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AN INVESTIGATION OF FAST NEUTRON
RADIATION DAMAGE IN AN
AUSTENITIC STAINLESS STEEL

(Thesis)

Everett E. Bloom

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METALS AND CERAMICS DIVISION

**AN INVESTIGATION OF FAST NEUTRON RADIATION DAMAGE
IN AN AUSTENITIC STAINLESS STEEL**

Everett E. Bloom

A dissertation presented to the Graduate Council of The University of Tennessee in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

AUGUST 1970

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ABSTRACT

The nature of irradiation damage in type 304 stainless steel has been deduced from a study of microstructure and density of specimens irradiated by neutrons in the temperature range 370 to 800°C to fluences of 1×10^{18} to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV).

No damage was detected at exposures less than 1×10^{18} neutrons/cm² ($E > 0.1$ MeV). At 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV), small defect clusters, which appeared as black dots under suitable diffraction conditions, were present in the microstructure. Most of these small defect clusters were dislocation loops with Burgers' vectors of the type $a/3 \langle 111 \rangle$. A small fraction of the dots exhibited diffraction contrast consistent with either that expected from $a/2 \langle 110 \rangle$ dislocation loops or from defect clusters having spherically symmetric strain fields. The concentration of the small defect clusters decreased as the irradiation temperature was increased above 370°C. After irradiation at 524°C, no defect clusters were observed by transmission electron microscopy, indicating the concentration to be less than about 10^{12} defects/cm³.

Specimens irradiated to fast neutron fluences in the range 2×10^{21} to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 370 to 470°C contained voids and faulted interstitial dislocation loops. After irradiation to the lower fluences in this range the damage was heterogeneously distributed. Dislocation loops were clustered around dislocation lines and voids were located on dislocation lines. The void concentrations were higher at 370-380°C than at 460-470°C over the entire range of fluence

investigated. The void concentrations increased as the fluence raised to the 0.66 and 1.66 power at 370-380°C and 460-470°C, respectively. After irradiation at 570-630°C, the damage structure consisted of a dislocation network, a few unfaulted dislocation loops, and voids nearly always associated with the dislocation lines. The only damage observed after irradiation at 770-840°C was helium bubbles which were present both at grain boundaries and within the matrix.

A given void was found to grow rapidly early in its life (i.e., at small void sizes). A short time after its formation (a few times 10^{21} neutrons/cm²) the void growth rate decreased sharply. As a result, the density change was closely related to the void nucleation rate.

The microstructures of specimens which contained cyclotron injected helium prior to their irradiation showed helium to have a pronounced influence on void formation. Specimens preinjected with helium contained a higher concentration of smaller voids.

These observations are consistent with the concept that void nucleation occurs by the stabilization of void nuclei by the helium produced by (n,α) reactions. At low fluences and thus low helium concentrations, helium collects on dislocations and the first voids appear at these defects. As the helium concentration increases, stable nuclei form in the matrix and give a more uniform void distribution. Helium stabilization of void nuclei gives a void nucleation rate which is initially low, then increases until saturation of the void concentration occurs. The decrease in void growth rate is thought to be due to the buildup of a shell around the void within which the vacancy diffusivity is lower than in the homogeneous alloy.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. NEUTRON IRRADIATION DAMAGE PROCESSES	3
Displacement of Atoms in Solids by Neutron Irradiation .	3
Transmutation Reactions	10
III. FORMATION OF DEFECT CLUSTERS	15
Stability of Various Defect Configurations	16
Irradiation Damage in Pure Face-Centered Cubic Metals . .	18
Irradiation Damage in Austenitic Stainless Steels	23
IV. EXPERIMENTAL PROCEDURE	42
Description of Reactor Components	42
Design of Irradiation Experiments	52
Transmission Electron Microscopy	57
Immersion Density Measurements	58
Experimental Errors	60
V. RESULTS	63
Transmission Electron Microscopy Observations	64
Damage at low neutron fluence	64
Dislocation loops and networks	69
Voids and swelling	84
Effects of Helium on Irradiation Damage	109
Immersion Density Measurements	112

CHAPTER	PAGE
VI. SUMMARY OF RESULTS AND DISCUSSION	122
General Observations	122
Irradiation damage at low fluences	122
Development of dislocation structure	123
Development of void structure	130
Discussion of Results: Nucleation and Growth	
Mechanisms	136
VII. CONCLUSIONS	149
LIST OF REFERENCES	151
APPENDICES	161
A. DESCRIPTION OF EXPERIMENTAL BREEDER REACTOR-II	161
B. MEASUREMENT OF VOID CONCENTRATION	165

LIST OF TABLES

TABLE		PAGE
I.	Characteristics of Voids in Irradiated Pure Metals	24
II.	Compositions of Typical Unirradiated EBR-II Components . .	44
III.	Composition of Type 304 Stainless Steel Used in EBR-II	
	Materials Irradiation Experiments	54
IV.	Comparison of Void Concentrations in Specimens Irradiated	
	to Approximately the Same Neutron Fluence at Different	
	Neutron Flux Levels	107
V.	Density Change of Specimens Removed from the EBR-II Safety	
	Rod Thimble	114
VI.	Density and Density Change in Type 304 Stainless Steel	
	Irradiated in EBR-II Experimental Subassembly XO-34 . . .	117
VII.	Void Concentration Data for Foils 1 and 2 of Irradiated	
	Specimen S-3	166

LIST OF FIGURES

FIGURE		PAGE
1.	Average Number of Atom Displacements as a Function of Neutron Energy in Iron (Atomic Weight 56)	7
2.	Calculated Helium Concentration in Type 304 Stainless Steel as a Function of the Fast Neutron Fluence	13
3.	Density Decrease in High Purity Nickel (Ni 270), Commer- cially Pure Nickel (Ni 200), and a Nickel Base Alloy (Inconel 600) as a Result of Neutron Irradiation	22
4.	Type 304 Stainless Steel Irradiated at 93°C	25
5.	Plate-Like Precipitates Formed in Type 304 Stainless Steel During Irradiation at 371°C	27
6.	Precipitates, with a Denuded Zone Adjacent to the Grain Boundary, Formed in Type 304 Stainless Steel During Irradiation at 454°C	27
7.	Temperature Dependence of the Rates of Void Nucleation and Void Growth in Type 304 Stainless Steel Irradiated in EBR-II as Calculated by the Model of Harkness and Li	36
8.	Predicted Temperature Dependence of Void Formation from Model of Harkness and Li	38
9.	Expected Void Volume as a Function of Temperature and Fluence from Model of Harkness and Li	39
10.	Microstructure of Unirradiated EBR-II Fuel Cladding	45
11.	Microstructure of Unirradiated EBR-II Safety Rod Thimble	46

FIGURE	PAGE
12. Irradiation Conditions for EBR-II Fuel Cladding	47
13. Irradiation Conditions for EBR-II Shroud Tube	49
14. Irradiation Conditions for EBR-II Safety Rod Thimble	51
15. Drawing of Specimen Used in EBR-II Materials Irradiation Experiments	53
16. Schematic Drawing of Specimen Holder Used in EBR-II Materials Irradiation Experiments	55
17. Transmission Electron Micrograph Showing Defect Clusters in Type 304 Stainless Steel Irradiated at 384°C to 1.4×10^{20} Neutrons/cm ² ($E > 0.1$ MeV)	65
18. Concentration of Defect Clusters in Type 304 Stainless Steel Irradiated at Temperatures Between 384 and 524°C to 1.4×10^{20} Neutrons/cm ² ($E > 0.1$ MeV)	66
19. Small Dot-Like Defects Observed Under Two Beam Diffraction Conditions	68
20. Dislocation Loops in Type 304 Stainless Steel Irradiated at 370°C to 2.0×10^{21} Neutrons/cm ² ($E > 0.1$ MeV)	70
21. Dislocation Structure in Specimens Irradiated at 370-380°C	71
22. Defect Clusters in Type 304 Stainless Steel Irradiated at 460-470°C to 1.4×10^{20} Neutrons/cm ² ($E > 0.1$ MeV) at a Neutron Flux of 1.9×10^{15} Neutrons/cm ² sec ($E > 0.1$ MeV)	73

FIGURE	PAGE
23. Dislocation Line - Precipitate Structure in Specimen Irradiated at 460-470°C to 5×10^{20} Neutrons/cm ² (E > 0.1 MeV) at a Neutron Flux of Approximately 4×10^{13} Neutrons/cm ² /sec (E > 0.1 MeV)	74
24. Examples of the Loop and Dislocation Structures Observed After Irradiation to 2×10^{21} Neutrons/cm ² (E > 0.1 MeV) at 460-470°C	77
25. Effect of Fast Neutron Fluence on the Loop Structure in Type 304 Stainless Steel Irradiated at 460-470°C	78
26. Geometric Representation of the Origin of Diffraction Contrast from an Edge Dislocation	80
27. Geometric Representation of the Image Produced by an Interstitial Dislocation Loop	81
28. Dislocation Loops with 002 and $00\bar{2}$ Diffraction Vectors Operating	83
29. Dislocation Network in Type 304 Stainless Steel Irradi- ated at 570-630°C to 3.7×10^{22} Neutrons/cm ² (E > 0.1 MeV)	85
30. Voids in Type 304 Stainless Steel Irradiated at 370-380°C to 2.0×10^{21} Neutrons/cm ² (E > 0.1 MeV)	86
31. Effect of Fast Neutron Fluence on the Void Concentration and Size Distribution in Type 304 Stainless Steel Irradiated at 370-380°C	88

FIGURE	PAGE
32. Histogram of the Void Size Distribution in Type 304 Stainless Steel Irradiated at 370-380°C to 5.0×10^{22} Neutrons/cm ² (E > 0.1 MeV)	89
33. Effect of Fluence on the Void Size Distribution Curve for Type 304 Stainless Steel Irradiated at 370-380°C . . .	90
34. Heterogeneous Void Distributions in Type 304 Stainless Steel Irradiated at 460-470°C to 4×10^{21} Neutrons/cm ² (E > 0.1 MeV)	92
35. Association of Voids with Dislocation Lines in Type 304 Stainless Steel	93
36. Voids Associated with Dislocation Lines in Specimen Irradiated at 460-470°C to 0.74×10^{22} Neutrons/cm ² (E > 0.1 MeV)	94
37. Type 304 Stainless Steel Irradiated at 420°C to 4.2×10^{22} Neutrons/cm ² (E > 0.1 MeV)	96
38. Effect of Fast Neutron Fluence on the Shape and Concen- tration of Voids in Type 304 Stainless Steel Irradi- ated at 460-470°C	97
39. Histogram of the Void Size Distribution in Type 304 Stainless Steel Irradiated at 460-470°C to 2.1×10^{22} Neutrons/cm ² (E > 0.1 MeV)	98
40. Effect of Fast Neutron Fluence on the Void Size Distri- bution in Type 304 Stainless Steel Irradiated at 460-470°C	99

FIGURE	PAGE
41. Effect of Irradiation Temperature on the Void Concentration and Size in Type 304 Stainless Steel Irradiated to 3.7×10^{22} Neutrons/cm ² ($E > 0.1$ MeV)	101
42. Variation of Void Concentration with Fast Neutron Fluence in Type 304 Stainless Steel Irradiated at 370-390 and 460-470°C	104
43. Variation of Void Concentration with Irradiation Temperature	106
44. Maximum Void Diameter Versus Fast Neutron Fluence	108
45. Maximum Void Diameter as Function of Irradiation Temperature for Specimens Irradiated to Fast Neutron Fluences in Excess of 1×10^{22} Neutrons/cm ² ($E > 0.1$ MeV)	110
46. Microstructure of Type 304 Stainless Steel Irradiated at 390°C to 7.6×10^{21} Neutrons/cm ² ($E > 0.1$ MeV)	111
47. Microstructure of Type 304 Stainless Steel Which Contained 20×10^{-6} Atom Fraction Helium Prior to Irradiation at 390°C to 7.6×10^{21} Neutrons/cm ² ($E > 0.1$ MeV)	113
48. Density Decrease as Function of Axial Distance from Reactor Midplane for EBR-II Safety Rod Thimble	115
49. Density Decrease Versus Fluence for Type 304 Stainless Steel Irradiated at 370-380°C	118
50. Density Decrease Versus Fluence for Type 304 Stainless Steel Irradiated at 460-470°C	119
51. Density Decrease Versus Temperature	121

FIGURE	PAGE
52. Energy of $a/3 \langle 111 \rangle$ and $a/2 \langle 110 \rangle$ Dislocation Loops as a Function of Loop Radius	129
53. Typical Loading Diagram for Rows 1 Through 8 of the EBR-II	162
54. Neutron Flux as a Function of Distance from the Reactor Midplane in Row 2 of the EBR-II	163

CHAPTER I

INTRODUCTION

When metals and alloys are subjected to neutron irradiation, vacancies and interstitials are produced by displacement reactions and impurity atoms such as hydrogen and helium are produced by transmutation reactions. Damage of both types is of interest because these defects (or clusters of these defects) strongly affect many of the mechanical and physical properties. From a practical or applied viewpoint it is important that the properties of a material which is to be used in a nuclear reactor are not degraded to the extent that either the safe or economical operation of the reactor system is affected.

Austenitic stainless steels have several properties which make them attractive for use as fuel cladding and structural components in Liquid Metal Cooled Fast Breeder Reactors (LMFBR). These alloys possess adequate strength and are compatible with liquid sodium (the reactor coolant) and with uranium-plutonium oxides (the reactor fuel) at the projected operating temperatures. In fast reactors the neutron fluxes and neutron fluences to which cladding and other components will be subjected are much higher than those encountered in most other reactor systems. It is thus important to know what changes in properties will occur as a result of irradiation at conditions similar to those expected during service in LMFBR's.

At the time when this investigation was initiated there had been two reports that an unexpected form of irradiation damage occurred when austenitic stainless steels were irradiated at temperatures between 350 and approximately 600°C to fast neutron fluences in excess of 10^{22} neutrons/cm². Cawthorne and Fulton (1,2) used transmission electron microscopy to examine fuel cladding and tensile specimens of type 316 stainless steel which had been irradiated in the Dounreay Fast Reactor to neutron fluences as high as 6×10^{22} neutrons/cm² at temperatures between 270 and 600°C. At irradiation temperatures above approximately 350°C voids which varied in size from the smallest resolvable to 1100 Å diameter were present. Murphy and Strom (3) demonstrated that when type 304L stainless steel was irradiated in the Experimental Breeder Reactor-II (EBR-II) at temperatures in the range 370 to 470°C large increases in strength and large reductions in ductility were observed in postirradiation tube burst tests at 500°C. These results were unexpected since previous investigations in which austenitic stainless steels were irradiated at the same temperatures but to neutron fluences an order of magnitude lower had not detected any changes in properties or microstructure. Moreover, fundamental studies on the nature of radiation damage indicated that in stainless steels displacement damage should be completely annealed even at lower temperatures. The present investigation was initiated to investigate more thoroughly the nature of this unexpected damage. After the nature was established, the relationships of the irradiation-induced voids and interstitial loops with the temperature, fluence, and flux were sought and an attempt was made to define possible void nucleation and growth mechanisms.

CHAPTER II

NEUTRON IRRADIATION DAMAGE PROCESSES

Metals or alloys subjected to neutron irradiation suffer two basic types of damage. Atoms are displaced from their normal equilibrium positions as a result of being struck by neutrons or other energetic particles. This process produces vacant lattice sites (vacancies) and leaves atoms in interstitial positions (interstitials). The second type of damage is transmutations of the constituent atoms by reactions initiated by neutron capture. The most important of these are the production of protons (hydrogen nuclei) or alpha particles (helium nuclei) by various transmutation reactions of the type (n,p) and (n,α) . When considering the changes in microstructure or mechanical or physical properties resulting from neutron irradiation, it is realized that two important quantities are the rate at which defects are produced and the distribution of defects throughout the lattice.

I. DISPLACEMENT OF ATOMS IN SOLIDS BY NEUTRON IRRADIATION

In order to displace an atom from its normal lattice site into an interstitial position a minimum amount of energy, called the displacement energy, E_d , must be supplied to that atom. Sietz (4) estimated the value of E_d to be approximately 25 eV. This estimate was based on the argument that the binding energy of an interior atom should be approximately twice the sublimation energy, i.e., to a first approximation twice as many bonds would have to be broken in removing an interior atom

from its lattice site as when removing a surface atom. In addition, this displacement of an atom from its normal lattice position does not occur in a reversible manner. Sietz estimated that a reasonable value of E_d was four to five times the sublimation energy or approximately 25 eV for a typical solid. This estimate is in good agreement with experimentally determined values listed by Kelly (5).

During neutron irradiation, atom displacements can occur by several different mechanisms. A neutron may elastically collide with an atom and transfer sufficient kinetic energy to the atom to displace it from its lattice site. Such an atom may receive sufficient kinetic energy to produce still further displacements. A second mechanism is a result of nuclear reactions of the type $^{10}\text{B}(n,\alpha)^7\text{Li}$ or $^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$. The recoil nucleus may leave its lattice site with sufficient energy to cause other displacements. Another possibility is the interaction of the reaction product (such as the α particle) with other lattice atoms.

Only the elastic scattering makes a significant contribution to the atomic displacements produced by the collision of fast neutrons with lattice atoms. Reactions of the type (n,γ) , (n,α) , (n,p) or $(n,2n)$ produce a very small fraction of the total displacements and can thus be ignored. In an elastic collision the maximum amount of energy, E_m , which may be transferred from a neutron of energy E_n to a nucleus of atomic weight A is given by

$$E_m = \frac{4A}{(A+1)^2} E_n \quad (1)$$

For isotropic scattering, the struck nucleus has equal probability of receiving any energy between 0 and E_m . The average energy transferred by such a collision is thus $E_m/2$.

If an atom which is struck by a neutron receives energy in excess of E_d it is displaced from its lattice site. Such an atom is called a Primary Knock-on Atom (PKA). As a PKA travels through the lattice it strikes other atoms, transferring energy to them and displacing them from their lattice sites. The quantity $v(E)$ is defined as the number of additional displacements made by a PKA as it slows down from energy E to the position in the lattice where it is in thermal equilibrium with its surroundings. To obtain $v(E)$ the model and calculations of Kinchin and Pease (6) are used. These authors give:

$$v(E) = \begin{array}{ll} 0 & \text{for } 0 \leq E \leq E_d \\ 1 & \text{for } E_d \leq E \leq 2E_d \\ E/2E_d & \text{for } 2E_d \leq E \leq L_c \\ L_c/2E_d & \text{for } E \leq L_c \end{array} \quad (2)$$

In this treatment, L_c is called the ionization cutoff energy and is defined as the energy of an atom moving through a solid above which energy is lost only by electronic excitation (i.e., ionization) and below which energy losses occur only by elastic collisions. Dienes and Vineyard (7) assume that L_c is given by

$$L_c = A \times 10^3 \text{ eV} \quad (3)$$

Consider neutrons of energy E_n producing PKA's having average energy

$$E_{\text{average}} = \frac{E_m}{2} = \frac{2A}{(A+1)^2} E_n = \frac{\bar{\alpha} E_n}{2} \quad (4)$$

where $\bar{\alpha} = 4A(A+1)^2$. The average number of displacements produced by these primary knock-ons is $\bar{v}(E_n)$, and is given by

$$\bar{v}(E_n) = \begin{cases} 0 & \text{for } E_n < E_d/\bar{\alpha} \\ 1 & \text{for } E_d/\bar{\alpha} \leq E_n \leq 2E_d/\bar{\alpha} \\ \bar{\alpha} E_n / 4E_d & \text{for } \frac{2E_d}{\bar{\alpha}} \leq E_n \leq L_c/\bar{\alpha} \\ \frac{L_c}{4E_d} \left[2 - \frac{L_c}{\bar{\alpha} E_n} \right] & \text{for } \frac{L_c}{\bar{\alpha}} \leq E_n \end{cases} \quad (5)$$

The expression for $\bar{v}(E_n)$ as a function of E_n for iron ($A = 56$) is plotted in Figure 1. The number of displacements per PKA increases linearly with neutron energy for energies between approximately 10^3 and 10^6 eV and then saturates rapidly for neutron energies above approximately 2×10^6 eV (2 MeV). The number of displacements per unit volume per unit time is given by

$$\frac{dn}{dt} = N_0 \int_{E_d/\bar{\alpha}}^{\infty} \phi(E_n) \sigma(E_n) \bar{v}(E_d) dE_n, \quad (6)$$

Figure 1. Average number of atom displacements as a function of neutron energy in iron (atomic weight 56).

where

$$\begin{aligned} N_0 &= \text{number of atoms per unit volume,} \\ \sigma(E_n) &= \text{atomic cross section for elastic scattering, and} \\ \phi(E_n)dE_n &= \text{flux of neutrons having energies between } E_n \text{ and} \\ &\quad E_n + dE_n. \end{aligned}$$

The spatial distribution of the displacement damage produced by fast neutrons is very important. First, the PKA's are distributed uniformly throughout the bulk of the material since the mean free path between neutron-atom collisions is of the order of centimeters. The defects produced by the individual PKA's, however, are not produced homogeneously on an atomic scale. Seitz and Koehler (8) calculate that an atom moving with energy less than L_a , where L_a is given by

$$L_a \approx 4Z^{7/3} R_h \quad (7)$$

will undergo hard-sphere collisions. In equation (7) Z is the atomic number and R_h is the Rydberg energy for hydrogen. In the case of iron ($Z = 26$), PKA's having less than about 10^5 eV energy undergo hard-sphere collisions. Calculations using equation (1) show that most of the PKA's have less than this amount of energy. The effective radius (R_e) of an atom for hard-sphere collisions is a function of the PKA energy and is given by

$$R_e \approx \frac{a_n}{(Z)^{1/3}} \ln \frac{Z^2 e^2}{R_h E} \quad (8)$$

where

a_n = Bohr radius of hydrogen atom,

e = electron charge, and

E = energy of moving atom.

The mean free path between hard sphere collisions L_{HS} is given by

$$L_{HS} = \frac{1}{\pi R_e^2 N_0} \quad (9)$$

Thus, as the energy of a moving atom decreases, R_e increases and L_{HS} decreases. As the kinetic energy of a moving atom is dissipated it begins to collide with essentially every atom in its path. Most of the atom displacements occur in a very small volume called a displacement spike. Several investigators have suggested what the final configuration of the atoms inside a displacement spike might be. Using the terminology of Beeler (9,10), this is the "primary damage state" or the defect distribution produced directly by the PKA at 0°K temperature where no thermally induced rearrangement can occur. Brinkman (11) has suggested that because of the large amount of energy dissipated in a small volume the atoms will recrystallize in correct registry with the surroundings but will leave small clusters of vacancies and interstitials. Seeger (12) argues that after immediate rearrangement the spike will be a region of high vacancy concentration. Kinchin and Pease (6) suggest that the spike will consist of volume having a high vacancy concentration surrounded by a shell which contains a high concentration of interstitials.

Computer calculations performed by Beeler (9,10) indicate that the primary damage state is similar to that proposed by Kinchin and Pease.

II. TRANSMUTATION REACTIONS

During neutron irradiation (n,p) , (n,γ) , and (n,α) reactions are initiated by the nuclei of atoms capturing neutrons. Each reaction of this type produces either a new isotope, as is the case with (n,γ) reactions, or a chemically different species, as is the case with (n,p) and (n,α) reactions.

With the exception of hydrogen and helium, the chemically different species produced by transmutation reactions usually do not have metallurgical significance since their concentration builds up slowly and usually does not exceed either the concentration of impurities initially present in the material or the solubility limits for the product species. Exceptions to this statement include the production of silicon in aluminum (13) and rhenium in tungsten (14).

Helium produced by (n,α) reactions poses a different situation. Because of its chemically inert electronic structure, helium is highly insoluble in the metal lattice. Cottrell (15) gives the atomic concentration C of a monoatomic gas dissolved with a free energy F in equilibrium with a gas phase at a pressure p and temperature T as:

$$C = \frac{p}{N_0 kT} e^{-F/kT} \quad (10)$$

Since there would be a large amount of strain energy associated with a helium atom in an interstitial position, Cottrell proposed that each atom would enter substitutional solution by capturing a vacancy. Thus the energy of solution would be primarily the energy of formation of a vacancy; about 1 eV for a face-centered cubic metal. Taking $p = 1 \text{ atm}$, $T = 1000^\circ\text{K}$, and $F = 1 \text{ eV}$ then the solubility is on the order of 10^{-9} .

Russell and Hastings (16) have followed the precipitation of helium from interstitial solution by measuring the changes in lattice parameter on post irradiation annealing of a copper-boron alloy. Initially, the helium atoms formed by the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction were in interstitial positions. The results indicated that, during annealing, each helium atom captured two vacancies and entered substitutional solution. Continuation of the annealing to higher temperatures caused the helium to precipitate in gas bubbles. These processes caused the lattice to contract initially, as the helium atoms captured vacancies and moved into solid solution, and then expand again and approach the unirradiated value as the helium precipitated in bubbles.

The formation of helium bubbles in irradiated materials has been reported by several investigators (17,18,19,20). The effects of helium on the mechanical properties have been extensively investigated and reviewed (17,18,19,20,21,22).

For irradiation in a fast reactor neutron spectrum most of the helium is produced by (n,α) reactions with high energy neutrons. Alter and Weber (23) and DePino (24) have estimated the amounts of helium produced in austenitic stainless steels irradiated in a fission neutron

spectrum and a typical fast reactor neutron spectrum, respectively. Calculations of this type are not accurate since cross sections for (n,α) reactions are in general not well known. The results are interesting, however, since they show the relative importance of the various elements present in a stainless steel to the total helium production. DePino examined all of the constituents in a type 304 stainless steel and concluded that, in a fast reactor neutron spectrum, over 90% of the total helium was produced from iron, chromium, nickel, nitrogen and boron. These calculations are summarized in Figure 2. Irradiation to a neutron fluence of $< 1.7 \times 10^{19}$ neutrons/cm² (thermal) and 6.6×10^{23} neutrons/cm² ($E > 0.18$ MeV) would produce approximately 150 ppm helium (2.3 ppm helium per 1×10^{22} neutrons/cm²). Similar calculations performed by Alter and Weber (23) give a helium production rate of approximately 5.5 atomic ppm helium per 1×10^{22} neutrons/cm² for 304 stainless steel irradiated in a fission neutron spectrum. To a first approximation, the helium production rate is constant with time over the duration of the irradiation.

Hydrogen is produced by (n,p) reactions. Calculations by Alter and Weber, for a fission neutron energy spectrum, indicate that in type 304 stainless steel, the hydrogen production rate is 109 atomic ppm hydrogen per 1×10^{22} neutrons/cm². Of the total hydrogen produced, approximately 30% comes from (n,p) reactions with the iron isotopes and approximately 66% from (n,p) reactions with the nickel isotopes. In austenitic stainless steels and nickel base alloys irradiated at elevated temperatures, it has been suggested that hydrogen will diffuse from the

Figure 2. Calculated helium concentration in type 304 stainless steel as a function of the fast neutron fluence.

A. DePino, Jr., "Helium Production by (n,α) Reactions in Stainless Steel," Nuclear Applications 3, 620 (1967).

material rapidly enough to prevent the concentration from exceeding the solubility limit (17).

CHAPTER III

FORMATION OF DEFECT CLUSTERS

As discussed previously, the primary damage state or the defect distribution produced directly by the PKA probably consists of a volume which has a high concentration of vacancies surrounded by a shell which has a high concentration of interstitials. Since reactor irradiations are nearly always carried out at temperatures at which one or more of the irradiation-produced defects are mobile, this primary damage state is highly unstable and dynamic recovery will occur. Many of the original irradiation-produced vacancies and interstitials will be annihilated by recombination, trapped at impurities or absorbed by dislocations and grain boundaries. Any irradiation produced defect which survives will be thermodynamically unstable (i.e., there will be a supersaturation of vacancies and interstitials) and may cluster with defects of like kind in order to lower the free energy of the system. The formation of defect clusters and the final damage state will thus depend upon material parameters such as surface and stacking fault energies, energy of formation of vacancies and interstitials, migration energy of vacancies and interstitials, the binding energy of vacancies and interstitials to defect clusters, and irradiation parameters such as the irradiation temperature, fast neutron flux, fast neutron fluence, etc.

In the following section, the calculation of the stability of various defect configurations will be considered and the experimental

mechanisms of irradiation damage, mainly in face-centered cubic metals and alloys, will be reviewed.

I. STABILITY OF VARIOUS DEFECT CONFIGURATIONS

In a pure metal quenched from an elevated temperature, the concentration of vacancies in equilibrium at that temperature may be maintained at a lower temperature to form a supersaturated condition. The vacancies can cluster on annealing to form several distinct types of defects. Similarly, during irradiation a vacancy supersaturation is maintained and one might expect various types of vacancy clusters to form. Because of their large energy of formation and high mobility, it is not possible to quench in a significant supersaturation of interstitials. During irradiation, however, interstitials are produced in equal numbers to vacancies and the formation of interstitial clusters must also be considered. Both vacancies and interstitials may precipitate to form defects such as "faulted" dislocation loops (loops which surround a stacking fault), "perfect" dislocation loops (loops which surround unfaulted material) and possibly stacking fault tetrahedra. In addition, vacancies may precipitate to form three-dimensional voids.

In principle, the defect having the minimum free energy should form. For dislocation loops, the total energy is the sum of the energy associated with the dislocation and the energy associated with any stacking fault. The energies associated with faulted and perfect loops of radius R_L are given by equations (11) and (12) respectively:

$$E_f = \frac{2}{3} \frac{1}{(1-\nu)} Gb^2 R_\ell \left(\ln \frac{4R_\ell}{r_0} - 2 \right) + \pi R_\ell^2 \gamma, \quad (11)$$

$$E_p = \left[\frac{2}{3} \frac{1}{(1-\nu)} + \frac{1}{3} \left(\frac{2-\nu}{2(1-\nu)} \right) \right] Gb^2 R_\ell \left[\ln \frac{4R_\ell}{r_0} - 2 \right], \quad (12)$$

where

ν = Poisson's ratio,

G = shear modulus,

b = Burgers vector,

r_0 = radius of dislocation core (3 to 5 times b), and

γ = stacking fault energy.

For vacancies precipitating as a spherical void of radius R_v , the energy associated with the void is given by:

$$E_s = 4\pi R_v^2 \sigma \quad (13)$$

where σ is the surface energy.

Sigler and Kuhlman-Wilsdorf (25) have calculated the relative stabilities of several different types of vacancy clusters in aluminum, nickel, platinum, copper, gold and silver. Their results indicated that when the ratio of surface energy to stacking fault energy was less than 10, e.g., aluminum and nickel, the void was the most stable vacancy cluster whereas when this ratio was greater than 10, e.g., platinum, gold, copper and silver, a stacking fault tetrahedron was the most stable cluster. The results for nickel agree with similar calculations performed by Johnson (26).

For the precipitation of interstitials, the stacking fault energy is again an important parameter. If the stacking fault energy exceeds a value given by

$$\gamma \geq \frac{Gb^2}{3\pi R_\ell} \left[\frac{2 - \nu}{2(1 - \nu)} \right] \ln \left[\frac{4R_\ell}{r_0} - 2 \right] \quad (14)$$

the loop will be a perfect loop; whereas if γ is less than this value, the loop will have an associated stacking fault.

Calculations of this type have only limited applicability to very small defect clusters. For small dislocation loops the core energy of the dislocation dominates the energy expression and this term is not well known. For three dimensional defect clusters surface energy terms and defect shapes are not well known. It is also possible that as a defect grows in size, some other configuration may have lower energy, but the defect may not be able to convert to this configuration because of an energy barrier or kinetic factors.

II. IRRADIATION DAMAGE IN PURE FACE-CENTERED CUBIC METALS

In pure face-centered cubic (fcc) metals irradiated at low temperatures below approximately $0.3 T_m$ (where T_m is the melting temperature in °K) two distinct types of defect clusters have been reported. Silcox and Hirsch (27) first reported prismatic dislocation loops in copper which had been neutron-irradiated at temperatures in the range 35 to 100°C. Barnes and Mazey (28) observed dislocation loops of approximately 200 Å diameter as well as a much higher density of smaller

defects, approximately 20 Å diameter, in both copper and aluminum which had been bombarded with α particles. The nature of these defects was inferred from post-bombardment annealing studies. The larger loops were thought to be interstitial in nature and the smaller loops were thought to be vacancy clusters. Similar observations of defects in neutron irradiated copper have been made by Makin et al. (29,30); and Koppenaal et al. (31), and Merkle (32).

The nature of the small dislocation loops in neutron irradiated materials has been the subject of considerable controversy. Quantitative electron microscopy studies which utilize the black-white contrast from the strain field of the loops have at various times been interpreted to show the loops in copper to be entirely interstitial in nature (33,34), entirely vacancy in character (35), and mixtures of both interstitial and vacancy loops (36). It thus appears quite possible that both cluster types may be formed.

Reports of damage in irradiated pure nickel are also conflicting. Greenfield and Wilsdorf (37) did not observe damage in nickel which was neutron irradiated at 70°C to a fast neutron fluence of 1×10^{18} neutron/cm². At the higher irradiation temperature of 200°C, damage was detected as dark spots in electron micrographs (approximately 2.3×10^{15} spots/cm³). In contrast, Bell (38) has observed defect clusters in nickel irradiated at 80°C to 5×10^{18} neutrons/cm² ($E > 1$ MeV) and Brimhall et al. (39) observed defect clusters in nickel irradiated at 40°C to 2.5×10^{18} neutrons/cm² ($E > 1$ MeV). Brimhall et al. found the majority of the defects to be vacancy clusters. More recently, Bourret and Dautreppe (40)

irradiated nickel at 77°K and then examined it at room temperature. After irradiation, the damage structure consisted of interstitial Frank dislocation loops and vacancy clusters thought to be small tetrahedral voids.

It was not until a report by Cawthorne and Fulton (1,2) (to be discussed later) of a complex damage structure consisting of voids and dislocation loops in an austenitic stainless steel irradiated at temperatures between 0.38 and 0.50 T_m that investigators began to examine pure metals irradiated at temperatures above 0.3 T_m . Since then there have been several reports of damage in pure face-centered cubic metals irradiated in the temperature range of 0.3 to 0.5 T_m .

In copper irradiated at about 0.5 T_m to 1×10^{18} neutrons/cm² (fast), Hulett et al. (41) found a nonhomogeneous distribution of vacancy and interstitial loops. Brimhall and Mastel (42) observed voids in copper irradiated to 1.2×10^{20} neutrons/cm² ($E > 1$ MeV) at 0.39 T_m . Brimhall and Mastel (42) and Mastel and Brimhall (43) have reported the presence of voids in pure nickel irradiated at temperatures in the range 0.31 to 0.42 T_m to fast neutron fluences as low as 4×10^{19} neutrons/cm² ($E > 1$ MeV). The voids appeared to be octahedra with surfaces bounded by {111} planes. Annealing experiments were used to demonstrate that the voids were not filled with gas.

Holmes (44) has measured the density decrease due to void formation as a function of fast neutron fluence in high purity (99.98%) nickel (nickel 270), a commercial purity (99.6%) nickel (nickel 200) and a nickel base alloy (Inconel 600) which contained 73% Ni, 17% Cr, and 8%

Fe. The irradiation temperature was $437 \pm 28^\circ\text{C}$. These results are shown in Figure 3. Nickel 270 exhibited the highest rate of volume change and the rate in nickel 200 was intermediate. Inconel 600 showed a small but consistent decrease in volume. This latter observation was thought to be due to surface reactions with the reactor coolant. Nickel exhibits a significant volume change at low fluences and follows a linear relationship between fluence and swelling. In stainless steel voids are not observed until much higher fluences and there is a power law between swelling and neutron fluence. Holmes suggested that this difference might be due to stacking fault energy. The high stacking fault energy of nickel makes a void an energetically more favorable configuration than a vacancy loop while the low stacking fault energy of stainless steel should make void formation less favorable.

Stiegler and coworkers (13) compared the damage structures produced in high purity (99.999%) and commercial purity (99%) aluminum as a result of irradiation at 50°C to a fluence of 3.5×10^{20} neutrons/ cm^2 ($E > 0.82$ MeV). Octahedral voids and dislocation loops were observed in the high purity aluminum. Contrast analysis of the larger loops proved them to be the vacancy type. The distribution of voids and loops was nonuniform; areas which contained large voids had small loops, and vice versa. The heterogeneous distribution of voids was thought to be due to dissolved impurities, possibly gases which might stabilize void nuclei. In commercial purity aluminum irradiated at 50°C to 3.5×10^{20} neutrons/ cm^2 ($E > 0.82$ MeV), the only visible damage was dislocation loops of both the vacancy and interstitial type. Brimhall and Mastel

Figure 3. Density decrease in high purity nickel (Ni 270), commercially pure nickel (Ni 200), and a nickel base alloy (Inconel 600) as a result of neutron irradiation.

J. J. Holmes, "Irradiation Induced Swelling in Nickel Alloys," Trans. Am. Nucl. Soc. 12, 117 (1969).

(42) have also observed voids in aluminum also irradiated at 50°C but to a fluence of 3.2×10^{19} neutrons/cm² ($E > 1$ MeV).

Table I summarizes the data on the observation of voids in pure fcc metals irradiated at temperatures between 0.3 and 0.5 T_m . Voids have been observed in metals having both low and high stacking fault energies, copper and aluminum respectively. With increasing irradiation temperature the mean void diameter increases and the void concentration decreases. The results of Stiegler et al. (13), Stiegler and Bloom (46) and Hulett et al. (41) suggest that early in the irradiation the damage may be heterogeneously distributed.

III. IRRADIATION DAMAGE IN AUSTENITIC STAINLESS STEELS

As is the case with pure fcc metals, the type of damage produced in austenitic stainless steels by neutron irradiation depends on the irradiation temperature and the fast neutron fluence. Wilsdorf and Kuhlmann-Wilsdorf (48) did not detect any damage in a type 304 stainless steel irradiated in the annealed condition to 1×10^{19} neutrons/cm² (fast) at ambient reactor temperature (approximately 50°C). Armijo et al. (49) observed damage in specimens irradiated at 43 and 343°C to fast neutron fluences of 1×10^{20} and 1×10^{21} neutrons/cm² ($E > 1$ MeV) respectively. Bloom et al. (50) studied the irradiation produced defects for irradiation temperatures between 90 and 454°C. The specimens, which were annealed type 304 stainless steel, were irradiated to 9×10^{20} neutrons/cm² (thermal) and 7×10^{20} neutrons/cm² ($E > 1$ MeV). The microstructure of a specimen irradiated at 93°C is shown in Figure 4. A high

TABLE I
CHARACTERISTICS OF VOIDS IN IRRADIATED PURE METALS

Metal and Reference	Irradiation Temperature °C	Irradiation Temperature Fraction of T_m	Neutron Fluence Neutrons/cm ² E > MeV	Mean Void Diameter Å	Void Concentration Voids/cm ³
Nickel					
42	260	0.31	1.2×10^{20}	60	2×10^{16}
43	380	0.38	5.7×10^{19}	83	4×10^{15}
45	500	0.45	5.7×10^{19}	165	8×10^{14}
	575	0.49	6.2×10^{19}	245	2.5×10^{14}
46	370-545	0.38-0.48	1.4×10^{20}	---	---
Copper					
42	260	0.39	1.2×10^{20}	230	3×10^{14}
Aluminum (High Purity)					
42	50	0.35	3.2×10^{19}	270	Not Reported
13	50	0.35	3.5×10^{20}	Not Reported	1.3×10^{14}
47	55	0.35	$1 \times 10^{19} - 1 \times 10^{22}$	---	---
Aluminum (Commercial Purity)					
13	50	0.35	1.5×10^{22}	Not Reported	Not Reported

Figure 4. Type 304 stainless steel irradiated at 93°C.

E. E. Bloom, W. R. Martin, J. O. Stiegler, J. R. Weir, "The Effect of Irradiation Temperature on the Strength and Microstructure of Stainless Steel," J. Nucl. Matl. 22, 68 (1967).

concentration of defect clusters which appeared as black dots in diffraction contrast was present. With increasing irradiation temperature, up to approximately 300°C, the concentration of such defect clusters decreased and their size increased slightly. Between 300 and 371°C (Figure 5) there was a marked change in the damage structure. The concentration of dot-like defect clusters decreased markedly and a rod or plate-like precipitate appeared. The small dot defects were completely absent in specimens irradiated at 398°C and well-defined precipitate particles whose contrast suggested the presence of a strain field were present. After irradiation at 454°C (Figure 6) the precipitates were coarser, and when the specimens were examined in absorption contrast, small white dots (indicating thin areas in the foil) were observed. The nature of the dots was not known. It was suggested that they were either helium bubbles or areas where small precipitates had fallen from the foil.

The character of the damage structure at irradiation temperatures below approximately 350°C does not appear to change with increasing fast neutron fluence. Cawthorne and Fulton (1,2) have examined specimens irradiated to approximately 3×10^{22} neutrons/cm² and at temperatures less than 350°C. Only a high density of dot-like defect clusters was observed.

At irradiation temperatures above 350-370°C and at high fast neutron fluences the damage has an entirely different character. Cawthorne and Fulton were the first to report a damage structure consisting of voids and dislocation loops in an austenitic stainless steel

Figure 5. Plate-like precipitates formed in type 304 stainless steel during irradiation at 371°C.

E. E. Bloom, W. R. Martin, J. O. Stiegler, J. R. Weir, "The Effect of Irradiation Temperature on the Strength and Microstructure of Stainless Steel," J. Nucl. Matl. 22, 68 (1967).

Figure 6. Precipitates, with a denuded zone adjacent to the grain boundary, formed in type 304 stainless steel during irradiation at 454°C.

E. E. Bloom, W. R. Martin, J. O. Stiegler, J. R. Weir, "The Effect of Irradiation Temperature on the Strength and Microstructure of Stainless Steel," J. Nucl. Matl. 22, 68 (1967).

irradiated at temperatures between 350 and 560°C to fast neutron fluences as high as 7.8×10^{22} neutrons/cm². The voids ranged in size from the smallest observable (approximately 50 Å) to 1100 Å in diameter. The total void volume increased with increasing fast-neutron fluence and appeared to be a maximum for irradiation at approximately 510°C. The void volume could not be accounted for solely in terms of helium production since the amount of helium required to balance the surface tension by an internal pressure was as much as 100 times that produced by transmutation reactions. The number of voids was greatly reduced by post-irradiation annealing for 1 hr at 900°C and the residual void volume was reasonably consistent with the amount of helium expected from transmutation reactions.

These results have been confirmed and extended by a number of investigators (51,52,53,54). Holmes et al. (51) and Claudson et al. (52) have examined type 304 stainless steel which had been irradiated in the EBR-II at temperatures between 370 and 470°C. Voids and loops (thought to be interstitial in nature) were observed. The voids were uniformly distributed except for a denuded zone near grain boundaries. The void concentration increased as the fluence raised to the 1.2 ± 0.3 power and no relationship between void concentration and irradiation temperature was reported. The void size increased with irradiation temperature and to a lesser extent with neutron fluence and, at least at the higher irradiation temperature (472°C), the voids were predominately octahedral in shape with surfaces on {111} planes and the ends truncated by {100} planes.

Stiegler and Bloom (53) examined type 304L stainless steel irradiated at temperatures between 370 and 470°C to neutron fluences in the range of 0.8 to 1.4×10^{22} neutrons/cm². After irradiation at 370°C to 0.8×10^{22} neutrons/cm² ($E > 0.1$ MeV) both loops and voids were present. The loops ranged in diameter from the smallest observable to approximately 500 Å diameter. With increasing irradiation temperatures the loop concentration decreased and the size increased. After irradiation at 472°C to 0.9×10^{22} neutrons/cm² ($E > 0.1$ MeV) the loops had diameters of approximately 100 to 1100 Å, were on {111} planes and were faulted. This suggested that they were Frank sessile loops. The voids appeared to be homogeneously distributed and ranged in size from the smallest observable to approximately 190 and 310 Å after irradiation at 370 and 470°C, respectively. Histograms of the void size distributions were determined. In general, the histograms had a bell shape. In this investigation, a wide variety of void shapes was observed. The smaller voids appeared spherical in shape. The larger voids often had faceted or crystallographic surfaces; however, few of these were regular polyhedra and many were very irregular in shape. A characteristic observed by all investigators has been the absence of voids on grain boundaries. This is important since, if the voids were bubbles stabilized by an equilibrium pressure of a gas such as helium, they would be present at the grain boundaries as well as in the matrix.

The density decrease associated with the formation of voids in type 304 stainless steel has been measured by several investigators (2,52,54,55) and the results were recently tabulated and discussed by

Claudson et al. (52). Nearly all values were from specimens irradiated at temperatures between 370 and 470°C, and over this range of temperature the data were fit to an expression:

$$\frac{\Delta\rho}{\rho_0} [(\phi t), T] = 6.5 \times 10^{-39} (\phi t)^{1.77} \exp \left[-\frac{5600}{RT} \right] \quad (15)$$

where

$\frac{\Delta\rho}{\rho_0}$ = density decrease,
 (ϕt) = fast neutron fluence in neutrons/cm² ($E > 0.1$ MeV), and
 R and T have their usual meanings.

The effect of temperature on the formation of voids and dislocation loops is not well known for temperatures above 470°C. Harkness et al. (54) have reported that no voids or loops were observed in type 304 stainless steel irradiated at $600 \pm 50^\circ\text{C}$ to 2.4×10^{22} neutrons/cm².

Although it is now well established that voids are formed in stainless steel as a result of fast neutron irradiation in the temperature range of 370 to approximately 600°C the precise nucleation and growth mechanisms are not known.

Several mechanisms have been proposed to explain how void nucleation might occur. Since there is continuous production and annihilation of vacancies during irradiation, the vacancy concentration in the lattice will exceed the thermal equilibrium concentration. If this vacancy supersaturation is sufficient, homogeneous nucleation can occur. The critical supersaturation for homogeneous nucleation, (C_v/C_{v0}) , is related to the critical void radius R_v^* by:

$$C_v/C_{v0} = \exp(2\gamma\Omega/R_v^*kT) \quad , \quad (16)$$

where

C_v = actual vacancy concentration,

C_{v0} = vacancy concentration in thermal equilibrium,

γ = surface energy,

Ω = atomic volume,

k = Boltzman's constant, and

T = temperature in °K.

Beeler (56) has suggested that void nucleation may occur by the overlapping of displacement cascades. If a second cascade occurs in the very close vicinity of an initial cascade before the high vacancy concentration present in the center of the initial cascade is eliminated, a void having radius R_v^* in equilibrium with the existing vacancy supersaturation may be formed.

Cawthorne and Fulton (1,2) have suggested that helium from (n, α) reactions may stabilize small embryo (i.e., voids having a radius R_v less than R_v^*) thus providing nuclei for subsequent precipitation of vacancies.

Harkness and Li (54) have recently published a theoretical treatment of the void formation phenomenon. Void nucleation was assumed to occur in vacancy rich regions created within displacement spikes. Growth was assumed to occur by the precipitation of vacancies from a supersaturated solution with the growth rate controlled by vacancy diffusion. A summary of the work of Harkness and Li (54) follows.

The free energy change (ΔG_v) associated with growth of a spherical cavity by an amount dR_v is given by:

$$\Delta G_v = -4\pi R_v^2 dR_v (P_g + \sigma + \mu_v \frac{\rho}{M}) + 8\pi\gamma R_v dR_v, \quad (17)$$

where

- P_g = internal gas pressure,
- R_v = cavity radius,
- σ = hydrostatic stress,
- ρ = density of metal,
- M = molecular weight of metal,
- μ_v = chemical potential of vacancy, and
- γ = surface energy.

The chemical potential of a vacancy is assumed to be expressed as

$$\mu_v = E_v + kT \ln C_v \quad (18)$$

where

- E_v = energy of vacancy formation,
- C_v = vacancy concentration,
- T = temperature, and
- k = gas constant.

Since

$$E_v = -kT \ln C_{v0}, \quad (19)$$

where C_{v0} = thermal equilibrium vacancy concentration at temperature, T ,

Eq. (18) can be rewritten as:

$$\mu_v = kT \ln (C_v/C_{v0}) \quad (20)$$

Eq. (17) thus becomes

$$\Delta G_v = -kT \frac{\rho}{M} \ln (C_v/C_{v0}) - P_g - \sigma + \frac{2\gamma}{R_v} \quad (21)$$

when divided by $4\pi R_v^2 dR_v$ to give the free energy change per unit volume. Harkness and Li obtain the steady state vacancy concentration by using the treatment of Greenwood et al. (57). They assumed that the most effective sink for the irradiation produced vacancies and interstitials is the dislocation network. The steady state vacancy concentration is then given by:

$$(C_v - C_{v0})D_v = (1/4)Br_1^2 [2 \ln (r_1/r_0) - 1] \dots \quad (22)$$

where

- D_v = vacancy diffusion coefficient,
- B = net creation rate of vacancies or interstitials,
- r_1 = dislocation spacing, and
- r_0 = dislocation core radius.

The net creation rate of point defects, A , is obtained by estimating the number of vacancies and interstitials that recombine during their migration toward dislocations. The probability of recombination is given by

$$1 - \exp(-10C_v v_i \tau) \quad (23)$$

and, thus, B is given by

$$B = B' \exp (-10 C_v v_i \tau) \quad (24)$$

where

- B' = actual defect generation rate,
- v_i = interstitial jump frequency, and
- τ = average interstitial lifetime.

Following the development given by Greenwood et al. (57) the expression for the steady state vacancy concentration is:

$$C_v - C_{v0} = B' r_1^2 / D_v [1/2 \ln (r_1/r_0) - 1/4] \exp [-10 (D_v/B' a^2) C_v (C_v - C_{v0})] , \quad (25)$$

where a is the lattice spacing.

Harkness and Li assumed that the nucleation occurs in displacement spikes and that this nucleation process had the same temperature dependency as homogeneous nucleation. The number of nuclei reaching critical size per unit time, N_c , is given as:

$$N_c = K_1 \phi \exp (-16\pi\gamma/3kT\Delta G_v^2) \quad (26)$$

where K_1 is a constant and ϕ is the neutron flux. The neutron flux appears in the equation since nucleation is assumed to occur in the displacement spikes. The nucleation rate $\dot{I}$ is the product of the concentration of critical size nuclei (Eq. 26) and the rate at which

vacancies are added to these nuclei, which is proportional to $\exp(-\Delta G_m/RT)$, where ΔG_m is the energy for vacancy diffusion. The final expression for the nucleation rate is then given by:

$$\dot{I} = K\phi \exp(-16\pi\gamma^3/3kT\Delta G_v^2) \exp(-\Delta G_m/kT) \quad (27)$$

where K is said to be a slowly varying function of temperature. The nucleation rate calculated from equation 27 is plotted as a function of temperature in Figure 7.

In the model of Harkness and Li void growth is assumed to occur by the precipitation of vacancies from supersaturated solution and is controlled by the rate at which vacancies can diffuse to the void surface. The growth rate $\dot{G}$ is given by the equation

$$\dot{G} = dR_v/dt = \alpha D_v C_v / R_v, \quad (28)$$

where

α = constant (< 1), and

R_v = void radius.

Harkness and Li integrate this expression between some nucleation time, t_0 , and time, t , and obtain:

$$R_v = (\alpha D_v C_v)^{1/2} (t - t_0)^{1/2}, \quad (29)$$

If this expression is substituted into equation 28 the growth rate is

Figure 7. Temperature dependence of the rates of void nucleation and void growth in type 304 stainless steel irradiated in EBR-II as calculated by the model of Harkness and Li.

S. D. Harkness and Che-Yu Li, "A Model for Void Formation in Metals Irradiated in a Fast-Neutron Environment," p. 189 in Radiation Damage in Reactor Materials, Vol. 2, International Atomic Energy Agency, Vienna, 1969.

$$\dot{G} = \frac{dR_v}{dt} = (\alpha D_v C_v)^{1/2} / (t - t_0)^{1/2} \quad (30)$$

The temperature dependence is proportional to $(D_v C_v)^{1/2}$.

The void volume fraction or density decrease was obtained from the Johnson-Mehl (58) expression, which gives $\bar{F}$, the fraction transformed (i.e., the void volume) as a function of the nucleation and growth rates:

$$\bar{F} = 1 - \exp[-K(D_v C_v)^{3/2} t^{5/2}] \quad (31)$$

For the small volume fractions which occur as a result of void formation the density decrease should follow a $t^{5/2}$ dependency. Equation 31 is plotted as a function of temperature at a constant fluence in Figure 8 and as a function of fluence for several temperatures in Figure 9.

An empirical approach to the determination of mechanisms controlling swelling was taken by Claudson et al. (52) who examined the flux and time dependence of the volume change which would occur if any combination of five possible nucleation mechanisms or seven growth mechanisms controlled the density decrease. The mechanism which gave best agreement with experimental results was nucleation in displacement spikes and the growth of faceted voids by vacancy absorption at their tips.

Recent experimental results of Lauritzen et al. (59) and Bloom and Stiegler (60) have indicated that compositional differences such as those which exist between types 304, 316, 321, and 347 stainless steels can have a marked influence on irradiation induced void formation and swelling when the microstructures in these alloys are compared at a

Figure 8. Predicted temperature dependence of void formation from model of Harkness and Li.

S. D. Harkness and Che-Yu Li, "A Model for Void Formation in Metals Irradiated in a Fast-Neutron Environment," p. 189 in Radiation Damage in Reactor Materials, Vol. 2, International Atomic Energy Agency, Vienna, 1969.

Figure 9. Expected void volume as a function of temperature and fluence from model of Harkness and Li.

S. D. Harkness and Che-Yu Li, "A Model for Void Formation in Metals Irradiated in a Fast-Neutron Environment," p. 189 in Radiation Damage in Reactor Materials, Vol. 2, International Atomic Energy Agency, Vienna, 1969.

common irradiation temperature and fluence. The reasons for these differences are not understood, and, because of the limited amount of data, definite trends regarding differences in temperature and fluence dependencies cannot be established. These results do, however, indicate the importance of minimizing the composition variations when attempting to examine other variables such as temperature, neutron flux and neutron fluence.

Examination of the published literature indicates that although some information exists regarding the irradiation induced density change, only a few detailed microstructural examinations have been reported. The details of the dependence of irradiation-induced void formation on temperature, fluence and material parameters are lacking. The model developed by Harkness and Li (54) is able to predict irradiation induced density changes since nearly all of the parameters in the model are adjusted on the basis of density change data. This same model, however, does not agree with several experimental observations. For example, the model predicts (Figure 7, page 36) that the void concentration at a constant fluence should increase as the irradiation temperature is increased, reaches a maximum at approximately 450°C, and then decrease with further increases in temperature. Experimental results of Claudson et al. show the void concentration to be independent of irradiation temperature. The model of Harkness and Li indicates that helium plays no role in the void nucleation or growth, yet results obtained by Nelson and Mazey (61) indicate that helium may be important in the void nucleation step.

The present investigation was initiated to investigate more thoroughly the temperature, fluence, and flux dependence of the irradiation-induced void and loop formation phenomena in austenitic stainless steels and to attempt to define the operative void nucleation and growth mechanisms.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The experimental variables of irradiation temperature, fast neutron fluence, fast neutron flux, and neutron energy spectrum may be important in controlling the microstructural changes which occur in metals and alloys when subjected to neutron irradiation. In order to investigate the effect of these variables in austenitic stainless steels over as wide a range as possible, materials from two sources were used. The first source included components that had been removed from the Experimental Breeder Reactor-II (EBR-II). During irradiation there was a gradient in both temperature and neutron flux along their length. The second source included specimens which were irradiated in the EBR-II in experimental subassemblies. Since these irradiation experiments had design-controlled temperatures a wider range of experimental variables was obtained.

Postirradiation examination included immersion density measurements and transmission electron microscopy (TEM).

I. DESCRIPTION OF REACTOR COMPONENTS

The reactor components used in this investigation were (1) the cladding from an EBR-II driver fuel element (Driver Fuel Element No. C-179-86), (2) a shroud tube which was removed from a 19 pin experimental subassembly (Subassembly XG05), (3) a containment tube which was removed from a 7 pin experimental subassembly (Subassembly X0-67), and (4) a

portion of an EBR-II safety rod thimble (Safety Rod Thimble 3-D-1 flat C). The components were made of AISI Type 304 stainless steel. The chemical analysis and exact thermal-mechanical history of each of the components prior to its irradiation in the EBR-II could not be ascertained. The composition of some typical unirradiated components, not necessarily from the same heat as the irradiated components, are listed in Table II. The microstructures of material taken from an unirradiated fuel cladding and a safety rod thimble are shown in Figures 10 and 11. These materials should have received similar thermal-mechanical treatments as was received by the respective irradiated components prior to their insertion into the EBR-II. The average grain diameter of the fuel cladding and safety rod thimble as determined by the intercept technique was 0.016 mm and 0.045 mm respectively.

The fuel cladding was a tube, 44 cm long, 0.40 cm inside diameter and an 0.023 cm wall thickness. During irradiation in the core of the EBR-II (row 2), the outside of the cladding was exposed to flowing sodium containing 10 to 15 ppm oxygen (by weight) and the inside was in contact with static sodium except for a small portion at the top which was in contact with helium. The irradiation temperature as a function of position along the length for this particular fuel element has been calculated by Cushman (62) and is given in Figure 12. The neutron fluence along the length of the cladding has been calculated on the basis of reactor exposure and is also shown in Figure 12. The maximum fluence, at the reactor midplane, was 1.4×10^{22} neutrons/cm² ($E > 0.1$ MeV). A brief description of the EBR-II and the method used to calculate the fast

TABLE II

COMPOSITIONS OF TYPICAL UNIRRADIATED EBR-II COMPONENTS

Component	Fe	Analysis (Weight Percent)					
		C	Cr	Ni	Mn	Si	Ti
Fuel Cladding	Balance	0.034	19.0	8.4	1.0	0.53	< 0.02
Safety Rod Thimble	Balance	0.046	19.0	9.6	1.2	0.60	< 0.05
		Mo	P	S	B	N	
Fuel Cladding		0.12	0.023	0.013	0.0001	0.048	
Safety Rod Thimble		0.01	0.012	0.013	0.00002	0.004

Figure 10. Microstructure of unirradiated EBR-II fuel cladding.

Figure 11. Microstructure of unirradiated EBR-II safety rod thimble.

Figure 12. Irradiation conditions for EBR-II fuel cladding.

neutron fluence is given in Appendix A. Murphy and Strom (3) have calculated that the internal pressure in the fuel element (due to fission gas release) at the end of irradiation was 20 to 30 kg/cm². This pressure would produce a hoop stress of 2 to 3 kg/mm² in the cladding.

After irradiation, the fuel was removed from the cladding, and the cladding was cleaned ultrasonically in ethyl alcohol. The cladding was then cut into five sections, each approximately 7.6 cm long. A jig was constructed to support the tube wall during all subsequent cutting operations in order to eliminate any deformation and to allow the exact positioning of the cuts. A water-cooled abrasive cutoff saw was used. Four longitudinal cuts were made at 90-deg intervals around the cladding. Transverse cuts at approximately 0.3 cm intervals then produced four electron microscopy specimens from any one position (63).

The shroud tube was contained in an experimental subassembly which was irradiated in a Row 4 position of the reactor. The shroud tube was 102.5 cm long, 1.25 cm inside diameter, 0.025 cm wall thickness and extended from the bottom of the reactor core to a point 68 cm above the core. Since there is little heat generated outside the reactor core the coolant temperature was nearly constant from the top of the core to the top of the shroud tube. During irradiation the tube was not subjected to any appreciable stresses and was exposed to flowing sodium on both the inside and outside surfaces. The calculated irradiation temperatures and fast neutron fluences along the length of the shroud tube are shown in Figure 13.

Figure 13. Irradiation conditions for EBR-II shroud tube.

Following irradiation the shroud tube was cleaned and transmission electron microscopy specimens were cut in a manner similar to that described for the fuel cladding.

The containment tube which was removed from the seven tube experiment subassembly (Subassembly X067) which was irradiated in a Row 4 position of the EBR-II. This tube had an outside diameter of 2.05 cm and a wall thickness of 0.071 cm. Transmission electron microscopy specimens were removed from this component from an area which was approximately 34.3 cm below the reactor midplane during irradiation. The irradiation temperature at this point was 370°C and the fast neutron fluence was 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV).

The safety rod thimble was a hexagonal shaped tube which was 116.6 cm long, approximately 5.82 cm across each flat and had an 0.10 cm thickness. The thimble was irradiated in a Row 3 position of the reactor to a peak neutron fluence of 6.75×10^{22} neutrons/cm² ($E > 0.1$ MeV). Since it extended both above and below the core of the reactor there were segments along which the irradiation temperature was approximately constant at either 370 or 462°C and along which the fast neutron fluence varied. Figure 14 shows the variation in irradiation temperature and fast neutron fluence along the length of the thimble. After irradiation, transmission electron microscopy specimens measuring 0.31 cm by 0.31 cm by 0.10 cm thick and immersion density specimens measuring 3.08 cm long by 2.86 cm wide by 0.10 cm thick were cut from the desired locations. As with the other components, all cutting operations were done with a water cooled abrasive cut-off saw.

Figure 14. Irradiation conditions for EBR-II safety rod thimble.

II. DESIGN OF IRRADIATION EXPERIMENTS

In order to expand the range of fast neutron fluence and irradiation temperature beyond that available through an examination of reactor components, specimens were irradiated in two experimental sub-assemblies.

In the first experiment, specimens of type 304 stainless steel were irradiated to neutron fluences of 1×10^{18} to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV). This experiment was designed to investigate the initial stages of the irradiation damage process. Specimens in a second experiment were irradiated at temperatures of 570–630°C and 770–840°C to a fluence of 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV). This experiment was to define the damage structure occurring at the higher irradiation temperatures.

Each was designed in a similar manner. Specimens of the design shown in Figure 15, having the composition listed in Table III, were held in specimen holders such as the one shown schematically in Figure 16.

A gas gap between the specimen holder surface and the inside surface of the tube element provided a barrier to radial heat flow and allowed temperatures above the reactor coolant temperature to be obtained. The experiment was designed and calibrated on the basis of nuclear heating rate as a function of axial position determined in a previous experiment (64).

A computer program was used to calculate the width of the gas annulus between the surface of the specimen holder and the inner wall of the tube. Briefly, the technique was as follows. The materials and

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Figure 15. Drawing of specimen used in EBR-II materials irradiation experiments.

TABLE III
COMPOSITION OF TYPE 304 STAINLESS STEEL USED IN EBR-II
MATERIALS IRRADIATION EXPERIMENTS

Element	Weight Percent
C	0.040
Cr	18.4
Ni	9.3
Si	0.7
Mn	1.5
S	0.020
P	0.012
N	0.092
B	0.0008
Fe	Balance

Figure 16. Schematic drawing of specimen holder used in EBR-II materials irradiation experiments.

desired irradiation temperature for each specimen holder within a given tube were determined. This information, the inlet sodium temperature, sodium flow rate, a sodium film coefficient, the fixed (cold) geometry, the material properties such as: emissivity, density, thermal expansion coefficients and thermal conductivities as a function of temperature, and the nuclear heating rates as a function of axial position were input to the computer. The computer was programmed to calculate the cold gas annulus required to attain the specified irradiation temperatures. Calculations for gas annulus were performed at three places (bottom, middle, and top) on each of the 5.72 cm long specimen holders. It was assumed that at steady state all heat transfer within the capsule tube was radial, and that the total heat transferred across the gas annulus was the sum of that transferred by conduction and by radiation. Standard equations applicable to these conditions and geometry were used.

During the latter stages of this investigation a second type of irradiation experiment was conducted in an attempt to demonstrate the importance of transmutation produced helium in the void formation process. In this experiment sheet specimens of annealed type 304 stainless steel were irradiated in the EBR-II in contact with the liquid sodium reactor coolant. The composition of the alloy was (by weight percent): Cr - 18.15, Ni - 9.60, C - 0.046, Mn - 1.77, Si - 0.62, Cu - 0.25, Mo - 0.33, Co - 0.03, P - 0.023, S - 0.010, Fe - balance. In one set of specimens a uniform concentration of 20×10^{-6} atom fraction helium was injected prior to irradiation by bombarding with variable energy α particles. The injection was conducted by R. T. King, who has described the

experimental procedure elsewhere (65). A second set of unbombarded specimens was irradiated at the same position in the reactor experiment. The irradiation temperature, fast neutron flux and neutron energy spectrum were identical for the two sets of specimens. The irradiation temperature was approximately 390°C and the fluence was 7.6×10^{21} neutrons/cm² ($E > 0.1$ MeV).

III. TRANSMISSION ELECTRON MICROSCOPY

Preparation of specimens for transmission electron microscopy studies was accomplished using a semiautomatic technique which has been described in detail by Dubose and Stiegler (66). The specimens were first "dimpled" on both sides by an electrolytic jet technique. This reduces the thickness of the specimen to about 0.08 mm and produces a flat bottom dimple. Final polishing was accomplished in an electrolytic cell in which breakthrough was detected by a photocell device. The electrolytes were 60% H_3PO_4 -40% H_2SO_4 for dimpling and 5% $HClO_4$ -95% C_2H_5OH for the final polishing operation. Only the center of the specimen remains after thinning by this technique and thus surface effects which may have occurred during irradiation are eliminated.

Specimens were examined on a 200 kv (Hitachi Hu-200E) electron microscope. At least two specimens of each irradiation condition were examined. Defect concentrations were determined by a count of the number of defects per unit area on a photograph and then determining the volume represented by this area through a determination of the foil thickness.

In specimens irradiated to low fast neutron fluences such that the damage was in the form of small defect clusters visible only under diffraction conditions the foil thickness was measured by a determination of the crystallography of a twin boundary and then measuring the projection of the twin boundary on the photomicrograph. In all other instances the foil thickness was measured by obtaining a stereo pair of photomicrographs from a given area and measuring the distance between points on the top and bottom surfaces of the foil. A discussion of the variation of the measured defect concentrations within specimens having the same irradiation history is given in Appendix B.

IV. IMERSION DENSITY MEASUREMENTS

The method used to determine the density changes which occurred as a result of irradiation was based on Archimedes' principle and was similar to the method used by Batcliff (67). The density ρ of a sample having weight W_a in air of density ρ_a and weight W_e in liquid of density ρ_e is given by

$$\rho = \frac{W_a \rho_e - W_e \rho_a}{W_a - W_e} \quad (32)$$

The densities of irradiated samples (ρ_I) and of unirradiated samples (ρ_0) having approximately the same weight and the same geometrical shape were determined by weighing in air and in carbon tetrachloride (CCl_4). The temperature of the air was constant to within $\pm 5^\circ\text{C}$ and the density of the air was assumed to be 0.0012 gm/cm^3 . The density of the liquid

was determined immediately before and immediately after the weighing of a given specimen in the liquid. This was obtained by weighing a calibrated dummy sample in the liquid and calculating the density of the liquid from the expression

$$\rho_e = \frac{(\rho_{DS}(W_{Sa} - W_{Sl}) - W_{Sl}\rho_a)}{W_{Sa}} \quad (33)$$

where

- ρ_{DS} = density of calibrated standard,
- W_{Sa} = weight of standard in air,
- W_{Sl} = weight of standard in liquid, and
- ρ_a = density of air.

It was then assumed that the density of the liquid at the time of the weighing of the experimental sample was the average of the before and after measurements as determined above.

The density change which occurred as a result of irradiation, hereafter referred to as $(\Delta\rho/\rho_0)$, was then determined from

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho_I - \rho_0}{\rho_0} \quad (34)$$

The density of each sample was measured a minimum of five times. In reporting the percent density change the number of measurements, as well as the standard deviation of these measurements is given.

V. EXPERIMENTAL ERRORS

Possible sources of errors associated with these experiments and measurements are: (1) the temperature, (2) the accuracy of the fast neutron fluxes and fluences, (3) the errors associated with measurement of defect densities and sizes by TEM, and (4) errors encountered in measurement of the immersion density. Throughout this investigation attempts were made to minimize the errors by adopting standard techniques of measurement. In those cases in which the error cannot be definitely established, such as with the irradiation temperature and the fast neutron fluxes and fluences, the methods used in obtaining the reported values are described. In this way other investigators can adjust these results as future measurements of the reactor environment dictate.

In order to minimize the errors in irradiation temperature emphasis was placed on specimens which were removed from positions along the length of EBR-II components at which the temperature was constant. At the bottom of the reactor core and extending downward the temperature was in the range of 370-380°C. This temperature is accurately known because the inlet coolant temperature is monitored and controlled. In like manner the temperature towards the top or slightly above the reactor core and extending upwards also remains constant. The exact position along the length of a component at which the temperature reaches its maximum value and then remains constant is determined by heat transfer conditions. Calculated temperature profiles for the various components were supplied by Argonne National Laboratory (62). Emphasis was placed

on specimens removed from positions at which the calculated temperatures were in the range of 460-470°C. For specimens irradiated in experimental subassembly X0-34 a range of irradiation temperatures is also specified (i.e., 570-630°C or 770-840°C). The lower and upper temperatures of this range are based on heating rates of 3.0 and 4.0 watts per gram (in iron) at the Row 2 reactor midplane at a reactor power level of 50 MW. This is believed to be a conservative estimate of the possible range of heating rates and thus the irradiation temperatures.

The method used in obtaining the fast neutron fluxes and fluences for the various components and experiments is described in Appendix A. This is probably the largest source of absolute error since there is approximately a 20% difference between the Row 2 midplane calculated flux and that measured by dosimetry. Fluence values are based upon the experimentally determined value of the flux [2.1×10^{15} neutrons/cm² sec (total)]. The flux distribution and energy spectrum measurements and calculations of Kamphouse et al. (68) are used consistently.

Magnification and determination of the foil thickness are the major errors associated with the quantitative transmission electron microscopy studies. The magnification of a given photomicrograph is estimated to be correct to within $\pm 5\%$. Errors in magnification were minimized by taking most of the TEM photomicrographs which were subsequently used for quantitative evaluations at common microscope settings (lens current, etc.). Determination of the foil thickness using stereomicroscopy is estimated to be accurate to $\pm 20\%$. The actual variation in void concentrations as determined in two different foils of the same irradiated specimen are presented in Appendix B.

The fractional change in density as determined by the immersion technique is calculated from Equation 34:

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho_I - \rho_0}{\rho_0} \quad (34)$$

The standard deviation associated with this fractional change in density can be shown to be:

$$\sigma\left(\frac{\Delta\rho}{\rho_0}\right) = \left\{ \frac{\partial}{\partial\rho_0} \left(\frac{\Delta\rho}{\rho_0}\right) \sigma_{\rho_0}^2 + \frac{\partial}{\partial\rho_I} \left(\frac{\Delta\rho}{\rho_0}\right) \sigma_{\rho_I}^2 \right\}^{1/2} \quad (35)$$

where

$\sigma\left(\frac{\Delta\rho}{\rho_0}\right)$ = standard deviation of density change,

σ_{ρ_0} = standard deviation associated with measurement of unirradiated density, and

σ_{ρ_I} = standard deviation associated with measurement of irradiated density.

If it is assumed that the standard deviation of the unirradiated specimens (σ_{ρ_0}) is equal to that of the irradiated specimen (σ_{ρ_I}) then Equation 35 becomes:

$$\sigma\left(\frac{\Delta\rho}{\rho_0}\right) = \sigma_{\rho_I} \frac{(\rho_0 - \rho_I)^{1/2}}{\rho_0} \quad (36)$$

Standard deviations for the density change determined by Equation 36 are listed with the results of the density measurements.

CHAPTER V

RESULTS

Radiation damage to type 304 stainless steel was studied through an examination of specimens which were removed from various EBR-II components and to specimens irradiated in EBR-II experimental subassemblies. Two main techniques used to characterize the damage were: (1) transmission electron microscopy (TEM), and (2) direct measurement of the irradiation produced density changes. The transmission electron microscopy observations are presented first, since they illustrate the nature of the damage. Since a large fraction of the specimens examined came from EBR-II components, emphasis was placed on characterizing the damage in considerable detail at irradiation temperatures of 370-380°C and 460-470°C. These two temperatures were picked because they were the most accurately known part of the temperature gradient along the components and because a wide range of fast neutron fluences could be obtained at these temperatures. The effect of irradiation temperature on the damage structure was investigated through a series of specimens irradiated to fluences of 3.75 to 4.0×10^{22} neutrons/cm² ($E > 0.1$ MeV) at four temperatures in the range 370 to 840°C. The possible importance of transmutation produced helium on the irradiation damage process was examined in a specimen of type 304 stainless steel containing 20×10^{-6} atom fraction helium and irradiated at 390°C to 7.6×10^{21} neutrons/cm² ($E > 0.1$ MeV). The damage structure in this specimen was compared to

that in a control specimen which contained no helium prior to an identical irradiation.

I. TRANSMISSION ELECTRON MICROSCOPY OBSERVATIONS

Damage at Low Neutron Fluence

In type 304 stainless steel irradiated to 1.1×10^{18} neutrons/cm² ($E > 0.1$ MeV) at 370°C no damage was observed when the specimens were examined in the electron microscope under either diffraction or absorption contrast conditions. After irradiation at 384°C to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) small defect clusters such as those shown in Figure 17 were observed. These clusters were visible only when the foil was oriented near a diffraction position thus indicating that the spots were defects having a small strain field associated with them. With the exception of a small degraded zone near grain boundaries, which can also be seen in Figure 17, the defect clusters appeared to be homogeneously distributed throughout the grains. As the irradiation temperature was increased and the neutron fluence held constant at 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) the concentration of defect clusters dropped sharply, Figure 18. Approximately 1.5×10^{13} clusters/cm³ were present in a specimen which was irradiated at 496°C and no defects were observed (indicating that the defect concentration was less than approximately 10^{12} defects/cm³) in a specimen irradiated at 524°C. For this value of fluence the temperature cutoff for visible damage is between 496 and 524°C. When the specimens were examined under absorption conditions no damage was observed.

Figure 17. Transmission electron micrograph showing defect clusters in type 304 stainless steel irradiated at 384°C to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV).

Figure 18. Concentration of defect clusters in type 304 stainless steel irradiated at temperatures between 384 and 524°C to 1.4×10^{20} neutrons/cm² ($E > 0.1$ Mev).

The nature of the defect clusters was studied in a specimen irradiated at 467°C. Small defect clusters such as those shown in Figure 17 exhibit black-white contrast under dynamical two beam conditions. As outlined by Rühle (69), the direction $\bar{l}$ of the black-to-white contrast depends on the type of defect causing the contrast and also on the diffraction vector which is operating. If the defect is planar, e.g., a dislocation loop, then the direction of $\bar{l}$ is the projection, in a plane perpendicular to the beam, of the Burgers' vector of the loop. In this case, $\bar{l}$ is an intrinsic property of the loop and is not dependent on the diffraction vector $\bar{g}$. If on the other hand, the defect has a spherically symmetric strain field the direction of $\bar{l}$ is dependent on $\bar{g}$ and is in the direction of $\bar{g}$. By observing the direction of $\bar{l}$ when various $\bar{g}$ vectors were operative, it was possible to identify three defect types:

1. A defect exhibiting contrast consistent with that expected from a dislocation loop with an $\frac{a}{3} \langle 111 \rangle$ Burgers' vector.
2. A defect exhibiting contrast consistent with that expected from a dislocation loop with an $\frac{a}{2} \langle 110 \rangle$ Burgers' vector.
3. A defect exhibiting contrast consistent with that expected from a spherically symmetric strain field.

Figure 19 shows defects observed under two beam conditions such that the black-white contrast is visible. In this particular area of the foil, defects exhibiting contrast as expected from $\frac{a}{3} \langle 111 \rangle$ dislocation loops are visible. Of the approximately 50 defects analyzed in this manner, more than 75% exhibited contrast expected from $\frac{a}{3} \langle 111 \rangle$ dislocation

Figure 19. Small dot-like defects observed under two beam diffraction conditions.

The direction of the black-to-white contrast remains the same for different $\bar{g}$ vectors; thus, labeled defects are dislocation loops.

loops. Stiegler (70) has determined that the $\frac{a}{3} \langle 111 \rangle$ defects exhibit contrast behavior consistent with that expected from interstitial dislocation loops.

At higher fast neutron fluences the damage was more and more complicated. For fluences up to approximately 1×10^{21} neutrons/cm² ($E > 0.1$ MeV), the visible damage continued to be dislocation loops. However, when specimens which had been irradiated to fluences in excess of approximately 1×10^{21} neutrons/cm² ($E > 0.1$ MeV) were examined under absorption contrast conditions, cavities ranging up to a few hundred Å diameter were observed. Examination of stereo micrographs showed the cavities to be contained within the foil and not in contact with the foil surface, thus, indicating that they were not polishing artifacts. Previous investigations (1,2,52,53,54,55) have made similar observations and have also concluded that these cavities are irradiation produced voids.

Because the loop structure is visible under diffraction conditions and the voids are visible under absorption conditions these two defects will be discussed separately from this point forward.

Dislocation Loops and Networks

The dislocation loop structure produced by different fast neutron fluence at constant irradiation temperatures of 370–380°C are illustrated in Figures 20 and 21. After irradiation to 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV) at 370°C (Figure 20), the dislocation loops were larger than after irradiation to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) at

Figure 20. Dislocation loops in type 304 stainless steel irradiated at 370°C to 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV).

Note the clustering of the loops.

(a) 5×10^{21} neutrons/cm² ($E > 0.1$ MeV).

(b) 5×10^{22} neutrons/cm² ($E > 0.1$ MeV).

Figure 21. Dislocation structure in specimens irradiated at 370-380°C.

approximately the same temperature (Figure 17, page 65). There was evidence that in the specimen irradiated to 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV) the loop structure was not homogeneously distributed. The concentration of loops in the immediate vicinity of grown-in dislocations was much higher than in the surrounding matrix. The only apparent difference between these two specimens is that the specimen irradiated to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) had a lower preirradiation dislocation density than the specimen irradiated to the higher fluence.

With increasing fast neutron fluence the dislocation loop structure becomes progressively more complex. Figure 21 shows specimens irradiated at 370-380°C to 5×10^{21} and 5×10^{22} neutrons/cm² ($E > 0.1$ MeV). Even at the lower of these two fluences the loop concentration is too large to be accurately measured. In the lower fluence specimen fringes can be seen in those loops having the correct orientation with respect to the plane of the foil. These fringes indicate the presence of a stacking fault. Because of the high loop concentration, inhomogeneities in the loop distributions are not apparent if they are present. In the specimen irradiated to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV) the loop concentration is so high that it is impossible to resolve individual loops.

After irradiation at 460-470°C to a neutron fluence of 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) a structure shown in Figure 22 was found. The specimen contained approximately 2×10^{14} defect clusters/cm³.

Figure 23 shows a specimen which was irradiated to 5×10^{20} neutrons/cm². This specimen did not contain defect clusters. However,

Figure 22. Defect clusters in type 304 stainless steel irradiated at 460-470°C to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) at a neutron flux of 1.9×10^{15} neutrons/cm²/sec ($E > 0.1$ MeV).

Figure 23. Dislocation line - precipitate structure in specimen irradiated at 460-470°C to 5×10^{20} neutrons/cm² ($E > 0.1$ MeV) at a neutron flux of approximately 4×10^{13} neutrons/cm²/sec ($E > 0.1$ MeV).

the grown in dislocations were decorated with what stereo microscopy suggested were small rod-shaped precipitates.

The different microstructures present in these two specimens apparently resulted from different irradiation conditions; i.e., the fast neutron flux and the irradiation time. The specimen containing the defect clusters was irradiated in a flux of 1.9×10^{15} neutrons/cm²/sec for 20.5 hr, whereas the specimen containing the dislocation-precipitate structure was irradiated in a flux of 1.7×10^{13} neutrons/cm²/sec for 8200 hr. Thus, the specimen irradiated to 1.4×10^{20} neutrons/cm² at a "high" fast neutron flux contained defect clusters which were apparently vacancy and interstitial in nature while the specimen irradiated to 5×10^{20} neutrons/cm² at a fast neutron flux which was about a factor of 100 lower did not contain such clusters.

The dislocation line - precipitate structure shown in Figure 23 is almost identical in appearance to precipitate structures observed by Singhal and Martin (71) and Beckitt and Clark (72). In these investigations the structures were identified as $M_{23}C_6$ carbides precipitated on dislocations in unirradiated austenitic stainless steels as a result of thermal aging at temperatures of 560 and 700°C for short times, near 1 hr. Brager and Kissinger (73) have shown that $M_{23}C_6$ carbides are formed in type 316 stainless during irradiation at 480°C, whereas in control specimens aged at the irradiation temperature for the irradiation time no precipitation occurred. In the present investigation, it appears that the dislocation precipitate structure resulted from the precipitation of carbides, probably of the $M_{23}C_6$ type on dislocations

which were present prior to irradiation.

Comparison of the appearance of the dislocation loop structure at different fluences for a constant irradiation temperature of 460-470°C is further illustrated in Figures 24 and 25. After irradiation to 2×10^{21} neutrons/cm² ($E > 0.1$ MeV) the concentration of the dislocation line - precipitate structure (labeled A in Figure 24) had not changed appreciably although the precipitates were larger, extending 500 to 1000 Å into the surrounding matrix. The specimens shown in Figures 23 and 24 were both taken from the ESR-II shroud tube and were subjected to similar thermal histories, i.e., 8200 hr at 460°C. The larger precipitates in the higher fluence specimen may be a result of the irradiation conditions: i.e., the higher fast neutron flux and/or fluence. In addition, defects exhibiting the characteristics of dislocation loops were also observed at this slightly higher fluence. Most of these loops were very irregular in shape (labeled B in Figure 24) although some of the smaller loops were more circular (labeled C in Figure 24). Stacking fault fringes were readily visible in the larger loops.

After the higher fluences, the dislocation line - precipitate structure and the irregularly shaped dislocation loops become more difficult to observe, possibly because the other forms of damage obscure them. The irregularly shaped loops still appear to be present in Figure 25. At fluences of approximately 1×10^{22} neutrons/cm² ($E > 0.1$ MeV) and higher, it was very difficult to determine the nature of the loop structure because of the high loop densities and large loop sizes.

Figure 24. Examples of the loop and dislocation structures observed after irradiation to 2×10^{21} neutrons/cm² ($E > 0.1$ MeV) at 460-470°C.

A. Dislocation line-precipitate structure. B. Irregular shaped defect exhibiting contrast similar to faulted dislocation loop. C. Regular faulted dislocation loop.

(a) 3.3×10^{21} neutrons/cm²
(E > 0.1 MeV)

(b) 8.8×10^{21} neutrons/cm²
(E > 0.1 MeV)

(c) 2.1×10^{22} neutrons/cm²
(E > 0.1 MeV)

Figure 25. Effect of fast neutron fluence on the loop structure in type 304 stainless steel irradiated at 460-470°C.

The nature of the dislocation loops, whether they were formed by the precipitation of vacancies or interstitials, was determined in a specimen which had been irradiated at 460°C to 2.8×10^{21} neutrons/cm² ($E > 0.1$ MeV). The technique was suggested by Stiegler (70) and was a modification of the method used by Mazey *et al.* (74) and Edmondson and Williamson (75). The technique is based on geometrical arguments describing the contrast around a dislocation. Figure 26 is a schematic representation of the distortion present in the vicinity of an edge dislocation. Let θ be the angle between the incident beam (I_0) and an undistorted lattice plane. If $\theta > \theta_B$ where θ_B is the Bragg angle, and $\bar{s} > 0$ (where $\bar{s}$ is the vector which brings the reciprocal lattice point into coincidence with the reflecting sphere) a clockwise rotation of the lattice at "A" reduces the angle of incidence to θ_B and diffraction will occur in the vicinity of "A." Thus, in Figure 26 the image of the dislocation appears to the right of the actual dislocation position. Note that at "B" the rotation of the lattice causes θ to deviate from, rather than approach, θ_B . Conversely, if $\theta < \theta_B$ and the sign of $\bar{g}$ is reversed, the image of the dislocation appears on the right side of the dislocation. When the dislocation is of opposite sign the rotations are opposite and for the same $\bar{g}$, $\bar{b}$, and $\bar{s}$ the dislocation image will appear on the opposite side of the dislocation to that just described.

The case of an interstitial dislocation loop inclined to the plane of the foil is illustrated in Figure 27. In this case $\theta > \theta_B$, and the clockwise rotation of the lattice planes at points A and B brings the lattice at these points into a diffracting position, and

ORNL-DWG 70-4681

Figure 26. Geometric representation of the origin of diffraction contrast from an edge dislocation.

Figure 27. Geometric representation of the image produced by an interstitial dislocation loop.

The angle θ of the incident beam relative to the set of lattice planes being considered is greater than θ_B , the Bragg Angle. The clockwise rotations of the lattice at A and B reduce θ to give an image. For this condition the image is outside the actual dislocation.

produces a dislocation image. For these conditions the image is on the outside of the dislocation loop. If the loop were a vacancy loop ($\bar{g}$ and $\bar{s}$ unchanged) the image would be on the inside of the dislocation. If in Figure 27 the sign of $\bar{g}$ were reversed the image would appear on the inside of the dislocation.

In order to determine whether a dislocation loop is a vacancy loop or an interstitial loop it is necessary to know the inclination of the loop with respect to the surface of the foil, the direction of $\bar{b}$ (which for a loop having a stacking fault in an fcc lattice is a $\langle 111 \rangle$ direction), the diffraction conditions, $\bar{g}$, and the sign of $\bar{s}$ (i.e., $\theta > \theta_B$, $\bar{s} > 0$; $\theta < \theta_B$, $\bar{s} < 0$). Since the position of the dislocation image depends on $\bar{g}$, $\bar{b}$, and $\bar{s}$, if we keep $\bar{b}$ and $\bar{s}$ constant and change the sign of $\bar{g}$ the position of the image will change from the inside to the outside of the actual location.

Figure 28 shows dislocation loops in a specimen irradiated at 460-470°C to 2.8×10^{21} neutrons/cm² ($E > 0.1$ MeV) with both plus and minus $\bar{g}$ vectors operating ($\bar{s}$ is positive in both cases). The loops which exhibit stacking fault fringes in Figure 28a appear larger in Figure 28c indicating that when $\bar{g}$ was changed from plus to minus the dislocation image shifted from inside to outside of the dislocation. Stereomicroscopy was used to determine the inclination of the loops to the surface of the foil. The behavior was that expected from interstitial dislocation loops. Note that in Figure 28, the defect labeled A is an unfaulted dislocation loop. A small fraction of the total

Figure 28. Dislocation loops with 002 and 00 $\bar{2}$ diffraction vectors operating.

Note that the loops which exhibit stacking fault fringes when the diffraction vector is 002 become larger and no longer exhibit these fringes when the diffraction vector is changed to 00 $\bar{2}$. This behavior would be expected from interstitial dislocation loops.

number of loops were observed to be of this type at this irradiation temperature.

Figures 20 through 25 (pages 70, 71, 73, 74, 77, and 78) show that the effect of increasing the irradiation temperature from 370 to 470 C at a constant fluence was to increase the loop size and decrease the loop density. Quantitative measurement of these parameters was impossible due to the complexity of the structure.

At an irradiation temperature of 570-630 C a dislocation network rather than faulted dislocation loops was formed. An electron micrograph of this dislocation structure in a specimen irradiated at 570-630 C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) is shown in Figure 29. The dislocation line density in this material was approximately 2×10^{10} cm/cm³. A few apparently unfaulted dislocation loops were also observed. This transition from a structure of faulted dislocation loops to a network of dislocation lines was a result of the difference in irradiation temperature. In this same heat of type 304 stainless steel irradiated at temperatures in the range of 370-470 C the faulted dislocation loop structure was present.

Voids and Swelling

At an irradiation temperature of 370-380 C the lowest fast neutron fluence at which voids were detected was 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV). In this specimen the concentration of visible voids was 8.5×10^{14} voids/cm³. As can be seen in Figure 30, the voids range in size from the smallest observable (about 50 Å diameter) to approximately 100 Å diameter. Examination of foils in which grown-in dislocations

Figure 29. Dislocation network in type 304 stainless steel irradiated at 570–630°C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV).

Figure 30. Voids in type 304 stainless steel irradiated at 370-380°C to 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV).

were visible in residual contrast (Figure 30) revealed that voids were often located on or very close to these dislocations.

The void size, void shape and void concentration were strongly dependent on the fast neutron fluence. Figure 31 illustrates the changes in the irradiation produced voids when the irradiation temperature was held constant at 370-380°C and the fluence was increased from 4.8×10^{21} to 5.0×10^{22} neutrons/cm² ($E > 0.1$ MeV).

It is readily apparent from these photomicrographs that a distribution of void sizes is present. Secondly, as the fast neutron fluence is increased the void concentration increases. After irradiation to 4.8×10^{21} neutrons/cm² ($E > 0.1$ MeV) and 1.2×10^{22} neutrons/cm² (Figure 31a and b) several void shapes within any one grain can be found. The smaller voids appear spherical and the larger voids appear polyhedral. In the case of the polyhedral shaped voids no one form or shape predominates. After irradiation to the highest fluence, 5.0×10^{22} neutrons/cm² ($E > 0.1$ MeV), many of the larger voids appear to have a common shape (e.g., in Figure 31c the larger voids project as squares) suggesting that they are approaching some equilibrium shape. Void size distributions were determined for a total of eight specimens irradiated at 370-380°C. A typical histogram of the void size distribution for one of these specimens is shown in Figure 32. At this irradiation temperature the smallest size interval contains the largest percentage of voids. All visible voids fall into a narrow size range, having diameters between approximately 60 and 170 Å. The void size distributions for the specimens shown in Figure 31 have been plotted in Figure 33. This plot

(a) 4.8×10^{21} neutrons/cm²
(E > 0.1 MeV).

(b) 1.2×10^{22} neutrons/cm²
(E > 0.1 MeV).

(c) 5.0×10^{22} neutrons/cm²
(E > 0.1 MeV).

Figure 31. Effect of fast neutron fluence on the void concentration and size distribution in type 304 stainless steel irradiated at 370-380°C.

Figure 32. Histogram of the void size distribution in type 304 stainless steel irradiated at 370-380°C to 5.0×10^{22} neutrons/cm² ($E > 0.1$ MeV).

Figure 33. Effect of fluence on the void size distribution curve for type 304 stainless steel irradiated at 370-380°C.

shows the void concentration within a size interval as a function of the void diameter. The points have been plotted at the center of the respective size intervals and smooth curves drawn through them. The most important feature of the distributions is that over a range of fluences from 4.8×10^{21} to 5.0×10^{22} neutrons/cm² ($E > 0.1$ MeV) the maximum void size remains constant at approximately 200 Å. After irradiation to 2×10^{21} neutrons/cm² the maximum void size is smaller, being near 100 Å.

Irradiation at 460–470°C to relatively low fast neutron fluences produced heterogeneous void distributions similar to those observed after a low fluence irradiation at 370–380°C. Figure 34 shows a specimen irradiated at 460–470°C to approximately 4×10^{21} neutrons/cm² ($E > 0.1$ MeV). Voids are associated with dislocations, which can be seen in residual contrast. The fact that the voids lie on the dislocations was confirmed by stereo microscopy.

In instances where the void was associated with line defects the void shape was very strongly affected. Figure 35 shows voids lying on very straight dislocations. These voids have a crystallographic appearance in contrast to the voids which do not appear to be associated with dislocations. In general there was a tendency for voids lying on dislocations to be elongated in the direction of the dislocation line.

After the higher fast neutron fluence, the void concentration was higher and it became progressively more difficult to detect inhomogeneities in the void distributions. Figure 36, however, shows a specimen irradiated to 0.74×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 460°C. Several voids are associated with the dislocation lines and these voids tend to

Figure 34. Heterogeneous void distributions in type 304 stainless steel irradiated at 460-470°C to 4×10^{21} neutrons/cm² ($E > 0.1$ MeV).

Stereo microscopy indicated that the voids lie on dislocation lines.

Figure 35. Association of voids with dislocation lines in type 304 stainless steel.

Note the difference in shape of those voids which lie on the dislocations compared to those which do not.

Figure 36. Voids associated with dislocation lines in specimen irradiated at 460-470°C to 0.74×10^{22} electrons/cm² ($E > 0.1$ MeV).

be elongated in the direction of the line, whereas voids in the matrix have more uniform shapes and project as squares or in some cases as circles.

In addition to heterogeneities in the void distributions within the matrix which were observed under certain irradiation conditions, a second heterogeneity, namely the lack of voids in a zone adjacent to the grain boundaries was observed at all irradiation temperatures. Grain boundaries in a specimen irradiated at 420°C to 4.2×10^{22} neutrons/cm² ($E > 0.1$ MeV) are shown in Figure 37.

Figure 38 shows the effect of fluence on the appearance of the voids in material irradiated at 460-470°C. After irradiation to a given neutron fluence the void concentration is much reduced as compared to specimens irradiated at 370-390°C. Although an admittedly qualitative observation, it also appears that the voids tend to have more polyhedral or crystallographic shapes than at the lower temperature. Void size distributions were determined for eight specimens irradiated at 460-470°C. The elongated voids such as those present in Figure 34 were not considered in determining the size distributions. A typical histogram is shown in Figure 39. In comparison to the lower irradiation temperature (Figure 32, page 89) at 460-470°C the range of void sizes is larger (approximately 60 to 300 Å diameter) and the interval containing the largest percentage of the voids is not the smallest size interval. A plot of three void size distribution curves for specimens irradiated at 460-470°C is shown in Figure 40. As was the case at the lower irradiation temperature of

Figure 37. Type 304 stainless steel irradiated at 420°C to 4.2×10^{22} neutrons/cm² ($E > 0.1$ MeV).

Note the regions along grain boundaries are denuded of voids.

(a) 2.8×10^{21} neutrons/cm²
($E > 0.1$ MeV).

(b) 0.9×10^{22} neutrons/cm²
($E > 0.1$ MeV).

(c) 1.1×10^{22} neutrons/cm²
($E > 0.1$ MeV).

Figure 38. Effect of fast neutron fluence on the shape and concentration of voids in type 304 stainless steel irradiated at 460-470°C.

Figure 39. Histogram of the void size distribution in type 304 stainless steel irradiated at 400-470°C to 2.1×10^{22} neutrons/cm² ($E > 0.1$ MeV).

Figure 40. Effect of fast neutron fluence on the void size distribution in type 304 stainless steel irradiated at 460-470°C.

370-380°C, a maximum void diameter which appears to be insensitive to the fast neutron fluence is also achieved at 460-470°C.

The effect of irradiation temperature on the void structure is illustrated in Figure 41 which shows voids present in specimens irradiated to fluences in the range of $3.75-4.0 \times 10^{22}$ neutrons/cm² ($E > 0.1$ MeV) at temperatures of 370-380°C, 430-440°C, 570-630°C, and 770-840°C.

Several observations relating to the effect of irradiation temperature were made. At this fluence, the void concentration was approximately the same in specimens irradiated at 370-380 and 430-440°C but was significantly lower in the specimen irradiated at 570-630°C. With increasing irradiation temperature the voids became larger and in general appear to have more uniform polyhedral shapes.

As in the case of specimens irradiated to relatively low fluences in the temperature range of 370-470°C (see Figures 30, 34 and 35, pages 86, 92 and 93), nearly all the voids in the specimen irradiated at 570-630°C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) were associated with dislocation lines. The dislocation structure differed inasmuch as the lower irradiation temperature the dislocations were present prior to irradiation while at the higher temperature the dislocations were apparently produced by the irradiation.

The specimen irradiated at 770-840°C contained approximately 1×10^{13} cavities/cm³ ranging in size from the smallest observable to approximately 75 Å diameter. In several instances the cavities were located on large precipitate particles and also at grain boundaries. These cavities are inherently different from the voids which formed

(a) Irradiated at 370-380°C.

(b) Irradiated at 430-440°C.

Figure 41. Effect of irradiation temperature on the void concentration and size in type 304 stainless steel irradiated to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV).

At 770-840°C helium bubbles rather than voids were formed.

(c) Irradiated at 570-630°C.

(d) Irradiated at 770-840°C.

Figure 41 (continued)

at lower temperatures since voids have never been seen at precipitate particle-matrix interfaces nor at grain boundaries. In addition, the high temperature cavities were smaller than the voids which formed at a lower irradiation temperature. The high temperature cavities thus have the characteristics reported previously for helium bubbles (17,18,19,20).

The void concentration and void size distribution was determined for each irradiated specimen. These results are presented as plots of void concentration and maximum void size as a function of fluence for a constant irradiation temperature and as a function of irradiation temperature for a constant fast neutron fluence.

Figure 42 shows the void concentration as a function of the fast neutron fluence for specimens irradiated at 370-380 and 460-470°C. At each temperature the void concentration increased monotonically with increasing fluence. Over the range of fluence for which data is available the void concentration increased at a faster rate and the concentrations were lower at 460-470°C than at 370-380°C. This must mean that at still lower fluences (i.e., less than 10^{21} neutrons/cm² [$E > 0.1$ MeV]) the void concentration was increasing at a faster rate at 370-380°C than at 460-470°C. A least square fit of the data shown in Figure 42 gives a variation of void concentration with fluence (i.e., the value of B in the expression $\rho_v = A(\phi t)^B$) of 0.66 at 370-380°C and 1.66 at 460-470°C.

Sufficient data were available to define the form of the curve of void concentration as a function of irradiation temperature for a fast neutron fluence of $3.7-4.0 \times 10^{22}$ neutrons/cm². Additional curves were then constructed from limited data available at fluences of 5×10^{21}

Figure 42. Variation of void concentration with fast neutron fluence in type 304 stainless steel irradiated at 370-380 and 460-470°C.

and 1.2×10^{22} neutrons/cm² ($E > 0.1$ MeV). At each fluence level the void concentration decreased with increasing irradiation temperature, Figure 43. This decrease in void concentration with increasing temperature occurred more rapidly at low fluences than at higher fluences. At a fluence of $3.7\text{--}4.0 \times 10^{22}$ neutrons/cm² the void concentration is nearly constant at irradiation temperatures between 370 and 450°C.

Several of the examined specimens had been irradiated to approximately the same fast neutron fluence but at fast neutron fluxes which differ by as much as a factor of six. The void concentrations for these specimens are listed in Table IV. Within the experimental error associated with these measurements, the void concentration did not depend on the value of the fast neutron flux. Void size distribution curves were also examined and did not appear to be influenced by the flux.

The maximum void diameter is plotted as a function of fast neutron fluence for specimens irradiated at 370–380°C and 460–470°C in Figure 44. At 370–380°C no voids were observed after irradiation to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) and voids having a maximum diameter of approximately 100 Å were observed after irradiation to 2.0×10^{21} neutrons/cm² ($E > 0.1$ MeV). Over the range of fluence from 5×10^{21} to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV) the maximum void size changed very little, remaining essentially constant at 200 Å diameter. It thus appears that a void grows quite rapidly early in its life but that after approximately 5×10^{21} neutrons/cm² the growth rate decreases very sharply thus giving an apparent maximum or limiting void size. A similar argument can be

Figure 43. Variation of void concentration with irradiation temperature.

TABLE IV

COMPARISON OF VOID CONCENTRATIONS IN SPECIMENS IRRADIATED
TO APPROXIMATELY THE SAME NEUTRON FLUENCE AT
DIFFERENT NEUTRON FLUX LEVELS

Irradiation Temperature °C	Neutron Fluence Neutrons/cm ² E > 0.1 MeV	Neutron Flux Neutrons/cm ² /sec E > 0.1 MeV	Void Concentration Voids/cm ³
370	0.80 x 10 ²²	1.4 x 10 ¹⁵	2.5 x 10 ¹⁵
370	0.76 x 10 ²²	2.1 x 10 ¹⁴	3.6 x 10 ¹⁵
472	0.9 x 10 ²²	1.2 x 10 ¹⁵	4.0 x 10 ¹⁴
465	0.9 x 10 ²²	3.7 x 10 ¹⁴	5.5 x 10 ¹⁴
465	1.3 x 10 ²²	1.8 x 10 ¹⁵	9.0 x 10 ¹⁴
462	1.2 x 10 ²²	3.3 x 10 ¹⁴	7.5 x 10 ¹⁴

Figure 44. Maximum void diameter versus fast neutron fluence.

made for specimens irradiated at 460-470°C. However, at the higher temperature the maximum void size is larger, being approximately 300 Å diameter. Maximum void diameter as a function of irradiation temperature is shown in Figure 45.

II. EFFECTS OF HELIUM ON IRRADIATION DAMAGE

In order to determine any role of transmutation produced helium on the irradiation damage processes, a specimen of type 304 stainless steel was injected with 20×10^{-6} atom fraction helium prior to irradiation at 390°C to 7.4×10^{21} neutrons/cm ($E > 0.1$ MeV) in the EBR-II. The damage structure in this specimen was compared to that in a specimen irradiated at identical conditions but which did not contain helium prior to irradiation.

The pre-irradiation microstructure of the specimen containing 20×10^{-6} atom fraction helium showed no evidence of damage which might have resulted from the α -particle bombardment.

Figure 46 shows the postirradiation microstructure of the specimen which contained no cyclotron injected helium prior to irradiation. Approximately 2.4×10^{15} voids/cm³ ranging in size from the smallest observable (approximately 40 Å diameter) to a maximum of 130 Å diameter were present. There was a zone approximately 1000 Å wide adjacent to the grain boundaries which was denuded of voids. This zone was also denuded of the loop structure, Figure 46b. There was some evidence of loop formation immediately adjacent to the grain boundaries. Similar observations of a zone denuded of dislocation loops near grain

Figure 45. Maximum void diameter as function of irradiation temperature for specimens irradiated to fast neutron fluences in excess of 1×10^{22} neutrons/cm² ($E > 0.1$ MeV).

(a) Voids. Note denuded zone adjacent to grain boundary.

(b) Dislocation loops. Note region adjacent to grain boundary which is denuded of loops.

Figure 46. Microstructure of type 304 stainless steel irradiated at 390°C to 7.6×10^{21} neutrons/cm² ($E > 0.1$ MeV).

boundaries with intense loop formation at the boundaries have been reported by Stiegler and Bloom (53).

The void and loop structure in the specimen which contained 20×10^{-6} atom fraction helium prior to irradiation is shown in Figure 47. The microstructure is in general much finer than that of the specimen which contained no helium. The maximum void diameter was approximately 60 Å and the concentration of visible voids was 5.2×10^{15} voids/cm³. Because of the very small void sizes, it is probable that a large fraction of the total void population probably was not resolved, and thus, the actual void concentration may be significantly higher. The zone adjacent to grain boundaries which was denuded of voids was only 100-200 Å wide and loop formation occurred up to the grain boundary. Comparison of Figure 46b and Figure 47b also indicates that the loop diameters were smaller and the concentration higher in the specimen which contained helium prior to irradiation.

III. IMMERSION DENSITY MEASUREMENTS

Results of immersion density measurements on specimens removed from the EBR-II safety rod thimble are listed in Table V. The density change was calculated by comparison with the density of specimens removed from the very ends of the thimble where TEM examination showed essentially no void formation. The reported values are the average of five independent measurements. These density decreases are plotted in Figure 48 as a function of the position of the specimen in the reactor during irradiation. The curve is nearly symmetrical but is displaced

(a) Voids.

(b) Dislocation structure.

Figure 47. Microstructure of type 304 stainless steel which contained 20×10^{-6} atom fraction helium prior to irradiation at 390°C to 7.6×10^{21} neutrons/cm² ($E > 0.1$ MeV).

TABLE V

DENSITY CHANGE OF SPECIMENS REMOVED FROM THE EBR-II SAFETY ROD THIMBLE

Irradiation Temperature °C	Neutrons/cm ² E > 0.01 MeV	Density of Irradiated Specimen gm/cm ³ ρ_I	Standard Deviation of ρ_I	Density Decrease $\frac{\Delta\rho}{\rho_0}$ (%)	Standard Deviation $\frac{\Delta\rho}{\rho_0}$ (%)
370	3.7 x 10 ²¹	7.8818	.0214	0.07	0.02
370	5.8 x 10 ²¹	7.8800	.0166	0.10	0.01
370	9.2 x 10 ²¹	7.8673	.0131	0.26	0.02
370	1.4 x 10 ²²	7.8621	.0160	0.32	0.03
370	3.1 x 10 ²²	7.8542	.0060	0.42	0.01
374	4.3 x 10 ²²	7.8399	.0168	0.60	0.04
381	5.8 x 10 ²²	7.7901	.0766	1.23	0.30
393	6.6 x 10 ²²	7.7033	.0110	2.34	0.05
410	6.5 x 10 ²²	7.6349	.0064	3.20	0.04
421	5.5 x 10 ²²	7.6609	.0214	2.49	0.12
432	4.2 x 10 ²²	7.7823	.0099	1.33	0.04
444	2.9 x 10 ²²	7.8282	.0059	0.75	0.01
455	2.1 x 10 ²²	7.8580	.0115	0.37	0.02
462	1.3 x 10 ²²	7.8611	.0199	0.34	0.04
462	9.2 x 10 ²¹	7.8748	.0267	0.16	0.03
462	5.8 x 10 ²¹	7.8796	.0219	0.10	0.02
462	3.6 x 10 ²¹	7.8861	.0168	0.02	< 0.01
462	2.0 x 10 ²¹	7.8867	.0040	0.01	< 0.01

Figure 48. Density decrease as function of axial distance from reactor midplane for EBR-II safety rod thimble.

to a position slightly above the reactor midplane. This displacement is due to the fact that the swelling is both fluence and temperature dependent. The swelling increases with increasing fluence (at constant temperature) or with increasing temperature (over the range 370-470°C) at constant fluence. Since the temperature increases from the bottom to the top of the reactor and the neutron flux peaks at approximately the reactor midplane, the maximum swelling occurs slightly above the midplane.

The density changes in type 304 and type 304L stainless steels irradiated at 570-630 and 770-840°C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) are listed in Table VI.

The density decrease as a function of fluence determined by immersion measurements and calculated from the void concentration and size distribution is shown in Figures 49 and 50 for irradiation temperatures of 370-380 and 460-470°C, respectively. At each temperature, the density decreases measured by the two different techniques are in reasonably good agreement. Data for these two irradiation temperatures were used to determine the fluence dependency X , of the density decrease in an expression of the form

$$\frac{\Delta\rho}{\rho_0} \propto (\phi t)^X \quad (37)$$

The values of X as determined by a least square fit of the data were 0.84 and 1.60 for irradiation temperatures of 370-380 and 460-470°C, respectively. These values for the fluence dependency of the density decrease are consistent with the fluence dependency of the void concentration as given in Figure 42, page 104. It thus appears that the

TABLE VI

DENSITY AND DENSITY CHANGE IN TYPE 304 STAINLESS STEEL IRRADIATED^a IN EBR-II
EXPERIMENTAL SUBASSEMBLY XO-34

Material	Irradiation Temperature °C	Density of Irradiated Specimen gm/cm ³ ρ_I	Standard Deviation of ρ_I	Density Decrease $\frac{\Delta\rho}{\rho_0}$ (%)	Standard Deviation of $\frac{\Delta\rho}{\rho_0}$ (%)
304	570-630	7.8758	0.0027	0.19	< 0.01
Stainless	770-840	7.8905	0.0026	0.01	< 0.01
Steel ^b	770-840	7.8916	0.0041	-0.01	---
304L	570-630	7.8674	0.0037	0.06	< 0.01
Stainless	570-630	7.8663	0.0038	0.07	< 0.01
Steel ^c					

^aIrradiated to 3.7×10^{22} neutrons/cm² (E > 0.1 MeV).

^bUnirradiated density 7.8911 gm/cm³.

^cUnirradiated density 7.8724 gm/cm³.

Figure 49. Density decrease versus fluence for type 304 stainless steel irradiated at 370-380°C.

ORNL DWG 70-4677
Y-99769

Figure 50. Density decrease versus fluence for type 304 stainless steel irradiated at 460-470°C.

fluence dependency of swelling is not temperature independent as was assumed in the analysis of Claudson et al. (52).

The density change as a function of irradiation temperature was examined by normalizing the data listed in Tables V and VI, pages 113 and 116, to a fast neutron fluence of 4.0×10^{22} neutrons/cm² ($E > 0.1$ MeV). This fluence was used because it is approximately equal to the fluence accumulated by the specimens irradiated at 570-630°C. Because of the limited data and the uncertainties in the fluence dependency at temperatures other than 370-380 and 460-470°C the data were normalized to the desired fluence using an assumed fluence dependency of 1. The results, shown in Figure 51, illustrate the strong temperature dependency of the density decrease.

Figure 51. Density decrease versus temperature.

Data are normalized to a fluence of 4×10^{22} neutrons/cm² ($E > 0.1$ MeV) using $\Delta\rho/\rho \propto (\phi t)^{1.0}$.

CHAPTER VI

SUMMARY OF RESULTS AND DISCUSSION

I. GENERAL OBSERVATIONS

Changes in the microstructure of type 304 stainless steel as a result of fast neutron irradiation at temperatures between 370 and 840°C to fast neutron fluences to 7×10^{22} neutrons/cm² ($E > 0.1$ MeV) have been followed by transmission electron microscopy. The materials were irradiated in the EBR-II either as reactor components or as specimens contained in reactor subassemblies specifically designed for materials irradiation experiments. The results of the investigation are summarized and discussed below.

Irradiation Damage at Low Fluences

No damage was observed at the lowest fluence at which specimens were examined [1.1×10^{18} neutrons/cm² ($E > 0.1$ MeV)]. After irradiation to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) small defect clusters which appeared as black dots when examined under diffraction contrast conditions (Figures 17 and 22, pages 55 and 73) were present. Diffraction contrast from these defects was consistent with that expected from three defect types: (1) dislocation loops having an $a/3 \langle 111 \rangle$ Burgers' vector, (2) dislocation loops having an $a/2 \langle 110 \rangle$ Burgers' vector and (3) a spherical or three dimensional cluster rather than a planar defect such as a loop. In excess of 75% of the defects were dislocation loops having an $a/3 \langle 111 \rangle$ Burgers' vector. Stiegler (70) has analyzed the

contrast arising from these loops and has concluded that they are mostly interstitial in nature. The three dimensional defects are assumed to be vacancy clusters. As the irradiation temperature was increased from 384 to 496°C, the defect cluster concentration decreased continuously. After irradiation to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) at 524°C no clusters were observed. This observation indicates that there is an incubation period before defect clusters begin to form or that the initial growth rate is very slow since damage is observed at fluences above 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) at temperatures above 500°C. Note, however, that because of the small volumes which are examined and the resolution of the microscope, approximately 10^{12} defects larger than about 15 Å diameter would have to be present in order to be detected.

Development of Dislocation Structure

As the fast neutron fluence was increased above 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) the dislocation loop concentration continued to increase and the loops continued to grow. On the basis of qualitative observations, it appeared that for a constant fluence the loop concentration decreased and the loop diameter increased the greater the irradiation temperature in the range 370 to 470°C (Figures 21 and 25, pages 71 and 78). The appearance of the dislocation loops under various diffraction conditions was consistent with that of interstitial dislocation loops having $a/3 \langle 111 \rangle$ Burgers' vector. This type of dislocation is sessile and bounds a stacking fault. At low neutron fluences, before the loop structure became too dense and complex for observation of the

individual loops, several different loop forms or shapes were present. The loop distribution was affected by the presence of structural irregularities, such as dislocations and grain boundaries.

After irradiation at 370°C to relatively low fluences, the clustering of dislocation loops about dislocation lines (Figure 20, page 70) was evident. This observation of clustering has been reported by Piercy and Whitton (76) and Stiegler et al. (13), for loops in irradiated aluminum and aluminum alloys. Piercy and Whitton attributed the clustering in deformed areas of the sample to the irradiation-induced vacancies enlarging submicroscopic vacancy loops produced by deformation prior to irradiation. This mechanism is unlikely to be operative in the case of stainless steel since the loops are interstitial instead of vacancy in character. However, dislocations might influence loop nucleation as a result of the segregation of impurities in the vicinity of the dislocation. Segregation of large atoms to the tension side of a dislocation and small atoms to the compression side was initially proposed by Cottrell and Bilby (77). Local variations in composition might reduce the stacking fault energy, making nucleation easier in such regions. Stiegler and Bloom (53) have reported that the loop distribution near grain boundaries in type 304 stainless steel was dependent upon the irradiation temperature. A specimen irradiated at 372°C to 0.8×10^{22} neutrons/cm² ($E > 0.1$ MeV) had a grain boundary zone between 750 and 1500 Å wide which was denuded of the loop structure whereas heavy loop formation occurred immediately adjacent to the boundary. For irradiation at 472°C the denuded zone was not observed and loops formed up to a

grain boundary. Examination of the grain boundaries revealed that at 372°C no grain boundary precipitate was visible, whereas at 472°C precipitates about 1000 Å in diameter were present.

It thus appears that solute or impurity atoms can play a role in interstitial loop nucleation. For stainless steel carbon is probably the responsible element. In the case of specimens irradiated at 372°C, carbon could be segregated to the boundary, giving a locally high concentration at the boundary, a zone depleted in carbon immediately adjacent to the boundary, and the nominal concentration at regions still further removed from the boundary. Similarly in specimens containing dislocations it is likely that carbon had segregated to the dislocations. In both cases loop formation was enhanced in regions containing excess carbon and in the case of grain boundaries, loop formation was depressed in the zone depleted of carbon. In contrast, when carbon segregates to the boundary and forms carbide precipitates, such as at 472°C, loop formation is not affected.

Also observed at an irradiation temperature of 460–470°C were small rod-shaped precipitates on dislocations which were present in the material prior to irradiation (Figure 23, page 74). These precipitates were quite uniformly spaced along the dislocation and nearly always occurred on the same side of the dislocation line. Similar structures have been observed by Beckitt and Clark (72) in an austenitic stainless steel which had been solution treated and aged for short periods of time at 700°C. The precipitates were about the same size and were uniformly spaced along the dislocations. Although not specifically

mentioned by Beckitt and Clark, some of their photomicrographs also suggest that the precipitates initially form on one side of the dislocation. These investigators identified the precipitates as $M_{23}C_6$ type carbides. On the basis of the similar morphologies one may conclude that the precipitates observed in this investigation may also be $M_{23}C_6$ type carbides. The occurrence of the precipitates on only one side of a dislocation may be a result of the stress field of the dislocation. There was some evidence that the growth of the precipitates was influenced by the fast neutron flux and/or fluence. For example, the precipitates were significantly larger in a specimen irradiated at a higher flux to a higher fluence but at the same temperature.

As the fast neutron fluence was increased for irradiation temperatures between 370 and 470°C the inhomogeneities in dislocation loop distributions, irregularly shaped loop structures and dislocation line-precipitate structures became progressively more difficult to observe due to the increase in density and size of the more regular, faulted, interstitial dislocation loops.

There was a marked change in dislocation structure for specimens irradiated at 570–630°C as compared to 470°C. The faulted dislocation loops present at the lower temperature were replaced by a network of dislocation lines and a few unfaulted dislocation loops (Figure 29, page 85). The possible reasons for this change in dislocation structure with increasing irradiation temperature can be discussed in terms of the energies associated with faulted and perfect dislocation loops with Burgers' vectors of $a/3 \langle 111 \rangle$ and $a/2 \langle 110 \rangle$, respectively. These

energies were given in Equations 11 and 12 which represent the elastic strain energy of the dislocation plus the energy associated with the stacking fault, if one is present. Using these equations, Friedel (78) shows that in metals having stacking fault energies γ such that

$$\gamma > \frac{Gb}{30} , \quad (33)$$

perfect or unfaulted loops are the lower energy configuration for all loop sizes. For metals with low stacking fault energy where Equation 38 is not fulfilled, faulted loops are the most stable for small loop sizes. However, as a faulted loop grows the energy of the stacking fault increases as the square of the loop radius, $(R_L)^2$, and the energy of the dislocation line increases as R_L . Thus, there is a loop radius such that for larger radii the perfect dislocation loop is more stable and for smaller radii the faulted loop is more stable. The loop radius at which this transition occurs is a function of the stacking fault energy.

Indirect evidence (79) obtained from a study of deformation and recrystallization textures indicates that austenitic stainless steels behave as if the stacking fault energy increases as temperature increases. If the stacking fault energy exceeds the right hand side of Equation 38 the interstitials should precipitate in perfect or unfaulted loops since this would be the lower energy configuration. Alternately, if the stacking fault energy is lower than that given by the right hand side of Equation 38, then the interstitials should initially precipitate to form faulted loops. As these faulted loops grow two factors tend to make the perfect loop the lower energy configuration. With increasing irradiation

temperature the loop concentration decreases and the loops grow to larger sizes and with increasing irradiation temperature the stacking fault energy increases thus increasing the energy of a faulted loop.

Figure 52 shows the energy of perfect dislocation loops and of faulted dislocation loops as a function of the loop radius calculated from Equations 11 and 12. In the case of faulted dislocation loops stacking fault energies of 20 ergs/cm^2 , which is a typical value for stainless steel at low temperatures (80), and a higher value of 100 ergs/cm^2 were used. For each of these stacking fault energies there is a loop radius above which the perfect loop is the more stable. This radius decreases with increasing stacking fault energy. Thus if the loops are initially faulted their growth will result in the perfect loop eventually becoming the lower energy configuration. The elimination of the stacking fault and conversion of a faulted dislocation loop to a perfect dislocation loop requires the nucleation of two Shockley partial dislocations. The dislocation reaction for the unfaulting of an $a/3 [111]$ loop can be written:

Since the strain energy of a dislocation is proportional to the square of the Burgers' vector this reaction is energetically favorable (i.e., the left side of Equation 39 is proportional to $2/3a^2$ and the right side is proportional to $1/2a^2$).

Ippohorski and Spring (81) have observed the unfaulting of interstitial Frank loops in copper. The loops were produced in the electron

Figure 52. Energy of $\frac{a}{3} \langle 111 \rangle$ and $\frac{a}{2} \langle 110 \rangle$ dislocation loops as a function of loop radius.

microscope by the electron displacement damage. No details of the unfaulting mechanism were given, however.

Development of Void Structure

Voids, ranging in size from the smallest observable in the electron microscope (approximately 50 Å diameter) to several hundred angstroms diameter were observed at irradiation temperatures between 370 and 570–600°C. In this report, the term void has been used to describe a cavity which has an internal gas pressure significantly less than that required to balance the surface tension. In contrast, a bubble is a cavity containing a gas whose pressure balances or nearly balances the surface tension.

The characteristics of the void structure were studied as a function of fast neutron fluence and irradiation temperature through observations of the void distributions within the material, changes in void shapes, and through measurement of void concentration, void size distributions, and changes in the density of the material.

Several qualitative observations concerning the irradiation produced voids had been reported previously and were confirmed during the course of this investigation. Voids did not form on grain boundaries nor in a region a few hundred angstroms wide on either side of the boundary (1,2,52,53,54). In general the void volume was orders of magnitude larger than that which could be stabilized by the irradiation produced helium (1,2,52,53,54). For example, the specimen shown in Figure 37, page 96, had a void concentration of 7.7×10^{15} voids/cm³ (see Appendix F). The mean void diameter was about 150 Å. Assuming

an ideal gas, the number of gas atoms (M_0) contained within a cavity having an equilibrium internal pressure is given by

$$M_0 = \frac{8\pi \gamma R_v^2}{3kT} \quad (40)$$

Using $R_v = 1.5 \times 10^{-6}$ cm, $\gamma = 1500$ ergs/cm², and $T = 700^\circ\text{K}$, each void would require 3×10^5 gas atoms to be at equilibrium. For the total void concentration, about 2.2×10^{21} helium atoms/cm³ would be required. The measured helium concentration for this specimen was 12.2×10^{-6} atom fraction (82) or about 10^{18} helium atoms/cm³, more than three orders of magnitude less than that required for each cavity to contain an equilibrium amount. Previously reported experiments on EBR-II driver fuel cladding (53) have shown that the voids are unstable and can be removed by postirradiation annealing at sufficiently high temperatures.

A number of results from this investigation either have not been reported previously or are in substantial disagreement with previous results.

Claudson et al. (52) and Stiegler and Bloom (53) have characterized voids in stainless steel as being uniformly distributed. In each case the conclusion was based on examination of specimens irradiated to fluences in excess of 1×10^{22} neutrons/cm² ($E > 0.1$ MeV). In this study specimens irradiated to lower fluences in the temperature range of 370-470°C contained a nonrandom, nonuniform distribution of voids. There was a strong tendency for the voids to be located on structural irregularities such as dislocations. At higher fluences (within this

temperature range), the void density was much greater and nonuniformities in the void distributions became more difficult to detect. In the specimens irradiated to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) at 570-630°C the void concentration was low and nearly all voids were associated with dislocation lines. Nonuniform void distributions have now been observed in several other irradiated materials: aluminum by Stiegler *et al.* (13), nickel by Stiegler and Bloom (46), iron by Farrell and Houston (83), vanadium by Wiffen and Stiegler (84). Nonuniform distributions have important implications concerning the mechanism of void nucleation. Classical homogeneous nucleation, nucleation in single displacement spikes and nucleation by multiple spike overlap would each lead to a random void distribution. The apparent uniform void distribution at neutron fluences exceeding approximately 1×10^{22} neutrons/cm² ($E > 0.1$ MeV) at temperatures between 370 and 470°C may be real, implying that other nucleation mechanisms become operative (i.e., mechanisms which would produce uniform distributions), or that the increased void density simply obscures the heterogeneous nature of the distribution. To the author's knowledge the homogeneity of the void distributions at high fast neutron fluences has not been established. At temperatures near 600°C, even at high fluences, the voids were always associated with structural irregularities.

Void concentration as a function of fluence for irradiation temperatures of 370-380 and 460-470°C and as a function of temperature for various fluences were illustrated in Figures 42 and 43, respectively, pages 104 and 106. In specimens irradiated to a constant fluence, the

void concentration decreased with increasing irradiation temperature. This latter result disagrees with data of Claudson et al. (52), which was reported to show that the void concentration was independent of irradiation temperature in the range 370 to 470°C. The results of Claudson et al. were not internally consistent since the density decrease varies by only a small amount between these two irradiation temperatures, yet the voids were significantly larger at the higher irradiation temperature. This requires the void concentration to be lower.

Over the range of fluences for which data were obtained, the void concentration was higher after irradiation at 370-380°C than after irradiation at 460-470°C, but was increasing with fluence at a slower rate at the lower temperature. In order for this situation to exist there must have been a transient or incubation period before significant void nucleation started. The length of this incubation period must have increased with increasing irradiation temperatures. This conclusion is supported by the fact that no damage was observed after irradiation at 524°C to 1.4×10^{22} neutrons/cm² ($E > 0.1$ MeV) but voids and loops were observed after a fluence of 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) at the higher temperature of 570-630°C.

Several specimens were examined after irradiation to approximately the same fluence but at fast neutron fluxes which were different by as much as a factor of six. Within the accuracy of the experimental determination, there was no effect of flux on the void concentration. The only evidence for an effect of the fast neutron flux upon the damage

structure was found in a comparison of a specimen irradiated in a flux of 1.9×10^{15} neutrons/cm²-sec to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV) with a specimen irradiated in a neutron flux of approximately 4×10^{13} neutrons/cm²-sec to a fluence of 5×10^{20} neutrons/cm². The specimen irradiated in the higher flux contained defect clusters but the specimen irradiated in the lower flux did not.

Early in its life a void apparently grows very rapidly, but after a relatively low neutron fluence (on the order of 5×10^{21} neutrons/cm² ($E > 0.1$ MeV)), the growth rate decreases. This was demonstrated by measurement of maximum void diameter as a function of the fast neutron fluence. These results (Figure 44, page 108) indicated that at 370-380°C voids of the maximum size (approximately 210 Å diameter) were observed after irradiation to approximately 1×10^{22} neutrons/cm² ($E > 0.1$ MeV) and that this maximum size did not change even when the neutron fluence was increased to 5.0×10^{22} neutrons/cm² ($E > 0.1$ MeV). Similar conclusions were made for an irradiation temperature of 460-470°C where the data indicated that the voids grow rapidly early in their life and that the growth rate then slows markedly. Limited data indicate that the maximum void size increases sharply with increasing irradiation temperature (Figure 45, page 110).

The conclusion that the voids grow rapidly early in their life, then almost stop growing, was supported by observations of the void shapes. Stiegler and Bloom (53) reported that the voids produced by irradiation to fluences near 1×10^{22} neutrons/cm² ($E > 0.1$ MeV) at temperature above approximately 400°C were often very irregular in

shape. At lower temperatures the voids were too small for their shape to be accurately determined. For higher fluences the voids were more regular in appearance, with the voids in a given grain often having a common shape (Figures 31 and 38, pages 88 and 97).

These observations on void shapes can be rationalized by an argument similar to that used by Stiegler et al. (85) to explain the shape of creep cavities in tungsten. Voids grow by the diffusion of vacancies into them. Early in the life of a void, the vacancies are entering the void so rapidly that surface diffusion cannot maintain the equilibrium polyhedral shape and the voids are nearly spherical. Later in the growth process experimental observation showed that the flux of vacancies into the voids decreases and surface diffusion allows the void to more closely approach its equilibrium shape.

Good agreement was obtained between the density decrease measured by immersion techniques and the density decrease calculated from measurements of the void concentration and the void size distribution curves. The fluence dependence (X) of the density decrease determined by a least square fit of the data in Figures 49 and 50, pages 118 and 119, to Equation 37 was 0.84 and 1.66 for irradiation temperatures of 370-380 and 460-470°C, respectively. The variation of the density decrease with fluence and temperature is not adequately expressed by the single equation (Equation 15) used by Claudson et al. (52).

Irradiation at 777-840°C to a fluence of 3.67×10^{22} neutrons/cm² ($E > 0.1$ MeV) did not produce damage in the form of voids and loops. Helium bubbles, formed by the precipitation of the helium produced by

(n, α) transmutation reactions were present. These bubbles were located along grain boundaries as well as in the matrix. The fact that these cavities were present on grain boundaries was evidence that they contained a gas and were not voids since voids do not form at grain boundaries.

II. DISCUSSION OF RESULTS: NUCLEATION AND GROWTH MECHANISMS

Several mechanisms of void nucleation and growth during fast neutron irradiation have been proposed. The present experimental results will be compared to the predictions of these models in an attempt to establish which mechanism or mechanisms are operative.

There is continuous production and annihilation of both vacancies and interstitials during irradiation, and as a result, the concentration of these defects exceeds the thermal equilibrium concentration at any given instant. The vacancy concentration during irradiation (C_v) is given by

$$C_v = \epsilon C_{v0} \approx \frac{\alpha \tau}{N}, \quad (41)$$

where

C_v = vacancy concentration,

C_{v0} = vacancy concentration at thermal equilibrium,

ϵ = vacancy supersaturation ratio,

α = vacancy production rate (vacancies $\text{cm}^{-3} \text{sec}^{-1}$),

τ = average vacancy lifetime (sec), and

N = lattice sites cm^{-3} .

If the vacancy supersaturation during irradiation is sufficiently large, then homogeneous nucleation of voids by random fluctuation in the size of vacancy clusters might occur.

The change in free energy (ΔG_v) when a vacancy is added to a void (containing no gas) is given by:

$$\Delta G_v = \frac{2\gamma\Omega}{R_v} - kT \ln \frac{C_v}{C_{v0}} \quad (42)$$

where

- R_v = void radius,
- Ω = atomic volume, and
- γ = surface energy.

The critical void radius, R_v^* , at which size the free energy change goes through a maximum, ($\Delta G_v = 0$), is related to the vacancy supersaturation (C_v/C_{v0}) by

$$R^* = \frac{2\gamma\Omega}{kT \ln \frac{C_v}{C_{v0}}} \quad (43)$$

If the vacancy supersaturation is sufficiently large, vacancy clusters produced in the displacement spikes will exceed the critical size and a void would be nucleated. The temperature, time and flux dependence for such spike nucleation would not be the same as for homogeneous nucleation. Spike nucleation will thus be discussed separately.

For vacancy supersaturations at which the critical void size is larger than the maximum cluster size produced in displacement spikes, homogeneous nucleation can occur. Under these conditions the nucleation rate, $\dot{I}$, as given by Turnbull and Fisher (86), will be

$$\dot{I} = K C_v \exp \frac{16\pi\sigma^3}{3 \left(kT \ln \frac{C_v}{C_{v0}} + \frac{2\gamma\Omega}{R_v^*} \right)} \exp - \frac{\Delta G_m}{kT} \quad (44)$$

where K is a constant, C_v is the vacancy concentration, the first exponential is the concentration of nuclei of the critical size (see Equation 26), and the second exponential is the vacancy mobility, with ΔG_m being the energy of vacancy motion.

It is difficult to relate the homogeneous nucleation rate to the irradiation parameters of neutron flux, irradiation time and irradiation temperature because of the complexity of the vacancy production and annihilation processes. For example, the vacancy concentration during irradiation depends on the number of vacancies produced per PKA (primary knock-on atom), the fraction of this total which are annihilated almost immediately, and the fraction which diffuse through the lattice and are annihilated by recombination, or absorption at sites such as grown in dislocations, grain boundaries, irradiation-produced dislocation loops or irradiation produced voids. Formulation of these quantities involves a large number of unknown parameters.

There are several qualitative considerations which indicate that homogeneous nucleation of voids does not predominate. In specimens

irradiated at the same temperature, to the same total fluence, but at fluxes which differed by a factor of six, no difference in void concentration was observed. Increasing the neutron flux at constant temperature should have increased C_v (54,57), and thus, both the pre-exponential and exponential parts of Equation 44 would increase. Integration of this equation over the irradiation time (t_1 and t_2 for the specimens irradiated at fluxes of ϕ_1 and ϕ_2 , respectively, where $\phi_1 = 6\phi_2$ and $\phi_1 t_1 = \phi_2 t_2$) leads to a higher predicted void concentration in the specimen irradiated at the higher flux. The data do not support this model.

Homogeneous nucleation can not explain the heterogeneous void distributions observed at low fluences nor can it explain the observation that specimens containing helium prior to irradiation had a larger concentration of smaller voids than specimens which contained no injected helium.

If the vacancy supersaturation during irradiation is sufficiently large a portion of the vacancy clusters produced in the displacement spikes are larger than the critical size and void nucleation in the displacement spike occurs. Until the void concentration begins to saturate, the nucleation rate should then be proportional to the flux and the void concentration should increase as $(\phi t)^{1.0}$. The present results show that the void concentration increases approximately as $(\phi t)^{0.8}$ and $(\phi t)^{1.4}$ at temperatures of 370-380 and 460-470°C, respectively. At 370-380°C saturation of the void concentration has probably begun and the fluence dependence is less than unity. However, at 460-470°C the fluence dependence of 1.4 is higher than that predicted by spike nucleation. If void

nucleation did occur in displacement spikes the presence of helium should have no effect on the void concentration and the void distribution should be uniform. The predictions of this model do not fit the observations of the present work.

If a single displacement spike cannot produce a vacancy cluster of the critical size, then possibly the overlapping of two or more spikes in a short period of time could. This is essentially the model proposed by Beeler (56). In this case, the nucleation rate would be proportional to $(\phi)^x$ where x is the number of spike overlaps necessary to produce a nucleus of the critical size. The void concentration after a given irradiation time would then be proportional to $\phi^x t = \phi^{x-1}(\phi t)$. If this mechanism is operative, the void concentration after a given irradiation would depend on the neutron flux in which the specimen was irradiated. Such flux dependence was not observed. As with homogeneous and single spike nucleation, the void concentrations should be independent of the presence of helium, and the voids should be homogeneously distributed contrary to the experimental observations.

Other nucleation mechanisms which have been suggested but which are not supported by the present experimental results include: (1) nucleation on sites which exist prior to irradiation; (2) the stabilization of displacement spikes by helium produced by (n,α) reactions and (3) the nucleation model proposed by Harkness and Li (54). For nucleation on pre-existing sites the void concentration would be expected to saturate early in the irradiation. However, the void concentration continuously increases for fluences between 2×10^{21} and

6×10^{22} neutrons/cm² ($E > 0.1$ MeV). The stabilization of displacement spikes by helium atoms would lead to a nucleation rate dependent on both the helium concentration (C_{He}) and the displacement spike concentration. In general, a spectrum of vacancy cluster sizes would be produced. The number of helium atoms required to stabilize a given cluster would depend upon that particular cluster size (more helium atoms the smaller the cluster). Since the helium concentration varies approximately as (ϕt) , and the concentration of displacement spikes as ϕ , the nucleation rate (if the clusters were all of the same size and if only one helium atom per cluster were required) would be approximately dependent on $\phi^2 t$ and the void concentration on $(\phi t)^2$, a higher power of the fluence than observed. In addition, this mechanism should lead to a homogeneous void distribution which, as pointed out previously is not observed at low void concentrations.

The Harkness and Li (54) model assumes that void nucleation occurs in displacement spikes but has the temperature dependence of homogeneous nucleation. The model contains a number of parameters which are adjusted by fitting the model to the total density change which occurs during irradiation due to both void nucleation and void growth. Although the model predicts density changes reasonably well over the range of temperature and fluence for which data are available, it does not predict many of the microstructural observations. This nucleation mechanism, for example, requires a homogeneous void distribution, and the nucleation should be independent of the presence of helium: neither of which are observed experimentally. The model predicts that the nucleation rate

(and thus the void concentration) should increase with increasing temperature, reach a maximum at approximately 425°C and then decrease at still higher temperatures: present results indicate that the void concentration decreases monotonically with increasing irradiation temperature. In a recent and revised version of the model (87), additional vacancy and interstitial sinks were assumed and it now predicts that at a given irradiation temperature the void concentration saturates at a fluence near 1×10^{22} neutrons/cm² and from that point on nearly all of the density change occurs as a result of void growth: the present results indicate that the void concentration continues to increase with increasing fluence and that the void growth rate decreases rapidly as a void grows. Further, this model predicts that the void concentration will be strongly dependent on the neutron flux: this was not observed in the present investigation.

On the basis of these arguments, it is concluded that none of the previously proposed void nucleation mechanisms predominate over a wide range of irradiation conditions. Many of the important experimental observations are consistent, however, with the concept that void nucleation occurs through the stabilization of void embryo by helium atoms when the embryo are below the critical size for the prevailing vacancy supersaturation given by Equation 41. The manner in which helium could influence the void nucleation process can be seen by considering the expression for the change in free energy per unit volume when a cavity of radius R_v , containing some internal gas pressure P_g , grows by an amount dR_v :

$$\frac{d\Delta G_v}{4\pi R_v^2 dR_v} = \frac{2\gamma}{R_v} - P_g - \frac{kT}{\Omega} \ln \frac{C_v}{C_{vo}} \quad (45)$$

An internal gas pressure thus decreases the free energy change per unit volume for the addition of a vacancy to a void embryo and, for a given vacancy supersaturation, the critical void size is decreased. In a simple case, this mechanism involves the nucleation and growth of helium bubbles. Because of the availability of vacancies, it is reasonable to assume that the internal gas pressure in such bubbles is balanced by the surface energy term. Once the bubble has reached a critical size, given by

$$R_v^* = \frac{2\gamma}{P_g + \frac{kT}{\Omega} \ln \frac{C_v}{C_{vo}}} \quad (46)$$

it continues to grow due to the driving force provided by the vacancy supersaturation, thus becoming essentially "void" in nature rather than a helium bubble.

If it is assumed that the vacancy supersaturation (C_v/C_{vo}) decreases as the irradiation temperature is increased (as has been shown by calculations of Greenwood et al. (57) and Harkness and Li (87)), several of the important experimental observations can be explained on the basis of helium stabilization of void embryo. At the beginning of irradiation ($t = 0$) the nucleation rate is zero since no helium is present. As irradiation proceeds, the concentration of helium increases approximately linearly with fluence. The helium atoms will migrate

through the lattice eventually colliding with other helium atoms or being trapped at structural irregularities such as dislocations. Early in the irradiation (i.e., at low fast neutron fluences) the helium concentration will be low and the probability of collision of two helium atoms or a single helium atom with a helium bubble of subcritical size will be small. Under these conditions dislocations and other structural irregularities will gather helium and enhanced diffusion along the dislocation core will assist in the formation of helium bubbles of the critical size. Thus, the first voids would form on dislocations. The tendency for voids which are located on dislocations to be elongated in the direction of the dislocation line could result if growth occurred by a mechanism proposed by Amelinckx et al. (88). The growth of a cavity located on a screw dislocation is envisioned to occur by the precipitation of vacancies along the steps produced at the ends of the cavity due to the displacement caused by the dislocation. In such a case the steps will wind into a spiral causing growth primarily along the direction of the dislocation line.

As the irradiation progresses, the concentration of helium will continue to increase. As the helium diffuses through the lattice it will collide with other single helium atoms or with helium bubbles. Given sufficient time, bubbles of the critical size for the existing vacancy supersaturation will be formed. These bubbles could then continue to grow without the addition of helium. This mechanism gives a nucleation rate-time behavior similar to that expected due to transient nucleation proposed by Turnbull (80); i.e., initially the nucleation

rate is low because no critical size nuclei exist, as critical size nuclei begin to form the nucleation rate increases rapidly to a steady state value. The transient or incubation period prior to the onset of significant nucleation would increase with increasing irradiation temperature since the lower vacancy supersaturation existing at the higher temperature would require larger critical size nuclei and thus longer times would be required for them to form.

As the irradiation temperature is increased and the vacancy supersaturation decreases nucleation becomes progressively more difficult due to the increased critical size. At 570-630°C nearly all of the critical nuclei which form are thus on dislocations or other preferred sites for helium precipitation. At still higher temperatures (770-840°C) the vacancy supersaturation is small enough that helium bubbles smaller than 100 Å diameter do not grow. The helium stabilization of small nuclei is consistent with the observation that the void concentration in specimens which contained helium prior to irradiation was much higher than that present in specimens which did not contain helium.

Saturation of the void concentration occurs when it becomes more probable for a newly created helium atom or for very small helium bubbles to reach an existing void as they diffuse through the lattice rather than meet another gas atom or bubble and form a new stable nucleus.

Claudson et al. (52) have examined several mechanisms of void growth, each dependent upon a different set of limiting processes. These mechanisms have time and neutron flux dependence which vary with the processes that control the net rate at which vacancies are absorbed into the voids.

The complicating factor in attempting to analyze the void size data in terms of void growth mechanisms is the observation that a void, once nucleated, grows very rapidly but after a relatively short period of time the growth rate decreases sharply. This phenomenon causes an apparent maximum or limiting void size which is dependent primarily on the irradiation temperature. The growth rate as a function of time at low fluences cannot be determined from the present experimental data and the growth mechanism cannot be established.

In pure metals the occurrence of a maximum or limiting void size is not observed. Packan (47) and Farrell and King (90) have examined high purity aluminum in which voids are observed at fluences as low as 10^{19} neutrons/cm² ($E > 0.1$ MeV). Stiegler (70) and Bloom (46) have examined nickel irradiated at fluences of 1.4×10^{20} and 1×10^{22} neutrons/cm² ($E > 0.1$ MeV) at a temperature of approximately 475°C. The maximum void size for these two fluences was 225 and 1500 Å respectively. Thus, in nickel the voids continue to grow, eventually reaching sizes much larger than those observed in stainless steel irradiated at the same temperature or same fraction of T_m . In addition, the void growth rate in nickel corresponds to that expected from the diffusion-controlled precipitation of vacancies from a supersaturated solution:

$$R_v = (2D_v C_v)^{1/2} (t - t_0)^{1/2} \quad (47)$$

where $(t - t_0)$ is the time the void has had to grow since nucleation.

It is possible that a similar growth process occurs in stainless steel early in the life of a void. The decreased growth rate appears to be

peculiar to stainless steel; or perhaps to alloys, since it is not observed in pure metals. The decreased growth rate does not appear to be due to a decrease in the vacancy supersaturation since void nucleation and growth of voids to the maximum size continues.

Stieglar et al. (91) have suggested that the decreased void growth rate may be caused by the formation of a shell of material around a void in which the activation energy for vacancy motion is increased above that of the homogeneous alloy. Since a void grows by the net flow of vacancies toward the void, atoms must move in the opposite direction. In an alloy, the region around the void will become depleted of those components which have the highest diffusivities. This depletion forms a shell of material in which the vacancy diffusivity is lower, and for a given vacancy supersaturation the void growth rate decreases. The concept of solute segregation in vacancy gradients has been discussed by Anthony (92). For a two component alloy (solute B in solvent A), in which the diffusivity of solute B is lower than that of solvent A, solute enrichment around vacancy sinks will occur due to the flux of vacancies into the sink. Kuczynski et al. (93) have detected this type of solute segregation in the initial stages of two-wire sintering of homogeneous alloys of Cu-In and Cu-Ag.

In a complex alloy such as stainless steel segregation of those elements having lower diffusivities in the regions around voids would be expected. Thus as a void grows a shell having a low vacancy diffusivity will form around the void and the growth rate will decrease.

In a pure metal such as aluminum or nickel no solute is present and such segregation cannot occur. Growth of voids in pure metals would thus continue, being limited only by other rate controlling processes.

CHAPTER VII

CONCLUSIONS

The nature of neutron irradiation damage in type 304 stainless steel has been deduced from a study of microstructure and density changes in specimens irradiated in the temperature range 370-800°C to neutron fluences of 1×10^{18} to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV).

The major experimental observations were:

1. Defect clusters, which appear as small black dots when observed by transmission electron microscopy, are present in specimens irradiated to 1.4×10^{20} neutrons/cm² ($E > 0.1$ MeV). The concentration of these clusters decreased in specimens irradiated at progressively higher temperatures in the range 370 to 524°C.
2. Specimens irradiated in the temperature range 370 to 470°C and to neutron fluences in the range 2×10^{21} to 5×10^{22} neutrons/cm² ($E > 0.1$ MeV) contained voids and faulted interstitial dislocation loops.
3. After irradiation at 570-630°C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) the damage structure consisted of a dislocation network, a few unfaulted dislocation loops and voids.
4. The only damage observed after irradiation at 770-840°C to 3.7×10^{22} neutrons/cm² ($E > 0.1$ MeV) was helium bubbles which were present both at grain boundaries and within the matrix.
5. After irradiation to lower fluences in the temperature range 370-470°C (i.e., $> 1 \times 10^{22}$ neutrons/cm²) or to 3.7×10^{22} neutrons/cm² at 570-630°C the damage was nonhomogeneous.

6. For specimens irradiated to a constant neutron fluence the void concentration decreased monotonically with increasing irradiation temperature in the range 370 to 630°C.

7. Measurement of the maximum void diameter as a function of fluence (at constant irradiation temperature) showed that a given void grows rapidly early in its life (i.e., at small void sizes). A short time after its formation the growth rate decreases sharply.

8. The microstructures of specimens which contained cyclotron injected helium prior to their irradiation showed helium to have a pronounced influence on void formation.

These experimental observations lead to the following major conclusions:

1. Void nucleation occurs by the stabilization of nuclei by the helium produced by (n, α) reactions.

2. The change in dislocation structure with increasing irradiation temperature (between 470 and 630°C) is thought to be a result of the increase in stacking fault energy with increasing temperature.

3. The decreased void growth rate can be caused by the buildup of a shell around the void within which the vacancy diffusivity is lower than in a homogeneous alloy of the same average composition.

4. The density change, caused by the buildup of voids, is closely related to the void nucleation rate and has a fluence dependency which is temperature dependent.

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APPENDIX A

DESCRIPTION OF EXPERIMENTAL BREEDER REACTOR-II

The Experimental Breeder Reactor-II (EBR-II) is an unmoderated, sodium cooled reactor with a full power design rating of 62.5 Mw (Th). The reactor assembly consists of 637 subassemblies spaced on a triangular pitch of 2.320 in. The present nominal core loading consists of 77 (total) enriched-uranium driver and experimental irradiation subassemblies, two safety rods, and 12 control rod subassemblies. The inner blanket contains 36 natural uranium and experimental subassemblies and the outer blanket contains 510 natural uranium subassemblies. A typical loading diagram for the eight inner rows of the reactor (the reactor core consists of the inner six rows) is shown in Figure 53. All of the materials discussed in this report were irradiated in rows 2, 3, or 4 of the reactor core. Flux and fluence calculations were based primarily on the dosimetry and spectrum calculations of Kamphouse et al. (68), and on information taken from the Guide for Irradiation Experiments in EBR-II (94).

The experimentally determined value of the neutron flux at the Row 2 midplane is 2.1×10^{15} neutrons/cm² (total) (68). Using this value of flux, and the dosimetry results and spectrum calculations of Kamphouse et al., the neutron flux as a function of axial distance from the midplane for Row 2 was obtained as shown in Figure 54. This graph was used to calculate the fluences received by specimens irradiated in Subassembly X-0-34. For the EBR-II driver fuel cladding (driver fuel element C-179-8) and the safety rod thimble (safety rod thimble 3-D-1

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Figure 53. Typical loading diagram for Rows 1 through 8 of the EBR-II.

ORNL-DWG 70-3817

Figure 54. Neutron flux as a function of distance from the reactor midplane in Row 2 of the EBR-II.

flat C) the fluence at the reactor midplane was supplied by Argonne National Laboratory (62,95) and the distribution of the neutron fluence as a function of axial distance from the midplane was assumed to be the same as shown in Figure 54.

The neutron fluences for the shroud tube which was irradiated in Subassembly XG05, Row 4, were calculated by Moteff (96) and were shown in Figure 13, page 49.

APPENDIX B

MEASUREMENT OF VOID CONCENTRATION

The determination of void concentration was accomplished by measuring the foil thickness by stereomicroscopy and then counting the number of voids in the same area of the photomicrograph. The void concentration, ρ_v , is then given by:

$$\rho_v = \frac{N_v M^3}{At} \quad (48)$$

where N_v is the number of voids counted in area A, t is the thickness of the foil as determined from the stereomicrographs, and M is the magnification. The determination of void concentration is thus subject to the errors involved in measuring t and M.

The accuracy of this determination was estimated by measuring the void concentration in two different areas of one foil and in one area of a second foil. These foils were both removed from the same axial position of the EBR-II shroud tube and thus composition and irradiation conditions were essentially identical. The foil thickness was determined at a point in the photomicrograph and the number of voids in 25 cm² areas near this thickness measurement was counted.

The results are listed in Table VII. It is apparent that the variation in void concentration within the same grain is small as can be seen from the sample standard deviations. A larger variation in void concentration was observed from one sample to another. The source of

TABLE VII
VOID CONCENTRATION DATA FOR FOILS 1 AND 2 OF IRRADIATED SPECIMEN S-3

Sample Number	Foil Thickness A	Number of Voids in 25 cm ²	Void Concentration Voids/cm ³ ρ_v	Mean Void Concentration $\bar{\rho}_v$	Sample Standard Deviation
S-3-1-A	900	174	9.78×10^{15}	9.53×10^{15}	0.19×10^{15}
		165	9.28×10^{15}		
		171	9.62×10^{15}		
		168	9.45×10^{15}		
S-3-1-B	1250	165	6.68×10^{15}	6.60×10^{15}	0.16×10^{15}
		170	6.69×10^{15}		
		158	6.43×10^{15}		
S-3-2-A	850	116	6.91×10^{15}	6.95×10^{15}	0.12×10^{15}
		118	7.03×10^{15}		
		117	6.97×10^{15}		
		113	6.73×10^{15}		
		119	7.09×10^{15}		

this variation does not appear to be the foil itself since the largest difference in void concentration was observed in two different areas of the same foil (i.e., sample 5-3-1-A and 5-3-1-B). Measurement of relative void concentrations in two different grains visible on the same photomicrograph exhibited variations of approximately the same magnitude as those measured within a given sample as listed in Table VII. The variation in measured void concentration thus appears to be due primarily to errors associated with determination of the foil thickness and magnification.

The mean void concentration for these three samples was 7.69×10^{15} voids/cm³. The standard deviation of the measurement was 1.3×10^{15} voids/cm³ (approximately 16% of the mean value).