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Radiation enhanced copper clustering processes in Fe–Cu alloys during electron and ion irradiations as measured by electrical resistivity

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Abstract

To study the mechanism of radiation-enhanced clustering of copper atoms in Fe–Cu alloys, in situ electrical resistivity measurements are performed during irradiation with 100 MeV carbon ions and with 2 MeV electrons at 300 K. Two kinds of highly pure Fe–Cu alloys with Cu content of 0.02 and 0.6 wt% are used. The results are summarized as follows:

(1) Although there is a steep initial resistivity increase below about 10 μdpa, the resistivity steadily decreases after this initial transient in Fe–0.6wt%Cu alloy, while in Fe–0.02wt%Cu alloy, the resistivity either decreases slowly or stays almost constant. The rate of change in resistivity depends on copper concentration.
(2) The rate of change in resistivity per dpa is larger for electron irradiation than for ion irradiation.
(3) Change in dose rate from 10^{-8} to 10^{-9} dpa/s slightly enhances the rate of resistivity change per dpa.

The decrease in resistivity with dose is considered to be due to clustering or precipitation of copper atoms. The initial abrupt increase in resistivity is too large to be accounted for by initial introduction of point defects before copper clustering. Tentatively the phenomenon is explained as due to the formation of embryos of copper precipitates with a large strain field around them. Quantitative evaluation of the results using resistivity contribution of a unit concentration of Frenkel pairs and that of copper atoms gives an important conclusion that more than one copper atom are removed from solid solution by one Frenkel pair. The clustering efficiency is surprisingly high in the present case compared with the ordinary radiation-induced or radiation-enhanced precipitation processes.

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1. Introduction

Mechanism of radiation embrittlement in pressure vessel steels of light water reactors is one of the most important subjects in recent years which is related to the plant life extension of light water reactors [1]. Copper has been known to have a strong effect on the embrittlement phenomena [2] and so-called copper-rich precipitates have been thought to be responsible for the

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embrittlement [3]. However, the exact mechanism of the role of copper has not been fully understood yet. Moreover, although the mechanism of copper transport during irradiation has been assumed via radiation enhanced diffusion by vacancy mechanism [4], the experimental evidence for the mechanism has been scarce. In particular, interstitials as well as vacancies are introduced during irradiation, so that copper migration mechanisms during irradiation have to be elucidated. In the present experiment, the role of radiation-induced point defects in the clustering of copper atoms in Fe–Cu model alloys has been studied by measuring electrical resistivity in situ during electron as well as heavy ion irradiations. In many cases, charged particle irradiations have been regarded as a means to give accelerated irradiations, but the experimental conditions chosen in the present experiments are such that the dpa rate is almost comparable to that in neutron irradiations in test reactors. To elucidate the effect of copper atoms exclusively, the specimens were prepared as pure as possible to eliminate the effects of the presence of other impurities as carbon atoms. Electrical resistivity measurements provide an excellent means to obtain information on various atomic size defects, i.e. their concentrations, interaction with each other and evolution, very sensitively and yet in a way that the results obtained are the average over the specimen volume.

In the present paper, specimens, irradiation conditions, a method of electrical resistivity measurements are described in Section 2. Experimental results are given in Section 3 in terms of dose dependence, dpa rate dependence, comparing those obtained by electron irradiations and by heavy ion irradiations. Important information can be derived from the experimental results such as copper clustering efficiency, dpa rate effects and cascade effects, which are discussed in Section 4. The conclusions are summarized in Section 5.

2. Experimental procedures

2.1. Specimens

Specimens used for electrical resistivity measurements were prepared from two kinds of highly pure Fe–Cu alloys with the copper concentration of 0.02 and 0.6 wt%. The specimens were taken from the same heat as those used in earlier experiments of the effects of high energy heavy ion irradiations on the hardness [5,6]. The chemical composition of the specimens is shown in Table 1. The final state of heat treatment was 850 °C for 10 min followed by quenching through gas cooling. The specimens were cut into ribbons of 1mm width. The thickness of the specimen was about 30 microns. Two kinds of the specimens were mounted on a copper or aluminum disk side-by-side, electrodes were spot-welded and then copper lead wires were soldered. The two specimens were electrically connected in series. The specimen geometry is shown in Fig. 1. The width of the specimens and the length between potential leads were measured using a travelling microscope.

2.2. Ion and electron irradiations

The specimens were irradiated at 300 K with 2 MeV electrons from a single-ended accelerator at Takasaki Research Establishment, JAERI and with 100 MeV carbon ions from a 20 MV tandem accelerator at Tokai Research Establishment, JAERI. The specimens were thin enough for the incident particles to penetrate completely. The specimens in position to be irradiated and the cryostat are schematically shown in Fig. 2. The same type of cryostat was used both for electron and ion irradiations. Irradiation chamber itself including the radiation shield and the specimen mounting block is isolated from ground potential, serving as a Faraday cup. To measure the beam current accurately, the specimens, the specimen holder and the radiation shield were surrounded by a secondary electron suppressor. The beam current was monitored and recorded throughout irradiation. The size of the beam-defining window was 8×8 mm^2 for electron irradiation and 10×10 mm^2 for ion irradiation.

In both irradiations, the dpa values were calculated using the displacement energy of 24 eV for pure iron [7]. We have experimentally confirmed that the same value of 24 eV can be applied to the Fe–Cu alloys as well by electron irradiations at 20 K with the electron energies ranging from 0.5 to 2 MeV [8].

The ranges of 2 MeV electrons and 100 MeV carbon ions in iron are 1.66 mm and 70.7 μm, respectively. Since the thickness of the specimen is ~30 μm, energy degradation during penetration of the incident electrons through the specimens is negligible. For 100 MeV carbon ions, there is slight energy degradation but practically all the ions penetrate through the specimen. The

Table 1
Chemical composition of the Fe–Cu alloy specimens (in wt%)

Alloy	Cu	C	Si	O	N	Fe
Fe–0.6wt%Cu	0.61	0.002	0.002	0.015	0.0006	Balance
Fe–0.02wt%Cu	0.022	0.003	0.003	0.015	0.0006	Balance

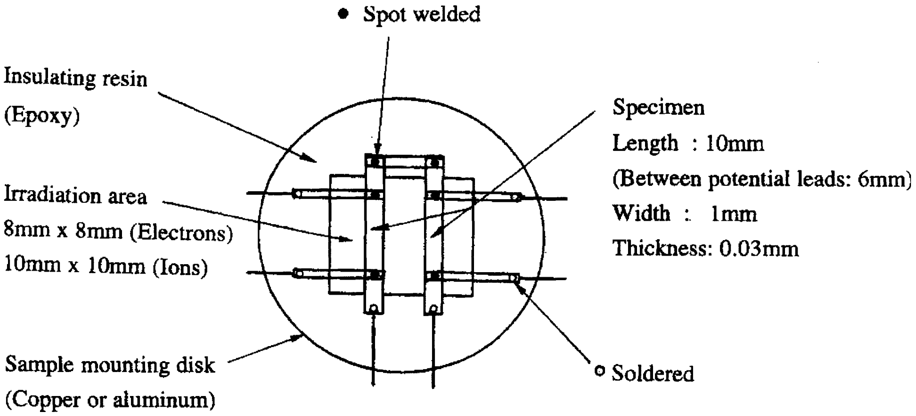

Fig. 1. Schematic drawing of a specimen holder. Two kinds of specimens are carefully glued on a copper or aluminum disk with epoxy resin. Two specimens are bridged by Fe–Cu alloy ribbon by spot welding. Potential leads are also Fe–Cu alloy ribbons, spot-welded on the sample. Bombarding area is a square, 8mm × 8mm for electron, and 10 mm × 10 mm for ion irradiations.

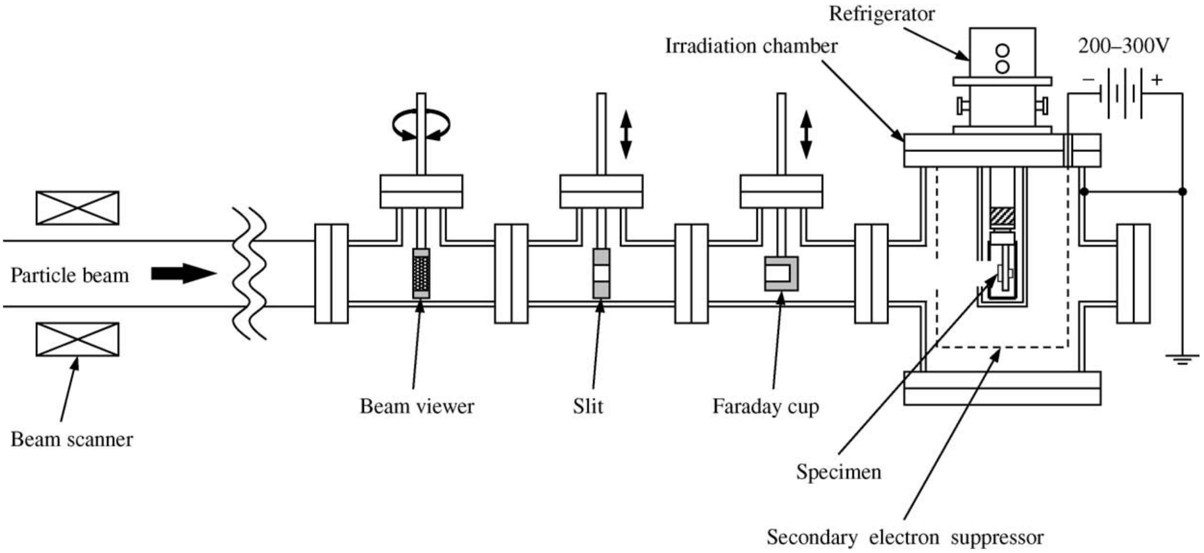

Fig. 2. Schematic drawing of an irradiation chamber. Similar setup is used for both electron and ion irradiations.

dpa values were calculated by using the TRIM code [9]. The energy loss through the specimen thickness was taken into account in the calculation.

2.3. Electrical resistivity measurements

The electrical resistivity was measured in situ by a conventional four-probe method at 300 K as a function of irradiation dose. The temperature of the specimens was measured with a platinum resistance thermometer simultaneously with the resistivity of the specimens. To assure the accuracy of the resistivity measurements, temperature must be controlled within less than 10^{-2} K. To obtain such an accuracy, temperature was slowly swept around 300 ± 0.2 K and the resistivity data were interpolated at a reference temperature, 300.00 K. The measuring system comprises two precision constant current sources, three digital voltmeters and a computer which controls the measurement sequence and for data acquisition.

3. Results

3.1. Dpa dependence of resistivity change

Fig. 3 shows the dpa dependence of resistivity change for (a) Fe–0.6wt%Cu and (b) Fe–0.02wt%Cu alloys

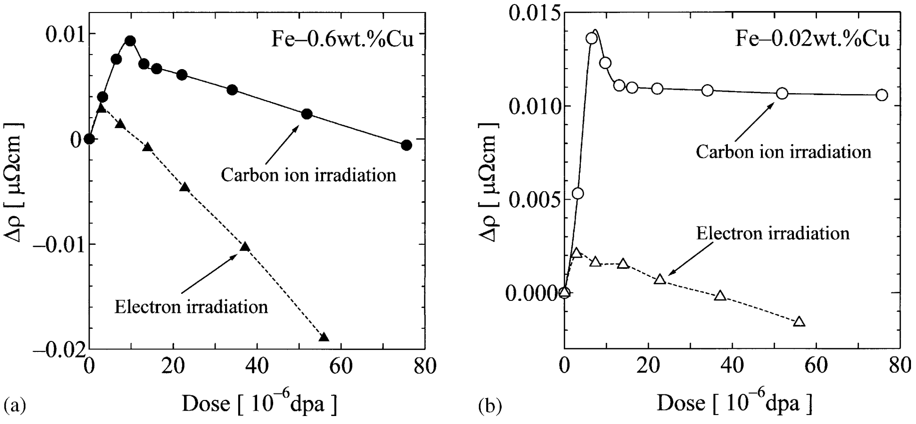

Fig. 3. Dpa dependence of electrical resistivity change by irradiations at 300 K with 2 MeV electrons and 100 MeV carbon ions; (a) Fe–0.6wt%Cu alloy, (b) Fe–0.02wt%Cu alloy.

under the same dpa rate of $(1.6–2)\times10^{-9}$ dpa/s. Several types of comparisons can be made for a set of figures. First, except for an anomalous transient behavior at the beginning of irradiation, the resistivity decreases steadily with dose. In some cases, linear steady decrease in resistivity extends to ∼140 μdpa for electron irradiation and to ∼450 μdpa for ion irradiation, which are, however, not shown in the figures. Secondly, the rate of change in resistivity is strongly dependent on copper concentration. In ion irradiation case, resistivity values become almost level off for Fe–0.02wt%Cu alloy, indicating that copper atoms are responsible for the resistivity decrease. Thirdly, the results obtained under high-energy carbon ion irradiation can be compared with those obtained under electron irradiation under almost the same dpa rate. The figure clearly shows that the electron irradiation gives higher rate of change in resistivity than heavy ion irradiation. The reason for the difference will be discussed later in terms of freely migrating defects and cascade damage.

There is a small transient region in the early stage of irradiation up to a few μdpa for electron irradiations, whereas in ion irradiations, an abrupt increase in resistivity is seen up to about 10 μdpa. It seems that the resistivity increase in the transient is larger for less Cu containing alloy for ion irradiations. However, the rate of resistivity increase in the transient regime is almost the same for electron and ion irradiations, being about 10^3 μΩ cm/dpa.

The transient behavior can be eliminated by a small amount of pre-irradiation. Even though the initial transient is eliminated, the rate of resistivity decrease in the steady state regime does not seem to be altered by the pre-irradiation.

3.2. Effect of dpa rate

Fig. 4 shows the effect of dpa rate on the resistivity change for (a) Fe–0.6wt%Cu and (b) Fe–0.02wt%Cu alloys. The dpa rate ranges from 10^{-9} dpa/s (low dpa

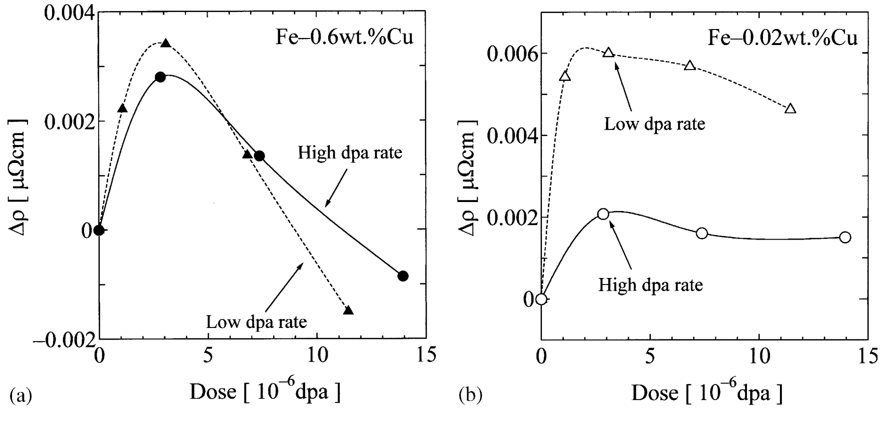

Fig. 4. Dpa rate dependence of electrical resistivity change by irradiation with 2 MeV electrons at 300 K. Here, high dpa rate is around 10^{-8}dpa/s, whereas low dpa rate is about 10^{-9}dpa/s. (a) Fe–0.6wt%Cu alloy, (b) Fe–0.02wt%Cu alloy.

rate) to 10^{-8} dpa/s (high dpa rate). Note these values are in a same order of magnitude to those of typical test reactor conditions. There is a general tendency in both electron and ion irradiations that for lower dpa rate, the rate of change in resistivity is larger as clearly observed in Fig. 4(a) for Fe–0.6wt%Cu alloy. Similar tendency has also been observed in ion irradiation case using hardness change measurements [10]. This is also consistent with the generally accepted view that the formation process of copper rich precipitates in commercial pressure vessel steels also depends on dose rate. For Fe–0.02wt%Cu alloy, similar trend seems to exist, i.e. the resistivity tends to decrease for both high and low dpa-rate, but the dpa-rate dependence is less clear because the change in resistivity is very small (Fig. 4(b)).

4. Discussion

4.1. The mechanism of resistivity decrease

It has been confirmed in our work using the same alloys on the recovery stages up to 300 K following ion irradiations at about 7 K, or electron irradiations at about 11 K [8], that the general trend of the annealing curves is quite similar to that for pure iron [11]. However, there are some indications that interaction between self interstitials and copper atoms does exist as evidenced by a slight decrease in the amount of Stage I_D and appearance of a bump at 130 K, which is presumably dependent on copper concentration. Although interstitial migration is not a central issue of the present paper, recent molecular dynamics studies in pure Fe and Fe–Cu alloys have indicated only a very modest effect of copper solute atoms on self interstitial atom and cluster migration [12]. Correspondingly, these authors consider that interstitials have negligible effect on copper atom transport. Vacancies in highly pure alloys may be mobile at about 250 K from the appearance of Stage III similar to the case of pure iron. Most of the radiation induced defects (90%) are annihilated by annealing up to 300 K.

From the background information stated above, vacancies should be mobile during irradiation at 300 K. Copper atoms, which have been postulated to be mobile via vacancy mechanism, may also migrate during irradiation at 300 K. The resistivity decrease may be due to removal of copper atoms from solid solution. The removed copper atoms may form copper clusters or copper precipitates. The initial transient may be due to the nucleation process of such clusters. It may be possible for the small embryos to increase the resistivity due to strain field around them. Alternatively, soon after the onset of irradiation, simple point defects, vacancies and interstitials, first accumulate but as the concentrations increase, point defect clusters are formed, acting as the precipitation sites for copper atoms. Both interstitial and vacancy clusters may provide site for copper precipitation according to a large-scale molecular static calculation for point defects-copper atom system [13]. If this is the case, interstitial annihilation and interstitial interaction with copper atoms occurring even at low temperature around 100–300 K may have some effects on copper precipitation under irradiation around 300 K. These arguments are speculative and further evidences are required to reach a final conclusion, e.g. from lifetime and coincidence Doppler broadening measurements of positrons at cryogenic temperatures. In any case, it might be suggestive that the slope of the initial resistivity change in the transient regime is about 10^3 μΩ cm/dpa, which is similar to the Frenkel pair resistivity of 12.5 μΩ cm/% Frenkel pair (= 1250 μΩ cm/dpa) [7], which is too large to be accounted for by the surviving defects at 300 K.

4.2. The role of point defects on copper clustering

At 300 K, vacancies can be mobile because the vacancy migration stage (Stage III) appears around 250 K [11]. There is evidence that the copper clustering process occurs during irradiation. The resistivity values after irradiation do not show any change with time, even after leaving the specimen overnight at 300 K. Therefore, we conclude that the copper clustering occurs during irradiation where production and annihilation of point defects are vigorously occurring. As discussed above, interstitials may contribute to the transport of copper atoms because of the presence of weak interaction shown in isochronal annealing curves. The number of copper atoms removed from solid solution per Frenkel pair can be estimated using the resistivity contribution of an atomic percent of copper atoms of about 2.5 μΩ cm/at.% Cu [8]. The slope of resistivity change in Fig. 3(a) is about 0.02 μΩ cm per 50 μdpa (∼400 μΩ cm per Frenkel pair), implying about 1.6 copper atoms are removed from solid solution per Frenkel pair introduced by electron irradiation. This is a very efficient process indicating that more than one copper atom is transported to cluster sites by one vacancy-interstitial pair produced. In the case of ion irradiation, the slope gives ∼120 μΩ cm per dpa. The difference between electron and ion irradiations may be ascribed to the difference in the fraction of freely migrating defects (FMD). If the fraction of FMD, ξ, for electrons is assumed to be 1, then $\xi = 0.3$ for 100 MeV carbon ions.

Copper atoms have been thought to migrate by vacancy mechanism for a long time. At the same time, there have been experimental evidences that copper atoms form clusters on dislocations or on grain boundaries, both of which act as sinks for point defects. This cannot be accounted for by a simple site-exchange mechanism with a vacancy. Soneda et al. have examined the effect of radiation induced point defects on copper atom clustering [13], arriving at a conclusion that copper atoms may migrate by 'soft' vacancy-drag mechanism, by which copper atoms can be transported to vacancy sinks. By this mechanism, a vacancy can carry copper atoms many times. The possibility of interstitial involvement in copper atom diffusion directly by a mixed dumbbell mechanism should be very low by energetical considerations. Needless to say, interstitials are indirectly involved in the clustering of copper atoms through recombination with vacancies during irradiation.

5. Conclusion

(1) Resistivity is a sensitive means to detect small changes in defect microstructure. Changes occurring during low dpa rate comparable to test reactor irradiations (10^{-9} dpa/s) can be measured.
(2) At 300 K, in Fe–0.6wt% Cu alloy, after initial transient, resistivity decreases steadily, indicating that copper precipitation process is taking place during irradiation.
(3) Change in resistivity takes place during irradiation. The change does not occur in such a way that the defects surviving after irradiation at 300 K are responsible for transporting copper atoms. In that sense, indirect role of interstitials cannot be discarded.
(4) From the rate of change in resistivity, the number of copper atoms removed from solid solution per Frenkel pair can be derived. The efficiency is very high, of the order of one copper atom removed from solid solution per Frenkel pair. Taking into account the fact that considerable fraction of point defects should be annihilated by mutual recombination, this high efficiency should imply that one point defect (probably vacancy) could transport many copper atoms before annihilation.
(5) From the comparison between resistivity decreasing rate in the steady state regime for electron and ion irradiations, the FMD fraction, ξ, is evaluated to be 1 for electrons, 0.3 for 100 MeV carbon ions.
(6) At 300 K, there is a slight dpa rate dependence on copper precipitation rate. In the dpa rate range from 10^{-9} to 10^{-8} dpa/s, the lower dpa rate gives higher rate of resistivity decrease.

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