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Stability of Y–Ti complex oxides in Fe–16Cr–0.1Ti ODS ferritic steel before and after heavy-ion irradiation

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ABSTRACT

The mechanical strength of oxide dispersion strengthened (ODS) ferritic steels depends on the dispersion and microstructural stability of the oxide particles. Yttria is normally selected as dispersion particles to strengthen ODS ferritic steels, and other additional elements such as titanium and aluminum are added to obtain finer dispersion particles for the improvement of the mechanical properties of the ODS steels. Kyoto University is involved with the development of new ODS ferritic steels. 16Cr–0.1Ti–0.35Y_2O_3 ODS steel is a fusion structural material. In this research, the irradiation resistance of 16Cr–0.1Ti–0.35Y_2O_3 (16Cr0.1Ti) ODS steel was investigated by high-resolution TEM and by performing an ion irradiation experiment. The ODS steel was consolidated by hot extrusion at 1150 °C and annealed at 1050 °C for 1 h for recrystallization. Oxides in 16Cr0.1Ti ODS steel were characterized by HRTEM and STEM-EDX and specified as (Y, Ti) complex oxides with an atomic ratio of Y:Ti = 2:1. A 1.7 MeV tandem accelerator for heavy-ion irradiation at the dual-beam material irradiation facility for energy technology (DuET), Kyoto University, was used to introduce irradiation damages in materials. The comparison of the dispersion, shape, and chemical composition of the oxides between the pre- and post-irradiated materials revealed that (Y, Ti) complex oxides were stable under the ion irradiation up to 60 dpa at 650 °C.

1. Introduction

Oxide dispersion strengthened (ODS) ferritic steels are potential high-temperature materials that are stabilized by dispersed particles at elevated temperatures. These dispersed particles improves the tensile strength and creep rupture strength of the ODS steels better than conventional reduced activation ferritic/martensitic (RAFM) steels. ODS steels are expected to increase the operation temperature up to approximately 650 °C and also enhance the energy efficiency of the fusion reactor [1,2]. The dispersed oxide particles determine the basic performance of the steel; fine and stable oxides are necessary for good performance. Yttria is a major material that is used as a dispersed oxide, but its particle size increases during the consolidation and thermal treatment of ODS steel. Some additional elements are necessary to make the dispersed oxides finer, and for this, titanium and aluminum are frequently used to form complex oxides with Yttria [3]. The dissolution and precipitation of oxide nano-clusters have been researched by small-angle neutron scattering (SANS) [4]. In the case of Y–Ti–O nano-clusters, the consolidation of ODS steel at 850 °C precipitates high nano-clusters with diameters of 1–6 nm, and the number density of such nano-clusters reduces with an increase in the consolidated temperature. SANS is useful for the statistical analysis of nano-clusters, and atom probe tomography (APT) is able to characterize each nano-cluster. APT measurements also indicate that the added Y_2O_3 powders dissolve perfectly in the ferrite matrix during the mechanical alloying and precipitate during consolidation and thermal treatments. The APT investigation also indicates that Y-, Ti-, and O-rich nano-clusters are not residual remnants of the original Y_2O_3 but a consistent of TiO because titanium is more than yttrium and the metal-to-oxygen ratio is approximately 1:1 in a nano-cluster [5]. On the other hand, TEM investigations [6,7] and XRD analysis [3] indicated that Y–Ti–O nano-particles with a diameter of several nanometers are cubic $Y_2Ti_2O_7$. Although the growth process of oxides is not apparent, Y-, Ti-, and O-rich nano-clusters may grow to a stoichiometric oxide. Such nano-clusters and nano-particles of (Y, Ti) complex oxide substantially contribute to the mechanical strength of ODS steels. The stability of (Y, Ti) complex oxides is a very important issue because it determines the mechanical properties. The APT research also revealed that nano-clusters are strongly resistant to coarsening by annealing up to 1000 °C [5], and nano-clusters do not change after ion irradiation up to 0.7 dpa at 300 °C [8]. Our previous work morphologically investigated the irradiation resistance of (Y, Al) complex oxides using heavy-ion irradiation and TEM; however, this work could not investigate the irradiation resistance of each oxide [9]. In the present research, the microstructural stability of ODS steel under high-temperatures and heavy-dose

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irradiation environments has been investigated, especially focusing on the microstructural construction of an oxide particle with a diameter of several nanometers by using a high-resolution TEM.

2. Experiments

16Cr–0.1Ti–0.35Y_2O_3 ODS ferritic steel, which was designated as 16Cr0.1Ti, was used for this research. The chemical composition of these materials is shown in Table 1. The pre-alloyed powders were prepared at KOBELCO Ltd. These powders were mechanically alloyed with Y_2O_3 in an argon gas atmosphere at room temperature. The powders were consolidated by a hot extrusion method at 1150 °C. Subsequently, the consolidated ODS steels were thermally treated at 1050 °C for 1 h. The disk-shaped specimens, with a diameter of 3 mm and a thickness of 0.25 mm, were cut and their surfaces were polished by mechanical polishing and electropolishing. The dual-beam material irradiation facility for energy technology (DuET) at the Institute of Advanced Energy, Kyoto University, was used for this research [10]. Fe ions (6.4 MeV) were irradiated on the materials by using a 1.7 MeV tandem accelerator. Fe ions, which are the self-ions of steels, were selected to minimize the effects of heavy-ion implantation. The depth profiles of the displacement damage and helium concentration were calculated by the SRIM98 code. The irradiation temperature was 650 °C. The nominal dose rate and the dose of ion irradiation were 5×10^{-4} dpa/s and up to 60 dpa at a depth of approximately 600 nm from the surface, respectively. Focused ion beam (FIB) processing was used for the preparation of TEM specimens from the irradiated ODS steels. The thin foils were electropolished for a very short time in order to remove the deformation layer introduced by the FIB processing. TEM investigation was performed using JEOL JEM2010 and JEM2200FS with EDX.

Table 1
Nominal chemical composition of ODS ferritic steel.

(wt%)	C	Cr	W	Al	Ti	Y_2O_3
16Cr0.1Ti	0.02	16	0	0	0.1	0.35

3. Results

Fig. 1 shows TEM images of the 16Cr0.1Ti ODS steel before and after ion irradiation up to 60 dpa at 650 °C. Irradiated 6.4 MeV Fe ions arrive at a depth of approximately 2 μm from the specimen surface. A depth profile of dpa calculated using SRIM98 is shown in the TEM image of irradiated 16Cr0.1Ti ODS steel in Fig. 1(a). Fig. 1(a) shows both high-temperature irradiated and unirradiated microstructures but thermally treated during the irradiation. It is impossible to distinguish between the areas of both microstructures. A TEM image of the as-received 16Cr0.1Ti ODS steel is shown in Fig. 1(b). The as-received 16Cr0.1Ti ODS steel includes high density dislocations. These dislocations were introduced during the hot extrusion, and the ODS steel was not completely recrystallized by the thermal treatment [2]. A HRTEM image of a typical or relatively large dispersed oxide particle with a diameter of ~9 nm is shown in Fig. 2. The image in Fig. 2(a) was obtained by using JEOL JEM 2200FS, and Fig. 2(b) is the fast Fourier transform (FFT) image of Fig. 2(a). This image (Fig. 2(b)) is taken from Z ≈ $[011]_{Fe}$, and because the oxide is on a grain boundary, the $[011]_{Fe}$ spots are overlapped by angled $[011]_{Fe}$ spots, as shown in Fig. 2(b). The HRTEM image of the oxide in Fig. 2(a) shows the complex contrast, and a diffusion ring with fine spots is shown in Fig. 2(b). The fine spots are attributed to the oxide. The lattice plane spacing estimated from each fine spot is 0.30 nm ± 0.02 nm. Fig. 3 shows the results of the EDX analysis for an oxide with a diameter of 11 nm and a ferrite matrix. The chemical composition of the oxide is investigated in the EDX analysis (Fig. 3) is summarized in Table 2. The diameter of the oxide is smaller than the thickness of the thin foil specimen, and the chemical composition of both the oxide and ferrite matrix is presented in Fig. 3(a). The important points with regard to the data listed in Table 2 are that the oxide obtained is (Y, Ti) oxide, the atomic ratio of Y and Ti is 2:1, and no titanium is detected in the matrix. On the basis of the data of unirradiated 16Cr0.1Ti ODS steel, the dispersion, shape, and chemical analyses of ion-irradiated 16Cr0.1Ti ODS steel are performed, as shown in Fig. 4. Fig. 4(a) and (b) show a comparison of the typical dispersion of oxides between unirradiated and irradiated 16Cr0.1Ti ODS steels. No significant difference is detected from the TEM images. Fig. 4(c) and (d) show a high-magnification TEM image and the results of the EDX analysis of an irradiated oxide, respectively.

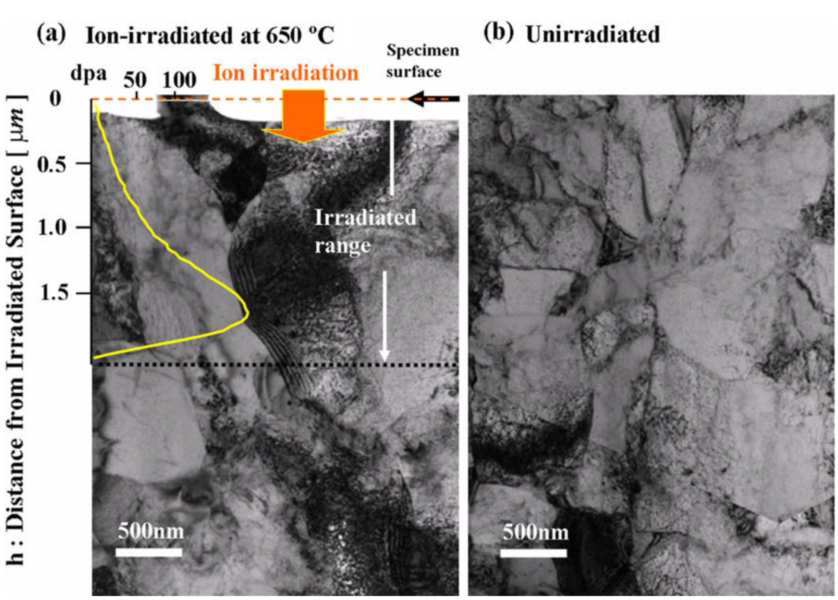

Fig. 1. Cross-sectional TEM images of 16Cr0.1Ti ODS steel: (a) after ion irradiation up to 60 dpa at 650 °C and (b) unirradiated.

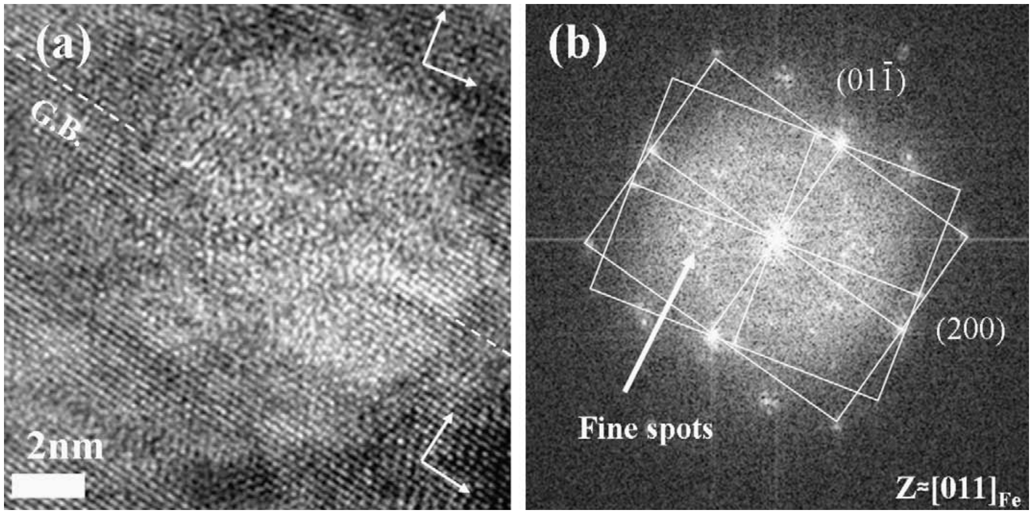

Fig. 2. TEM images of a typical dispersed oxide on a grain boundary: (a) high-resolution TEM image and (b) FFT image.

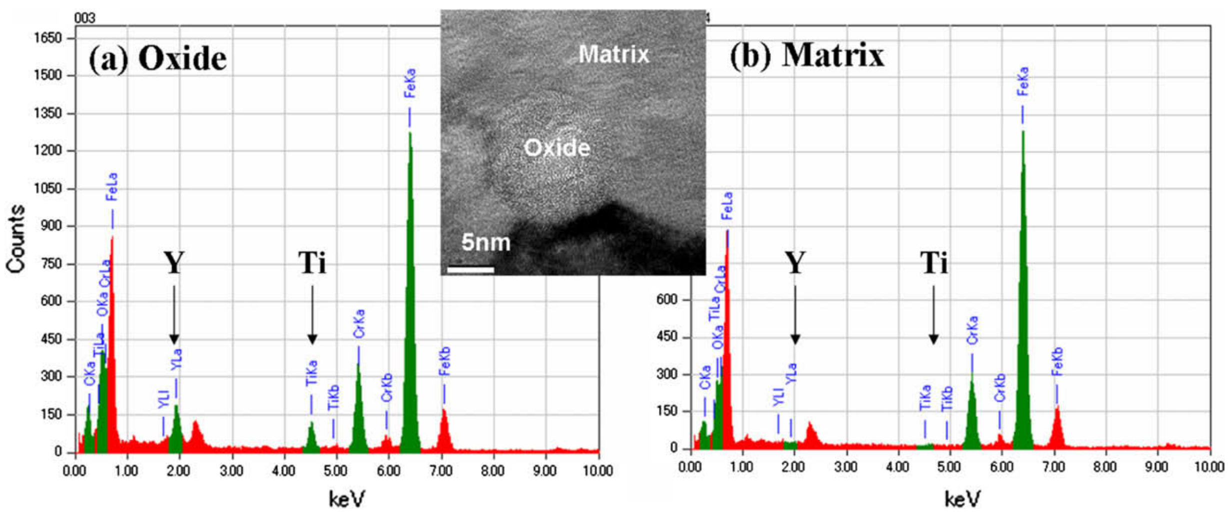

Fig. 3. EDX analysis of (a) an oxide and (b) a ferrite matrix.

Table 2
Chemical composition of the oxide investigated by EDS analysis.

at.%	Fe	Cr	Ti	Y	O
Oxide	51.3	11.9	3.68	6.47	26.6
Matrix	67.8	13.6	0.00	0.12	18.4

Although the thicker thin foil and the strain of dislocations surrounding the oxides prevent a clear view, the shape and atomic ratio of Y and Ti are retained after the heavy-ion irradiation up to 60 dpa at 650 °C.

4. Discussion

The TEM image of unirradiated 16Cr0.1Ti ODS steel in Fig. 1(b) indicates that the ODS steel is not completely recrystallized by the thermal treatment at 1050 °C for 1 h, and therefore, there are high density dislocations in the grains. These dislocations are formed due to the dispersion of the oxides during the hot extrusion and heat treatment procedure. In the irradiation temperature range from 300 °C to 700 °C, the contrast due to the occurrence of irradiation damages is visible in the TEM image at 300 °C [11]. The contrast is invisible at above 500 °C, and it is considered that the dislocations are annealed and merged with the original dislocations introduced during the consolidation procedure. The dislocations and grains of the as-received and irradiated (above 500 °C) ODS steels are not identical; however, they are not distinguishable by TEM. In fact, a slight relaxation of the dislocations is considered to occur due to the irradiation and thermal effects after the ion irradiation experiment. The dispersed oxides appear to be effective in stabilizing the microstructure at temperatures above 500 °C. Published researches using HRTEM [6] and XRD analysis [3] have revealed that the (Y, Ti) complex oxides of non-stoichiometric nano-clusters [5] are considered to grow to yield cubic $Y_2Ti_2O_7$. The type of oxides present in the 16Cr0.1Ti ODS steel is unclear. Fig. 2(a) shows an oxide showing the complex contrast. This complex contrast was observed from the direction of two zone axes $Z \approx [0\,1\,1]$ and $Z \approx [0\,1\,0]$. There is a diffusion ring with fine spots in the FFT image as shown in Fig. 2(b). These fine spots are possibly originated from the oxide. The lattice plane spacing calculated from the measurements of each fine spot in Fig. 2(b) is 0.30 nm ± 0.02 nm. The lattice plane spacing of 0.291 nm for cubic $Y_2Ti_2O_7$ (2 2 2) and 0.301 nm for orthorhombic Y_2TiO_5 (2 0 1) is close to the lattice plane spacing in Y–Ti–O systems.

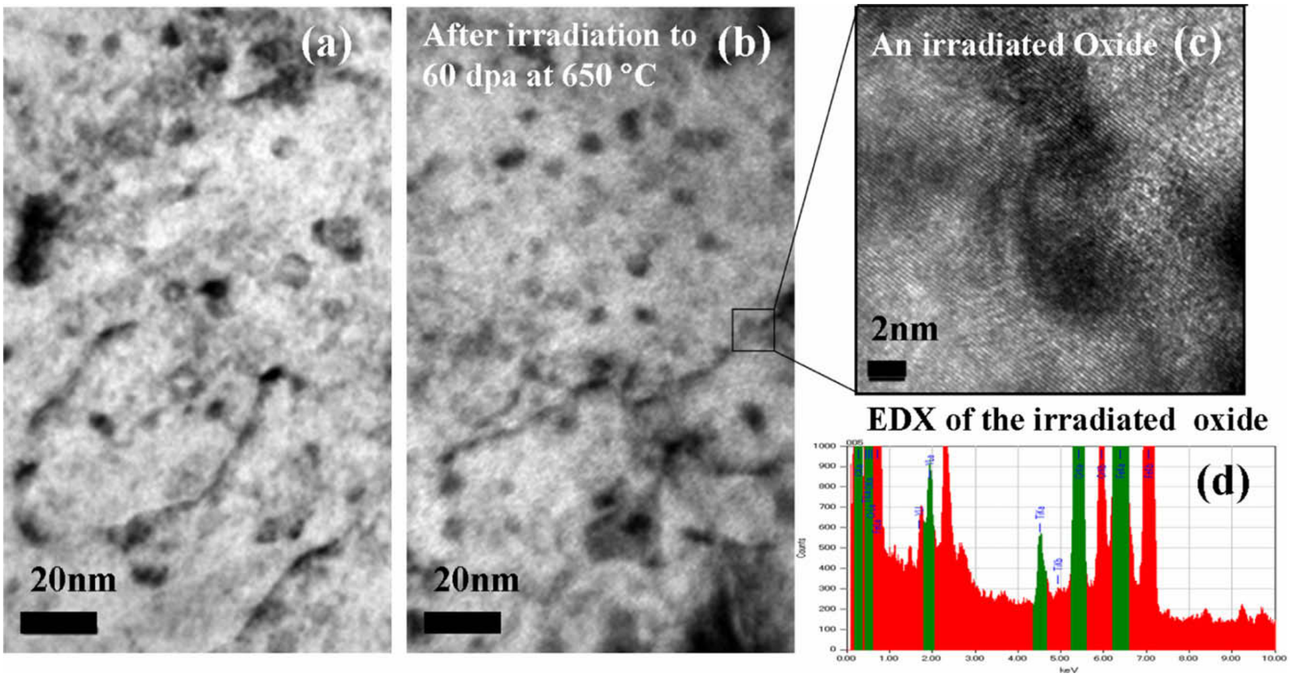

Fig. 4. TEM and EDX investigation of ion-irradiated 16Cr0.1Ti ODS steel: (a) unirradiated, (b) ion-irradiated up to 60 dpa at 1200 °C, (c) high-resolution TEM image of irradiated oxide, and (d) EDX analysis of an irradiated oxide.

Because the oxide with a diameter of 11 nm is smaller than the thickness of the foil having several tens nm thick, the EDX data of oxides includes both the matrix and oxide. However, the oxide is a (Y, Ti) complex oxide with a Y:Ti ratio of 2:1 before the irradiation. There is a possibility of the HRTEM image of the oxide showing a complex contrast because the oxide was observed from an out-of-zone axis. On the basis of these data, the irradiation effects were investigated. The irradiated oxide is buried in a thick foil, and the observation of oxides in the stress fields of dislocation or sub-grain boundaries in the irradiated materials was more difficult than unirradiated materials. This fact may mean that the oxides serve as obstacles against the movement of dislocations and grain boundaries under the ion irradiation environment at 650 °C. No change was detected in the dispersion of oxides and shape of each oxide. Although the higher background in the EDX analysis indicated that the TEM specimen was thicker than the unirradiated specimen, the atomic ratio of Y:Ti was maintained at 2:1. From these results, this research may be summarized as follows: no change was observed in the microstructure and oxides in the 16Cr0.1Ti ODS steel after ion irradiation up to 60 dpa at 650 °C.

5. Conclusion

The stability of dispersed oxides in ODS steels under irradiation at elevated temperatures was investigated using a heavy-ion irradiation method and TEM investigation. The materials used for this research were 16Cr–0.1Ti–0.35Y_2O_3 (16Cr0.1Ti) ODS ferritic steels. EDX analysis indicated that the oxides were (Y, Ti) complex oxides with the atomic ratio Y:Ti = 2:1. Although the lattice plane spacing estimated from the FFT image of HRTEM investigation indicated that the oxides were cubic $Y_2Ti_2O_7$ or orthorhombic Y_2TiO_5, the specifications of the oxide are still unknown. The ion irradiation experiment was performed up to 60 dpa at 650 °C using 6.4 MeV Fe ions at a dose rate of 5×10^{-4} dpa/s. No change was observed in the dispersion of the oxides and the shape of each oxide. The atomic ratio Y:Ti was also constant at 2:1. No change was detected in the microstructure and oxides present in the 16Cr0.1Ti ODS steel after ion irradiation up to 60 dpa at 650 °C.

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