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Effects of oxygen and hydrogen at low pressure on the mechanical properties of V–Cr–Ti alloys ☆

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Abstract

Exposure of V–Cr–Ti alloys to low oxygen partial pressures at high temperature results in oxygen absorption and internal oxidation. Characterization of a V–4Cr–4Ti alloy after oxidation at 500°C revealed a microstructure with ultrafine oxide precipitates in the matrix and along grain boundaries. Heat treatment at 950°C following oxidation resulted in large TiO_x precipitates in the matrix and grain boundaries. Tensile ductility was reduced by exposure to low-pressure oxygen under the temperature and pressure conditions. However, heat treatment at 950°C following oxidation was generally effective in recovering ductility irrespective of initial annealing treatment or grain size. Without increases in oxygen, >500 wppm hydrogen was required to cause significant decreases in tensile elongation. When oxygen was added either during or prior to hydrogen exposure, significant embrittlement occurred with 100 wppm hydrogen. Because of this synergism with hydrogen, oxygen pick-up remains a major concern for V–Cr–Ti alloys in fusion reactor applications. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In the fusion neutron energy spectrum, hydrogen is produced as a transmutation product in vanadium, and deuterium and tritium are present as primary fuel components. Oxygen, on the other hand, is a ubiquitous component of air, vacuum, or inert gas environments. At temperatures of interest, vanadium alloys have a strong affinity for reaction with oxygen and hydrogen even at relatively low partial pressures of the gases.

Reactions of unalloyed vanadium with hydrogen and oxygen have been previously reported [1–5]. Embrittlement of vanadium in hydrogen environments can occur depending upon temperature, strain rate and impurity content of the metal. Hydrogen in vanadium increases the ductile-to-brittle transition temperature (DBTT) consistent with the temperature dependence of the hydrogen solvus line.

Oxygen has a significant solubility in vanadium (e.g., 1.1 wt% at 500°C) [6]. 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.

2. Experimental

Two alloys with the following nominal compositions were investigated: V–5Cr–5Ti and V–4Cr–4Ti (concentrations are in wt%). Two heats of V–5Cr–5Ti and one of V–4Cr–4Ti were tested, and the respective chemistries are shown in Table 1. Note that the heat made at ORNL

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Table 1
Compositions of V–Cr–Ti alloys

Nominal composition (wt%)	Heat ID	Concentration (wt%)			Concentration (wppm)			
		Cr	Ti	Fe	O	N	C	Si
V–5Cr–5Ti	ORNL	4.0	5.6	0.1	324	512	204	1100
V–5Cr–5Ti	832394	4.2	5.4	<0.045	427	52	40	<310
V–4Cr–4Ti	832665	3.1	4.1	0.022	310	85	86	780

contains a higher concentration of nitrogen and carbon than the other two heats. The alloys were tested in the form of small tensile specimens, nominally 0.76-mm thick with 1.5 × 7.6 mm^2-long gage sections, that were either machined or stamped from warm-reduced sheet stock. Prior to oxidation, specimens were annealed for 1 h in vacuum at temperatures from 1050°C to 1200°C to produce a recrystallized grain structure.

For exposure to low-pressure hydrogen or oxygen, the vanadium alloys were loaded in an ultra-high vacuum testing apparatus. Prior to introducing hydrogen or oxygen, the system was outgassed at 500°C until a vacuum of 10^{-6} Pa (10^{-8} Torr) was established. High-purity gas was admitted through a controllable leak valve while the system was being evacuated by a turbomolecular pump. Pressure of the specimen was determined from the pumping speed, conductance of the system, and pressure-gage measurements at the entrance and exit of the reaction tube. The amounts of gas picked up by the specimens were monitored by weight changes and by selective chemical analyses after the exposures. Despite the use of high-purity hydrogen (99.9999%) and an ultra-high vacuum containment system, concomitant oxygen contamination was a persistent problem during initial hydrogen exposures. Accordingly, the gas supply used for the hydrogen system was modified by addition of a hydrogen purifier that contained a palladium–silver alloy membrane to exclude oxygen and water vapor from the test environment.

3. Results and discussion

3.1. Hydrogen effects

Samples of the two V–5Cr–5Ti heats were exposed to hydrogen at 500°C at 10^{-2}–10 Pa (10^{-4}–10^{-1} Torr), generally for 24 or 100 h. At the end of the test, specimens were either left in the hydrogen atmosphere to cool to room temperature (slow-cooled, i.e. furnace-cooled at ~10°C/ min) or immediately pulled from the hot zone to an unheated region (fast-cooled, i.e. cooled at ~100°C/ min). As shown in Fig. 1, slow-cooled specimens showed significantly higher hydrogen concentrations than fast-cooled specimens. Hydrogen uptake by V–4Cr–4Ti was determined at 450°C and 10 Pa (~10^{-1} Torr) and between 25 and 250 Pa (0.2–2.5 Torr) at 325°C (Fig. 1). Excepting specimens slow-cooled from 500°C, data under these conditions fit calculated isotherms for unalloyed vanadium [7,8].

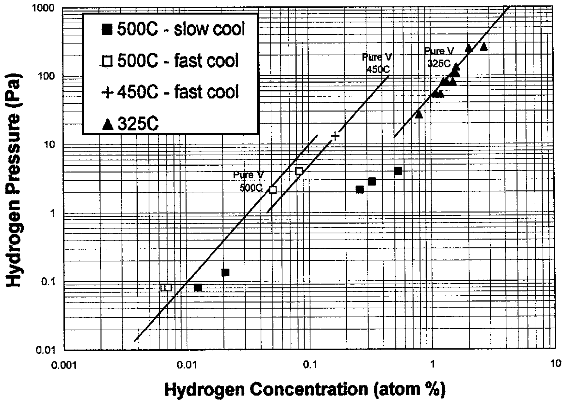

Fig. 1. Hydrogen concentrations in V–5Cr–5Ti and unalloyed vanadium [7,8] after exposure to low-pressure hydrogen at 500°C.

Hydrogen increased the room temperature yield stress and ultimate tensile strength of V–4Cr–4Ti while decreasing its total elongation [9]. Effects of hydrogen uptake on the room temperature ductility of V–4Cr–4Ti are shown in Fig. 2. When oxygen was excluded, hydrogen concentrations up to 400 wppm produced only a small reduction in ductility; however, above 500 wppm the ductility fell precipitously. Natesan and Soppet [10] also reported a significant decrease in the room temperature elongation of V–4Cr–4Ti in a sample with a hydrogen concentration of 358 wppm. Hydrogen significantly increases the DBTT of pure vanadium. Hahn et al. [11] attributed this increase to interstitial hardening of vanadium, that inhibits dislocation movements and reduces the resistance to crack propagation. Spitzig et al. [12], on the other hand, attributed the hydrogen effect to strengthening by equilibrium hydride precipitates, or stress-induced hydrides at a propagating crack tip. In the case of pure vanadium, the data cited pertain to hydrogen concentrations of 60 ppm or less, and the highest DBTT was well below room temperature. Accordingly, although the pure vanadium results may have

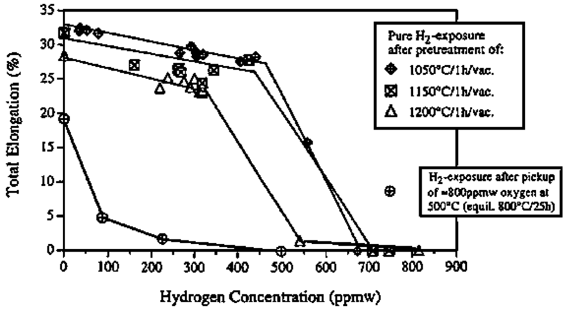

Fig. 2. Effect of hydrogen on the room temperature tensile ductility of V–4Cr–Ti.

relevance to the V–4Cr–4Ti results in terms of the hydrogen-embrittling mechanisms, they cannot be tied directly into our study of room temperature properties. However, given that 500 wppm hydrogen corresponds to the solubility threshold for hydride formation in pure vanadium below 80°C, hydride formation does offer a plausible explanation for the observed drop in room temperature ductility of V–4Cr–4Ti above 500 ppm.

3.2. Oxygen effects

Oxidation kinetics of V–4Cr–4Ti at 400°C and 500°C are shown in Fig. 3. Rates at 400°C were quite low at oxygen pressures of 10^{-2} and 10^{-3} Pa (10^{-4}–10^{-5} Torr). At 500°C, the rates were significantly higher, but they were essentially independent of pressure 10^{-2}–10^{-4} Pa (10^{-4}–10^{-6} Torr). Rates at 500°C parabolically decreased with time, indicative of a diffusion limited oxidation process.

Oxygen had little effect on the room temperature yield and tensile strengths of the V–Cr–Ti alloys up to a concentration of 3000 wppm. However, as shown in Figs. 4 and 5, the corresponding room temperature ductility was significantly reduced. Coarse grain material appeared to be more adversely affected by the same level of oxygen addition at 500°C than fine grain material [13]. Heat treating oxidized samples at 950°C after oxidation at 500°C resulted in a significant recovery of ductility (Fig. 4).

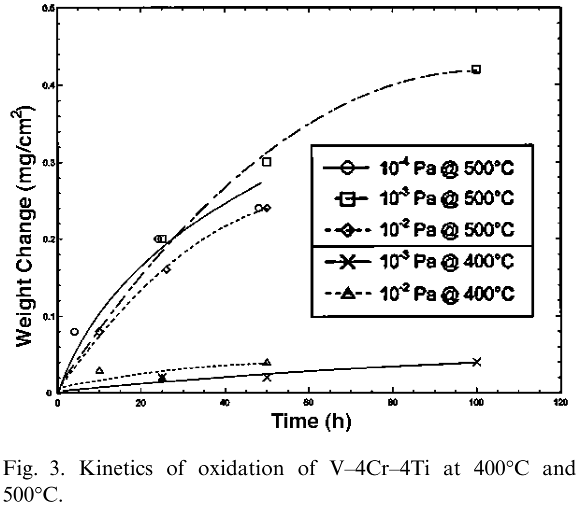

Fig. 3. Kinetics of oxidation of V–4Cr–4Ti at 400°C and 500°C.

After oxidation at 500°C and 10^{-4} Pa (10^{-6} Torr), selected samples were subsequently heat treated for 100 h at 600°C to homogenize the oxygen distribution, and the same samples were further heat treated for 4 h at 950°C. After heat treatment at 600°C, TEM characterization of an alloy with a ~1400 wppm oxygen addition revealed a uniform matrix microstructure with ultrafine oxide precipitates as shown in Fig. 6. At every grain

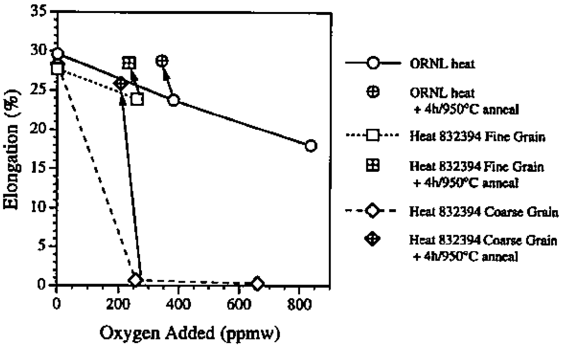

Fig. 4. Room temperature elongation of two nominal V–5Cr–5Ti alloys after oxidation at 10^{-4} Pa/500°C. Samples were heat treated for 100 h in vacuum at 500°C following oxidation.

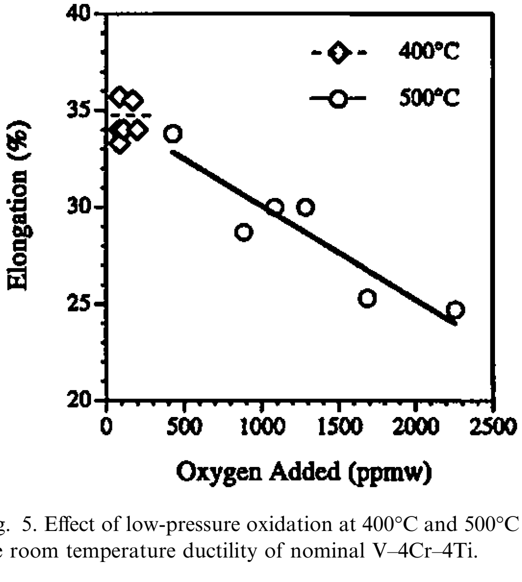

Fig. 5. Effect of low-pressure oxidation at 400°C and 500°C on the room temperature ductility of nominal V–4Cr–4Ti.

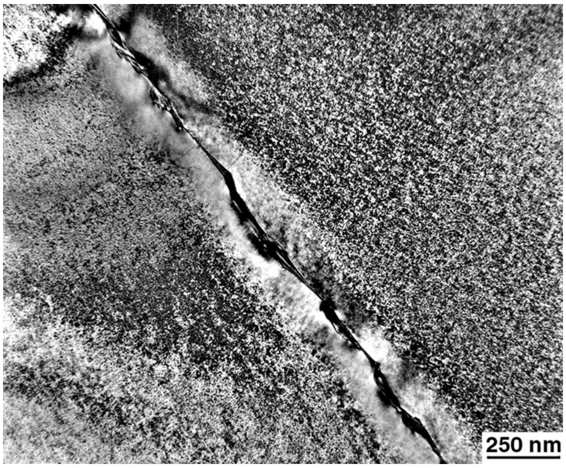

Fig. 6. TEM bright field image of V–4Cr–4Ti after the addition of ~1400 ppmw O at 500°C and annealing for 100 h at 600°C. Fine oxide precipitates are observed in the matrix and larger precipitates at the grain boundary which is surrounded by a precipitate-denuded zone.

boundary, there was a 100–200 nm denuded zone adjacent to the boundary and precipitates along the boundary. The composition of these precipitates has not been conclusively determined.

After a similar oxygen addition at 10^{-4} Pa and 500°C (1160 wppm oxygen) followed by annealing for 4 h at 950°C, the microstructure was remarkably different (Fig. 7). Large TiO_x precipitates were observed in the matrix and on the boundaries. The platelets followed established crystallographic patterns in the vanadium alloy. The denuded zone appeared to be retained adjacent to grain boundaries indicating that the fine precipitates present prior to annealing at 950°C grew significantly. The 950°C anneal improved room temperature ductility from near 0% to 15–20%. Without the anneal, the fracture was predominantly intergranular. Since grain boundary precipitates were observed before and after annealing, their presence does not appear to affect ductility. The denuded zone adjacent to the boundaries has been proposed to be an important factor in the failure [14].

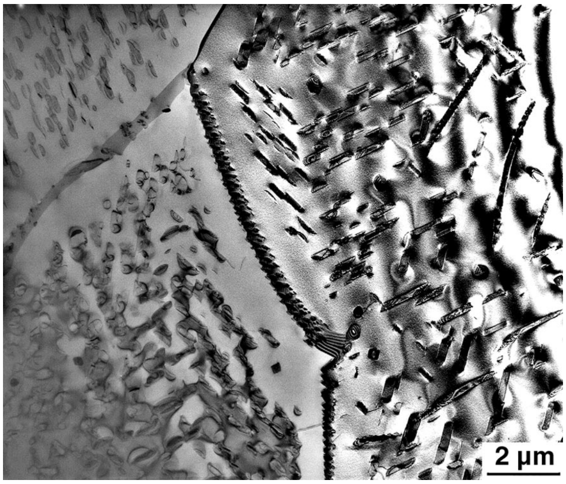

Fig. 7. TEM bright field image of a similarly exposed alloy as in Fig. 4 (~1200) ppmw O but including 4 h at 950°C anneal. In this case, large oxide precipitates are observed.

3.3. *Oxygen plus hydrogen*

Fig. 2 indicates that a controlled addition of 850 wppm of oxygen to V–4Cr–4Ti at 500°C drastically lowered the amount of hydrogen required to embrittle the alloy. Without the addition of oxygen, >500 wppm hydrogen was required before room temperature ductility decreased precipitously; however, 100 wppm hydrogen was sufficient to significantly embrittle the oxidized sample.

When vanadium alloys were deliberately or inadvertently oxidized at 500°C prior to or during hydrogen exposure, the resulting embrittlement, in terms of fracture appearance and response to remedial heat treatment, was similar to that of oxygen alone, but the degree of embrittlement at a given oxygen level was significantly enhanced. As with oxygen added singly (reported above), the ductility reductions were a function of grain size, being much greater in coarse-grained specimens.

4. Conclusions

Hydrogen in V–Cr–Ti alloy affects its room temperature tensile properties. In the absence of an increase in oxygen concentration, matrix hardening and a slight effect on total elongation were noted up to ~400 ppm (~2.2 at.%) hydrogen in the alloys. At higher concentrations, brittle behavior occurred.

At low oxygen partial pressures ($\leqslant 10^{-2}$ Pa), oxygen uptake at 400°C was below measurable limits after the first 10–25 h. At the low pressures, the rate of uptake at 500°C was parabolic and did not vary over the pressure range 10^{-2}–10^{-4} Pa. The primary effect of oxidation at 500°C on room temperature tensile properties was to reduce ductility. There was little or no effect on yield strength or ultimate tensile strength.

Oxygen pick-up remains as one of the major concerns in the use of V–Cr–Ti alloy for fusion reactor applications, particularly in the case of welds. Because of synergistic effects, the uptake of hydrogen isotopes during reactor operation will be an important factor in setting the permissible level of oxygen contamination.

Acknowledgements

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