Effects of Helium and Displacement Damage on Microstructural Evolution in Helium-Implanted Martensitic Steel HCM12A Examined by TEM and Positron Annihilation Lifetime Measurement

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The effects of helium concentration and displacement damage on microstructural evolution were mainly investigated in a high chromium martensitic steel (HCM12A) implanted uniformly with helium at 823 K to 1, 10, and 30 appm-He by 50 MeV cyclotron accelerator using an energy degrader under 2x10^4 dpa/appm-He. After the helium implantation, the microstructures were examined by a transmission electron microscopy (TEM) and positron annihilation lifetime (PAL) measurement. 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. Preset results of the long lifetime in the HCM12A implanted with 10 appm-He and 30 appm-He are 345 ps in $\tau_3$ and 308 ps in $\tau_2$, respectively, and these values were found to close to the value of 360 ps which was obtained by the other study in F82H steel irradiated in the SINQ irradiation program.

KEYWORDS: DPA, Helium, Microstructure, Positron Annihilation Lifetime Measurement (PAL), TEM, Bubble

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 such as voids and dislocation loops, and also induce chemical composition changes such as radiation induced precipitate formation and solute atom segregation to dislocations, defect clusters, and grain boundaries. 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 spectroscopy through the interaction of positrons with matter [16-21] is a useful non-destructive examination tool of microstructural change analysis and configuration and property studies at the atomic level in materials irradiated by high energy protons and spallation neutrons. This technique was developed to study vacancies, voids and defects in solids in the early 50s and has been advancing. In the annihilation process of a positron and an electron, 511 keV photons are released and detected.

In this study, the microstructural changes in materials with helium implantation at higher temperature about 823 K from 1 appm-He and 2x10^-4 dpa to 30 appm-He and 6x10^-3 dpa were mainly investigated in a high-chromium martensitic steel, HCM12A steel, using by positron annihilation lifetime measurement and transmission electron microscope. HCM12A steel is considered as the structural material in nuclear power plants.

2. Experimental Procedures

2.1 Specimens

A martensitic steel HCM12A (12Cr martensitic steel) was used in this study, and a chemical composition of the steel is given in Table I. The material was prepared as a hot-rolled plate with normalizing (1323 K, 1 h) and tempering (1043 K, 7 h) followed by air cooling.

| 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 |

2.2 Helium Implantation by Cyclotron Accelerator
He implantation experiments [14,15] were carried out using AVF Cyclotron accelerator of Radioisotope Center of Tohoku University, under 50 MeV He\textsuperscript{2+} ion about 823 K±10 K and 1, 10, and, 30 appm in helium concentration. As shown in Fig. 1, helium was uniformly implanted from the specimen surface to about 0.4 mm in thickness by using a rotating energy degrader consisting of Al foils. The depth distribution of He concentration and displacement damage in the specimen calculated by SRIM (The Stopping and Range of Ions in Matter) code. The average ratio of helium concentration to displacement damage was about 5300 appm/He/dpa. The temperature was monitored to the specimen spot-welded with thermo-couples during He implantation. The time for 10 appm-He implantation was about 6 hours. The HCM12A specimen aged at 550°C for 6 hours was prepared to compare the properties between short time aging specimen and helium implantation specimen with a same aging time at 823 K. The helium implantation rates were 0.3 appm/h for 1, 10, and 30 appm-He or 2.7appm/h for 10 and 30 appm-He. The displacement damage rate was 2\times10^{-4} dpa/appm-He.

2.3 Transmission Electron Microscopy

Microstructural observation for the helium-implanted specimens was conducted using a transmission electron microscope operated at 200 kV (TEM, JEM-2000FX) at International Research Center for Nuclear Materials Science of Tohoku University. The specimens were electro-polished for thin foil preparation for TEM observation in an electrolyte solution of acetic acid and perchlorate.

2.4 Positron Annihilation Spectroscopy

Positrons and gamma rays with 1.28 MeV are emitted from \textsuperscript{22}Na source. Positron annihilation lifetime measurements were performed at room temperature using three photon simultaneous measurement positron system as shown in Fig. 2, and three scintillator detectors are arranged for these particles. This system was installed in JAEA Tokai-site. The time dependence of two-photon yield was determined using standard pulse-counting techniques. Three-parameter events consisting of the two pulse heights and the time difference between the two photons were recorded in list mode and sorted off-line. The lifetime resolution full width at half maximum (FWHM) was about 140 ps.
3 Experimental Results

3.1 Positron lifetime measurement

In case of positrons annihilate from some different states in general, positron lifetime spectra, $T(t)$, can be described as a sum of some power functions, if the time resolution is ideally very high:

$$T(t) = \sum \left( \frac{I_i}{\tau_i} \right) \exp\left(-\frac{t}{\tau_i}\right)$$  \hspace{1cm} (1)

where $I_i$ is a relative intensity for each component, $i$, of the positron lifetime, $\tau_i$, for each component $i$.

Figure 3 shows some of positron spectrums for as-received HCM12A, HCM12A aged at 823 K for 6 hr, 1 appm-He, 10 appm-He, and 30 appm-He implanted HCM12A. Positron annihilation lifetimes and the intensities measured in HCM12A steel are given in Table II. Single component intensity $I_1$ was observed in as received HCM12A and the aged one, and the life time was about 125 ps. Two components were observe in the 1 appm-He HCM12A and long lifetime component appeared slightly. In 10 appm-He implanted HCM12A, three components were observed. In this case first component seemed to be changed and the intensity largely decreased. As increasing implantation helium concentration, the intensity of the second component with long lifetime increased. Also, third component with longer lifetime about over 300 ps was detected in the 10 appm-He implanted case.

In the aged HCM12A steel at 823 K for 6 hr, no change of positron lifetime was observed. The long lifetime component of positron appeared to increase with helium implantation concentration, and DPA from 1 appm to 10 appm-He and the intensity also increased. This result indicates that some defects and defect clusters were formed in these specimens. Over 10 appm-He implantation it seems to be decreasing to be the sizes and number densities of vacancy-type cluster. In the specimens more than 10 appm-He implantation, the long lifetime component of positron increased clearly. The lifetime of positron tended to increase with helium implantation concentration and the...
intensity of long lifetime component also tended to increase, and it is shown that the sizes and number densities of vacancy clusters are increased. The difference of the intensities of long lifetime components in 10 appm-He and 30 appm-He implanted specimens may be influenced by helium implantation rate.

Table II. Positron annihilation lifetimes and the intensities measured in HCM12A steel.

| Material        | $\tau_1$(ps) | $I_1$ (%) | $\tau_2$(ps) | $I_2$ (%) | $\tau_3$(ps) | $I_3$ (%) |
|-----------------|--------------|-----------|--------------|-----------|--------------|-----------|
| As received     | 127.5        | 100       | -            | -         | -            | -         |
| 550C, 6h        | 125.8        | 100       | -            | -         | -            | -         |
| 1 appm*         | 124.5        | 92.8      | 236.6        | 7.2       | -            | -         |
| 10 appm*        | 54.4         | 16.6      | 159.8        | 51.1      | 345.3        | 32.2      |
| 30 appm**       | 119.9        | 69.4      | 307.5        | 30.6      | -            | -         |

*0.3 appm-He/h, **2.7 appm-He/h

3.2 Transmission Electron Microscopy

HCM12A steel is lath-martensitic structure, and carbides are formed on lath boundaries and grain boundaries. Helium trap site in HCM12A exists in high density dislocations and lath boundaries and grain boundaries. In Fig. 4, microstructure of the HCM12A steel with He-implanted at 823 K were observed, and bubbles 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. Figs. 4(a'), 4(b'), and 4(c') are magnified images of Figs. 4(a), 4(b), and 4(c), respectively. Largest bubbles were observed in HCM12A implanted to 10 appm-He. The number density of bubbles was tended to increase with helium implantation concentration. The formation of helium bubbles in HCM12A steel were confirmed on dislocations, precipitates, and lath-boundaries from 1 appm-He. In 10 appm-He implanted specimen, bubbles were grown in lath boundaries and grain boundaries. The size of bubbles formed in the boundaries was more than 50 nm. In 30 appm-He implanted specimen, many bubbles
are clearly formed in the matrix and they are also formed in lath boundaries and dislocations, and grain boundaries as seen in Fig. 4(c’). The size of bubbles formed in the boundaries was about 50 nm.

**Fig. 4.** Microstructures of HCM12A steel implanted at 823 K by 50 MeV-He ions. Pictures (a) and (a’) are 1 appm-He implanted condition. Pictures (b) and (b’) are 10 appm-He condition. Pictures (c) and (c’) are 30 appm-He condition.
4. Discussion

Recent result [17] in positron annihilation lifetime measurements of austenitic stainless and ferritic/martensitic steels irradiated in the SINQ target irradiation program at the Swiss Spallation Neutron Source of Paul Scherrer Institute (PSI) showed that the decrease in the positron annihilation lifetime of vacancy clusters, which is corresponds to the long lifetime about 360 ps (estimated as $V_{15}$ vacancy clusters), by the absorption of He atoms was detected from about 9 dpa and 700 appm-He in a ferritic/martensitic steel, F82H, as the irradiation dose was shifted to the lifetime level about 250 ps under irradiation conditions from about 6 dpa, 370 K, and 410 appm-He to about 20 dpa, 560 K, and 1800 appm-He. The decrease was also detected by isochronal annealing. In the irradiated an austenitic stainless steel, JPCA, with about 6 dpa and about 410 K, the long lifetime was about 240 ps and it was estimated as $V_4$ vacancy clusters. Dissociation of small He bubbles due to the annealing led to an increase in the positron annihilation lifetime of the bubbles in JPCA steel irradiated with about 6 dpa and about 410 K. Preset results of long lifetime in the HCM12A implanted with 10 appm-He and 30 appm-He are 345 ps in $\tau_3$ and 308 ps in $\tau_2$ and these values are very closed to the previous data of F82H, 360 ps.

According to a study of lower dpa irradiation experiments [18], the effect of neutron irradiation at room temperature on positron annihilation lifetime in F82H steel was detected even at a low irradiation dose of $10^6$ dpa. The long lifetime was less than the positron lifetime for single vacancies [22] and the defects produced by the neutron irradiation were vacancies and dislocation loops. While, the results of positron lifetime measurement for specimens irradiated at 673K in F82H steel showed that defects were detected only in fusion neutrons irradiation with energy of 14 MeV to F82H with 6.5x$10^5$ dpa under about 10 appm-He/dpa in the FNS (Fusion Neutron Source) facility of JAEA Tokai-site, and the mean lifetime increased slightly. Since the irradiation temperature was high and the irradiation dose was small, the defects produced by the neutron irradiation were expected to migrate to sinks and disappear. Judging from the long lifetime of fusion-neutron irradiated F82H, the defects formed in the specimen were interstitial type dislocation loops [22]. It was considered that the defects remained only in fusion-neutron-irradiated F82H steel due to the effect of cascade size. On the other hand, irradiation experiments of F82H steel irradiated at 673 K with high dpa in the HFIR (High Flux Isotope Reactor) at the Oak Ridge National Laboratory (ORNL) showed that dislocation loops and cavities were formed by the irradiation [5,23]. The cavity formation and growth tended to be enhanced by helium production amount even at higher temperature of 673 K and the higher temperatures [5,8,23-24].

In this study, the displacement damage rate was $2x10^{-4}$ dpa/appm-He. In the 1, 10, and 30 appm-He implanted specimens, the displacement damage are $2x10^{-4}$ dpa, $2x10^{-3}$ dpa, and 6 $x10^{-3}$ dpa, respectively. The dpa level in this study is comparable to the FNS experiments, but the ratio of helium concentration to dpa in this study is very high compared to it. Therefore, it is thought that He-V clusters under higher He/dpa is easy to be formed even in low dpa level of $10^{-4}$ dpa, and the clusters can be grown with helium implantation concentration and dpa.

5. Conclusion
In this study the main objective is to understand the effects of helium concentration and displacement damage on microstructural evolution in a high chromium martensitic steel HCM12A in low dpa regime about $10^{-4}$ to $10^{-3}$ dpa under high temperature irradiation environment. The specimens were implanted uniformly with helium at 823 K up to 50 appm-He by 50 MeV cyclotron accelerator using energy degraders. The displacement damage rate was $2 \times 10^{-4}$ dpa/appm-He. In the 1, 10, and 30 appm-He implanted specimens, the displacement damage are $2 \times 10^{-4}$ dpa, $2 \times 10^{-3}$ dpa, and $6 \times 10^{-3}$ dpa, respectively. The dpa level in this study is comparable to previous study of FNS experiments, but the ratio of helium concentration to dpa in this study was very high compared to it. After the helium implantation, the microstructures were examined by a transmission electron microscopy and positron annihilation lifetime measurement. The long lifetime component of positron tended to increase with helium implantation concentration in the regime more than 10 appm-He. From present study, it is thought that He-V clusters under higher He/dpa irradiation environment is easy to be formed even in low dpa of $10^{-4}$ dpa, and the He-V clusters can be grown with helium implantation concentration and dpa.

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