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A MODEL FOR VOID FORMATION IN METALS
IRRADIATED IN A FAST-NEUTRON ENVIRONMENT

by

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A MODEL FOR VOID FORMATION IN METALS IRRADIATED IN A FAST-NEUTRON ENVIRONMENT

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ABSTRACT

This report presents experimental observations of void formation in Type 304 stainless steel irradiated with fast neutrons. The irradiated microstructure is characterized by a homogeneous distribution of both polyhedral voids and Frank dislocation loops. The number densities for each species were about $10^{15}/\text{cm}^3$; the defects were up to several hundred angstroms in size. Neither defect type, however, formed at grain boundaries. The temperature dependence of void formation is discussed from observations of three samples that received a fluence of $2 \times 10^{22} \text{ n/cm}^2$ at 375, 460, and 600°C. No observable voids formed at 600°C, whereas void formation was greater at 460°C than at 375°C.

A model to explain these observations has been developed, based on classical nucleation and growth theory. The results from the model were then incorporated into a Johnson-Mehl expression to determine a theoretical temperature dependence for void formation. This approach gave good agreement with experimental results.

The presence of helium atoms is suggested as an important factor in void nucleation in stainless steel. The gas atoms may stabilize the voids, which, in austenitic stainless steel, are a higher energy form than planar defects.

I. INTRODUCTION

Void formation in face- and body-centered-cubic structural materials subjected to fast-neutron ($E > 1 \text{ MeV}$) bombardment has become a problem of major concern in fast-reactor development. This phenomenon was first reported by Cawthorne and Fulton¹ in austenitic stainless steel and has since been discovered in aluminum,² nickel,³ and vanadium^{4,5} after they have been exposed to fast-neutron fluxes. Cawthorne and Fulton noted, in their initial observation, that the cavities were too numerous to

be explained in terms of gas-filled bubbles and thus were probably the result of vacancy agglomeration. This conclusion has since been borne out by annealing studies.⁶

The effect of void formation on the dimensional stability of reactor coolant channels in both present and future liquid-metal fast breeder reactors has been a subject of great interest at Argonne National Laboratory. As a result, a program was launched aimed at experimentally determining the characteristics of void formation, as well as at gaining a theoretical understanding of the phenomenon that could lead to its control. This report summarizes the present results of this investigation.

II. EXPERIMENTAL RESULTS

The results reported in this section were obtained from Type 304 or 304L austenitic stainless steel irradiated in the EBR-II reactor. This facility is not instrumented, so that both temperatures and neutron fluxes must be calculated. As a result, temperatures are known only, in some cases, to within $\pm 50^\circ\text{C}$. Neutron fluxes are also subject to considerable error. Relative values of temperatures and fluxes may be known much more accurately, however, so that, when possible, samples were examined from axial positions along an element irradiated in EBR-II.

Examination of a large number of irradiated Type 304 stainless steel samples by transmission electron micrography revealed three general characteristics. First, after irradiation between 371 and 650°C , the microstructure exhibited a large number density ($\sim 10^{15}/\text{cm}^3$) of polyhedral voids and Frank dislocation loops. At times it appeared that other dislocation forms might also be present, but no positive identification could be made. Figure 1a is a micrograph of an area in which the Frank dislocation loops are in strong contrast; Fig. 1b shows an adjacent area in which the loops are out of contrast, so that the polyhedral voids are shown more prominently.

The second characteristic observed in these microstructures is that no defects appeared to form at grain boundaries (see Fig. 2). This behavior is in direct contrast to that found in austenitic stainless steel irradiated at elevated temperatures in thermal reactors. In the latter, a large number of gas-filled cavities are formed at the grain boundaries. The difference between microstructures that result from fast and thermal irradiations may make it dangerous to extrapolate data on the mechanical properties of thermally irradiated material to the behavior of material in a fast-neutron environment.

Fig. 1. Characteristic Microstructure of Type 304L Stainless Steel Irradiated with Fast Neutrons at 460°C to a Fluence of 1.4×10^{22} n/cm². (a) Note Frank dislocation loops and (b) adjacent area with loops out of contrast. Note polyhedral voids.

Fig. 2
Characteristic Grain-boundary Region in Type 304L Stainless Steel Irradiated with Fast Neutrons (Note absence of any defect along grain boundary)

The third characteristic applicable to all the irradiated microstructures was that the size distributions of voids were quite narrow. In general, the standard deviation of the size-distribution curve was from 0.3 to 0.4 of the mean void size.

Table I summarizes the results for typical void diameters, number densities, size distribution, standard deviations, and immersion density. These results were taken from a Type 304 stainless steel control-rod thimble (CRT) and from Type 304L stainless steel Mark-IA cladding.

TABLE I. Void Formation in Type 304 Stainless Steel

Sample	Irradiation Temp, °C	Neutron Exposure, 10^{22} n/cm ²	Average Void Diameter, ^a Å	Standard Deviation, Å	Number Density of Voids, ^b 10^{15} /cm ³	Immersion Density Change, %
CRT	375	2.4	101	38	1.06	0.53
CRT	410	4.5	101	46	2.16	1.26
CRT	450	4.1	118	51	4.08	1.67
CRT	463	3.1	198	70	1.71	1.15
CRT	470	2.4	160	-	2.0	0.39
Cladding	462	1.3	117	32	2.5	-
Cladding	465	1.4	105	-	4.0	-
Cladding	492	1.1	140	-	1.5	-

^a $\pm 10\%$.

^bValues accurate within a factor of two.

The effect of temperature on void formation is striking. The phenomenon appears to be limited to a relatively narrow temperature range of about 300°C. Voids have not been observed below about 350°C or above 650°C, but do reach a maximum at about 500°C. Figure 3 illustrates the effect of temperature on void formation. The three samples were irradiated at nearly the same neutron exposure ($\sim 2.4 \times 10^{22}$ n/cm²) at temperatures of 375, 460, and 600°C. The void diameter increases from 100 to 160 Å, although the number density remains about the same as the irradiation temperature increases from 375 to 460°C. No voids or Frank loops are observed at the 600°C temperature. This latter temperature value is only known to within $\pm 50^\circ\text{C}$.

The effect of neutron exposure on void volume appears to be exponential. Experimental observations supporting this behavior are presented later (in Fig. 13) in comparison with theoretical predictions for void formation.

III. A MODEL FOR VOID FORMATION

In general, void formation appears to be the result of the condensation of vacancies from a matrix that has been supersaturated with point defects by the neutron bombardment. Irradiation by high-energy neutrons

Fig. 3

Micrographs Illustrating Temperature Dependence of Void Formation (fluence = 2.4×10^{22} n/cm²).
 (a) $T_{\text{Irr}} = 375^{\circ}\text{C}$, average void diameter = $100 \text{ \AA}$,
 (b) $T_{\text{Irr}} = 460^{\circ}\text{C}$, average void diameter = $160 \text{ \AA}$
 and (c) $T_{\text{Irr}} \approx 600^{\circ}\text{C}$, not absence of voids.

results in the formation of displacement spikes. For example, 1-MeV neutron bombardment of iron causes spikes that are typically ellipsoidal in shape. The computer studies of Beeler⁷ and others demonstrated that these spikes contain vacancy-rich cores surrounded by a region rich in self-interstitial atoms. Lück and Sizmann⁸ showed that this initial separation of species leads to a statistical clustering of each species. The net result of fast-neutron bombardment is the creation of small clusters of vacancies and interstitials in a matrix containing both free vacancies and interstitials. The free vacancies and interstitials each will generally maintain some steady-state concentration dependent on the neutron flux, the distances to available sinks, and the rate of vacancy-interstitial recombination. If these steady-state concentrations are in excess of those in thermal equilibrium, the system will be supersaturated and there will be a strong driving force for point-defect precipitation. The small vacancy clusters that are formed nearly instantaneously by the displacement spike could serve as precipitation sites for further vacancy condensation. Other nucleation sites could operate, but their effectiveness is assumed to be minor compared with the vacancy cluster formed by the displacement spike.

The purpose of this study is to show that the tools of classical nucleation and growth theory can be used to treat void formation in irradiated metals. A model has been developed to help explain the temperature dependence of the void formation and to indicate possible means of control.

IV. FREE-ENERGY CHANGE DURING VOID FORMATION

Consider a spherical cavity containing some gas at pressure P_G that is in a vacancy-supersaturated matrix to which a stress has been applied. Fine and Herring⁹ determined that, when the size of the cavity is near the critical size for nucleation, the free-energy change associated with cavity formation may be written as follows:

$$d(\Delta F) = -4\pi r^2 dr \left(P_G + \sigma + \frac{\rho}{M} \mu_v \right) + 8\pi r dr \gamma, \quad (1)$$

where

r = cavity radius,

σ = hydrostatic component of the applied stress,

ρ = density of the metal,

M = molecular weight of the metal,

μ_v = vacancy chemical potential = $E_v + kT \ln C_v$,

E_v = energy of vacancy formation,

C_v = vacancy concentration,

and

γ = surface energy of the metal.

The plastic strain energy around the void has not been included in Eq. 1 and, in this study, will be assumed small.

As Greenwood *et al.*¹⁰ showed, when no vacancy supersaturation exists, Eq. 1 leads to an expression for the vacancy concentration in equilibrium with a cavity of radius r that contains a gas at pressure P_G . When a vacancy supersaturation does exist, μ_v becomes

$$\mu_v = E_v + RT \ln N_v, \quad (2)$$

where, for our purposes, N_v is the steady-state concentration of vacancies due to the fast-neutron irradiation. Since the energy of vacancy formation is related to the vacancy population in thermal equilibrium, N_{v0} , through

$$E_v = -RT \ln N_{v0}, \quad (3)$$

Eq. 2 becomes

$$\mu_v = RT \ln (N_v/N_{v0}). \quad (4)$$

Substituting this result in Eq. 1 leads to the final expression for the free-energy change per unit volume associated with void nucleation,

$$\Delta F = -RT \frac{\rho}{M} \ln (N_v/N_{v0}) - P_G - \sigma + 2\gamma/r. \quad (5)$$

This expression for free-energy change illustrates a basic difference between the two types of cavities discussed in the literature; voids are the result of a dominant vacancy-supersaturation term, whereas bubbles exist under conditions in which the internal gas-pressure term is the most important.

A calculation of the magnitude of the vacancy-supersaturation term for austenitic stainless steel under EBR-II conditions will emphasize its importance. First, note that the coefficient, $RT \rho/M$, is quite large. For example, at 500°C,

$$RT \frac{\rho}{M} = 1.29 \times 10^5 \text{ psi}. \quad (6)$$

This high value means that the vacancy-supersaturation term in Eq. 5 becomes quite important even at small supersaturations.

V. STEADY-STATE CONCENTRATION OF VACANCIES

The actual vacancy concentration due to neutron irradiation that is present in-reactor has been estimated by Greenwood *et al.*,¹⁰ who showed that of the two most probable point-defect sinks (grain boundaries and dislocations), the dislocation network will probably be the controlling factor. Their result for the steady-state concentration of vacancies is

$$(N_V - N_{V0}) D_V = (1/4) A r_1^2 [2 \ln (r_1/r_d) - 1], \quad (7)$$

where D_V is the vacancy diffusion coefficient, A is the net creation rate of point defects, r_1 is the dislocation spacing, and r_d is the dislocation core radius. A similar expression may be written for the interstitial concentration. The net creation rate of point defects is evaluated by realizing that the probability of the occurrence of vacancy-interstitial recombination during migration to a dislocation is given by

$$1 - \exp(-10N_V\nu_i\tau); \quad (8)$$

therefore,

$$A = A' \exp(-10N_V\nu_i\tau), \quad (9)$$

where

A' = actual defect generation rate = $\phi\sigma_D\eta$,

ν_i = interstitial jump frequency,

τ = average interstitial lifetime,

ϕ = neutron flux,

σ_D = displacement cross section,

and

η = number of vacancies (or interstitials) not immediately annihilated upon creation of a displacement spike.

The only modification to the work of Greenwood *et al.* is the multiplication of the exponent by 10 to increase the effective recombination volume. This modification is based on computer studies,¹¹ which have indicated that recombination will occur if an interstitial comes within a 10-atom volume of a vacancy.

The final expression for the steady-state vacancy concentration becomes

$$N_V - N_{V0} = A'r_1^2/D_V[(1/2) \ln(r_1/r_d) - 1/4] \times \exp[-10(D_V/A'a^2)N_V(N_V - N_{V0})], \quad (10)$$

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Fig. 4. Steady-state and Thermal Vacancy Populations in Fast-neutron-irradiated Type 304 Stainless Steel

where a is the lattice spacing. Figure 4 shows the variation of both N_V and N_{V0} with temperature when values for the variables representative of solution-treated stainless steel in EBR-II are used; the values are $\phi = 2 \times 10^{15}$ n/cm²-sec, $\sigma_D = 3 \times 10^{-24}$ cm², $\eta = 300$ vacancies/primary knock-on atom (pka), $r_1 = 10^{-4}$ cm (corresponds to a dislocation density of 10^8 cm/cm³), $r_d = 10^{-7}$ cm, $D_V = 10^{-2} \exp(-30,000/RT)$, $N_{V0} = \exp(-38,000/RT)$, and $a = 3 \times 10^{-8}$ cm. Substitution of the relative vacancy concentration at, for example, 500°C in Eq. 6 yields a value for the vacancy-supersaturation term of

$$RT \frac{\rho}{M} \ln(N_V/N_{V0}) = 1.7 \times 10^6 \text{ psi.}$$

This value is much larger than any expected applied stress, indicating that the stress will not be an important factor during void nucleation.

VI. TEMPERATURE DEPENDENCE OF VOID FORMATION

The observed temperature dependence of void formation in Type 304 stainless steel may be understood through a consideration of nucleation theory. If one assumes that the void nucleation sites are the vacancy clusters formed by the displacement spike, then the temperature dependence will be the same as that for homogeneous nucleation. The basic result* of nucleation theory is that the nucleation rate is the product of the concentration of critical nuclei and their rate of growth. This approach is valid under the important assumption that the growth process is sufficiently slow so that the steady-state and equilibrium numbers of critical nuclei are the same. For void formation, the number N_{eq} of nuclei reaching critical size is given by

$$N_{eq} = k_1 \phi \exp(-16\pi\gamma^3/3RT\Delta F_V^2).$$

*See, for example, M. E. Fine, Introduction to Phase Transformation in Condensed Systems, Macmillan, New York (1965).

The neutron flux is included, since the vacancy clusters created by the displacement spikes are assumed to be the nucleation sites. It is assumed, for the present calculation, that these clusters are formed independently of time, and linearly with flux. The growth rate of the critical-size cavities is given by

$$k_2 \exp(-\Delta F_A/RT).$$

The rate of nucleation, I , then is the product, or

$$I = k\phi \exp(-16\pi\gamma^3/3RT\Delta F_V^2)(-\Delta F_A/RT), \quad (11)$$

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Fig. 5. Temperature Dependence of Rates of Void Nucleation and Void Growth in Type 304 Stainless Steel Irradiated in EBR-II

where $k = k_1k_2$ is a slowly varying function of temperature involving the vacancy concentration, the vibrational frequency, and the number of available nucleation sites; ΔF_A is the energy of vacancy diffusion; γ is the surface energy; and ΔF_V is the volume free energy, which, from Eq. 5, is $(RT\rho/M) \ln (N_V/N_{V0}) + P_G + \sigma$.

The temperature dependence of the nucleation rate is presented in Fig. 5. The values used to evaluate the expression were the same as those used previously to represent the irradiation of Type 304 stainless steel in EBR-II. Values for N_V and N_{V0} were obtained from Fig. 4, and γ was assigned a value of 1000 ergs/cm².

To compare this result with the observed temperature dependence of void formation, the temperature dependence of the growth rate must also be included. By assuming that only vacancies condense at voids, we may derive a first approximation of the cavity-growth rate in the following manner.

Consider a cavity of size r ($r > r_{\text{critical}}$) that grows to $r + dr$ by vacancy agglomeration in time dt while in a spherical cell of radius y ($y \gg r$). The increase in volume, dv , in time dt , is the difference between the vacancy and interstitial fluxes arriving at the surface of the cavity; that is,

$$dv = 4\pi r^2 dr = 4\pi r^2 dt(\Omega J_V - \Omega J_I). \quad (12)$$

The vacancy flux, J_V , is given by $(D_V/\Omega)\nabla C_V$, where C_V is the mole-fraction vacancy concentration and Ω is the atomic volume. The interstitial flux, J_I , is, by comparison, given approximately by $(D_I/\Omega)\nabla C_I$, where C_I is the interstitial concentration.

Insertion of these terms in Eq. 12 yields

$$dv = 4\pi r^2 dt(D_V \nabla C_V - D_I \nabla C_I). \quad (12a)$$

The flux terms are equal to a first approximation, unless a net attractive force exists between like species.

Since the formation of voids and interstitial loops is an experimental fact, one must presume that there is a preferential attraction of vacancies for voids and of interstitials for loops. Thus, void growth should proceed as a net difference between the vacancy and interstitial fluxes.

Since the temperature dependence of the two flux terms is nearly equal, the preferential migration of vacancies to voids will be presented for the present purpose of modeling the temperature and flux dependence of void formation by

$$dv = \alpha 4\pi r^2 dt D_V \nabla C_V,$$

where α is some temperature-independent positive constant much less than unity.

The concentration gradient around a spherical sink evaluated at the cavity surface is given by

$$\left. \nabla C_V \right|_r = \frac{N_V}{r} \quad (13)$$

when the steady-state vacancy population N_V is much greater than that in equilibrium with the cavity.

Substitution of Eq. 13 in Eq. 12a thus results in the following expression for the radial growth rate G :

$$G = \frac{dr}{dt} = \alpha D_V N_V / r. \quad (14)$$

Integration of Eq. 14 between some nucleation time τ and time $t > \tau$ results in the following expression for the void radius:

$$r = (\alpha D_V N_V)^{1/2} (t - \tau)^{1/2}. \quad (15)$$

Insertion of this result in Eq. 14 yields the time dependence of the growth rate, given by

$$G = \frac{dr}{dt} = (\alpha D_V N_V)^{1/2} / (t - \tau)^{1/2}. \quad (16)$$

The temperature dependence of the growth rate, plotted in Fig. 5, is proportional to $(D_V N_V)^{1/2}$.

To compare these results with experimental measurements, we must derive an expression that relates the void volume fraction to the theoretical nucleation and growth rates. If one assumes that the nucleation rate is time-independent and that the total void volume fraction is low enough so that no cavity impingement occurs, then the approach used by Johnson and Mehl¹² may be employed. This approach yields the following expression for the void volume fraction:

$$f = 1 - \exp[-KI(D_V N_V)^{3/2} t^{5/2}], \quad (17)$$

where f is the void volume fraction and K is a constant. This result implies that the temperature dependence of void formation is proportional to $(D_V N_V)^{3/2} I$.

Equation 17 is plotted in Fig. 6 as a function of irradiation temperature. The theoretical curve displays a maximum at about 500°C. If a reduction from the maximum of two orders of magnitude is used as the criterion for the disappearance of detectable void formation, then this approach predicts that voids should be observed over a 300°C range (325-625°C). This agrees with the experimental results, which also indicate a maximum at about 500°C and void formation over a range of about 300°C (350-650°C).

The constant, K , in Eq. 17 can be evaluated from the experimental results. This allows construction of a plot that relates expected void volume to irradiation temperature and neutron exposure.

Figure 7 is presented as an aid in predicting the swelling of austenitic stainless steel under various combinations of irradiation temperature and neutron exposure. The predicted swelling may be easily read by choosing the appropriate irradiation temperature line.

As a further check of the model, the swelling profiles along various flats of sub-assembly guide thimbles have been plotted from the data of Table II and compared with immersion-density results. The calculated

Fig. 6. Temperature Dependence of Void Formation Predicted by Eq. 17

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Fig. 7

Expected Void Formation as
a Function of Temperature
(in °C) and Fluence

irradiation temperatures and fluences for positions along each flat are used to calculate the expected swelling values according to the model. These calculations were performed according to the computer program presented in the appendix. Figure 8 shows the excellent agreement that was obtained with a flat of a control-rod guide thimble irradiated in position 5-C-12 to a peak exposure of 4.8×10^{22} n/cm².

Figure 9 shows a further extension of the model. Swelling profiles from two flats of a safety-rod guide thimble irradiated in position 3-D-1 to a peak fluence of 10^{23} n/cm² were calculated. The curves were constructed solely from the fluences and the irradiation temperatures at positions along the flats and involved no adjustable parameters.

TABLE II. Comparison of Observed and Predicted Density Changes for Three Axial Reactor Components

Sample Source	Estimated Total Fluence, 10^{22} n/cm ²	Irradiation Temp, °C	Predicted Density Decrease, %	Observed Density Decrease, %
CRT 5-C-12	2.4	375	0.1	0.5
	4.5	410	1.2	1.3
	4.3	425	1.5	1.0
	4.1	450	1.7	1.7
	3.1	463	0.8	1.1
	2.4	463	0.4	0.4
A Flat, SRT 3-D-1	0.5	460	0.006	0.5
	0.9	460	0.01	0.9
	5.6	426	2.2	2.5
	9.1	413	4.8	4.1
	10.0	401	4.0	1.3
	1.4	371	0.02	0.4
D Flat, SRT 3-D-1	0.5	446	0.006	0.00
	5.6	418	1.8	1.9
	9.1	405	3.9	3.7
	10.0	395	3.4	2.6
	9.1	385	1.7	0.6
	2.7	371	0.07	0.5
	2.4	371	0.02	0.3

51543

Fig. 8. Comparison of Theoretical and Experimental Results for the Swelling Profile of a Flat of a Control-rod Guide Thimble Irradiated in Position 5-C-12 to a Peak Fluence of 5×10^{22} n/cm²

51542

Fig. 9

Comparison of Theoretical and Experimental Results for the Swelling Profiles of Two Flats of a Safety-rod Thimble Irradiated in Position 3-D-1 to a Peak Fluence of 10^{23} n/cm²

The two flats received almost the same neutron dose, but were calculated to have been irradiated at different temperatures. The cause of the expected temperature differential was that one flat was adjacent to driver-fuel subassemblies during most of its exposure, while the other was usually next to a structural subassembly. This resulted in a calculated difference of about 20°C between the sodium outlet temperatures of A and D flats. The agreement between the predicted swelling profiles and the immersion-density data for both flats is quite good.

VII. SENSITIVITY ANALYSIS

Although the present model involves several assumptions that may not be realistic, the good agreement with experimental results helps to confirm the general approach.

For this reason, other consequences of the model are interesting to examine in terms of controlling void formation. The analysis indicates that the material properties that most affect void formation are the energy of vacancy formation, the energy of vacancy motion, and the surface energy of the metal.

As Fig. 10 shows, an increase in the energy of vacancy formation causes void formation to increase in magnitude and to occur at higher temperatures.

50265

Fig. 10
Effect of Energy of Vacancy Formation (E_F) on Void Formation

Changing the energy of vacancy formation, however, would be difficult. A more feasible parameter to change is the energy of vacancy motion. Increasing this energy shifts the peak of the void-volume-fraction curve toward higher temperatures and lower magnitudes, as seen in Fig. 11.

Increases in the surface energy of the material sharply decrease the magnitude of void formation and shift it to lower temperature ranges. This behavior (shown in Fig. 12) implies that void formation could be controlled by increasing the surface energy of the material.

Currently, most reactor exposures are reported as the product of flux and time. For some phenomena, it is important to separate the flux and time variables. However, for void formation, the model indicates (as shown in Fig. 13) that, for practical purposes, it is sufficient to report results in terms of integral exposure. In the construction of the plot shown in Fig. 13, agreement between experimental and theoretical results was obtained by evaluating the constant K in Eq. 17 through comparison with experimental measurements. The experimental points presented in Fig. 13 are from measurements made at ANL and Pacific Northwest Laboratory (PNL) on Type 304 stainless steel irradiated in EBR-II at temperatures between 450 and 500°C. The

51545

Fig. 12

Effect of Surface Energy (γ) on
Void Formation (surface energy
in ergs/cm²)

51544

Fig. 11
Effect of Energy of Vacancy Motion
(E_m) on Void Formation

50266

Fig. 13

Predicted Dependence of Void Formation
on Integral Exposure as a Function of Flux
Level and Irradiation Temperature

experimental points indicate the possibility of a neutron-exposure threshold below which no appreciable void formation occurs. The large amount of void formation predicted for fluences in excess of 10^{23} n/cm² emphasizes the severity of the problem.

VIII. DISCUSSION

The previous discussion ignored an important factor in void nucleation. For any irradiated material, a certain probability exists that the small initial cavities formed by the displacement spike will collapse into a planar defect. In face-centered materials, the Frank dislocation loop and the stacking-fault tetrahedron are possible resultant defects.

For any particular metal, one would expect the formation of the defect with the lowest energy of formation. These energies are roughly independent of temperature, but are functions of the defect size, the elastic modulus, and the stacking-fault and surface energies of the metal.

The tendency for a defect to transform into another defect of lower energy decreases with increasing defect size. For example, if clusters become stable past some small size, they can continue to grow into voids by vacancy agglomeration with only a low probability of collapse, even though the Frank loop or the stacking-fault tetrahedron may be a lower energy configuration. The possibility of void stabilization is enhanced by the fact that materials irradiated in a fast-neutron flux generate helium atoms homogeneously by (n, α) reactions. Helium atoms could diffuse into the small cavities created by the displacement spike and, by exerting an internal pressure, could stabilize void formation. Therefore, in materials in which the void is not the lowest energy form, void formation may depend on whether there are, statistically, enough gas atoms in the neighborhood of a cluster to prevent its collapse into a Frank loop or into a stacking-fault tetrahedron. Clarebrough *et al.*¹³ observed void stabilization by gas atoms in both copper and silver when each was quenched from a hydrogen-bearing atmosphere.

Voids due to irradiation have been observed in at least three face-centered-cubic materials: nickel, aluminum, and austenitic stainless steel. These voids occurred after fast-neutron irradiation in the same homologous temperature range (one-fourth to one-half the melting-point temperature, in degrees K). The only apparent difference between the void-formation phenomena in these materials is the fluence at which voids are first observed. Mastel and Brimhall³ found voids in nickel after a fast fluence of 10^{19} n/cm², Cunningham² reported voids in aluminum at fast fluences of less than 10^{21} n/cm²; however, voids have not been reported in stainless steel until fluences in excess of 10^{22} n/cm² have been attained. This difference (three orders of magnitude) in fluence prior to void formation appears

to depend on the importance of helium atoms in void stabilization. Since the rate of helium generation by the (n, α) reaction is approximately the same in the three materials, a different concentration of helium appears to be necessary for void formation in each material. Hydrogen generation is not thought to be an important factor in void stabilization, since the high mobility of hydrogen under reactor conditions would prevent any concentration buildup with time. For materials in which the void is the most stable secondary defect, little gas would be required to aid void formation. However, as the relative energy of void formation increases, the gas concentration in the material becomes more critical. One means of evaluating the relative energies of formation for the various secondary defects is through the equations compiled by Sigler and Kuhlmann-Wilsdorf.¹⁴ These equations are not meant to give quantitative results, but are used here merely to show expected trends. The void is the most stable defect form in nickel, principally because of the high stacking-fault energy (300 ergs/cm^2). Gas, therefore, would not be needed to stabilize void formation, and voids would be expected to form at low fluences. This corresponds with experimental observation. In aluminum, the relative position of the void as a low-energy defect is not as clear-cut as in nickel. Some gas may be re-

quired, which would be reflected in a higher fluence for the onset of void formation. This behavior has been observed experimentally.

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Fig. 14. Energy of Defect Formation in Type 304 Stainless Steel at 500°C

In austenitic stainless steel (see Fig. 14), void formation clearly is not the lowest energy defect, primarily because of the very low ($\sim 15 \text{ ergs/cm}^2$) stacking-fault energy of the material. Both the Frank loop and the stacking-fault tetrahedron are significantly lower energy forms (see Fig. 8), which implies that a relatively high gas concentration is necessary to stabilize void formation. This would explain the fact that voids are not observed in austenitic stainless steel until fluences in excess of 10^{22} n/cm^2 are reached, or until a significant concentration of helium is generated.

If this picture of void nucleation is correct, it would imply that austenitic stainless steel is one of the best face-centered-cubic materials for resisting void formation, for in few other face-centered-cubic materials is the void such a relatively high-energy configuration.

IX. CONCLUSIONS

A discussion of void formation from a classical thermodynamic viewpoint resulted in the following conclusions:

1. Cavity formation at EBR-II reactor temperatures should be little affected by applied stress.
2. The temperature dependence of void formation in Type 304 stainless steel is predictable from a consideration of nucleation and growth theory.
3. The model was able to accurately predict the swelling in two flats of material irradiated under different conditions.
4. The model predicts that lowering the energy of vacancy formation decreases the amount of void formation and shifts the occurrence to lower temperatures.
5. The model predicts that an increase in the surface energy of the material also decreases the amount of void formation and shifts the occurrence to lower temperatures.
6. The model predicts that an increase in the energy of vacancy motion decreases the void volume fraction and shifts the occurrence to higher temperatures.
7. The model indicates that the reporting of neutron exposure as an integral value is suitable for characterizing void formation.
8. It was suggested that the onset of void formation is influenced by the energy of the void relative to the energies of planar defects.

APPENDIX

Computer Input for Fuel-element Modeling Codes

The model for void formation discussed in the body of this report has been incorporated into a computer subroutine for inclusion in fuel-element modeling codes.

Briefly, the subroutine first reads the neutron fluence, the irradiation temperature, and the exposure time. From these data, the subroutine first computes the steady-state vacancy concentration, then the void nucleation rate, the void growth rate, and, finally, the void volume fraction and the expected increase in cladding diameter.

The subroutine consists of the following:

30 Read Z1, T1; Z1 = neutron fluence in units of n/cm^2

and

T1 = irradiation temperature in $^{\circ}C$.

35 Let T = T1 + 273; converts temperature to $^{\circ}K$.

40 Let Y6 = 2.4×10^7 ; exposure time in seconds.

45 Let X1 = $Z1/Y6 \cdot 3.5 \cdot 10^{(-30)}$,

since $X1 = A' r_1^2 [(1/2) \ln(r_1/r_d) - 1/4]$,

where

A' = number of vacancies generated by neutron damage per second

= $Z1/Y6 \cdot \sigma_D \cdot n$,

σ_D = nuclear cross section of stainless steel

$\approx 3.1 \times 10^{-24} \text{ cm}^2$,

n = number of vacancies that escape instant recombination after one displacement event ≈ 300 ,

r_1 = sink distance = $(1/\rho)^{1/2}$,

ρ = dislocation density $\approx 10^{-9}$ for commercially annealed material,

and

r_d = dislocation core distance $\approx 10^{-7} \text{ cm}$.

50 Let X2 = $Z1/Y6 \cdot 9/3 \cdot 10^{(-38)}$,

since $X2 = A' a^2/10$,

where

$a = \text{lattice spacing} \approx 3.1 \times 10^{-8} \text{ cm.}$

- 60 Let $X3 = 10^{(-38,000/(4.6*T))}$; gives the vacancy atom
 fraction in thermal equilibrium.
- 70 Let $X4 = ((X1/X2)*X3)-1$; involved in calculation of the
 steady-state vacancy population, N_v .
- 80 Let $X9 = 10^{(-2)}*10^{(-30,000/(4.6*T))}$; calculates the
 vacancy diffusion coefficient.
- 85 Let $X5 = 4*(X1/X2)*((X1/X9)+X3)$; involved in calculation
 of N_v .
- 90 Let $X6 = (X4+((X4)^2+X5)^{0.5})$; involved in calculation of N_v .
- 100 Let $X7 = X6/(2*X1/X2)$; the steady-state vacancy atom
 fraction.
- 110 Let $Y2 = (\log(X7/X3))$; involved in calculation of the
 nucleation rate.
- 120 Let $X8 = 3.23*10^{11}/(T^3*Y2^2)$; involved in calculation
 of the nucleation rate.
- 130 Let $Y4 = (X9*X7)^{1.5}$; temperature dependence of the
 void growth rate.
- 140 Let $Y5 = Y4*10^{(-X8)}*X9*10^{40}$; involved in calculation
 of the void volume.
- 145 Let $Y7 = Z1/Y6*Y5*Y6^{2.5}*1.62*10^{(-32)}$; void volume,
 in percent.
- 150 Let $Z6 = 0.150$; cladding tube diameter.
- 160 Let $Z7 = (Y7/3)*Z6*10^{-2}$; gives the increment of cladding
 diameter increase.

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