



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Nuclear Materials 322 (2003) 73–79

journal of
nuclear
materialswww.elsevier.com/locate/jnucmat

The recovery and recrystallization of cold rolled V–W–Ti alloys

Jiming Chen^{a,b,*}, Takeo Muroga^c, Takuya Nagasaka^c, Ying Xu^a, Shaoyu Qiu^b^a Southwestern Institute of Physics, P.O. Box 432, Chengdu 610041, China^b National Key Laboratory for Nuclear Fuel and Materials, Nuclear Power Institute of China, P.O. Box 436, Chengdu 610041, China^c National Institute for Fusion Science, Oroshi, Toki, Gifu 509-5292, Japan

Received 10 March 2003; accepted 2 July 2003

Abstract

Several V–W–Ti alloys with about 50% reduction in thickness by cold rolling were isochronally annealed at temperatures from 100 to 1100 °C. Hardness was measured after the annealing. By comparison with V4Cr4Ti and V4Ti alloys, the V6WTi alloy was found to begin recovery at a temperature about 100 °C higher, while the full recrystallization temperature was around 900 °C for all of the alloys. Hardness decreased successively above 500 °C in V8W, as is the case in pure V. Impurity induced hardening was observed around 300 °C only in the alloys without Ti. Precipitation and the interaction between interstitial impurities and dislocations were supposed to be the main contributors to the different recovery and recrystallization behaviors of the alloys.

© 2003 Elsevier B.V. All rights reserved.

PACS: 28.52.Fa; 81.05.Bx; 81.40.Ef

1. Introduction

Vanadium alloys, especially that of V4Cr4Ti, are considered to be a promising candidate structural material for fusion applications due to their good thermal properties, high temperature strength and inherent low activation characteristics [1–4]. However, in recent years, many researches have reported that the alloy has to be used within a temperature window of ~400–700 °C because of the low temperature neutron irradiation hardening and the limitation of the high temperature strength or the high temperature creep properties [5]. Besides, the alloy also has the disadvantage of easy oxidation at elevated temperature and high sensitivity to hydrogen embrittlement [6]. Based on these limitations

and demerits, several V–W–Ti alloys were developed in China especially for the purpose to increase their resistance to hydrogen embrittlement [7]. Full assessment of the alloys will be carried out later and, as a first step, the recovery and recrystallization behavior was studied. This paper presents the detailed alloying process and the results of the recovery and recrystallization study.

2. The preparation of the alloys

The alloys were melted in a magnetic floating furnace using inductive heating method. Fig. 1 shows the vanadium-rich portion phase diagram of the V–W system [8]. V and W form a continuous solid solution due to their similar atom size. A V–W alloy will begin to melt when its temperature meets the solid line and the melting will complete at the dashed line. The melting temperature of the alloy increases with increasing tungsten concentration. The increase is not so significant in the lower tungsten concentration regime. However, pure W

* Corresponding author. Address: Southwestern Institute of Physics, P.O. Box 432, Chengdu 610041, China. Tel.: +86-28 2932225; fax: +86-28 2932202.

E-mail address: chenjm@swip.ac.cn (J. Chen).

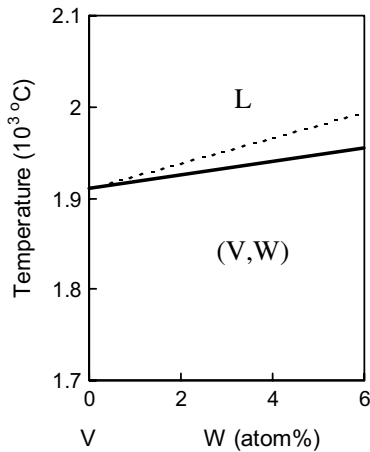


Fig. 1. Phase diagram of the V–W alloy [8].

has much higher melting point and thus could hardly be melted by common heating method such as the inductive heating. In this case, V will be melted first and then W gradually dissolves into the molten vanadium. Fig. 2 shows the process to prepare the alloys. The original raw materials of V, W, Al and Ti have purity of more than 99.5%. V was in a small powder state and was pressed into large cylindrical rods of about 40 mm in diameter prior to the melting. Higher inductive electrical current could be formed around the outer layer of the cylinder during the heating, leading to a high heating efficiency. Very thin W foils were used with a thickness of about 0.1 mm to shorten the dissolution durations. The alloy ingot weight was about 340 g. The melting was usually conducted for three times, 20 min each, for the homogenization.

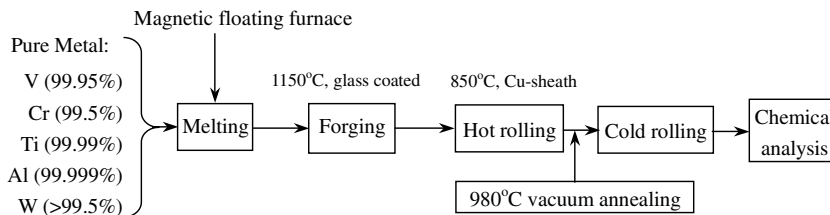


Fig. 2. The flow chart showing the process for the alloy preparation.

The alloy ingots were forged into ~ 15 mm thick plates at 1150 °C in air. To protect the alloy from the air contamination of oxygen and nitrogen pickup, the ingots were coated with a glass film at ~ 200 °C before the heating. A sandblasting treatment was employed to remove the surface coating layer after the forging. The plates were then canned with a copper plate and hot rolled at ~ 850 °C in air to a thickness of ~ 2 mm. Some copper plates were found to be mounted on the rolled plate and were removed by grinding with sandpapers. A heat treatment was then conducted at 980 °C in a vacuum of $\sim 2 \times 10^{-3}$ Pa, to reduce the hardness for further rolling. Finally, the plates were cold rolled to a thickness of ~ 1 mm. Therefore, the final plates have a cold work (CW) of $\sim 50\%$ reduction in thickness and were used for the recovery and recrystallization experiments. Chemical analysis results showed that the alloys had low O, C and N concentrations. The chemical compositions of the alloys were listed in Table 1.

3. Experimental procedures

Samples for the recovery and recrystallization experiments were cut from the cold-rolled plates to a size of 10×5 mm². They were mechanically ground and electro-polished. Some of the samples were ground carefully by hand with oil, for the purpose to eliminate any hydrogen pickup from the water. These hand-ground samples were used for the annealing treatment below 400 °C. Separated by tantalum plates and wrapped in zirconium getter foils, the samples were annealed at 100 – 1100 °C for an hour in a vacuum less than 1×10^{-5} Torr, with a heating rate of ~ 20 K/min. Followed the annealing, the samples were cooled down to

Table 1
Chemical compositions of the alloys (mass%)

Alloy	Ti	Al	Si	W	O	N	C
V4Ti	3.99	–	0.014	<0.5	0.028	0.003	0.012
V8W	–	0.00	0.014	8.28	0.023	0.004	0.010
V7WAl	–	0.34	0.014	7.35	0.029	0.003	0.011
V6WTi	1.10	0.12	0.014	6.48	0.025	0.003	0.009

room temperature in the furnace. The cooling took 2–3 h approximately. Some samples were heat-treated first at 1100 °C for 1 h for the purpose of resolution of impurities and removal of dislocations introduced by the cold rolling. Optical microscope observation showed that these samples were fully recrystallized. Consequently the contribution of the precipitation to the recovery and recrystallization of the alloys could be evaluated without the effect of the cold rolling induced dislocations. Vickers hardness tests with a load of 500 g and microstructure observations with an optical microscope and a scanning electron microscope (SEM) were conducted after annealing. The grain sizes of the alloys were measured from these observations. All was measured on the LT plane along the transverse (T) direction. Here L represents the rolling direction.

4. Results

Fig. 3 shows the measured hardness of the cold-rolled alloys after isochronal annealing, together with the data for a 90% CW V with 260 wppm oxygen concentration [9] and for a 90% CW V4Cr4Ti alloy (NIFS-Heat-2) [10]. The alloys could be divided into two categories

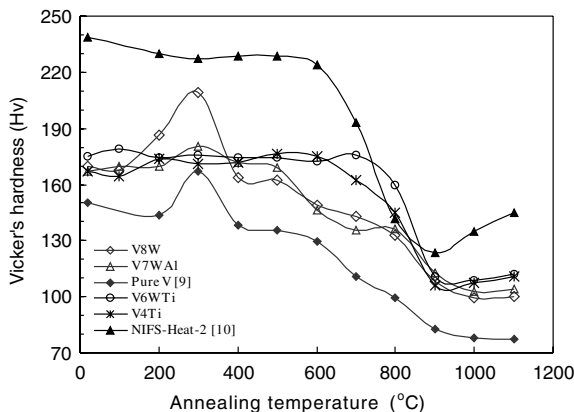


Fig. 3. The hardness of the isochronally annealed alloys as a function of temperature.

Table 2
The temperatures (°C) of T_B and T_C for each alloy

	Alloy			
	V8W	V7WAl	V6WTi	V4Ti
T_B	500	500	700	600
T_C	1000	1000	900	900

according to the results, those with Ti and those without Ti. The V–W alloys behaved just like pure V, a hardness peak appeared at 300 °C, followed by a successive decrease of the hardness with increasing temperature to ~1000 °C. With the addition of 0.34% Al (in mass), the peak at 300 °C decreased significantly. On the other hand, the peak at 300 °C disappeared in the Ti-bearing alloys. For each curve, there were another two characteristic temperatures: the beginning recovery temperature (T_B) above which the hardness began to decrease and the one above which the hardness did not decrease any more (T_C). The temperatures were summarized in Table 2 for each alloy. Obviously the Ti-bearing alloys have higher T_B but lower T_C than the non-Ti bearing alloys. V6WTi has the highest T_B temperature. Despite the difference, all of the alloys showed similar hardness after annealing around 900 °C. V4Cr4Ti was a little harder than the others. It was found in the optical observations of the annealing samples that recrystallization has completed for all alloys after 900 °C annealing according to the totally equiaxed grains, as opposed to the elongated shape below the temperature. As an example, Fig. 4 shows the optical microstructure after annealing at 400 and 900 °C for V4Ti.

Fig. 5 shows the dependence of the mean grain size of the alloys on the annealing temperature. The size decreased with increasing temperature from 600 to 900 °C. The decrease might be caused by the recovery of the alloys and the formation of sub-grains within the elongated grains. Since the measurement was one-dimensional, the size had little meaning before recrystallization. It is evident from the figure that the alloys with Ti have smaller full recrystallization grain size than the others. The grain size of the V6WTi was the smallest,

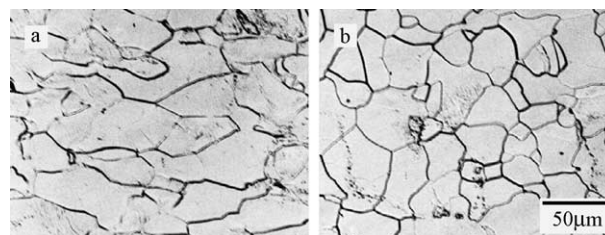


Fig. 4. Optical photos showing the microstructure in V4Ti after 400 °C (a) and 900 °C (b) annealing.

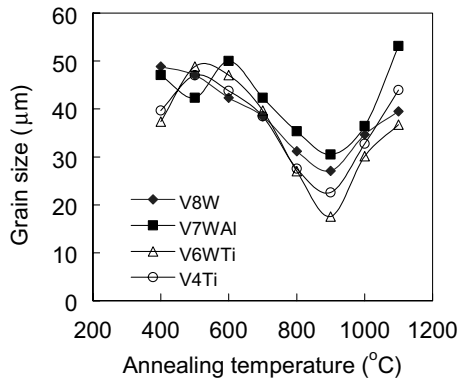


Fig. 5. Dependence of the mean grain size on the annealing temperature.

about 18 μm in diameter on average. Above 900 $^{\circ}\text{C}$ the grains grew drastically with increasing the temperature.

Many precipitates were observed in the alloys with Ti, as shown in Fig. 6 for the annealing at 600, 700, 900 and 1100 $^{\circ}\text{C}$. But nearly no or very small numbers of precipitates were observed in the alloys without Ti. It seemed that the precipitates are related to Ti. Most of the precipitates are less than 0.4 μm in diameter. The precipitates distributed heterogeneously, but were found to be much smaller with less number in V6WTi than those in V4Ti. There was no precipitate observed in both alloys after annealing at 900 $^{\circ}\text{C}$. This result indicates that the precipitation varies with the alloy composition and the annealing temperature. Precipitation was found to take place again at 1100 $^{\circ}\text{C}$ where some of the precipitates distributed along the grain boundaries in V4Ti (see the right bottom photo in Fig. 6).

Fig. 7 shows the SEM-EDS analysis results for the V4Ti alloy. The analysis results showed that there was no enrichment of alloying element in the precipitates. It is obvious that the precipitate has much higher carbon concentration than that in the matrix. In the case for V6WTi, the carbon concentration was also found to be high. The value of N, O concentration cannot be identified from the spectra because of overlapping of the N, O, Ti and V peaks.

The precipitation behavior may influence the temperature dependence of the hardness. To evaluate its effects, the alloys were first annealed at 1100 $^{\circ}\text{C}$ to release dislocations and then annealed again at different temperatures. Consequently the change of the hardness could reveal the contribution of the precipitation. Fig. 8 shows the results of the measured hardness as a function of the annealing temperatures for these repeatedly annealed alloys. The plot also includes the data of the as-rolled specimens. V6WTi and V4Ti exhibited similar hardness at any temperatures, while that for V8W and V7WAl showed similarly but smaller hardness than the

Ti-bearing ones. For the two types of the alloys with or without Ti, the first peak appeared at different temperatures. This peak hardness temperature (marked as T_p in the figure) is much higher for the Ti-bearing alloys than that for those without Ti, 600 and 400 $^{\circ}\text{C}$ respectively. Besides, all alloys had a much lower peak at 900 $^{\circ}\text{C}$.

5. Discussions

It was reported that C, N and O impurities have strong effects on the recovery behaviors [9,11]. These interstitial impurities are known to be mobile below 300 $^{\circ}\text{C}$. They migrate to the dislocations during the annealing heat treatment and reduce the mobility of the dislocations during the hardness test. This interaction causes the alloy harder and a hardness peak appears on the hardness-temperature curves around 300 $^{\circ}\text{C}$ as shown in Fig. 3 for the alloys without Ti. Titanium and aluminum have strong affinity to the impurities which, as a result, can hardly move to the dislocation sites. Thus the interaction between the impurities and the dislocations becomes weaker, leading to the absence of the hardness peak for the Ti-bearing alloys around 300 $^{\circ}\text{C}$.

Comparing the beginning recovery temperature T_B in Table 2 with the peak hardness temperature T_p in Fig. 8, both temperatures are equal to each other for V4Ti. But T_B is 100 $^{\circ}\text{C}$ higher than T_p for the other alloys. Precipitation must be the main contributor to the hardness increase at temperatures around T_p in Fig. 8. The precipitation may also delay the beginning of the recovery or recrystallization during the annealing of the cold-rolled alloys, since precipitates retard dislocation movements. That is why the Ti-bearing alloys had a higher beginning recovery temperature than the non-Ti bearing alloys. However, the notable hardness decrease and recovery seemed to have already started for V4Ti at 700 $^{\circ}\text{C}$ where large number of precipitates still existed. It seemed that the precipitates were not strong enough to suppress the recovery at the temperature. But the hardness of V6WTi did not decrease or even increased a little at 700 $^{\circ}\text{C}$. In fact, judged from Fig. 8, the increase could not have resulted from the precipitation in the alloy because the contribution of the precipitation to the hardness had become smaller as compared to that at 600 $^{\circ}\text{C}$. One possibility is the contribution of the O, N and C impurities in the alloy, just like that happened in V8W around 300 $^{\circ}\text{C}$. It has been stated above that the presence of Ti would restrict the interaction between the impurities and the dislocations by binding the impurities. But the interaction may become active at high temperature since Ti atoms are mobile at temperatures higher than 500 $^{\circ}\text{C}$ [1]. The occurrence of dynamic strain ageing gives a direct evidence for the interaction in V4Cr4Ti when tested at 400–700 $^{\circ}\text{C}$ in low tensile rate

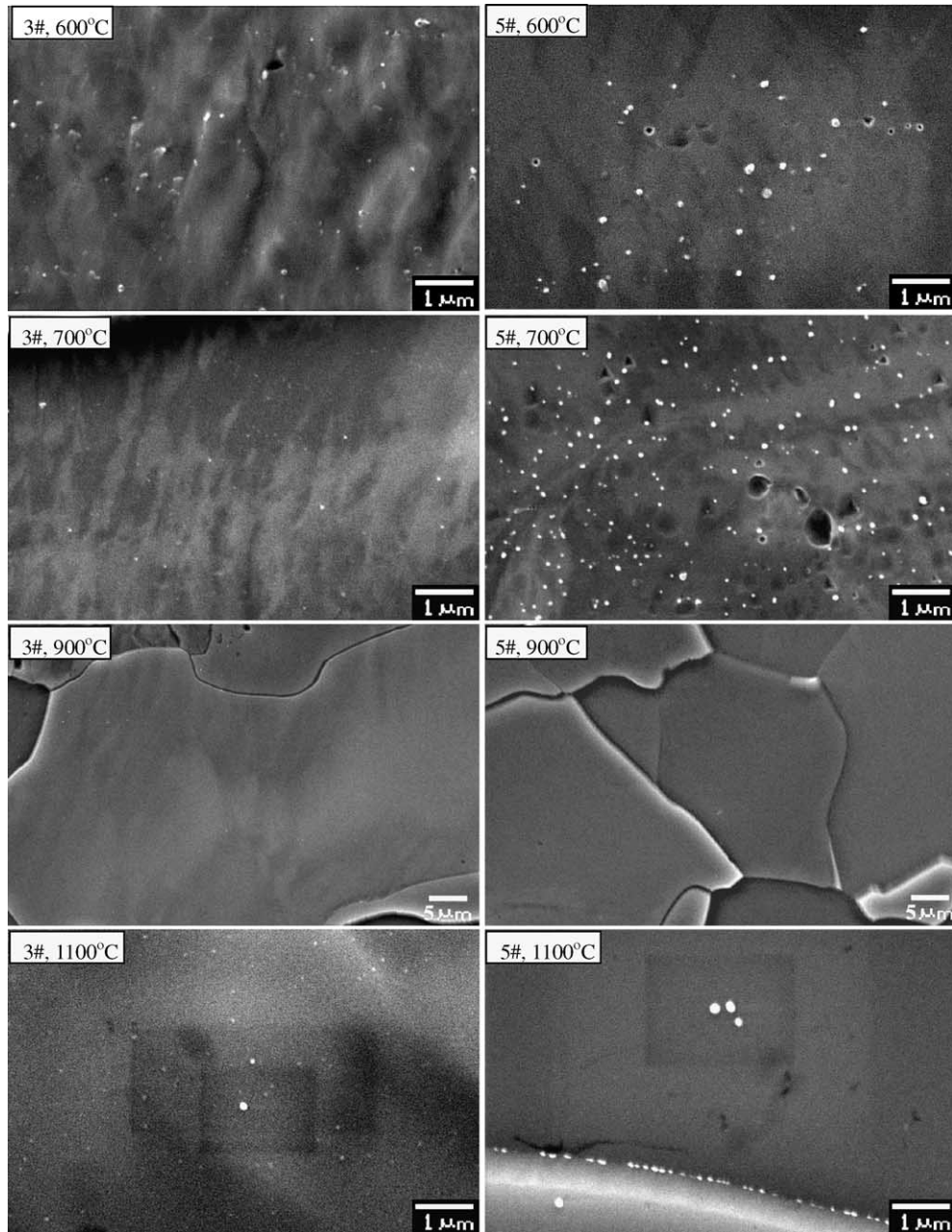


Fig. 6. SEM photos showing the precipitates in the alloys annealed at 600, 700, 900 and 1100 °C, 3#: V6WTi, 5#: V4Ti.

[5]. The strength of the interaction should be closely related to the concentration of the mobile impurities. Nagasaka reported that the additional anneal hardening at 200–400 °C for metal vanadium became smaller with decreasing nitrogen content [9]. In the present study, the alloys had similar O, N and C concentration. But the mobile impurity content would vary a lot for each of the alloys at high temperature due to the different precipitation behavior. Precipitation consumed part of the in-

terstitial impurities. It has been observed that the precipitation was more pronounced in V4Ti than that in V6WTi (see Fig. 6). As a result, the mobile interstitial impurities in V6WTi must be more than those in V4Ti, resulting in the additional hardening at 700 °C in V6WTi due to their interaction with dislocations. For other alloys, this hardening must be weaker because of the recovery-induced decrease in dislocation density and was used up by the recovery. It could be found in Fig. 3

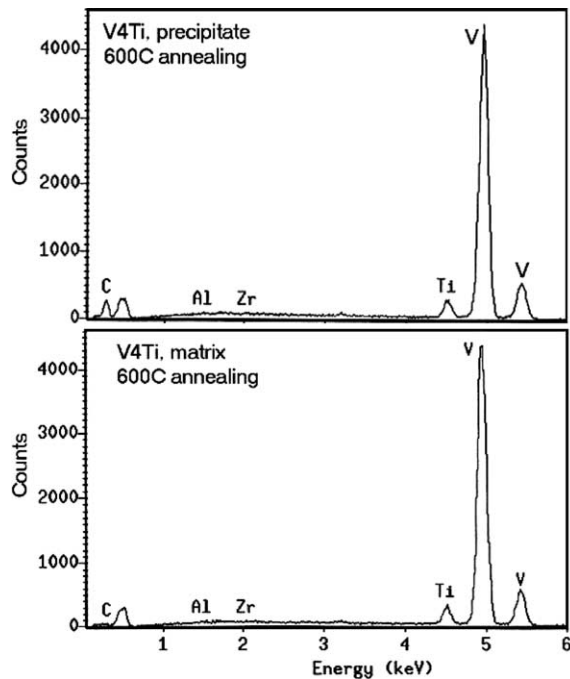


Fig. 7. EDS spectra for the precipitate and the matrix showing the different C content.

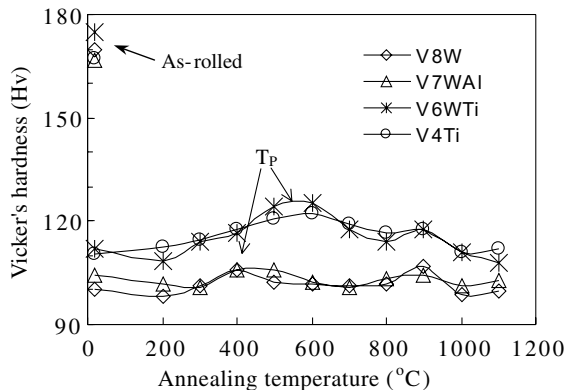


Fig. 8. The measured hardness as a function of annealing temperature for the solid solution heat-treated alloys.

that the recovery of the hardness became slower around 700 °C for both V8W and V7WAl alloys. Besides, this interaction itself should have roles to slow down the recovery.

On the other hand, even if the binding of the Ti atoms to the impurities were still in active at high temperature, it would become weaker because the precipitation consumed the Ti atoms. This was especially the case for the V6WTi alloy since its Ti content was much lower than that in V4Ti. Thus there would be a case that all the Ti atoms in the V6WTi alloy were depleted by the precipitation but there were still enough Ti atoms in

V4Ti to bind the impurities. Consequently, it is possible that the interaction between the interstitial impurities and the dislocation became active in V6WTi but was still inactive in V4Ti.

6. Conclusions

The recovery and recrystallization behavior of some V–W–Ti–Al alloys were investigated by isochronal annealing heat treatment. The results could be summarized as follows.

1. The addition of W in the alloys up to 8% in mass does not significantly increase the hardness. The V–W (–Ti) alloys exhibited similar hardness to V4Ti but lower hardness than V4Cr4Ti.
2. The V–W alloy behaved similarly to pure V. Hardness decreased above 500 °C to a minimum at ~1000 °C.
3. Impurity getter species such as Al and Ti could suppress the additional hardening at 300 °C by reducing the interaction between the impurities and the dislocations.
4. Ti-bearing alloys have higher beginning recovery temperature than the non-Ti bearing alloys. This was attributed to the precipitates in the Ti-bearing alloys due to their strong resistance to dislocation movement.
5. V6WTi has the highest temperature for beginning recovery among the alloys including V4Cr4Ti. The possible reason comes from the resumed interaction between the mobile interstitial impurities and the remained dislocations in the alloy at high temperature. Precipitation consumed more impurities and part of the Ti atoms in V4Ti, leading to a relatively lower beginning recovery temperature in the alloy due to the absence of the interaction.

Acknowledgements

This work is conducted under the support by the China–Japan Core University Program and the support of the National Nature Science Foundation of China (project #50271025). The author would like to thank Dr N.J. Heo and the others in NIFS who aided in the experiment.

References

- [1] A.F. Rowcliffe, S.J. Zinkle, D.T. Hoelzer, J. Nucl. Mater. 283–287 (2000) 508.
- [2] D.L. Smith, H.M. Chung, H. Matsui, et al., Fusion Eng. Des. 41 (1998) 7.
- [3] N.P. Taylor, C.B.A. Forty, D.A. Petti, G. Le Marois, J. Nucl. Mater. 283–287 (2000) 28.

- [4] E.E. Bloom et al., *J. Nucl. Mater.* 122&123 (1984) 17.
- [5] R.J. Kurtz, K. Abe, V.M. Chernov, et al., *J. Nucl. Mater.* 283–287 (2000) 70.
- [6] J. Chen, S. Qiu, L. Yang, et al., *J. Nucl. Mater.* 302 (2002) 135.
- [7] Jiming Chen, Takeo Muroga, et al., *Acta Metall. Sinica* 38 (2002) 839 (in Chinese).
- [8] T.B. Massalski, *Binary Alloy Phase Diagrams*, ASM, 1986.
- [9] T. Nagasaka, H. Takahashi, T. Muroga, T. Tanabe, H. Matsui, *J. Nucl. Mater.* 283–287 (2000) 816.
- [10] N.J. Heo, T. Nagasaka, T. Muroga, *J. Nucl. Mater.*, in press.
- [11] D.T. Hoelzer, M.K. West, S.J. Zinkle, A.F. Rowcliffe, *J. Nucl. Mater.* 283–287 (2000) 616.