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The influence of hydrogen on tensile properties of V-base alloys developed in China

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Abstract

Several V–Cr–Ti–Al–Si alloys were studied with respect to their mechanical performances after exposure to hydrogen environments. The alloys were developed in China by using a melting process in a magnetic floating furnace. Most of the alloys had a high oxygen concentration from 700 to 1100 wppm since the forging and hot rolling were performed in air at elevated temperature. The results showed a synergistic effect of oxygen and hydrogen. The ductility loss correlated largely with the hydrogen concentration up to 113 wppm. Both V4Ti and V4TiSi showed a relatively higher resistance to hydrogen embrittlement in comparison with other alloys such as V4Cr4Ti and V4Ti3Al.

1. Introduction

V4Cr4Ti is regarded as one of the most promising candidate structural materials for fusion applications because some of its properties are superior to other materials such as ferritic and austenitic stainless steels [1–12]. However, there are still some critical issues for the engineering use in a fusion reactor [13]. In recent years many studies have reported the reduction in ductility of the alloy after the exposure in oxygen, hydrogen environments and low temperature neutron irradiations [14–17]. Some progress has been made in improving the low temperature irradiation performance of the alloy by reducing the total impurity 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 these additions [19]. Some results showed that V4Cr4Ti could keep its high ductility when the hydrogen concentration was less than 400 wppm [15]. But the synergistic effects of hydrogen and oxygen have not been studied carefully. In the present paper new experimental results are given on the effect of hydrogen and the combined effect of oxygen and hydrogen for some vanadium alloys developed in China.

2. Experimental procedure

Several vanadium alloys were developed on a small scale in China. Table 1 lists their chemical compositions and hot-working temperatures. The alloys, melted in a magnetic floating furnace using high purity raw materials, were hot-rolled in air and cold-rolled to 0.5–1 mm thick sheets with a ratio of $\simeq$50% CW. An acid solution of $HNO_3 + 5\%$ HF was used to remove the surface oxidation scale. Each alloy was finally annealed at 1020 °C for 20 or 60 min in a vacuum better than 1×10^{-3} Pa. The grain sizes were in the range from 20 to 40 μm.

Tensile specimens with a gauge area of 20×8 mm^2 for each alloy were cut from the annealed sheets with the length of specimens parallel to the rolling direction. Placed in a 2×10^{-3} Pa vacuum vessel and preheated to 420 °C for several minutes, the specimens were then charged with hydrogen at 700 °C in a hydrogenation apparatus. High purity hydrogen gas was admitted through a controllable leak valve while the vessel was being evacuated. The hydrogen concentration in the alloys was controlled and adjusted by controlling the flow rate of the hydrogen gas and the time of the

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

Alloy	Chemical composition (wt%)						Hot-rolling 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
V4Ti-1	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
V4Ti3Al-1	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

admittance. 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 MTS810 machine with a strain rate of $\simeq 4 \times 10^{-3}$ s^{-1}. The fracture surfaces were observed using a scanning electron microscope.

3. Results

3.1. The effects of alloy process variation on the properties

It can be seen from Table 1 that the hot-rolling temperature was not the same for all alloys. The differences directly affected the oxygen concentrations of the alloys since the alloys were hot-rolled in air. The original vanadium had an oxygen concentration of 350 wppm. Small increments in the oxygen concentration were obtained in the alloys which were hot-rolled at lower temperature in the range from 400 to 500 °C. On the contrary, the concentration was more than doubled for the alloys with a hot-rolling temperature of 850 °C. Besides, V4Ti3Al had a lower oxygen concentration than the other alloys with the same hot-rolling process.

Table 2 lists the mechanical properties of the vanadium alloys. One can clearly see that the alloying elements Al, Si and Cr considerably strengthen the alloy but do not significantly affect the ductility. Oxygen exhibited an opposite effect on the properties of V4Ti and V4Ti3Al. The strength of the V4Ti alloy increased a little while the total elongation decreased from 26.9% to 19% as the oxygen concentration increased from 0.046% to 0.085%. On the contrary, V4Ti3Al showed an increase in elongation with a small loss in strength as the oxygen increased from 0.039% to 0.07%.

3.2. Hydrogen effects

Fig. 1 shows the tensile curves of the V4Ti and V4Ti3Al alloys with lower oxygen concentration (390–460 wppm). The hydrogen concentration was 29 and

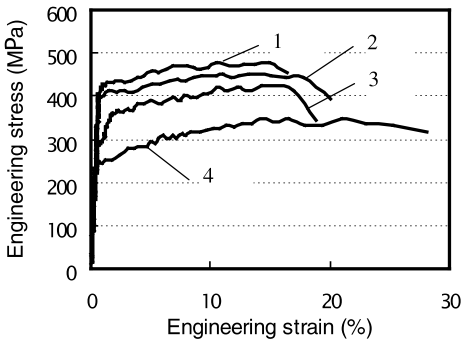


Fig. 1. Tensile curves for the alloys with (1,3) and without (2,4) hydrogen. 1,2: V4Ti3Al-1, 3,4: V4Ti-1.

Table 2
Mechanical properties of the vanadium alloys with oxygen concentration listed

	Alloy						
	V4Cr4Ti	V3TiAlSi	V4Ti-1	V4Ti	V4TiSi	V4Ti3Al-1	V4Ti3Al
OC (wt%)	0.09	0.08	0.046	0.085	0.11	0.039	0.07
σ_y (MPa)	326.3	438.5	237.8	262.0	256.3	404.5	382.5
σ_u (MPa)	402.7	501.9	338.5	341.5	335.7	461.6	425.4
δ (%)	19.0	19.5	26.9	19.0	21.8	20.3	23.0
σ_y/σ_u	0.81	0.87	0.70	0.77	0.76	0.88	0.90

OC: Oxygen concentration, σ_y: yield strength, σ_u: ultimate tensile strength, δ: total elongation.

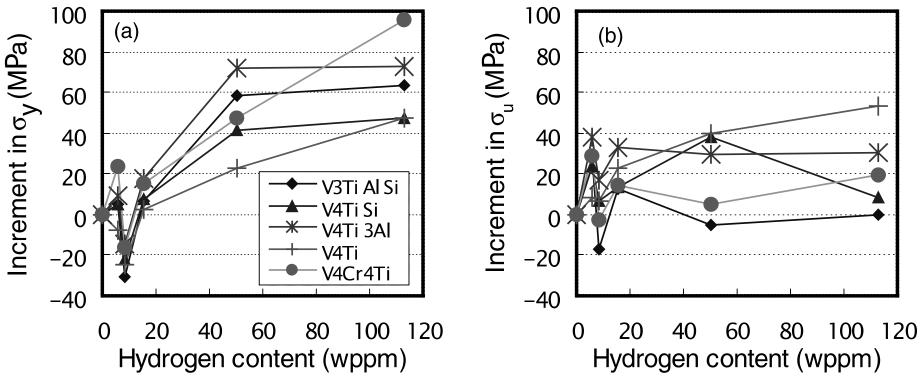


Fig. 2. The increment in yield and ultimate tensile strength caused by hydrogen in various vanadium alloys.

20 wppm for V4Ti-1 and V4Ti3Al-1 alloys, respectively. Evidently hydrogen causes increases both in the yield strength and ultimate tensile strength. On the contrary, the total elongation decreased with hydrogen. The V4Ti alloy seems to lose more in ductility and gain more in strength. Accordingly the V4Ti alloy is likely to be more susceptible to hydrogen embrittlement.

The alloys with high oxygen concentration behaved similarly. Fig. 2 shows the increments of yield strength and ultimate tensile strength at various hydrogen concentrations. The yield strengths of the alloys increase with increasing hydrogen concentration (see Fig. 2(a)). It is assumed that these increases are caused by the reduced dislocation mobility due to the solute hydrogen in the alloys [15]. Their ultimate tensile strengths were increased too, but the increments were small and nearly independent of the hydrogen level for most of the alloys, except V4Ti (see Fig. 2(b)) whose ultimate tensile strength increased successively with increasing hydrogen concentration.

Fig. 3 shows the results of the total elongation for the alloys with different hydrogen concentrations. The elongation decreased with increasing hydrogen concentration for all of the alloys. It even falls below 2.5% at 113 wppm hydrogen concentration for the V4Cr4T, V4Ti3Al and V3TiAlSi alloys, while V4Ti and V4TiSi show better ductility over the whole range of hydrogen concentrations, with the lowest elongation of more than 6%.

There was another notable distinction on the mechanical performances between the V4Ti alloy and the others. Both the yield strength and ultimate tensile strength increased successively with the hydrogen content for the V4Ti alloy, in contrast to the other alloys. Fig. 4 compares the strengths for the V4Ti and V4Cr4Ti alloys. The difference between the two strengths is almost unchanged over the whole hydrogen range for the V4Ti alloy while that for V4Cr4Ti gradually decreased to zero. This difference might be even more pronounced for V4Ti3Al or V3TiAlSi.

The fracture surfaces of the alloys showed mainly transgranular cleavage under the scanning electron microscope. However, many examples of intergranular fracture were found for the V4Ti3Al, V3TiAlSi and V4Cr4Ti alloys. The fracture appeared to be associated with the fine grains (see Fig. 5(a)–(c)). Many fine precipitates smaller than 1 μm in diameter were found on the surfaces of the grains in the V4Ti3Al alloy (Fig. 5(d)), which may weaken the grain boundaries of the alloy. Therefore, the tensile strength of these alloys was

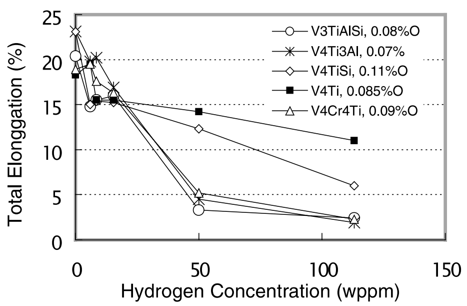


Fig. 3. Effect of hydrogen plus oxygen on the total elongation of several vanadium alloys.

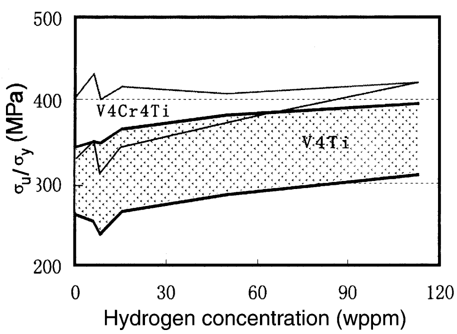
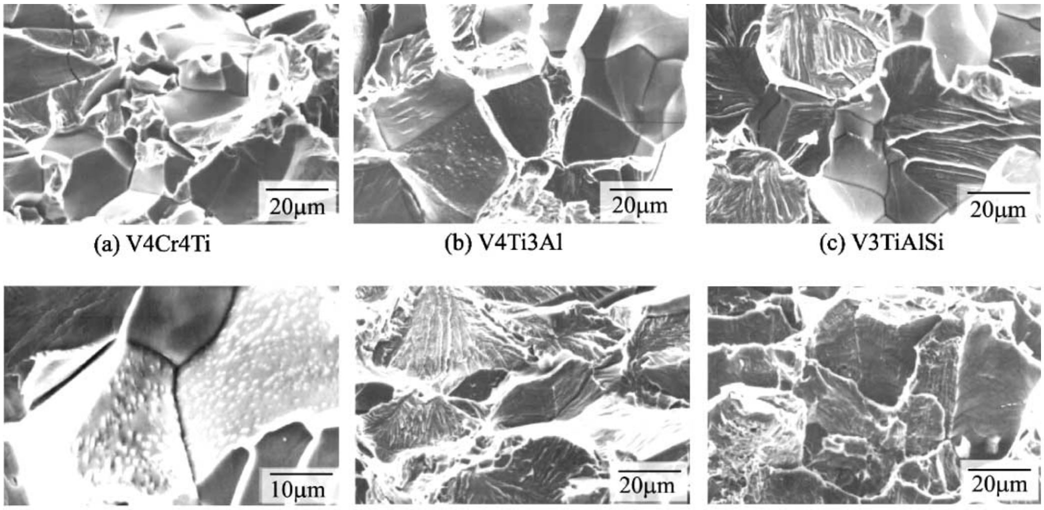


Fig. 4. The change of the yield and ultimate strength of V4Ti and V4Cr4Ti alloys with hydrogen concentration.



(a) V4Cr4Ti (b) V4Ti3Al (c) V3TiAlSi
(d) V4Ti3Al (e) V4TiSi (f) V4Ti

Fig. 5. SEM fractographs of the vanadium alloys. Hydrogen concentration: 50 wppm.

mainly determined by the grain boundary strength and thus showed a weak dependence on the hydrogen level. V4Ti and V4TiSi alloys were found to have many small cleavage planes (see Fig. 5(e) and (f)), indicative of more energy being exhausted during the fracture process.

4. Discussion

Alloying elements in vanadium alloys may affect the oxygen concentration level. The relatively lower oxygen concentration of the V4Ti3Al alloy shows that aluminum could prevent the alloy from absorbing too much oxygen from the atmosphere. On the other hand, as pointed out in [15], an alloying element in vanadium with higher affinity to oxygen, such as titanium, will significantly affect the solubility and distribution of oxygen in the alloy, and could also influence the effect of oxygen on mechanical properties. In comparison, aluminum has ever a stronger affinity to oxygen than titanium. Thus, oxygen in the V4Ti3Al alloy would be nearly totally absorbed by aluminum during the annealing heat treatment if the annealing time was long enough. So the matrix would have much lower oxygen concentration and the ductility of the alloy could remain high. The annealing time for the higher oxygen concentration V4Ti3Al was 1 h in this experiment, while that for the lower oxygen concentration V4Ti3Al (V4Ti3Al-1) was only 20 min. This may account for the higher total elongation of V4Ti3Al at the higher oxygen concentration.

The fact that the elongation decreases slowly with hydrogen concentration for V4Ti in Fig. 3 indicates that this alloy is less susceptible to hydrogen embrittlement than other alloys when their oxygen concentration is high. Consequently, the addition of Al, Si and Cr to V–4Ti with high oxygen concentration lowers its resistance against hydrogen embrittlement. It was found that both V4Ti and V4TiSi had a lower yield strength and smaller ratio of yield strength to ultimate tensile strength (see Table 2). This may partially account for their better resistance against hydrogen embrittlement since hydrogen increases the yield strength of the alloys and raises it closer to the ultimate tensile strength. Furthermore, as the V4Ti alloy fractured in transgranular cleavage, its grain boundary strength is higher than the grain strength. It must be the solid solution hardening from the hydrogen in the grains that causes the yield strength and the ultimate tensile strength of the alloy to increase almost in an equal rate with increasing hydrogen concentration. As a result, the V4Ti alloy kept a higher ductility than the other alloys at the same hydrogen concentration.

5. Conclusions

Some vanadium alloys were developed in China. The alloys were V4Cr4Ti, V4Ti, V4TiSi, V4Ti3Al and V3TiAlSi. Their mechanical performances were studied at different hydrogen concentration levels. The results showed a synergistic effect of hydrogen and oxygen.

(1) Both the yield strength and the ultimate tensile strength of the V–Ti alloy could be significantly increased by adding Al, Si and Cr to the alloy without changing the total elongation much. Furthermore, the addition of Al was proven to be not only helpful

to lower the oxygen concentration of the alloy but also to retain high ductility of the alloy even at high oxygen concentration levels. Its effect on the hydrogen embrittlement sensitivity seems to be associated with the oxygen concentration level in the alloy. When the oxygen concentration was low, it lowered the sensitivity.

(2) V4Ti and V4TiSi showed better properties against hydrogen embrittlement among the alloys because they had a smaller ratio of yield strength over ultimate tensile strength. The hydrogen seemed to cause solid solution hardening in the V4Ti but to weaken the grain boundaries in other alloys. The drastically decreasing ductility with the hydrogen content was caused by intergranular fracture for V4Cr4Ti, V4Ti3Al and V3TiAlSi alloys.

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