Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Journal of Nuclear Materials 334 (2004) 143–148

journal of nuclear materials

www.elsevier.com/locate/jnucmat

The hydrogen-induced ductility loss and strengthening of V-base alloys

J.M. Chen [a,b,*], S.Y. Qiu [b], T. Muroga [c], Y. Xu [a], T. Nagasaka [c], Y. Chen [b], Y. Deng [a], Z.Y. Xu [a]

[a] *Southwestern Institute of Physics, P.O. Box 432, Chengdu 610041, China*
[b] *National Key Laboratory for Nuclear Fuel and Materials, China Nuclear Power Institute, P.O. Box 436, Chengdu 610041, China*
[c] *National Institute for Fusion Science, Oroshi, Toki, Gifu 509-5292, Japan*

Received 4 March 2004; accepted 19 May 2004

Abstract

Several V-base alloys were exposed to hydrogen gas at 700–800 °C for hydrogen charging. Tensile tests were performed after the exposure to evaluate the hydrogen embrittlement behavior. The results showed that neither the uniform nor the total elongation was significantly affected by the hydrogen before a critical hydrogen concentration (C_{CH}) was reached when the alloys were tested at high strain rate of 1.1×10^{-3}/s. However the total elongation of the V–4Cr–4Ti alloy (NIFS-Heat 2) decreased notably with increasing hydrogen concentration at the strain rate of 4.4×10^{-4}/s. Hydrogen-induced hardening occurred for all of the alloys, which was thought to be a solid solution hardening. The hardening rate was found to decrease significantly with the addition of Ti/Al to the alloy and the increase of the strain rate. And also, the alloys with Ti or Al were shown to have better properties against the hydrogen embrittlement.
© 2004 Elsevier B.V. All rights reserved.

PACS: 28.52.Fa; 62.20.Fe; 62.20.–x; 81.40.Np

1. Introduction

As one of the candidate structural materials for fusion reactors, vanadium alloys possess many advantages such as low long-term activation [1–4], high operating temperature [5–7] and acceptable post-irradiation properties [8–10] in the temperature range interested in. V–Li self-cooling blanket has been expected having the potential for high performance with attractive safety and environmental features [11–13]. As an attempt to pursue higher performance of the V–Li blanket, it is required to develop a candidate alloy with even higher operating temperature. Recently some new alloys have been developed in China by alloying V with tungsten and other elements. The primary recovery and recrystallization characterization of the alloys have been done. The results indicated that the V–6W–1Ti alloy could bear higher annealing temperature than V–4Cr–4Ti (NIFS-Heat-2), below the temperature hardness recovery could hardly be detected for the ~50%CW samples [14].

There are several issues for vanadium alloys in the application as the structural materials of a V–Li blanket [15], one of which is hydrogen embrittlement. In the fusion neutron energy spectrum, hydrogen will be produced as a transmutation product in vanadium and its alloy. Moreover, vanadium alloys have a strong affinity for reaction with hydrogen and its isotopes. The alloys will pick up deuterium and tritium from the fusion fuel in the reactor [16]. Previous studies showed that hydrogen accumulation would take place in vanadium

---

[*] Corresponding author. Address: Southwestern Institute of Physics, P.O. Box 432, Chengdu 610041, China. Tel.: +86-28 8293 2225; fax: +86-28 8293 2202.
E-mail address: chenjm@swip.ac.cn (J.M. Chen).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.05.013

in hydrogen environment even at low partial pressure [17]. Some results have been reported on the hydrogen embrittlement recently [18–21], but most of the studies concentrated on the reference V–4Cr–4Ti alloy. It was found that hydrogen-induced ductility loss may not be a major issue but the embrittlement at a critical hydrogen concentration. These results also showed that oxygen will enhance the embrittlement, but nobody showed the role of the alloying element of Ti and the effect of tensile strain rate on the properties. With the accumulation of the experiment data for more alloys, these effects could be evaluated. The present paper showed the results for some of the newly developed vanadium base alloys with or without Ti, together with that for the conventional V–4Cr–4Ti alloy.

2. Experimental procedure

Four newly developed alloys with the following nominal compositions were investigated: V–4Ti, V–6W–1Ti, V–7W–0.3Al and V–8W. The alloys were prepared from 99.8% pure vanadium and other pure metals by an induction melting in 99.9999% argon gas. The weight of each ingot was about 340 g. The ingots were forged into ~15 mm thick plates at 950–1150 °C in air with a glass film coated on the surface for protection from air contamination. The plates were then wrapped with copper sheets and hot rolled at ~850 °C in air to a thickness of ~2 mm, followed by an annealing treatment at 980 °C for 1 h in vacuum of $\sim 2\times 10^{-3}$ Pa. Finally, the plates were cold rolled to a thickness of ~0.5 mm and annealed again under the same condition as that stated above. Table 1 listed their chemical compositions.

Tensile specimens were cut from the plates with gauge dimensions of $25\times 8\times 0.5$ mm^3. The specimens, together with $ZrH_{1.8}$ hydride in weight ratio of 0.1 to the specimens, were enclosed in evacuated quartz tubes for hydrogen charging. Each tube had a diameter of ~20 mm and a length of ~200 mm, with a vacuum in the level of 10^{-5} Torr. The tubes, containing the specimens and the hydride, were heated to 800 °C and kept at the temperature for 20–180 min, then water quenched to room temperature. Chemical analysis showed scarcely any oxygen pickup during the charging. As an example, the oxygen concentration in V–4Ti is still 280 wppm after 1 h hydrogen charging. Hydrogen concentration in the specimens was measured with a RH404 type hydrogen-measuring device that was made by the Leco Co. in United States.

Tensile tests were performed using an Instron 4302 machine at room temperature in air. The strain rate was 1.1×10^{-3}/s. Load and displacement were recorded by a computer. The elongations and strengths were determined from the stress–strain curves.

In addition to the alloys stated above, this paper also concerned another previous studied alloy. The alloy was V–4Cr–4Ti (NIFS-heat-2, termed as NIFS V44 in the following text). Its chemical composition is also shown in Table 1. Tensile specimens have gauge dimensions of $19\times 4\times 1.9$ mm^3. Tensile testing of the specimens with or without hydrogen charging was performed also at room temperature in air but at a relatively lower strain rate of 4.4×10^{-4}/s. The hydrogen charging was conducted in a hydrogenation furnace at 700 °C with 99.9999% hydrogen gas. An equilibrium heat treatment was conducted at the temperature for 2 h in the same furnace followed the hydrogen charging. Detailed process for the preparation of the alloy and the experimental procedures were listed elsewhere [22,23]. Chemical analysis was performed again to detect the change of the oxygen concentration after the hydrogen charging and the equilibrium heat treatment. The as-received NIFS V44 had an oxygen concentration of ~220 wppm, which increased to ~360 wppm after the treatment. Followed the same treatment without the admittance of hydrogen gas, the alloy was tensile tested. Results showed a little increase in strength and nearly no change in elongations. These data was used as the elementary tensile properties of the alloy in the present paper in order to delete the effect of the oxygen pickup on the evaluation of the hydrogen embrittlement behavior.

3. Experimental results

Fig. 1 shows the engineering stress–strain curves of NIFS V44 alloy with hydrogen charging (215.3 wppmH)

Table 1
Chemical compositions of the alloys (mass%)

Alloy	Cr	Ti	Al	Si	W	O	N	C	H
V–4Ti	/	3.99	/	0.014	<0.5	0.028	0.003	0.012	0.0016
V–8W	/	/	/	0.014	8.28	0.023	0.004	0.010	0.0014
V–7W–0.3Al	/	/	0.34	0.014	7.35	0.029	0.003	0.011	0.0016
V–6W–1Ti	/	1.10	0.12	0.014	6.48	0.025	0.003	0.009	0.0015
NIFS V44*	4.03	3.73	0.0059	0.027	/	0.022	0.0084	0.0062	0.0024

* V–4Cr–4Ti (NIFS-Heat-2).

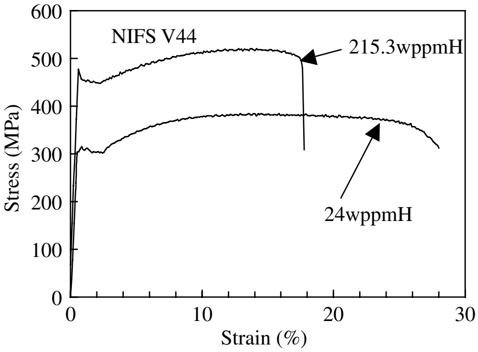

Fig. 1. Engineering stress–strain curves of the NIFS V44 alloy with 24 wppmH and the hydrogen charged one (215.3 wppmH) tensile tested at room temperature at strain rate of 4.4×10^{-4}/s.

and without hydrogen charging (24 wppmH). Evidently the tensile properties were greatly changed by the hydrogen charging. Strengths increased while elongations decreased. The hydrogen dependences of the properties are presented as follows.

3.1. The elongations of the alloys

The most concerned property for the hydrogen effects is the hydrogen-induced ductility loss and the critical hydrogen concentration required to embrittle the alloy. Fig. 2 and Fig. 3(a) show the measured tensile elongations, total elongation (TE) and uniform elongation (UE), as a function of the hydrogen concentration for the alloys. Fig. 3(b) shows the results for the US V–4Cr–4Ti (832665 heat, named as US V44 next) reported by

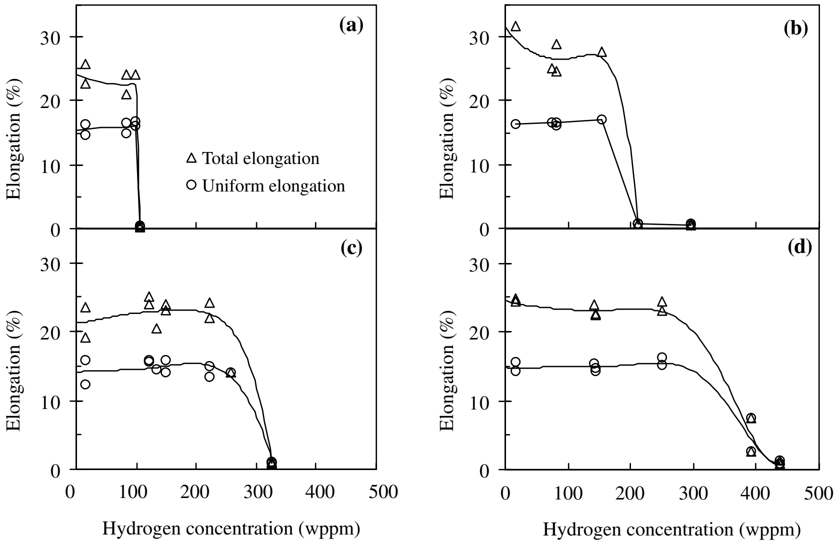

Fig. 2. Tensile elongations as a function of the hydrogen concentration for (a) V–8W, (b) V–7W–0.3Al, (c) V–6W–1Ti and (d) V–4Ti. All was tested at room temperature at strain rate of 1.1×10^{-3}/s.

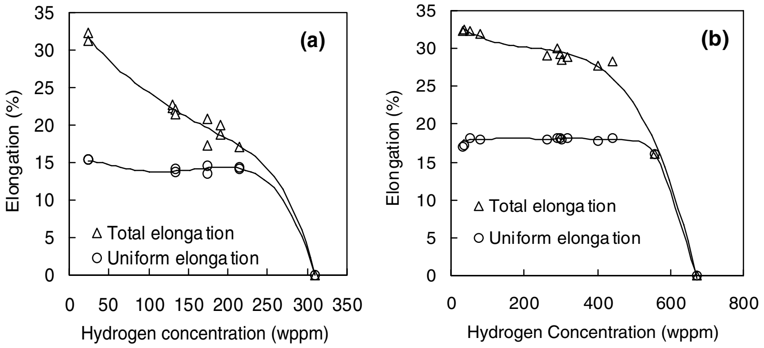

Fig. 3. Tensile elongations as a function of the hydrogen concentration for (a) NIFS V44 tested at strain rate of 4.4×10^{-4}/s and (b) US V44 tested at strain rate of 1.1×10^{-3}/s [18].

Rohrig et al. [18], for which the tensile test employed a strain rate of 1.1 × 10^{-3}/s and the tensile specimen had a thickness of 0.76 mm. It is a little thicker than the specimens of the newly developed alloys but much thinner than those of the NIFS V44. Fig. 2 shows that neither TE nor UE changed much with the hydrogen until a critical hydrogen level (C_{CH}) was reached, beyond which the elongations decreased drastically. Comparing the results, C_{CH} tended to decrease with reducing Ti content in an alloy: V–4Ti has the highest C_{CH} while that for V–8W is the lowest among the alloys. Evidently, the property is also benefited from the doped aluminum. Despite of the small Al content in V–7W–0.3Al, its C_{CH} is much higher than that of the V–8W alloy.

The hydrogen dependence of the uniform elongation for the NIFS V44 and US V44 is similar to that of the other alloys. The change of it is very small below the critical hydrogen concentration. However, the total elongation decreased with increasing hydrogen concentration for both alloys. The strongest reduction happened for the NIFS V44, for which the tensile strain rate is much slower as compared to other alloys. It seems that tensile strain rate has strong effect on the hydrogen dependence of the total elongation. And yet, the C_{CH} for both alloys is quite different though they are both V–4Cr–4Ti alloys. The data of the C_{CH}, the loss rate of the UE and TE on hydrogen concentration (R_{UE} and R_{TE}, respectively) and the tensile strain rate are summarized in Table 2. Here a linear relationship between the hydrogen concentration and UE or that with TE was assumed at hydrogen concentrations below C_{CH}, which was in a range for each alloy because the exact value could not be determined from the insufficient tensile test data. Evidently, the US V44 has higher C_{CH} than the NIFS V44. It seems that the US V44 is better at the property.

3.2. The strengths of the alloys

It was observed that hydrogen-induced hardening happened for any of the alloys. Fig. 4 is an example showing the hydrogen concentration dependence of the yield strength and ultimate tensile strength for V–7W–0.3Al. The yield strength nearly increased linearly with the hydrogen at the level below 212 wppm, where brittle fracture occurred (see Fig. 2(b)). On the other hand, the ultimate tensile strength increased in the low hydrogen concentration region but started to decrease around the C_{CH}, which is between 154 and 212 wppmH for the alloy. When the hydrogen concentration got higher than the C_{CH}, there is a trend that both strengths decrease with increasing hydrogen concentration.

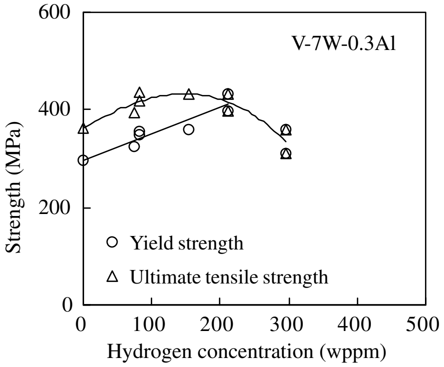

Fig. 4. The dependence of the yield strength and the ultimate tensile strength on the hydrogen concentration for V–7W–0.3Al tested at room temperature at strain rate of 1.1 × 10^{-3}/s.

Other alloys showed similarly in the hydrogen-induced hardening behavior. Fig. 5 shows the dependence of the yield strength on the hydrogen concentration for all alloys, including that for the US V44 reported by Rohrig et al. [18]. The tensile strain rate was also shown in the figure. Approximately, all exhibited a linear increase in yield strength with the hydrogen concentration. However, the increasing rate is quite different from one another. The rate was listed in Table 2 as R_{YS}. It looks like that the hardening is likely related to the Ti addition in the alloy and is strongly affected by the tensile strain rate. The alloy with Ti addition, such as V–6W–1Ti, V–4Ti and the US V44, has much smaller hardening rate

Table 2
Summary of the results and the corresponding tensile strain rate

	Alloy					
	V–6W–1Ti	V–4Ti	V–7W–0.3Al	V–8W	NIFS V44	US V44
Strain rate (/s)	1.1 × 10^{-3}	1.1 × 10^{-3}	1.1 × 10^{-3}	1.1 × 10^{-3}	4.4 × 10^{-4}	1.1 × 10^{-3}
C_{CH} (wppm)*	258–327	249–391	154–212	98–107	215–310	558–673
R_{UE} (10^{-5}/wppmH)	0.64	−3.52	−4.96	−10.1	6.43	−1.4
R_{TE} (10^{-5}/wppmH)	−8.53	4.19	25.3	12.4	77.3	11.7
R_{YS} (MPa/wppmH)	0.37	0.34	0.6	1.03	0.71	0.3

* C_{CH}: the critical hydrogen concentration required to embrittle the alloy, R_{UE}: linear loss rate of the uniform elongation, R_{TE}: linear loss rate of the total elongation, R_{YS}: linear increase rate of the yield strength by hydrogen.

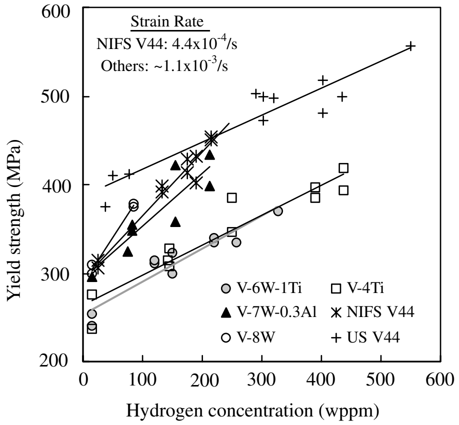

Fig. 5. The increase of the yield strength with hydrogen concentration for each alloy. Data for the US V44 is from Ref. [18].

than that without Ti. It is about half or even less as compared to the latter one. NIFS V44 and US V44 are both V–4Cr–4Ti alloy. If no other factor is considered, the decrease in strain rate from 1.1×10^{-3}/s to 4.4×10^{-4}/s produced a 1.37 times increase in the hardening rate, from 0.3 to 0.71 MPa/wppmH.

4. Discussions

4.1. The effect of Ti/Al addition to the vanadium alloys

The results could be summarized as that either Ti or Al addition was helpful in increasing the abilities of the alloys against the hydrogen embrittlement. This benefit should partially come from the fact that the addition decreases the hydrogen-induced hardening of the alloy (see Fig. 5). The linear increase of the yield strength with the hydrogen indicated a solid solution strengthening by the doped hydrogen in the hydrogen concentration range below C_{CH} for any of the alloys. It should account for the little change of the uniform elongation in the hydrogen range.

The hydrogen-induced hardening in the alloys, though being thought to be a solid solution hardening, would be affected by the interaction between the hydrogen and the dislocations. It is just like the DSA (dynamic strain aging) happened in high temperature tensile tests of vanadium alloys. In the tests the interstitial impurities in the alloy, such as C, N, O, move to the dislocation sites at certain temperature and impede the motion of the dislocations [6]. This interaction causes serrations of the tensile stress–strain curve and increases the strength of the alloy. Hydrogen is also interstitial atom in vanadium alloy and it has higher mobility than C, N and O due to its smaller atomic size. Therefore, it is possible that similar behavior (called as DSA also in the following text) caused by hydrogen occurred in the present tensile testing. The V–4Cr–4Ti alloy shown in the present paper, the NIFS V44 and US V44, exhibited a significant increase of the hydrogen-induced hardening rate (R_{YS} in Table 2) when the tensile strain rate decreased from 1.1×10^{-3}/s to 4.4×10^{-4}/s. It is because the hydrogen in the NIFS V44 had longer time to move to the dislocation sites due to the slower strain rate and consequently led to a stronger DSA. However, further study may be needed because there were some differences in the preparation and the hydrogen charging of NIFS V44 and US V44. For the US V44, another study by Natesan et al. showed that the critical hydrogen concentration required to embrittle the alloy is less than 360 wppm [20], which is quite lower than that reported by Rohrig (see Table 2). The former study utilized a much lower tensile strain rate of 1.8×10^{-4}/s, while that for the latter is 1.1×10^{-3}/s. Though no data is available in Ref. [20] to show the hydrogen-induced hardening rate, it is still reasonable to think that the stronger DSA due to the lower strain rate resulted in a higher hardening rate and the lower C_{CH} of the alloy in Natesan's study.

On the other hand, the present stress–strain curves look a little serrated (see Fig. 1). This serration is very small and is most probably caused by the data acquisition system rather than by DSA. In fact, serrations of stress–strain curve by DSA is due to the trap of interstitial solutes in dislocations and the de-trap (extrication) of the trapped interstitial solutes from the dislocations. H atoms are believed to be able to move together with the dislocations at room temperature. The de-trap could not occur for the DSA caused by H. Therefore, serrations could not appear. Perhaps, if the tensile test temperature were lower where hydrogen atoms are less mobile, then serration would occur.

The effect of Ti/Al on the behavior is attributed to the strong interaction between the elements and the hydrogen. It was well known that Ti and Al are strong interstitial scavenging species which might bind hydrogen, resulting in a weaker interaction between the hydrogen and the dislocations in the alloy. Consequently the effect of the hydrogen on the tensile properties got smaller. Evidence to support the strong interaction is that Ti could decrease the diffusion coefficient of H in the Ti-bearing alloy [24]. In another study reported by Nishimura et al. [25], the hydrogen permeability in V–Al alloys decreased with increasing Al content up to 40 wt%. Though no explanation was given but the hydrogen diffusivity must be lowered by the Al addition. Due to the lower mobility of H in the Ti/Al-bearing alloys, DSA becomes weaker and so does the hydrogen-induced hardening. That is why the alloys with Ti or Al have better properties against hydrogen embrittlement.

4.2. The effect of strain rate on the hydrogen-induced ductility loss

It was reported that stress-assisted hydrogen diffusion might play an important role to the hydrogen embrittlement of the NIFS V–4Cr–4Ti alloy [22]. In the tensile tests, hydrogen moves to the necking center due to the high tensile stress at it and the stress gradient around it. This enrichment at the necking center decreases the plastic deformation ability. As a result, the total elongation rather than the uniform elongation is more reduced by the hydrogen. However, in the present study, this behavior seemed to be influenced by the tensile strain rate. The NIFS V44 alloy showed a much stronger loss of the total elongation with the hydrogen while the strain rate for it was lower as compared to other alloys. It indicates that the stress-assisted hydrogen diffusion is a time controlling process. For other alloys the total elongation changed more tenderly with the hydrogen because the strain rate is higher. The effect gets weaker at higher strain rate because the hydrogen enrichment would be smaller due to insufficient diffusion time. Therefore, the uniform elongation is more significant in evaluating the effect of hydrogen on the ductility loss as compared to the total elongation.

5. Conclusions

The tensile properties of several V–W–Ti–Al alloys were measured with their hydrogen concentration up to 438 wppm. With the additional data from the previous studied V–4Cr–4Ti, the effects of tensile strain rate and the alloying elements on the properties were clearly shown. Results could be summarized as follows.

(1) The addition of Ti/Al to a vanadium alloy could increase its resistance to the hydrogen embrittlement significantly due to the strong binding force of the alloying elements to the hydrogen in solid solution. The binding decreases the mobility of the doped hydrogen and weakens the DSA resulted from the interactions between the hydrogen and the dislocations in the alloy. Hydrogen-induced hardening is thus decreased with the Ti/Al addition and the critical hydrogen concentration required to embrittle the alloy increases a lot.

(2) Tensile strain rate has strong effect on the hydrogen concentration dependence of the total elongation instead of the uniform elongation. Lower strain rate leads to more loss of the total elongation induced by the hydrogen. Therefore, the uniform elongation is more significant in evaluating the effect of hydrogen on the ductility loss as compared to the total elongation.

Acknowledgements

This work is conducted with the support of the National Nature Science Foundation of China (project #50271025). The author would like to thank Professor Q. Lu in Nanjing University who aided in the alloy preparation.

References

[1] E.V. Dyomina, P. Fenici, V.P. Kolotov, M. Zucchetti, J. Nucl. Mater. 258–263 (1998) 1784.
[2] R.H. Jones, H.L. Heinisch, K.A. McCarthy, J. Nucl. Mater. 271&272 (1999) 518.
[3] N.P. Taylor, C.B.A. Forty, D.A. Petti, et al., J. Nucl. Mater. 283–287 (2000) 28.
[4] E.E. Bloom, R.W. Conn, J.W. Davis, R.E. Gold, et al., J. Nucl. Mater. 122&123 (1984) 17.
[5] M. Satou, K. Abe, H. Kayano, J. Nucl. Mater. 179–181 (1991) 757.
[6] A.F. Rowcliffe, S.J. Zinkle, D.T. Hoelzer, J. Nucl. Mater. 283–287 (2000) 508.
[7] R.J. Kurtz, M.L. Hamilton, J. Nucl. Mater. 283–287 (2000) 628.
[8] H.M. Chung, B.A. Loomis, D.L. Smith, Fus. Eng. Des. 29 (1995) 455.
[9] B.A. Loomis, D.L. Smith, F.A. Garner, J. Nucl. Mater. 179–181 (1991) 771.
[10] D.L. Smith, H.M. Chung, B.A. Loomis, H.-C. Tsai, J. Nucl. Mater. 233–237 (1996) 356.
[11] D.L. Smith et al., Fus. Technol. 8 (1) (1985) 10.
[12] I.R. Kirillov et al., Fus. Eng. Des. 39&40 (1998) 669.
[13] Y. Gohar, S. Majumdar, D.L. Smith, Fus. Eng. Des. 49&50 (2000) 551.
[14] J. Chen, T. Muroga, T. Nagasaka, Y. Xu, S. Qiu, J. Nucl. Mater. 322 (2003) 73.
[15] R.J. Kurtz, K. Abe, V.M. Chernov, et al., J. Nucl. Mater. 283–287 (2000) 70.
[16] Y. Hirohata, T. Oda, T. Hino, S. Sengoku, J. Nucl. Mater. 290–293 (2001) 196.
[17] J.R. DiStefano, J.H. De Van, D.H. Rohrig, L.D. Chitwood, J. Nucl. Mater. 273 (1999) 102.
[18] H.D. Rohrig, J.R. DiStefano, L.D. Chitwood, J. Nucl. Mater. 258–263 (1998) 1356.
[19] J.R. DiStefano, B.A. Pint, J.H. De Van, D.H. Rohrig, L.D. Chitwood, J. Nucl. Mater. 283–287 (2000) 841.
[20] K. Natesan, W.K. Soppet, J. Nucl. Mater. 283–287 (2000) 1316.
[21] J. Chen, Z. Xu, L. Yang, J. Nucl. Mater. 307–311 (2002) 566.
[22] J. Chen, Y. Xu, S. Qiu, T. Muroga, et al., J. Nucl. Mater. 325 (2004) 79.
[23] T. Muroga, T. Nagasaka, K. Abe, et al., J. Nucl. Mater. 307–311 (2002) 547.
[24] S. Yano, M. Tada, H. Matsui, J. Nucl. Mater. 179–181 (1991) 779.
[25] C. Nishimura, T. Ozaki, M. Komaki, Y. Zhang, J. Alloys Compd. 356&357 (2003) 295.