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Oxygen embrittlement of vanadium alloys with and without surface oxide formation

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Abstract

Specimens of V–4Cr–4Ti have been exposed to low pressure oxygen and high purity He environments from 10^5 Pa down to 10^{-1} Pa in order to determine oxidation kinetics at 600–700 °C and effects on mechanical properties at 25 and 600 °C. At lower pressures ($p(O_2) \leqslant 10^{-5}$ Pa), linear reaction kinetics were measured for exposures up to 2000 h and the data was used to develop a mathematical expression for the oxidation rate as a function of temperature and oxygen pressure. At higher pressures, linear-parabolic reaction kinetics were measured associated with high oxygen uptake and the formation of an external oxide layer. Room-temperature and 600 °C tensile ductility was reduced by these exposures, but specimens which formed an external oxide retained some tensile ductility after exposure. However, similar specimens with an external oxide that were subsequently annealed for 2000 h at 700 °C were severely embrittled. These results suggest that a surface oxide on V–4Cr–4Ti can be a source of oxygen for further embrittlement and does not prevent embrittlement in extended exposures at 700 °C.

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1. Introduction

Vanadium alloys are being considered as a structural material in fusion reactors [1]. Some reactor designs involve vanadium alloys in high temperature environments such as vacuum or helium. These environments will contain some level of oxygen and hydrogen impurities that can react with vanadium-based alloys and cause degradation of their mechanical properties. Even a lithium-cooled design may have such an environment on the exterior side of the vanadium wall. Also, recent evaluations have suggested that the operating window for vanadium alloys is 400–700 °C as set by low temperature radiation embrittlement and thermal creep [2]. Thus, it is important to fully understand the effect these environments will have on the mechanical properties of vanadium alloys up to 700 °C so that appropriate operating conditions can be defined.

Refractory metal oxidation is often poorly understood because it is fundamentally different from the oxidation of more conventional Fe- and Ni-base alloys where oxidation resistance is predicated on the formation of a protective external oxide scale. Wagner's original work [3] on the conditions necessary for protective scale formation include an extremely important factor – a low solubility of oxygen in the metal. This issue is often overlooked because most Fe- and Ni-base alloys of interest for oxidation studies have a low oxygen solubility. However, for metals that have a high solubility for oxygen, like many refractory metals, this is a fundamental problem. In the case of a refractory metal like vanadium, the oxide needs to prevent solute embrittlement of the alloy in order to be considered protective. Furthermore, all refractory metals do not perform similarly when exposed to an oxygen-containing environment because there are differences in the volatility of the oxidation product and the oxygen solubilities.

Previous work on environmental effects on vanadium have considered lower temperatures and oxygen pressures from 10^{-4} to 10^5 Pa (1 atm) [4–8]. The present

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work includes lower pressures (10^{-5}–10^{-6} Pa) and higher temperatures (600–700 °C) in an attempt to provide data obtained under conditions closer to what has been proposed. Also, testing was performed in high-purity He to simulate a He-cooled system. At these higher temperatures, the oxidation behavior is strongly affected by the oxygen pressure. At the lowest oxygen pressures ($\leqslant 10^{-5}$ Pa), linear kinetics was observed.

2. Experimental procedure

All of the experiments were conducted on V–4%Cr–4%Ti (Heat#832665). (Compositions are given in weight percent except for volume percent in gas phase.) Prior to exposure, the specimens were vacuum annealed for 1 h at 1050 °C to produce a 20–30 μm diameter grain size. Specimens were 0.76 mm thick tensile specimens (type SS-3). Low pressure exposures were conducted in an ultra high vacuum system in which a base vacuum of 10^{-7} Pa (10^{-9} Torr) could be achieved. A leak valve was used to achieve oxygen partial pressures of 10^{-3}–10^{-6} Pa (10^{-5}–10^{-8} Torr). For testing in helium at 76 000 Pa (1 atm), the pumping system was closed after pressurization and excess gas pressure was removed through an oil bubbler. To achieve He partial pressures of 76 or 7.6 Pa, a micrometering valve was used with a mechanical pumping system. The oxygen content was determined by weighing the samples before and after exposure. A power law was then used to fit the data at each pressure and temperature:

$$\Delta M = kt^{1/n}, \tag{1}$$

where M is mass, k and n are constants and t is time. For linear reaction kinetics, $n = 1$ and for parabolic, $n = 2$. Mechanical properties were measured in tension tests at room temperature, 25 and 600 °C. Specimens were tested with a crosshead speed of 0.051 cm/min. Uniform and total elongation and the yield and ultimate strengths were measured.

3. Results and discussion

3.1. Reaction kinetics 600–700 °C

The oxidation rate of V–4Cr–4Ti was measured at oxygen pressures in vacuum from 10^{-3}–10^{-5} Pa at 600 °C and from 10^{-3}–10^{-6} Pa at 700 °C. Rather than trying to force fit linear or parabolic kinetics the data were plotted on a log–log plot in Fig. 1 where examples of linear ($n = 1$) and parabolic ($n = 2$) kinetics are included. From this type of plot, n values can be calculated for each condition, Table 1. In general, the results showed near linear behavior at 10^{-4}–10^{-5} Pa at 600 °C and at 10^{-6} Pa at 700 °C. At higher pressures at both temperatures, greater deviations from linearity were observed up to $n = 1.63$. However, values of $n = 2$ (parabolic kinetics) were not observed as has been previously assumed [7,8]. The linear-parabolic behavior at 10^{-3} Pa was attributed to the formation of a surface oxide which then inhibited oxygen uptake into the substrate. Under these conditions, specimen surfaces became discolored as mass gains exceeded 0.5–2%. However, at lower pressures, the specimen surfaces remained shiny and no surface oxide was observed. In a previous study at oxygen pressures of $<10^{-4}$ Pa [7], a surface oxide was observed which may explain the different observations.

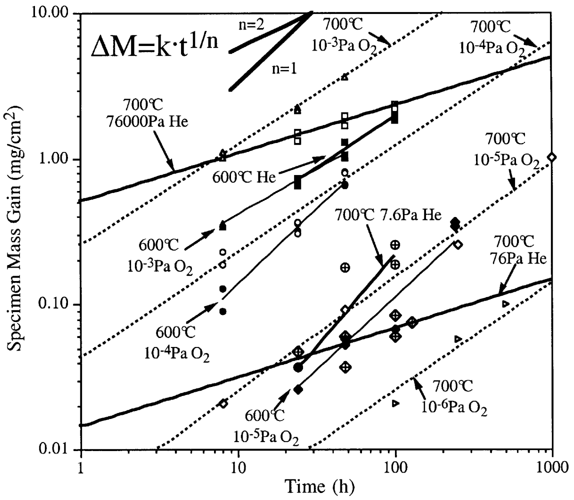

Fig. 1. Log–log plot of the mass gains for V–4Cr–4Ti at 600 °C (closed symbols-solid lines) and 700 °C (open symbols-dashed lines) at oxygen pressures of 10^{-3}–10^{-6} Pa and in He at 700 °C (bold lines). At lower oxygen pressures, the data fit a linear relationship ($n = 1$) whereas at higher pressures the value of n increased.

In order to compare the various results in this study, a linear rate was fitted where appropriate, Table 1. At 10^{-4}–10^{-6} Pa, the change in oxidation rates was proportional to the oxygen partial pressure. However, comparing the rates at 10^{-3} and 10^{-4} Pa, the rates were less than an order of magnitude different and thus did not scale with the oxygen pressure. The linear pressure relation appears to be most applicable for high temperature/low pressure oxidation where a significant surface film does not form.

Mass gain results from tests at 600 and 700 °C in He at 76 000 Pa (1 atm) also are shown in Fig. 1 and summarized in Table 1. Data from tests in pure He (<0.1 vppm oxygen) had n values of 1.39 at 600 and 3.02 at 700 °C. The deviation from linear behavior at 600 °C was similar to that observed with an oxygen pressure of 10^{-3} Pa. The high mass gains in 76 000 Pa He are not

Table 1
Oxidation data for V–4Cr–4Ti at low pressure and in high purity helium (research grade He with <0.1 vppm oxygen)

Temperature (°C)	Pressure (Pa)	Mass gain rate, average normalized to 10^{-3} (Pa)	Power law fit (n)	Fitted linear rate (mg/cm^2 h)
Oxygen				
600	10^{-3}	1	1.63	
	10^{-4}	0.4	0.98	1.4×10^{-2}
	10^{-5}	0.04	1.00	1.5×10^{-3}
700	10^{-3}	1	1.44	
	10^{-4}	0.19	1.38	1.6×10^{-2}
	10^{-5}	0.016	1.28	9.5×10^{-4}
	10^{-6}	0.002	1.02	2×10^{-4}
Helium				
600	7.6×10^4 He	0.97	1.39	1.6×10^{-2}
700	7.6×10^4 He	0.67	3.02	
700	76 He	0.021	2.95	
700	7.6 He	0.017	0.80	2.4×10^{-3}

surprising because, even with high purity ($\approx$1 vppm O_2) He, the oxygen partial pressure would be $\approx 10^{-1}$ Pa. In a He-cooled fusion reactor, the total He pressure would be significantly higher but, with purification, the O_2 pressure possibly could be lower. In order to simulate that environment, the He pressure was dropped to levels of 76 and 7.6 Pa in an attempt to achieve oxygen pressures of $\approx 10^{-4}$ and 10^{-5} Pa, respectively. The mass gain results for tests at each pressure are shown in Fig. 1 (bold fitted lines) and summarized in Table 1. At 7.6 Pa He, the data fell near the previous results for 10^{-5} Pa O_2 which corresponds very well to the predicted oxygen level in the gas. The n value was 0.8. At 76 Pa He, the mass gain values were lower and n was 3.0, identical to the value at 76 000 Pa He. The specimens exposed to 76 Pa He had a slight tarnish suggesting that at the higher pressure there may have been oxide film formation which inhibited oxygen uptake. The change in rate also could be due to a change in the rate of oxygen adsorption due to the higher He pressure.

3.2. Oxidation model

It is clear from the experimental results that no single mathematical relationship likely describes the oxidation rate over the entire range of temperature and pressures of interest. However, if it is assumed that the data generated thus far for the lower oxygen pressures at 600–700 °C fit an equation of the form:

$$r = k \cdot p(O_2), \tag{2}$$

and

$$k = k_0 e^{-Q/RT}, \tag{3}$$

where r is the oxidation rate in mg/cm^2 h, k_0 the constant, R the gas constant, $p(O_2) = O_2$ partial pressure in Pa, Q the activation energy and T the temperature in Kelvin. Then a fit of the data at low oxygen pressures yields:

$$r = 4.7 \times 10^2 e^{-821/T} p(O_2). \tag{4}$$

This equation can be used to calculate the approximate oxidation rate of V–4Cr–4Ti at 600–700 °C for partial pressures of oxygen in vacuum between 10^{-4} and 10^{-6} Pa. These levels correspond approximately to residual oxygen pressures for vacuum levels between 10^{-1} and 10^{-3} Pa. This equation would not apply to lower temperatures where previous work indicated that at 500 °C, the oxidation rate was independent of pressure at 10^{-2}–10^{-4} Pa ($\simeq 4 \times 10^{-3}$ mg/cm^2 h) [4]. It also would not apply to higher oxygen pressures including exposures to 76 000 Pa He with 1 vppm O_2. However, under these conditions, the mass gains are high and the material is embrittled after short exposures. Of more technological importance are the low oxygen pressures where longer times show a relatively low oxygen uptake and the material retains some ductility. Under these conditions, the oxidation reaction tends to follow the linear kinetics model.

Based on the relationship in Eq. (4), if a vanadium alloy specimen needed to maintain an oxygen level below 0.1 mg/cm^2 after 25 000 h in order to retain a room temperature tensile ductility >10%, the oxygen pressure would need to be $< 2 \times 10^{-8}$ Pa. For a He cooled system operating at 10 bar, that oxygen pressure suggests an oxygen content of <1 part per *trillion* in the gas. However, that calculation assumes that the high density of He in the environment would not alter the rate of oxygen absorption. Previous work on Nb–1Zr reported a reduced oxygen uptake rate in He due to a 'shielding' effect [9]. The model rates also are based on one specimen thickness (0.76 mm) and geometry, i.e. surface area to volume ratio. The effect of these factors on the predicted rates needs to be further investigated.

3.3. Mechanical properties

As previously reported [4], sub-size sheet tensile specimens (SS-3) of unoxidized, annealed V–4Cr–4Ti have a room temperature elongation of ≃30% and a yield strength of 350 MPa, but oxygen uptake can significantly lower the ductility and slightly increase the strength. The room temperature and 600 °C tensile properties were measured as a function of oxygen pick-up by the V–4Cr–4Ti specimen. Selected values are shown in Table 2 and more results are available in a summary report [10]. Tests were completed on the specimens exposed at 10^{-3} and 10^{-4} Pa at 600 and 700 °C with and without a post-oxidation anneal for 4 h at 950 °C. Previous work at 400–500 °C had shown that a 950 °C anneal could restore some lost ductility [4]. In general, specimens with $\leqslant 1000$ ppm O showed improved ductility when annealed at 950 °C, Fig. 2. However, most of the 10^{-3} Pa exposures at both temperatures resulted in much higher mass gains which led to severe embrittlement that was not improved by the 950 °C anneal. In most cases, the anneal reduced the ductility further, Fig. 2 This negative effect is attributed to the higher temperature anneal allowing the diffusion of oxygen throughout the specimen. For example, the oxygen uptake (1991 ppm) after 8 h at 600 °C in 10^{-3} Pa was likely concentrated at the specimen surface, leaving a less-affected ductile core and resulting in a total elongation of 12%. When a similarly exposed specimen (1856 ppm O) was annealed at 950 °C, thus allowing more oxygen diffusion throughout the specimen cross-section, its ductility dropped to 4.3%.

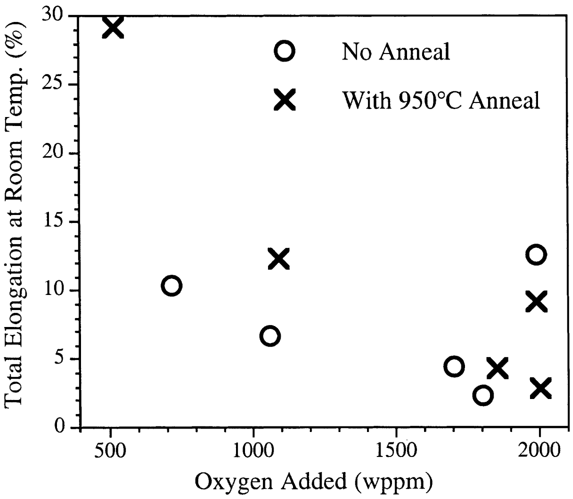

Fig. 2. Room temperature total elongation for V–4Cr–4Ti with and without a 4 h, 950 °C anneal with various levels of added oxygen.

Post-oxidation tensile data at room temperature and 600 °C are reported in Table 2 for specimens exposed to 10^{-5} and 10^{-6} Pa oxygen or 76 000 Pa He at 600 and 700 °C. Although pre-oxidation elongation at 600 °C was

Table 2
Mechanical properties at 25 and 600 °C of V–4Cr–4Ti after exposure

Temperature (°C)	Pressure (Pa)	Time (h)	Oxygen content (wppm)	Surface oxide	Yield strength (MPa)	Ultimate strength (MPa)	Uniform elongation (%)	Total elongation (%)
No anneal					*Properties at 25 °C*			
700	10^{-6}	100	117		407	486	14	25
		100	291		375	415	15	29
	10^{-5}	48	408		406	499	14	24
		250	1353		430	543	3	7
		257	1347		427	472	4	11
600	10^5 (He)	48 ☆	5805	Visible	387	457	8	10
Annealed for 2000 h at 700 °C					*Properties at 25 °C*			
600	10^5 (He)	100 ☆	3827	Visible[a]	Broke on loading			
700	10^5 (He)	24	8282	Visible[a]	Broke on loading			
		100	11 836	Visible[a]		422	0	
No anneal					*Properties at 600 °C*			
	No exposure				272	394	9	15
700	10^{-6}	500	323		248	388	13	21
	10^{-5}	48	606		307	424	9	16
	10^{-5}	257	1433		319	440	2	5
600	10^5 (He)	48	5937	Visible	298	371	5	6

[a] After annealing, the surface oxide was no longer visible.

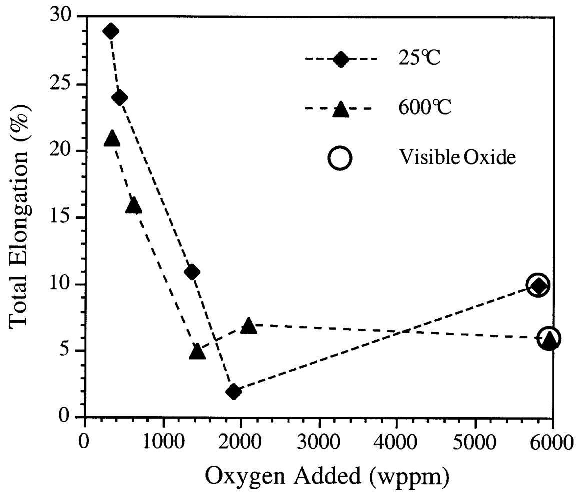

Fig. 3. Total elongation for V–4Cr–4Ti measured at 25 and 600 °C as a function of oxygen added. At the highest oxygen levels, a surface oxide was observed and no further drop in ductility was measured. These specimens were not annealed after oxidation.

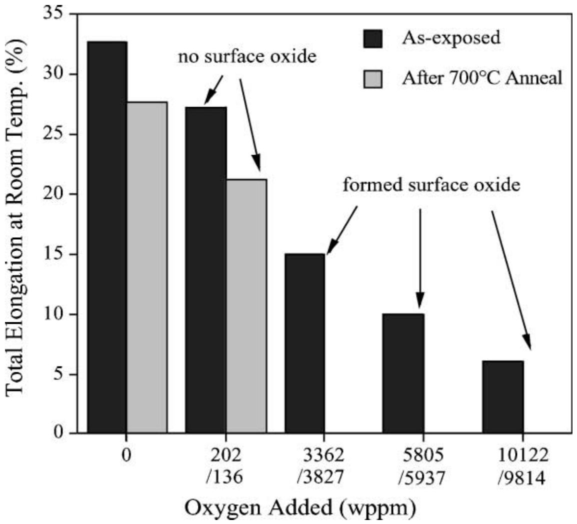

Fig. 4. Total elongation at room temperature as a function of added oxygen with and without annealing for 2000 h at 700 °C. Specimens which formed a surface oxide and were annealed (3827, 5937 and 9814 ppm O) were severely embrittled and had zero ductility.

initially lower than at room temperature (9–15%), values as low as 2–5% uniform elongation were obtained after oxidation. At both test temperatures, the total elongation dropped with increasing oxygen added up to $\approx$2000 ppm, Fig. 3. However, specimens with a surface oxide retained significant ductility ($\sim$10% total elongation at 25 °C) for total mass gains up to $\simeq$6000 ppm O, whereas samples with no visible surface oxide had little ductility ($\simeq$2% total elongation) after mass increases of $\simeq$2000 ppm O, Fig. 3.

The results in Fig. 3 appear to indicate that the formation of a surface oxide protects the alloy from further embrittlement. However, because the solubility of oxygen in vanadium is relatively high, the oxide may not initially contribute to tensile embrittlement but, over time, it could be a source of oxygen for further internal oxidation to occur. One way to determine if the surface oxide is protective is to anneal the sample for an extended period. If the surface film is truly protective the specimen should retain its ductility after continued exposure at high temperature. For example, a sample exposed to He picked up 5805 ppm O (marked by star in Table 2), and contained a visible surface oxide. When tensile tested at room temperature, total elongation was 10% at room temperature. Another sample with 3827 ppm O (marked by star in Table 2) also had a visible surface oxide; but it was subsequently heat treated for 2000 h at 700 °C in static argon. After this heat treatment there was no longer a visible surface oxide but the sample had such low ductility that it failed on loading during the tensile test. This result and another for a sample with 8382 ppm indicated that the formation of a surface oxide does not represent a long-term protective state for V–4Cr–4Ti. To confirm this hypothesis, a series of specimens were oxidized to create a range of added oxygen levels up to $\simeq$1%. The higher oxygen levels were achieved by exposure at 600 °C in 76 000 Pa He where a surface oxide was formed. Half of the specimens were fractured after exposure and the other half were annealed in a He-filled quartz ampule for 2000 h at 700 °C. Fig. 4 shows the room temperature ductility results for this set of specimens. As a control, a specimen with no added oxygen and one with a low level of added oxygen (136 ppm) also were annealed in the same ampule for 2000 h at 700 °C. Compared to the unannealed results, the specimens with little or no added oxygen showed only a small loss in ductility after annealing. However, the ductility of those specimens which had an external oxide before annealing was reduced to zero, Fig. 4, and the specimen surface changed to a dull metallic color. During prolonged high temperature exposure even in the absence of further oxidation, the presence of a surface oxide provided a source for oxygen which embrittled the underlying substrate.

4. Summary

Oxidation kinetics of V–4Cr–4Ti in vacuum with low oxygen pressures, 10^{-3}–10^{-6} Pa (10^{-8}–10^{-11} bar), and in high-purity helium at 600–700 °C were determined. After exposure, mechanical properties were measured at 25 and 600 °C. Oxidation at 600–700 °C generally produced linear kinetics when the oxygen pressure was $\leqslant 10^{-5}$ Pa including exposures in 7.6 Pa He. A general linear relationship also was observed with respect to oxygen pressure in vacuum. Higher oxygen partial pressures (including higher He pressures) can result in external film formation and linear-parabolic or even sub-parabolic kinetics. Oxygen uptake resulting in oxygen concentrations >2000 ppm generally led to significant tensile embrittlement. Higher total oxygen levels could be tolerated (without significant embrittlement) in cases where an external oxide layer formed. However, when specimens which formed an external layer were given an additional vacuum anneal for 2000 h at 700 °C, embrittlement occurred. This indicates that, rather than being protective, surface oxides on vanadium are a source of oxygen for further internal oxidation and thus embrittlement. Given the system purity requirements, it appears unlikely that a vanadium alloy would have sufficient environmental resistance to be used in a high pressure He environment.

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