Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 367–370 (2007) 179–184
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Heavy-ion irradiation effects on the morphology of complex oxide particles in oxide dispersion strengthened ferritic steels

H. Kishimoto [a,*], K. Yutani [b], R. Kasada [a,b], O. Hashitomi [a], A. Kimura [a,b]

[a] *Institute of Advanced Energy, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan*
[b] *Graduate School of Energy Science, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

Abstract

The mechanical strength of oxide dispersion strengthened (ODS) ferritic steels depends on the oxide particles, such as Yttria. Other elements such as titanium and aluminum are added to refine the dispersed particles of ODS steels. The addition of elements results in the formation of complex oxides such as (Y, Al) and (Y, Ti) oxides. Because the ODS steels are proposed for the higher temperature operation of fusion applications, the stability of the complex oxides under irradiation environments is important. In this work, a microstructural stability investigation under heavy-ion irradiation was carried out for ODS steels focusing on the morphology of (Y, Ti) and (Y, Al) complex oxides. The 19Cr ODS steel strengthened by (Y, Ti) complex oxides and 19Cr–2W–4Al steel with (Y, Al) complex oxides were ion-irradiated and investigated using TEM. The results revealed that the complex oxides were stable after the ion irradiation at 670 °C and 150 dpa.

1. Introduction

Reduced activation ferritic/martensitic (RAFM) steels have been developed as structural materials for the first wall of fusion reactors. The highest operation temperature of a fusion reactor using RAFM steels is limited at 550–600 °C because of low creep strength of the RAFM steels. Oxide dispersion strengthened (ODS) steels are expected to increase the operation temperature up to about 650 °C and thus increase the energy efficiency of fusion reactors [1,2]. There are many kinds of ODS steels. The most popular oxide element for ODS alloys is yttria (Y_2O_3). Yttria is added to the pre-alloyed powders and dissolves into solid solution in the metal powder during mechanical alloying. The yttria precipitates during the consolidation process such as hot extrusion and HIPing, and recrystallization thermal treatments [3]. The finely dispersed oxides having the diameter of nano-meter scale are known to improve the mechanical properties of ODS steels at high temperature [4]. Larger oxides and other precipitates such as carbides do not contribute to the dispersion strengthening, or in the worst case, they might result in degradation of mechanical properties. Titanium

* Corresponding author. Tel.: +81 774 38 3565; fax: +81 774 38 3467.
E-mail address: hkishi@iae.kyoto-u.ac.jp (H. Kishimoto).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.03.149

and aluminum form finer complex oxides with yttrium [2,5]. For example, Japanese ODS 12Y (Fe–12Cr–0.25Y_2O_3) is strengthened by yttria, but 12YWT (Fe–12Cr–2.5W–0.4Ti–0.25Y_2O_3) has yttrium–titanium complex oxides. Transmission electron microscope (TEM) investigation and the atom probe analysis showed the diameters of yttria particles and (Y, Ti) complex oxides are 10–40 nm and 3–5 nm, respectively [6]. 14YWT (Fe–14Cr–3W–0.4Ti–0.25Y_2O_3) and a commercial ODS MA957 (Fe–14Cr–0.9Ti–0.3Mo–0.25Y_2O_3) are also strengthened by the yttrium–titanium complex oxides [7]. Aluminum is also a popular element for ODS steels. PM2000 (Fe–20Cr–5.5Al–0.5Ti–0.5Y_2O_3) and MA956 (Fe–20Cr–4.5Al–0.5Ti–0.5Y_2O_3) are typical materials which are reinforced by yttrium–aluminum complex oxides. It was reported that the mean diameters of (Y, Al) complex oxides are shown to range from 9 nm to 24 nm [5,8]. In the present research, microstructural stability of ODS steel in the irradiation environment, especially focusing on the stability of oxide particles, are investigated using heavy-ion irradiation and TEM observation.

2. Experiments

Two kinds of ODS steels, 19Cr–0.3W–0.3Ti–0.35Y_2O_3 and 19Cr–2W–4Al–0.3Ti–0.35Y_2O_3 ODS ferritic steels which were designated K1 and K4, respectively, were used for this research. These ODS steels were developed as high corrosion resistant ODS steels based on 12YWT. The K1 and K4 alloys were reinforced by (Y, Ti) and (Y, Al) complex oxides, respectively [9]. The chemical composition of these materials is shown in Table 1. The pre-alloyed powders were prepared at COBELCO Ltd. These powders were mechanical alloyed with Y_2O_3 powder in an argon gas atmosphere at room temperature. The powders were consolidated by a hot extrusion method at 1150 °C. After the hot extrusion, the consolidated ODS steels were annealed at 1050 °C for 1 h. Disk-shaped specimens, 3 mm in diameter and 0.25 mm in thickness, were cut and their surfaces were polished by mechanical- and electro-polishing. The dual-Beam Material Irradiation Facility for Energy Technology (DuET) at the Institute of Advanced Energy, Kyoto University, was used for this research [10]. The materials were irradiated by 6.4 MeV Fe^{3+} ions by using a 1.7 MeV tandem accelerator. The Fe^{3+} ion is a self-ion for steels and was selected to minimize the effects of heavy-ion implantation. The depth profiles of the displacement damage were calculated by SRIM98 code. The irradiation temperature was from 300 °C to 700 °C. The values of nominal dose rate and dose were 1×10^{-3} dpa/s and up to 150 dpa at about 600 nm depth from the surface. A focused ion beam (FIB) processing was used for the preparation of longitudinal cross-section TEM specimens from the irradiated ODS steels. The thinned foils were electro-polished for very short time to remove the surface layer damaged by FIB processing. The thin foils were cut from the specimens and lifted using a micro pick-up system. The lifted samples were put on carbon-film supported copper grids, or settled on molybdenum meshes. The TEM investigation was performed using JEOL JEM2010 and JEM2200FS.

3. Results

Fig. 1(a) and (b) shows the back scattered electron images of unirradiated K1 and K4 alloys, respectively. These materials had elongated grains along the hot extrusion direction. The back scattered electron images indicated that aluminum-oxide particles (Black particles in Fig. 1(b)) and chromium-rich phases (White phases in Fig. 1(b)) existed in the K4 alloy. The aluminum-oxide particles were not observed in the K1 alloy. TEM image of unirradiated K4 alloys is shown in Fig. 2. XRD and TEM-EDX investigation revealed two kinds of oxides, alumina and (Y, Al) complex oxides, and carbides which were determined to be $M_{23}C_6$ and titanium carbonitrides, Ti (C, N), existed in the K4 alloy. The K1 alloy had simpler precipitation of (Y, Ti) complex oxides and $M_{23}C_6$. Fig. 3 shows a cross-sectional TEM image of K4 alloy after ion-irradiation at 670 °C. A result of depth profile of

Table 1
Chemical composition of investigated ODS ferritic steels

ID	Materials	C	Si	Mn	Cr	W	Al	Ti	Y_2O_3
K1	19Cr–0.3W–0.3Ti–0.35Y_2O_3	0.05	0.041	0.06	18.37	0.29	<0.01	0.28	0.368
K4	19Cr–2W–4Al–0.3Ti–0.35Y_2O_3	0.09	0.039	0.06	18.85	1.83	4.61	0.28	0.368

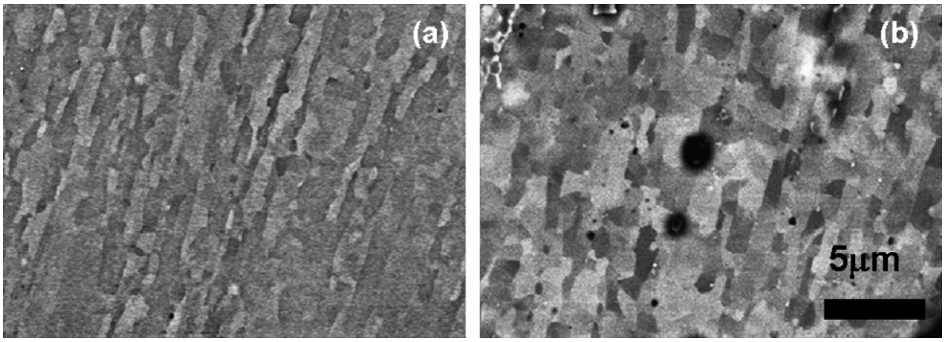

Fig. 1. Back scattered images of microstructure: (a) K1 alloy and (b) K4 alloy.

Fig. 2. TEM image of unirradiated K4 alloy.

displacement damage for steels calculated by SRIM 98 is also shown in Fig. 3. The heavy-ion beam entered from the specimen surface and stopped at the depth of about 2 μm. Though both irradiated and unirradiated microstructures were included in Fig. 3, no significant difference between the two microstructures was observed. Because a high density of dislocations exists along the grain boundaries, it is difficult to see the real grain shapes and precipitates. Scanning TEM (STEM) was convenient for the observation of this alloy. Fig. 4(a) and (b) are the STEM images of cross-sectional microstructures of K1 and K4 alloys, respectively. Fig. 4(a) shows that a heavy-ion irradiation at 670 °C did not modify the shape of microstructure, significantly. There were no large precipitates except for $M_{23}C_6$ phase along the grain boundaries of extruded direction in the K1 alloy. On the other hand, there were some Ti(C, N) precipitates and an alumina particle in the K4 alloy as shown in Fig. 4(b). Ti(C, N) precipitates in the irradiated range looked smaller than those in unirradiated material, but the number density of Ti(C, N) was too small to perform statistic analysis. TEM images in Fig. 5 show the (Y, Al) complex oxides before and after the ion-irradiation. The dispersion and shapes of (Y, Al) complex oxides seems not to be changed by ion-irradiation up to 150 dpa at 670 °C. The mean diameter of fine oxides observed for (Y, Al) complex oxides in the K4 alloy and

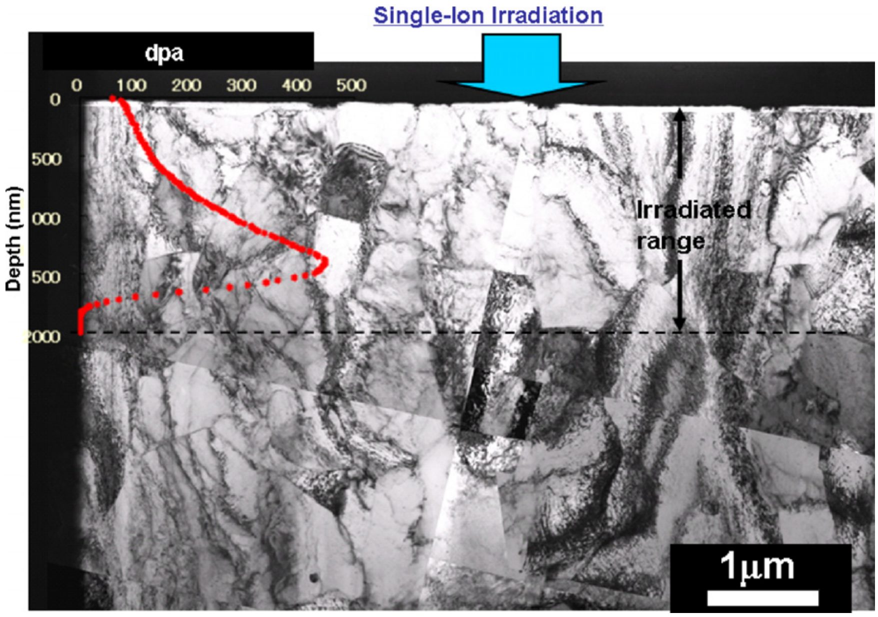

Fig. 3. Cross-sectional TEM image of K4 alloy after ion irradiation up to 150 dpa at 670 °C.

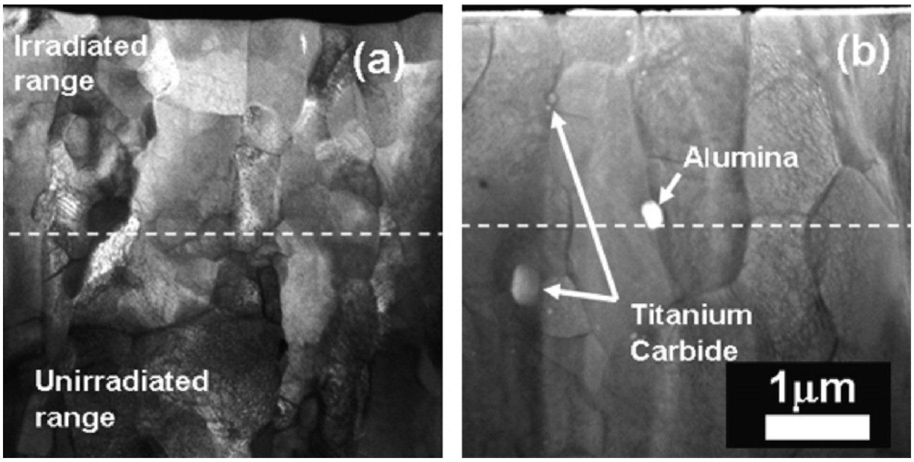

Fig. 4. Cross-sectional STEM images of K1 and K4 alloys after ion irradiation up to 150 dpa at 670 °C: (a) K1 alloy and (b) K4 alloy.

(Y, Ti) complex oxides in the K1 alloy are shown in Fig. 6. Though the diameters slightly rise and fall, it seemed that both (Y, Al) and (Y, Ti) complex oxides remain stable under the heavy-ion irradiation of the present condition.

4. Discussion

The mechanical properties of ODS steels depend on the dispersed particles, especially at elevated temperature. Monnet, et al. reported precise research on dispersed oxides under neutron irradiation for ODS alloys and showed the possibility of morphologic instability of dispersed particles against neutron irradiation [11]. In the present research, no morphologic instability or changes of particle dispersion for both (Y, Al) and (Y, Ti) complex oxides could be detected. A precise analysis of construction of fine particles is in progress. There is a possibility that at least two kinds of (Y, Al) complex oxides might exist in the K4 alloy. This means that the K4 alloy has similar precipitates to MA956 [5], and we need

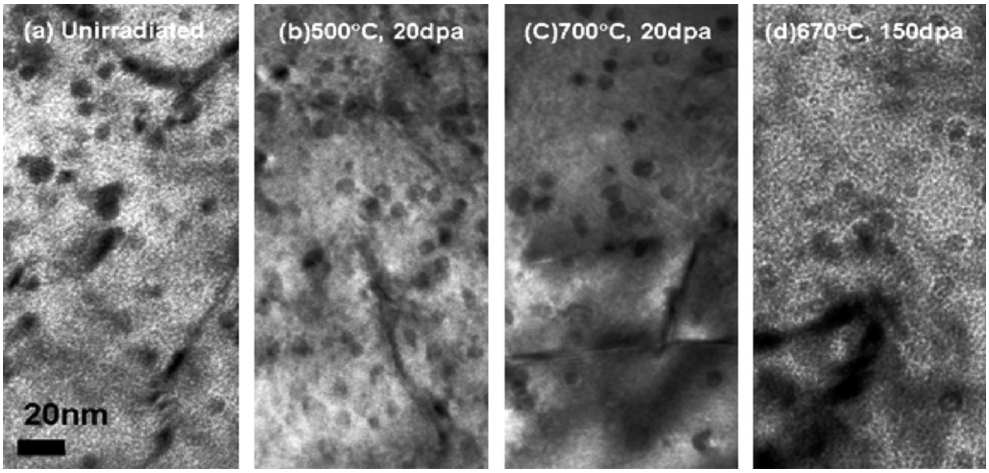

Fig. 5. TEM image of (Y, Al) oxides in K4 alloys: (a) Unirradiated, (b)irradiated at 500 °C and 20 dpa, (c) irradiated at 700 °C and 20 dpa and (d) irradiated at 670 °C and 150 dpa.

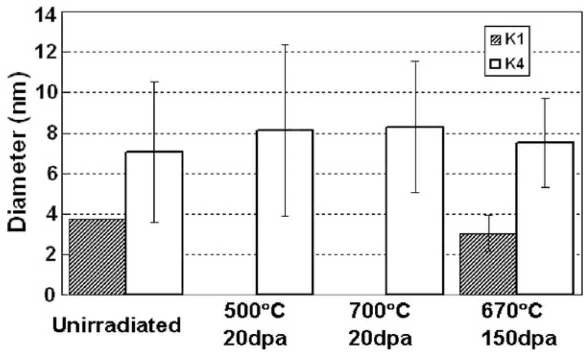

Fig. 6. Irradiation effects on diameter of dispersed oxides of both (Y, Ti) complex oxides in K1 alloy and (Y, Al) complex oxides in K4 alloy.

to consider the possibility that the finest precipitates which contribute to the dispersion strengthening and the coarser oxides which are easy to investigate may be different species. Actually, it is difficult to investigate the finest precipitates because of the size of particles. Many techniques, such as atom probe tomography and small angle neutron scattering (SANS) [7,12], should be employed for the investigation of oxide particles on ODS steels.

The grains of both K1 and K4 alloys were not significantly changed but were surrounded with a high density of dislocations after the irradiation up to 150 dpa at 670 °C. This phenomenon might indicate that the dispersed particles prevented grain growth. Because such dislocations were not in the K4 alloy irradiated up to 20 dpa at 500 °C and 700 °C. Because of the limit of ion range, the lower half of a cross-sectional TEM image of thin foil is not damaged by the ion irradiation. The dislocations surrounding grains existed in both unirradiated and irradiated ranges, thus, this grain growth seemed to be a thermal effect. This means that both K1 and K4 alloys were not recrystallized during the hot extrusion and thermal treatments as was 12YWT and MA957 [4]. As shown in Figs. 4 and 5, the grain morphology and size in irradiated range was not different from that in unirradiated material, so it is considered that the fine dispersed oxides in irradiated range remained stable against the ion-irradiation up to 150 dpa and resisted the grain modification at 670 °C.

5. Conclusion

The morphologic stability of dispersed oxides in ODS steels under irradiation environment at elevated temperature was investigated using a heavy-ion irradiation method and TEM investigation. The materials used for this research were 19Cr–0.3W–0.3Ti–0.35Y_2O_3(K1) and 19Cr–2W–4Al–0.3Ti–0.35Y_2O_3 (K4) ODS ferritic steels which were reinforced by (Y, Ti) and (Y, Al) complex oxides, respectively. The ion irradiation experiment was performed up to 150 dpa and 700 °C using 6.4 MeV Fe^{3+} ions with a dose rate of 1×10^{-3} dpa/s. No significant modification of microstructure occurred in both K1 and K4 ODS alloys after the ion irradiation up to 150 dpa at 670 °C. TEM investigation demonstrated the microstructural stability of both (Y, Ti) and (Y, Al) complex oxides under the ion irradiation of the present condition.

References

[1] D.S. Gelles, ISIJ Int. 30 (1990) 905.
[2] S. Ukai, M. Fujiwara, J. Nucl. Mater. 307–311 (2002) 749.
[3] H.K.D.H. Bhadeshia, Mater. Sci. Technol. 16 (2000) 1404.
[4] R.L. Klueh, J.P. Shingledecker, R.W. Sweindeman, D.T. Hoelzer, J. Nucl. Mater. 341 (2005) 103.
[5] A. Czyrska-Filemonowicz, B. Dubiel, J. Mater. Process. Technol. 64 (1997) 53.
[6] R.L. Klueh, D.S. Gelles, S. Jitsukawa, A. Kimura, G.R. Odette, B. Van der Schaaf, M. Victoria, J. Nucl. Mater. 307–311 (2002) 455.
[7] M.K. Miller, D.T. Hoelzer, E.A. Kenik, K.F. Russel, Intermetallics 13 (2005) 387.
[8] A. Wasilkowska, M. Bartsch, U. Messerschmidt, R. Herzog, A. Czyrska-Filemonowicz, J. Mater. Process. Technol. 133 (2003) 218.
[9] R. Kasada, N. Toda, H.S. Cho, A. Kimura, in: Proceedings of the 2005 International Congress on Advances in Nuclear Power Plants (ICAPP '05), Seoul, Korea (2005). p. 5328.
[10] A. Kohyama, Y. Katoh, M. Ando, K. Jimbo, Fusion Eng. Des. 51&52 (2000) 789.
[11] I. Monnet, P. Dubuisson, Y. Serruys, M.O. Ruault, O. Kaïtasov, B. Jouffrey, J. Nucl. Mater. 335 (2004) 311.
[12] M.J. Alinger, G.R. Odette, D.T. Hoelzer, J. Nucl. Mater. 329–333 (2004) 382.