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EFFECT OF Ti ADDITION ON THE PRECIPITATION BEHAVIOR OF MARTENSITIC STEEL IRRADIATED WITH IRON IONS AND SUBSEQUENT HYDROGEN IONS

VPLIV DODATKA Ti NA PROCES IZLOČANJA V MARTENZITNEM JEKLU, OBSEVANEM Z IONI ŽELEZA IN Z IONI VODIKA

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The effect of titanium addition on the precipitation behavior of martensitic steel induced by the irradiation of iron ions and subsequent hydrogen ions at 300°C was investigated using two different steels: 9Cr2W0.25V and 9Cr2W0.25V-Ti. The new Cr/W-rich phase formed around the pre-existing precipitates in the two martensitic steels. The MX phase (Ti(C, N)) formed in the matrix of the 9Cr2W0.25V-Ti steel after the irradiation. Ti-added martensitic steel has good performance in delaying the increase of precipitates and the implantation of hydrogen atoms could accelerate the precipitation behavior.

Keywords: precipitation, ion irradiation, ferritic/martensitic steel, hydrogen

Avtorji so raziskovali vpliv dodatka titana na potek izločanja izločkov (precipitatov) v martenzitnem jeklu. Potek izločanja je bil induciran z obsevanjem z ioni Fe in nato še z ioni vodika pri 300 °C. V raziskavi so uporabili dve različni jekli: 9Cr2W0.25V in 9Cr2W0.25V-Ti. Ugotovili so, da se je v obeh jeklih tvorila nova s Cr in W bogata faza, ki je nastajala okoli primarnih izločkov. Po obsevanju je nastajala faza MX (Ti(C, N)) v matrici jekla 9Cr2W0.25V-Ti. Dodatek Ti k martenzitnemu jeklu ugodno vpliva pri zaviranju nastajanja in rasti izločkov. Obsevanje z vodikovimi ioni lahko pospeši proces tvorbe izločkov.

Ključne besede: izločanje, obsevanje z ioni, feritno/martenzitno jeklo, vodik

1 INTRODUCTION

The reduced-activation ferritic/martensitic (RAFM) steels have been regarded as one of the most promising structural materials for future fusion-power reactors.[1] They have excellent mechanical properties, low thermal expansion coefficient, high thermal conductivity[2] and good resistance to radiation-swelling and helium embrittlement.[3,4] It is well known that several typical RAFM steels, such as CLAM Eurofer97, 9Cr2WVTa and F82H, are selected as the primary first-wall and blanket structural materials in the prospective International Thermonuclear Experimental Reactor (ITER). All these above-mentioned steels are often melted by vacuum induction melting and modified by adding a small quantity of tantalum in order to reduce the prior-austenite grain size and form small, spherical, Ta-rich precipitates (TaC) in the RAFM steels.[3]

The effect of Ti is better than that of Ta in the reduced activation of RAFM steel.[4] Adding a suitable amount of Ti can form small Ti-rich precipitates (Ti(N, C)), and the Ti(N, C) is more stable than TaC. $M_{23}C_6$ and MX precipitates are mentioned as the primary precipitates in RAFM steel. $M_{23}C_6$ carbides are amorphous after irradiation under 0.5 dpa at low temperatures, while MC carbides remain crystalline in 9Cr-1Mo ferritic/martensitic steel.[5] This means that the phase stability of MC is better than that of $M_{23}C_6$. However, neither $M_{23}C_6$ nor MC would be stable in neutron-irradiated RAFM steels, and they would increase with the irradiation dose and a corresponding reduction in the number density occurring in the 9Cr-2WV steels during neutron irradiation.[6] Therefore, the mechanism of nucleating and the coarsening of precipitates in RAFM steels still require further investigation. With regards to a fusion power reactor, the structural materials would suffer 14 MeV neutron irradiation doses of ~100 dpa. Large quantities of hydrogen and helium would be produced in the structural materials by the nuclear transmutation reactions (n, p) and (n, α). To date, the studies of helium's effect on the microstructure of RAFM steels under irradiation were common.[7–10] The effect of hydrogen on the swelling and mechanical properties in ferritic alloys has also been demonstrated.[11,12] However, studies of the hydrogen effect for the irradiation-induced precipitation behavior of RAFM steels is still limited. Finding the condition of irradiation-induced precipitation in the matrix of RAFM steels caused by small additional elements and implanting

Table 1: Chemical compositions of the RAFM and RAFM-Ti steels (*w*/%)

	Ti	C	V	Cr	Mn	W	Si	N/ppm	Fe
RAFM	~	0.088	0.25	9.24	0.49	2.29	0.25	170	Bal.
RAFM-Ti	0.015	0.097	0.25	9.27	0.46	2.34	0.0083	700	Bal.

hydrogen atoms may be useful to evaluate the composition optimization of RAFM steels.

In the present study we report on the formation of minor precipitates and the effect of Ti addition on the precipitate formation in RAFM steels irradiated with single iron and subsequent hydrogen ions at 300 °C. The hydrogen effect on irradiation-induced precipitation behavior in RAFM steels is also discussed.

2 EXPERIMENTAL PART

The materials used in the present study are two different RAFM steels with 0.25 *w*/% of element V. The compositions of the materials are given in **Table 1**. The heat-treatment conditions consist of twice quenching and twice tempering, and the detailed steps include: quenching at 980 °C for 0.5 h and oil cooled, tempered at 760 °C for 2 h and air cooled; quenching at 960 °C/0.5h and oil cooled, tempered at 760 °C/2h and air cooled. This refines the austenite grains and the martensitic laths.

The TEM specimens were prepared by a conventional jet electropolishing method, using 5% perchloric acid and 95% ethanol polishing solution at –30 °C. The specimens were irradiated with single iron ions and subsequent hydrogen ions in an ion implanter supported by the Accelerator Laboratory of Wuhan University. The single iron-ion irradiation was at 300 °C with an energy of 100 keV to a peak damage dose of 40 dpa. For the sequential ion irradiation (Fe^+ plus H^+), the specimen was first irradiated to 40 dpa with 100-keV iron ions at 300 °C, 50-keV hydrogen ions were used for the irradiation at 300 °C, subsequently, and the irradiation fluence was 2×10^{17} H^+/cm^2, corresponding to 60 appm/dpa at the peak damage zone of the iron ions. The damage profiles were calculated by SRIM 2008,[13] where the displacement energy (Ed) was set to 40 eV, as recommended in ASTME 521-89.[14] The damage profiles and H atomic concentration calculated by SRIM 2008 were shown in **Figure 1**. The examination of the TEM specimen was conducted with a JEM-2010HT microscope, which was operated at 200 kV. The compositions of the irradiation-induced small precipitations in the matrices were measured using a JEM-2010FEF field-emission-gun analytical TEM equipped with an energy-dispersive X-ray (EDX) analyzer with a nominal spot size of 0.5 nm.

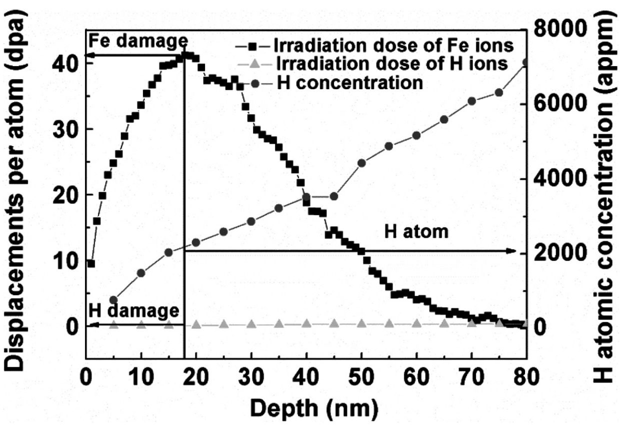

Figure 1: SRIM calculation of the damage profiles induced by irradiation with 100-keV Fe and 50-keV H ions to 1×10^{16} Fe^+/cm^2 and 2×10^{17} H^+/cm^2, respectively. The H atomic concentration is also shown in the image

3 RESULTS AND DISCUSSION

Figure 2 shows the microstructural evolution of the irradiation-induced precipitation in RAFM and RAFM-Ti steels irradiated with single irons and

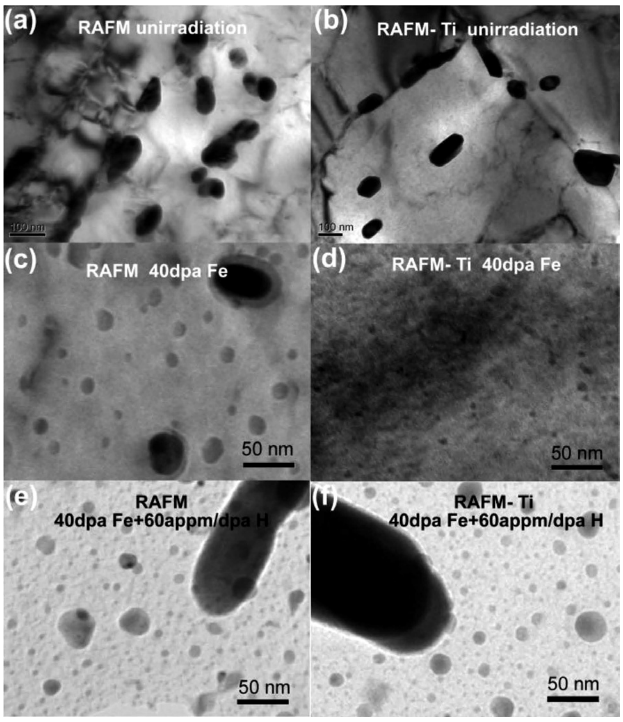

Figure 2: Microstructural evolution of irradiation-induced precipitation in RAFM steels irradiated with single iron and sequential hydrogen ions: a) un-irradiated bright-field image in RAFM steel, b) un-irradiated bright-field micrograph in RAFM-Ti steel; bright-field micrographs in RAFM steel, c) and RAFM-Ti steel, d) irradiated with 40 dpa single iron ions. Microstructure of small precipitations in RAFM steel, e) and RAFM-Ti steel, f) irradiated with 40 dpa iron ions plus 60 appm/dpa H^+ ions subsequently

sequential hydrogen ions. The microstructure of the un-irradiated RAFM and RAFM-Ti steels contains many $M_{23}C_6$ (M = Cr, W and Fe elements) carbides with a size range of ~100–300 nm in the matrices (as shown in **Figure 2a** and **2b**). However, microscopy reveals smaller size precipitates (SPs) formed in all the irradiated specimens, as shown in **Figure 2(c-f)**.

Figure 2c and **2d** show the TEM micrographs of RAFM and RAFM-Ti irradiated with 40 dpa Fe ions at 300 °C, respectively. The average size of the Cr/W-rich carbides in the RAFM steel is about twice as large as the mean size of the Ti-rich (Ti(N, C)) precipitates formed in the RAFM-Ti steel under the same irradiation conditions. However, it is much smaller than the average size of the pre-existing $M_{23}C_6$. The formation of Cr/W-rich carbides requires the enrichment of both the Cr and W elements. The likely source of Cr, W and C would be the pre-existing $M_{23}C_6$ in the matrix. The pre-existing $M_{23}C_6$ grew/coarsened in the RAFM steel irradiated to 40 dpa at 300 °C, as shown in **Figure 2(c)**. This implies that the dissolution of the pre-existing $M_{23}C_6$ appeared.[15] The effect of irradiation would accelerate the Cr/W-rich carbides' nucleation process through irradiation-enhanced diffusion. The RAFM-Ti steel consists of 700 ppm N and 0.015 *w*/% Ti. The reason that the precipitation of the Ti-rich Ti(N, C) in the RAFM-Ti steel occurred could be the role of the irradiation-enhanced diffusion of Ti, N and C elements and the Ti(N, C) precipitates that grew and coarsened.

Figure 2e and **2f** are the bright-field images of the RAFM and RAFM-Ti steels under sequential-ion irradiation at 300 °C. In the RAFM steel, after subsequent hydrogen ion irradiation, the mean diameter and the number density of the precipitates were estimated to be 6.8 nm and 2.17×10^{16} cm^{-3}, respectively. Comparing with single ion-irradiated RAFM steel, the precipitate density in **Figure 2e** is about four times as large as that in **Figure 2c**. Similarly, in the matrix of RAFM-Ti steel, the precipitate density in **Figure 2f** is about three times as large as that in **Figure 2d**. However, the displacement damage at the peak damage zone of iron ions because of the hydrogen implantation was only 0.1 dpa. In short, comparing with single ion-irradiated RAFM steel at 300 °C, the hydrogen effect on irradiation-induced precipitation behavior was detectable. The implantation of hydrogen atoms could accelerate the precipitation of the minor precipitates.

Figure 3 shows the energy-dispersive X-ray spectroscope (EDX) analysis for titanium, vanadium, chromium, manganese, iron and tungsten obtained by using a

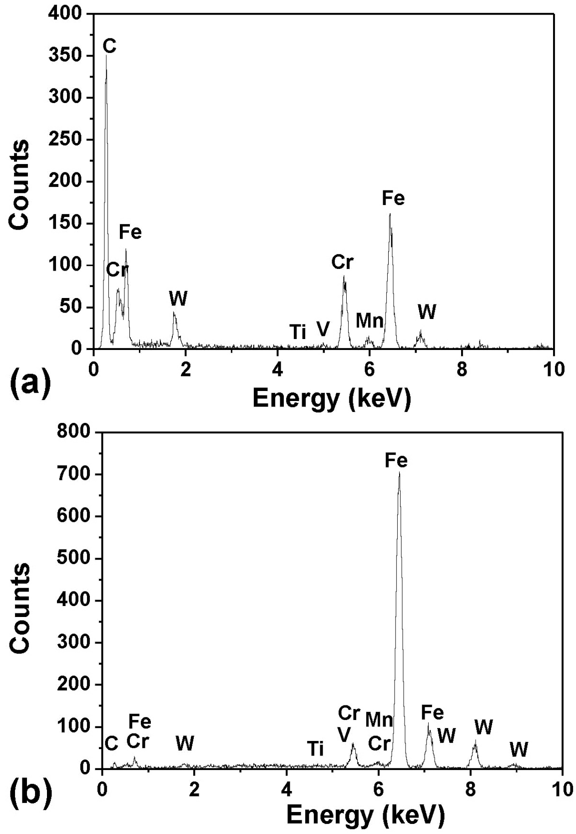

Figure 3: a) EDX results of the smaller size precipitates in the RAFM steel and b) the RAFM-Ti steel irradiated sequential-beam ions (40dpa Fe + 60 appm/dpa H ions)

TEM for the minor precipitations in RAFM steel irradiated with sequential-beam ions (40 dpa Fe + 60 appm/dpa H ions). The irradiation-induced SPs were seen to be strongly enhanced in W and Cr in the irradiated RAFM steel, and the weight percent of W was as high as 8.08 %, as shown in **Table 2**. Previous work showed that $M_{23}C_6$ and M_6C carbides were formed in Fe-9Cr-2W steel irradiated in a fast flux test facility to 60 dpa at 500 °C.[16] Tanigawa et al.[17] predicted the formation possibility of M_6C (W-rich carbides) in the F82H after irradiation at 300 °C. Bachhav et al.[18] observed the chromium-rich α' phase in neutron-irradiated Fe-Cr alloys at 290 °C. Thus, it could be considered that the type of irradiation-induced SPs in RAFM steel is Cr/W-rich carbides. The phases in the irradiated RAFM-Ti steel were seen to be enriched in Ti. Most of the irradiation-induced SPs in RAFM-Ti steel should be the Ti-rich Ti(N, C) precipitates. Noticeably, since the SPs contained 6.18 *w*/% of Cr and 2.85 *w*/% of Ti, it was

Table 2: EDX results obtained from **Figure 3**

	Ti		V		Cr		Mn		Fe		W	
	w/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%
RAFM	~	~	0.89	1.02	17.52	19.66	~	~	73.54	76.76	8.08	2.56
RAFM-Ti	1.27	1.50	0.69	0.76	6.18	6.72	0.67	0.69	88.34	89.45	2.85	0.88

likely that most of the Cr/W-rich carbides also formed in the matrix of RAFM-Ti steel.

Table 3: Average characteristics of SPs in specimens irradiated under different conditions

Steels	First Irradiation (dpa)	Sequential Irradiation (appm/dpa)	Mean size of SPs (nm)	Concentration of SPs (cm^{-3})	Upper limit size of SPs (nm)
RAFM	40 Fe^+	~	11.2	5.4×10^{15}	21.6
	40 Fe^+	60 H^+	6.8	2.17×10^{16}	34.2
RAFM-Ti	40 Fe^+	~	4.7	7.2×10^{15}	8.9
	40 Fe^+	60 H^+	6.9	2.06×10^{16}	25.3

Table 3 summarizes the quantitative results of irradiation-induced SPs in RAFM and RAFM-Ti steels. **Figure 4** shows the size distribution of the irradiation-induced precipitate density in RAFM and RAFM-Ti steels. Under 40 dpa iron ion irradiation at 300 °C, the average diameter and the mean size of the SPs was 11.2 nm and 4.7 nm, as shown in **Figure 2c** and **Figure 2d**, respectively. Comparing **Figure 4a** with **Figure 4b**, it could indicate that the behavior of the precipitation in **Figure 4a** was more severe than that in **Figure 4b**. After an additional 60 appm/dpa H ion implantation, comparing **Figure 4c** with **Figure 4d**, the average size of the SPs in the RAFM and RAFM-Ti steels was similar, but the proportion of the SPs (< 8 nm) in the RAFM steel was larger than that in RAFM-Ti steel, which could shorten the mean size of the SPs in the RAFM. This further indicated that the size of the Ti-rich (Ti(N, C)) precipitates in the ion-irradiated RAFM-Ti steel was smaller than that of the Cr/W-rich carbides in RAFM steel. Therefore, the Ti-added RAFM-Ti steel has good performance in delaying the increase in the number of precipitates.

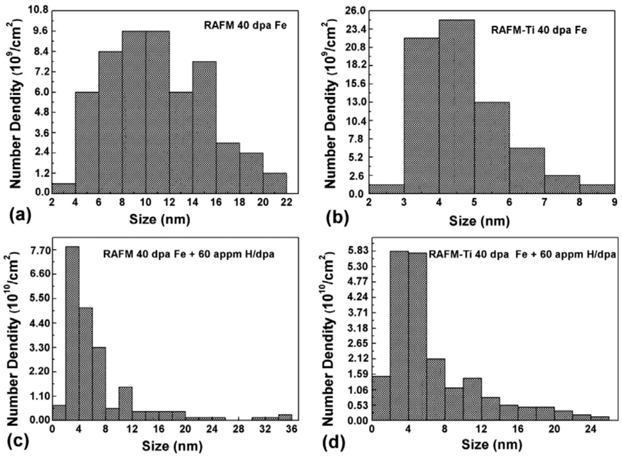

Figure 4: Size distribution of irradiated-induced precipitate density in RAFM steel: a) and RAFM-Ti steel, b) irradiated with 40dpa single iron ions; RAFM steel, c) and RAFM-Ti steel, d) irradiated with 40dpa iron ions plus 60 appm/dpa hydrogen ions subsequently

4 CONCLUSIONS

The energy-dispersive X-ray spectroscope analysis indicated that the precipitates in ion-irradiated RAFM steel were Cr/W-rich carbides and the Ti-rich Ti(N, C) formed in the post-irradiated RAFM-Ti steel. The Ti-added RAFM-Ti steel had good performance in delaying the increase of precipitates, comparing the sizes of the Ti-rich Ti(N, C) precipitates with the Cr/W-rich carbides. The hydrogen effect in RAFM steels indicates that the implantation of hydrogen atoms could accelerate the precipitation of the minor precipitates.

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