Effect of Deuterium Ion Implantation on Microstructures of Fe- M ($M=V, W, Ta$) Alloys

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To study the effect of tungsten, vanadium and tantalum on the microstructures in CLAM (China Low Activation Martensitic) steel after irradiation respectively, the microstructures of Fe- M ($M=V, W, Ta$) model alloys were investigated after implanted deuterium ions using an ion accelerator at 773 K. After implanted deuterium ion, TEM (Transmission Electron Microscope) observation and EDX (Energy Dispersive X-ray Spectrom) analysis have been carried out. The result showed that tiny voids were observed in all model alloys after implanted the same dose of deuterium ions. The swelling rate in FeTa alloy was the smallest among the three alloys. Unlike FeW and FeV alloys, there was the segregation in FeTa alloy under a fluence of $5 \times 10^{17} \text{ D}^+/\text{cm}^2$ at 773 K. A theoretical analysis showed that the void growth in FeTa alloy slowed down due to tantalum segregation near voids. It indicates that tantalum plays an important role in the improved irradiation resistance of CLAM steel.

KEY WORDS: Ions implantation; Void; Radiation-induced segregation; Swelling

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1. Introduction

As is well known, the study on fusion reactor attracts great interest because it can produce pollution-free energy rather than present fission reactors. However, deuterium-tritium fusion reaction releases neutron energy up to 14 MeV which makes the microstructures of the first wall structural materials using in fusion reactor suffer from severe irradiation damages, resulting in the deterioration of the mechanical properties^[1]. Traditional structural materials included long half-life elements Mo, Nb and Ni which hadn't met the need of environment protection. RAFMs (Reduced Activation Ferritic/Martensitic steels) are considered as the primary structural materials for fusion DEMO and reactor in the future. One of the improvements is that short half-life elements V, W, Ta replace Mo, Nb and Ni in

keeping with reduced activation in RAFMs. Versions of RAFMs, which are world-widely studied nowadays, include F82H, EUROFER97, 9Cr-2WVTa^[2] and CLAM steel. CLAM steel is expected as the candidate structural material using in FDS (Fusion Driven Subcritical System) series fusion reactors^[3,4] and ITER (International Thermonuclear Experimental Reactor) liquid LiPb test blanket module of China. The designed compositions of CLAM steel include 9 wt%Cr, 1.5 wt.%W, 0.2 wt.%V, 0.07 wt.%Ta and so on. After irradiation Cr enrichment could lead to precipitation of additional phases in CLAM steel. The additional phases may contain tungsten, vanadium and tantalum^[5]. However, whether tungsten and vanadium enrich^[6], more advanced microscopic analysis is needed due to the complexity of additional phases. Tantalum can refine the grain and improve the properties of the steels. Whereas, the segregation of tantalum in CLAM steel during irradiation still needs to be verified^[7].

To study the effect of tungsten, vanadium and tantalum on the microstructures of CLAM steel after irradiation respectively, the microstructures charac-

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Fig. 1 Microstructures of post-implanted FeV alloy in three different view fields at 773 K: (a), (b), (c) different view fields

teristics of Fe-*M* (*M*= V, W, Ta) model alloys were investigated after implanted deuterium ions at 773 K. The data was analyzed theoretically.

2. Experimental

Fe-*M* (*M*= V, W, Ta) model alloys were prepared by vacuum arc melting furnace. Their nominal compositions are Fe-0.2 wt%V, Fe-1.5 wt%W, Fe-0.07 wt%Ta. The contents (wt%) of alloying elements are the same with CLAM steel as follows: Cr 9, C 0.10, Mn 0.45, W 1.50, Ta 0.07, V 0.20, Fe balanced. The alloys were cold rolled to a thickness of 0.1 mm and punched into 3 mm disks. These disks were annealed (1023 K/1 h /air cooling). Then twin-jet electropolisher was used to prepare TEM specimens.

Deuterium ion implantation was performed at 773 K up to a fluence of 5×10^{17} D⁺/cm² by an ion accelerator at Institute of Semiconductors of the Chinese Academy of Science. The accelerator voltage was 58 keV for Fe calculated by SRIM (the Stopping and Range of Ions in Matter). After implantation, TEM observation and EDX analysis were done using Tecnai F20 FETEM (Field Emission Transmission Electron Microscope).

3. Results and Discussion

3.1 Microstructures of Fe-*M* (*M*= V, W, Ta) model alloys

Fig. 1 illustrates microstructures of post-implanted FeV alloy. TEM examinations of the post-implanted specimen revealed a low void density. The size of which was approximately 14 nm and the number density was 7.4×10^9 /cm². When materials are irradiated, there would produce point defects (interstitials and vacancies). At high temperature ($T=(0.3-0.55)T_m$, T_m means melting point),

vacancy concentration will increase due to migration. When the vacancy concentration reaches a definite value, vacancies will accumulate together to form three-dimensional voids. Meanwhile, deuterium implantation also affect the formation of voids^[8].

Vanadium has evident elevated temperature strengthening effect on steels especially at above 773 K. Xin *et al.*^[9] thought the enrichment of vanadium would reduce the strength of RAFMs. In this study, the segregation of vanadium was unobserved after implanted deuterium ions up to a fluence of 5×10^{17} D⁺/cm² at 773 K. The compositions (wt%) of FeV alloy before and after implantation are Fe 99.69, V 0.30 and Fe 99.72, V 0.27, respectively. Therefore, the addition of vanadium can enhance the strengthening of CLAM steel.

Fig. 2 illustrates microstructures of post-implanted FeW alloy. The same as microstructures in post-implanted FeV alloy, voids were observed. However, the size was a little smaller, which was about 9 nm while the number density was 2.2×10^{10} /cm², larger than that in post-implanted FeV alloy.

In addition to the voids, some black dots were also observed. High resolution image showed there was no precipitate. Likewise, the result of EDX (Table 1) showed the compositions of black dot were almost the same with that of matrix in post-implanted FeW alloy. These black dots were thought voids with directions parallel to electron beam.

Tungsten can strengthen steel through solid solution. It is also an important element to decrease DBTT of ferritic/martensitic steel. The existence

Table 1 Composition (wt%) of FeW alloy before and after implantation

Element	Pre-implanted	Post-implanted	
		Matrix	Black dot
Fe	99.98	99.07	98.87
W	1.01	0.92	1.12

Fig. 2 Microstructures of post-implanted FeW alloy in three different view fields at 773 K: (a), (b), (c) different view fields; (d) a representative high-resolution image of black dots in post-implanted FeW

Fig. 3 Microstructures of post-implanted FeTa in three different view fields at 773 K: (a), (b), (c) different view fields; (d) a representative high-resolution image of black dots in post-implanted FeTa

of segregation would weaken solid solution strengthening, increase brittleness and decrease ductility^[10]. There is no obvious segregation or the precipitate of tungsten in this study. This makes CLAM steel enough strength.

Fig. 3 showed the microstructures of post-implanted FeTa alloy. When implanted deuterium ions at 773 K, voids appeared with the mean size of 8 nm and the number density of $3.0 \times 10^{10}/\text{cm}^2$. The size of the void in FeTa alloy was the smallest while the number density was the largest among the three model alloys.

Like FeW alloy, there were also some black dots like petty precipitate with a size of 4 nm in post-implanted FeTa alloy. Analyzed by EDX (shown in Table 2), the compositions of tantalum in black dot increased while no precipitate fringe appeared in high resolution image. This may be RIS (Radiation-Induced Segregation).

RIS can be caused by a small amount of added element as solute during irradiation. The alloying solute atoms interact with point defects (interstitials and vacancies) produced by irradiation. As a over-sized solute atom, tantalum diffuses by exchange with vacancies. Besides, temperature performs a role in the interaction between solute atoms and point defects^[11]. At higher temperature the main interaction is solute-vacancy complexes. Implanted by deuterium ions at

Table 2 Compositions (wt%) of FeTa alloy before and after implantation

Element	Pre-implanted	Post-implanted	
		Matrix	Black dot
Fe	99.89	99.99	99.22
Ta	0.10	*	0.77

Note: * The content of Ta cannot be detected well because of quite low content

773 K ($T=0.43T_m$), tantalum migrates with vacancy toward to defect sinks^[12] which can include voids and result in the segregation around the sinks. The result is a coated void in which the void develops a shell of composition that is different from that in the matrix. A primary effect of the composition change is a change in diffusion coefficient leading to a change in the void capture efficiency^[13].

3.2 The swelling rate of Fe-M ($M=V, W, Ta$) model alloys

Void is not regular spherical. It is polyhedron. In this study, we assume it is spherical when calculating the swelling rate. The equation is as follows:

$$S = \frac{\Delta V}{V} = \frac{\pi}{6xyt} \sum d^3$$

where, xy means the area of the field of view, t means

Table 3 Swelling rate of Fe-*M* (*M*= V, W, Ta) model alloys

Alloy	Size of void (nm)	Density of void (cm ⁻²)	Segregation	Swelling rate (%)
FeV	14	7.4×10^9	×	0.013
FeW	9	2.2×10^{10}	×	0.004
FeTa	8	3.1×10^{10}	✓	0.003

the thickness of the field of view calculated by extinction coefficient $\xi_{\text{effg}(3g)}$, d is the mean diameter of voids. According to Fig. 1, Fig. 2 and Fig. 3, the swelling rate is shown in Table 3.

From Table 3, the swelling rate of FeTa alloy is the lowest. This may be due to RIS in post-implanted FeTa alloy. Tantalum segregation can slow down void growth. It may provide a barrier to nucleation of the voids^[13]. If, for example, a void nucleus which needs more vacancies to grow finds itself surrounded by tantalum. That will effectively be a barrier tending to prevent more vacancies jumping into it. And the segregation of tantalum to the vicinity of a growing void would make its growth more difficult. Besides, the segregation that leads to a reduction in the vacancy flux to a void increases as the void grows, so that the growth rate of void decreases. This provides a possible link between diffusion behavior in alloys and their resistance to void swelling.

Tantalum segregation will influence mechanical properties of steels. Klueh *et al.*^[7] thought tantalum played an important role in the improved irradiation resistance of the 9Cr-2WVTa steel. Segregation of tantalum from solution during irradiation was hypothesized to cause difference in behavior of a tantalum-containing steel compared to the one without tantalum when fluence or temperature is increased. Laha *et al.*^[14] found prior austenitic grain size of RAFMs decreased from 15 μm to 9 μm on increasing tantalum from 0.06 wt% to 0.14 wt% after heat treatment. However, creep rupture strength and tensile strength of the steel decreased with the increase in tantalum content. Therefore, they thought RAFMs having 0.06 wt% tantalum tended to have better properties.

The accurate explanation needs more experiments and computer simulation for CLAM steel under certain irradiation conditions. We will go on doing related experiments and simulation.

4. Conclusions

Fe-*M* (*M*= V, W, Ta) model alloys were implanted deuterium ions at 773 K. Voids appeared in post-implanted FeW and FeV alloys. The segregation existed in FeTa alloy besides voids. The swelling

rate in FeTa alloy was the lowest among the three model alloys due to the tantalum segregation. The segregation is caused by the interaction between vacancy and tantalum atoms. Tantalum-vacancy complexes migrate with dissociation to the same direction at high temperature during deuterium ions implantation. Then the segregation occurs. Tantalum plays an important role in improving resistance for CLAM steel.

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