SUPPRESSION OF VOID FORMATION IN NICKEL BY A DYNAMIC TRAPPPING MECHANISM

S. M. Sorensen, Jr.* and C. W. Chen
Ames Laboratory-USERDA and Department
of Materials Science and Engineering
Iowa State University
Ames, Iowa 50010

ABSTRACT

The effect of carbon on void formation in high purity nickel under neutron irradiation to four fluences ranging from $4 \times 10^{18}$ to $2 \times 10^{20}$ n/cm$^2$ (E>$0.1$ MeV) at 500°C was investigated using transmission electron microscopy. In samples containing up to 84 wt ppm C, cubic voids were observed, and the void size tended to increase with increasing C content, while the void density decreased at much greater rates. Consequently, the associated swelling was seen to be steadily reduced. In samples containing 600 ppm C, void formation was completely suppressed, and an irradiation-induced dissolution of graphite precipitates occurred. The suppression of void formation in the irradiated Ni is attributed to an effective trapping mechanism associated with the interstitial C atoms in solution. Quantitative analyses on the size and density of voids reveal that the suppressing effect of C is mainly on void nucleation, not on growth. This trapping mechanism is considered to be dynamic in nature because the traps served by the C atoms can move through the lattice rapidly during irradiation until they are anchored in defect complexes.

It is now recognized that several different types of trapping mechanisms are effective in suppressing void formation in irradiated metals and alloys. Grain boundaries$^1$, dislocations$^2$, precipitates$^3$ and substitutional solute atoms$^4$ have all been shown to exert suppressing effects on void formation. These mechanisms display the common feature that the traps are static in nature because they remain essentially stationary in the lattice during irradiation. Recently we reported that a dynamic

*Now at the Inland Steel Research Center, East Chicago, Indiana 46312.
trapping mechanism is also capable of suppressing void formation in irradiated metals. In the latter case, interstitial solute atoms of carbon were observed to suppress void formation in Ni which had been irradiated by neutrons to a fluence of $9 \times 10^{19} \text{n/cm}^2$ (E>0.1 MeV) at 710°C. The suppression was either partial or complete, depending on the carbon content.

Since 710°C is near the upper limit of the temperature range for void formation in Ni, the observed swelling at that temperature is extremely small, being less than $5 \times 10^{-6}$. To further confirm the suppressing effect of carbon and to explore its dependence on the temperature and fluence of irradiation, it is deemed necessary to irradiate the Ni-C alloys at lower temperatures and to various fluences. The present report describes the results obtained from a series of new experiments.

**EXPERIMENTAL PROCEDURE**

Sheet samples of high purity (>99.99 wt%) Ni were prepared with five different carbon concentrations (4, 16, 27, 84 and 600 wt ppm; carbon analysis performed by combustion chromatography). Prior to irradiation, all samples received a high-vacuum anneal at 1000°C for 24 hrs under a residual pressure <2x10^{-7} Torr. Four sets of samples were irradiated in the central thimble of the Ames Laboratory Research Reactor (ALRR) to fluences ranging from $4 \times 10^{18} \text{n/cm}^2$ to 0.26, 0.53, and $2 \times 10^{20} \text{n/cm}^2$ (E>0.1 MeV). Sample temperature was maintained at 500±10°C throughout the irradiations by Joule heating. The samples were examined by transmission electron microscopy (TEM) using a Hitachi 100 kV electron microscope. Voids produced at 500°C are cubic in shape, with little or no truncation. For such cubic voids, the edge length was used to characterize the void size, which was measured on the electron photomicrographs enlarged to 150,000x by a Zeiss particle-size analyzer. Foil thicknesses were determined by the slip-trace method, the extinction contour method, or (and) the method developed by Wolff.
RESULTS

Despite the variation of fluence by a factor of 50, the irradiation experiments yielded essentially the same results as far as void formation is concerned. Table 1 lists the results of quantitative analyses on the size and density of voids produced at 0.4 and $5.3 \times 10^{19} \text{ n/cm}^2 (E>0.1 \text{ MeV})$ fluences. In samples containing up to 84 ppm C, while the mean void size was observed to increase with increasing C content, the void density decreased at much greater rates. Consequently, the associated swelling decreased progressively with increasing C content. As might be expected, the maximum swelling increased steadily with fluence from 0.006% at $4 \times 10^{18} \text{ n/cm}^2$ to 0.38% at $2 \times 10^{20} \text{ n/cm}^2$. Typical examples of the induced cubic voids are shown in Fig. 1. Samples with 600 ppm C showed no voids at all four fluences, thus reconfirming the behavior previously observed after irradiation at 710°C.

Because of the temperature dependence of the solubility limit for C in Ni, a related phenomenon was observed in the Ni-5 samples. The maximum solubility of C is about 600 ppm at 710°C but it is decreased to about 155 ppm at 500°C. Thus, aging of the Ni-5 samples at 500°C for 100 hrs allowed carbon to be precipitated out in nodular form (Fig. 2A). The selected-area electron-diffraction patterns of the aged samples showed diffuse rings, indicating the amorphous structure of graphite in the precipitates consistent with the Ni-C phase diagram. Upon irradiation, however, neither graphite precipitates nor voids were observed. Dislocations with heavy decorations of precipitates, presumably carbides, are the main defects in the irradiated lattices of Ni-5 samples (Fig. 2B).

DISCUSSION

The experimental results have confirmed that carbon is capable of suppressing void formation in Ni under neutron irradiation at 500°C as is at 710°C. The void suppression is only partial when the C content is relatively low; and the suppression becomes complete at the concentration of 600 ppm. Moreover, the same suppressing effect prevails in the fluence
range tested. It is therefore concluded that the effectiveness of the present method for the suppression of void formation is independent of the irradiation temperature and fluence up to at least \(2 \times 10^{20} \, \text{n/cm}^2\) (\(E > 0.1 \, \text{MeV}\)). Although this fluence is still a low value relative to the dosage expected for the core components of fast breeder reactors, nevertheless it is about three orders of magnitude higher than the critical fluence required for void formation in \(\text{Ni}^{10}\).

To elucidate the trapping mechanism associated with the C atoms, we note that the void density decreased eventually to zero, but the void size increased with increasing C content. Thus, we further conclude that the effect of carbon is largely to suppress void nucleation, not void growth. A similar conclusion was reached in a recent study by Smidt et al.\(^4\), who ascribed the suppressing effect of certain substitutional solutes on void formation in irradiated iron to a reduction of vacancy supersaturation, thereby making it difficult, and eventually impossible, for void nuclei to be formed. In this connection, it is pertinent to refer to another recent study by Makin and Walter\(^11\), who examined the effect of C on the swelling of 316-type stainless steel under 1 MeV electron irradiation in the temperature range 500-600°C. They also found a reduction in swelling with increasing C content. However, they observed that carbon tended to increase the void density and to reduce the void growth rate. The latter observations are contrary to our results shown in Table 1. To reconcile the differences, it is important to realize that increasing the C content in 316-type stainless steel would also promote carbide precipitation, which is capable of reducing swelling through the formation of denuded zones around the carbide precipitates. This is in contrast to our Ni-5 samples, in which most of the carbon is in solution by virtue of the irradiation-induced dissolution of the graphite nodules. The dissolution effect of irradiation on graphite precipitates in Ni alloys was discussed by Nelson et al.\(^12\).

To support the trapping capability of carbon atoms for vacancies, it was previously cited\(^5\) that computer simulation studies have shown stable configurations of monovacancy-, divacancy-, and split interstitial-carbon atom complexes and their binding energies are given at 0.30, 0.86, and
0.46 eV, respectively. The positive, relatively large binding energy for the divacancy-carbon atom complex implies that each carbon atom is capable of capturing at least two vacancies. It is not known at present whether or not the suppressing effect of carbon will eventually be saturated at high fluences. Additional experiments are needed to test this possibility.

The unique feature of this trapping mechanism is the dynamic behavior of the carbon atoms in solution. The jump frequency of C-atoms can be calculated applying the expression given in the previous paper. Using the activation energy of 34.8 kcal/mole deduced by Berry for the migration of C-atoms in Ni, and other appropriate constants, the jump frequency of C-atoms is calculated to be \(3.5 \times 10^7\) jumps/s at 500°C. This jump frequency should be compared with \(1.3 \times 10^5\) jumps/s for monovacancies in Ni at the same temperature. The comparison clearly shows that interstitial-carbon atoms are indeed highly mobile in the Ni lattice at 500°C.

In summary, we conclude that the presence of carbon atoms in the Ni lattice exerts a suppressing effect on void formation which is independent of the irradiation temperature and fluence up to \(2 \times 10^{20}\) n/cm² (E>0.1 MeV). The trapping mechanism associated with the C-atoms is characterized by the dynamic behavior of the interstitial-atom traps in contrast to the static nature of all other trapping mechanisms.

REFERENCES

4. F. A. Smidt, Jr., J. A. Sprague, J. E. Westmoreland and P. R. Malmberg, Defect and Defect Clusters in BCC Metals and Their Alloys, p. 341,
Table 1. Void formation data for high purity nickel irradiated in the ALRR to fluences of (I) $4.0 \times 10^{18}$ and (II) $5.3 \times 10^{19}$ n/cm$^2$ (E>$0.1$ MeV) at $500\pm10^\circ$C.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Carbon Content, wt ppm</th>
<th>Mean Void Size, A</th>
<th>Void Number Density, Voids/cm$^3$</th>
<th>Swelling ($\Delta V/V$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>4</td>
<td>146, 198</td>
<td>Fluence I: $0.2 \times 10^{14}$, Fluence II: $2.5 \times 10^{14}$</td>
<td>Fluence I: 0.006%, Fluence II: 0.19%</td>
</tr>
<tr>
<td>Ni-2</td>
<td>16</td>
<td>148, 205</td>
<td>Fluence I: $0.15 \times 10^{14}$, Fluence II: $1.8 \times 10^{14}$</td>
<td>Fluence I: 0.005%, Fluence II: 0.15%</td>
</tr>
<tr>
<td>Ni-3</td>
<td>27</td>
<td>157, 214</td>
<td>Fluence I: $0.1 \times 10^{14}$, Fluence II: $1.3 \times 10^{14}$</td>
<td>Fluence I: 0.004%, Fluence II: 0.13%</td>
</tr>
<tr>
<td>Ni-4</td>
<td>84</td>
<td>~200, 247</td>
<td>Fluence I: ~$0.01 \times 10^{14}$, Fluence II: $0.6 \times 10^{14}$</td>
<td>Fluence I: ~0.001%, Fluence II: 0.09%</td>
</tr>
<tr>
<td>Ni-5</td>
<td>600</td>
<td>NO VOIDS OBSERVED</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>