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The Influence of Radiation-Produced Defects on the Precipitation of Carbon in Iron*

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The severe local damage caused by neutron irradiation of an alloy can create extra sites for the nucleation of phase changes. This effect of enhanced nucleation has been studied in the iron-carbon system. Measurements were made by electrical resistivity, internal friction, and electron microscopy. Two effects were found. When the alloy is irradiated at ambient temperature (~60°C) the number of precipitation particles formed and, hence, the rate of precipitation of carbon, is ten times the number in the unirradiated alloy. Further irradiation does not increase the number of precipitate particles. When the alloy is irradiated at low temperature (~−100°C) the disappearance of carbon from solution is one thousand times faster than the thermal rate. It is deduced that the carbon is temporarily trapped by vacancies and later released to precipitate at a temperature higher than the precipitation temperature in the unirradiated alloy.

Introduction

It is known that the severe local damage caused by neutron irradiation of a metal can create extra sites for the nucleation of phase changes. The iron-carbon system was selected for study because the carbon diffuses interstitially and is therefore not accelerated by the vacancies and interstitials created by the irradiation. Careful studies of thermal precipitation of the carbon in this system exist,[1] and it was hoped that a simple comparison of the relative rates of precipitation in irradiated and unirradiated specimens would yield the increased number of nuclei. This proved to be the case only for short time irradiation at ambient reactor temperatures; low temperature irradiation followed by warming accelerates the disappearance of the carbon from the solid solution in a manner not believed to be associated with precipitation.

Ambient Temperature Irradiation

The rate of disappearance of carbon which had been quenched into solution in iron (0.01 wt. % carbon) was measured by its contribution to the internal friction (Snoek) peak.[2] A typical decay rate of this peak is shown by the right-hand curve of Fig. 1. The irradiation data we taken in the following manner.[3] The internal friction peak height was measured at 57°C, by selection of the proper frequency, in several samples. These were then placed in the reactor at 57°C for various lengths of time and, after removal, the decay rate of the internal friction peak at 57°C was measured. The data are shown by the middle curve of Fig. 1. It is seen that after a 4-hour irradiation all data fall on the same curve and that this decay is about ten times as fast as the thermal one. These data imply that the excess nuclei are all formed within the first 4 hours of irradiation and that further irradiation has no effect. Random walk considerations show that roughly ten times as many nuclei are required in the irradiated samples as in the unirradiated sample to cause this acceleration of the disappearance of the carbon.

Hull and Mogford[4] performed a similar experiment with electron microscopy. They measured the density and size of precipitate particles in 0.004 wt. % carbon in iron after both thermal and irradiation treatment. After several days of aging at 60°C, the precipitate particle density was about $3\times10^{13}/cm^3$. When quenched iron-carbon was irradiated at 60°C in a neutron flux of similar magnitude to the internal friction work, the particle density increased to $2\times10^{14}/cm^3$ after 5 hours irradiation. Subsequent irradiations up to 144 hours

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showed essentially no change in the number of particles although their size increased. This independent observation of a factor of 10 increase in the number of precipitation sites is in excellent agreement with the implications of the internal friction studies. The number of primary knock-ons from such irradiation doses is about $2.5\times10^{14}/cm^3$ after 2 hours. If each forms a nucleation site then not 4, but 2 hours should be sufficient time to yield the above results. It is not known however, why the incipient nuclei created by the primary knock-ons of further irradiation do not form sites of precipitate particles. Further studies of this phenomenon need to be made, particularly with irradiations of under 4 hours duration.

Low Temperature Irradiation

When the quenched iron-carbon is irradiated at low temperature (-100°C) an entirely different effect occurs. Measurements of the rate of decay of the internal friction peak after a 12 day low temperature irradiation show that the carbon disappears over a thousand times faster than in unirradiated iron. Fig. 2 illustrates the normalized curves of this decay at different temperatures after a 12 day irradiation. Similar decays for a 4 day irradiation and no irradiation are also shown. It should be noted that the decay of the 4 day specimen does not go to completion. This faster rate of disappearance is illustrated also in Fig. 1 in which the 50°C curve of Fig. 2 is plotted for comparison. When the curves of Fig. 2 are analyzed it is found that the disappearance of carbon obeys a second order reaction rate and is governed by the migration energy of carbon in iron, 19.8 Kcal/mol. The average number of jumps a carbon atom makes before disappearance is calculated to be about 20,000. This number requires a far greater density of nuclei than could have been created by the 12 day irradiation.

The behavior of the carbon in iron after low temperature irradiation is also being studied by electrical resistivity and a somewhat more revealing picture is emerging.[5] Fig. 3 shows the comparison of isochronal annealing of irradiated and unirradiated quenched iron-carbon. The lower curves show the temperature derivatives which assist in identifying the steps. The unirradiated

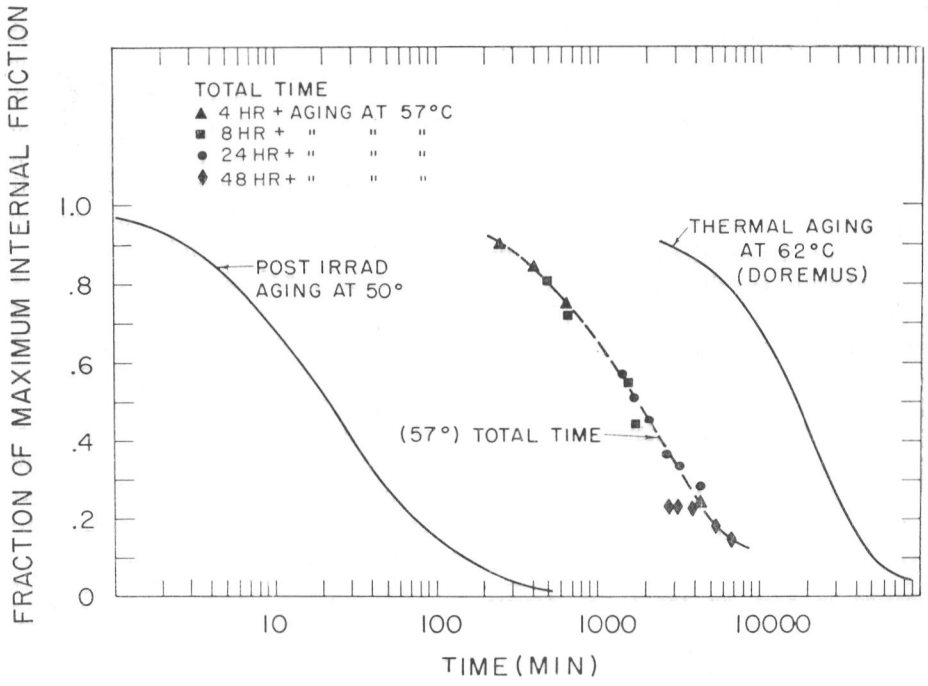

Fig. 1. Summary of internal friction studies of carbon in iron. Right curve—thermal rate (Ref. 1). Middle curve—irradiation and aging at 57°C. Left curve—aging at 50°C after irradiation at −100°C (Ref. 2).

specimen shows two distinct steps, one around 170°C and the other around 250°C. The lower temperature step is the one observable by internal friction techniques and is related to the precipitation of carbon from solution. The high temperature step is associated with the rearrangement of the precipitate into the Fe_3C phase.[6] The irradiated specimen shows considerably more complexity. A 19 day low temperature irradiation has increased the electrical resistivity by about 20% (all resistivities were measured at liquid nitrogen temperature). A low temperature decay occurs around −30°C with an activation energy of about 5 Kcal/mol. This probably arises from the annealing of one of the point defects, possibly the interstitial since this step occurs in decarburized iron. A second step occurs around 50°C which corresponds to the internal friction observation. The activation energy of this decay

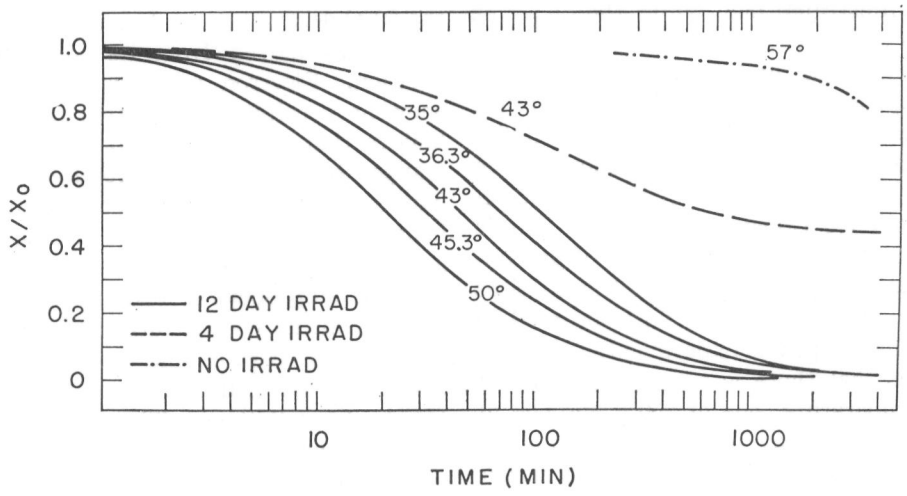

Fig. 2. Normalized decay curves of internal friction peak.

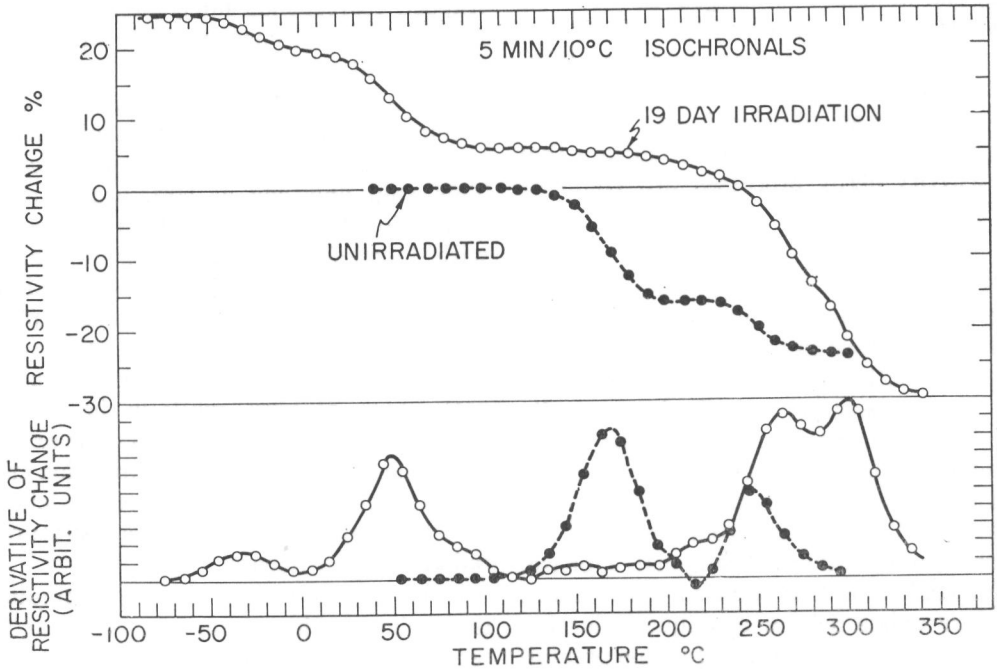

Fig. 3. Resistivity and temperature derivative of resistivity during isochronal annealing of iron-carbon irradiated for 19 days at −100°C compared with an unirradiated specimen.

step, measured by isothermal annealing, is 19.8 Kcal/mol and the kinetics are of second order for a slightly unequal initial concentration, in agreement with the internal friction findings. A very slight decay of resistivity can be seen at 150°C in both the resistivity and derivative curves of Fig. 3. In another experiment (not shown) the irradiation time at low temperature was 2 days. Subsequent isochronal annealing showed that the decay at 150°C was considerably larger than the illustrated one, while the decay at 50°C was smaller. It is clear that shorter irradiations cause the 150°C decay to increase at the expense of the 50°C and, in the limit, to approach the unirradiated case. Irradiation has also caused an acceleration of the decay of resistivity in this region, *i.e.* it occurs around 150°C instead of 170°C. This is in agreement with the acceleration of precipitation caused by the extra nucleation sites formed by irradiation that was observed in ambient temperature experiments. Fig. 3 also shows that there is a two-step decay at higher temperature, one at 260°C and one at 300°C. After a 2 day irradiation the relative size of the step at 260°C is considerably larger than the one at 300°C, although in absolute magnitude it is always about the same size, and in the limit it has merged into the unirradiated curve and the 300°C decay has disappeared. Irradiation has caused the 250°C step to shift to a higher temperature and the development of an additional step at 300°C. Other experiments, not shown, indicate that all resistivity decay processes are complete by 350°C.

Discussion

There are five decay steps in the irradiated specimens and two in the unirradiated specimen. We shall now propose a model to explain these observations. It is generally recognized that the two decay steps in the unirradiated iron-carbon are caused by precipitation of the interstitial carbon atoms. The first step, at 170°C, arises from the clustering of carbon atoms into the hexagonal, ε, phase. Careful studies of this reaction have shown that there exists neither a unique activation energy nor order of reaction for this precipitation process.[1] However, internal friction studies have shown that the activation energy for the migration of carbon in iron is about 19.8 Kcal/mol. The step at 250°C arises from the transformation of the hexagonal phase into the orthorhombic Fe_3C phase.

It has already been stated that the -30°C decay step is probably the motion of a point defect since it occurs in pure iron and the magnitude is proportional to the radiation dose. We assume this point defect to be the interstitial.

From internal friction measurements of the 50°C decay step, we know that the carbon has been removed from its free interstitial position. Electron microscope observations show no precipitation in this region.[7] We believe that the carbon atoms have become trapped by the radiation produced vacancies. This hypothesis is substantiated by the kinetic behavior of this step. Both internal friction and electrical resistivity measurements show that the step obeys second order kinetics for unequal initial concentration of the reactive components, carbon and vacancies, and, as shown in Fig. 2, does not go to completion for short irradiations. The activation energy of the decay step is 19.8 Kcal/mol, the activation energy for the migration of carbon in iron. Furthermore, the average number of jumps a carbon atom makes before becoming trapped corresponds fairly well with the expected vacancy concentration produced by the irradiation.

The step at 150°C probably arises from the precipitation of carbon that remains free because of an insufficient number of vacancies. This step and one at 50°C are coupled by irradiation dosage. The 150°C peak decreases with increasing irradiation while the 50°C peak increases with increasing irradiation. This explanation of residual carbon precipitation at 150°C therefore seems likely. In unirradiated material the carbon precipitation peak occurs at 170°C while in the irradiated material it is at 150°C. This is to be expected from the acceleration of precipitation caused by the increase of precipitation nuclei, demonstrated by the ambient temperature irradiation experiments.

It is expected that there is a binding of the carbon to the vacancy traps and at some temperature the carbon will boil out of the traps. Although not shown here, the shorter irradiation curves exhibit an increase in resis-

tivity around 210°C, which we believe to arise from the carbon released from traps.

The decay step which occurs at 250°C is probably the precipitation of carbon into a metastable phase which may or may not be identical in phase to the ε phase in unirradiated carbon. The step at 300°C would correspond to the transformation of the metastable precipitate into Fe_3C.

Annealing of pure iron irradiated for an equivalent time shows no unique decay in this temperature region which substantiates the assignment of these steps to a carbon precipitation model rather than to annealing of damage in the iron lattice.

Studies by electron microscopy verify the above model in part. In unirradiated iron-carbon traces of precipitates are first evident around 150°C. In the irradiated iron-carbon the first precipitate appears around 220°C, clearly demonstrating the retardation of precipitation by low temperature irradiation.

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DISCUSSION

Sugeno, T.: I should like to comment something to Dr. Fujita's work. I and Miss K. Yokogawa of our laboratory studied the resistometric recovery of cold-worked iron containing a minute concentration of carbon (~0.0005 wt.% C). The isochronal recovery curve obtained for wire specimens strained 10% by twisting at liquid nitrogen temperature showed one minimum point at about 0°C over the range from −120°C to 60°C. It is supposed that the decreasing part of the curve may be caused by the trapping of vacancy clusters by interstitial carbon atoms and the increasing part may be caused by the interstitial atoms escaping from the trapped states. The study is now under way.

Fujita, F. E.: At present we can not say anything about a precise model for our first recovery step below 0°C, although there may be a close relation between it and your observation. From three isochronal annealing curves, the activation energy of the first step was found by rough estimate to be about 5 Kcal/mol.

Wert, C.: Do you have any comment to make about the geometrical model of the *C-V* defect?

Fujita, F. E.: No, we have not. At present, we can hardly say that the defects trapping carbon atoms are vacancies, although it is almost clear from the kinetics and electron microscopy that they are point defects.

Bullough, R.: Could you clarify the kinetics of migration of the carbon atoms to the isolated traps (vacancies)?

Fujita, F. E.: Yes, a pure random walk consideration is applicable to this case, and the second order kinetics should be expected. Actually, we could experimentally obtain the kinetics of this process from isothermal and isochronal measurements. The result is pure second order kinetics with different initial concentrations of the two reactants, in good agreement with our theoretical calculation.