Effects of Helium Production and Displacement Damage on Microstructural Evolution in Helium-Implanted Austenitic Stainless Steel and Martensitic Steel Examined By HIT Experiment and kMC Simulation

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The effects of helium concentration and displacement damage on microstructural evolution were mainly investigated in specimens of austenitic stainless steel (304 steel) and a high chromium martensitic steel (HCM12A) irradiated at 773 K under single ion beam of He ions and dual ion beams of Fe or Ni ion and He ions. After the irradiation, the nano indentation test was performed to examine the difference of radiation hardening between 304 (fcc structure) and HCM12A (bcc structure). kMC simulation was also examined to understand the effects of helium production and displacement damage and swelling behaviors in bcc Fe and fcc Fe. The kMC simulation result was similar to the related some experimental research results.

KEYWORDS: DPA, Helium, Microstructure, HIT, Bubble, kMC Simulation, Irradiation Hardening

1. Introduction

High energy particle irradiation to solid-state material can induce displacement damage of atoms, and then point defects such as vacancies and interstitial atoms migrate and aggregate to form defect clusters and chemical composition changes such as voids, dislocation loops, solute atom segregation, and precipitates. These defects can often lead irradiation hardening and embrittlement in materials [1-2]. Through the nuclear reaction process between the incident particles and materials, transmutation atoms and spallation products such as helium are produced and can be also affected on their microstructural evaluation and mechanical properties [3]. Therefore, irradiation dose and transmutation helium content are recognized as key parameters to be strongly influenced on the mechanical properties and microstructures [4-8]. Some studies for effects of DPA and helium content on microstructural changes and mechanical properties were performed.
Non-destructive measurement methods utilized with developed surface acoustic wave (SAW) technique [9-10] and a magnetic flux density measurement system [11] were examined in the irradiated specimens. Nano-indentation techniques for examination of irradiation hardening behavior were evaluated in HIT ion irradiation experiment [12], and tensile and creep tests of irradiated materials were also investigated in the materials irradiated in nuclear reactors [13] and helium implantation accelerator facility [14-15]. Positron annihilation lifetime measurements of austenitic stainless and ferritic/martensitic steels irradiated in the SINQ target irradiation program were examined by Sato [17]. The result showed that the decrease in the positron annihilation lifetime of vacancy clusters by the absorption of He atoms was detected in ferritic/martensitic steel F82H as the irradiation dose was increased. The decrease was also detected by isochronal annealing. Dissociation of small He bubbles due to the annealing led to an increase in the positron annihilation lifetime of the bubbles in an austenitic stainless steel JPCA.

In this study, the microstructural changes in materials with helium implantation and ion irradiation in HIT were mainly investigated in a high-chromium martensitic steel HCM12A and an austenitic stainless steel 304, which are considered as the structural material in nuclear power plants.

2. Experimental Procedures

2.1 Specimens

Table I. Chemical composition (wt%) of materials used in this study

| Material | B  | C  | N  | Si | P  | S  | V  | Cr | Mn | Ni | Cu | Nb | Mo | W  |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| HCM12A   | 0.0031 | 0.11 | 0.063 | 0.27 | 0.016 | 0.002 | 0.19 | 10.83 | 0.64 | 0.39 | 1.02 | 0.054 | 0.30 | 1.89 |
| 304      | 0.0005 | 0.05 | 0.022 | 0.60 | 0.026 | 0.002 | 0.05 | 18.39 | 0.87 | 8.94 | 0.09 | -   | -   | -   |

A martensitic steel HCM12A was used in this study, and chemical composition of the steel is given in Table I. Martensitic steel with chromium content of 12 mass% (12Cr martensitic steel) is used in this study. The material was obtained as a hot-rolled plate with normalizing (1323 K, 1.05 h) and tempering (1043 K, 7.03 h) followed by air cooling.

2.2 HIT ion irradiation

The specimens for the ion irradiation were mechanically polished by the following series: SiC paper up to #4000, and 3 μm diamond powder, and then 0.3 and 0.05 μm alumina powder, and finally completed by electrolytic surface finish. Ion irradiations at 773 K were conducted at HIT facility [17] operated by the University of Tokyo. 4.0 MeV Ni³⁺ ions for 316FR steel or 2.8 MeV Fe⁵⁺ ions for HCM12A steel were ejected from the Tandem accelerator, and He⁺ ions were ejected from the Van de Graff accelerator. The helium injection ratio to dpa (He/dpa) was set to 1 appm He/dpa at the depth between 500 - 700 nm from the incident surface with an energy degrader for 1 MeV He⁺ ions [18]. The both ions were irradiated onto the target simultaneously. A Ni foil energy degrader was used for helium. The displacement damage was calculated by the TRIM code assuming a 40 eV average displacement threshold energy.
2.3 Nano-Indentation Measurement for HIT Ion Irradiation Specimens

The irradiated specimens were indentation-tested at a load of 7 mN using UMIS-2000 (CSIRO, Australia) ultra-micro-indentation testing system. The direction of indentation was chosen to be parallel to the ion-beam axis, or normal to the irradiated surface. The indenter tip was triangular pyramid the Berkovich. The micro-hardness (H) was analyzed in the manner outlined by Oliver and Pharr [19] and Mencik and Swain [20]. The indentation load was controlled at 7 mN, and the incident depth was about 250 nm. The indentation depth was basically determined from Katoh's analysis between indentation depth and micro-hardness in austenitic stainless steel irradiated by dual ion beams [21]. The indentation data for each measurement were obtained about 30 points, and the average value was evaluated.

3 Results and Discussion

3.1 HIT Ion Irradiation

In irradiation hardening of austenitic stainless steel and martensitic steel, the dependency of irradiation hardening on dpa and He/dpa was examined in HIT ion experiment and the result is given in Figure 1. Highest hardening was observed in highest dpa specimens in 304 and HCM12A steels with 10 dpa under 10 appm-He/dpa, but the increment of hardening in HCM12A steel was small. In the HCM12A steels irradiated with He only and 100appm-He/dpa, no hardening was observed. The changes of irradiation hardening in the austenitic stainless steel was larger than that in the martensitic steel.

The irradiation hardening is generally induced by the formation and growth of defect clusters. The defects that contribute to the strength in an irradiated steel are given

![Graph](image)

Fig. 1. Irradiation hardening of 304 and HCM12A irradiated at 773 K up to 100 appm-He under some conditions by single beam of 1 MeV He⁺ ions through energy degrader and dual ion beams of the He⁺ ions and 4.0 MeV Ni³⁺ ions for 316FR steel or 2.8 MeV Fe⁵⁺ ions for HCM12A steel.
as: Frank type dislocation loops, black dots, precipitates, cavities (either bubbles or voids), and dislocation network. These defects can be divided into two classes: short-range and long-range obstacles. The short-range obstacles are defined as those which influence moving dislocations only on the same slip plane as opposed to long-range obstacles which impede dislocation motion on slip planes not containing the obstacle [22]. The contributions to hardening by short- and long-range obstacles are combined as follows [23-24]:

\[ \Delta \sigma_{YS} = \Delta \sigma_{SR} + \Delta \sigma_{LR}, \]  

(1)

where \( \Delta \sigma_{YS} \), \( \Delta \sigma_{SR} \), and \( \Delta \sigma_{LR} \) represent the strength estimated from all defect clusters, the short-range obstacles, and the long-range obstacles, respectively. In this model, only the network dislocations are long-range obstacles. In the case of the experiment [24], after 400°C irradiation, the radiation-induced defect clusters observed were Frank-type loops, bubbles, voids, and carbides, and the latter part \( \Delta \sigma_{LR} \) was no changed. \( \Delta \sigma_{YS} \) is therefore described such as:

\[ \Delta \sigma_{YS} = \Delta \sigma_{SR} = \{(\Delta \sigma_{\text{loops}})^2 + (\Delta \sigma_{\text{bubbles}})^2 + (\Delta \sigma_{\text{voids}})^2 + (\Delta \sigma_{\text{precipitates}})^2\}^{1/2} \]  

(2)

where \( \sigma_{\text{loops}} \), \( \Delta \sigma_{\text{bubbles}} \), \( \Delta \sigma_{\text{voids}} \), and \( \Delta \sigma_{\text{precipitates}} \) represent the strength increase estimated from dislocation loops, bubbles, voids, and precipitates, respectively. The contribution from each type of short-range obstacle is described as follows:

\[ \Delta \sigma_i = M a \mu b (N_i d_i)^{1/2} \]  

(3)

\[ \Delta \sigma_{YS} = 0.3 \Delta H \]  

(4)

where \( M, a, \mu, b, N_i, d_i \), and \( \Delta H \) are factors converting critical resolved shear stress in a single crystal to the uniaxial yield stress in a random crystal, the barrier strength of i-type of obstacle such as dislocation loops, the shear modulus of matrix, the Burgers vector of moving dislocation, the number density of the obstacles, the mean diameter of the obstacles, and the difference of hardness measured before and after irradiation by nano-indentation measurement, respectively.

Present result of radiation hardening indicates that resistance for radiation and helium in martensitic steel at high temperature seems to be larger than austenitic stainless steel due to higher sink density such as higher dislocation density and many lath boundaries. At high temperatures, the number densities of dislocation loops and bubbles are relatively low, and it can be expected that the size of bubble will increase with increasing dpa under helium implantation due to strong binding between vacancies and helium atoms. The irradiation hardening can be changed by the sizes and number densities of defect clusters as given in an equation (3), and there is a possibility that the hardening of FCC Fe is higher than that of BCC Fe shown in Figure 2.

### 3.2 Modeling Simulation of Bubble Formation and Growth

For the difference of bubble formation and growth in BCC and FCC iron, modeling simulation was evaluated by Suzudo [25]. It derived ab initio energies related to the
nucleation of He-vacancy clusters under irradiation. Atomic structure with a specified defect was relaxed using Vienna Ab initio Simulation Package (VASP) with Projector Augmented Wave potential [26,27]. In this calculation it was used the cutoff energy of 280 eV for the plane wave basis, the Monkhorst-Pack 3x3x3 k-point mesh, and the Meshfessel-Paxton smearing with 0.1 eV width. Only for the cases of bcc Fe, spin-polarized calculations were performed. It was calculated migration energies of point defects such as vacancy, He atom at tetrahedral interstitial sites, and dumbbell-type self-interstitial atom (SIA), using the Nudged Elastic Band method. The migration energies of point defects by ab-initio method are given as below: In bcc Fe, the migration energies of vacancy, interstitial He, and self interstitial atom (SIA) are 0.67 eV, 0.06 eV, and 0.32 eV, respectively; In fcc Fe, these migration energies are 1.36 eV, 0.24 eV, and 0.32 eV, respectively. The migration energy of interstitial He atoms in bcc Fe is extremely small, and the vacancy migration energy in bcc Fe is significantly smaller than that in fcc Fe. It was also calculated He and vacancy binding energy and the value was comparable, while many bcc metals have larger binding energies between He and vacancy than fcc metal [28]. The bubble growth is modeled by a process driven by energy minimization of the surface energy and thermal fluctuation within the framework of a Monte Carlo simulation method. In Figure 2, the related new result in present study shows that the simulation of He-V cluster formation was calculated in a condition of 1 He-appm and 0.001 dpa under 1000He-appm/dpa and 0.1 dpa/s. In BCC Fe, larger V clusters were formed, comparing the V and HeV clusters formed in FCC Fe under the same condition.

Recent experiment of BCC ferritic steel (HCM12A) implanted with helium atoms is performed and the helium bubble formation behavior as a function of helium concentration from 1 to 30 appm was examined by a transmission electron microscopy (TEM) and positron annihilation lifetime (PAL) measurement [29]. Bubbles (He-V clusters) with about 10 nm to a few 10 nm in diameter were formed on grain boundaries, sub-boundaries, and dislocation lines, and bubbles with a few nm were also observed in matrix. The long lifetime component of positron tended to increase with helium implantation concentration, especially, in the regime more than 10 appm-He implantation. The results of the long lifetime in the HCM12A implanted with 10 appm-He and 30 appm-He are 345 ps in $\tau_1$ and 308 ps in $\tau_2$, respectively, and these values were found to

![Fig. 2. Defect cluster formation in bcc Fe and fcc Fe by kMC calculation. Blue : HeV Cluster Red : V Cluster (V, SIA, and Interstitial He were not shown).](image)
close to the value of 360 ps which was obtained by the other study in F82H steel irradiated in the SINQ irradiation program, i.e., \( \tau_2 \) of JPCA steel was shorter than that of F82H steel [16]. Thus the kMC simulation result was similar to the experimental result. Additional experimental analysis of swelling behaviors in the difference between BCC Fe and FCC Fe will be presented in a paper [30,31]. Further analysis is needed to understand the swelling behavior in the difference between FCC and BCC as functions of DPA and He amount.

5. Summary

The effects of helium concentration and displacement damage on microstructural evolution were mainly investigated in specimens of a high chromium martensitic steel HCM12A and an austenitic stainless steel, 304. These specimens were irradiated in HIT facility at 773 K up to 100 appm-He under some different conditions of the ratio of He/dpa. Highest hardening was observed in highest dpa specimens in 304 and HCM12A steels with 10 dpa under 10 appm-He/dpa, but the increment of hardening in HCM12A steel was small. In the HCM12A steels irradiated with He only and 100ppm-He/dpa, no hardening was observed. The changes of irradiation hardening in the austenitic stainless steel was larger than that in the martensitic steel.

Defect cluster formation and growth were performed in BCC Fe and FCC Fe by kMC simulation, and the bubble growth behavior was examined to understand the effects of helium production and displacement damage on mechanical properties and microstructures. In BCC Fe, the larger V clusters were formed, comparing the V and HeV clusters formed in FCC Fe in the same calculation condition with 1 He-appm and 0.001 dpa under 1000He-appm/dpa and 0.1 dpa/s. The kMC simulation result was similar to the related experimental research results.

Further analysis is needed to understand the swelling behavior in the difference between FCC and BCC as functions of DPA and He amount.

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