The effect of carbon on void formation in neutron-irradiated nickel

Sigurd Martin Sorensen Jr.
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The effect of carbon on void formation in neutron-irradiated nickel

by

Sigurd Martin Sorensen, Jr.

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INTRODUCTION

One of the basic processes of radiation damage by neutrons and energetic particles in crystalline solids is the displacement of atoms from their lattice sites, thus creating equal numbers of vacancies and interstitials initially. The 1966 discovery (1) of three-dimensional vacancy aggregates, or voids, in stainless steel after irradiation at elevated temperatures in the Dounreay Fast Reactor, however, came as a complete surprise as well as a shock. Neither had the phenomenon been predicted, nor would it be appreciated in the development of breeder reactor technology. Following the original observations on stainless steel, void formation has been shown in numerous pure metals, with the first report being made by Mastel and Brimhall (2) on neutron-irradiated nickel. It soon became apparent that void formation was a common phenomenon in most metals and alloys irradiated in the temperature range 0.30 to 0.55 $T_m$, where $T_m$ is the absolute melting temperature of the material, and the associated swelling poses a serious materials problem in the design of fast breeder reactors.

Many studies have been devoted to a basic understanding of the phenomenon, and others to the development of effective methods for the elimination or reduction of swelling in irradiated metals. Consequently, the addition of certain substitutional solutes has been found to depress swelling in pure
metals. The alloying of nickel with Fe and other elements (3-8) are cases in point. However, the effect of interstitial solutes on void formation is much more complex. Leitnaker et al. (9) reported that the presence of small quantities of carbon and nitrogen and possibly silicon reduced the swelling in neutron-irradiated Type 316 stainless steel by more than an order of magnitude over high purity material. It was subsequently concluded (10) that the swelling resistance of commercial stainless steel is improved by interstitial solutes. On the other hand, Wiffen (11) revealed that the void density and swelling increased with an increase in interstitial impurity content (carbon, nitrogen and oxygen) in neutron-irradiated vanadium. It should be noted in the latter study that gaseous impurities tend to stabilize vacancy clusters, thereby promoting void nucleation (12).

The effect of carbon alone on void formation is also highly controversial. Bramman et al. (13,14) disclosed that increasing the carbon content from 0.02 to 0.05% in M316 stainless steel increased the swelling under neutron irradiation by virtue of the formation of \( M_{23}C_6 \) precipitates. Garr et al. (15) also detected that the swelling increased in Type 316 stainless steel with the extent of carbide precipitation prior to irradiation, implying that carbon in solution could impede void formation. However, Makin and Walters (16) found that increasing the carbon content from 0.16 to 1.0% in Type 315 stainless steel reduced the swelling under 1 MeV electron
irradiation because of a decrease in void growth rate. Furthermore, they claimed that carbon in solution increased the void density and decreased the swelling. Meanwhile, they also observed void suppression due to the formation of denuded zones around carbide precipitates. Smidt et al. (17) examined the effect of carbon on void formation in iron. After irradiation to $4.9 \times 10^{20} \, \text{n/cm}^2 \, (E>0.1 \, \text{MeV})$ at $280^\circ \text{C}$, void formation appeared to be enhanced in the $0.1 \, \text{at.\% C-alloy}$, which also featured some carbide precipitates on dislocation loops. Irradiation of the same C-alloy to $7.4 \times 10^{21} \, \text{n/cm}^2 \, (E>0.1 \, \text{MeV})$ at $596^\circ \text{C}$, however induced large dendrite-like defects, probably voids, nonuniformly distributed in association with precipitates, presumably carbides. The complex shape and nonuniform distribution of the dendritic voids made any meaningful evaluation and comparison of the swelling impossible. Moreover, the solubility limit for carbon in iron is only about $0.025 \, \text{at.\%}$ at $600^\circ \text{C}$ (18), so again the role of carbon was clouded by the appearance of carbide precipitates.

It is easily seen from the existing information that carbon could significantly affect void formation, but generalization on the role of carbon in void formation would be impossible. For this reason it was decided to undertake a crucial study on the effect of carbon on void formation. By crucial is meant the selection of a simple metallic system of high purity as the base material and a close control of the
amount and distribution of carbon in the matrix. Nickel was chosen as the base metal for several reasons. First, nickel requires the lowest neutron fluence of any metal or alloy to produce voids. Harbottle and Dickerson (19) reported that at 400°C the critical fluence for void formation in nickel was only $4 \times 10^{17} \text{ n/cm}^2 (E>1. \text{ MeV})$. This is more than three orders of magnitude less than that for stainless steel (20), which is currently the chief structural material for cladding in the liquid-metal fast breeder reactor (LMFBR), and about two orders of magnitude less than those for body-centered cubic refractory metals (21) currently under consideration for the first wall material in the controlled thermonuclear reactor (CTR). This low critical fluence allowed the irradiation experiments to be conducted in the Ames Laboratory Research Reactor (ALRR). Second, nickel is an important constituent in stainless steel, and it has the same face-centered cubic crystal structure as the austenitic stainless steels (Types 304 and 316) being tested in the EBR-II and other LMFBR testing facilities. Third, carbon is moderately soluble in nickel. The solubility limit of graphite in nickel in the temperature range 500°-1200°C can be expressed (22) by

$$C_{\text{carbon}}^{\text{Ni}} \text{ (wt %) } = 12.4 \exp(-5160/T).$$

(1)

By knowing the amount of carbon dissolved in the nickel lattice at the absolute temperature, T, precisely, the role of carbon in void formation would not be obscured by carbide precipitation.
EXPERIMENTAL PROCEDURE

Sample Preparation

Two lots of high purity nickel were used to prepare sheet samples with five different carbon concentrations (4, 16, 27, 84, and 600 parts per million by weight) designated Ni-1, Ni-2, Ni-3, Ni-4 and Ni-5, respectively. One lot was prepared at Ames Laboratory (AL) in the form of an arc-melted finger with 84 ppm carbon. The other lot was supplied commercially in sheet form 0.005 cm thick and initially contained 27 ppm carbon. The Ni-5 samples were prepared by arc-melting 5 grams of the AL lot with 0.3 grams of high purity graphite. The resulting finger was homogenized for 24 hours at 1200°C under a helium atmosphere, and subsequently cold-rolled to a thickness of about 0.010 cm. The remainder of the AL lot was then cold-rolled to a thickness of about 0.010 cm. The Ni-1 and Ni-2 samples were prepared by decarburizing samples of Ni-4 and Ni-3 through methanation for 4 hours at 1100°C according to the reaction C(s) + 2H₂(g) → CH₄(g). Prior to irradiation all samples were annealed at 1000°C for 24 hours under a residual pressure less than 5x10⁻⁷ Torr. A complete chemical analysis of the annealed samples gave the concentrations of major impurities listed in Table 1. For an accurate determination of the carbon content, which was considered to be of vital importance in this study, combustion chromatography was used with the uncertainty indicated in the table.
## Table 1. Chemical analysis of the nickel samples in weight parts per million

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Ni-1</th>
<th>Ni-2</th>
<th>Ni-3</th>
<th>Ni-4</th>
<th>Ni-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4±1</td>
<td>16±5</td>
<td>27±6</td>
<td>84±8</td>
<td>600±10</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>19</td>
<td>13</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>N</td>
<td>ND(^a)</td>
<td>ND</td>
<td>&lt;1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>H</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>Al</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Si</td>
<td>2.4</td>
<td>0.1</td>
<td>0.1</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>S</td>
<td>21</td>
<td>15</td>
<td>15</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Ti</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>V</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe</td>
<td>60</td>
<td>30</td>
<td>30</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;10</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;1.0</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Zr</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>W</td>
<td>2.2</td>
<td>2.5</td>
<td>2.5</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\(^a\) ND indicated "None Detected".
Irradiation Experiments

Five neutron irradiation experiments were conducted on nickel sheet samples with five different carbon concentrations inside the flux converter in the central thimble of the ALRR. One experiment was conducted at 710°C, in order that a maximum amount of carbon would be in solution during irradiation. The other experiments were conducted at 500°C, which, according to Brimhall et al. (23), is the optimum temperature for swelling in neutron-irradiated nickel. The sample packages consisted of two stainless steel cans. The inner can contained the samples and was filled with high purity helium to ensure good thermal equalization during irradiation. A nichrome heating element was silver-soldered onto the outside wall of the inner can to act as an external heat source. Two chromel-alumel thermocouples were used, one near the inside wall of the inner can to control the current of the heating element, and one attached to samples to monitor the temperature. A nickel wire was included in each sample package for monitoring the fast neutron flux. Flux determinations were made from measurements of the γ-decay of Co\textsuperscript{58} induced in nickel by the Ni\textsuperscript{58}(n,p)Co\textsuperscript{58} reaction. The conditions of the five irradiation experiments are compared in Table 2.

Electron Microscopy

Disk specimens, 3 mm in diameter, were punched from the irradiated samples for examination by transmission electron
Table 2. Neutron irradiation experiments

<table>
<thead>
<tr>
<th>Irradiation experiment number</th>
<th>Irradiation temperature, °C</th>
<th>Neutron flux, n/cm²-sec (E&gt;0.1 MeV)</th>
<th>Neutron fluence, n/cm² (E&gt;0.1 MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>710 ± 15</td>
<td>2.7x10¹³</td>
<td>9.0x10¹⁹</td>
</tr>
<tr>
<td>44</td>
<td>500 ± 10</td>
<td>2.7x10¹³</td>
<td>4.0x10¹⁸</td>
</tr>
<tr>
<td>42</td>
<td>500 ± 5</td>
<td>3.3x10¹³</td>
<td>2.6x10¹⁹</td>
</tr>
<tr>
<td>40</td>
<td>500 ± 10</td>
<td>2.1x10¹³</td>
<td>5.3x10¹⁹</td>
</tr>
<tr>
<td>43</td>
<td>500 ± 10</td>
<td>2.7x10¹³</td>
<td>2.0x10²⁰</td>
</tr>
</tbody>
</table>

Microscopy (TEM). Most of the disk specimens were electrolytically thinned using an electrolyte of 10% perchloric acid, 10% ethylene glycol, and 80% ethyl alcohol under 13 V and 50 mA at 0°C. However, this procedure resulted in severe pitting in Ni-5 specimens irradiated at 500°C. The latter specimens were prepared using an electrolyte of 15% aqua regia and 85% methyl alcohol under 15 V and 25 mA at -65°C.

The electron microscopy was conducted using a 100 kV Hitachi HU-11A electron microscope equipped with a 30° tilting stage and a liquid nitrogen cold finger. To accurately determine the size and shape of voids it was important to perform the TEM observations under the "two-beam" diffraction condition. Furthermore, as Chen (24) pointed out, to unambiguously determine void shape, it was necessary to make observations exactly on (001) and (011) planes of the specimens. A Zeiss Particle Size Analyzer was used to obtain void size distribu-
tions from electron photomicrographs enlarged to a total magnification of 150,000X. The outer edge of the dark fringe surrounding the void image was taken as the best measure of true void size, although this is strictly true only for pure absorption contrast (25). The cube edge length was used to characterize void size for cubic voids, while a spherical diameter was adopted for octahedral voids.

A computer program was written to evaluate the void size distribution. The program determined the mean void size, standard deviation of the void size and the mean void volume. The mean void size was calculated on a volume-averaged basis using the expression,

\[ \bar{d} = \left( \frac{\sum f_i d_i^3}{N} \right)^{1/3}, \]  

where \( f_i \) is the number of voids in size class \( i \), \( d_i \) the midpoint of size class \( i \), and \( N \) the total number of voids counted. This volume-averaged size was 5-10% larger than the arithmetic average. The void-size standard deviation was estimated by applying the formula (26),

\[ \text{SD} = \sqrt{\frac{\sum f_i d_i^2 - \left( \frac{\sum f_i d_i}{N} \right)^2}{N(N-1)}} \]  

Depending upon void shape the mean void volume was calculated from either the relation,

\[ \bar{V}_{\text{cubic}} = \frac{\sum f_i d_i^3}{N} \]  
or
Equation 5 is derived for spherical voids, and results in about a 10% error when applied to pure octahedral voids. Because the observed octahedral voids were truncated by an estimated 5-30%, the error in using Equation 5 was somewhat reduced. In an area \( A \) having \( N_A \) voids, the void density is given by \( N_v = N_A / \tau \), where \( \tau \) is the foil thickness. To attain a representative value of \( N_v \), at least ten different areas were evaluated in each specimen. Foil thicknesses were determined by several methods. The slip trace and extinction contour methods (27) were used whenever applicable, along with the method developed by Wolff (28) for neutron irradiated foils containing voids. Foil thicknesses varied from 500 to 1500 Å. The void volume fraction, or swelling, \( \Delta V/V \), was calculated from the product \( \bar{V} \cdot N_v \).
RESULTS

Irradiation at 710°C

After neutron irradiation to a fluence of $9.0 \times 10^{19}$ n/cm$^2$ (E 0.1 MeV) at 710°C, defect clusters were observed in specimens containing carbon up to 84 wt ppm. Although the defect clusters appeared to be voids, the possibility that they could be gas bubbles should not be ruled out without critical tests for two reasons. First, 710°C is equivalent to 0.57 $T_m$, which slightly exceeds the usual temperature range for void formation. Secondly, the only previous report (29) of neutron-induced voids in nickel at temperatures above 650°C has been reinterpreted (23) as gas bubbles. For a critical identification of the defect clusters, we recalled that Brimhall and Mastel (30) had reported a complete disappearance of voids in neutron-irradiated nickel after a vacuum anneal for two hours at 800°C, whereas Kulcinski et al. (31) had confirmed the persistent appearance of gas bubbles in nickel after annealing for two hours at 1150°C. Hence we subjected the irradiated samples to a high-vacuum anneal at 1000°C for two hours, followed by the same TEM foil preparation and examination. The post-irradiation anneal was found to bring about a complete disappearance of the defect clusters. This result has thus provided conclusive evidence that the defect clusters were indeed voids, not gas bubbles. The voids were observed to be in the shape of octahedra, bounded by {111} planes and trun-
cated to a small degree by \{100\} planes. The degree of truncation increased from about 5 to 30% with increasing void size. Typical examples of void formation in the samples containing up to 84 ppm carbon are shown in Figure 1.

An extensive TEM examination of the specimens containing 600 ppm carbon failed to detect any voids. Instead, these specimens exhibited high concentrations of "black spots", few of which appeared in the specimens containing voids. Since the "black spots" were apparently formed in place of voids, it is reasonable to assume that they are aggregates of irradiation-induced defects and carbon atoms. An example of this microstructure is shown in Figure 2, along with the microstructure of an unirradiated Ni-5 specimen after aging at 710°C for 50 hours. The aging treatment produced a clean microstructure in which very few dislocations were observed, and there were no signs of graphite precipitation. The latter observation is of great importance, because it not only confirms the solubility limit of about 650 ppm for carbon in nickel at 710°C given by Equation 1, but it also demonstrates that the observed void suppression is due to the presence of carbon in solution, not to carbide precipitates.

The results obtained from quantitative analyses of the void formation parameters are listed in Table 3. The results indicate that as the carbon content is increased, the void size increases steadily, while the void density decreases. This increase in void size and decrease in void
Figure 1. TEM photomicrographs showing the suppressing effect of carbon on void formation in high-purity nickel irradiated to a fluence of $9.0 \times 10^{19}$ n/cm$^2$ (E $>$ 0.1 MeV) at 710°C.
Figure 2. Typical microstructure in (a) an unirradiated Ni-5 specimen aged at 710°C for 50 hours and (b) a Ni-5 specimen irradiated to a fluence of $9.0 \times 10^{19}$ n/cm$^2$ ($E>0.1$ MeV) at 710°C.
Table 3. Void formation data from irradiation experiment #37

\[ \Phi t = 9.0 \times 10^{19} \text{ n/cm}^2 (E > 0.1 \text{ MeV}), T_i = 710^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Carbon content, wt ppm</th>
<th>Mean void diameter (d), Å</th>
<th>Standard deviation of diameter, Å</th>
<th>Mean void volume (v), cm$^3$</th>
<th>Average void density ($N_v$), voids/cm$^3$</th>
<th>Swelling ($\Delta V/V$), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>4</td>
<td>204</td>
<td>50</td>
<td>$4.4 \times 10^{-18}$</td>
<td>$10.4 \times 10^{13}$</td>
<td>0.046</td>
</tr>
<tr>
<td>Ni-2</td>
<td>16</td>
<td>207</td>
<td>26</td>
<td>$4.6 \times 10^{-18}$</td>
<td>$8.8 \times 10^{13}$</td>
<td>0.041</td>
</tr>
<tr>
<td>Ni-3</td>
<td>27</td>
<td>215</td>
<td>32</td>
<td>$5.2 \times 10^{-18}$</td>
<td>$8.2 \times 10^{13}$</td>
<td>0.043</td>
</tr>
<tr>
<td>Ni-4</td>
<td>84</td>
<td>390</td>
<td>80</td>
<td>$31 \times 10^{-18}$</td>
<td>$0.3 \times 10^{13}$</td>
<td>0.009</td>
</tr>
<tr>
<td>Ni-5</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td>NO VOIDS OBSERVED</td>
<td></td>
</tr>
</tbody>
</table>


density is also seen qualitatively in Figure 1. The swelling also tends to decrease with increasing carbon content, and this variation is shown in Figure 3. The solid line represents a least squares fit of the data, and the dashed line is a linear extrapolation. The extrapolation implies that the critical carbon concentration needed to completely suppress void formation is about 105 ppm under the specified conditions of irradiation. Although there is no theoretical justification for a linear relationship between swelling and carbon content, the extrapolation to 105 ppm is consistent with the experimental observation that void formation was completely suppressed by a carbon content of 600 ppm. However, the general validity of an extrapolation of this nature is uncertain.

Irradiation at 500°C

Four neutron irradiation experiments were conducted at 500°C with the fluence varying from \(4.0 \times 10^{18}\) to \(2.0 \times 10^{20}\) n/cm\(^2\) (E>0.1 MeV). At all four fluences voids were observed in the specimens containing up to 84 ppm carbon. TEM photomicrographs of the observed void formation at \(2.0 \times 10^{20}\) n/cm\(^2\) are shown in Figure 4. The morphology of the voids was cubic, with very little or no truncation. In specimens containing 600 ppm carbon, however, no voids were found at any of the fluence levels. Data from the quantitative analysis of the TEM observations are listed in Tables 4-7 as a function of carbon content at each fluence. Again, it is seen that as the
Figure 3. Swelling as a function of solute carbon content in neutron-irradiated high purity nickel at 710°C.
Figure 4. Voids and other types of defects induced in irradiated nickel containing varying amounts of carbon. Irradiation fluence - $2.0 \times 10^{20} \text{ n/cm}^2$ ($E>0.1 \text{ MeV}$) and irradiation temperature - $500^\circ \text{C}$
Table 4. Void formation data from irradiation experiment #44

\[ \Phi t = 4.0 \times 10^{18} \text{n/cm}^2 \ (E > 0.1 \text{ MeV}), \ T_i = 500^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Carbon content, wt ppm</th>
<th>Mean void size (d), Å</th>
<th>Standard deviation of diameter, Å</th>
<th>Mean void volume (v), cm$^3$</th>
<th>Average void density (N$_v$), voids/cm$^3$</th>
<th>Swelling (ΔV/V), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>4</td>
<td>146</td>
<td>20</td>
<td>(3.1 \times 10^{-18})</td>
<td>(0.2 \times 10^{14})</td>
<td>0.006</td>
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<td>Ni-2</td>
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<td>24</td>
<td>(3.2 \times 10^{-18})</td>
<td>(0.15 \times 10^{14})</td>
<td>0.005</td>
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<td>Ni-3</td>
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<td>157</td>
<td>28</td>
<td>(3.9 \times 10^{-18})</td>
<td>(0.1 \times 10^{14})</td>
<td>0.004</td>
</tr>
<tr>
<td>Ni-4</td>
<td>84</td>
<td>~200</td>
<td>-</td>
<td>~8.0 \times 10^{-18}</td>
<td>~0.01 \times 10^{14}</td>
<td>~0.001</td>
</tr>
<tr>
<td>Ni-5</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td>NO VOIDS OBSERVED</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Void formation data from irradiation experiment #42

\[ \phi t = 2.6 \times 10^{19} \text{n/cm}^2 (E>0.1 \text{MeV}), T_i = 500^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Carbon content, wt ppm</th>
<th>Mean void size ((d)), Å</th>
<th>Standard deviation of diameter, Å</th>
<th>Mean void volume ((\bar{V})), (\text{cm}^3)</th>
<th>Average void density ((N_V)), voids/cm(^3)</th>
<th>Swelling ((\Delta V/V)), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>4</td>
<td>198</td>
<td>43</td>
<td>(7.8 \times 10^{-18})</td>
<td>(0.5 \times 10^{14})</td>
<td>0.04</td>
</tr>
<tr>
<td>Ni-2</td>
<td>16</td>
<td>204</td>
<td>32</td>
<td>(4 \times 10^{-18})</td>
<td>(0.4 \times 10^{14})</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni-3</td>
<td>27</td>
<td>210</td>
<td>50</td>
<td>(4 \times 10^{-18})</td>
<td>(0.3 \times 10^{14})</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni-4</td>
<td>84</td>
<td>228</td>
<td>55</td>
<td>(4 \times 10^{-18})</td>
<td>(0.2 \times 10^{14})</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni-5</td>
<td>600</td>
<td>NO VOIDS OBSERVED</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table 6. Void formation data from irradiation experiment #40
[$\phi t = 5.3 \times 10^{19} \text{n/cm}^2 (E>0.1 \text{MeV}), T_i = 500^\circ\text{C}$]

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Carbon content, wt ppm</th>
<th>Mean void size ($d$), Å</th>
<th>Standard deviation of diameter, Å</th>
<th>Mean void volume ($v$), cm$^3$</th>
<th>Average void density ($N_v$), voids/cm$^3$</th>
<th>Swelling ($\Delta V/V$), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>4</td>
<td>198</td>
<td>30</td>
<td>$7.8 \times 10^{-18}$</td>
<td>$2.5 \times 10^{14}$</td>
<td>0.19</td>
</tr>
<tr>
<td>Ni-2</td>
<td>16</td>
<td>205</td>
<td>35</td>
<td>$8.6 \times 10^{-18}$</td>
<td>$1.8 \times 10^{14}$</td>
<td>0.15</td>
</tr>
<tr>
<td>Ni-3</td>
<td>27</td>
<td>214</td>
<td>40</td>
<td>$9.7 \times 10^{-18}$</td>
<td>$1.3 \times 10^{14}$</td>
<td>0.13</td>
</tr>
<tr>
<td>Ni-4</td>
<td>84</td>
<td>247</td>
<td>43</td>
<td>$15 \times 10^{-18}$</td>
<td>$0.6 \times 10^{14}$</td>
<td>0.09</td>
</tr>
<tr>
<td>Ni-5</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7. Void formation data from irradiation experiment #43
\[ \phi = 2.0 \times 10^{20} \text{ n/cm}^2 (E > 0.1 \text{ MeV}), T_i = 500^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Carbon content, wt ppm</th>
<th>Mean void size (d), Å</th>
<th>Mean void volume ( \bar{V} ), cm(^3)</th>
<th>Average void density ( N_V ), voids/cm(^3)</th>
<th>Swelling ( \Delta V/V ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>4</td>
<td>223</td>
<td>29</td>
<td>1.1x10(^{-17})</td>
<td>3.4x10(^{14})</td>
</tr>
<tr>
<td>Ni-2</td>
<td>16</td>
<td>271</td>
<td>68</td>
<td>2.0x10(^{-17})</td>
<td>1.8x10(^{14})</td>
</tr>
<tr>
<td>Ni-3</td>
<td>27</td>
<td>292</td>
<td>69</td>
<td>2.5x10(^{-17})</td>
<td>1.5x10(^{14})</td>
</tr>
<tr>
<td>Ni-4</td>
<td>84</td>
<td>324</td>
<td>71</td>
<td>3.4x10(^{-17})</td>
<td>1.0x10(^{14})</td>
</tr>
<tr>
<td>Ni-5</td>
<td>600</td>
<td>NO VOIDS OBSERVED</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
carbon content was increased to 84 ppm, the mean void size increased, while the void density and swelling tended to decrease, and at the 600 ppm carbon content, void formation was completely suppressed. The results also reveal that at constant carbon concentrations up to 84 ppm, void size, density and swelling all increase with increasing fluence. This can be seen qualitatively in Figure 5, which contains a set of micrographs of irradiated Ni-4 specimens shown as a function of fluence at 500°C.

Although Brimhall et al. (23) showed that 500°C was the optimum temperature for swelling in neutron-irradiated nickel, it did introduce a complication in the present study. Since the solubility limit for carbon in nickel at 500°C was 157 ppm, calculated from Equation 1, three-fourths of the carbon in the Ni-5 specimens were in excess of the limit at 500°C. Indeed, nodular precipitates were observed in unirradiated Ni-5 specimens aged at 500°C for 100 hours, as shown in Figure 6. The selected-area electron-diffraction patterns of the latter specimens showed diffuse rings, indicating that the precipitates were amorphous, as expected for graphite. However, these precipitates were not present in the Ni-5 specimens after irradiation at 500°C. An example of the irradiated microstructure of a Ni-5 specimen is included in Figure 6 for comparison. The irradiated microstructure features dislocations heavily decorated with impurities, presumably excess graphite precipitating out from solution.
Figure 5. The effect of neutron fluence on the production of voids and other defects in Ni-4 samples irradiated at 500°C
Figure 6. A drastic change in the main feature of the microstructure of (a) an unirradiated Ni-5 specimen aged at 500°C for 100 hours and (b) a Ni-5 specimen irradiated to a fluence of $5.5 \times 10^{19}$ n/cm$^2$ (E>0.1 MeV) at 500°C.
DISCUSSION

The experimental results at 710°C clearly show that the presence of carbon in solution suppresses void formation in neutron-irradiated nickel. These results are in qualitative agreement with those by Stiegler et al. (10), who concluded that interstitial elements in solution are responsible for the swelling resistance of commercial stainless steel. The results are in disaccord with those of Wiffen (11), however, which imply an increase in void density and subsequently in the swelling in neutron-irradiated vanadium caused by interstitial impurities. This apparent discrepancy may be attributed in part to the fact that over two-thirds of the interstitial impurities in the vanadium specimens were gaseous. Since gaseous impurities are known to promote void nucleation, any suppressing effect due to carbon may have been overshadowed by the enhancing effect of the gaseous impurities. The discrepancy may also be ascribed to differences in crystal structure, which may play an important role in determining the interaction between radiation-induced point defects and interstitial impurity atoms.

While the results at 710°C are essential in establishing the suppressing effect on void formation of carbon in solution, the results at 500°C are of greater practical importance, because the latter temperature is the optimum temperature for maximum swelling in neutron-irradiated nickel (23). Two
schools of thought have emerged on the functional relationship between swelling and neutron fluence (32). American workers have adopted the empirical relation

$$\Delta V/V \propto (\phi t)^x,$$  \hspace{1cm} (6)

where $x$ is a fluence exponent evaluated experimentally. Figure 7 is obtained by fitting the present data at each carbon concentration to this empirical relation. The fluence exponent is seen to increase from 1.11 to 1.52, as the carbon content increases from 4 to 84 ppm. Although several theoretical attempts have been made on the physical significance of the fluence exponent (e.g. (33)), none accounts for a change in exponent with composition.

In another approach, British workers have used a linear relationship between swelling and fluence beginning after some "initial fluence":

$$\Delta V/V \propto (\phi t - \phi t_0)$$  \hspace{1cm} (7)

where the induction period $t_0$ is chosen to best fit the data and is not the same as the incubation period, which denotes the initial time for any observable radiation damage to emerge. Harbottle and Dickerson (19) applied this relation to their data for nickel after neutron irradiation at 400°C with excellent results. Their "initial fluence" of $4 \times 10^{17}$ n/cm$^2$ was interpreted as the critical fluence of void formation in nickel at 400°C. The present data obtained from irradiation at 500°C are also fitted to this linear relation, and different initial
Figure 7. Experimental data for swelling ($\Delta V/V$) in nickel are plotted against neutron fluence at different carbon concentrations. Irradiation temperature: 500°C
fluences were obtained at each carbon concentration, as shown in Figure 8. Following the interpretation by Harbottle and Dickerson, the deduced "initial fluence" values may also be taken as critical fluences for void formation in nickel at 500°C. It is significant to note that the deduced values increased from $1.3 \times 10^{18}$ to $3.4 \times 10^{18}$ n/cm$^2$, as the carbon content was increased from 4 to 84 ppm. Moreover, these deduced values fit a semi-logarithmic relation with carbon content, as shown in Figure 9. A linear extrapolation to 600 ppm carbon gives a critical fluence of $1.3 \times 10^{21}$ n/cm$^2$, which is consistent with the observation that void formation was completely suppressed in Ni-5 specimens irradiated at 500°C to fluences up to $2.0 \times 10^{20}$ n/cm$^2$. Table 8 lists all deduced and extrapolated values of the critical fluence for void formation in Ni-C alloys.

Table 8. Values deduced for the critical fluence required for void formation in high purity nickel under neutron irradiation at 500°C as a function of carbon content

<table>
<thead>
<tr>
<th>Carbon content, wt ppm</th>
<th>Critical neutron fluence, n/cm$^2$ (E&gt;0.1 MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$1.3 \times 10^{18}$</td>
</tr>
<tr>
<td>16</td>
<td>$1.6 \times 10^{18}$</td>
</tr>
<tr>
<td>27</td>
<td>$2.0 \times 10^{18}$</td>
</tr>
<tr>
<td>84</td>
<td>$3.4 \times 10^{18}$</td>
</tr>
<tr>
<td>600</td>
<td>$1.3 \times 10^{21}$ (extrapolated)</td>
</tr>
</tbody>
</table>
Fig. 8. Alternatively, the swelling data delineated in Figure 7 may be analyzed as a function of an adjusted neutron fluence, $\phi_t - \phi_0$, where $\phi_0$ may be viewed as the critical fluence required for void formation.
Figure 9. The deduced values of critical fluence $\phi t_0$ display a linear relationship with the concentration of carbon dispersed in the matrix of nickel.
The magnitude of the critical fluence is, of course, affected by other variables besides composition. Since dislocations act as preferential sinks for interstitials (34), thus creating the vacancy supersaturation necessary for void formation, the density and distribution of dislocations are expected to affect the critical fluence. Indeed, recent electron irradiation experiments conducted on pure nickel indicate that a minimum dislocation density is required for void formation (35,36), while increasing the dislocation density above certain levels by cold work tends to reduce void formation (37). Other studies indicate that the irradiation temperature has a pronounced effect on the critical fluence. For example, Brimhall et al. (23) found the critical fluence to lie between 2 and $7 \times 10^{18}$ n/cm$^2$ at 280°C. At 370°C, Stiegler and Bloom (38) observed small voids, all less than 60 Å in diameter, after irradiation to a fluence of $1.1 \times 10^{18}$ n/cm$^2$. Hence the critical fluence may be set to be below $10^{18}$ n/cm$^2$. On the basis of the deduced values for $\Theta t_0$ in the present study and that obtained by Harbottle and Dickerson (19) at 400°C, it is reasonable to conclude that the critical fluence for void formation in high purity nickel goes through a minimum near 400°C and increases as the irradiation temperature is either increased or decreased. This variation in critical fluence with irradiation temperature is most likely due to the exponential increase in vacancy mobil-
ity with temperature. At low temperatures vacancies migrate slowly, and the recombination of vacancies with fast-moving interstitials keeps vacancy supersaturation low. As vacancy mobility increases, recombination decreases, and void formation occurs more readily, until the temperature becomes high enough that the increase in the equilibrium thermal vacancy concentration reduces vacancy supersaturation and delays void formation.

In principle, void formation may be suppressed through the reduction of vacancy supersaturation by inhibiting either the nucleation and/or growth of the voids. The experimental results obtained in this investigation furnish evidence to conclude that the effect of carbon is mainly to suppress void nucleation, not void growth. This important conclusion is drawn for the following reasons. First, the increase in critical fluence with increasing carbon content suggests that carbon retarded void nucleation. Second, the size distribution of the voids induced at the lowest fluence did not extend down to the limit of visibility implying that once voids were nucleated, they grew rapidly. Third, and most important, while the void density decreased drastically as the carbon content was increased, the mean void size actually underwent a slight increase. This increase in void size was probably a consequence of the reduction in void nucleation, although Beeler (39) cited a possible enhancement of void growth by
virtue of multiple carbon atom attachment to split-interstitials in face-centered cubic metals. The present void size data was examined to see whether carbon had any discernible effect on void growth. Heald and Speight (40) recently derived an expression for void size as a function of dose and obtained

$$d^2 \propto (\phi - \phi_0).$$  \hspace{1cm} (8)\

The present results at 500°C are plotted in Figure 10 using this relation. The lines represent a least-squares fit of the data at each carbon concentration. The data fit the relation better as the carbon content was increased, in agreement with the conclusion that solute carbon did not inhibit void growth.

Smidt et al. (17) examined the suppressing effect of various substitutional solutes on void formation in irradiated iron and concluded that their effect was also mainly to reduce void nucleation. In another recent study, Makin and Walters (16) analyzed the swelling in Type 316 stainless steel under 1 MeV electron irradiation in the temperature range 500-600°C as a function of carbon content. At 600°C the swelling in the 1% carbon steel was low, and they, too, arrived at the conclusion that the low swelling was a consequence of the effect of carbon on void nucleation, rather than on void growth. Here, however, caution should be exercised in assessing the effect of carbon on void formation in Type 316 stainless steel, because the addition of carbon essentially results in carbide
Figure 10. Using the functional relation derived by Heald and Speight (40), the mean void size data obtained at 500°C are plotted as a function of neutron fluence above the critical fluence.
precipitation, instead of simple dissolution. Since denuded zones were observed around carbide precipitates, the effect on void formation originally attributed to carbon could be more accurately related to the carbide precipitates. Therefore, despite the striking similarities, the suppressing mechanism proposed to explain the present results need not be identical to that for the stainless steel investigated by Makin and Walters (16).

It is now recognized that several types of traps are available for vacancies in suppressing void formation in irradiated metals and alloys. Grain boundaries (41), dislocations (42), precipitates (43) and substitutional solute atoms (17) have all been shown to be effective traps in different materials. Since the present investigation has clearly shown that the suppression and eventual elimination of voids in neutron-irradiated nickel was a result of the dissolution of carbon in the lattice, the observed suppression must be due to a trapping mechanism associated with the carbon atoms. There are several ways in which carbon atoms might affect void formation. Norris (44) recently proposed a mechanism in which impurity atmospheres modify the stress field of dislocations, which leads to a reduction in their preferential bias for interstitials. This type of dislocation poisoning is effective if the impurity atoms remain in solution during irradiation, and are surrounded by large strains. In the present study, the carbon atoms did remain in solution during irradiation. In
fact at 500°C, irradiation aided the dissolution of carbon in the Ni-5 specimens, thus extending the solubility limit for carbon well beyond the equilibrium value of 157 ppm. An irradiation enhancement of precipitate dissolution in nickel alloys had been previously reported by Nelson et al. (45). However, since the most important interaction between a point defect and a dislocation is elastic in nature and controlled by the size effect (46), it is doubtful that interstitial carbon atoms could generate enough strain in the nickel lattice to make the dislocation poisoning mechanism effective.

A trapping mechanism based on point defects is most likely responsible for the void suppression in the present case. Although there is no direct information on the binding energies of carbon atoms with other lattice defects in nickel, Beeler (47) has performed computer simulation studies on various configurations of point defect-carbon atom complexes. He found positive binding energies for monovacancy-, divacancy-, and split interstitial-carbon atom complexes with values of 0.30, 0.86 and 0.46 eV, respectively. These values suggest that carbon atoms may be effective in trapping vacancies as well as interstitials. Koehler (48) has proposed an interstitial trapping mechanism for undersized substitutional impurity atoms. His mechanism emphasized the enhancement of recombination and the ultimate suppression of void formation through a reduction in the rate of void growth. On the other hand, Smidt and Sprague (49) cited a different trapping
mechanism whereby vacancies are attracted by oversized substitutional solute atoms, giving rise to a suppression of void formation via the reduction in void nucleation. Although the latter workers' arguments in support of their mechanism are debatable, they have subsequently added (17) that interstitial impurity trapping would also be important, if the binding energies of interstitial-impurity atom complexes are sufficiently large.

Assuming that the binding energies obtained by Beeler (47) for defect complexes in nickel are reasonable, the large binding energy between a divacancy and a carbon atom implies that it is the most stable defect complex of the three considered, and that each carbon atom would be effective in trapping at least two vacancies. Moreover, while the computer calculations considered only elastic interactions in determining defect complex binding energies, a simple consideration of electrostatic interactions also favors the formation of vacancy-carbon atom complexes. In a metallic solid, such as nickel, vacancies and interstitials are considered to be centers of negative and positive charges, respectively. Therefore, it is the effective charge of the carbon atoms in solution that determines which type of defect complex would be electrostatically more favorable. Electrotransport work (50) on a 0.2 wt % carbon-nickel alloy over the temperature range 600°-1400°C indicates that carbon atoms have an effective charge of +1.8. Therefore, from an electrostatic considera-
tion the formation of vacancy-carbon atom complexes is favored over interstitial-carbon atom complexes. The formation of vacancy-carbon atom complexes may have two plausible effects on the irradiation-induced defect structure of the nickel lattice. One possibility is to enhance the recombination of trapped vacancies with moving interstitials. The enhancement of recombination would reduce vacancy supersaturation, which, in turn, would reduce the rate of void nucleation, as seen in the following argument. From the extensive theoretical studies by Russell (51) on the homogeneous nucleation of voids, it is reasonable to express the rate of void nucleation as

$$\dot{N} \sim \exp(-\Delta G_{nC}/kT),$$

where the free energy for the formation of critical size void nuclei, $\Delta G_{nC}$, is given by

$$\Delta G_{nC} \propto \frac{\gamma^3\Omega^2}{[kT \ln\left(\frac{C_v}{C_v^0}\right)^2]}.$$

In the last expression $\gamma$ is the surface energy, $\Omega$ the atomic volume, $C_v$ the irradiation-induced free vacancy concentration and $C_v^0$ the equilibrium thermal vacancy concentration. A decrease in $C_v$ due to recombination would cause an increase in $\Delta G_{nC}$, thus leading to a rapid decrease in $\dot{N}$. It is also possible that trapped vacancy complexes might act as nuclei for the formation of "black spot" defects by attracting more
vacancies, interstitials and carbon atoms. The "black spots" shown in Figure 2 may be evidence of the onset of this second possibility.

The unique feature of the present trapping mechanism is the dynamic behavior of the carbon atoms in solution. It is this dynamic nature, which makes vacancy trapping possible. The jump frequency of any point defect can be calculated from the general expression

$$
\Gamma_i = \Gamma_i^0 \exp(-Q_i^M/kT)
$$

where $\Gamma_i$ is the jump frequency of the defect, $\Gamma_i^0$ the pre-exponential frequency factor and $Q_i^M$ the activation energy for the migration of the mobile defect. For interstitials $\Gamma_I^0 = Z_I \nu_I$, where $Z_I$ is the number of nearest interstitial sites (presumably 12 octahedral sites) and $\nu_I$ is the interstitial vibration frequency ($10^{13} \text{s}^{-1}$). For monovacancies $\Gamma_v^0 = Z_v$, with $Z$ the lattice coordination number (12) and $\nu$ the lattice vibration frequency ($1.1 \times 10^{13} \text{s}^{-1}$), and for divacancies $\Gamma_{v_2}^0 = Z_v \nu_{v_2}/2$, where $\nu_{v_2}$ is the divacancy vibration frequency ($3.3 \times 10^{12} \text{s}^{-1}$). For solute carbon atoms $\Gamma_c^0 = Z_I D_o^1/a_o^2$, where $D_o^1$ is the frequency factor for carbon diffusion ($2.48 \text{ cm}^2/\text{s}$) and $a_o$ is the lattice parameter (3.526 Å). Jump frequencies were calculated at 500°C and 710°C for interstitials, monovacancies, divacancies and solute carbon atoms in nickel, using migration activation energies of 0.21 eV (52), 1.38 eV (53), 0.82 eV (53) and 1.74 eV (54), respectively, and the
values are listed in Table 9.

Table 9. The jump frequency of point defects in nickel

<table>
<thead>
<tr>
<th>Migrating defect</th>
<th>Jump frequency at 500°C, jumps/second</th>
<th>Jump frequency at 710°C, jumps/second</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials, $\Gamma_I$</td>
<td>$5.1 \times 10^{12}$</td>
<td>$1.0 \times 10^{13}$</td>
</tr>
<tr>
<td>Monovacancies, $\Gamma_V$</td>
<td>$1.3 \times 10^5$</td>
<td>$1.1 \times 10^7$</td>
</tr>
<tr>
<td>Divacancies, $\Gamma_{V2}$</td>
<td>$8.9 \times 10^7$</td>
<td>$1.2 \times 10^9$</td>
</tr>
<tr>
<td>Solute carbon atoms, $\Gamma_C$</td>
<td>$1.1 \times 10^5$</td>
<td>$2.9 \times 10^7$</td>
</tr>
</tbody>
</table>

These calculations reveal that interstitials are the most mobile species, and without the appreciable mobility of the carbon atoms, vacancy trapping would be unlikely. This is in contrast to previously reported "static" trapping mechanisms involving substitutional solute atoms (17), precipitates (43), dislocations (42) or grain boundaries (41), which remain essentially stationary at $T_i \sim (0.3-0.6)T_m$. In the latter cases the mobility of the interstitials is so much larger than that of the vacancies that interstitial trapping would dominate in the absence of mobile traps, such as solute carbon atoms. It is therefore concluded that the reduction in void swelling observed in this investigation is most likely due to a trapping mechanism in which solute carbon atoms are capable of effectively trapping vacancies and suppressing void formation via the inhibition of void nucleation.
The variation in void morphology found in this investigation was not entirely expected. The octahedral voids, which were observed after irradiation to a fluence of $9.0 \times 10^{19}$ n/cm$^2$ at 710°C, exhibited a small degree of $\{100\}$ truncation, increasing from about 5 to 30% with increasing void size and carbon content. Irradiation at 500°C, however, produced cubic voids with little or no truncation over the entire fluence range of $4.0 \times 10^{18}$ to $2.0 \times 10^{20}$ n/cm$^2$. All previous work citing void shape in neutron-irradiated nickel at fluences less than $10^{19}$ n/cm$^2$ reported cubic voids (19,38), and the present results are in agreement with these earlier findings. Previous information on the shape of voids induced in nickel at fluences greater than $10^{19}$ n/cm$^2$ was less consistent. Octahedral or truncated octahedral voids were usually reported (2,19,30, 31,55-57), with Brimhall and Mastel (29) finding octahedral voids over the temperature range 380° to 750°C. However, Stiegler and Bloom (38) observed a change in void shape with irradiation temperature, from cubic at low temperatures (385°-410°C), to nearly equiaxed polyhedral at intermediate temperatures (440°-470°C), and finally to an elongated shape along $<110>$ directions at 525°C. Harbottle (58) also found cubic voids after neutron irradiation to a fluence of $1.1 \times 10^{20}$ n/cm$^2$ at 400°C, while octahedral voids were observed after irradiation to $5.1 \times 10^{19}$ n/cm$^2$ at 450°C. However, his study was conducted in a 1 MV electron microscope, and during subsequent
electron irradiation at 450°C, the octahedral voids underwent progressive {100} truncation until their shapes became purely cubic. The change in shape was seen to coincide with the onset of linear void growth during the electron irradiation procedure. Moreover, the most common void morphology observed in electron irradiated nickel has been cubic (59), while predominantly truncated voids have been found in ion-bombarded nickel.

In the present study, where octahedral voids were observed after irradiation at 710°C, the increase in {100} truncation with increasing void size and increasing carbon content might be attributed to a preferential adsorption of carbon atoms on 100 void surfaces. This is supported by recent studies (60-62) on the surface structure of nickel, where carbon atoms have a tendency to diffuse from the interior of bulk crystals toward free {100} surfaces. From the standpoint of the thermodynamic criterion that $\gamma dA = \text{minimum}$ for the equilibrium shape of voids, the emergence of purely octahedral voids necessitates the ratio $\gamma_{(111)}/\gamma_{(100)} = 1/\sqrt{3} = 0.577$, which is unlikely to be met. Nor is it likely that impurity adsorption would raise the $\gamma_{(111)}/\gamma_{(100)}$ ratio to exceed unity sufficiently to permit the formation of untruncated cubic voids. Therefore, the appearance of untruncated octahedral and cubic voids in nickel must represent a non-equilibrium condition. Little is known theoretically on the
nonequilibrium formation and growth of voids. Nelson et al. (63) have suggested that void shape is affected by elastic strain fields in the lattice. Strain fields are often found in association with voids (64). It is possible that the observed variation in void shape with irradiation temperature in this investigation is due to the effect of temperature on lattice strains.

The results obtained in this investigation may be of great practical importance when applied to other material systems, such as vanadium, tantalum, and their alloys. These materials are now under consideration in the development of advanced (fast breeder and fusion) reactor technology. In theory, the present trapping mechanism is expected to work in any material so long as the system displays sufficiently extensive solubility for carbon. The Group 5A body-centered cubic refractory metals (V, Nb, and Ta) are all capable of dissolving large amounts of carbon. Furthermore, V and Nb exhibit superior neutronic properties and are therefore considered as attractive base metals for the vacuum-wall construction of a fusion reactor. Meanwhile, tantalum has been suggested as the control-rod material in fast breeder reactors. Should the vacancy trapping mechanism based on carbon atoms prove to be applicable to these metallic systems, the potentially serious swelling problem could be alleviated. In this endeavor, however, it is well to remember that carbon is
probably the only interstitial solute capable of suppressing void formation by virtue of its nongaseous nature. The other interstitial solutes, such as nitrogen, oxygen, and hydrogen, being gaseous, should be ruled out as desirable dopants for the purpose of suppressing void formation. In fact, the very nature of these gaseous elements would actually enhance void formation because of their tendency to promote void nucleation.
SUMMARY

Neutron irradiation to a fluence of $9.0 \times 10^{19}$ n/cm$^2$ (E>0.1 MeV) at 710°C produced octahedral voids in high purity nickel samples containing up to 84 wt ppm carbon. The void size increased with increasing carbon content, while the void density and associated swelling decreased. In samples containing 600 wt ppm carbon, void formation was completely suppressed, and a high concentration of "black spots" was observed.

The neutron irradiation of high purity nickel at 500°C to four fluences ranging from $4.0 \times 10^{18}$ to $2.0 \times 10^{20}$ n/cm$^2$ (E>0.1 MeV) produced cubic voids in samples containing up to 84 wt ppm carbon. At $4 \times 10^{18}$ n/cm$^2$ and, to a lesser degree, at the other fluences, the void size tended to increase with increasing carbon content, while the void density and swelling decreased. At each carbon concentration the void size, void density and swelling all increased with increasing fluence. Deduced values of the critical fluence for void formation were found to increase with increasing carbon content. In all specimens containing 600 wt ppm carbon, void formation was again completely suppressed.

The suppression of void formation observed in this investigation was attributed to a trapping mechanism for vacancies of the interstitial carbon atoms in solution. A quantitative analysis of the void formation data indicated
that the effect of carbon was mainly to suppress void nucleation, with little or no effect on void growth. A trapping mechanism, based on a large divacancy-carbon atom complex binding energy, was proposed so as to enhance interstitial-vacancy recombination, which, in turn, suppresses void nucleation. The trapping mechanism is considered to be dynamic in nature because interstitial carbon atoms are quite mobile in the nickel lattice during irradiation.
BIBLIOGRAPHY


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