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B. L. Shriver

Manfred Wuttig
Missouri University of Science and Technology

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IRRADIATION ENHANCED DECOMPOSITION OF A NICKEL–CARBON SOLID SOLUTION*†

B. L. SHRIVER‡§ and M. WUTTIG‡

This investigation was performed to determine the effects of room temperature neutron irradiation on the distribution of carbon in a nickel–0.3 wt.% carbon alloy. The experiment consisted of comparing the amount of carbon in solid solution and the internal stresses of both unirradiated and irradiated (10^{13} fn-cm^{-2} $< \Phi_F <$ 10^{18} fn-cm^{-2}) samples following isochronal anneals between 100 and 1200°C by using the magnetic disaccommodation technique. The results indicate that the amount of carbon remaining in solid solution decreases with increasing neutron dose. At temperatures below 200°C this is due to the trapping of carbon by mobile irradiation-produced defects. Between 200 and 600°C the formation of metastable carbides is enhanced by the presence of irradiation-produced defects. No differences are observed in irradiated and unirradiated samples above 600°C.

AUGMENTATION DE LA DECOMPOSITION D'UNE SOLUTION SOLIDE NICKEL–CARBONE PAR IRRADIATION

Cette étude a été effectuée pour déterminer les effets de l'irradiation aux neutrons à température ambiante sur la distribution du carbone dans un alliage nickel–0,3% carbone en poids. L'expérience consiste à comparer la quantité de carbone en solution solide ainsi que les contraintes internes de deux échantillons, l'un non irradié et l'autre irradié (10^{13} fn-cm^{-2} $< \Phi_F <$ 10^{18} fn-cm^{-2}), après des recuits isochrones entre 100°C et 1200°C, en utilisant la méthode de désaccommodation magnétique. Les résultats montrent que la quantité de carbone restant dans la solution solide diminue quand la dose de neutrons augmente. Aux températures inférieures à 200°C, ceci est dû au piégeage du carbone par les défauts mobiles produits par irradiation. Entre 200°C et 600°C, la formation de précipités métastables augmente par suite de la présence des défauts produits par irradiation. Au-dessus de 600°C, aucune différence n'est observée entre les échantillons non irradiés et irradiés.

VERSTÄRKTE ENTMISCHUNG EINER NICKEL–KOHLENSTOFF-LEGIERUNG NACH NEUTRONENBESTRAHLUNG

Das Ziel dieser Untersuchung war, den Einfluß der Raumtemperatur-Neutronenbestrahlung auf die Verteilung von Kohlenstoff in einer Nickel–0,3 Gew.% Kohlenstoff-Legierung zu untersuchen. Es wurden der gelöste Anteil des Kohlenstoffs und die inneren Spannungen von unbestrahlten und bestrahlten (10^{13} fn/cm^2 $< \Phi_F <$ 10^{18} fn/cm^2) Proben nach isochronen Anlaßbehandlungen zwichen 100 und 1200°C mit Hilfe der Methode der magnetischen Disakkomodation verglichen. Die Ergebnisse deuten darauf hin, daß der Anteil des gelösten Kohlenstoffs mit zunehmender Neutronendosis abnimmt. Unterhalb 200°C wird der Kohlenstoff durch bewegliche, bei der Bestrahlung erzeugte Defekte eingefangen. Zwischen 200 und 600°C wird die Entstehung metastabiler Ausscheidungen durch die Gegenwart von Bestrahlungsdefekten begünstigt. Oberhalb 600°C wurden keine Unterschiede zwischen bestrahlten und unbestrahlten Proben beobachtet.

1. INTRODUCTION

It has been shown that neutron irradiation greatly accelerates the rate of decomposition of supersaturated Fe–C alloys.[1–7] This decay of the solid solution was due to both the trapping of carbon at irradiation-produced defects[2–7] and enhanced precipitation due to the nucleation of carbides at defect clusters.[1,2]

This paper reports on a survey type study of irradiation enhanced decomposition in a nickel–0.3 wt.% carbon alloy. The objective of this investigation was to see if this interstitial solid solution is also affected by neutron irradiation and, if so, to characterize the type of interaction responsible for the change.

The nickel–carbon alloy was utilized because its crystal structure is the same as that of austenitic stainless steels which are commonly used in structural components of nuclear reactors. Nickel is also ferromagnetic so that the magnetic disaccommodation technique could be used to obtain information about the internal stresses and the amount of carbon in solid solution.

2. EXPERIMENTAL PROCEDURE

(a) *Introduction*

This investigation consisted of a series of isochronal anneals between 100 and 1200°C performed on three samples: an unirradiated sample used as a reference and two samples exposed to fast fluences of 5×10^{13} and 2×10^{17} fn-cm^{-2} at 40°C. After each 30 min anneal the amount of carbon in solid solution and the formation of defect clusters or precipitates were checked by using the magnetic disaccommodation technique.

(b) *Magnetic disaccommodation technique*

Magnetic disaccommodation is a useful technique for studying changes in solid solutions since it yields information about both the amount of alloying element in solid solution and its distribution. The value of the magnetic permeability immediately

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‡ Department of Metallurgical and Nuclear Engineering, University of Missouri-Rolla, Rolla, Missouri 65401.

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following demagnetization, μ_0, is sensitive to the formation of small precipitates or defect clusters if the stress field caused by them is of the same order as the magnetostrictive stresses.[8] Furthermore, the amplitude of the magnetic disaccommodation, $\Delta\mu$, is proportional to the concentration of the defect causing it.[9] Since the reorientation of dicarbons is believed to be responsible for the disaccommodation in dilute nickel–carbon alloys,[10] $\Delta\mu$ is proportional to the square of the amount of carbon in solid solution. Applications of this technique to related problems are discussed elsewhere.[10–13]

Thus, by measuring both $\Delta\mu$ and μ_0 after each isochronal anneal, it is possible to detect the redistribution of carbon in nickel and characterize the stresses associated with the change. These measurements were made in an oil bath at 105 $\pm$ 3°C since this was the temperature which gave the optimum disaccommodation amplitude during the first 10 min after demagnetization.[10]

(c) *Electron microscopy*

In order to further characterize the effects of neutron irradiation on this alloy, transmission electron microscopy studies were made on thin foils which had received the same treatment as the magnetic disaccommodation samples. Although the magnetic disaccommodation experiment indicated the formation of both defect clusters and precipitates neither was observed in the thin foils by using a 100 kV electron microscope. This was probably due to the relatively low neutron dose and the low stresses caused by the nickel–carbon precipitates. (Also see Discussion.)

(d) *Sample preparation*

The samples were prepared from commercially available nickel wire (1 mm diameter) which contained about 20 ppm substitutional impurities; mainly silver and iron. Reactor grade graphite powder was used for the carburization. Each sample consisted of three, 5 cm long, wires.

The wires were initially recrystallized for 24 hr at 1200°C and in 20 μ of air. They were subsequently carburized by packing in graphite (500 μ of air) and quenching in ice water after 20 min at 1200°C. All samples contained about 0.3 wt.% carbon. The values of the initial permeability and the disaccommodation amplitude indicated nearly equal carbon contents and distributions in all samples.

One of the samples (*S*-2) was irradiated for 3 hr at about 40°C in the University of Missouri-Rolla Reactor ($\phi_f \simeq 5 \times 10^9$ fn-cm^{-2}-sec^{-1}).* A second sample (*S*-3) was irradiated for 100 hr at 40°C in the University of Missouri Research Reactor Facility ($\phi_f \simeq 5 \times 10^{11}$ fn-cm^{-2}-sec^{-1}).*

(e) *Annealing conditions*

Samples *S*-1 (unirradiated standard) and *S*-2 ($\Phi_F \simeq 5 \times 10^{13}$ fn-cm^{-2}) were annealed in 25°C steps in either an oil or salt bath at temperatures between 50 and 500°C. In this range the temperature was controlled within $\pm$1°C. At higher temperatures (500–1200°C) a wire wound electric tube furnace and 50°C steps were used. The temperature control for this furnace was better than $\pm$3 per cent. The samples were sealed in fused quartz with about 20 μ of air for all anneals above 400°C.

Because of the high radioactivity of sample *S*-3 ($\Phi_F \simeq 2 \times 10^{17}$ fn-cm^{-2}) it was annealed in the electric tube furnace with a pressure of about 500 μ of air for all temperatures above 225°C. Fifty degree steps were used between 100 and 600°C, and 100°C steps for higher temperatures. Some oxidation of the sample was apparent after annealing above 1000°C.

3. EXPERIMENTAL RESULTS

Neutron irradiation at room temperature and subsequent annealing have a marked effect on the distribution of carbon in nickel as shown by the changes of initial permeability and disaccommodation amplitude as a function of annealing temperature in Figs. 1 and 2. The observed effects may be divided into groups. The first group consists of quantitative phenomena associated with the normal decomposition of the supersaturated solid solution and the second group is associated with the irradiation induced decomposition that is not seen in the unirradiated case.

The principle features of the variations in μ_0' and $\Delta\mu'$, except those between 100 and 200°C, are common to all samples and, thus, reflect the formation and dissolution of metastable precipitates. These

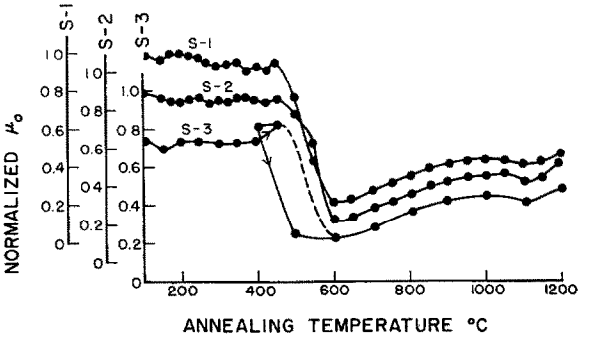

FIG. 1. Normalized initial permeability, μ_0', as a function of annealing temperature. $\mu_0' = \mu_0(T)/\mu_0$ (105°C).

* Approximate fast neutron flux ($E > 1$ MeV) at irradiation position.

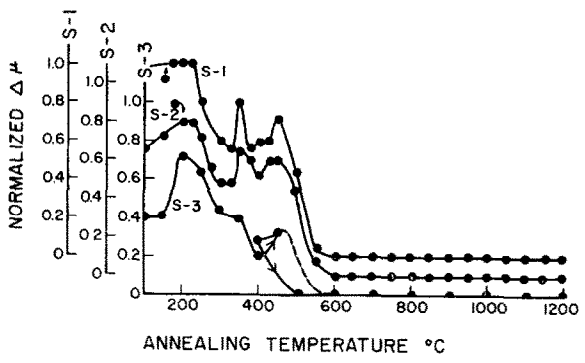

FIG. 2. Normalized disaccommodation amplitude, $\Delta\mu'$, as a function of annealing temperature. $\Delta\mu' = \Delta\mu(T)/\Delta\mu$ (105°C).

decomposition processes are quantitatively altered by the presence of the irradiation-produced defects. The apparent disappearance of up to 40 per cent ($\langle C\rangle^2 \propto \Delta\mu' \simeq 0.4$; $\therefore \langle C\rangle \simeq 0.6$) of the carbon solute below 200°C, however, is a qualitatively new phenomenon. No differences are observed in irradiated and unirradiated samples above 600°C.

4. DISCUSSION

In order to discuss the changes in the Ni–C solid solution it is necessary to know what types of defects are produced by neutron irradiation and how these defects will interact with the interstitial solutes. Since carbon has a low absorption cross section (3.4 mb) the defects formed in the alloy should be basically the same as found in pure nickel irradiated under similar conditions.[14] This was also indicated by the nearly identical drop of μ_0' that was observed during the irradiation of both carbon-free and carbon-doped samples early in this study. A survey of recent literature[15–21] reveals that both vacancy and self-interstitial defects will be formed in nickel during room temperature irradiation. Point defects are produced during irradiation and defect clusters may be formed either during irradiation or upon annealing at temperatures where the respective point defects are mobile. There will be an attractive interaction between the carbon interstitials and irradiation-produced defects[22,23] which may lead to an enhanced decomposition of the solid solution if either the solute or the defects are mobile.

The irradiation-produced quantitative changes in the decomposition of the supersaturated Ni–C alloys at temperatures above 200°C are ultimately the result of solute-defect interactions, which probably result in the enhanced nucleation of carbides, as seen in iron alloys irradiated under similar conditions.[1,2,24] The present data, however, is insufficient to warrant a detailed discussion of this effect. The difficulties that were encountered in trying to find the cause of these changes were compounded by the apparent similarity of the precipitates formed, as indicated by the relatively constant values of μ_0' in the temperature range of 100–450°C. Only the formation of the precipitate at around 550°C is accompanied by a stress field which is large enough to be reflected in the initial permeability data. Ni–C alloys are, therefore, different from Fe–C alloys where the formation of carbides and carbon-defect trapping cause significant changes of μ_0.[7] It may be concluded that the strain energy of the Ni–C alloy is relatively independent of the solute distribution between 100 and 500°C. This is most likely the main reason for the failure of the electron microscopy studies mentioned above.

Since both carbon-doped and carbon-free nickel samples showed the same decrease in μ_0' upon irradiation, neither this drop nor the accompaning drop in $\Delta\mu'$ can be related to the formation of nickel carbides. These changes must, instead, be associated with the trapping of carbon at irradiation-produced defects. This trapping cannot occur by the migration of carbon atoms to stationary defects since long range carbon diffusion will not be possible at either the irradiation temperature or the magnetic permeability measuring temperature.[25] It is more likely that the trapping takes place between stationary carbon atoms and mobile point defects or small defect clusters. The carbon interstitials would then act as preferential sinks for the migrating defects. Self-interstitials and divacancies are two mobile[10–12] defects that may be present in sufficient numbers[22] to account for the amount of trapping observed. The increase in $\Delta\mu$ between 100 and 200°C indicates the dissociation of the carbon-defect traps.

5. CONCLUSIONS

Room temperature neutron doses of 10^{13} and 10^{17} fn-cm^{-2} affect the nickel–carbon solid solution in two ways. During irradiation up to 40 per cent of the carbon may be removed from solid solution due to the trapping of carbon by mobile defects; possibly self-interstitials or divacancies. These carbon-defect traps are unstable above 150°C as carbon is returned to solid solution upon annealing between 150 and 200°C. Above 200°C the normally occurring decomposition of the solid solution appears to be enhanced by the presence of the irradiation-produced defects, which may act as additional nucleation sites. The form and type of the defects responsible for this effect are unknown, but they appear to anneal at about 600°C since both irradiated and unirradiated samples have the same values of μ_0 and $\Delta\mu$ above that temperature.

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