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THE EFFECT OF RADIATION ON ATOMIC
REARRANGEMENTS IN Fe-N, Cu-Ni, AND Cu-Al ALLOYS

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J. T. Stanley, J. M. Williams, and M. S. Wechsler

Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

The effect of neutron and electron irradiations at below room temperature on the precipitation, segregation, and short-range ordering processes in Fe-N, Cu-Ni, and Cu-Al alloys, respectively, has been studied. Neutron irradiation, but not electron irradiation, is found to accelerate the precipitation of nitrides, which is attributed to the introduction of nucleation sites. However, at high electron doses, evidence is found for the trapping of nitrogen by radiation-produced point defects. For the segregation process in Cu-Ni and short-range ordering in Cu-Al, the reaction rate is increased by irradiation with neutrons and electrons. These are believed to be cases of radiation-enhanced diffusion, which occurs when radiation-produced defects become mobile at temperatures above -50°C . However, the identity of the defect responsible for the diffusion has not been definitely established.

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I. Introduction

The relative arrangement of the different types of atoms in alloys often has a profound effect on properties. Therefore, it is important to understand better how and why radiation causes atomic arrangements in alloys to be altered. The three alloys considered here, Fe-N, Cu-Ni, and Cu-Al, exhibit three different types of metallurgical reactions: precipitation, segregation, and short-range ordering, respectively. In each case, the effect of neutron and electron radiations on these processes has been studied. The principal mechanisms whereby radiation-produced defects affect the kinetics of metallurgical reactions are by the enhancement of diffusion and by providing additional nucleation sites. A comparison of the relative effects of neutron and electron bombardments is helpful in determining the relevant mechanism in particular cases because large clusters of defects should be necessary for nucleation and these are produced upon neutron irradiation but not upon electron irradiation. A third mechanism that may play a role is the trapping of solute atoms by radiation-produced defects. We will see that trapping appears to be a factor in the precipitation of nitrogen in electron-irradiated iron, but only after relatively high exposure.

II. Precipitation in Fe-N Alloys:

For the work on Fe-N alloys, the amount of nitrogen in solid solution was determined from the magnitude of the Snoek internal friction peak. The foil samples of Ferrovac E iron, 1 1/2-in. x 3/16-in. x 0.005-in. in dimensions, were decarburized and nitrided to give a concentration of about 0.015 wt. % nitrogen. The internal friction was measured in flexure at a

frequency of about 35 cps. At this frequency the nitrogen internal friction peak occurs at 65°C. The details of sample treatment and measurement have been given elsewhere.¹

No change in the temperature of the internal friction peak is observed upon irradiation, which demonstrates that the nitrogen jump rate is not affected. However, as is shown in Fig. 1, the loss of nitrogen from supersaturated solid solution in alpha iron at 65°C is accelerated by a factor of five following neutron irradiation below -120°C for 23 days. Furthermore, it was found¹ that the same degree of acceleration takes place upon irradiation under similar circumstances for only one day, corresponding to a neutron dose of about 6×10^{15} neutrons/cm² ($E > 0.6$ Mev). Now, the accelerated loss of nitrogen from solid solution upon neutron irradiation is most likely due to enhanced nucleation of the precipitating nitride particles. The nucleation site is probably the damage cluster which results from a primary neutron-atom collision. Therefore, a dose of 6×10^{15} neutrons/cm² corresponds to a density of damage clusters of about 2×10^{-8} , since the cross section for a primary collision is about 3×10^{-24} cm² in iron. It is interesting that the concentration of precipitate particles in a normal aging experiment² is about $(1-5) \times 10^{-9}$. An increase by ten-fold in the number of particles will produce a decrease in the inter-particle spacing by a factor of $(10)^{1/3}$ and a decrease in the time for a given loss of nitrogen at the particles by a factor of $(10)^{2/3} \approx 5$, which is consistent with the five-fold decrease in the reaction time observed upon neutron irradiation. However, the reason for the saturation in the radiation-enhanced reaction rate is not entirely clear, although it may be a consequence of the rapid reduction in supersaturation in the neighborhood of the damage clusters when a large number of them is present.

As we have said, electron irradiation should not give rise to enhanced nucleation of the precipitation process, inasmuch as the electron damage

consists largely of isolated interstitial-vacancy pairs rather than damage clusters as for neutron irradiation. That this is so for electron-irradiated Fe-N is shown in Fig. 2, where the aging curves at 65°C are seen to coincide for the unirradiated sample and for the sample irradiated with 2-Mev electrons at 0°C to a dose of 1.8×10^{16} electrons/cm². The fractional number of displacements produced by this electron irradiation, about 10^{-16} , corresponds roughly to that for the neutron irradiation discussed above. Although some clustering of the defects may have occurred upon electron irradiation at 0°C, apparently no clusters large enough to nucleate the precipitation reaction were formed.

We have also mentioned that solute atoms may be trapped by radiation-produced defects, due to a binding energy between the defect and the solute atom. In fact, this mechanism provides an explanation of certain observations for irradiated Fe-C^{3,4}. However, trapping is not likely to be an important factor unless the concentration of defects approaches the concentration of solute atoms, which is about 6×10^{-4} atomic fraction nitrogen for our Fe-N samples. Therefore, it is not surprising that the irradiation of 1.8×10^{16} electrons/cm² (Fig. 2), producing about 10^{-6} defects, did not give rise to any trapping, as is seen in the fact that in the irradiated state the sample exhibited the same internal friction at the outset of the aging reaction as it did in the unirradiated condition. However, an irradiation at 77°K to a dose of 7.8×10^{18} electrons/cm² caused about a 16% decrease in the internal friction measured in the temperature range 25-65°C (Fig. 3, closed circles). This indicates that between 77°K and 25°C the radiation-produced defects migrated to the nitrogen atoms and trapped about 16% of them. This is perhaps reasonable since the dose of 7.8×10^{18} electrons/cm² is expected to produce about 6×10^{-4} defects, which is of the same order as the nitrogen concentration. A still higher dose of 1.5×10^{19} electrons/cm² gave a decrease in

internal friction of about 38% (Fig. 3, open squares).

A further point should be made with reference to Fig. 3. As the legend indicates, after the sample was irradiated to 7.8×10^{18} electrons/cm², it was aged for 31.6 hrs at 65°C; then it was annealed for 15 min at 370°C and water quenched. The closed triangle points show that the internal friction returned to the value it had after the irradiation to 7.8×10^{18} electrons/cm². Thus, the heat treatment at 370°C was sufficient to redissolve into solid solution those nitrogen atoms that had not been trapped upon irradiation or upon raising the temperature to the test temperature following the irradiation, but the nitrogen atoms that became trapped upon irradiation remained trapped when the 370°C heat treatment was applied. On the other hand, the closed squares in Fig. 3 show that a heat treatment at 450°C was sufficient to free most of the nitrogen atoms from the radiation-produced traps and put them back into solid solution. Finally, the open triangle point shows that, once the nitrogen atoms are freed from their traps, a heat treatment of 370°C will put them back into solid solution. The major point underlying the above remarks is that the defect-solute atom complex probably dissociates at a temperature between 370°C and 450°C.

There remains the question of the kinetics of the aging at 65°C following the irradiation to 7.8×10^{18} electrons/cm² (Step 5, Fig. 3) as compared to that for the sample in the unirradiated condition (Step 2, Fig. 3). The aging curves, normalized to the initial nitrogen in solid solution, are shown in Fig. 4. As for the lower electron dose (Fig. 2), no acceleration of the reaction was observed. In fact, a slight retardation is noted in Fig. 4, which may be due simply to the lower concentration of nitrogen in solid solution after irradiation because of the loss of nitrogen from solution by trapping.

III. Segregation in Cu-Ni Alloys:

In the past, it has been thought that the Cu-Ni system displays a continuous series of FCC substitutional solid solutions. However, as a result of magnetic susceptibility⁵ and other⁶ measurements, a tendency toward segregation of the copper and nickel at lower temperatures has been noted. Under usual conditions, the atomic mobilities are too low to allow the segregation to occur to any appreciable extent. But when the alloy is irradiated, the segregation process is accelerated and the segregation takes place at lower temperatures than is normally possible. The decrease in electrical resistivity of Cu-37 at. % Ni upon neutron irradiation at 70-100°C has been ascribed to the radiation-enhanced segregation.⁷

In experiments at the Oak Ridge National Laboratory⁸, Cu-Ni foil samples of compositions 37, 48, 62, and 77 at. % nickel were irradiated at -180°C to a dose of about 10^{17} neutrons/cm² ($E > 0.6$ Mev). Upon subsequent isochronal annealing, the three samples of higher nickel content underwent an anomalous decrease in resistivity. The largest decrease was observed for the Cu-62 at. % Ni alloy. Figure 5 shows that the decrease in resistivity for this sample started at about -50°C and reached its largest value (-1.0 $\mu\text{ohm-cm}$) at about 300°C. A similar control sample given the same isochronal annealing treatment showed a maximum decrease in resistivity of only 0.3 $\mu\text{ohm-cm}$ ⁸. The decrease in resistivity for the unirradiated sample indicated that there is a tendency toward segregation even in the absence of radiation. However, the process occurs at a lower temperature and to a greater extent in a sample previously irradiated at -180°C.

When a Cu-62 at. % Ni sample is irradiated with 2-Mev electrons at -196°C to a dose of 9×10^{17} electrons/cm², the isochronal annealing behavior is very similar to that observed for the neutron-irradiated sample (Fig. 5).

The two irradiations are expected to have produced comparable numbers of defects. The fact that the same result was observed after electron irradiation suggests that the radiation-enhanced segregation is not caused by nucleation sites introduced upon irradiation. Instead it would appear that the enhancement is due to the diffusion attendant upon the motion of point defects above -50°C . The annealing curves in Fig. 5 show a gradual decrease in resistivity over the large temperature interval of -50 to 300°C . Since the annealing spectrum is so diffuse, it is difficult to identify the defect or defects responsible. Isochronal annealing experiments on quenched and on quenched-and-irradiated samples have also been conducted in the attempt to better understand the mechanism of the radiation-enhanced segregation in Cu-Ni alloys.

IV. Ordering in Cu-Al Alloys:

Although no superlattice has been observed for alpha solid solutions of aluminum in copper, several x-ray diffuse scattering studies^{9,10} have demonstrated the presence of short-range order for alloys with aluminum contents near 15 at. %. Furthermore, it has been shown that upon neutron irradiation at 100°C the degree of short-range order is increased¹⁰. Neutron^{11,12} and electron¹³ irradiation at 100°C is known also to give rise to a decrease in electrical resistivity, which is therefore attributed to an increase in short-range order.

In view of the previous discussion of the low-temperature electron and neutron irradiations in precipitating and segregating systems, it is interesting to examine the results of similar irradiations in the short-range ordering system Cu-Al. In Fig. 6, we see that the isochronal annealing curves are quite similar following neutron irradiation at -120°C to about 10^{17} neutrons/cm² ($E > 0.6$ Mev) and 1-Mev electron irradiation at -196°C to about 2×10^{17} electrons/cm². The decrease in resistivity sets in at about -50°C , as was true

or Cu-Ni (Fig. 5), but the magnitude of the decrease in resistivity is much smaller. Since low-temperature electron irradiation is effective in stimulating the short-range ordering, we conclude that in Cu-Al as for Cu-Ni the introduction of nucleation sites is not an important aspect of the effect of the irradiation. Again, the explanation of the radiation-enhancement is sought in terms of the atomic rearrangement brought about upon the motion of the radiation-produced point defects.¹⁴

V. Concluding Remarks:

A comparison of the results of annealing (or aging) experiments in Fe-N, Cu-Ni, and Cu-Al alloys following low-temperature neutron and electron irradiation leads to the conclusion that the precipitation reaction in Fe-N is accelerated by virtue of the introduction of nucleation sites, whereas the segregation process in Cu-Ni and short-range ordering in Cu-Al are enhanced by the diffusive motion of radiation-produced point defects. This is perhaps not surprising, since the segregation and ordering processes constitute atomic rearrangements on the matrix crystal lattice, and therefore the reactions are not limited by the need to overcome an interfacial energy between two crystal structures. On the other hand, the precipitation of nitrides in Fe-N does involve the formation of a second phase. Therefore, nucleation is expected to be an important factor. Furthermore, the diffusion of nitrogen in iron is interstitial in character and, thus, radiation-produced defects do not provide a simple mechanism for enhanced diffusion. However, isolated point defects may serve as trapping centers for the nitrogen atoms. Our experiments indicate that trapping may occur upon electron irradiation, provided that the concentration of radiation-produced defects approaches the nitrogen concentration.

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Figure Captions

1. The fractional amount of nitrogen remaining in solid solution versus aging time at 65°C. Internal friction measurements at about 35 cps on unirradiated and neutron-irradiated Fe-0.015 wt. % N.
2. Internal friction versus aging time at 65°C for unirradiated and electron-irradiated Fe-0.015 wt. % N. Irradiation temperature, 0°C.
3. Internal friction at about 35 cps versus test temperature for Fe-0.015 wt. % N after various treatments. Electron energy, 2 Mev.
4. The effect of 2-Mev electron irradiation on the precipitation of nitrogen in iron. Fractional amount of nitrogen remaining in solid solution versus aging time at 65°C. Internal friction measurements at about 35 cps on Fe-0.015 wt. % N.
5. Change in resistivity of Cu-62 at. % Ni during isochronal annealing following neutron and electron irradiation. All measurements made at liquid nitrogen temperature.
6. Change in resistivity of Cu-15 at. % Al upon isochronal annealing ($t = 30$ min) following neutron and 1 Mev electron irradiation. All measurements made at liquid nitrogen temperature.

Aging of the Nitrogen Peak in Iron-Nitrogen Alloy at 65°C .

SPECIMEN HISTORY

- (1) ○ UNIRRADIATED
- (2) AGED 18.9 hr AT 65°C
- (3) SOLUTION ANNEALED AT 590°C, 1 hr; W.Q.
- (4) ● IRRADIATED TO 7.8×10^{18} electrons/cm² AT 77°K
- (5) AGED 31.6 hr AT 65°C
- (6) ▲ SOLUTION ANNEALED AT 370°C, 15 min; W.Q.
- (7) ■ SOLUTION ANNEALED AT 450°C, 15 min; W.Q.
- (8) △ AGED 24 hr AT 65°C; SOLUTION ANNEALED AT 370°C, 15 min; W.Q.
- (9) □ IRRADIATED TO 1.5×10^{19} electrons/cm² AT 170°K

Fig. 3 The Effect of 2-Mev Electron Irradiation on the Nitrogen Internal Friction Peak in Iron.

FRACTION OF NITROGEN REMAINING IN SOLUTION

The Effect of 2-Mev Electron Irradiation on the Precipitation of Nitrogen in Iron.

Fig. 5

Change in Resistivity of Cu-Al (15 at. % Al) Upon Isochronal Annealing ($t = 30$ min) Following Low Temperature Reactor Neutron Irradiation and 1 Mev Electron Irradiation.