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Use of high energy ions for the mechanistic study of irradiation embrittlement in pressure vessel steels using Fe–Cu model alloys

K. Morita [a,b,1], S. Ishino [a,*], T. Tobita [b], Y. Chimi [b], N. Ishikawa [b], A. Iwase [b]

[a] *Department of Applied Science, Tokai University, 1117 Kitakaname, Hiratsukashi, Kanagawa-ken 259-1292, Japan*

[b] *Japan Atomic Energy Research Institute (JAERI), Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan*

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Abstract

To study the mechanism of irradiation embrittlement in pressure vessel steels, it is necessary to sort out the irradiation parameter dependence, which is particularly complex in the neutron irradiation case. Irradiation with high energy heavy ions allows us to carry out single parameter experiments, thereby providing basic data for the modelling of irradiation embrittlement. In this study using Fe–Cu model alloys, three important parameters (ion fluence, irradiation temperature and copper concentration) are selected and irradiation induced Vickers hardness change is measured. The hardness change shows a steep increase with fluence after a certain incubation dose. The irradiation temperature dependence of hardness change at fixed fluence shows a peak at around 250–300 °C. Shift of irradiation temperature dependence from neutron irradiation case may be ascribed to the difference in dose rate. Copper concentration dependence shows that the change in hardness seems to depend on the square root of copper concentration. This supports the dispersed barrier hardening model.

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1. Introduction

Pressure vessel of a light water reactor is a demanding component, required to have a full integrity throughout the reactor lifetime with high credibility. There are various degradation modes known for the pressure vessel as neutron irradiation embrittlement, stress corrosion cracking, fatigue and so on. Among them, the most important mechanism is the neutron irradiation embrittlement [1] and in fact power reactors currently in service have been equipped with surveillance test coupons, thereby confirming the integrity during the whole lifetime of the reactor. This is a corroborative approach, having its own limitations such that the generic application to other reactor types or to different service conditions is difficult. Large allowance to cover inherent ambiguity is imposing drawback for the demand of plant life extension. There has been a growing need to establish a novel method of evaluation of degradation based on the understanding of the mechanisms of neutron irradiation embrittlement. One way to the understanding of the mechanisms is establishing a modelling using a number of reliable data obtained under simplified experimental conditions. In this context, use of ion irradiation is growing rapidly for the study of embrittlement

* Corresponding author. Tel.: +81-463 58 1211x4153/+81-3 3488 2756; fax: +81-463 50 2017/+81-3 3488 0589.

E-mail address: ishino@keyaki.cc.u-tokai.ac.jp (S. Ishino).

[1] Present address: Japan Power Engineering and Inspection Corporation (JAPEIC), Shin-Toranomon Bldg., 5-11 Akasaka 1-chome, Minato-ku, Tokyo 107-0052 Japan.

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mechanisms under well controlled conditions, which are difficult to obtain for neutron irradiations.

Since the damage production process by ion irradiations is different from that by neutron irradiations, it is not possible to directly compare the ion irradiation results with neutron irradiation results. However, displacement damage produced by elastic collisions is essentially the same for both cases. Moreover, ion irradiations have great advantages over neutron irradiations in that

(1) the degree of activation is much lower for ion irradiation case to allow efficient post irradiation experiments mostly without using hot laboratories,
(2) high damage levels are easily attainable within a short irradiation time,
(3) irradiation parameters can be controlled without much difficulty.

One of the biggest disadvantages is that the displacement damage is distributed non-uniformly near the specimen surface, if the energy of the heavy ions used is in a medium or low energy range mostly below several MeV [2,3]. Experimental methods to quantify the radiation damage is greatly restricted with such relatively low energy ion irradiations; transmission electron microscopy and micro-indentation hardness measurements are examples of available methods. Ambiguity comes in to interpret the experimental results because the damaged region is very close to the specimen surface. Use of high energy ions will resolve major parts of these difficulties, but such a trial has seldom been reported largely because such facilities are not readily available. In this paper, we will report the first results of applying high energy heavy ions with an energy range of around 100 MeV to solve a practical material problem.

Generally accepted mechanism of irradiation embrittlement in pressure vessel steels has been that radiation hardening, $\Delta\sigma_{total}$, is the sum of matrix hardening and the hardening due to radiation-enhanced copper precipitation [4,5]. In recent years, most extensive studies have been focused on the so-called copper precipitates, which are now regarded not as pure copper precipitates but as copper-rich precipitates (CRP) formed during neutron irradiation by radiation-enhanced diffusion at the reactor operating temperature of ~300 °C. However, the details of the nature, structure and the process of formation of the CRPs have not been fully clarified yet.

Objective of the present study is to investigate the radiation embrittlement mechanisms by measuring the change in hardness in Fe–Cu model alloys using high energy heavy ion irradiations. The experimental matrices were chosen as simple as possible to obtain clear-cut information. Experimental parameters systematically varied were ion fluence, irradiation temperature and copper concentration in Fe–Cu alloys.

In this paper, experimental details are described in Section 2, followed by experimental results for three major irradiation parameters in Section 3. The results are discussed in Section 4, comparing with existing neutron irradiation data and with other experimental data.

2. Experimental procedure

2.1. Specimen

Several high purity Fe–Cu alloys were prepared. The copper concentrations were varied to be 0.02, 0.1, 0.6 and 1.2 wt%. Chemical analysis of the specimens is shown in Table 1. The specimens were supplied in a block form after hot rolling and heat treatment by Hitachi Kyowa Engineering Co. The final heat treatment was solution-annealing at 850 °C for 2 h and then water quenching. Specimens were cut from a large ingot into small plates of $7 \times 7 \times 1$ mm^3 by wet polisher, mechanically polished carefully and finally electrolytically polished just before irradiation.

2.2. Irradiation

Irradiations were performed using a 20 MV tandem accelerator at Japan Atomic Energy Research Institute, Tokai Research Establishment with 200 MeV $^{197}Au^{13+}$ ions. The damage distribution by the 200 MeV Au^{13+} ions was calculated by the TRIM code using a displacement energy of 40 eV. The result is represented in Fig. 1.

Table 1
Chemical analysis of Fe–Cu model alloys after final heat treatment

Specimen	Chemical composition (wt%)					
	Cu	C	Si	O	N	Fe
Fe–0.02 wt%Cu	0.022	0.003	0.003	0.015	0.0006	Balance
Fe–0.1 wt%Cu	0.10	0.002	0.003	0.014	0.0005	Balance
Fe–0.6 wt%Cu	0.61	0.002	0.001	0.013	0.0006	Balance
Fe–1.2 wt%Cu	1.19	0.002	0.001	0.013	0.0006	Balance

Schematic representation of an irradiation chamber is shown in Fig. 2(a). The chamber was electrically insulated from the ground, being served as a Faraday cup, i.e. the ion beam current passing through a beam-defining slit could be collected and measured. The voltage of −250 V was applied to a secondary electron suppressor surrounding the specimen holder. Specimen mount was a copper block embedded with a K-type thermocouple, at the rear side of which a halogen lamp heater was equipped. This allowed irradiation at elevated temperatures up to 400 °C. Because of low beam current, beam heating was negligibly small. Thermal trap tank was filled with coolant water to avoid heating of the other parts of the chamber except the specimen block. Specimen temperature was calibrated against the copper block temperature. The difference between both temperatures was small so that irradiation temperature was represented by the copper block temperature. Irradiation conditions are summarized in Table 2. In each experimental condition, four types of the alloys were irradiated simultaneously side by side to give the same irradiation conditions for them as shown in Fig. 2(b). By using an appropriate masking plate, irradiated and

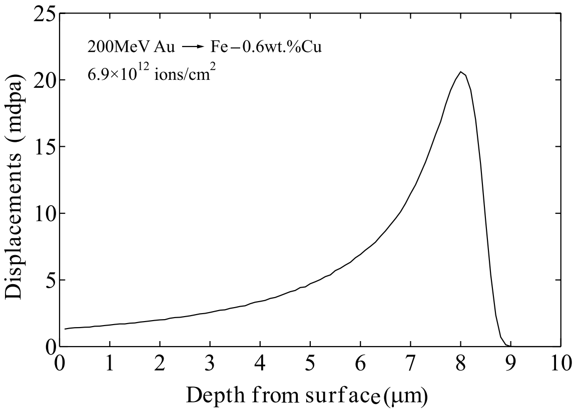

Fig. 1. Damage distribution in Fe–0.6 wt% Cu alloy irradiated with 200 MeV Au ions as calculated by the TRIM code. Dpa values are for an ion fluence of 6.9×10^{12} ions/cm^2.

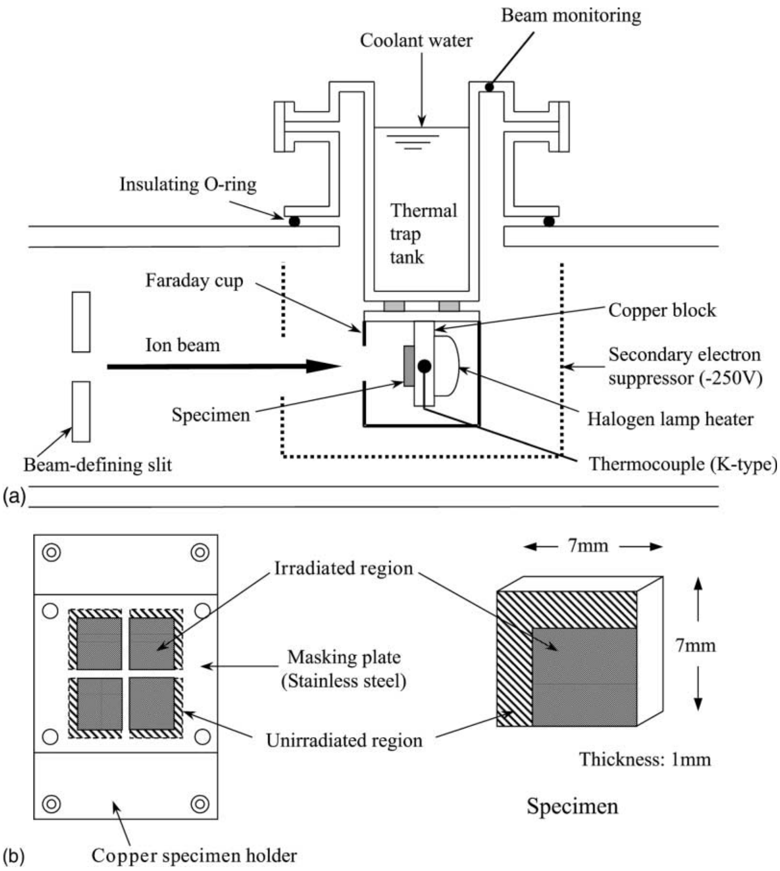

Fig. 2. (a) Schematic representation of irradiation chamber with specimen in position to be irradiated. (b) Specimen mounting, showing that four kinds of specimens are in side-by-side position to be irradiated simultaneously. With an appropriate masking, unirradiated regions with the same thermal history as the irradiated regions are formed.

Table 2
Irradiation conditions (ions: 200 MeV Au^{13+})[a]

	Irradiation temperature (°C)					
	Room temperature	200	250	300	350	400
Fluence (ions/cm^2)	8.4×10^{10}	–	9.0×10^{10}	–	–	–
	8.6×10^{11}	–	9.2×10^{11}	–	–	–
	5.7×10^{12}	5.0×10^{12}	6.7×10^{12}	5.1×10^{12}	5.0×10^{12}	5.2×10^{12}

[a] Four kinds of specimens with varied copper concentrations were irradiated side by side exactly under the same condition.

unirradiated regions were made in each of the specimens.

2.3. Hardness measurement

An Akashi MVK-E Microhardness tester was used for hardness measurements. Conventional Vickers hardness number was derived for irradiated and unirradiated regions. From these results, hardness changes, ΔH_v, were obtained.

The load of hardness measurements reflects damage distribution from the surface. We have examined the load dependence of hardness with fixed holding time of 15 s [6], selecting the load of 10 gf throughout the present experiment.

3. Results

3.1. Ion fluence dependence

Fig. 3(a) and (b) show the ion fluence dependence of ΔH_v for irradiation (a) at room temperature and (b) at 250 °C, respectively. For irradiation at room temperature, hardness change is small except for Fe–1.2 wt% Cu alloy irradiated to a fluence of 6×10^{12} ions/cm^2. For irradiation at 250 °C, the alloys with higher copper content show a remarkable increase in hardness, whereas for a low fluence and in specimens with lower Cu content, the hardness changes are small. It seems that beyond a certain fluence level and above a certain copper concentration, ΔH_v increases with fluence with almost an identical slope. The tendency is similar to the trend curve for ΔDBTT [7].

3.2. Irradiation temperature dependence

Fig. 4 shows the dependence of ΔH_v on irradiation temperature for the highest fluence of 200 MeV Au ion irradiation, i.e. 5.0–6.7 $\times 10^{12}$ ions/cm^2. Dependence of the effect of irradiation temperature on copper concentration is clearly observed, but for Fe–0.02 wt% Cu and Fe–0.1 wt% Cu alloys, the irradiation temperature dependence of hardening is small and the difference is not clear. Probably due to copper clustering or 'precipitation' which is controlling the hardness change in this regime, the hardening is most remarkable for irradiations around 250–300 °C. Conversely, the peak temperature does not depend on copper concentration as shown by arrows. Above the peak temperature, the hardening decreases presumably due to decomposition of the precipitates or coarsening of the precipitates.

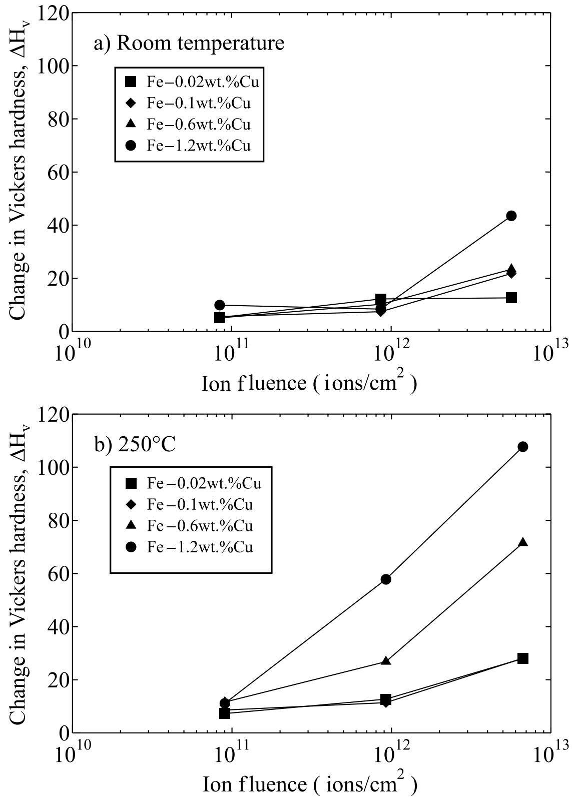

Fig. 3. Fluence dependence of hardness change (a) at room temperature and (b) at 250 °C.

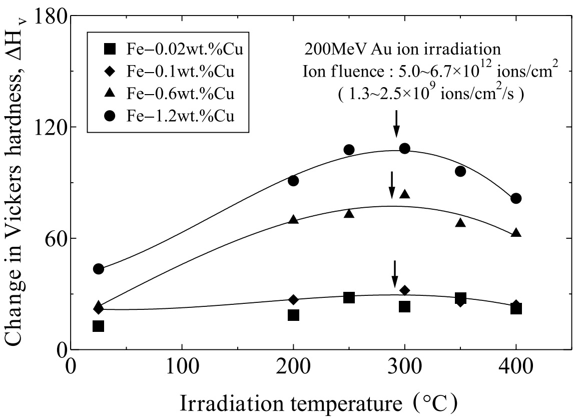

Fig. 4. Irradiation temperature dependence of hardness change for a common constant fluence of 5.0–6.7 × 10^{12} ions/cm^2 for specimens containing various concentration of copper. Arrows indicate peak positions.

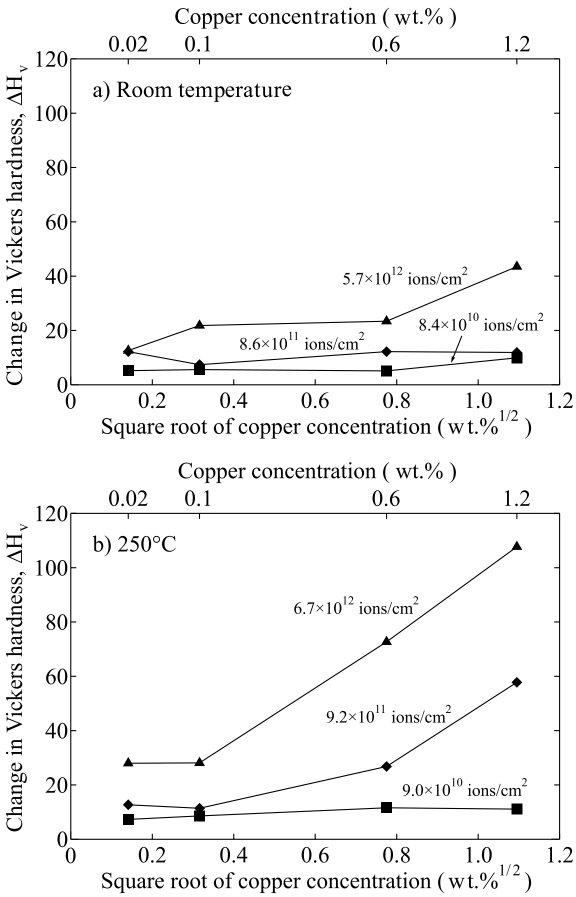

Fig. 5. Copper concentration dependence of hardness change (a) at room temperature and (b) at 250 °C. Abscissa is scaled by square root of copper concentration.

Below the peak temperature, the process of copper clustering may be more sluggish at lower temperatures and less precipitates are formed.

3.3. Copper concentration dependence

Fig. 5 shows the change in hardness plotted as a function of square root of copper concentration for irradiations (a) at room temperature and (b) at 250 °C for three fluence levels. Above a certain fluence, irradiation temperature and copper content, the hardness change seems to be proportional to the square root of copper concentration.

4. Discussion

4.1. General remarks

Present results have shown that heavy ions with high energies in the range of 100 MeV can be successfully applied to the study of radiation effects of materials on mechanical property changes by using conventional microhardness measurements.

4.2. Fluence dependence

For irradiation at room temperature, a hardness change can be observed only for Fe–1.2 wt% Cu alloy irradiated to the highest fluence of 5.7 × 10^{12} ions/cm^2. Although vacancy mobility should be very low at room temperature, there might be a fair chance for copper atoms to form a cluster with only a small number of jumps if the degree of supersaturation of solute copper is large. In fact, we have an independent evidence by electrical resistivity measurements that copper precipitation does occur during electron or ion irradiation at 300 K [8].

For irradiation at 250 °C, Fe–0.6 wt% Cu and Fe–1.2 wt% Cu alloys show a remarkable increase in hardness. To confirm that the hardness changes are definitely due to irradiation and not due to thermal aging, control thermal treatment at 250 °C was performed for a time period longer than the irradiation time for the highest fluence. Since no changes were observed in the control thermal treatment at the same temperature for all kind of specimens, irradiation is definitely responsible for the change in hardness.

4.3. Irradiation temperature dependence

Studies on the effect of irradiation temperature on irradiation embrittlement have been relatively scarce,

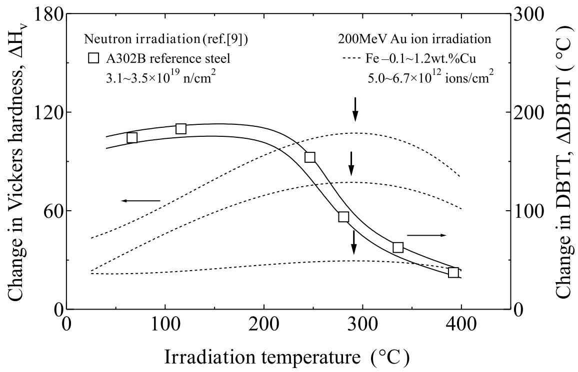

Fig. 6. Comparison of irradiation temperature dependence of the present data with neutron irradiation data taken from Ref. [9].

may be because the operating temperature of the pressure vessel in a light water reactor is in a relatively narrow range. However, typical pressure vessel temperature of about 300 °C is by no means in a temperature-insensitive regime. In fact, a few existing data on ductile–brittle transition temperature (DBTT) shifts by neutron irradiation show the strong temperature dependence around 300 °C [9,10]. Fig. 6 shows the comparison of these data with the present results. Such a comparison assumes that ΔDBTT is proportional to a change in yield stress, $\Delta\sigma_y$, which is again proportional to a hardness change, ΔH_v. As shown in Fig. 6, the curves of temperature dependence of hardness change shift to higher temperature in the present experiment by about 100 °C compared with the temperature dependence of ΔDBTT in neutron irradiation case. The shift may be ascribed to the difference in dose rate. In the case of the present ion irradiation, although the dpa rate varies with the depth from the surface, the typical value is of the order of 10^{-6} dpa/s, whereas in the neutron irradiation case, it ranges from 10^{-9} to 10^{-11} dpa/s. The effect of dose rate is very complex, being currently one of the most intriguing subjects.

Downward slope of hardening above 300 °C seems to show that some sort of defect centers involving copper atoms may become unstable and may decompose or disappear. Mader et al. have discussed this from annealing experiment after irradiation at 150 °C, concluding that so-called unstable matrix defects disappear around 290 °C [11]. Detailed positron annihilation studies using a positron lifetime and novel coincidence Doppler broadening measurements have shown that vacancy clusters decorated with small copper particles on the internal surface of the vacancy aggregates are annihilated by annealing between 200 and 400 °C with a slight increase of the positron lifetime, still leaving hardening which is eliminated by further annealing at 600–650 °C [12]. There is, without doubt, a certain kind of defects involving both vacancies and copper atoms which become unstable at or a little above 300 °C.

4.4. Effect of copper concentration

Clustering of copper atoms during irradiation seems to occur in Fe–Cu dilute alloys with low copper concentration even below the solubility limit. Auger et al. have reported that electron irradiation in Fe–0.1 wt% Cu at 290 °C does not show any copper precipitation whereas in neutron irradiation, copper accumulation in the precipitate has been observed [13]. There are a number of evidences showing that the size of the so-called 'precipitates' does not grow, remaining almost constant at about 3 nm. Instead, the number density of the precipitates increases with increasing fluence at least in the case of neutron irradiation [13]. Then, assuming the dispersed barrier model, the yield stress change, $\Delta\sigma_{ppt}$ may be expressed as

$$\Delta\sigma_{ppt} = \alpha\mu\, b\sqrt{N_p d_{ppt}} = \alpha\mu\, b\sqrt{d_{ppt}}\sqrt{N_p} = \mathrm{const}\sqrt{N_p} \propto \sqrt{C_{Cu}},$$

where α is a constant representing the strength of the barrier $(0 \leqslant \alpha \leqslant 1)$, μ the shear modulus, b the Burgers vector, N_p the number density of the precipitates, d_{ppt} the diameter of the precipitates, C_{Cu} the copper concentration. The present result (Fig. 5) seems to show that this is actually the case. Close correlation of the 'precipitation' sites with the number of cascades is suspected [13].

4.5. The nature of defects contributing to hardening and the effect of cascade

Basic understanding of the differences and similarities of radiation effects with different particles is necessary to correlate charged particle irradiation results with those obtained by neutron irradiation. However, the nature of the defects which cause hardness change is still remaining to be clarified. Accumulating information to date seems to indicate that the defect center responsible to hardness change is not a simple copper precipitate as observed in thermal aging treatment at least for fast neutron irradiations [12,13] producing cascade damage. It has been argued that electron irradiation may give similar copper precipitates as in the case of thermal aging. On the other hand, electron and neutron irradiations at 250 °C give similar hardening in terms of dpa scale, showing that cascade may not have a strong effect on copper-related hardening [14]. Irradiations with heavy ions in the energy range of 100 MeV in the present study will produce mostly simple Frenkel pairs with a few high energy cascades. It is interesting to compare the present results with those obtained in neutron and in electron irradiations.

The effect of cascade is one of the key elements for the basic understanding of radiation damage. Akamatsu et al. have conducted comparative study of electron and neutron irradiations on Fe–Cu model alloys using hardness, small angle neutron scattering, atom probe and positron annihilation [15]. Neutron irradiation increases hardening in pure iron, which is not observed in electron irradiation [15]. If copper concentration is below the solubility limit, no copper cluster formation occurs in electron irradiation, whereas, in neutron irradiation, copper clustering occurs under such conditions [13,15]. These results seem to show some involvement of cascade effect. However, as mentioned above, Tobita et al. have performed comparative experiments using electron and neutron irradiations at 250 °C and have found that fluence dependence of hardening in both kinds of irradiations in Fe–0.6 wt% Cu alloy is not much different on a dpa bases except at very low doses [14]. Similar comparison is underway for GeV energy heavy ion irradiations [16].

Dependence of hardening on damage distributions is important in relating ion irradiation data to neutron irradiation results. This is examined in detail by load dependence of microhardness measurements. The results of the load dependences together with the effect of ion species will be published elsewhere [6].

5. Summary

(1) Heavy ions with high energies in the range of 100 MeV could be successfully applied to the mechanistic study of irradiation embrittlement in pressure vessel steels using conventional microhardness measurements. Single parameter experiments, i.e. the experiments in which only one irradiation or material parameter is systematically varied with other parameters fixed, can be performed using a high energy heavy ion accelerator.

(2) Fluence dependence of hardening at 250 °C shows that after a certain incubation fluence, hardness increases with the same slope for both Fe–0.6 wt% Cu and Fe–1.2 wt% Cu specimens. For irradiation at room temperature, only Fe–1.2 wt% Cu alloy shows hardness increase at the highest fluence.

(3) Irradiation temperature dependence shows the hardening peak around 250–300 °C. No copper concentration dependence on the peak temperature is observed.

(4) Copper concentration dependence of hardening can be reasonably interpreted to be proportional to square root of copper concentration. This seems to support the dispersed barrier hardening model with constant size of copper-involving clusters.

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