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Hardening and microstructural evolution of A533b steels irradiated with Fe ions and electrons

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ABSTRACT

Radiation hardening and embrittlement of A533B steels is heavily dependent on the Cu content. In this study, to investigate the effect of copper on the microstructural evolution of these materials, A533B steels with different Cu levels were irradiated with 2.4 MeV Fe ions and 1.0 MeV electrons. Ion irradiation was performed from room temperature (RT) to 350 °C with doses up to 1 dpa. At RT and 290 °C, low dose (<0.1 dpa) hardening trend corresponded with $\Delta H \propto (dpa)^n$, with n initially approximately 0.5 and consistent with a barrier hardening mechanism, but saturating at ≈0.1 dpa. At higher dose levels, the radiation-induced hardening exhibited a strong Cu content dependence at 290 °C, but not at 350 °C. Electron irradiation using high-voltage electron microscopy revealed the growth of interstitial-type dislocation loops and enrichment of Ni, Mn, and Si in the vicinities of pre-existing dislocations at doses for which the radiation-induced hardness due to ion irradiation was prominent.

1. Introduction

Radiation-induced embrittlement of reactor pressure vessel (RPV) steels used for the construction of thermal fission reactors is clearly of considerable importance to the safe operation of the reactors and plays a major role in plant life extension considerations. The neutron irradiation of these steels leads to an increase in the ductile-to-brittle transition temperature and a decrease in the upper shelf energy [1,2]. Cu has a strong effect on such embrittlement phenomena, and it has been proposed that the Cu-rich precipitates are responsible. On the other hand, studies on mechanical properties of steels with different Cu levels have shown that so-called matrix defects are dominant during the embrittlement of steels with both low [3] and high Cu fluences [4]. In addition, the Cu-rich precipitation mechanism occurs relatively rapidly compared to that due to matrix defects, which is a slow process with a rate that is typically proportional to the dose. Recently, a series of ion and neutron irradiation studies were conducted for RPV steels and model alloys containing various solutes, and the radiation-induced hardening of these alloys was evaluated [5–10]. However, studies of matrix defect formation in RPV steels have been very limited [11].

It is also known that the nucleation and growth processes for dislocation loops during neutron irradiation are strongly controlled by various factors, including the neutron flux, irradiation temperature, chemical composition, and applied stress [12,13]. On the other hand, the effects of dislocation loop formation on hardening are not clearly understood. In this study, therefore, to elucidate the effects of dislocation loop formation on radiation hardening in RPV steels, Fe ion irradiation was performed on steels with three different Cu contents. UCSB's Irradiation VARiable (IVAR) program database [14] and the same A533B steels used in the IVAR program [14] were investigated to compare the effects of the Cu content on radiation-induced hardening due to both the Fe ion and neutron irradiation. Previously, we demonstrated, using conventional transmission electron microscopy (TEM), that ion irradiation of A533B steels at doses of less than 0.5 dpa did not result in the formation of any visible defect clusters [7]. Therefore, in this study, scanning transmission electron microscopy (STEM) was used to analyze the irradiated regions and changes in the radiation-induced hardness resulting from low dose ion irradiation, and the results were compared with the microstructural changes observed during in situ electron irradiation using high-voltage electron microscopy (HVEM), that gives a guidance to the fundamental defect

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clustering processes resulting from irradiation.

2. Experimental procedures

Three A533B steels with different Cu levels were used in this study. The A533B steels are referred to as A533B(LG) without Cu, A533B(LH) with a low Cu content (0.11 wt%), and A533B(LI) with a high Cu content (0.20 wt%). The results of the chemical analyses [14] of these steels are shown in Table 1. The specimens for ion irradiation and in situ observation via HVEM were annealed (austenitized) at 900 °C for 1 h, air cooled, tempered at 664 °C for 4 h, air cooled, stress relieved at 600 °C for 40 h, and finally air cooled. Ion irradiation with 2.4 MeV Fe^{2+} was conducted from room temperature (RT) to 350 °C using the tandem accelerator at Kyushu University. Fig. 1 (a) shows the SRIM calculation of damage distribution of Fe irradiated by 2.4 MeV Fe^{2+} ions. Nanoindentation tests were conducted at RT before and after ion irradiation using an Elionix ENT-1100 with a load of 1 gf. A triangular pyramidal diamond indenter (Berkovich type) with a semi-apex angle of 65° was used. The indenter load (L) and displacement (d) were continuously monitored using a computer system. L and d are given by the following equation [15]:

$$L/d = Ad + B, \quad (1)$$

where A and B are dependent on the material but independent of the load and indenter displacement. A is proportional to the Vickers hardness (Hv) and is given as follows [15]:

$$A(GPa) = 0.287\ Hv. \quad (2)$$

Fig. 1 (b) shows the typical L/d–d curves of unirradiated and 1.0 dpa irradiated at 290 °C of A533B(LI). In this study, A in the region of about 50–150 nm were compared to obtain the hardness of ion irradiated materials.

For the LI (0.2 wt% Cu) sample, atom probe tomography (APT) was also conducted after ion irradiation to 1 dpa at 290 °C and 350 °C. The atom probe samples were run in a LEAP 3000x HR at the University of California, Santa Barbara in voltage mode using a pulse fraction of 20% at a specimen temperature of 50 K. Previous experiments by Hyde et al. revealed that these conditions prevent the preferential evaporation of Cu in typical RPV Steels [16]. Reconstructions and data analyses were performed using the CAMECA Integrated Visualization and Analysis Software (IVAS). The cluster analysis was performed using the density-based clustering algorithm (DBSCAN) outlined here [17]. DBSCAN is a modified version of the more well-known maximum separation method that measures the distance between solute atoms and their nearest solute neighbors and classifies them as clustered if this distance is less than some threshold distance, d_{max}. The DBSCAN method measures the distance between a solute and its Nth nearest neighbor, where N was set at five in this case. Furthermore, any clusters with less than N_{min} atoms were excluded from the analysis. The precipitate number density was calculated by dividing the total number of clusters present in the sample by the total volume of the sample, which was given by $V = N_{atoms}\Omega/\eta$, where Ω is the atomic volume of Fe and η is the efficiency of the instrument, 0.37% in this case. The total number of solute atoms (Cu, Ni, Mn, and Si) in each cluster was divided by the total number of atoms in the sample to determine the precipitate mole fraction.

Table 1
Chemical compositions of the materials used in the present study (wt%).

ID	Cu	Ni	Mn	Mo	P	C	Si	S	Fe
LG	0	0.74	1.37	0.55	0.005	0.16	0.22	<0.015	Balance
LH	0.11	0.74	1.39	0.55	0.005	0.16	0.24	<0.015	Balance
LI	0.20	0.74	1.37	0.55	0.005	0.16	0.24	<0.015	Balance

For samples with large clusters and significant solute depletion from the matrix, there typically was a range of d_{max} values that yielded a relatively constant number density [18]. In these samples with an extremely high density of very small clusters, a slight change in d_{max} resulted in a correspondingly large change in the precipitate number density and volume fraction. As a result, it was difficult to determine the "correct" selection parameters to be used for determining the actual volume fraction, precipitate size, and number density. Selection of a very large d_{max} resulted in the detection of clusters that would be present in any random solid solution. Styman et al. [18] reported that for a typical RPV steel, these "random" clusters can be avoided by using $d_{max} \leq 0.50$ nm and $N_{min} \geq 24$ atoms, although the steel analyzed in their paper had a considerably higher solute (Cu, Ni, Mn, and Si) content ($\approx$4.25%) compared to the steel presented here ($\approx$2.5%). Lower alloy solute concentrations enable the selection of a smaller N_{min} or larger d_{max} without including these random clusters. Consequently, values for d_{max} in the range of 0.50–0.60 nm and for N_{min} in the range of 15–25 atoms were used. Note that a d_{max} value less than 0.50 nm left visible clusters present in the matrix. Thus, using the above ranges for d_{max} and N_{min}, it was possible to determine the mean and uncertainty values for the precipitate mole fraction and number density.

Electron irradiation with in situ observations was also performed using 1.0 MeV electrons and a high-voltage electron microscope (JEM-1000) in the HVEM Laboratory at Kyushu University. Electron irradiation was conducted at 290 °C and 350 °C. To reduce the temperature rise due to electron beam heating during irradiation, a relatively low electron dose rate of 2.5×10^{-4} dpa/s (the same as that for ion radiation) was selected. The TEM samples were prepared by electropolishing using 50 mL of perchloric acid and 950 mL of acetic acid as the electrolyte at RT and 15–30 V. After electron irradiation, solute enrichment around pre-existing dislocations due to irradiation was analyzed via STEM (Hitachi HD-2700).

3. Results

3.1. Temperature and dose dependence of radiation-induced hardness due to ion irradiation

The dose dependence of the radiation-induced hardness of alloys with different Cu levels after irradiation up to 1.0 dpa at RT, 290 °C, 320 °C, and at 350 °C is shown in Fig. 2 (a)–(d), respectively. Here, radiation-induced hardness is defined by the difference in the hardness before and after irradiation, $\Delta H = H_{irrad} - H_{unirrad}$. In this study, indentation measurements were performed before and after irradiation using the same samples. At all irradiation temperatures, radiation-induced hardening occurred at the beginning of ion irradiation, became saturated at approximately 0.1 dpa, and then gradually increased to 1.0 dpa with the dose. The irradiation temperature dependence of hardening for doses from 0.1 to 1.0 dpa is shown in Fig. 3 (a) through (d), respectively. The dashed line indicates the temperature dependence proposed by Bolton et al. [19] for matrix defects normalized to the observed RT hardening. In this previous study, a qualitatively similar general trend was observed at 0.1 dpa, with the hardness decreasing as the irradiation temperature increased, and the level of radiation-induced hardness was nearly the same with or without added Cu at all temperatures. However, the temperature dependence of the hardness observed in the present study was slightly less than that reported by Bolton et al. In addition, at 1.0 dpa in the present study, greater irradiation