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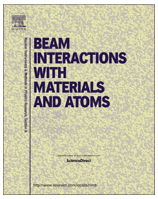

Characterization of the martensite phase formed during hydrogen ion irradiation in austenitic stainless steel

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ABSTRACT

Microstructural changes in austenitic stainless steel caused by hydrogen ion irradiation were investigated using transmission electron microscopy (TEM). It has been confirmed that the irradiation induced the formation of martensite along the grain boundary; the martensite phase exhibited a crystal orientation relationship with the adjacent austenite phase. The results of this study also indicate that the concentration of Cr in the martensite phase is lower compared to that in the austenite matrix. The TEM results showed the development of asymmetric radiation-induced segregation (RIS) near the grain boundary, which leads to local changes in the chemical composition such as reduction of Cr near the grain boundary. The asymmetric RIS serves as a prerequisite for the formation of the martensite under hydrogen irradiation.

1. Introduction

The internal structures of nuclear reactors, which are made of commercial austenitic stainless steels, are exposed to high-energy neutron radiation of up to approximately 100 dpa (displacement per atom) at the end of the operation. The degradation in the corrosion resistance of the internal structure of nuclear reactors has been attributed to irradiation-assisted stress corrosion cracking (IASCC), which significantly affects the integrity of nuclear reactor systems [1,2]. IASCC is attributed to the microstructural changes caused by the neutron radiation, such as defects in the metallic matrix and radiation-induced segregation (RIS) at the grain boundary (GB), which leads to the depletion of chromium and the enrichment of nickel, silicon, and phosphorus [1–5]. Apart from the typical microstructural changes mentioned above, a remarkable modification observed in highly irradiated austenitic stainless steels is the formation of martensite along the GB [6–7]. This is recognized to be of importance since the IASCC occurs along the GBs in austenitic stainless steels upon irradiation.

In this work, hydrogen ion irradiation induced formation of martensite in austenitic stainless steels was investigated using transmission electron microscopy (TEM). Based on the previous studies on martensite formation in austenitic stainless steels by implantation of gas ions [8–10], hydrogen ions were used in this work to produce the radiation-induced martensite at the GB of commercial austenitic stainless steel. Transmission electron microscopy was used to characterize the microstructural changes in the irradiated metal sample.

2. Experimental

Commercial SS316 austenitic stainless steel was used in the present work. The composition of the steel was 10.8% Ni, 16.7% Cr, 2.0% Mo, 1.3% Mn, 0.047% C, and 0.59% Si, and remaining Fe. The mechanical polishing of the sample was carried out with diamond suspensions of sizes 3 and 0.25 μm, which was followed by fine polishing with colloidal silica (0.02 μm) using a vibratory polisher (Vibromet 2).

The multi-purpose ion implanter at the Korea Institute of Geoscience & Mineral Resources was utilized for the hydrogen ion (H_2^+) irradiation that was carried out at different energies ranging from 100 to 490 keV at an irradiation temperature of 400 °C. In order to obtain uniform radiation damage (∼2–3 dpa) and implanted ion concentration in the ion-irradiated sample, the conditions for ion irradiation were modeled using the Stopping Range of Ions and Matter (SRIM) program [11,12]. Fig. 1 shows the radiation damage profiles as functions of the sample depth. The accumulated radiation damage was found to be uniform in the depth range of 0.25 to 1 μm, and the concentration of the implanted hydrogen ions was calculated to be approximately 50000 appm.

A TEM (JEOL 2100F) equipped with an energy-dispersive X-ray spectrometer (EDS) was used to analyze the radiation-induced microstructural changes in the steel samples. The samples for

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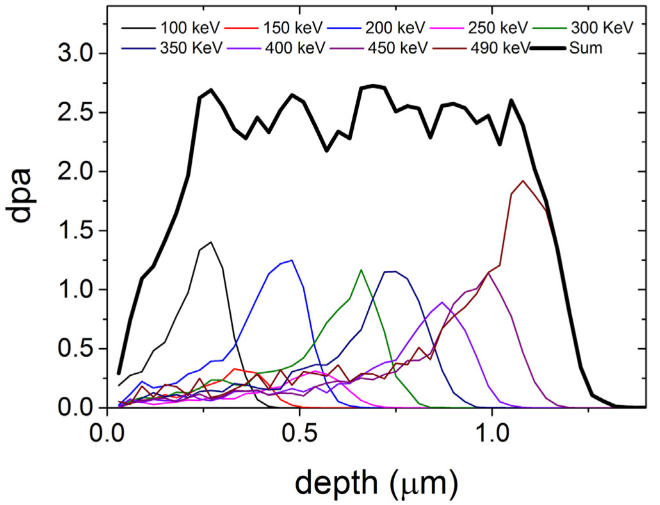

Fig. 1. Radiation-induced damage as a function of depth, calculated using SRIM in full cascade mode [11]. Displacement energy of 40 eV [12] was used for the calculation.

TEM studies were prepared by focused ion beam (FIB) milling. This was followed by low energy ion milling to reduce the radiation damage induced by Ga^+ ions during the FIB milling. We used a focused ion beam system (Helios 600, FEI) for the FIB milling. A low energy Ar ion miller (Gentlemill, Technoorg Linda) that can be operated at energy as low as 200 V was used for the low energy ion milling.

3. Results

The low-magnification TEM image of the irradiated austenitic stainless steel sample is presented in Fig. 2. A layered structure was observed along the GB near the surface. It should be noted that only a few samples showed the formation of the layered structure along the GB. The thickness of the layer was found to be less than 28 nm. The crystal orientation relationship between the layer structure and an adjacent austenite was analyzed using high-resolution electron microscopy (HREM). The phase identification of the layered structure and the crystal orientations of the layer and the austenitic grain AG2 was obtained from the Fast Fourier Transform (FFT) image and the corresponding schematic diagram in Fig. 3(a). The HREM analysis showed that the FFT pattern of the layered structure matches well that of the martensite phase with body centered cubic crystal structure. Furthermore, the direction of the electron beam in the HREM analysis was parallel to the [1 1 1] zone axis of martensite and the [1 0 1] zone axis of AG2, suggesting that the martensite phase exhibits the Kurdjumov-Sachs (K-S) orientation relationship with the AG2 austenitic grain. This indicates that the martensite has a semi-coherent interface with the AG2 austenitic grain. No crystal orientation relationship was found between the martensite and another austenitic grain AG1, indicating that there is an incoherent interface between the martensite and the AG1 austenitic grain. It was confirmed that there was no martensite or delta ferrite in the experimental steel prior to the irradiation through electron backscattered diffraction analyses.

We also observed the formation of carbides ($M(Cr)_{23}C_6$) along the GB as indicated in Fig. 2. The HREM image in Fig. 3(b) shows that the $M(Cr)_{23}C_6$ carbide has a cube-cube orientation relationship with the AG1 austenitic grain. However, these carbides are believed to have formed before the ion irradiation or during the thermal treatment, as they were observed in the non-irradiated regions of the sample as well.

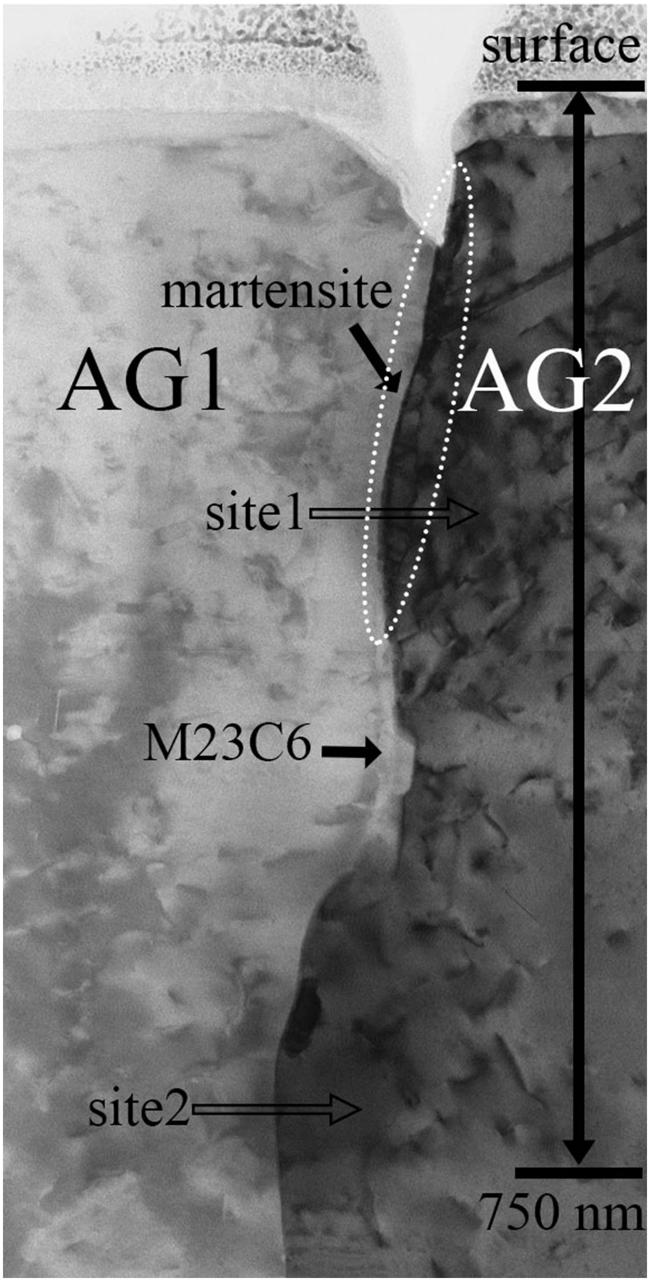

Fig. 2. Low-magnification TEM image showing the microstructure near the GB in the damaged layer after hydrogen ion irradiation.

The changes in the chemical composition near the martensite phase were measured using the TEM-EDS line scan method. The site of analysis is indicated as “site 1” in Fig. 2. The EDS analysis across the martensite layer presented in Fig. 4(a) clearly shows large variations in the chemical compositions of Cr and Ni. The incoherent interface between the martensite and the AG1 austenitic gain exhibited distinct depletion of Cr and enrichment of Ni. A weak RIS was observed at the semi-coherent interface with the AG2 austenitic grain that exhibited the K-S orientation relationship. The Cr content of the martensite phase was lower compared to that in the austenite matrix. Fig. 4(b) shows the result of the EDS analysis across the GB, obtained at a depth of 0.7 μm in the same TEM sample, where no martensite layer was observed. This site

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