Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 329–333 (2004) 377–381
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Nano-oxide particle stability of 9–12Cr grain morphology modified ODS steels under neutron irradiation

S. Yamashita [a,*], N. Akasaka [a], S. Ohnuki [b]

[a] *Irradiation Center Oarai Engineering Center, Japan Nuclear Cycle, Development Institute, Materials Monitoring Section, Fuels and Materials Division, 4002, Narita-cho, Oarai-machi, Ibaraki 311-1393, Japan*
[b] *Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8628, Japan*

Abstract

ODS steels based on a 9–12Cr composition were developed with modified grain morphology and incorporation of recrystallization heat treatment and martensitic transformation process into previous tube fabrication methods. The modifications were for improving strength anisotropy in hoop and longitudinal directions of cladding tubes. Specimens were irradiated in the experimental fast reactor JOYO at temperatures of 670–807 K to 15.0 dpa maximum. TEM and/or HRTEM observation indicated that nano-scale sized oxide particles were finely distributed in each alloy and were relatively stable under neutron irradiation. Quantitative constitution analyses showed that most of the oxide particles were comprised of yttrium and titanium, and that they were in most case non-stoichiometric. Comparing with past reports on neutron-irradiated ODS steels, the main factors determining oxide stability under neutron irradiation are shown to be irradiation temperature and/or type of oxide.

1. Introduction

In design of water-cooled solid breeder blankets, reduced activation ferritic steels are promising structural materials because of their high swelling resistance and well established industrial base. To achieve higher thermal efficiency in the system, use of oxide dispersion strengthened (ODS) ferritic steels that possess excellent high-temperature mechanical properties and superior swelling resistance has been considered [1].

Considerable efforts have been made to produce ODS ferritic steel fuel cladding tubes for a commercial liquid metal fast reactor [2–5]. As the results, two technological breakthroughs in their application for cladding material were achieved. The first breakthrough was success in the production of thin-walled cladding tubes from the mechanically alloyed ODS ferritc steels with low formability [2]. With this success, the second need arose; the thin-walled cladding tubes indicated unexpected strength anisotropy in the hoop and longitudinal directions, which was attributed to strongly elongated grain morphology with high aspect ratio. It was desired to improve the unique grain morphology induced by the previous fabrication process. Ukai et al. demonstrated that introduction of a recrystallization heat-treatment process [4] or a martensitic transformation heat-treatment [5] into the previous course of tube fabrication were highly effective for those modifications.

The development of ODS ferritic steels has made remarkable progresses, but studies on irradiation effects, i.e. from post-irradiation examinations, of those ODS steels are limited because of few irradiation opportunities [6–9]. Oxide particle effect on microstructural evolution, in particular, is important since these stable obstacles are believed to enhance the irradiation creep resistance at high temperature due to interaction with dislocations, but there is little data to support this tentative prediction.

This study focuses on oxide particle behavior under neutron irradiation in the modified ODS steels, and

* Corresponding author. Tel.: +81-29 267 4141; fax: +81-29 266 3713.
E-mail address: yamashita.shinichirou@jnc.go.jp (S. Yamashita).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.041

evaluates the nano-oxide particle stability in those steels by means of transmission electron microscope (TEM) and/or high resolution TEM (HRTEM). Microstructural evolution except for oxide particle effects [10] and mechanical responses [11] in the same neutron-irradiated ODS steels are discussed in the other papers referenced.

2. Experimental procedure

The materials investigated are, in wt%, Fe–0.06C–12Cr–2W–0.3Ti–0.25Y_2O_3 (F95) and Fe–0.12C–9Cr–2W–0.2Ti–0.35Y_2O_3 (M93). Details of the tube manufacturing process and the chemical composition can be found elsewhere [3,11].

The fast neutron irradiation in the experimental fast reactor JOYO was done at a temperature between 670 and 807 K to a fluence of 0.5 to 3.0×10^{26} n/m^2 ($E > 0.1$ MeV), equivalent to 2.5–15.0 dpa, respectively.

Samples were prepared by the following three processes: (i) sheets sliced along the longitudinal direction of the tube were mechanically thinned to $\leqslant 0.2$ mm, and then 3 mm diameter discs were punched from the sheets. Those discs were electro-polished with an electrolytic solution of CH_3COOH:$HC1O_4 = 19$:1. (ii) Rings cut from the transverse direction of the tube were mounted in a resin for mechanical reduction to $\leqslant 0.7$ mm. A micro-sample for mass reduction was made of the rings by using a FIB (focused ion beam) device. Dimensions of the FIB fabricated part were around $15^{l} \times 15^{w} \times 1^{t}$ μm^3. These parts were removed from the substrate, and fixed on non-magnetic substrates by W deposition. Finally, those micro-samples were electro-polished using the same electrolyte as (i) to remove the defect layer introduced by FIB fabrication, (iii) For an extracted replica specimens, surfaces of the specimen were cleaned using electrolyte of HC1:$CH_3OH = 10$:90. A 100–200 nm thick carbon film was then deposited on the surface. Finally, the film was floated off, washed in CH_3OH and retrieved on a copper grid.

Microstructural observations of those samples were conducted by both conventional transmission electron microscope (TEM) and high resolution TEM (HRTEM). Composition analyses were performed by utilizing the energy dispersive spectrum (EDS) device mounted on each microscope.

3. Results and discussion

3.1. Grain morphology in the unirradiated and irradiated ODS steels

TEM micrographs of the unirradiated ODS steels (M93 (a), F95 (b)) and the irradiated ODS steels (M93 (c), F95 (d)) are shown in Fig. 1. It was confirmed that

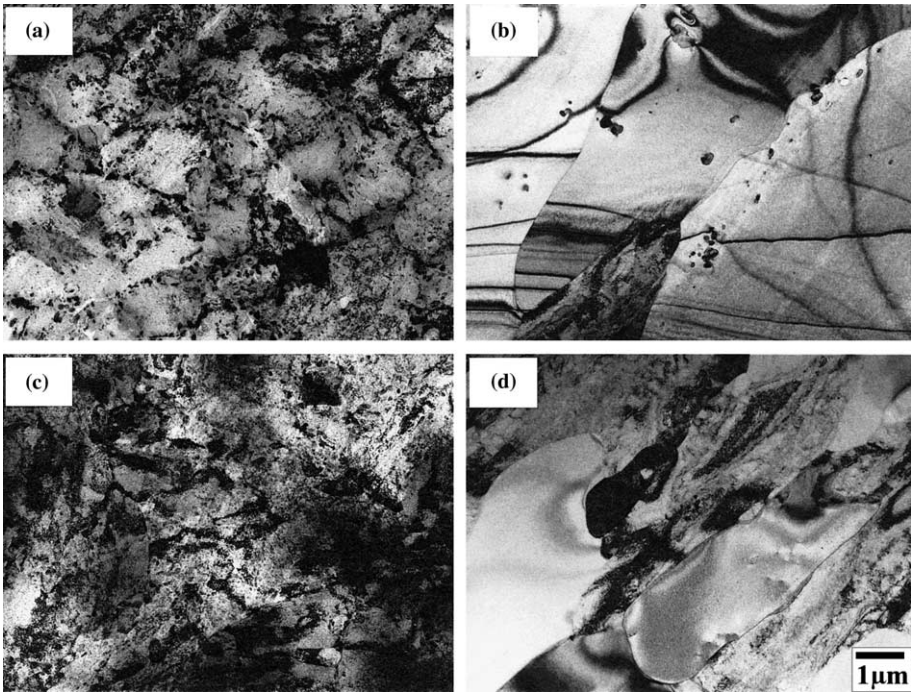

Fig. 1. Bright field TEM micrographs of M93 (a) and F95 (b) specimens before irradiation, and those of the M93 (c) and F95 (d) after irradiation at 770 K to 15.0 dpa.

initial structures of the both unirradiated F95 and M93 contained equiaxed grains due to the recrystallization heat-treatment for F95 and the martensitic transformation for M93, and also that macroscopic structural changes such as grain growth and/or recovery of the lath boundary due to irradiation were not seen. Further information on the microstructural evolution during neutron irradiation can be obtained from Ref. [10].

3.2. Nano-oxide particle distribution

Distribution of the oxide in the ODS steels is extremely important since the high temperature strength of the ODS steels is associated with the existence of oxide particles in the matrices. In Fig. 2 bright field TEM micrographs shows the distribution of the nano-scale sized oxide particle in unirradiated and irradiated F95 steel specimens. In these micrographs, the small, black contrast images represent oxide particles; the size and distribution seemed to be relatively uniform. Subsequently, dispersion parameters such as number density and average size of the oxide particles were measured from the TEM micrographs and are summarized in Table 1. Within experimental uncertainty, it could be said that there were slight changes but not significant in the dispersion parameters of the oxide particles before and after irradiation.

Table 1
Dispersion parameters of the oxide particles measured from TEM micrographs in Fig. 2

	Unirrad.	727 K, 14.0 dpa	788 K, 12.5 dpa
Average size (nm)	4.13	4.18	5.26
Number density ($\times 10^{22}$ N/m^3)	2.43	1.92	1.22

Table 2
Quantitative EDS analyses of oxide particles included in extracted replica specimens

	Ti (at%)	Y (at%)	Y/Ti (N*)
MP3			
Unirrad.	31.9–43.0	57.0–68.1	1.33–2.14 (7)
2.5 dpa (670 K)	43.8–56.9	43.1–56.2	0.87–1.26 (5)
15.0 dpa (770 K)	35.6–48.5	51.5–64.4	1.06–1.81 (2)
7.0 dpa (807 K)	39.8–48.7	51.3–60.2	1.05–1.51 (4)
F95			
Unirrad.	36.1–41.4	58.6–63.9	1.42–1.77 (5)
2.5 dpa (670 K)	26.2–32.5	67.5-73.8	2.08–2.82 (7)
15.0 dpa (770 K)	34.0–49.4	50.6–66.0	1.02–1.94 (6)
7.0 dpa (807 K)	37.2–42.3	57.7–62.8	1.36–1.69 (3)

*N represents the number of analyzed oxide particles.

3.3. Characterization of nano-oxide particles

Quantitative chemical analyses of nano-oxide particles in the extracted replicas of the unirradiated and irradiated ODS steels were carried out using the EDS analysis device mounted on the HRTEM, and the results are summarized in Table 2. It was found that most of the nano-oxide particles were compounds consisting of titania and yttria. Atomic ratio of yttrium to titanium, Y/Ti, indicated that these compounds had a wide constitution range. Although corresponding chemical forms for yttria–titania complex oxides in ODS steels, Y_2TiO_5 (Y_2O_3–TiO_2) or $Y_2Ti_2O_7$ (Y_2O_3-$2TiO_2$), can be found in the literature [12], the results obtained were not always in accordance with the ratio of either 2 for Y_2TiO_5 or 1 for $Y_2Ti_2O_7$. These results would suggest that most of the complex oxides in these ODS steels were non-stoichiometric.

Crystal structures of the complex oxides were investigated from the high resolution image analyses. Fig. 3 shows a representative HRTEM image for the extracted replica specimen. The power spectrum of the complex

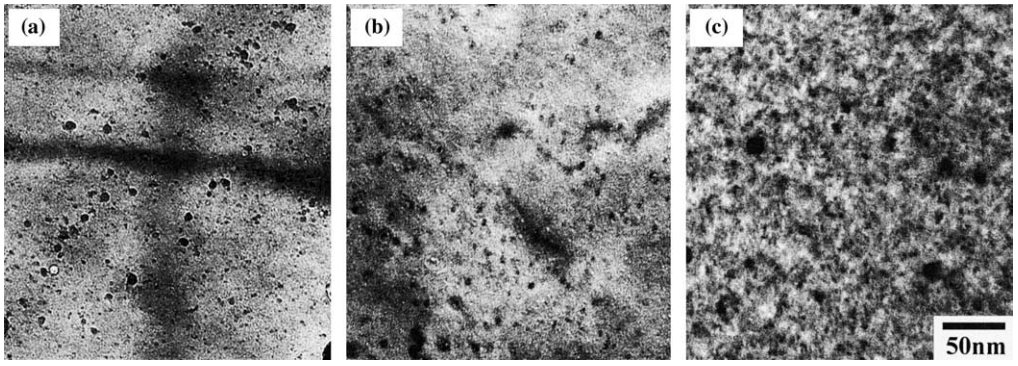

Fig. 2. Bright field TEM micrographs showing the distribution of nano-scale sized oxide particles in unirradiated F95 specimen (a) and irradiated F95 specimens, 14.0 dpa at 727 K (b) and 12.5 dpa at 788 K (c).

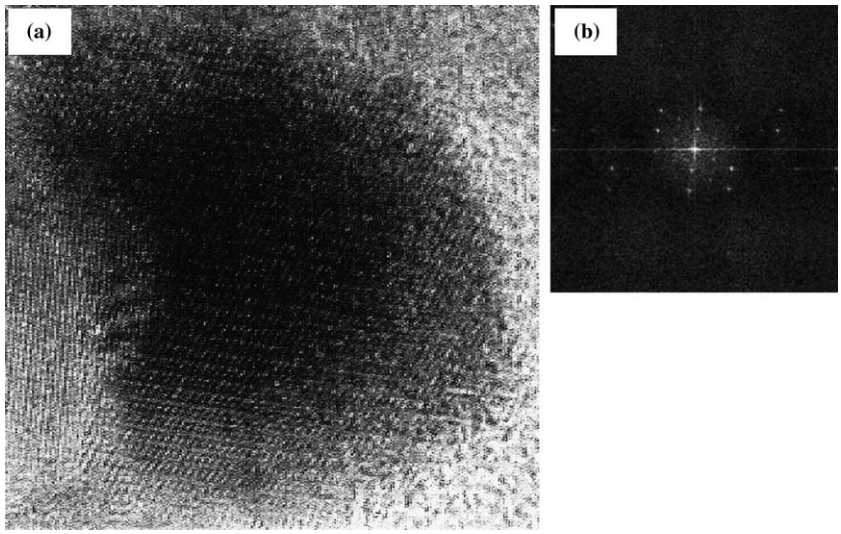

Fig. 3. HRTEM image of the complex nano-scale sized oxide particle in the extracted replica specimen of unirradiated M93 steel specimen (a) and the power spectrum (b).

oxide was very similar to that of the [0 1 1] reflection of a face-centered cubic lattice. According to past X-ray studies, a compound with the composition of $A_2B_2O_7$ was generally interpreted to have a complicated pyrochlore-type structure with a cubic lattice [13]. Therefore, it is believed that the primary compound of the yttria–titania complex oxide was $Y_2Ti_2O_7$ and that, in cases that the ratio of yttrium and titanium were unbalanced locally, the constitution changed.

3.4. Nano-oxide particle stability during neutron irradiation

As discussed in Section 3.2, oxide particles in this study showed relatively high stability under neutron irradiation to 15.0 dpa. However, it is significant to compare our experimental evidence with the others to understand roughly oxide stability under neutron irradiation even if experimental details such as chemical composition, irradiation temperature/dose and fabrication history differ among them. A few reports on microstructural evolution including oxide behavior in neutron-irradiated MA957 [6], DT2203Y05 [7], 1DS and 1DK [8] have been published. A comparison between MA957 and DT2203Y05 provides a clue to oxide stability determining factors under neutron irradiation, since they show opposite results on oxide stability. Compared with the results in over 200 dpa-irradiated MA957 and 81 dpa-irradiated DT2203Y05, oxide particles dissociated during irradiation in the latter, and the irradiation dose were considered not to affect so much on the oxide stability. How about the effect of irradiation temperature on that? The temperature was about 100 K higher in the DT2203Y05. A slight coarsening of oxide particles in this study was recognized as well at higher temperature irradiation (Fig. 2). Therefore, it is believed that irradiation temperature is one of the oxide stability determining factors. Besides irradiation temperature, another factor could be considered; type of complex oxide. DT2203Y05 oxde particles were not a pure yttria–titania compound like 1DS and 1DK in previous our work and M93 and F95 in this study, but included aluminum in that alloy. Further investigation would be needed to know which complex oxide is more stable under neutron irradiation. Taking into account all experimental results, oxide stability determining factors were believed to be irradiation temperature and/or type of complex oxide.

4. Conclusion

The nano-oxide particle stability in both grain morphology modified ODS ferritic steels and martensitic steels under neutron irradiation were evaluated by microstructural observations and chemical analyses using conventional TEM and HRTEM. The results were summarized as follows.

(1) Nano-oxide particles that consisted of yttrium and titanium were finely distributed in the matrices before and after irradiation, and they were confirmed to be stable for neutron irradiation to 15.0 dpa.
(2) Most of the complex oxide particles in these ODS steels were found to be $Y_2Ti_2O_7$ which had a complicated pyrochlore-type structure, but the composition was non-stoichiometric.

References

[1] S. Konishi, S. Nishio, K. Tobita, Fusion Eng. Des. 63&64 (2002) 11.
[2] S. Ukai, M. Harada, H. Okada, M. Inoue, S. Nomura, S. Shikakura, T. Nishida, M. Fujiwara, K. Asabe, J. Nucl. Mater. 204 (1993) 74.
[3] S. Ukai, S. Mizuta, T. Yoshitake, T. Okuda, M. Fujiwara, S. Hagi, T. Kobayashi, J. Nucl. Mater. 283–287 (2000) 702.
[4] S. Ukai, T. Okuda, M. Fujiwara, T. Kobayashi, S. Mizuta, H. Nakashima, J. Nucl. Sci. Technol. 39 (8) (2002) 872.
[5] S. Ukai, S. Mizuta, M. Fujiwara, T. Okuda, T. Kobayashi, J. Nucl. Sci. Technol. 39 (7) (2002) 778.
[6] D.S. Gelles, Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1994, DOE/ER-0313/16, 1994, p. 146.
[7] P. Dubuisson, R. Schill, M. Hugon, I. Grislin and J. Seran, Effect of Radiation on Materials: 18th International Symposium, ASTM STP 1325, 1999, 882.
[8] S. Yamashita, K. Oka, S. Ohnuki, N. Akasaka, S. Ukai, J. Nucl. Mater. 307–311 (2002) 283.
[9] T. Yoshirake, T. Ohmori, S. Miyakawa, J. Nucl. Mater. 307–311 (2002) 788.
[10] N. Akasaka, S. Yamashita, T. Yoshitake, S. Ukai, A. Kimura, these Proceedings.
[11] T. Yoshitake, Y. Abe, N. Akasaka, S. Ohtsuka, S. Ukai, A. Kimura, these Proceedings.
[12] T. Okuda, M. Fujiwara, J. Mater. Sci. Lett. 14 (1995) 1600.
[13] F. Jona, G. Shirane, R. Repinsky, Phys. Rev. 98 (1955) 903.