

OXIDATION BEHAVIOR OF V-Cr-Ti ALLOYS IN LOW-PARTIAL-PRESSURE OXYGEN ENVIRONMENTS*

K. Natesan and M. Uz (Argonne National Laboratory)

OBJECTIVE

The objectives of this task are to (a) quantify the oxygen partial pressure (pO_2) in argon and helium environments of various different purity levels, (b) determine the oxygen uptake of V-Cr-Ti alloys as a function of temperature and pO_2 in the exposure environment, (c) examine the microstructural characteristics of oxide scales and oxygen trapped at the grain boundaries in the substrate alloys, and (d) establish performance relationships between exposure time, exposure temperature, and oxygen concentration in the alloy for application in fusion reactor systems.

SUMMARY

A test program is in progress at Argonne National Laboratory to evaluate the effect of pO_2 in the exposure environment on oxygen uptake, scaling kinetics, and scale microstructure in V-Cr-Ti alloys. The data indicate that the oxidation process follows parabolic kinetics in all of the environments used in the present study. From the weight change data, parabolic rate constants were evaluated as a function of temperature and exposure environment. The temperature dependence of the parabolic rate constants was described by an Arrhenius relationship. Activation energy for the oxidation process was fairly constant in the oxygen pressure range of 1×10^{-6} to 1×10^{-1} torr for both the alloys. The activation energy for oxidation in air was significantly lower than in low- pO_2 environments, and for oxidation in pure O_2 at 760 torr was much lower than in low- pO_2 environments. X-ray diffraction analysis of the specimens showed that VO_2 was the dominant phase in low- pO_2 environments, while V_2O_5 was dominant in air and in pure oxygen at 760 torr.

EXPERIMENTAL PROGRAM

The heats of vanadium alloy selected for the study had nominal compositions of V-5 wt.%Cr-5 wt.%Ti (designated BL-63) and V-4 wt.%Cr-4 wt.%Ti (designated BL-71). Sheets of the alloys were annealed for 1 h at 1050°C prior to oxidation and tensile testing. Coupon specimens that measured $\approx 15 \times 7.5 \times 1$ mm were used for the oxidation studies. Our earlier work on oxidation of these alloys was conducted in air in a thermogravimetric test apparatus at temperatures of 300 to 650°C [1-4]. During this period, several oxidation experiments were conducted on V-4Cr-4Ti (identified as 44) and V-5Cr-5Ti (identified as 55) alloys at oxygen partial pressures in the range 1×10^{-6} to 1×10^{-1} torr at several temperatures in the range of 400 - 700°C . Specimens were exposed to these environments in a reaction chamber with an O_2 bleed/feed system to maintain the desired oxygen pressure. Specimens were retrieved periodically and weighed, and dimensions were measured. The oxidation products were examined by X-ray diffraction (XRD) analysis, and the scale microstructures were evaluated by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis. In addition, microhardness was measured on cross sections of exposed specimens to obtain hardness profiles and correlate them with oxygen concentration in the alloys.

RESULTS AND DISCUSSION

Extensive studies were conducted on the oxidation kinetics of 44 and 55 alloys in air over a temperature range of 300 - 650°C ; the results were reported earlier [1-4]. The current oxidation study on the two alloys involves exposure of the alloys to low- pO_2 environments. Tables 1 and 2 list the experimental variables such as pO_2 in the exposure environment and test temperature used in several of the experiments for the 44 and 55 alloys, respectively. Figure 1 shows normalized weight changes (in mg/mm^2) for 44 and 55 alloys after exposure at 500°C in several low- pO_2 environments. Similar data were obtained at other temperatures listed in Tables 1 and 2.

Table 1. Oxidation parameters of V-4Cr-4Ti alloy at various oxygen pressures

Oxygen pressure (torr)	Temperature (°C)	k_p ($\text{mg}^2\text{mm}^{-4}\text{h}^{-1}$)	k_o ($\text{mg}^2\text{mm}^{-4}\text{h}^{-1}$)	Q (kJ/mol)
5×10^{-6}	500	1.6×10^{-7}	8.6×10^4	174
	600	3.1×10^{-6}		
	700	4.1×10^{-5}		
5×10^{-4}	500	1.3×10^{-7}	3.9×10^5	185
	600	3.2×10^{-6}		
	700	4.7×10^{-5}		
1×10^{-1}	500	4.0×10^{-8}	9.9×10^5	199
	600	1.7×10^{-6}		
	700	2.2×10^{-5}		
160 (air)	400	1.4×10^{-7}	2.2×10^2	120
	500	1.1×10^{-6}		
	575	1.2×10^{-5}		
	620	2.5×10^{-5}		
760	450	2.6×10^{-8}	1.5×10^9	231
	525	1.6×10^{-6}		
	600	1.9×10^{-5}		

Table 2. Oxidation parameters of V-5Cr-5Ti alloy at various oxygen pressures

Oxygen Pressure (torr)	Temperature (°C)	k_p ($\text{mg}^2\text{mm}^{-4}\text{h}^{-1}$)	k_o ($\text{mg}^2\text{mm}^{-4}\text{h}^{-1}$)	Q (kJ/mol)
5×10^{-6}	500	1.3×10^{-7}	1.4×10^4	168
	600	2.1×10^{-7}		
	700	3.4×10^{-5}		
5×10^{-4}	500	1.1×10^{-7}	8.8×10^4	177
	600	2.3×10^{-6}		
	700	3.0×10^{-5}		
1×10^{-1}	500	3.6×10^{-8}	4.8×10^5	195
	600	9.4×10^{-7}		
	700	1.8×10^{-5}		
160 (air)	400	8.9×10^{-8}	2.3×10^3	137
	500	7.1×10^{-7}		
	575	4.6×10^{-6}		
	650	9.0×10^{-5}		
760	450	1.8×10^{-8}	1.5×10^{10}	247
	525	1.7×10^{-6}		
	600	2.0×10^{-5}		

The weight change data were correlated with time by the parabolic relationship $w^2 = k_p t$, where w is weight change, t is exposure time, and k_p is a parabolic rate constant. The k_p values calculated for various exposure conditions are also listed in Tables 1 and 2. Figure 2 shows the temperature dependence of the parabolic rate constant for the two alloys exposed to different oxygen pressures. The temperature dependence of the parabolic rate constant was described by the

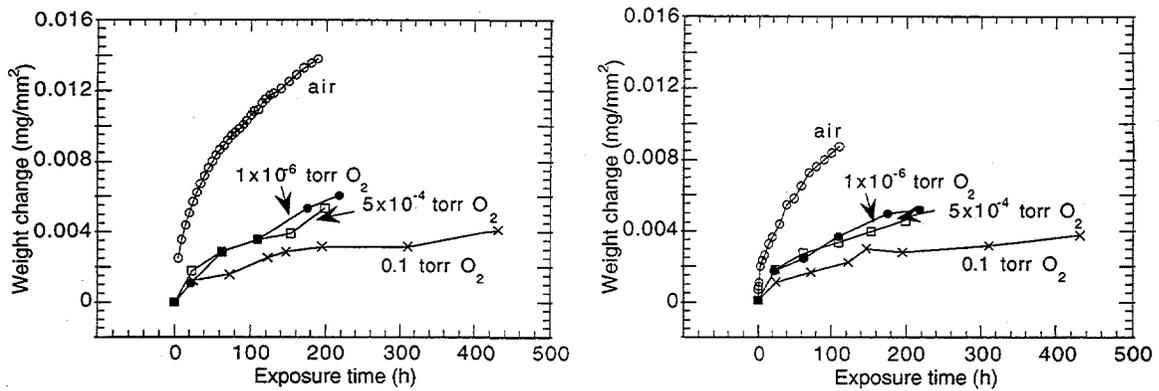


Fig. 1. Thermogravimetric weight change data for 44 (left) and 55 (right) alloys after exposure in low- p_{O_2} and air environments at 500°C.

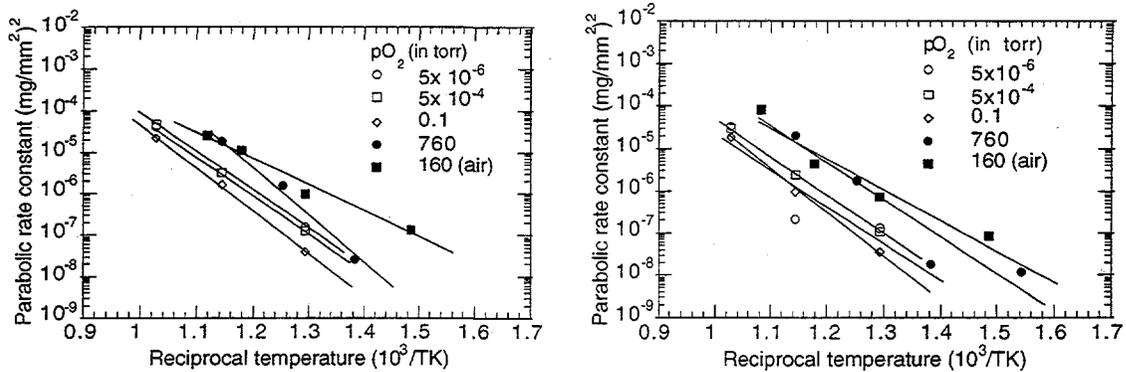


Fig. 2. Temperature dependence of parabolic rate constant for oxygen uptake of 44 (left) and 55 (right) alloys in several low- p_{O_2} and air environments.

relationship $k_p = k_0 \exp[-Q/(RT)]$, where k_0 is a preexponential term, Q is the activation energy for the oxidation process, R is a gas constant, and T is absolute temperature. The values for k_0 and Q , calculated from the best fit of the experimental data at various oxygen pressures, are also listed in Tables 1 and 2. The results show that the activation energy for the oxidation process is fairly constant at oxygen pressures in the range 10^{-6} to 10^{-1} torr. The activation energy calculated from data in the air tests was significantly lower, and in pure oxygen-tests (at 760 torr) was substantially higher than the values obtained at low- p_{O_2} conditions. It is not clear at present whether the type of scale (predominantly V_2O_5) that forms in air and in pure O_2 is the cause for this difference.

Table 3 lists the XRD data obtained on several specimens exposed to various oxygen pressures. The oxide VO_2 was the predominant phase that formed in both alloys when exposed to oxygen pressures in the range 10^{-6} to 10^{-1} torr. V_2O_5 was the primary phase in specimens exposed to air and to pure oxygen at 760 torr. Detailed microstructural evaluation of the specimens, especially those exposed to low- p_{O_2} environments, is in progress to characterize the role of p_{O_2} variation on the morphology of the scales and substrate penetration of oxygen.

REFERENCES

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Table 3. Phases identified^a in V-4Cr-4Ti and V-5Cr-5Ti alloys by X-ray diffraction^b analysis

Oxygen pressure (Torr)	Temperature (°C)	Phases identified in alloy	
		V-4Cr-4Ti	V-5Cr-5Ti
5 x 10 ⁻⁶	500	VO ₂ , TiV ₄ O ₁₀	VO ₂ , V ₂ O ₄
	700	VO ₂ , V ₁₆ O ₃ , CrV ₂ O ₆	V ₂ O ₅ , V ₅ O ₉ , V ₁₆ O ₃
5 X 10 ⁻⁴	600	VO ₂ , V ₂ O ₄ , CrVO ₄	VO ₂ , V ₂ O ₄ , CrVO ₄
	700	VO ₂ , V ₂ O ₄ , CrVO ₄	VO ₂ , V ₂ O ₄ , CrVO ₄
0.1	600	VO ₂ , V ₂ O ₄	VO ₂ , V ₂ O ₄ , CrVO ₄
	700	VO ₂ , V ₂ O ₄ , CrVO ₄	VO ₂ , V ₂ O ₄ , CrVO ₄
760	375	V ₂ O ₅ , V ₂ O ₃ , V ₃ O ₇	V ₂ O ₅ , VO ₂ , V ₂ O ₄
	600	V ₂ O ₅ , V ₂ Ti ₃ O ₉ , VO ₂	V ₂ O ₅ , VO ₂

^aPhases identified in all samples oxidized in air (pO₂ = 160 torr) were primarily V₂O₅.

^bX-ray diffraction unit was run at 1 degree/min.

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