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# Hardening of Fe–Cu alloys by swift heavy ion irradiation

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**Abstract**

Two kinds of model alloys, Fe–0.6 wt.% Cu and Fe–1.2 wt.% Cu, are irradiated with GeV heavy ions at 250 °C and at room temperature. Vickers microhardness test at room temperature shows that the change in hardness due to irradiation strongly depends on the irradiation temperature and the copper content. For Fe–1.2 wt.% Cu alloy irradiated at 250 °C, the hardness change is much larger than that for 2.5 MeV electron irradiation at the same dpa (displacements per atom through elastic collisions). The experimental result implies that the electronic excitation by GeV ions enhances the copper precipitation. This effect is, however, hardly observed for Fe–0.6 wt.% Cu alloy or for the irradiation at room temperature.



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## 1. Introduction

Irradiation-induced hardening of ferritic alloys is one of the important phenomena concerning the nuclear reactor safety, since it may result in the embrittlement of reactor pressure vessel steels. From such a practical point of view, much work on irradiation-induced hardening in ferritic alloys has been carried out so far by using test reactor neutron irradiation [1] and under commercial reactor surveillance programs [2]. Electron irradiation has also been performed to simulate the effects of gamma-rays on hardening [3–5]. The role of copper atoms on the hardening has been of great interest because the precipitates of copper atoms, which are produced under irradiation, have been regarded as effective obstacles against the motion of dislocations, leading to the hardening of materials [6,7].

To study the mechanism of irradiation induced Cu precipitation and the effects on the mechanical properties, irradiation with high energy (>1 MeV/u) ions is very useful [8] since some important

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parameters which dominate the Cu precipitation, i.e. irradiation temperature, irradiation dose (dpa), dose rate and energy of primary knock-on atoms, can be controlled independently by changing the mass and the energy of ions. Also, the projected range of high energy ions is several μm or more and we can easily measure the Vickers microhardness at the surface of the irradiated specimens.

In the case of high energy ion irradiations, most of the ion energy is lost in the target through the excitation of target electrons. However, the irradiation-induced Cu precipitation has been discussed so far in terms of the elastic collisions between irradiating particles and target atoms, and the effect of the electronic excitation has scarcely been considered.

About 3 years ago, Barbu et al. reported that the effect of electronic excitation on copper precipitation appeared in Fe–1.3 wt.% Cu alloy irradiated with 5.1 GeV Kr ions at 290 °C [9]. They measured the change in electrical resistivity due to irradiation, and compared the result with those for 188 MeV O ion irradiation and for 2.5 MeV electron irradiation [10]. They found that the decrease in electrical resistivity by Kr irradiation was much larger than those by the other particles on a dpa basis, and concluded that the electronic excitation by GeV Kr ions induced copper precipitation along the ion path. They confirmed the phenomenon by Vickers microhardness measurement; even at a small fluence of Kr ions, a remarkable increase in hardness was observed. This phenomenon is very interesting from a fundamental point of view, and also we need the details of the role of the electronic excitation to simulate the neutron irradiation effect on copper precipitation by using high energy ions. The mechanism of copper precipitation through the electronic excitation has, however, still remained uncertain. To clarify the mechanism, we have to investigate the dependence of copper precipitation on several parameters which will dominate the phenomenon, i.e. irradiation temperature, copper content and so on.

In this paper, we report the result of Vickers microhardness measurements in Fe–0.6 wt.% Cu and Fe–1.2 wt.% Cu alloys irradiated with 3.54 GeV Xe at 250 °C and with 3.80 GeV Ta ions at room temperature. The dependences of hardness change due to irradiation on copper content and irradiation temperature are discussed.

## 2. Experimental procedure

Two model alloys, Fe–0.6 wt.% Cu and Fe–1.2 wt.% Cu, were selected for the present experiment. As shown in Table 1, the content of impurities other than copper was very small. Specimens, 7 mm × 7 mm × 1 mm in dimension, were solution annealed at 850 °C and then were quenched into water. This process made Cu atoms dissolve supersaturatedly in the iron lattice. The specimens were irradiated with 3.54 GeV (26 MeV/u) Xe ions at 250 °C, and with 3.80 GeV Ta (21 MeV/u) Ta ions at room temperature using RIKEN ring cyclotron. To assist the irradiation uniformly on the target, the ion beam was wobbled in horizontal and vertical directions. The ion beam current was kept below 0.6 particle nA during irradiation to avoid the beam heating. The specimen temperature, which was controlled by a lamp heater, was monitored using a type-K thermocouple attached to the specimen holder.

Before and after irradiation, Vickers microhardness was measured at room temperature with a load of 100 gf, where the indent depth was about 6 μm. Hardness was measured at 10 points for each specimen. The experimental uncertainty of measured hardness was about ±5. As it is believed that

Table 1
Element compositions of the Fe–Cu model alloys in wt.%

| Specimen | Chemical composition (wt.%) | | | | | |
|---|---|---|---|---|---|---|
| | Cu | C | Si | O | N | Fe |
| Fe–1.2 wt.% Cu | 1.19 | 0.002 | 0.001 | 0.013 | 0.0006 | Balance |
| Fe–0.6 wt.% Cu | 0.61 | 0.002 | 0.001 | 0.013 | 0.0006 | Balance |

Table 2
Characteristics of the irradiations with Xe and Ta ions for Fe–1.2 wt.% Cu and Fe–0.6 wt.% Cu targets

| ion | $E$ (GeV) | $R_p$ (μm) | $S_e$ (MeV/(mg/cm$^2$)) | $\sigma_d$ (cm$^2$) | $T_{1/2}$ (keV) |
|---|---|---|---|---|---|
| $^{136}$Xe | 3.54 | 117 | 34 | $6.6 \times 10^{-18}$ | 6.7 |
| $^{181}$Ta | 3.80 | 83 | 60 | $1.5 \times 10^{-17}$ | 9.3 |

Incident energy ($E$), projected range ($R_p$), electronic stopping power ($S_e$), cross-section for defect production through elastic collisions ($\sigma_d$) and PKA median energy ($T_{1/2}$). $S_e$ and $\sigma_d$ are average values over the depth interval of 0–30 μm. $T_{1/2}$ is calculated for pure iron and not for Fe–Cu target.

the depth of resulting plastic deformation is about five times as large as that of indent depth [11], the deformation area is expected to extend to the depth of 30 μm in the present experiment.

The projected range, $R_p$, the electronic stopping power, $S_e$, and the cross-section for defect production through elastic collisions, $\sigma_d$, were calculated by means of TRIM98 code for each combination of irradiating ion and target material. In the calculation, we used the value of 40 eV as the threshold energy for atomic displacement [12]. The values of these parameters are almost the same for Fe–1.2 wt.% Cu and Fe–0.6 wt.% Cu alloys. The result is listed in Table 2. As can be seen in the table, the projected range is several times larger than the depth of plastic deformation. This means that the change in $S_e$ and $\sigma_d$ is small through the depth of plastic deformation. In fact, the values of $S_e$ and $\sigma_d$ for Xe ions vary only 10–25% over the depth interval of 0–30 μm. In the table, we list the average values of $S_e$ and $\sigma_d$ over this depth. To calculate the value of dpa for each irradiation, we multiplied the averaged $\sigma_d$ by the ion fluence.

For some specimens, we measured the depth dependence of hardness by varying the applied load from 3 to 500 gf.

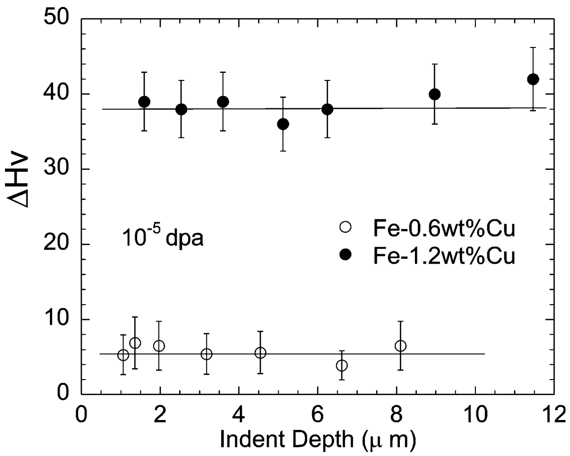


Fig. 1. Dependence of microhardness change on indent depth for Fe–1.2 wt.% Cu and Fe–0.6 wt.% Cu specimens irradiated with 3.54 GeV Xe ions up to $10^{-5}$ dpa at 250 °C.

## 3. Results and discussion

Fig. 1 shows the profile of the change in Vickers microhardness obtained in Fe–0.6 wt.% Cu and Fe–1.2 wt.% Cu specimens irradiated with Xe ions up to $10^{-5}$ dpa at 250 °C. The abscissa indicates the indent depth. For the both alloys, the microhardness change does not depend on the indent depth. This means that the irradiation affects the specimen nearly homogeneously over the observed depth, which is expected from the depth profile of $S_e$ and $\sigma_d$. Under such a condition, we do not need to consider the distribution of damage through the specimen depth, and can obtain the irradiation effect more quantitatively as a function of dpa and/or $S_e$ than in the case of inhomogeneous damage distribution.

In Fig. 2(a) and (b), the change in Vickers microhardness measured with the load of 100 gf, is plotted against the calculated dpa for Fe–1.2 wt.% Cu and Fe–0.6 wt.% Cu specimens, respectively. In the figures, data for Ta irradiation at room temperature are also plotted. For comparison, the results for 2.5 MeV electron-irradiated specimens are shown [5]. Their irradiation temperature is the same as for Xe ion irradiation (250 °C). The dpa rate for electron irradiation ($6.5 \times 10^{-9}$ dpa/s) is, however, a little smaller than that for Xe and Ta

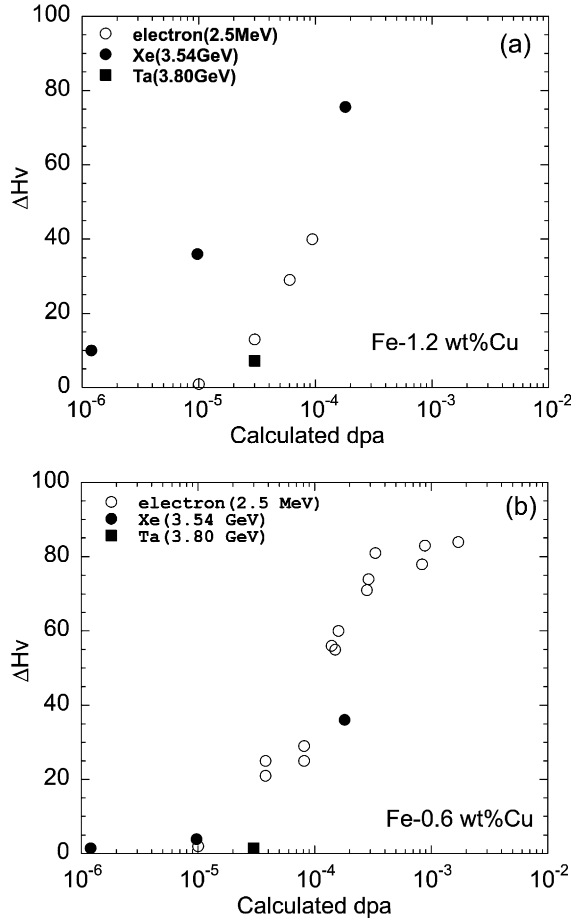


Fig. 2. Dpa dependence of irradiation-induced changes in microhardness for Fe–1.2 wt.% Cu (a) and Fe–0.6 wt.% Cu (b) specimens irradiated with 3.54 GeV Xe ions at 250 °C and 3.8 GeV Ta ions at room temperature. Data for electron irradiation at 250 °C [5] are also plotted for comparison.

irradiations ($1 \times 10^{-8}$–$1.6 \times 10^{-8}$ dpa/s). An ion irradiation experiment of Fe–Cu alloys has shown that the dependence of hardness change, $\Delta H_v$, on the dpa rate can be expressed as $\Delta H_v \approx (\text{dpa rate})^n$, where $n$ is $-1/3$ to $-1/5$ [13]. Therefore, a small difference in dpa rate does hardly affect the value of irradiation-induced hardness change, and we can directly compare the results for electrons with those for the GeV ions.

As can be seen in Fig. 2(a), the microhardness change for Fe–1.2 wt.% Cu alloy irradiated with Xe ions at 250 °C is much larger than that for electron irradiation. The hardness change can be observed even at $1 \times 10^{-6}$ dpa, and the value of $\Delta H_v$ reaches 40 at $1 \times 10^{-5}$ dpa. For electron irradiation, the dose of $1 \times 10^{-4}$ dpa is needed to obtain the same $\Delta H_v$ value. On a calculated dpa basis, the 3.54 GeV Xe irradiation is about 10 times as effective as the electron irradiation. On the other hand, in the case of Fe–0.6 wt.% Cu alloy, we can hardly observe any marked difference in hardness change between Xe ion irradiation and electron irradiation (Fig. 2(b)). Considering the experimental uncertainty, the data for both irradiations can well be scaled with the calculated dpa. For 3.80 GeV Ta ion irradiated specimen, where the irradiation temperature is room temperature and not 250 °C, the microhardness change due to irradiation is quite small in the both alloys.

One of the remarkable differences between GeV ion irradiation and electron irradiation appears in the energy spectrum of the atoms primarily knocked-on elastically from the regular site. Fig. 3 shows $W(T)$, the fraction of energy of displacements elastically produced by primary knock-on atoms with energies below $T$ for 3.5 GeV Xe ions, 3.8 GeV Ta ions and 2.5 MeV electrons. The value of $T$, which meets the equation of $W(T) = 0.5$, is called the PKA median energy, $T_{1/2}$ [14,15]. The

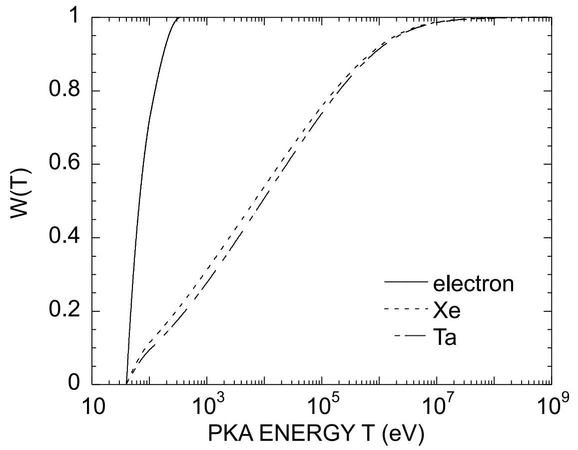


Fig. 3. Fraction of energy of displacements elastically produced by primary knock-on atoms with energies below $T$ for 3.54 GeV Xe ions, 3.8 GeV Ta ions and 2.5 MeV electrons. Target is pure iron.

parameter, $T_{1/2}$ expresses how dense the energy of irradiating particles is deposited elastically in the target material. The values of $T_{1/2}$ for the Xe and Ta irradiations are listed in the last column of Table 2. Although they are calculated for pure iron, the values are expected to be almost the same as for the Fe–Cu alloys.

Through ion irradiation experiments, Rehn et al. have found that the amount of radiation-induced segregation (RIS) in some alloys is strongly correlated with the value of $T_{1/2}$ for irradiating ions [16,17]. They have explained the $T_{1/2}$ dependence of RIS in terms of production efficiency of freely migrating defects (FMDs). For the irradiation with larger $T_{1/2}$, the efficiency of FMD production is smaller, and the amount of RIS, which is caused by the interaction of FMDs with solute atoms, becomes smaller. If FMDs, which were produced by elastic collisions, also dominated the copper precipitation during the irradiation in the present Fe–Cu alloys, the hardness change due to Xe ion irradiation would be smaller than that due to electron irradiation, $T_{1/2}$ for which is 67 eV. This is not what we observe in Xe ion irradiated Fe–1.2 wt.% Cu specimen. The remarkably large hardening in Xe irradiated Fe–1.2 wt.% Cu alloy is, therefore, not attributed to the production efficiency of FMDs which are induced by elastic collisions.

As the present result cannot be explained within the framework of elastic collisions, we next consider the effect of the high density electronic excitation by GeV ions. The present experiment shows that the remarkably large hardness change is observed clearly in Fe–1.2 wt.% Cu alloy and not in Fe–0.6 wt.% Cu alloy. This means that the Cu precipitation plays an important role in the phenomenon. As the copper precipitation can occur only under the existence of point defects (vacancies) and their thermal diffusion, we can qualitatively explain the large change in hardness in Fe–1.2 wt.% Cu alloy irradiated with GeV Xe ions at 250 °C as follows; high density electronic excitation induced by GeV ions produces point defects, and their thermal diffusion enhances the precipitation of copper atoms, leading to the additional increase in hardness. At room temperature, even if point defects are produced through electronic excitation, their thermal diffusion is not sufficient for the occurrence of Cu precipitation which causes the hardness change.

The above explanation, in which we assume that the number of defects produced through electronic excitation is larger than expected from the result of elastic collisions, is not consistent with the result obtained by the low temperature irradiation experiments in pure Fe. Dunlop et al. have shown that the role of swift ions with $S_e$ around 35 MeV/(mg/cm$^2$) is mainly the annihilation of already existing defects and not the defect production [18]. Our recent experiments also show that the damage efficiency, which is defined as the ratio of experimental defect production cross-section to the cross-section calculated by TRIM code, is still smaller for 3.5 GeV Xe ions than that for 2.0 MeV electrons [19]. To explain the difference in electronic excitation effects between at low temperature and at elevated temperatures, we may have to consider the effect of thermal lattice vibration on the electronic excitation induced defect production in pure Fe and Fe based alloys.

For Fe–0.6 wt.% Cu specimen, though the Xe irradiation was also performed at 250 °C, the electronic excitation effect was hardly observed. This result shows that there exists some threshold value of copper content, below which the effect of high density electronic excitation does not appear as the change in hardness.

## 4. Summary

Two model alloys, Fe–0.6 wt.% Cu and Fe–1.2 wt.% Cu, were irradiated with 3.54 GeV Xe ions at 250 °C and with 3.80 GeV Ta ions at room temperature. The change in hardness due to irradiation was measured by using Vickers microhardness tester. The change in hardness observed in Fe–1.2 wt.% Cu alloy irradiated with Xe ions at 250 °C is remarkably larger than for electron irradiation on a calculated dpa basis. For both of Fe–0.6 wt.% Cu and Fe–1.2 wt.% Cu alloys irradiated with 3.80 GeV Ta ions at room temperature, the change in microhardness is quite small. The experimental result implies that the thermal diffusion of defects produced through the electronic excitation by GeV ions enhances the precipitation of copper atoms in Fe–1.2 wt.% Cu alloy.

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