

Effect of Oxidation on Tensile Properties of a V-5Cr-5Ti Alloy*

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Abstract

Oxidation studies were conducted on V-5Cr-5Ti alloy specimens at 500°C in an air environment to evaluate the alloy's oxygen uptake behavior as a function of temperature and exposure time. Oxidation rates, calculated from measurements of thermogravimetric testing, are 5, 17, and 27 μm after a 1-yr exposure at 300, 400, and 500°C, respectively. Uniaxial tensile tests were conducted on preoxidized specimens of the alloy to examine the effects of oxidation and oxygen migration on tensile strength and ductility. Microstructural characteristics of several of the tested specimens were characterized by electron-optical techniques. Correlations have been developed between the tensile strength and ductility of the oxidized alloy and microstructural characteristics such as oxide thickness, depth of hardened layer, depth of intergranular fracture zone, and transverse crack length.

Introduction

Refractory alloys in general, and V alloys in particular, are susceptible to pickup of interstitials such as oxygen, carbon, and nitrogen, which can affect the short- and long-term mechanical properties of the materials. The vanadium alloy with composition V-5Cr-5Ti contains 5 wt.% Ti (a much more stable oxide-former than V and Cr), which can have an even stronger effect on mechanical properties, especially tensile and creep ductility. The degree of influence of interstitial oxygen on the alloy's properties will be dictated by alloy grain size, (the amount of grain-boundary area), amount and distribution of oxygen in the alloy, amount and size of second-phase oxide precipitates (such as Ti oxide), service temperature and time of exposure. This study examines the role of oxygen and oxidation rate on tensile properties of the alloy.

Experimental Procedure

The vanadium alloy heat selected for the study had a nominal composition of V-5 wt.%Cr -5 wt.%Ti and was designated as BL-63. Actual composition of the alloy is given in Table 1. A sheet of the alloy was annealed for 1 h at 1050°C prior to its use in oxidation and tensile testing; coupon specimens measuring $\approx 15 \times 7.5 \times 1$ mm were used for the oxidation studies. Oxidation experiments were conducted in air in a thermogravimetric test apparatus. Test temperatures ranged from 300 to 650°C.

Tensile specimens were fabricated according to ASTM specifications and had a gauge length of ≈ 19 mm and a gauge width of ≈ 4.5 mm. Grain size of the specimens was ≈ 32 μm . The specimens were preoxidized in air at 500°C for 24, 250, 600, 1000, and 2060 h prior to tensile testing in air at 500°C. As-annealed specimens were tensile tested on an Instron machine at constant crosshead speeds of 0.0005 to 0.2 cm/min, which correspond to initial strain rates of 4.3×10^{-6} to 1.8×10^{-3} s^{-1} . The preoxidized specimens were tested at a strain rate of 1.75×10^{-4} s^{-1} . All tests were performed in air at 500°C $\pm 2^\circ\text{C}$.

The specimens were loaded by pins that pass through holes in the enlarged end sections, thus minimizing misalignment. Total elongation was measured by vernier calipers on the tested specimens and load/elongation chart records. The fracture surfaces and longitudinal- and axial- cross sections of tested specimens were examined by scanning electron microscopy (SEM) and optical metallography. In addition, Vickers hardness measurements were made on several of the tested specimens. Coupon specimens of the alloy that were oxidized along with the tensile specimens were analyzed for their bulk oxygen content by the vacuum-fusion technique.

Table 1. Composition of V-5Cr-5Ti alloy*

Cr	Ti	Si	Al	B	C	H	N	Nb	O	P	S	V
4.4	5.1	300	200	<5	75	4	25	<50	420	<30	305	Bal**

* Cr, Ti, and V concentrations are in wt.%; all others are in wppm.

** Bal = balance.

Results and Discussion

Oxidation Behavior. Figure 1 shows weight-change data for the alloy oxidized in air at several temperatures. The oxidation kinetics followed a parabolic relationship with time. Detailed SEM analysis of the oxidized samples showed that the outer layer was predominantly vanadium-rich oxide and the inner layer was (V,Ti) oxide. A parabolic rate equation was used to calculate oxide scale thicknesses, which were in agreement with the values determined by metallography. Figure 2 shows the scale thicknesses (calculated on the basis of parabolic kinetics) for a 1-yr exposure in air as a function of temperature in the range 300-575°C. Scale thicknesses are 5, 10, 17, and 27 μm after a 1-yr exposure in air at 300, 400, 450, and 500°C, respectively. Even though the oxide thicknesses are low at these temperatures, the alloy also exhibits an oxygen-enriched region ahead of the oxide scale, and this can lead to hardening and possible embrittlement of the alloy. Figure 3 shows the Vickers hardness profiles of the specimens exposed to air for different times at 500°C. Oxide scale thickness is ≈ 10 μm , but hardness increase is noted to a depth as great as 120 μm , indicating an oxygen-enriched zone ahead of the oxide scale. Detailed analysis of this oxygen-enriched zone is currently in progress.

Baseline Tensile Properties. The engineering stress/engineering strain curves were obtained from the load-elongation data using the initial cross-sectional area of the specimen. Figure 4 shows the stress/strain curves for the as-annealed specimens tested at different strain rates. Negligible effect of strain rate is seen on the yielding phenomenon and on yield stress at 500°C. The tensile ductility of the alloy was 0.21-0.24 over the strain rates of this study. The maximum engineering stress increased with a decrease in strain rate, as shown in Fig. 5. Maximum engineering stress was ≈ 460 and 392 MPa at strain rates of 4.3×10^{-6} and $1.8 \times 10^{-3} \text{ s}^{-1}$, respectively. The variation in maximum engineering stress with strain rate can be described by the relation

$$\text{UTS(MPa)} = 319 - 24.4 \log \dot{\epsilon},$$

where UTS is ultimate tensile strength in MPa, and $\dot{\epsilon}$ is strain rate.

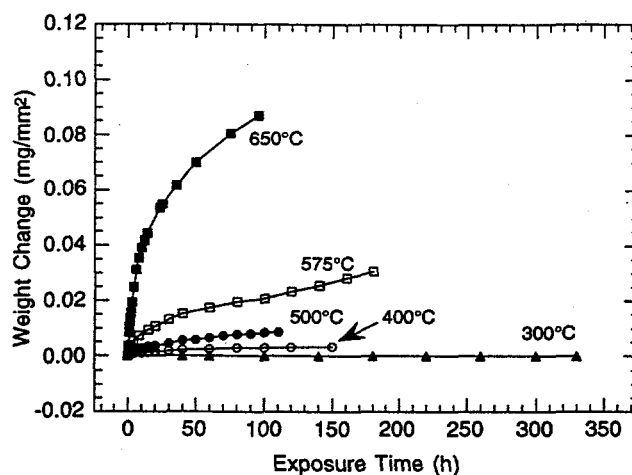


Figure 1. Weight change data for oxidation of V-5Cr-5Ti alloy in air at several test temperatures.

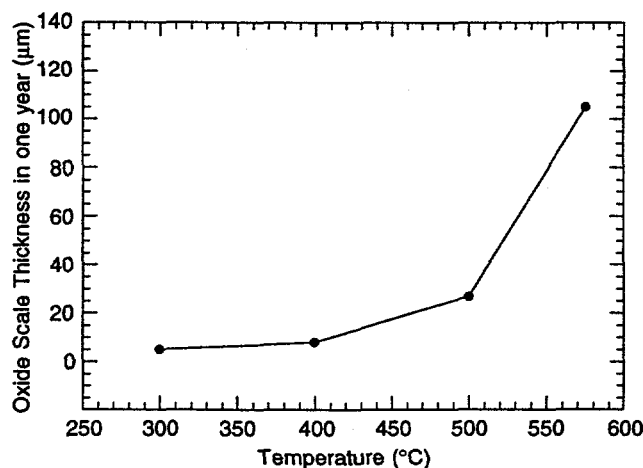


Figure 2. Scale thicknesses on V-5Cr-5Ti alloy in air as a function of exposure temperature.

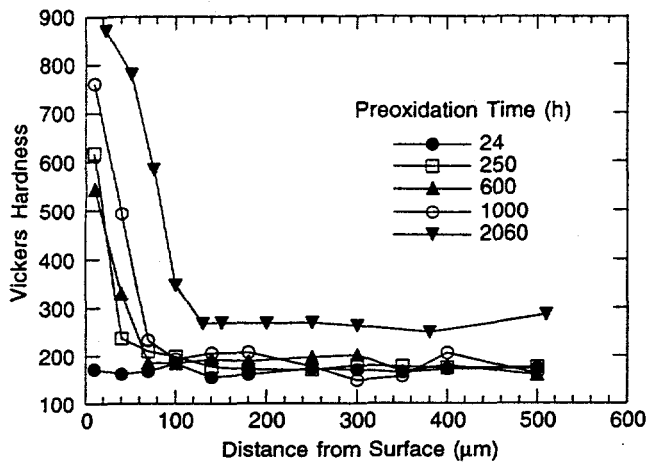


Figure 3. Vickers hardness data for specimens of V-5Cr-5Ti alloy oxidized at 500°C in air for different times.

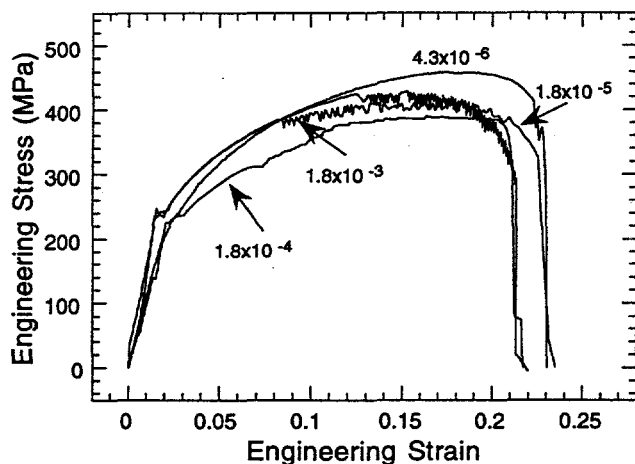


Figure 4. Stress/strain behavior of V-5Cr-5Ti alloy tested at 500°C in air at several different strain rates

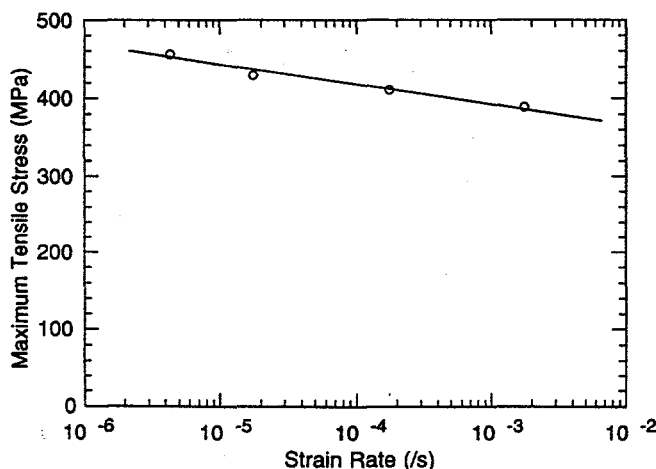


Figure 5. Maximum tensile stress as a function of strain rate for specimens of V-5Cr-5Ti alloy tested at 500°C in air.

Effect of Oxidation on Tensile Properties. To evaluate the effect of oxidation and oxide penetration into the substrate alloy, several tests were conducted to examine the tensile behavior of the alloy as a function of oxygen ingress and oxide scale formation. Tensile specimens were exposed to air for 24-2060 h in air at 500°C and then tensile tested in air at the same temperature. Most of the tests were conducted at a strain rate of $1.8 \times 10^{-4} \text{ s}^{-1}$.

Figure 6 shows the engineering stress/engineering strain curves for specimens after oxidation for several exposure times in the range 0-2060 h. The data indicate that stress/strain behavior of the alloy is virtually unaffected by a 24-h exposure in air at 500°C. As exposure time increases to 250 h, alloy strength increases, but there is some loss in tensile ductility. In the exposure period of 250-1000 h, the alloy essentially has the same ultimate tensile strength but shows reductions in tensile ductility from 0.21 at 24 h exposure to 0.14 at 1000 h exposure. Further exposure of the alloy to air at 500°C results in loss of strength and tensile ductility, as evidenced by the stress/strain curve for the specimen preoxidized for 2060 h. Figures 7 and 8 show variations in maximum engineering stress and rupture strain as a function of preoxidation time in air at 500°C. Figure 9 shows the variation in area under the stress/strain curve as a function of rupture strain for as-annealed and preoxidized alloy at 500°C. The area can be represented by an expression

$$\text{Area} = -4.22 + 369\varepsilon,$$

where ε is rupture strain.

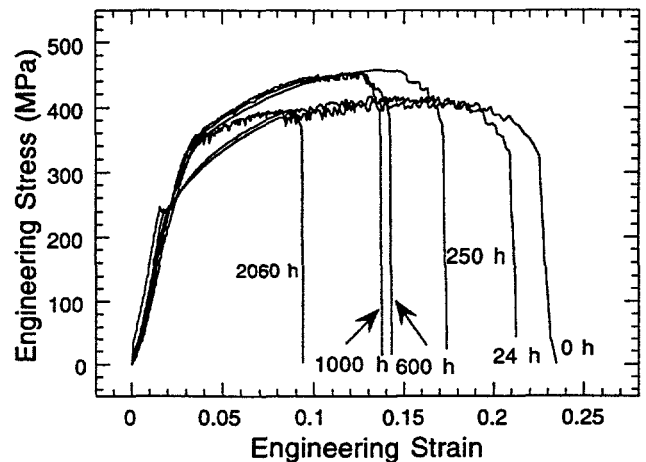


Figure 6. Effect of preoxidation at 500°C on stress/strain behavior of V-5Cr-5Ti alloy tested at 500°C in air at a strain rate of $1.75 \times 10^{-4} \text{ s}^{-1}$.

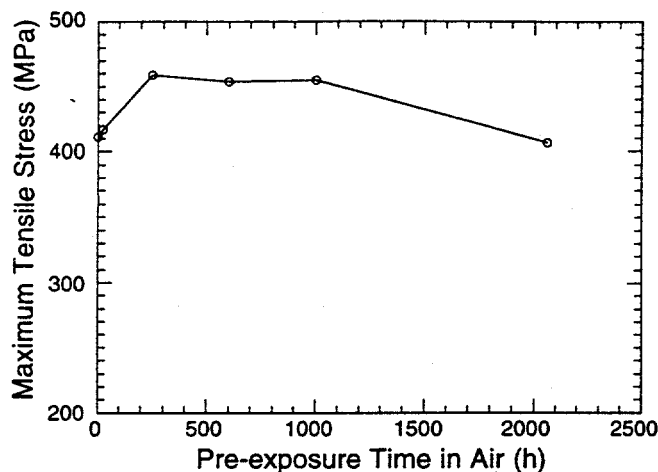


Figure 7. Maximum tensile stress as a function of pre-exposure time in air for specimens of V-5Cr-5Ti alloy tested at 500°C in air.

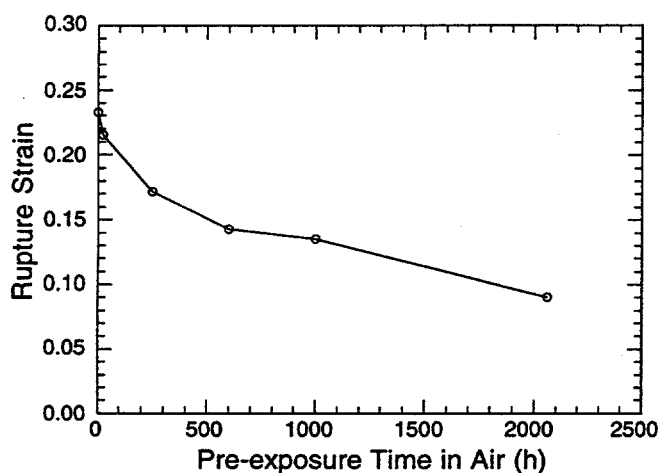


Figure 8. Rupture strain as a function of pre-exposure time in air for specimens of V-5Cr-5Ti alloy tested at 500°C in air.

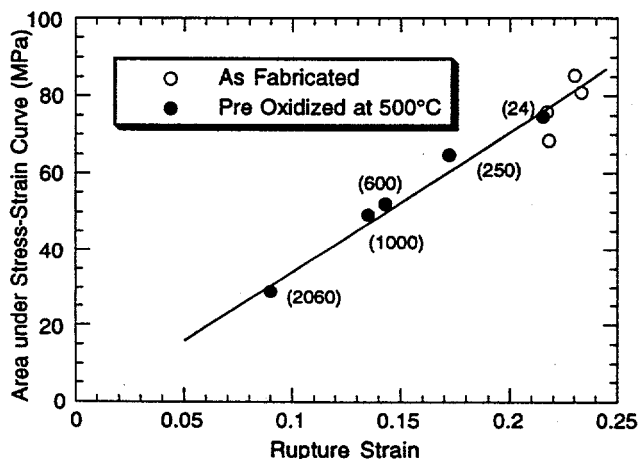


Figure 9. Correlation between area under stress/strain curve and rupture strain for specimens tested in air at 500°C. Numbers in parentheses indicate specimen pre-exposure time in air at 500°C.

Microstructural Observations. Axial cross sections of several of the tested specimens were examined by SEM. Figure 10 shows sections of specimen tested in as-annealed condition and after oxidation for 24, 250, 1000, and 2060 h in air at 500°C. Depths of cracks in the transverse direction increase as oxidation time increases. Further, crack spacing in the axial direction increases as oxidation time is increased. As the oxidation time continues to increase, the alloy undergoes only slight necking during the tensile test. It is evident, especially from the 1000 and 2060 h exposed specimens, that fracture occurred by the propagation of one of these axial cracks and that because the core of the alloy is somewhat ductile, the crack propagation direction in the core region is at $\approx 45^\circ$.

Figure 11 shows SEM photomicrographs of fracture surfaces of specimens tested in as-annealed condition and after oxidation for several time periods. The fracture mode was predominantly ductile in the as-annealed specimen. The specimen exposed for 24 h to air at 500°C showed a layer of grain-boundary or cleavage morphology to a depth of $\approx 25 \mu\text{m}$, beyond which a ductile fracture mode was observed. With increases in oxidation time, the zone of intergranular fracture increased; for the 2060-h oxidized specimen, the depth of this zone was $165 \mu\text{m}$.

Table 2 lists the calculated and measured thicknesses of oxide layers, depths of hardened layers (from Vickers hardness measurements), thicknesses of intergranular fracture zone, and transverse crack lengths for as-annealed/preoxidized specimens and tensile tested at 500°C. The data show that the oxide layer thickness is fairly small even after 2060 h of exposure to air at 500°C. However, oxygen diffusion into the substrate alloy and its enrichment in the surface regions of the specimens alter the fracture mode from ductile to cleavage. Further, the thicknesses of the zone of intergranular fracture is in agreement with the crack lengths measured in the transverse direction. The difference in the intergranular fracture zone thickness and crack length can be attributed to a subsurface oxygen-enriched layer that is not fully brittle. The results also indicate that there is a threshold oxygen concentration in the alloy for embrittlement to ensue, and this aspect is presently being investigated.

Figure 12 shows variations in hardened layer, intergranular fracture zone thickness, and transverse crack length as a function of oxidation time; tensile rupture strain values are also shown. Results to date indicate that the alloy is not subject to catastrophic embrittlement due to oxygen ingress into the material. Additional exposures as a function of oxygen partial pressure in the exposure environment, as well as tensile tests at lower temperatures, are in progress to establish the performance envelope for the alloy in an oxygenated environment.

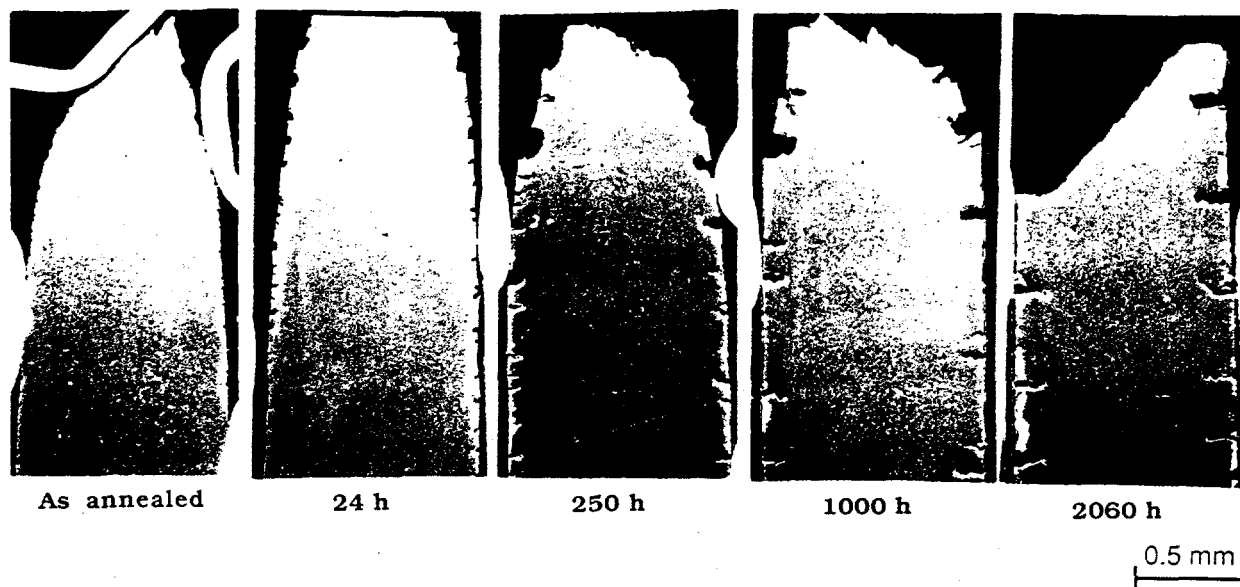


Figure 10. Scanning electron photomicrographs of axial sections of V-5Cr-5Ti specimens tensile tested in as-annealed condition and after oxidation in air at 500°C for several exposure times

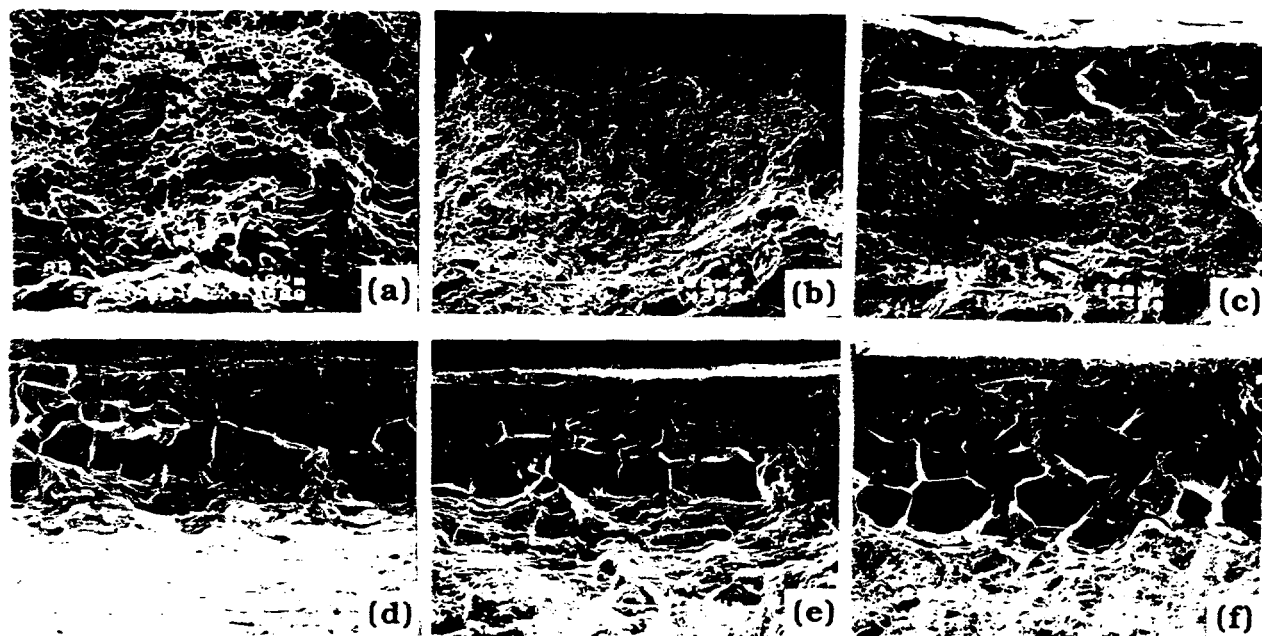


Figure 11. Scanning electron photomicrographs of fracture surfaces of V-5Cr-5Ti specimens tensile tested (a) in as-annealed condition and after oxidation in air at 500°C for (b) 24 h, (c) 250 h, (d) 600 h, (e) 1000 h, and (f) 2060 h.

Table 2. Oxidation, hardness, and fracture data for V-5Cr-5Ti alloy at 500°C

Exposure time (h)	Calculated oxide thickness (μm)	Measured oxide thickness (μm)	Depth of hardened layer (μm)	Thickness of intergranular fracture zone (μm)	Measured crack length (μm)	Rupture strain
0	0	0	0	0	10	0.233
24	1.4	1.2	<25	25	22	0.215
250	4.6	5.0	45	65	50	0.172
600	7.1	7.1	68	100	90	0.143
1000	9.1	9.0	80	120	110	0.135
2060	13.1	14.0	120	165	160	0.090

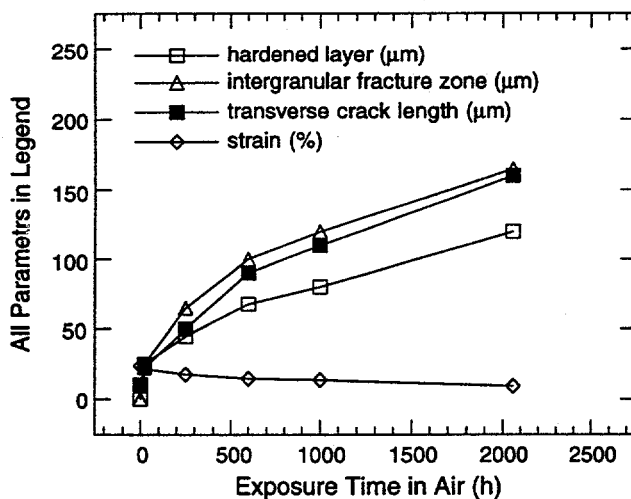


Figure 12. Variation in hardened-layer thickness, intergranular fracture zone depth, transverse crack length, and rupture strain as a function of exposure time at 500°C for V-5Cr-5Ti alloy.

Summary

Oxidation studies were conducted on V-5Cr-5Ti alloy specimens at 500°C in an air environment. The oxidation process followed a parabolic rate law. The oxide scale exhibited a dual layer, with the outer layer predominantly of V oxide and the inner layer of (V,Ti) oxide. Tensile specimens were preoxidized for 24-2060 h in air at 500°C and subsequently tensile tested under the same conditions. Effects of oxidation on the stress/strain behavior of the alloy are then evaluated. The fracture and cracking propensity of the alloy to oxidation are analyzed and correlated with hardness, fracture morphology, and rupture strain.

Acknowledgments

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