Available online at www.sciencedirect.com

ScienceDirect

Journal of Nuclear Materials 367–370 (2007) 132–136

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Radiation induced phase instability of precipitates in reduced-activation ferritic/martensitic steels

H. Tanigawa [a,*], H. Sakasegawa [a], H. Ogiwara [b], H. Kishimoto [b], A. Kohyama [b]

[a] Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
[b] Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan

---

Abstract

Irradiation effects on precipitation were investigated in detail utilizing ion irradiation. F82H IEA heat, JLF-1 HFIR heat, aged F82H-IEA (873 K × 30 k h) and model alloy (Fe–Ta–C, aged) were used for experiments. The specimens were irradiated up to 10 or 20 dpa at 573 K or 773 K with 6.4 MeV Fe^{3+} ion or with degraded 1 MeV He^{+}. It turned out that the size distribution of precipitates changed by ion irradiation just the same as it was observed in neutron irradiated RAFs, and precipitates in the ion irradiated region become amorphous. Laves phase in aged F82H was also amorphized. An aged Fe–Ta–C model alloy contained a high density of TaC in the matrix, but those TaC precipitates disappeared in the ion-irradiation region after 20 dpa single/dual ion irradiation. This amorphization of precipitates and TaC re-solution in these RAFs was also observed in neutron irradiated RAFs.

© 2007 Elsevier B.V. All rights reserved.

---

1. Introduction

Reduced-activation ferritic/martensitic steels (RAF) F82H(Fe–8Cr–2W–VTa) [1,2] have mostly been irradiated in fission reactors to investigate irradiation induced mechanical property changes, but spallation neutron sources, such as SINQ (swiss spallation neutron source) and high energy light ions have also been used to investigate the microstructure changes in the low temperature range [3–7]. In those studies, the dislocation microstructure evolution, as well as the phase stability of typical precipitates ($M_{23}C_6$) was studied and amorphization of $M_{23}C_6$ below 508 K was reported. The stability of precipitates in RAFs under neutron irradiation at 573 K has been studied [8–10], and it is reported that F82H, ORNL9Cr–2WVTa, and JLF-1 show various changes in precipitates after neutron irradiation up to 5 dpa at 573 K. To investigate this phenomenon with higher accuracy, those RAFs and a model alloy were irradiated with heavy ion beam. Our work includes precipitate size distribution and phase stability.

2. Experimental

The materials used were IEA-modified F82H (F82H-IEA), ORNL9Cr-2WVTa (ORNL9Cr) and the JLF-1 HFIR heat (JLF-1). Aged F82H-IEA (873 k for 30 k h), which contain Laves phase, and an aged Fe–Ta–C model alloy (923 K for 500 h),

---

[*] Corresponding author. Tel.: +81 29 282 6498; fax: +81 29 284 3589.
E-mail address: tanigawa.hiroyasu@jaea.go.jp (H. Tanigawa).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.03.155

Table 1
Chemical compositions of RAFs (wt%)

	C	Cr	W	V	Ta	Ti	N	Ni
F82H- IEA	0.11	7.7	2.00	0.16	0.02	0.01	0.008	–
JLF-1	0.1	8.9	1.95	0.20	0.09	0.002	0.0215	–
ORNL9Cr	0.1	8.8	1.97	0.18	0.065	<0.01	0.023	–
F82H + 2Ni	0.1	7.9	1.99	0.19	0.06	0.005	0.004	1.97
Fe–Ta–C	0.015	–	–	–	0.20	–	–	–

Table 2
Heat treatment conditions for RAFs

F82H aged	(F82H-IEA) + 873 K × 30 k h aging
JLF-1	1323 K/1 h/AC + 1053 K/1 h
ORNL9Cr	1323 K/1 h/AC + 1023 K/1 h
F82H + 2Ni	1313 K/30 min/AC + 1023 K/1 h
Fe–Ta–C	1273 K/1 h + 923 K × 500 h aging

which contain TaC, were also irradiated for comparison. Neutron irradiated F82H-IEA, ORNL9Cr, JLF-1 and 2 wt% Ni doped F82H (F82H + 2Ni) [8–10] were provided for detailed TEM analyses. Details of the chemical compositions and the heat treatments are listed in Tables 1 and 2. Irradiation was performed at the DuET facility, at the Inst. of Advanced Energy, Kyoto University up to 10 or 20 dpa at 573 K or 773 K with 6.4 MeV Fe^{3+} ion, and with degraded 1 MeV He^{+} for dual irradiation. The helium injection ratio to dpa (He/dpa) was set to 15 appmHe/dpa for a depth between 500 nm and 700 nm from the incident surface with an energy degrader. Cross sectional TEM thin film specimens of the ion irradiated region were made utilizing focused ion beam (FIB) micro-processor with a micro-sampling system, HITACHI FB-2000 A, at the WASTEF facility, JAEA. The details of the FIB processing are given elsewhere [11]. TEM observations are performed with JEOL 2200FS and JEOL 2010FX electron microscopes at the MUSTER facility, at the Inst. of Advanced Energy, Kyoto University.

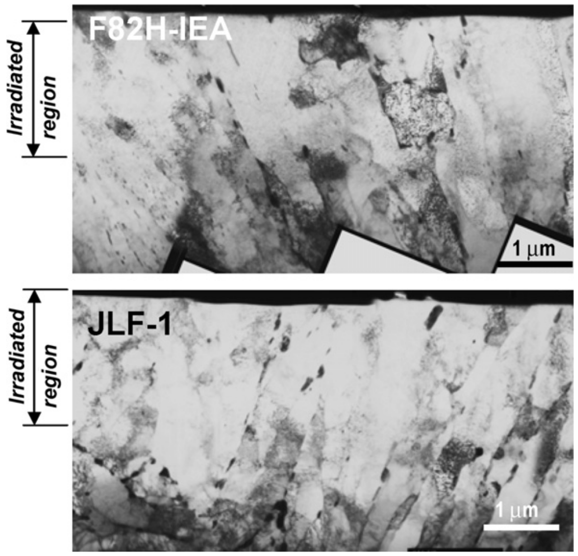

Fig. 1. STEM images of Fe ion irradiated F82H-IEA and JLF-1 at 573 K up to 10 dpa.

3. Results

The TEM microstructures of single ion irradiated F82H and JLF-1 at 573 K up to 10 dpa are shown in Fig. 1. These bright field STEM images show that

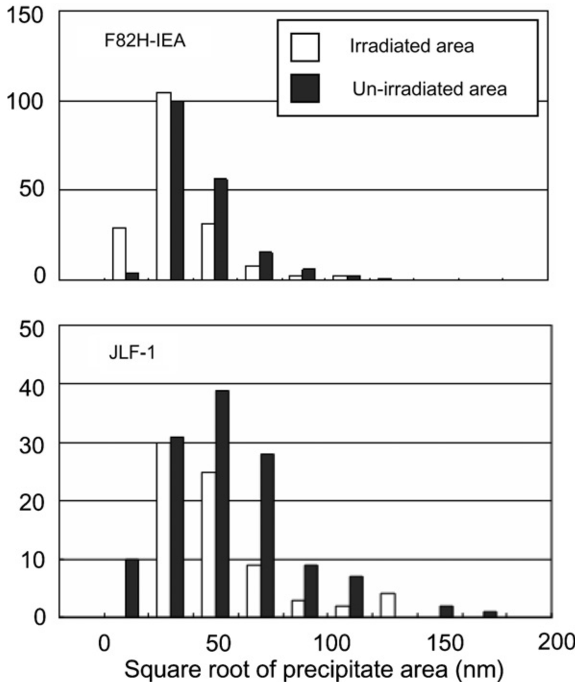

Fig. 2. Size distributions of precipitates in irradiated regions and un-irradiated regions of F82H-IEA and JLF-1 Fe-ion irradiated up to 10 dpa.

the precipitate distribution and morphology in irradiated regions are different from those in un-irradiated regions in both steels, and the lath structure become unclear in irradiated regions. The size distributions of precipitates were analyzed in irradiated regions (600–1000 nm from irradiation surface) and un-irradiated regions (2200–2600 nm) (Fig. 2). The size distributions suggest that the smaller precipitates became dominant and decreased in number in irradiated regions of F82H, but in JLF-1, the precipitates became smaller but the smallest precipitates were gone. These results suggests that these microstructures are refined in both steels but more so in JLF-1, and the same tendency was observed in neutron irradiated JLF-1 at lower dose (5 dpa/573 K) [10].

The dark filed images shown in Fig. 3 revealed that the precipitates of $M_{23}C_6$ in irradiated regions of F82H became amorphous. In aged F82H, the Laves phase also became amorphous phase (Fig. 4).

Microstructural observations on neutron irradiated RAFs (5 dpa/573 K) were performed with emphasis on the phase stability of $M_{23}C_6$ (Fig. 5). It turned out that the amorphization of $M_{23}C_6$ is very faint in F82H and JLF-1, but the amorphization was very obvious in ORNL9Cr and in F82H + 2Ni. This tendency is in agreement with the XRD analyses results on extraction residues from neutron irradiated RAFs which were previously reported [10], which showed that the X-ray peaks for all irradiated specimens tended to have broadening and lower intensity with the median at about 45°, especially on F82H + 2Ni. Those results support the presence of amorphous $M_{23}C_6$.

The aged Fe–Ta–C model alloy was irradiated at 773 K up to 20 dpa with single and dual ion beams. The microstructural observation suggests that the TaC, which is the dominant precipitate in un-irradiated regions disappeared from irradiated regions in both single/dual irradiation conditions (Fig. 6). This instability of TaC due to irradiation was also observed in XRD analysis results on extraction residues of neutron irradiated RAFs [10] as the MX peaks for JLF-1 and ORNL9Cr disappeared after irradiation.

4. Discussion

The amorphization of $M_{23}C_6$ in F82H or other 9Cr ferritic/martensitic steels has been reported by

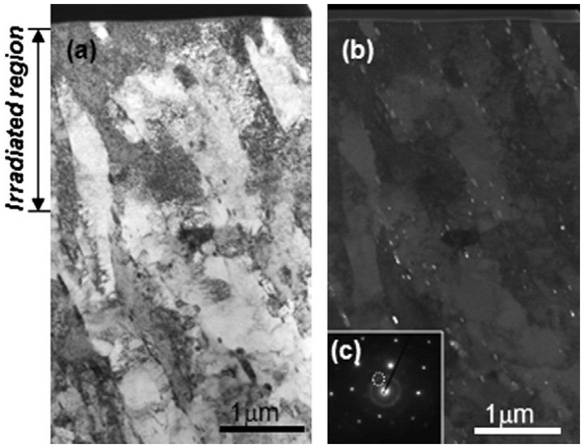

Fig. 3. TEM images of Fe-ion irradiated F82H at 573 K up to 10 dpa: (a) bright field image; (b) dark field image; and (c) diffraction pattern. White circle on (c) indicates the position of objective aperture to image the dark field image.

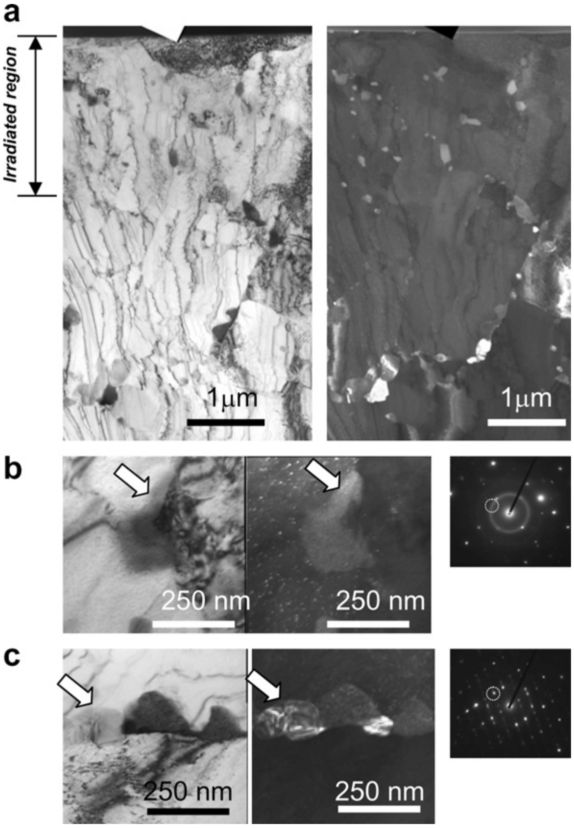

Fig. 4. (a) Bright field and dark field images of Fe ion irradiated aged F82H-IEA, irradiated at 573 K up to 10 dpa, and magnified images of Laves (indicated by open block arrow) and $M_{23}C_6$ in (b) irradiated region and (c) un-irradiated region with diffraction pattern from the area. White circles on diffraction patterns indicate the position of objective aperture to image dark field images.

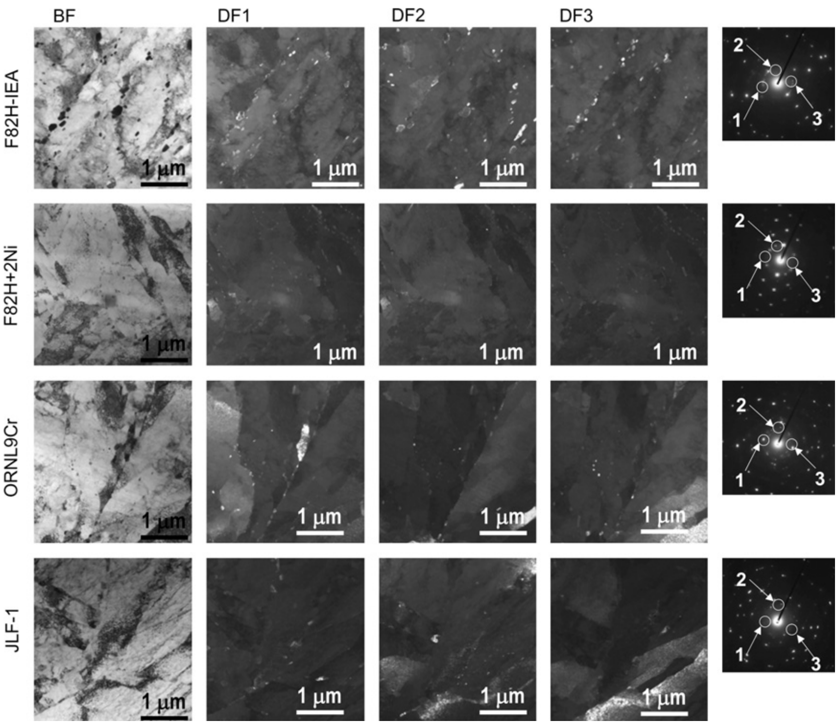

Fig. 5. TEM images of neutron irradiated RAFs, up to 5 dpa at 573 K. Dark field images DF1, 2 and 3 were taken by selecting the arrowed region of each diffraction pattern.

Dai et al. [3,5] Schaublin and Victoria [4], Jia et al. [6], and Sence et al. [7]. Schaublin examined F82H at room temperature and 523 K with proton and/or neutron irradiation, and suggested that the amorphization of $M_{23}C_6$ was observed only for specimens which were irradiated at room temperature [4]. Jia examined an F82H microstructure which was irradiated up to 10–12 dpa in the temperature range of 413–633 K at SINQ, and concluded that the glass transition temperature (T_g) was 508 K [6]. The results provided by Dai and Sence on the $M_{23}C_6$ amorphization after lower temperature irradiation are also in good agreement with the result of Jia.

However, the results provided in this work demonstrate the amorphization of $M_{23}C_6$ at 573 K, well above the value for T_g given by Jia. This discrepancy could be interpreted by the generalized Lindeman criterion (GLC) theory for radiation induced amorphization (RIA) provided by Okamoto et al. [12]. Based on GLC, the RIA occurs when the mean square displacement of the phase reaches a critical value, and this condition depends on how the displacements were induced and accumulated. It should be noted that there is a threshold temperature (T_x; $T_x > T_g$) below which the radiation induced re-crystallization could not occur. In the temperature range between T_g and T_x, the material cannot be 100% amorphous, or re-crystallized.

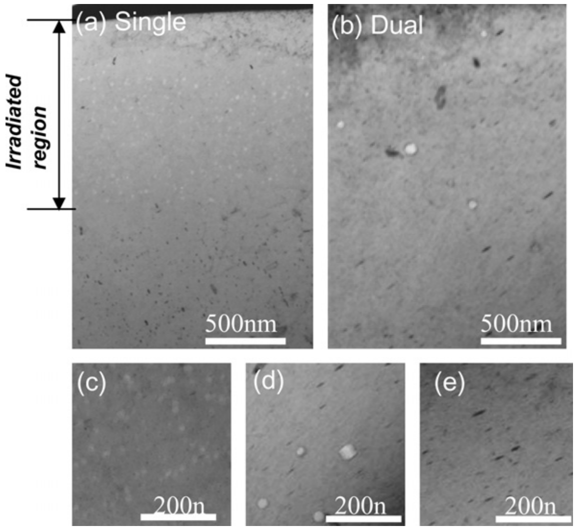

Fig. 6. TEM bright field image of Fe–Ta–C model alloy irradiated by (a) single ion and (b) dual ion at 773 K up to 20 dpa. Black contrasts in un-irradiated region correspond to TaC. Magnified bright field images of 20 dpa region of (c) single ion irradiated and (d) dual ion irradiated region, and (e) un-irradiated region.

The amorphization of $M_{23}C_6$ observed in Fe ion irradiated F82H at 573 K is possible because the displacement damage induced by Fe ion is highly efficient at producing damage compared to proton or neutron irradiation. The higher threshold temperature for RIA with heavy ion irradiation compared to light ion irradiation has also been observed for various inter-metallic materials [12]. The T_g of $M_{23}C_6$ under Fe ion irradiation must be below 773 K as there is no amorphization observed in that specimen.

The amorphization of $M_{23}C_6$ observed in neutron irradiated RAFs could be interpreted as the phenomenon between T_g and T_x. Differences for JLF-1 could arise because JLF-1 is tempered at higher temperature (1053 K) compared to other RAFs, and that makes the driving force for recovery stronger than for the other RAFs. The amorphization of $M_{23}C_6$ in F82H + 2Ni could be understood as the result of the complex composition of $M_{23}C_6$, because the chemical analyses on extraction residues indicates the presence of Ni in $M_{23}C_6$, and an increase in the mean square displacement and an increase in the threshold temperature of RIA.

The amorphization of Laves phase observed in aged F82H is expected, as the Laves phase, typically Fe_2W, is an inter-metallic and its melting temperature is above 1300 K. This result provides an alternate interpretation for the results reported by Kohno et al. [13] that the temperature time condition for the appearance of Laves phase under irradiation shifted to the higher temperatures compared to thermal aging condition, because this result suggests that the Laves phase would not appear as the stable phase below T_g of Laves phase, although the Laves phase must be present under thermal equilibrium conditions at that temperature.

The size distribution change of M_{23} C_6, and re-solution of TaC could be understood with the GLC theory, because the theory predicts that the temperature dependence of the diffusion coefficient under irradiation changes around the temperature range between T_g and T_x, and the effect of irradiation on diffusion is significant below that temperature in comparison with thermal diffusion. Since the melting temperatures for $Cr_{23}C_6$ and TaC are 1823 K and 4258 K, T_x of $M_{23}C_6$ or TaC could be assumed to be well above 573 K, and this suggests the possibility that the size distribution change or re-solution occurs with the help of diffusion enhanced by irradiation. This interpretation could also apply for the density change of defect clusters above T_g which was also reported by Jia et al. [6]

5. Summary and conclusions

Irradiation effects on precipitation were investigated in detail utilizing ion irradiation in which irradiation condition could be controlled with high accuracy, as well as on neutron irradiated specimens, with the emphasis on the phase stability of precipitates. The conclusions obtained were as follows:

(1) Radiation induced amorphization of $M_{23}C_6$ were observed in Fe ion irradiated F82H at 573 K, but not at 773 K, and the glass transition temperature T_g of $M_{23}C_6$ in F82H could be estimated between 573 K and 773 K.
(2) Radiation induced amorphization of Laves phase as observed in Fe ion irradiated aged-F82H at 573 K.
(3) The size distribution change and re-solution of TaC, which was observed in ion and neutron irradiated RAFs and in a Fe–Ta–C model alloy, could be related to the radiation induced amorphization and the radiation enhanced diffusion at that temperature range.

References

[1] K. Shiba, A. Hishinuma, J. Nucl. Mater. 283–287 (2000) 474.
[2] K. Shiba, M. Suzuki, A. Hishinuma, J. Nucl. Mater. 233–237 (1996) 309.
[3] Y. Dai, G.S. Bauer, F. Carsughi, H. Ullmaier, S.A. Maloy, W.F. Sommer, J. Nucl. Mater. 265 (1999) 203.
[4] R. Schaublin, M. Victoria, J. Nucl. Mater. 283–287 (2000) 339.
[5] Y. Dai, S.A. Maloy, G.S. Bauer, J. Nucl. Mater. 283–287 (2000) 513.
[6] X. Jia, Y. Dai, M. Victoria, J. Nucl. Mater. 305 (2002) 1.
[7] B.H. Sence, F.A. Garner, D.S. Gelles, G.M. Bond, S.A. Maloy, J. Nucl. Mater. 307–311 (2002) 266.
[8] H. Tanigawa, M.A. Sokolov, K. Shiba, R.L. Klueh, Fusion Sci. Tech. 44 (2003) 206.
[9] H. Tanigawa, N. Hashimoto, H. Sakasegawa, R.L. Klueh, M.A. Sokolov, K. Shiba, S. Jitsukawa, A. Kohyama, J. Nucl. Mater. 329–333 (2004) 283.
[10] H. Tanigawa, H. Sakasegawa, R.L. Klueh, Mater. Trans. 46 (2005) 469.
[11] H. Tanigawa, M. Ando, Y. Katoh, T. Hirose, H. Sakasegawa, S. Jitsukawa, A. Kohyama, T. Iwai, J. Nucl. Mater. 297 (2001) 279.
[12] P.R. Okamoto, N.Q. Lam, L.E. Rehn, Physics of Cyrstal-to-Glass Transformations, Solid State Physics, vol. 52, Academic, San Diego, CA, USA, 1999.
[13] Y. Kohno, A. Kohyama, M. Yoshino, K. Asakura, J. Nucl. Mater. 212–215 (1994) 707.