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Effects of oxygen, hydrogen and neutron irradiation on the mechanical properties of several vanadium alloys

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Abstract

Several V–Cr–Ti–Al–Si alloys were studied or reviewed of their mechanical properties after their exposure to oxygen, hydrogen and neutron irradiation environments. The results showed that the oxidation kinetic of V4Cr4Ti alloy exhibited parabolic behavior in a flowing argon gas with low partial pressure oxygen over the temperatures from 450 to 600 °C. Most of the alloys showed ductility losses with the increasing oxygen concentration with an exception of V4Ti3Al. Strong sensitivity to hydrogen embrittlement was found for the alloys with the combination of high oxygen concentration and high mechanical strength. It was found that the effect of hydrogen and neutron irradiation on the uniform deformation capability caused by their hardening are equivalent with that of the strain hardening. Fine grain was recommended for the alloys to improve their properties against hydrogen embrittlement and neutron irradiation induced ductility loss.

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1. Introduction

Vanadium alloys such as V4Cr4Ti were regarded as the most promising candidate structural materials for fusion application because of their superior properties to other materials such as ferritic and austenitic stainless steels [1–12]. However there are still some critical issues for the engineering use in fusion reactor [13]. Recent years many studies reported the reduction in ductility of the alloys exposed to oxygen, hydrogen environments and low temperature neutron irradiation [14–17]. Some progresses have been achieved to improve the low temperature irradiation performance of a V4Cr4Ti alloy by reducing the total impurities concentration or by adding from 0.1% to 1% Al, Si and Y to the alloy [18]. High temperature oxidation performance of the alloy was also improved by the additions [19]. These results were reviewed in this paper and some new experimental results were given. Discussions were taken to give the relations among the hydrogen embrittlement, neutron irradiation performance and the strain hardening of the alloy.

2. Experimental procedure

Several vanadium alloys were developed on a small scale in China. Table 1 listed the chemical compositions and the hot-working temperature. The alloys were melted in a magnetic floating furnace using high purity raw materials, hot rolled in air and cold rolled to 0.5–1 mm thick sheets with a ratio of ~50% CW. Each alloy was annealed at 1020 °C for 20 or 60 min in a vacuum less than 1×10^{-3} Pa before any experiment. The grain size was of 20–40 μm.

V4Cr4Ti was selected for the oxidation experiment. Specimens in size of $\sim 6 \times 8 \times 2$ mm were used. The oxidation was conducted in a flowing argon gas with

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Table 1
Chemical compositions of the vanadium alloys and the hot-working temperature

Alloy	Chemical composition (wt%)						Hot-working temperature (°C)
	Si	Cr	Ti	Al	N	O	
V4Cr4Ti	0.023	3.61	4.11	0.21	0.046	0.09	850
V3TiAlSi	0.95	0.02	3.20	1.07	0.006	0.08	850
V4TiL[a]	0.005	–	4.32	0.19	0.002	0.046	400–500
V4Ti	0.012	0.22	4.23	0.23	0.002	0.085	850
V4Ti3AlL[a]	0.016	–	4.24	2.82	0.001	0.039	400–500
V4Ti3Al	0.008	0.02	4.23	2.89	0.005	0.07	850
V4TiSi	0.24	0.02	3.96	0.26	0.052	0.11	850

[a] Here L means low oxygen concentration.

different oxygen content in a thermalgravimetric test apparatus at temperatures of 450, 520 and 600 °C. The flow rate of the gas was 15 l/h with the oxygen content of 6.7 vppm (5.1×10^{-3} Torr) and 12.0 vppm (9.1×10^{-3} Torr). A micro-gram balance was utilized to weigh the specimen in situ during the experiment. Specimen surfaces were examined by X-ray diffraction (XRD) analysis after the oxidation.

All alloys in Table 1 were hydrogenated in a hydrogenation apparatus in order to study the effects of hydrogen on their mechanical properties. Tensile specimens cut from the annealed sheets with a gauge length of 20 mm and width of 8 mm were placed in a 2×10^{-3} Pa vacuum vessel. The specimens were firstly preheated to 420 °C for several minutes before hydrogenation at 700 °C. High purity hydrogen gas was admitted through a controllable leak valve while the vessel was being evacuated. An equilibrium heat treatment was conducted at the same temperature for 2 h after the hydrogenation.

Tensile specimens with or without hydrogen were tested in a MTS machine with a strain rate of $\sim 4 \times 10^{-3} s^{-1}$. The fracture surfaces were observed using a scanning electron microscope to show their fracture features.

3. Results of oxidation and oxygen effects on mechanical performance

3.1. Oxidation behavior in different oxidizing atmosphere

Oxidation kinetics of V4Cr4Ti in a flowing argon gas are shown in Fig. 1. All of them exhibited parabolic behavior in the temperature range from 450 to 600 °C, indicative of a diffusion controlled oxidation process. The correlation between the weight gain (W) and the exposure time (t) could be expressed as $W^2 = K_p t$, where K_p is a parabolic rate constant. It was found from Fig. 1 that the parabolic rate constant increased with the exposure temperature and the oxygen content of the flowing gas. The temperature dependence of the para-

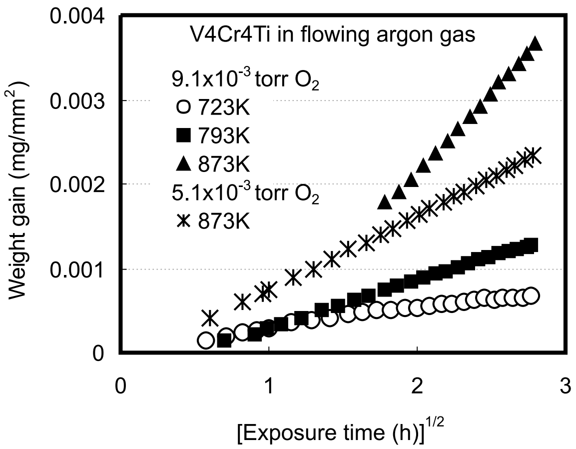

Fig. 1. Weight gain data plotted against the square root of exposure time for V4Cr4Ti alloy exposed to a flowing argon gas.

bolic rate constant shown in Fig. 2 was described by using a relationship $K_p = K_0 \exp[-Q/(RT)]$, where K_0 is a preexponential term, Q is the activation energy of the oxidation process, R is a gas constant and T is absolute temperature. The calculated activation energies were also marked in the figure. It is about 157.4 kJ/mol for the exposure in the flowing argon gas, a little lower than that in 5×10^{-6} Torr oxygen. It is obvious that the energy decreased with the increasing oxygen pressure.

Many forms of oxide would be formed during the oxidation process [20]. The oxide was predominately V_2O_5 both in air and in high-pressure oxygen. While that in low-pressure oxygen was mainly VO_2. The formed oxide in this experiment at 600 °C was found to be V_2O_4 according to the XRD analysis result.

It has been reported [19] that addition of Al, Si and Y in V4Cr4Ti could improve its high temperature oxidation performance by decreasing its oxidation rate in air. The fact that the alloy with Al element (V4Ti3Al) had relatively lower oxygen content in this study in com-

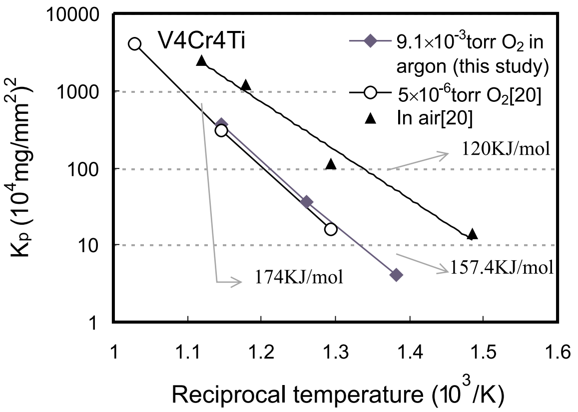

Fig. 2. Temperature dependence of parabolic rate constant for V4Cr4Ti exposed to different environments. The oxygen pressure was 5×10^{-6} Torr of the low-pressure O.

parison with the other alloys in Table 1 also suggested that the alloy element Al could increase the oxidation resistance of the vanadium alloys in air since all of the alloys were hot rolled in air in the temperatures ranging from 400 to 850 °C. The next section will show that the alloy with Al had better mechanical performance under high oxygen concentration.

3.2. Oxygen effects on mechanical properties

High temperature oxidation had small effects on the strength of vanadium alloys, but obviously decreased the ductility of the alloys [13,14]. The brittle fracture was mainly intergranular [13]. Fig. 3 shows the yield strength of V4Ti3Al and V4Ti. The yield strength of V4Ti increased by ~10% with the oxygen concentration from 460 to 850 wppm. While that for V4Ti3Al decreased a

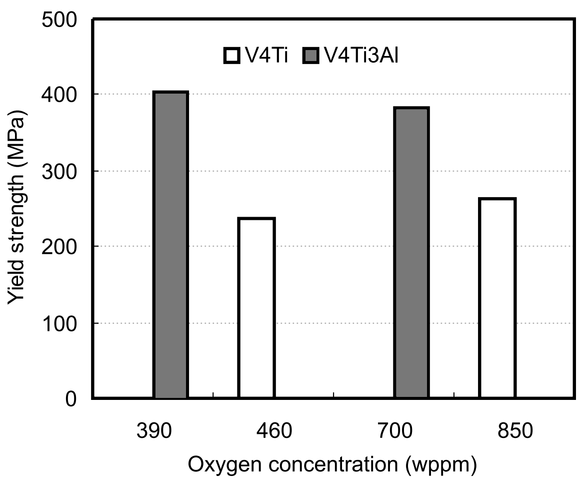

Fig. 3. The yield strength of V4Ti and V4Ti3Al at different oxygen concentration.

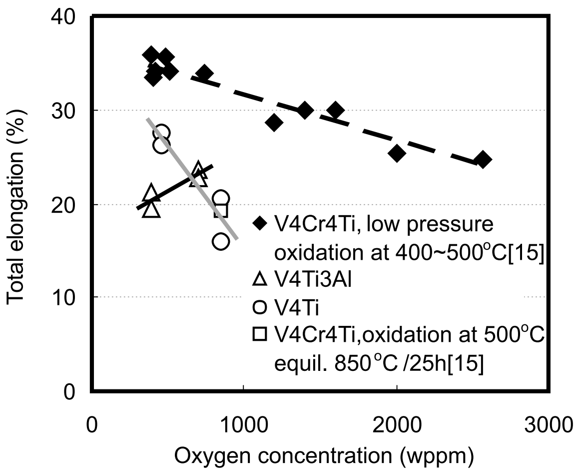

Fig. 4. The tensile properties of the vanadium alloys with different oxygen concentration.

little with the oxygen concentration. Fig. 4 shows the oxygen dependence of the total elongation for V4Ti3Al, V4Ti and V4Cr4Ti (heat 832665) [15]. The elongation decreased gently with oxygen for V4Cr4Ti but quickly for V4Ti. However, with an equilibrium treatment at 800 °C for 25 h, the elongation of V4Cr4Ti also lost largely [15]. This difference may be caused by the non-equilibrium distribution of oxygen in the oxidized specimen. In opposite to the results of V4Ti and V4Cr4Ti alloys, the elongation of V4Ti3Al increased a little with the oxygen increased from 390 to 700 wppm. Fig. 5 shows the fracture features of V4Ti and V4Ti3Al alloys with different oxygen concentration. All fractured in dimple structure. It was found that the size of the dimples became small for V4Ti and did not change significantly for V4Ti3Al as the oxygen concentration increased. The features again indicated that V4Ti3Al had higher resistance to oxygen induced ductility loss.

DiStefano described the role of alloy elements on the oxygen effects as: 'since oxygen has a stronger affinity for titanium than vanadium, oxygen in vanadium–titanium alloys may be preferentially associated with the titanium. If titanium significantly affects the solubility and distribution of oxygen in the alloy, effects of oxygen on mechanical properties could be affected as well' [15]. In comparison, aluminum has ever stronger affinity for oxygen than titanium. The oxygen in the base alloy would be nearly totally absorbed by aluminum during the annealing heat treatment if the time for annealing was long enough. Thus the matrix would have much lower oxygen concentration and the ductility of the alloy could remain high. The annealing time for higher oxygen concentration V4Ti3Al was 1 h in this experiment, while that for the lower oxygen concentration V4Ti3AlL was only 20 min. This may account for the higher total elongation of V4Ti3Al.

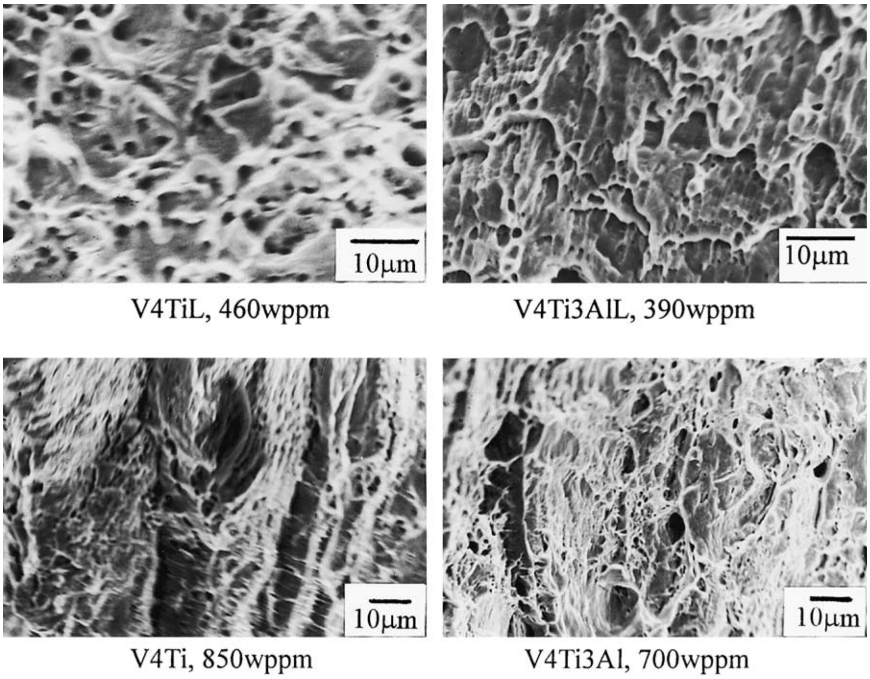

Fig. 5. SEM fractographs of the tensile specimens with different oxygen concentration.

4. Hydrogen effects and the effects combined with oxygen

Vanadium alloys are sensitive to hydrogen embrittlement. Fig. 6 shows the tensile curves of V4TiL and V4Ti3AlL alloys without hydrogen or with 29 and 20 wppm hydrogen, respectively. It was found that hydrogen caused increases both in yield strength and ultimate strength. In contrast, the total elongation decreased with hydrogen.

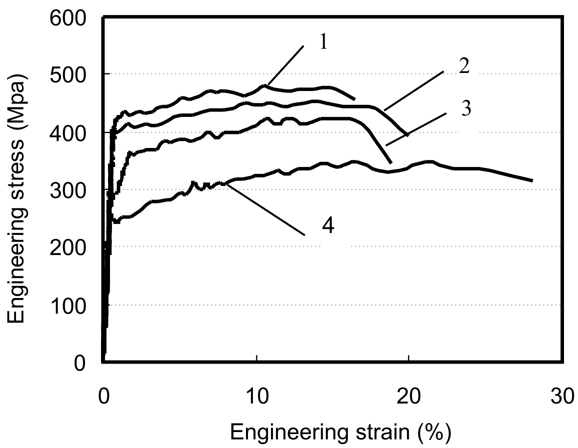

Fig. 6. Tensile curves for the alloys with (1, 3) or without (2, 4) hydrogen. 1, 2:V4Ti3AlL, 3, 4:V4TiL.

DiStefano et al. [15] reported that when oxygen was excluded, hydrogen concentration up to ~400 wppm produced only a small reduction in ductility for V4Cr4Ti alloy; however, above 500 wppm the ductility fell precipitously. The grain size had slightly affected the total elongation and the critical hydrogen concentration required to embrittle the alloy. The concentration seems to shift to lower levels and the total elongation decreased with increasing grain size. Fracture due to hydrogen embrittlement was predominantly transgranular cleavage [21]. In this study, most of the alloys (except V4TiL and V4Ti3AlL) had higher oxygen concentrations ranging from 700 to 1100 wppm. Their hydrogen effects on mechanical performance should take the synergistic effects of oxygen into consideration. Fig. 7 showed that their elongation decreased quickly with the increasing hydrogen concentration. Obviously this behavior is much different from that stated above for a low oxygen V4Cr4Ti alloy. It must be the oxygen that enhanced the hydrogen embrittlement of the alloy. However, the effect of oxygen on the behavior seemed to be nonuniform among other alloys. Fig. 8 showed the hydrogen concentration dependence of the total elongation for V4Ti and V4Ti3Al with different oxygen concentration. It was evident that the oxygen in V4Ti3Al speeded up its elongation-decreasing rate with hydrogen. But the rate appeared to be little affected for V4Ti alloy. V4Ti alloy also exhibited better ductility than other alloys at

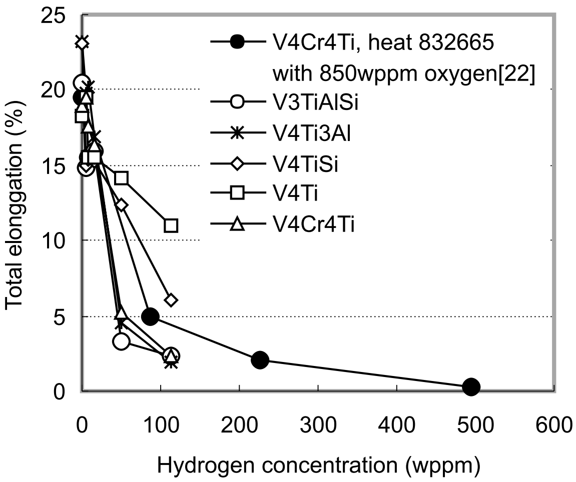

Fig. 7. Effect of hydrogen plus oxygen on the total elongation of the vanadium alloys [22].

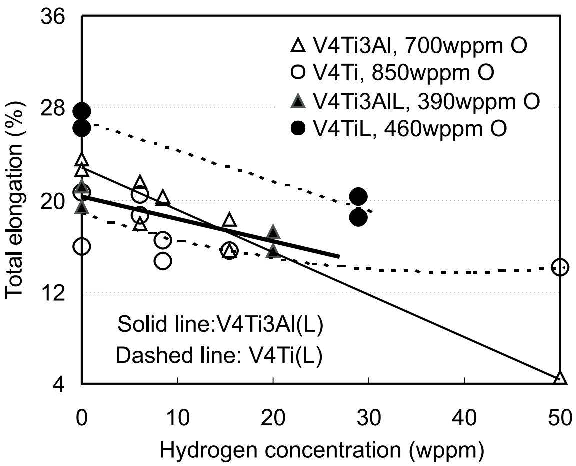

Fig. 8. The hydrogen dependence of V4Ti3Al and V4Ti alloys with different oxygen concentration.

the hydrogen concentrations $\geqslant 50$ wppm as shown in Fig. 7.

The vanadium alloys in this study took in oxygen from the atmosphere during the forging and hot-rolling process. According to the result reported by DiStefano [15], the oxygen was most likely distributed along the grain boundaries. It weakened the grain boundary and led the alloy to a higher trend to intergranular fracture. As the oxygen concentration in the alloys was not high enough in this experiment, the alloys showed ductile fracture without any feature of intergranular fracture (see Fig. 5). However, when hydrogen was taken in, the grain boundary of the alloys would be further weakened while the strength of the grain would increase since hydrogen could inhibit dislocation movement. Thus the strength of the grain boundary may become lower than the strength of the grain at a critical hydrogen concentration over which intergranular fracture might occur, resulting in great loss in ductility.

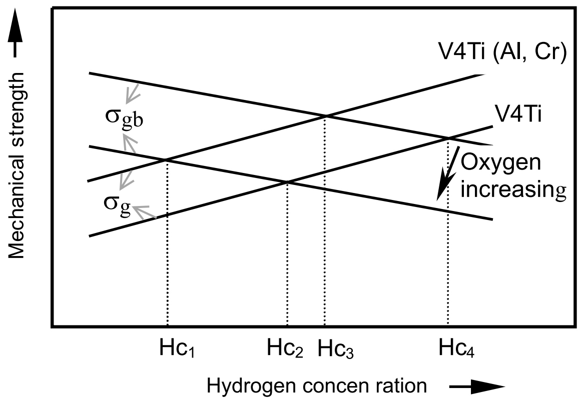

Fig. 9. Schematic representation of the changes of the grain boundary strength (σ_{gb}) and the grain strength (σ_g) with hydrogen. H_{c1}, H_{c2}, H_{c3} and H_{c4} represented the critical hydrogen concentrations.

Fig. 9 schematically showed the changes of the grain boundary strength and the grain strength with hydrogen for V4Ti and the alloys with addition of Al or Cr element in different oxygen concentration. In comparison with other alloys with Al or Cr, V4Ti alloy had much lower tensile strength (see Table 2). Besides, V4Ti should also have lower grain strength but similar grain boundary strength because the Al or Cr was substitutional atom in other alloys. It could be clearly seen from the figure that oxygen caused the critical hydrogen concentration shift to lower level and the concentration was higher for V4Ti alloy than that for the alloy with Al or Cr element. Therefore, the hydrogen embrittlement sensitivity of a vanadium alloy is affected by the combination of oxygen concentration and mechanical strength of the alloy. The increase in the grain strength by oxygen was not considered in the figure. If the effect was considered, the critical hydrogen concentration would be decreased further. Eventually, if the oxygen concentration was very low, intergranular fracture would not occur because the applied stress first exceeds the

Table 2
Room temperature yield strength and ultimate strength of several vanadium alloys

Alloy (MPa)	V4Cr4Ti	V3TiAlSi	V4Ti	V4TiSi	V4Ti3Al
σ_y	326.3	438.5	262.0	256.3	382.5
σ_{UT}	402.7	501.9	341.5	335.7	425.4

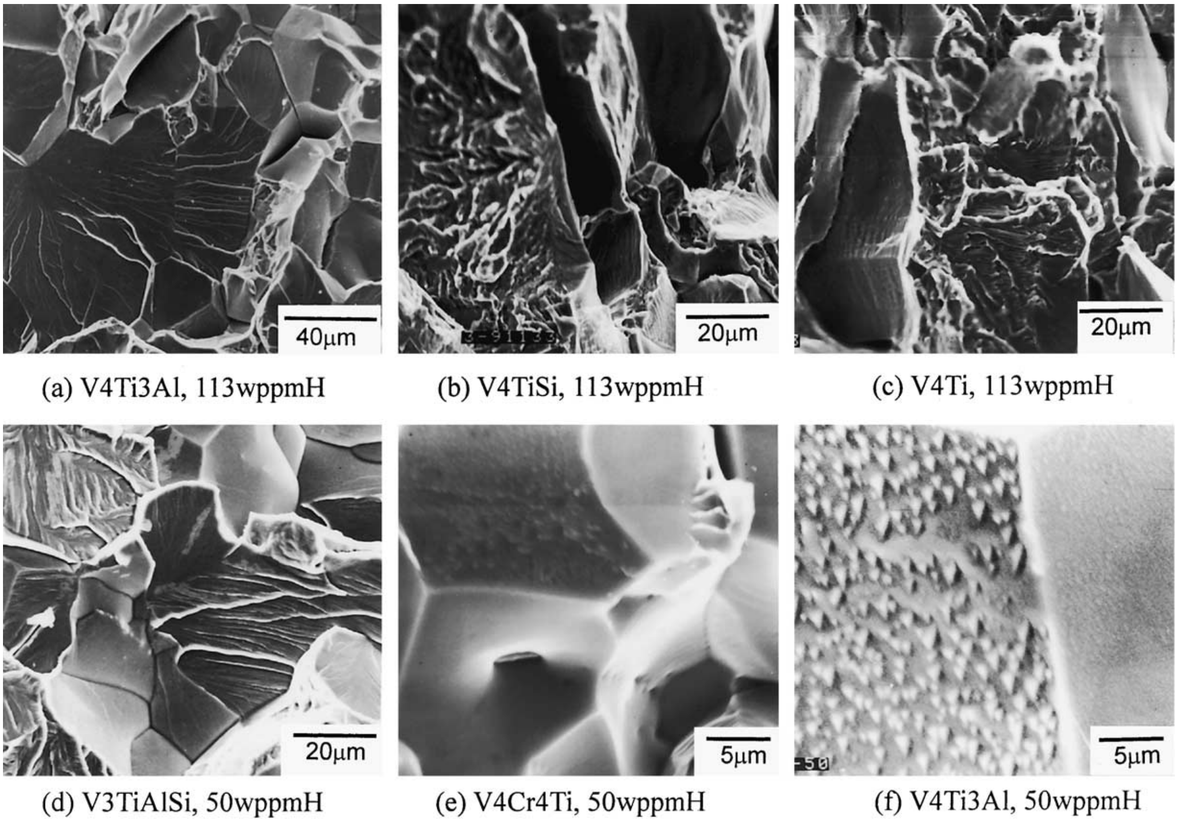

Fig. 10. SEM fractographs of V4Ti3Al, V4TiSi, V4Ti, V3TiAlSi and V4Cr4Ti tensile specimens with 113 or 50 wppm hydrogen.

grain strength for transgranular cleavage fracture prior to the grain boundary strength.

The hydrogen embrittlement fracture surfaces were observed to be mainly transgranular cleavage under a scanning electron microscope. However some intergranular fractures were found for the V4Ti3Al, V3TiAlSi and V4Cr4Ti alloys (see Fig. 10(a), (d) and (e)). The fractures seem to be associated with the fine grains (Fig. 10(a)) since a fine grain has higher strength than a coarse grain. Many fine precipitates in diameter lower than 1 μm were found on the grain surface of V4Ti3Al alloy (Fig. 10(f)), which may weaken the grain boundary of the alloy. V4TiSi and V4Ti alloys were found to have very small cleavage planes and many secondary cracks (see Fig. 10(b) and (c)), indicative of that more energy was exhausted during the fracture process. Therefore, the critical hydrogen concentration for V4Ti and V4TiSi alloys must exceed 113 wppm while that for other alloys must be less than 50 wppm according to the fracture modes. It gave the reason for the better property of V4Ti and V4TiSi alloys against hydrogen embrittlement and the nearly unchanged hydrogen embrittlement sensitivity for V4Ti alloy with the different oxygen concentration in this experiment.

5. Effects of neutron irradiation

Neutron irradiation of materials causes microstructure changes, which make changes in material properties. The change in microstructure varied with the irradiation temperature for V–Cr–Ti alloys [9–11]. Neutron irradiation produced coarse Ti_5Si_3 precipitates at temperature over 400 °C and high number density Ti_x (O,N,C) precipitates in diameter smaller than 4 nm in the temperature range from 300 to 400 °C. At even lower temperature the irradiation led to high number density of dislocations in the alloy. All of these changes increased the strength of the post-irradiated alloys and reduced their ductility because of their high resistance to dislocation movement. Fig. 11 indicated that both the yield strength and the ultimate strength of a V4Cr4Ti alloy was increased by 0.1–0.5 dpa neutron irradiation. The increments got higher as the irradiation/test temperature got lower. It was found from the figure that at a temperature below 400 °C the yield strength of the irradiated alloy exceeded the ultimate strength of the unirradiated alloy with the decreasing temperature. On the other hand, many researches [17,23] have found that great loss in uniform elongation occurred in neutron

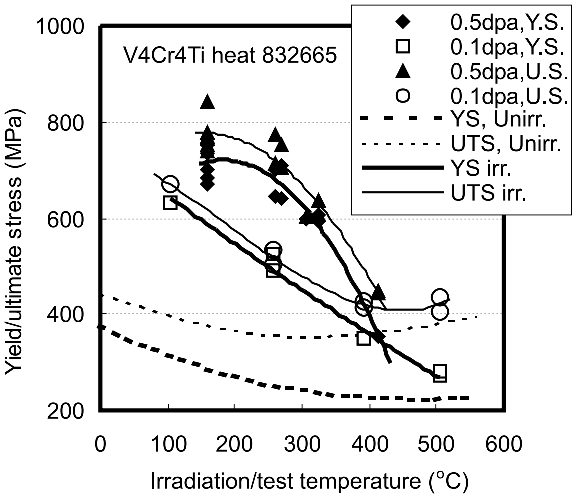

Fig. 11. The temperature dependence of yield and ultimate strength for V4Cr4Ti with or without irradiation. Data from Refs. [24,25].

irradiated vanadium alloys below this temperature (also see Fig. 12(a)). There may be some correlation between the two events.

Fig. 12(b) shows replots of uniform elongation as a function of yield strength. Data of hydrogenated V4Cr4Ti was also included in the figure. The solid lines, obtained by unloading the tensile specimen and then retest it at different points on the real tensile stress–strain curves, represent the results of the unirradiated alloy with different stain hardening. They reached a surprisingly good accordance with the irradiated and the hydrogenated alloys. Thus, it can be concluded that the effect of hydrogen and neutron irradiation on the uniform deformation capability caused by their hardening are equivalent with that of the strain hardening.

Plastic deformation is a result of dislocation motion. Both the hydrogen and the irradiation induced precipitates or dislocations in an alloy produce not only high resistance to dislocation motion, but also accelerate dislocation-breeding rate. Thus great numbers of dislocations might be produced in a very short time during the tensile loading of the alloy. It has been found that dislocation channeling occurred during the tensile test of a post-irradiated V4Cr4Ti alloy [11]. Since strain hardening is also resulted from dislocation motion resistance by great number of other dislocations, it is reasonable to take the equivalent effects of hydrogen, neutron irradiation and strain hardening on the uniform deformation capability of the alloy.

6. Discussion on the measures used to improve the mechanical performance under oxygen, hydrogen environment and neutron irradiation

As we know, the remained uniform deformation capability of an alloy after strain hardening is mainly dependent on the difference between the ultimate strength and the yield strength of the alloy. Therefore any way that could increase the difference could increase the uniform deformation capability. This result is just suitable for the cases of neutron irradiation and hydrogenation because of the equivalent effects.

There are many ways to strengthen an alloy, such as solid solution hardening, precipitation hardening and so forth. However, only grain refinement measure could increase the strength, the ductility and the strain hardening capability at the same time, give a result that the difference between the ultimate strength and the yield strength increased largely. Thus it seems that only grain refinement could improve the properties of an alloy against hydrogen embrittlement and neutron irradiation induced brittleness, otherwise the strength of the alloy

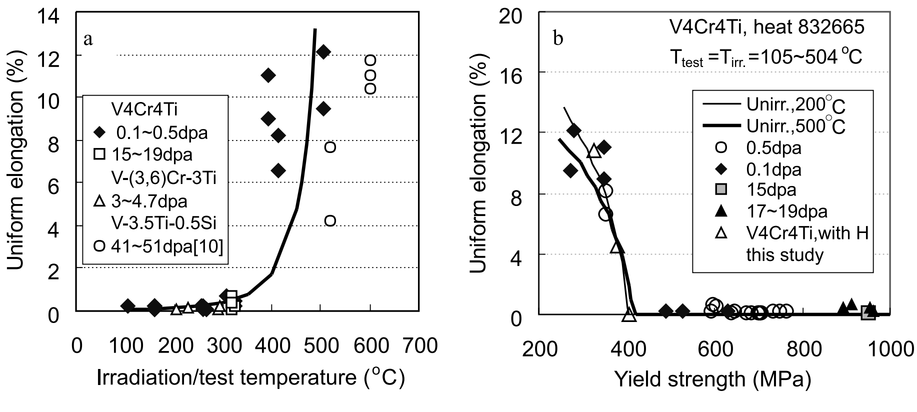

Fig. 12. The dependence of uniform elongation on irradiation temperature (a) and yield strength (b) of post-irradiated V4Cr4Ti. Data from Refs. [4,24].

must be decreased, just like that V4Ti alloy had better property against hydrogen embrittlement than V4Cr4Ti because of its lower yield strength. On the other hand, because fine grains have more grain boundaries, the impurity concentration such as oxygen and hydrogen could be lowered in the grain boundary. The grain boundary became so stronger that intergranular fracture could be inhibited. Thus the measure could be helpful to the oxidation performance of the alloy and the property against hydrogen embrittlement.

It has been proved that V4Cr4Ti alloy with fine grain had better resistance to hydrogen embrittlement [15] and oxidation induced ductility loss [14]. In Ref. [18], Satou reported that the 900 °C preheated V5Cr5TiAlSiY alloy had excellent ductility after 300 °C neutron irradiation in comparison with the one preheated at 1000 to 1100 °C. The former should certainly have smaller recrystallization grain size since the recrystallization annealing temperature was lower.

7. Conclusions

The oxidation and hydrogen embrittlement behaviors of several vanadium alloys were experimentally studied. Neutron irradiation effects on mechanical behavior were reviewed and analyzed in the paper. The results are summarized as follows:

1. The oxidation of V4Cr4Ti in a flowing argon gas with low partial pressure oxygen followed a parabolic kinetic. The activation energy of the process was 157.4 kJ/mol.
2. Addition of $\sim$3% Al in weight in V4Ti alloy led to a reduction in oxygen concentration and kept the alloy in high ductility at high oxygen concentration. Since the experimental data were limited, this result needs further investigation.
3. Most of the vanadium alloys except V4Ti and V4TiSi in the present study showed great sensitivity to hydrogen embrittlement because of the combination of their high oxygen concentration and high mechanical strength. Grain boundary weakening by oxygen was the main reason for the enhanced hydrogen embrittlement.
4. Neutron irradiation hardening, hydrogen induced hardening and strain hardening have the equivalent effects on the loss of the uniform deformation capability for V4Cr4Ti alloy or maybe other vanadium alloys.
5. Grain refinement was suggested to take to improve the mechanical performance of vanadium alloys under oxygen, hydrogen environment and neutron irradiation.

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References

[1] N.P. Taylor, C.B.A. Forty, D.A. Petti, G. Le Marois, J. Nucl. Mater. 283–287 (2000) 28.
[2] E.E. Bloom et al., J. Nucl. Mater. 122&123 (1984) 17.
[3] M. Satou, K. Abe, H. Kayano, J. Nucl. Mater. 179–181 (1991) 757.
[4] A.F. Rowecliffe, S.J. Zinkle, D.T. Hoelzer, J. Nucl. Mater. 283–287 (2000) 508.
[5] H. Matsui, J. Plasma, Fusion Res. 70 (8) (1994) 807.
[6] B.A. Loomis, A.B. Hull, D.L. Smith, J. Nucl. Mater. 179–181 (1991) 148.
[7] D.L. Smith, H.M. Chung, H. Matsui, et al., Fusion Eng. Des. 41 (1998) 7.
[8] B.A. Loomis, L.J. Nowicki, D.L. Smith, J. Nucl. Mater. 212–215 (1994) 790.
[9] H.M. Chung, B.A. Loomis, D.L. Smith, J. Nucl. Mater. 212–215 (1994) 804.
[10] H.M Chung, D.L. Smith, J. Nucl. Mater. 191–194 (1992) 942.
[11] P.M. Rice, S.J. Zinkle, J. Nucl. Mater. 258–263 (1998) 1414.
[12] B.A. Loomis, D.L. Smith, F.A. Garner, J. Nucl. Mater. 179–181 (1991) 771.
[13] R.J. Kurtz, K. Abe, V.M. Chernov, et al., J. Nucl. Mater. 283–287 (2000) 70.
[14] K. Natesan, W.K. Soppet, M. Uz, J. Nucl. Mater. 258–263 (1998) 1476.
[15] J.R. DiStefano, B.A. Pint, J.H. DeVan, et al., J. Nucl. Mater. 283–287 (2000) 841.
[16] H. Tsai, T.S. Bray, H. Matsui, et al., J. Nucl. Mater. 283–287 (2000) 362.
[17] M.L. Hamilton, M.B. Toloczko, J. Nucl. Mater. 283–287 (2000) 488.
[18] M. Satou, T. Chuto, K. Abe, J. Nucl. Mater. 283–287 (2000) 367.
[19] M. Fujiwara, K. Natesan, Fusion Materials Semiannual Progress Report, DOE/ER-0313/27, 1999, p. 45.
[20] K. Natesan, M. Uz, Fusion Eng. Des. 51&52 (2000) 145.
[21] J.R. DiStefano, J.H. DeVan, H.D. Roehrig, et al., J. Nucl. Mater. 273 (1999) 102.
[22] H.D. Rohrig, J.R. DiStefano, L.D. Chitwood, J. Nucl. Mater. 258–263 (1998) 1356.
[23] H.M. Chung, D.L. Smith, J. Nucl. Mater. 258–263 (1998) 1442.
[24] S.J. Zinkle, L.L. Snead, A.F. Rowcliffe, et al., Fusion Materials Semiannual Progress Report, DOE/ER-0313/24, 1998, p. 33.
[25] S.J. Zinkle, A.F. Rowcliffe, C.O. Stevens, Fusion Materials Semiannual Progress Report, DOE/ER-0313/24, 1998, p. 11.