nuclei with the same vacancy concentration but with the interstitials in equilibrium with the vacancies. Thus we obtain

$$\beta_i + \beta_v \frac{s(x) n^0(x)}{s(x+1) n^0(x+1)} = \frac{\beta_v s(x) n(x)}{s(x+1) n(x+1)} \quad (17)$$

which can be rearranged into a recursive equation for $n(x)$

$$n(x+1) = n(x) P_x n^0(x+1)/n^0(x) \quad (18)$$

where P_x is defined as

$$P_x \equiv \left[1 + \frac{\beta_i}{\beta_v m^0(x, x+1)} \right]^{-1} = \frac{\beta_v / m^0(x, x+1)}{\beta_v / m^0(x, x+1) + \beta_i} \quad (19)$$

with

$$m^0(x, x+1) \equiv \frac{s(x+1) n^0(x+1)}{s(x) n^0(x)}$$

The recursive equation (Eq. 18) has the solution

$$n(x) = n^0(x) \prod_{j=1}^{x-1} P_j \quad (20)$$

where we have chosen $n(1) = n^0(1)$, i.e., the concentration of vacancies is considered the independent variable, whether or not the interstitials are in equilibrium. Thus, from the distribution $n^0(x)$ obtained from thermodynamic considerations for a given arbitrary vacancy concentration, one can obtain the constrained distribution $n(x)$ at any concentration of interstitials. It should be emphasized that the distribution $n(x)$ is neither in equilibrium with the vacancies nor with the interstitials. In fact, it is maintained kinetically by an equal and opposite flow of embryos $J_v(x) = -J_i(x)$ caused by addition and emission of vacancies and of interstitials, respectively.

We can now express the net flow of void embryos $J(x, t)$ in terms of $n(x)$ and $n^0(x)$. Substituting Eq. 16 into Eq. 13, one has

$$J(x,t) = \beta_v s(x) n(x) \left[\frac{f(x,t)}{n(x)} - \frac{f(x+1,t)}{n(x+1)} \right] \quad (21)$$

Note that Eq. 21 does not explicitly depend on the actual concentration of interstitials. Yet, obviously, Eq. 21 *must* depend strongly on the interstitial concentration; in the limit of large interstitial concentrations, so many more interstitials than vacancies would arrive at voids that it would be impossible for voids to nucleate. *The effect of the interstitials is hidden in $n(x)$* , the constrained distribution of voids for arbitrary independent interstitial and vacancy concentrations as given by Eqs. 19 and 20.

Following the standard procedures of nucleation theory, Eq. 21 can be solved (see our recent paper^{2,7} for details), with the result,

$$J = \beta_v N s^0 \left[\left(g''(\bar{x}) + \frac{2}{9} \bar{x}^{-4/3} \right) / 2\pi \right]^{1/2} \exp [g(\bar{x}) - x g'(\bar{x}) - \xi \bar{x}^{2/3} / 3] \quad (22)$$

where

$$g(x) = \sum_{j=1}^{x-1} \ell_n P_j + \frac{2}{3} \ell_n x \quad (23)$$

where P_j is defined in Eq. 19 and where $\bar{x}$ is defined by the equation

$$\left[g'(x) + \ell_n S - \frac{2}{3} \xi x^{-4/3} \right]_{x=\bar{x}} \equiv 0 \quad (24)$$

For any given value of the supersaturation S , Eq. 24 determines a critical size, $\bar{x}$, which in turn determines the nucleation rate, J , via Eq. 22. Alternatively, for any given nucleation rate, Eqs. 22 and 24 can be solved for the supersaturation and critical size by iteration.

EVALUATION OF THE NUCLEATION EQUATIONS

In this section we evaluate Eqs. 22 and 24 and discuss the interrelations among some of the more important quantities, e.g., supersaturation, critical size of nuclei, and the constrained distribution of voids. The material parameter values listed in Table 1, appropriate for nickel, were used, and they thus give results that should be useful for actual structural reactor materials at least semiquantitatively. A surface free energy of 1000 ergs/cm² was assumed. This value is typical of alloys and is somewhat lower than values quoted usually for nickel. The nucleation rates of $J = 10^8$ and 10^{12} cm⁻³ sec⁻¹ used in these calculations would produce the typically observed density of 10^{15} voids/cm³ in

TABLE 1
VALUES OF VACANCY PROPERTIES USED
IN CALCULATIONS*

Formation energy, E_v	1.39 eV
Energy of motion, U_v	1.38 eV
Formation pre-exponential, C_0	$4.1 \times 10^{23} \text{ cm}^{-3}$
Frequency factor, ν_0	$5 \times 10^{13} \text{ sec}^{-1}$
Jump distance, b_v	$2.49 \times 10^{-8} \text{ cm}$

*These values are given for nickel by A. Seeger and H. Mehrer in *Vacancies and Interstitials in Metals*, p. 1, A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (Eds.), North Holland Publishing Company, Amsterdam, 1970.

$\frac{1}{3}$ year and $\frac{1}{3}$ hr, respectively; they thus correspond to time scales applicable to reactors and ion-bombardment experiments, respectively.

To evaluate Eqs. 22 and 24, one needs to express the quantities β , the rates at which defects arrive and are incorporated into voids per unit area and unit time (hereafter called "arrival rates") in terms appropriate for solids, i.e., $\beta = \nu bc / (4\omega)$,

where ν = jump frequency
 b = jump distance
 C = atomic fraction
 ω = atomic volume

The following expressions have been used for the jump frequencies and the concentration of vacancies

$$\nu = \nu_0 \exp(-U/kT) \quad (25)$$

and

$$C = S \cdot C_e = SC_0 \exp(-E/kT) \quad (26)$$

where U and E = energies of motion and formation, respectively
 ν_0 and C_0 = proper pre-exponentials including entropy factors
 $S(\equiv C/C_e)$ = supersaturation
 C_e = thermal-equilibrium concentration of vacancies

We shall now consider the constrained equilibrium size distribution of voids, Eq. 20. Figure 1 shows the effect of increasing the interstitial arrival rate at a fixed vacancy arrival rate. The concentration of nuclei containing x vacancies

Fig. 1 Concentration of void embryos as function of their size when the net flow of embryos is constrained to be zero. The parameters are the arrival-rate ratios β_i/β_v , and the nucleation rates (in $\text{sec}^{-1} \text{ cm}^{-3}$) of the unconstrained system. $T = 900^\circ \text{ K}$, $S = 430$. Solid circles indicate the minima of $s(x) n(x)$.

drops rapidly from its value at $x = 1$ (i.e., the vacancy concentration), reaches a minimum at about the critical nucleus size, and then starts to increase. With increasing interstitial arrival rate (increasing β_i/β_v), the slope of the distribution, dn/dx , decreases everywhere (it becomes more negative where it is negative). The reason is that increasing the interstitial flux increases the fraction of embryos of a given size x which actually shrink to the next smaller size ($x - 1$), whereas to maintain the constrained distribution requires that the increased fraction be balanced by a decreased concentration of nuclei of size x relative to that of size ($x - 1$).

Increasing the arrival-rate ratio shifts the minimum in the distribution $n(x)$ to larger sizes and to lower concentrations. Since the nucleation rate is proportional to $n(x)$, it is tremendously decreased by the deepening and widening of the minimum in $n(x)$. The nucleation rates, as shown in Fig. 1, decrease by about six orders of magnitude as the arrival-rate ratios increase from 0 to 0.97. Note that the nucleation rate decreases very rapidly as β_i/β_v approaches unity. In fact, for ratios equal to 1 (or larger), nuclei are incapable of growth and void nucleation is therefore impossible. To obtain any given rate of nucleation as β_i/β_v approaches unity requires higher and higher vacancy supersaturations. Furthermore, the very strong dependence of the nucleation rate on the supersaturation, which is a characteristic of ordinary nucleation, i.e., when $\beta_i/\beta_v = 0$, is essentially unchanged even by large values of the arrival-rate ratio, as shown in Fig. 2. A factor of 10 increase in supersaturation causes the

Fig. 2 Nucleation rate as function of the vacancy supersaturation. The parameters are the arrival-rate ratios β_i/β_v and temperature.

nucleation rate to increase from 1 to 10^{15} nuclei/(cm³)(sec) at 900°K or from 1 to 10^{10} nuclei/(cm³)(sec) at 700°K independent of the arrival-rate ratios.

The effect of temperature on the vacancy concentration, C , required to give a fixed nucleation rate is shown in Fig. 3 by the set of curves identified by the arrival-rate ratios, β_i/β_v . Over most of the temperature range, C increases with increasing temperature even though the supersaturation $S \equiv C/C_{ve}$ decreases, as can be seen by the diminishing distances between these curves and the curve labeled C_{ve} , giving the thermal-equilibrium concentration of vacancies. The curves labeled by the parameter p represent the steady-state concentrations of vacancies, C_n , which result from the continuous production of defect pairs ($\dot{n}$ in at. fraction/sec) by irradiation, balanced by the loss of interstitials and vacancies by recombination or sink annihilation.²⁶ The parameter p is the probability per

Fig. 3 Steady-state vacancy concentration caused by a production rate of $\dot{n} = 10^{-3}$ atom fraction of defect pairs per second; the parameter p on the curves is the probability per jump that a defect is annihilated at existing sinks, such as dislocations. The curve labeled C_{ve} is the thermal-equilibrium concentration of vacancies. The set of curves labeled by the arrival-rate ratio, β_i/β_v , indicates the vacancy concentration required to give a nucleation rate of 10^{12} voids/(cm³)(sec). Such a nucleation rate is thus obtained at the temperature and vacancy concentration at the intersection of the curves under the conditions characterized by the curve parameters. The nucleation rate will be higher (lower) at temperatures below (above) the intersection temperature at fixed values of the parameters.

defect jump that the defect is annihilated at a sink, such as dislocations, grain boundaries, and surfaces. The values chosen for p range from those typical for an annealed metal (10^{-7}) to those typical of a heavily cold-worked metal (10^{-3}). At low temperature, C_n is large because the mean lifetime of a vacancy before annihilation is long on account of its low jump frequency. Increasing the temperature increases the jump frequency (see Eq. 25) and thus lowers the lifetime and hence the radiation-induced steady-state vacancy concentration. At

high temperature, C_n approaches the thermal-equilibrium concentration of vacancies, C_{ve} .

The indicated rate of nucleation [$J = 10^{12}$ voids/(cm³)(sec¹)] occurs where the curves intersect. It is evident from Fig. 3 that the irradiation produces vacancy concentrations high enough for very large nucleation rates at low temperatures. However, as the temperature increases, the radiation-induced vacancy concentrations drop below the concentrations required for nucleation. The temperature of the crossover is sensitive to the sink-annihilation probability, p , the arrival-rate ratio, β_i/β_v , and other physical quantities. Nevertheless, a high-temperature limit to the homogeneous nucleation of voids exists over a wide range of parameters, as is shown in Figs. 3 and 4. The defect production rates $\dot{n}$, used as parameters, range from those expected in a fast breeder reactor

Fig. 4 Steady-state vacancy concentrations for several defect production rates $\dot{n}$ and a sink-annihilation probability $p = 10^{-7}$; and vacancy concentrations required for several nucleation rates J (in cm⁻³ sec⁻¹) at an arrival-rate ratio of 0.99. Such nucleation rates are obtained at the indicated defect production rates at the temperature where the curves intersect.

($\sim 10^{-6} \text{ sec}^{-1}$) to the practical limit achievable by ion bombardment ($\sim 10^{-2} \text{ sec}$). The temperature of the cutoffs for nucleation is about the same as that observed as the high-temperature limit of void formation in nickel and in stainless steels. Therefore one might conjecture that the observed limit is caused by the lack of nucleation of voids. Finally, it should be pointed out that the nucleation of interstitial precipitates probably occurs prior to the nucleation of voids in a metal that initially has no sinks. Since interstitials and vacancies are produced in equal numbers by the radiation and, in the absence of sinks, their concentrations build up equally, and since the jump frequency of interstitials is appreciably higher than that of vacancies, then the arrival-rate ratio, β_i/β_v , will be greater than unity and void nucleation is not possible. However, with sufficient supersaturation and an arrival-rate ratio larger than unity, the nucleation of *interstitial* precipitates, e.g., dislocation loops, *will* occur and provide defect sinks. The higher mobilities of interstitials will reduce their concentration more effectively than that of the vacancies, and β_i/β_v will approach unity. To reduce β_i/β_v below unity requires sinks that annihilate interstitials preferentially. This requirement is similar to that for the growth of voids, as has been discussed previously.^{2,3-2,6}

SUMMARY

A procedure has been developed that obtains the rate of homogeneous nucleation of voids in a material supersaturated with regard to both vacancies and interstitials. The constrained distribution of void embryos, i.e., the distribution that would result when the system is constrained to a zero nucleation rate in the presence of a prescribed vacancy and interstitial concentration, gives a convenient means to calculate the steady-state nucleation rate. However, unlike the usual case in nucleation, this distribution cannot be obtained by thermodynamics because arbitrary vacancy *and* interstitial concentrations cannot be in equilibrium with a single void-embryo size distribution. The competing arrival of interstitials and vacancies leads to a kinetically determined constrained distribution in which the flow of embryos to larger sizes resulting from the reactions of embryos with vacancies is balanced by a counterflow to smaller sizes caused by reactions with interstitials. The nucleation rate is expressed analogously to the form used in classical nucleation theory but with the kinetically constrained size distribution replacing the equilibrium distribution.

The method developed here can be extended to treat other types of defect precipitates, such as dislocation loops and stacking-fault tetrahedra. Similarly, the presence of insoluble gases or stresses in the material can be incorporated into the treatment by proper modifications of the constrained equilibrium distribution.

The presence of excess interstitials has a number of effects on the nucleation process: At a fixed vacancy supersaturation, an increase in interstitial concentra-

tion decreases the void nucleation rate and increases the size of the critical nuclei. For a given nucleation rate, higher vacancy supersaturations are required at an increased interstitial concentration. The very steep increase in nucleation rate as a function of supersaturation is retained in the presence of excess interstitials but occurs at higher values of the vacancy supersaturation.

Void nucleation is possible only when the rate of arrival (per unit area) of vacancies is larger than that of interstitials. This can be viewed as a consequence of the fact that growth of large void nuclei can proceed only under this condition. The arrival rates of defects are proportional to the product of their mobility and concentration. Since irradiation produces equal numbers of interstitials and vacancies and the mobility of the former is larger in metals, we expect the nucleation of interstitial precipitates to precede that of voids if the material contains initially insufficient defect sinks to drain the interstitials to low concentrations. The observation of interstitial loops in many irradiated materials showing voids indicates that this sequence may occur frequently.

The steady-state concentration of vacancies achieved in a high fast-neutron flux or during bombardment with energetic ions at intermediate temperatures is sufficient to cause profuse void nucleation. However, there is a temperature limit over a wide range of parameters above which the vacancy supersaturation is insufficient for void nucleation. Possibly the observed high-temperature limit of void formation is a consequence of nucleation difficulties. It should be emphasized that insoluble gases will ease the nucleation and may be vital to the formation of voids in certain cases by, e.g., preventing void embryos from collapsing to dislocation loops. But it appears that insoluble gases are not an absolute prerequisite for void nucleation.

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27. A more extensive version of this paper has recently been published. See J. L. Katz and H. Wiedersich, *J. Chem. Phys.*, **55**(3): 1414-1425 (Aug. 1, 1971).
28. Recently, another paper with many of the same ideas has also been published. See K. C. Russell, *Acta Met.*, **19**(8): 753 (August 1971).
29. In our extensive paper, Ref. 27, we do not neglect γ_i .

DISCUSSION BY ATTENDEES

Chen: In a simplified case of only the presence of supersaturated vacancies, a calculation of classical nucleation theory indicated a cluster smaller than a divacancy being a nucleus at annealing temperatures below -80°C for aluminum quenched from 600° . This shows a discrepancy in this type of calculation. How would the results of your calculation compare with that derived from experiments?

Katz: If the supersaturation is large enough, there is no barrier to nucleation. The observed rate of nucleation will in such cases be determined by the mobility of the vacancies. We have not compared our results to experiment since I know of no such experiments, that is, quenching experiments in the absence of heterogeneous nuclei such as trapped gas and in the absence of stress. As far as the small critical nucleus is concerned, that comes from ignoring the interstitials. If you include them, the size is ~ 1000 vacancies.

Balluffi: The basic assumption that the rate of point-defect emission from an embryo is a function only of size may not always be a completely satisfactory one. In general, the emission rate might be expected to depend upon the embryo surface and edge density (which should be a function of supersaturation) and the ability of absorbed defects to diffuse on the surface. It would probably be exceedingly complicated to include these factors in the formalism.

Katz: The complications you suggest may be correct. However, assuming an embryo is a function only of size is the usual approach in nucleation theory, and until other more obvious complications have been included in the theory, such as trapped gas and stress, these should probably be neglected. In any case, it may not be possible to fashion a theory that includes them.

Straalsund: Would you comment on the possible application of your theory to the nucleation of loops?

Katz: The same ideas will apply. However, it will be quite complicated since to describe the surface free energy of a loop will require at least two terms. Furthermore, the nucleation equation (Eq. 13) will have to be generalized for the more complicated shape and the probably different arrival rates at a loop edge vs. the loop surface.

Note Added in Proof for the Following Paper by Garner et al.

Recent analysis* of irradiation creep data obtained in fast-flux environments (EBR-II and DFR) indicates that irradiation creep can be described by a volume conservative process. The current FFTF design equation is given by an athermal equation (250 to 650°C) of the form:

$$\epsilon_i = A\sigma\bar{E}\phi + B\sigma\bar{E}\phi t \quad (1)$$

where ϵ_i is the uniaxial irradiation creep strain, σ the applied stress (psi), $\bar{E}$ the average neutron energy (MeV), ϕ the total neutron flux (neutrons/cm²·sec), t the equivalent full power time (hours), and A and B are material constants. The values of A and B for solution-treated and 20% cold-worked 316 stainless steel are given by:

Solution-Treated 316

$$A = -5.13 \times 10^{-23} \quad \text{when } \sigma < 22,000 \text{ psi}$$

$$= \frac{0.99 \times 10^{-18}}{\sigma} \quad \text{when } \sigma > 22,000 \text{ psi}$$

$$B = 3.94 \times 10^{-26}$$

20% Cold-Worked 316

$$A = 1.73 \times 10^{-23}$$

$$B = 2.74 \times 10^{-26}$$

*Westinghouse Electric Corporation, Advanced Reactors Division, Oxide Fuel Element Development Quarterly Progress Reports for Periods Ending September 30, 1971; and December 31, 1971, USAEC Reports WARD-4210T-3-10 and WARD-3045T-3-2.

THE EFFECT OF STRESS ON RADIATION-INDUCED VOID GROWTH

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ABSTRACT

The possible effects of applied stress on radiation-induced void growth are reviewed. A previous stress-induced void-growth model used in LMFBR design is critiqued and a new void-growth-rate equation is developed which includes the effects of applied stress. The primary influence of stress is shown to be the alteration of the activation energies for point-defect formation and migration.

A successful liquid-metal-cooled fast breeder reactor (LMFBR) design requires that the dependence of radiation-induced density changes in core structural materials must be determined for the significant variables. The current experimental effort is therefore focused on the characterization of radiation-induced swelling as a function of material composition, microstructure, prior mechanical and thermal history, as well as the ambient temperature, flux, and accumulated fluence to which the material is subjected. For fuel-element cladding and many core structural components, however, there is concern that the state of stress imposed on the swelling material may strongly influence or even dominate the swelling behavior, leading to important reactor-design implications.

Three candidate mechanisms are currently being considered as having the potential for creation or enhancement of voidage in structural materials under the combined effects of irradiation and stress.

1. The growth of cavities or helium bubbles located on grain boundaries under tension.
2. The volume changes associated with the hydrostatic component of irradiation creep.
3. The enhancement of void growth within grains due to stress-motivated point-defect currents.

The stress-induced growth of grain-boundary cavities or gas bubbles has been reported by numerous investigators.¹⁻⁵ Stress-rupture tests at a temperature of 700°C on stainless steel containing 40 ppm helium indicate that the major mode of deformation is due to the growth of grain-boundary cavities.³ However, at typical LMFBR operating temperatures, this mechanism is not expected to yield significant density changes.

Current irradiation-creep correlations employed in the Fast Flux Test Facility design⁶ predict that the hydrostatic component of irradiation creep will yield substantial volume changes. These volume changes have been attributed to the relative mobility of interstitials and their enhanced annihilation at stressed dislocations, giving rise to an incremental increase in the residual concentration of vacancies and vacancy clusters.⁷ Unfortunately the available data^{6,8} were obtained at temperatures below the LMFBR operating range and at fluences well below design requirements. Although the existing correlations predict a reduction of irradiation creep with increasing temperature, the extrapolation to high fluences introduces a large source of uncertainty in design. See "Note Added in Proof" on page 840.

Externally applied stresses have been previously considered as providing an additional driving force for defect migration in the vicinity of void surfaces, resulting in enhanced void growth for applied tensile stresses.⁹⁻¹¹ Li et al.¹² have considered the behavior of interstitial migration in the vicinity of a void subjected to a unidirectional tension. Although the vacancy migration was not considered, the interstitial current into the void was found to be enhanced, which would tend to decrease the void growth rate.

PREVIOUS TREATMENTS OF STRESS-ENHANCED VOID GROWTH

On the basis of thermodynamic considerations, Gulden and Kaae⁹ expanded a previous treatment of Harrison's¹⁰ and derived a formula for the stress-enhanced void growth in an irradiated material. They argued that the applied stress provides an additional force $\pi a^2 \sigma$ acting to expand or contract the void, where a is the void radius and σ is the "mean normal stress in the vicinity of the void." Therefore they concluded that the total force acting on the void surface is

$$F = \pi a^2 \left(\sigma + p - \frac{2\gamma}{a} + kT \ln \frac{C^v}{C_{eq}^v} - kT \ln \frac{C^i}{C_{eq}^i} \right) \quad (1)$$

where p is the internal gas pressure, γ is the surface tension, and C^v, C_{eq}^v and C^i, C_{eq}^i are the vacancy and interstitial concentrations far away from the void and the equilibrium concentrations, respectively.

Gulden and Kaae then derived the following radial growth-rate equation, assuming steady-state vacancy and interstitial fluxes to the void

$$\frac{da}{dt} = \frac{D_v}{a} \left\{ \frac{C^v}{C_{eq}^v} - \exp \left[\frac{2\gamma\Omega}{akT} - \frac{\Omega}{kT} (p + \sigma) \right] \right\} - \frac{D_I}{a} \left\{ \frac{C^i}{C_{eq}^i} - \exp \left[-\frac{2\gamma\Omega}{akT} + \frac{\Omega}{kT} (p + \sigma) \right] \right\} \quad (2)$$

where D_v and D_I are the self-diffusion coefficients for vacancies and interstitials and Ω is the atomic volume. Boltax et al.¹¹ condensed Eq. 2 considerably in terms of an "effective vacancy self-diffusion coefficient" D_v^E . They considered that the total volumetric swelling rate is composed of the experimentally observed stress-free component $\frac{d\left(\frac{\Delta V}{V}\right)_{SF}}{dt}$ and an additional stress-induced component that is proportional to the total stress-free swelling accumulated. Thus

$$\frac{d\left(\frac{\Delta V}{V}\right)}{dt} = \frac{d\left(\frac{\Delta V}{V}\right)_{SF}}{dt} + \frac{3a^2 \left(\frac{\Delta V}{V}\right)_{SF} D_v^E \Omega \sigma_H}{R_{SF}^4 kT} \quad (3)$$

where R_{SF} is the experimentally observed mean radius in stress-free swelling and σ has been replaced by the hydrostatic stress σ_H . This model is considered by its authors to be semiempirical; it has been correlated with limited data which show that, in the range 550 to 650°C, significant swelling increases over the stress-free prediction occur.¹³⁻¹⁵

Other investigators^{16,17} have also used the hydrostatic stress in treatments of stress effects on swelling, particularly in such force-balance statements as Eq. 1. Some confusion apparently exists as to the identity of the "mean normal stress σ " and its utilization in force-balance statements. Although it appears that the radial stress at the void surface is the only stress that can participate in a mechanical force balance at the surface, the hydrostatic stress is often substituted for σ with arguments directed toward chemical-potential changes that occur. The supersaturation terms in Eq. 1 are "chemical forces" or potential terms and cannot participate in the instantaneous mechanical force balance. Therefore in a correct treatment the effects of stress and supersaturation must be considered in terms of chemical-potential changes that occur in the void-matrix system. The radial stress at the surface of the void is always determined by the difference between the forces generated by the gas pressure and the surface tension. This induced radial stress is always equal to $\left(p - \frac{2\gamma}{a}\right)$

regardless of the magnitude of hydrostatic stress that may exist in the bulk of the material, which is determined by the externally applied stresses. The sum of

the first three terms in the parentheses of Eq. 1 is therefore always equal to zero, and stress would appear to have no effect on swelling.

A somewhat different approach to the void-growth problem under stress was taken by Harrison.¹⁰ He treated the problem by integrating the currents of defects over the void surface, and his result agrees in principle with the formula derived by Gulden and Kaae. However, he assumed that the defect currents due to concentration gradients are supplemented by currents that are proportional to the radial stress gradient at the surface of the void. This assumption is based on an argument advanced by Pines¹⁸ which states that the stress-induced defect currents depend only on the gradient of the stress component in the direction of the currents. However, this treatment ignores the fact that at the void surface there exist gradients in the other principal stresses as well, the net effect of which is to produce currents that would be directed against those produced by the radial gradient.

Bullough¹⁹ recently noted that Harrison's analysis would also be in error in the purely hydrostatic case if the gradient of the hydrostatic stress is employed in place of the gradient of the normal stress. Bullough noted that there is no gradient of the hydrostatic stress in a purely hydrostatic field and thus no additional driving forces are available for growth. In the general triaxial case, both positive and negative gradients in the hydrostatic stress will exist over the surface of a void, and these gradients will not be equal to the gradients in the radial stress.

ASSUMPTIONS REQUIRED FOR THIS TREATMENT

In the following section an expression is derived for the growth of a void in an isotropic elastic matrix subjected to irradiation and a triaxial stress state. The effect treated here considers void growth due to vacancy and interstitial currents only. It should be noted, however, that a void may grow or shrink by plastic deformation of the matrix around the void. This problem has been treated for the hydrostatic case allowing the matrix to be deformed by creep* and for the triaxial case of voids in a rigid-plastic matrix.²⁰ An atomistic process of this deformation around a void is, for example, dislocation climb near the void,²¹ which has been considered recently for a cylindrical void.

The void under consideration is assumed to adjust under growth in such a manner as to retain a spherical shape, even though the defect fluxes will not be uniform across the void surface. This assumption is supported by electron microscopic evidence of stressed fuel cladding. Nolfi²² has treated the shape changes of voids due to the effect of capillarity and applied stress in the absence

*For typical values of cladding stress, the unpublished work of W. G. Wolfer indicates that this mechanism may be neglected.

of irradiation and has demonstrated that capillarity would be an important effect at low defect supersaturations. It is also assumed that point-defect concentrations far from the void can be determined from the time- and position-dependent averages, employing a quasi-steady-state approach. Li et al.^{1,2} have discussed in detail the limitations of this approach.

The only effect of stress on void growth is expected to be the alteration of the free energies of formation and migration of the point defects, with resultant changes in equilibrium concentrations and defect mobility.

Symmetry considerations require that, in an isotropic medium, the effect of stress on diffusion can only depend on stress invariants, such as the hydrostatic stress and the equivalent stress. The derivation is therefore directed toward the anticipation that the final growth equation will be expressed in terms of stress invariants.

As has been shown by Shewmon,^{2,3} the driving force for diffusion is to a first order proportional to the gradient of the hydrostatic stress. The departure from cubical symmetry due to stress also results in an additional driving force depending on the deviatoric stresses. This effect, however, was shown to be negligible.^{2,4}

VOID GROWTH UNDER STRESS

The defect concentration gradients, as well as the gradients of the hydrostatic stress

$$\sigma_H = \frac{1}{3} (\sigma_1 + \sigma_2 + \sigma_3) \quad (4)$$

induce fluxes of vacancies and interstitials, j^v and j^i , as given by^{2,3}

$$j = -D(\sigma_H) \left(\nabla C + \frac{CW_m}{kT} \nabla \sigma_H \right) \quad (5)$$

where

$$D(\sigma_H) = D(0) \exp \left(\frac{W_m \sigma_H}{kT} \right) \quad (6)$$

is the diffusion coefficient for the migration of the defect under consideration, C is the local concentration of these defects, and W_m is the activation volume for migration. The activation volume is not strictly a volume but represents the derivative of the free energy of migration of the defect with respect to the local pressure.

For a spherical void of radius a , the growth rate can be expressed as

$$\frac{da}{dt} = \frac{\Omega}{4\pi} \int_S dS (j_n^v - j_n^i) \quad (7)$$

where j_n^v and j_n^i are the vacancy and interstitial fluxes normal to the void surface S and Ω is the atomic volume.

To obtain the net defect flux at the void surface, solve the steady-state diffusion equation for the differences between the two defect fluxes, and note that the generation and recombination terms cancel. Thus

$$\nabla \left(D^v \nabla C^v + D^v C^v \frac{W_m^v}{kT} \nabla \sigma_H - D^i \nabla C^i - D^i C^i \frac{W_m^i}{kT} \nabla \sigma_H \right) = 0$$

or

$$\nabla^2 \left[D^v(0) C^v \exp \left(\frac{W_m^v \sigma_H}{kT} \right) - D^i(0) C^i \exp \left(\frac{W_m^i \sigma_H}{kT} \right) \right] = 0 \quad (8)$$

which is recognized as the Laplace equation, to be solved with the following boundary conditions. At distances far from the void,

$$C^v = C_\infty^v \quad C^i = C_\infty^i \quad (9)$$

The boundary conditions in the vicinity of the void surface can be determined from the assumption that local thermal equilibrium exists there. Then

$$C^v(a, \sigma_H) = C_0^v \exp \left[- \left(p - \frac{2\gamma}{a} - \frac{W_f^v}{\Omega} \sigma_H \right) \frac{\Omega}{kT} \right] \quad (10)$$

and

$$C^i(a, \sigma_H) = C_0^i \exp \left[\left(p - \frac{2\gamma}{a} + \frac{W_f^i}{\Omega} \sigma_H \right) \frac{\Omega}{kT} \right]$$

where C_0^v and C_0^i = bulk equilibrium concentrations

W_f^v and W_f^i = activation volumes for vacancy and interstitial formation

γ = surface tension

p = gas pressure in the void

Equation 8 can be solved in terms of spherical harmonics for the boundary conditions (Eqs. 9 and 10). With Eq. 5 one can then calculate the net defect flux $(j^v - j^i)$ and obtain finally for the growth rate

$$\frac{da}{dt} = \frac{\Omega}{a} [D_v(\bar{\sigma}_H) C_\infty^v - D^i(\bar{\sigma}_H) C_\infty^i] - \frac{\Omega}{4\pi a} \int ds \left[D^v(0) C^v(a) \exp\left(\frac{W_m^v \sigma_H}{kT}\right) - D^i(0) C^i(a) \exp\left(\frac{W_m^i \sigma_H}{kT}\right) \right] \quad (11)$$

where $\bar{\sigma}_H$ is the externally applied hydrostatic stress. The local hydrostatic stress distribution around the void is^{2,5}

$$\sigma_H = \bar{\sigma}_H - \frac{5(1-\nu)}{3(7-5\nu)} [\sigma_1 (3 \sin^2 \theta \cos^2 \phi - 1) + \sigma_2 (3 \sin^2 \theta \sin^2 \phi - 1) + \sigma_3 (3 \cos^2 \theta - 1)] \quad (12)$$

where $\sigma_1, \sigma_2, \sigma_3$ are the externally applied principal stresses.

Expanding the exponentials of form $\exp(W\sigma_H/kT)$ in the integrand of Eq. 11, one can obtain an analytical expression for the growth rate. If terms higher than second order are neglected and the integration is performed, the growth rate can then be written as

$$\frac{da}{dt} = \frac{\Omega}{a} D^v(\bar{\sigma}_H) \left\{ C_\infty^v - C^v(a, \bar{\sigma}_H) \left[1 + \left(\frac{W_t^v \bar{\sigma}_{eq}}{kT} \right)^2 \right] \right\} - \frac{\Omega}{a} D^i(\bar{\sigma}_H) \left\{ C_\infty^i - C^i(a, \bar{\sigma}_H) \left[1 + \left(\frac{W_t^i \bar{\sigma}_{eq}}{kT} \right)^2 \right] \right\} \quad (13)$$

where

$$W_t^v = 0.264 (W_t^v + W_m^v) \quad (14)$$

and

$$W_t^i = 0.264 (W_t^i + W_m^i) \quad (15)$$

and Poisson's ratio ν was assumed to be $1/3$. The equivalent stress in the matrix σ_{eq} is of course defined by the applied principal stresses as

$$\bar{\sigma}_{eq}^2 = \frac{1}{2} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2] \quad (16)$$

Equation 13 gives the total growth rate of a void, including the following stress-free contribution.

$$\left(\frac{da}{dt}\right)_{\sigma=0} = \frac{\Omega}{a} D_v(0) \left\{ C_{\infty}^v - C_0^v \exp \left[- \left(p - \frac{2\gamma}{a} \right) \frac{\Omega}{kT} \right] \right\} \\ - \frac{\Omega}{a} D_i(0) \left\{ C_{\infty}^i - C_0^i \exp \left[\left(p - \frac{2\gamma}{a} \right) \frac{\Omega}{kT} \right] \right\} \quad (17)$$

Comparing Eqs. 17 and 13, one can see that the applied stresses give rise to a change in growth rate because the diffusivities, as well as the overall concentration gradients, of the defects are modified.

To assess the magnitude of the effect of stress on swelling, one has to make some assumptions about the activation volumes. Since no estimates for gamma iron are available, theoretical estimates were used for copper as hopefully representative of gamma iron. Girifalco and Welch²⁴ have calculated the following values for the case that the stresses arise from internal sources, accounting for lattice relaxation, elastic inhomogeneity, and electronic and vibrational changes around the defect.

$$W_m^v = +0.3\Omega, \quad W_f^v = -0.3\Omega, \quad W_m^i = -0.01\Omega, \quad W_f^i = +2.3\Omega \quad (18)$$

Note that the effect of applied stress on interstitial migration is negligible compared to that of interstitial formation and that the changes in the activation volumes for vacancies are equal and of opposite sign. Using these activation volumes and supersaturation balances obtained from the work of Harkness and Li,²⁶ one can assess the magnitude and direction of this effect for a stress situation typical of fuel-pin cladding. For a hoop stress of 20,000 psi, Table 1 shows the enhancement of swelling by stress.

Current efforts are directed toward the calculation of activation volumes appropriate for gamma iron. These growth relations will then be included in a computer routine developed from the work of Harkness and Li²⁷ which allows the sink densities and defect supersaturations to develop and change under irradiation. This work will be reported elsewhere.²⁸

CONCLUSIONS

It has been shown that externally applied stresses do not operate in a mechanical sense directly on the void surface. The effect of stress is only to alter the free energies for point-defect formation and migration. In the general triaxial case, the presence of a void leads to a modulation of the local hydrostatic stress over the void surface with deviations above and below the level of hydrostatic stress present in the undisturbed matrix. This modulation then leads to altered point-defect diffusivities and currents and generates nonuniform concentration gradients and fluxes across the void surface.

TABLE 1
ENHANCEMENT OF SWELLING RATE BY STRESS

Irradiation temperature, °C	Total fluence, neutrons/cm ²	Supersaturations*		Void radius, Å	$\left[\left(\frac{da}{dt} \right)_\sigma - \left(\frac{da}{dt} \right)_0 \right]$, cm/sec
		Vacancy	Interstitial		
400	7.2×10^{19}	2.87×10^4	5.35×10^{15}	20	3.51×10^{-13}
	7.2×10^{21}	1.99×10^3	3.59×10^{14}	20	2.43×10^{-14}
	7.2×10^{21}	1.99×10^3	3.59×10^{14}	100	4.86×10^{-15}
	7.2×10^{22}	597	1.08×10^{14}	100	1.46×10^{-15}
500	7.2×10^{19}	294	1.99×10^{13}	20	2.07×10^{-12}
	7.2×10^{21}	28.7	1.90×10^{11}	20	2.02×10^{-13}
	7.2×10^{21}	28.7	1.90×10^{11}	100	4.05×10^{-14}
	7.2×10^{22}	9.69	6.45×10^{10}	100	1.37×10^{-14}
600†	7.2×10^{19}	25.1	1.29×10^{10}	20	2.38×10^{-11}
	7.2×10^{21}	3.96	2.04×10^9	20	4.11×10^{-12}
	7.2×10^{21}	3.96	2.04×10^9	100	8.67×10^{-13}
	7.2×10^{22}	1.22	6.25×10^8	100	3.54×10^{-13}

Cladding hoop stress = 20,000 psi

*Other parameters needed for these calculations, such as surface tension and activation energies are substantially equal to the values for best fit of Harkness and Li.²⁷

†At this temperature, many of the stress-free growth rates are negative for the supersaturation balances used.

The predicted enhancement of the void growth rate in a tensile field is largely due to the enhanced diffusivity of vacancies in the matrix and to the fact that the interstitial equilibrium concentrations are altered near the void surface. If the applied stresses give rise to deviatoric components, as in the case of a fuel-pin cladding, an additional effect then arises. This leads to the physically interesting prediction that volume changes would arise in pure torsion, such as irradiation-creep experiments on springs.

The detailed numerical evaluation of the model is presently being performed. The crucial parameters of the model are the activation volumes for point-defect migration and formation. A preliminary numerical evaluation of the model showed stress-activated components of growth that are of the same magnitude as the stress-free growth rates predicted by Harkness and Li.²⁶ The enhanced growth rates under stress are expected to reduce the defect bulk supersaturations below the stress-free levels, retarding somewhat the enhanced growth under stress.

Experimental Westinghouse Electric Corporation subassemblies²⁹ are being prepared for insertion in EBR-II to characterize the effects of cladding hoop stress on irradiation-induced swelling over the temperature range of interest. Dimensional-change information as well as electron microscopic evidence from

these experiments will be used to illuminate the mechanisms by which stress affects dimensional changes of fuel-pin cladding.

ACKNOWLEDGMENT

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DISCUSSION BY ATTENDEES

Harkness: Under a uniaxial stress, do you expect more or less void growth?

Garner: We have considered the most crucial part of this question to be the definition of the appropriate activation volume. The ones we used were those supplied by Girifalco and Welch. If you put these into the equation, you get an *increase* under tension. I recognize that this is somewhat in opposition to the results of your paper (Franklin, Li, and Harkness) where you get a decrease, at least due to the interstitial component.

Huebotter: Why is it considered valid to separate out the effect of stress on swelling (thus obtaining a stress-free swelling expression) and then use that expression to design core components that will be under high stress?

Boltax: By comparison of essentially stress-free swelling data with that from stressed stainless steel, we obtain the net effect due to stress. This approach is the basis of the semiempirical model referenced in the paper. For design purposes, the major effects of stress on swelling occur at temperatures above 550°C. The sensitivity of this effect on fuel-pin behavior is under active study.

Zwilsky: The available data suggest that voids may grow under stress at elevated temperatures. Why is there such a sharp dependence on temperature, and where does it show up in your equations?

Garner: Since we are considering the effect of stress on the diffusion of point defects, the temperature dependence of the defect diffusivities dominates the temperature behavior. The diffusivities contain exponential terms in temperature, the effect of which overshadows that of other terms in the equations.

Norris: Have you considered the effect of stress on the void denuded zone at a grain boundary? If there were an effect tending to remove this zone, there could be potentially catastrophic effects on mechanical properties.

Garner: We have not considered this possibility to date. The stress-affected growth mechanism discussed in this paper requires the presence of a void to distort the local stress field and defect currents and therefore would not be a factor in the formation of the denuded zone. If the application of stress somehow acts to stabilize voids near the grain boundary such that the denuded zone did not form, the mechanical properties of irradiated material might indeed be strongly affected.

Carpenter: If you look at the chemical-potential gradient at grain boundaries, except under absurdly high stresses (much greater than the yield stress), the vacancy concentration gradient is always toward the grain boundary.

PREPARED DISCUSSION: THE EFFECT OF STRESS ON THE SHAPE OF VOIDS

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The effect of stress on the shape of voids in an isotropic elastic continuum is presently being studied. In our model, a uniaxial compression is applied to an elliptical hole, under boundary conditions of zero normal component of stress at the surface of the hole. The free energy of this system is determined as a function of the a/b ratio of the ellipse, the volume being held constant. The energy contributions in the analysis include the elastic stored energy in the stress field, the surface energy of the hole, and the work done by the applied stress. With no stress, the equilibrium shape of the hole is a cylinder. As the stress is increased, the a/b ratio for equilibrium increases, where the a axis is perpendicular to the stress axis. This is not just a strain effect, and it would require diffusion for equilibrium to be attained. The change in equilibrium shape is negligible for small voids and small stresses; however, as larger voids and higher stresses are considered, the a/b ratio for equilibrium increases, eventually leading to spontaneous collapse of the void at a rate determined by the diffusion mechanism.

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DISPLACEMENT RATES FROM THE LINDHARD MODEL AND THEIR USE IN THE ANALYSIS OF SWELLING DATA

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ABSTRACT

A major problem in predicting swelling behavior for reactor-design purposes is the proper correlation of data obtained under different irradiation conditions. As part of a study of the implications of a spectrally sensitive displacement model on the analysis of swelling data, a new displacement cross section has been calculated for stainless steel based on the energy partition theory of Lindhard et al. Void volume data are being collected from several laboratories and the best possible spectrum and fluence values associated with each data point. These spectra are being used to calculate the fraction F of flux exceeding 0.1 MeV, the spectrally averaged gross displacement cross section $\bar{D}$, and mean neutron energy $\bar{E}$. The relations between $\bar{D}$, $\bar{E}$, and F are presented for a wide range of EBR-II spectra and for several other reactors. An example is given to illustrate the differences in predictions of void formation that may result from using different measures of exposure. The relation between helium production rate, another important spectrally dependent quantity, and displacement rate in EBR-II spectra is presented.

A major problem in predicting the radiation-induced swelling behavior of metals for reactor-design purposes and in developing models of swelling is the proper correlation of data obtained under different irradiation conditions. Swelling data have usually been resolved into a fluence and a temperature dependence. The most commonly used measure of fluence is the number of neutrons having energies exceeding 0.1 MeV, but other limits from 10^{-10} to 1 MeV have also been used. Clearly, the apparent temperature dependence is a function of the measure of fluence, or, more generally, exposure. The purpose of this paper is to call attention to the need to consider the dependence of swelling on the neutron spectrum.

It has been recognized for a number of years¹ that the measure of exposure should encompass differences in neutron-energy spectrum encountered in various irradiation facilities and by various reactor components. It is generally

assumed that displacement of atoms is the primary source of radiation-induced changes in material properties. Knowledge of neutron spectra, scattering cross sections, and a model for the production of displacements by the knock-on atoms permits the calculation of relative displacement rates in different environments.

In earlier work on radiation-induced changes in mechanical properties, several investigators attempted with some success to improve data correlations by replacing fluence with a measure of the total displacements produced. The Kinchin-Pease model for displacement production per knock-on atom was used

Fig. 1 The displacement cross section for stainless steel based on a Lindhard model and ENDF/B scattering cross sections (Ref. 2).

initially, but it has given way to models that treat energy partition more realistically. The treatment of the production of primary knock-on atoms has evolved also from a hard-sphere elastic-scattering model to inclusion of anisotropic elastic scattering and inelastic scattering.

To determine the implication of an energy-sensitive displacement model on the analysis of swelling data, Doran² has calculated a new displacement cross section for stainless steel (see Fig. 1), based on the energy-partition theory of Lindhard et al.³ Void-volume data are being collected from several laboratories, and the best possible spectrum and fluence value is being assigned to each data point, using the results of the EBR-II Run 31F dosimetry test.⁴ From each spectrum the following quantities are computed: the spectral averaged neutron

energy $\bar{E}$, the spectral averaged gross displacement cross section $\bar{\Sigma}$, and the fraction F of the flux exceeding 0.1 MeV.

The relation between $\bar{\Sigma}$ and F is shown in Fig. 2. The points for EBR-II define a smooth, single-valued function. When points for reactors⁵ other than the metal-fueled EBR-II are included in Fig. 2, the relation between $\bar{\Sigma}$ and F becomes multivalued. In general, there will be a separate curve for each type of reactor, such as the oxide-fueled Fast Test Reactor (FTR).

Fig. 2 The relation between the spectral averaged displacement rate and the fraction of flux exceeding 0.1 MeV for several reactors. Here dpa means displacements per atom.

Presently available swelling data for stainless steel are not appreciably better correlated by $\bar{\Sigma}$ than by F , which is not surprising in view of the experimental uncertainties in the data, the source of the data being one type of reactor, and the relatively mild departure from proportionality in the relation shown in Fig. 2. Perhaps the most extensive data from a single reactor component (hence single material) are from a safety-rod thimble removed from EBR-II. Some of

these data⁶⁻⁸ are shown in Figs. 3 and 4 for two temperature ranges.* The scatter is unaffected by replacing F with $\bar{D}$ as the independent variable. Extrapolations of the data are affected, however, as are interpolations to other reactors, e.g., EBR-II to FTR. For example, the FTR driver spectrum, typical of the hardest spectrum expected in oxide-fueled liquid-metal-cooled fast breeder

Fig. 3 Some swelling data for a safety-rod thimble removed from EBR-II for the temperature range 370 to 372°C.

reactors, is appreciably softer than the hardest EBR-II spectrum. Consequently a total fluence at EBR-II core center of 6×10^{22} neutrons/cm² corresponds, in terms of gross displacements, to a total fluence of $\sim 10^{23}$ neutrons/cm² in the FTR fuel cladding.

For purposes of illustration, the swelling data shown in Figs. 3 and 4 were fitted to a power law using either F or $\bar{D}$ as independent variables (dashed curves). From these curves the density changes were determined for four different spectra at two fluences, 6×10^{22} neutrons/cm², for which no extrapolation was required, and 1×10^{23} neutrons/cm², for which some extrapolation was required for the harder (core) spectra. The parameters for the

*No temperature corrections have been made. Current data analyses are in disagreement as to whether significant corrections are necessary for the temperature ranges used. The data have been normalized to a common value of initial density (7.900) for comparison purposes.

Fig. 4 Some swelling data for a safety-rod thimble removed from EBR-II for the temperature range 420 to 480°C.

four spectra are included in Table 1 and the relative swelling values in Table 2. It can be seen that appreciable discrepancies exist for relatively soft spectra. It must be emphasized that this exercise is for illustrative purposes and represents only a preliminary treatment of a portion of the available data. Nor does the inclusion of an FTR reflector spectrum imply that swelling is expected to be a problem at this position. The point is that the neutron spectrum is expected to have a significant influence on void production, and spectral effects should be considered in interpreting data for modeling studies and for reactor-design purposes.

TABLE 1
SPECTRA CHARACTERISTICS

Parameter	EBR-II		FTR	
	Core	Blanket	Core	Shield
F	0.87	0.38	0.63	0.37
$\bar{D}$, displacements/ (cm ³)(neutrons/cm ²)	57.	18.	37.	15.
$\bar{E}$, MeV	0.80	0.17	0.49	0.14

TABLE 2
RELATIVE SWELLING VALUES FROM
CURVES OF FIGS. 3 AND 4

Total fluence, neutrons/cm ²	Nominal temp., °C	$(\Delta\rho/\rho \text{ based on } F) \div (\Delta\rho/\rho \text{ based on } \bar{D})$			
		EBR-II core	FTR core	EBR-II blanket	FTR shield
6×10^{22}	371	0.95	0.97	1.04	1.12
	450	0.94	1.0	1.19	1.38
1×10^{23}	371	0.98	1.0	1.06	1.15
	450	1.02	1.07	1.26	1.50

There have been attempts to apply data from thermal reactors to the design of fast reactors. The difficulty in choosing a proper basis for doing so is illustrated by the Engineering Test Reactor (ETR) and High Flux Isotope Reactor (HFIR) points plotted in Fig. 2. Both the unperturbed spectra and the hardened (by boron shielding) ETR-trap spectrum lie well away from the fast reactor points.

The mean energy $\bar{E}$ is a convenient parameter with which to characterize a spectrum. The relation between $\bar{D}$ and $\bar{E}$ is shown in Fig. 5 for essentially the same data as plotted in Fig. 2. The points for EBR-II and FTR nearly fall on a single curve that is almost linear except near the origin. Even the point for a fission spectrum [$\bar{E} = 2.0$ MeV, $\bar{D} = 117$ displacements/(cm³)(neutrons/cm²)] lies close to a linear projection of this curve. For the spectra considered, $\bar{E}$ is generally a closer approximation to $\bar{D}$ than is F if comparisons are made between medium and hard spectra, whereas F may be a better approximation if the comparison is between soft and medium spectra.

Although the gross displacement rate has been emphasized, it is clearly a crude parameter for use in correlating high-fluence data. Work is proceeding to include defect annealing and the changing damage state of the material.

Another important parameter that is sensitive to the neutron spectrum is the production rate of gaseous* transmutation products, particularly helium. This is discussed at some length in another paper⁹ of this conference. It has been demonstrated in both reactor irradiations¹⁰ and ion-bombardment experiments¹¹ that helium concentrations of several parts per million cause an increase in void concentration and a decrease in void size.

In using data to test models of swelling, it is important that the effect of helium production be considered; for example, the accumulation of helium at very high fluences may raise the maximum temperature at which significant

* Ultimately, at very high fluences, solid products may assume major importance.

Fig. 5 The relation between the spectral averaged displacement rate and the mean neutron energy for several reactors.

swelling is observed. To aid in such analyses, we show in Fig. 6 the spectral dependence of the ratio of the measured helium production rate to the gross displacement rate in a typical stainless steel. For a discussion of the factors determining the production rate of helium, see Ref. 9.

In summary, the inclusion of the influence of the neutron spectrum in the interpretation and application of swelling data, in terms of both displacement damage and transmutation effects, is believed to be important. The information presented in this paper concerning common irradiation facilities and the FTR, which is under construction, is intended to aid in this endeavor.

ACKNOWLEDGMENT

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Fig. 6 The ratio of the measured helium production in a typical stainless steel to the calculated number of displacements for EBR-II spectra.

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DISCUSSION BY ATTENDEES

Odette: Did you assume any ionization losses on the basis of a threshold energy in the Kinchin and Pease model?

Doran: Yes. The threshold was taken to be 56 keV.

Robinson: What did you do about including the effects of inelastic neutron scattering in calculating your displacement rates? A program called RICE, by J. D. Jenkins of ORNL, exists which uses the ENDF/B cross sections and the Lindhard partition theory to calculate displacement rates. This might give a convenient "working standard" for comparisons.

Doran: Inelastic neutron scattering was computed below ~ 4 MeV as the sum of contributions from discrete nuclear energy levels; at higher energies, an evaporation model was used. The angular distribution was assumed to be isotropic for inelastic scattering.

Thank you for calling attention to Jenkins' RICE program. We do not have at present a program that retrieves data directly from the ENDF/B tapes. I might mention that Jenkins' treatment of inelastic scattering appears to be slightly different from ours.

**BACK ROW STANDING
(LEFT TO RIGHT)**

W. G. Johnston
I. Y. Komen
K. Farrell
T. Elleman
R. W. Siegel
J. H. Austin
G. J. C. Carpenter

MIDDLE ROW STANDING (LEFT TO RIGHT)

H. Wiedersich
M. O. Marlowe
T. P. Papazoglou
R. Perrin
E. Metzbower
G. Martin
H. Huntington

O. S. Plail
P. S. Ho
Y. Adda

**FRONT ROW SEATED
(LEFT TO RIGHT)**

D. Gurinsky
S. Pugh
J. Cost
L. T. Chadderton
H. Conrads
R. Bullough
R. S. Nelson
K. Appleby

**BACK ROW STANDING
(LEFT TO RIGHT)**

A. J. Ardell
A. R. Wazzan
D. Stevens
J. Galligan
J. O. Stiegler

MIDDLE ROW STANDING (LEFT TO RIGHT)

S. K. Bhatnagar
H. Andresen
R. B. Adamson
J. H. Rosolowski
J. M. Donhowe
R. N. Duncan
J. S. Armijo

C. J. McHargue
E. E. Bloom

**FRONT ROW SEATED
(LEFT TO RIGHT)**

J. Beeler
M. S. Wechsler
P. Mohr
A. Turkalo
R. Scanlan
T. Anthony
F. Garner
W. G. Wolfer

BACK ROW STANDING
(LEFT TO RIGHT)

K. Ehrlich
J. Sprague
W. Schilling
R. Behrisch
J. R. Hawthorne
R. J. Price

MIDDLE ROW STANDING
(LEFT TO RIGHT)

A. Goland
J. M. Dupouy
A. Boltax
W. Bauer
C. W. Krapp
W. D. Wilson
A. Sosin

FRONT ROW SEATED (LEFT TO RIGHT)

M. T. Robinson	C. Y. Li
T. E. Mitchell	D. J. Michel
T. Blewitt	
F. Young	
R. Odette	
J. Moteff	
I. Torrens

**BACK ROW STANDING
(LEFT TO RIGHT)**

E. Bond
D. W. Keefer
J. L. Brimhall
T. Lauritzen
B. N. Singh

MIDDLE ROW STANDING (LEFT TO RIGHT)

P. R. Okamoto
S. Harkness
J. Jackson
A. Taylor
S. G. McDonald
A. A. Dykes
H. K. Birnbaum

D. Franklin
F. A. Comprelli

**FRONT ROW SEATED
(LEFT TO RIGHT)**

E. E. Gruber
M. Rühle
J. L. Katz
A. F. Rowcliffe
J. A. Spitznagel
P. R. Huebotter
J. R. Weir
B. C. Larson

BACK ROW STANDING
(LEFT TO RIGHT)
D. N. Seidman
P. Petroff
K. L. Merkle
A. S. Berger
D. I. R. Norris

MIDDLE ROW STANDING (LEFT TO RIGHT)
L. Ianniello
H. Van Den Broeck
F. Smidt
I. Manning
R. W. Balluffi
G. L. Kulcinski
K. L. Wilson
F. W. Wiffen
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FRONT ROW SEATED
(LEFT TO RIGHT)
S. Siegel
J. Washburn
W. Green
W. N. McElroy
D. M. Brudnoy
S. T. Byrne
W. E. Burchill
J. Bramman

BACK ROW STANDING
(LEFT TO RIGHT)

T. K. Bierlein
S. Saito
F. V. Strnisa
K. Russell
R. Johnson
J. Bourgoïn

MIDDLE ROW STANDING (LEFT TO RIGHT)

D. Peak
J. L. Straalsund
D. G. Doran
J. T. Robinson
J. W. Corbett
C. Weigel
O. Neilson
R. Raffaele
P. Brosious
K. Y. Chen

FRONT ROW SEATED (LEFT TO RIGHT)

Y. H. Lee
M. St. Peters
A. Wolfenden
D. W. Sandusky
W. A. Jesser
J. J. Laidler
K. Zwilsky
R. Dutton
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