

CHEMICAL AND MECHANICAL INTERACTIONS OF INTERSTITIALS WITH VANADIUM ALLOYS-J. R. DiStefano, L. D. Chitwood and J. H. DeVan*, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6157

OBJECTIVE

Liquid lithium contained by a vanadium alloy structure is the favored concept for an advanced breeding blanket for certain fusion reactor concepts. The objective of this task is to determine the kinetics of reactions of vanadium alloys with hydrogen and oxygen as a function of alloy composition and microstructure, and to determine their effects on mechanical properties.

SUMMARY

Oxidation studies of V-4Cr-4Ti were conducted in air and reduced oxygen partial pressures (10^{-4} , 10^{-5} and 10^{-6} Torr). Reaction rates were determined by weight change measurements and chemical analyses. Mechanical properties after the exposures were determined by room temperature tensile tests.

In air at 400 and 500°C, oxide films form on the surface. Initially, rates are high but decrease with time reaching similar values to those found in oxygen partial pressures of 10^{-4} , 10^{-5} and 10^{-6} Torr. At 400°C, oxygen pick-up followed a logarithmic function of time and was confined to regions near the surface. Little change in room temperature tensile properties were noted for oxygen increases up to 1500 ppm. Thermal cycling specimens from 400°C to room temperature up to 14 times had no apparent effect on oxidation rate or tensile properties. At 500°C, oxygen pick-up appeared to follow a parabolic relation with time. Rates were ~10 times those at 400°C and correspondingly larger oxygen increases occurred when compared with the 400°C tests after similar time periods. This resulted in a significant decrease in total elongation after 240 h.

At reduced oxygen partial pressures, rates were measured for times ≤ 100 h. Data are relatively sparse but generally show a slightly higher initial rate before slowing down. At 400°C increases to ~200 ppm oxygen were found with no effect on room temperature elongation. At 500°C increases in oxygen of ~2400 ppm after 50 h/ 10^{-5} Torr resulted in a decrease of around 25% in room temperature elongation. By comparison, exposure to air at 500°C for 12 h caused nearly the same results.

Results and Discussion

Air The oxidation of V-4Cr-4Ti has been studied in air at 400 and 500°C. As was previously done with V-5Cr-5Ti, we are continuing to use small tensile specimens (SS-3), nominally 0.76 mm thick with 1.5 mm x 7.6 mm gage sections that were stamped from sheet.

Cyclic oxidation behavior of annealed material (1050°C) was determined by repeatedly heating samples to 400°C for 24 h and then cooling to room temperature (1 cycle). Weight changes and room temperature tensile properties after exposure for 1 - 14 cycles (24 - 337 h) are shown in Table 1. The weight change data best fit a logarithmic time dependence:

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$$\Delta W (\text{mg/cm}^2) = 1.1 \times 10^{-1} \log t (\text{h}) - 5.27 \times 10^{-2},$$

an indication that chemisorption of oxygen or electric-field-induced transport of electrons or ions across the oxide film may be rate limiting. The weight change data in Table 1 show considerable scatter; therefore, in a separate experiment, a single specimen was given 9 cycles in air while its weight was continuously monitored in a microbalance system. In this case a slightly different logarithmic function fit the data:

$$\Delta W (\text{mg/cm}^2) = 0.8 \times 10^{-1} \log t (\text{h}) - 3.3 \times 10^{-2},$$

Table 1. Results of Cyclic Oxidation of V-4Cr-4Ti at 400°C in Air

Spec. No.	Time (h)	Cycles	Weight Change mg/cm ²	Rate mg/cm ² /h	Room Temp. Tensile		
					Y.S. (MPa)	U.T.S. (MPa)	Elong. (%)
WE-43	24	1	.085	3.5×10^{-3}	363	449	30.8
WE-44	48	2	.135	2.8×10^{-3}	350	441	31
WE-45	72	3	.165	2.3×10^{-3}	347	446	31
WE-46	96	4	.215	2.2×10^{-3}	352	441	28.8
WE-47	120	5	.205	1.7×10^{-3}	350	445	30.7
WE-48	144	6	.185	1.3×10^{-3}	354	445	29.5
WE-49	169	7	.160	9.5×10^{-4}	339	438	32
WE-50	193	8	.265	1.4×10^{-3}	359	458	28.6
WE-51	217	9	.205	9.5×10^{-4}	357	451	29.3
WE-52	265	11	.190	7.2×10^{-4}	368	467	26.8
WE-53	289	12	.190	6.6×10^{-4}	357	452	26.0
WE-54	313	13	.200	6.4×10^{-4}	356	452	28.8
WE-55	337	14	.280	8.3×10^{-4}	361	452	28.7
WE-58	577	None	.270	4.7×10^{-4}	358	458	27.8

Even though oxygen increases up to 1500 ppm occurred, room temperature tensile properties were essentially unchanged by the exposures to air at 400°C. Total elongation averaged 29.3% with a standard deviation of only 1.7%. An oxide scale was observed on the surface to a thickness of $< 2 \mu\text{m}$ (0.1 mil). The specimens also showed a hardness increase immediately below the scale, an indication of internal oxidation. However, the depth of the increase was limited to $\sim 10 \mu\text{m}$, further confirmation that bulk properties should not have been affected.

The non-cyclic oxidation of V-4Cr-4Ti was measured in air at 500°C for times to 240 h as shown in Table 2. Based on a parabolic rate law, the parabolic rate constant was found to be 4.8×10^{-3} ($\text{mg}^2/\text{cm}^4 \text{ h}$). At this temperature, oxygen increases were higher than at 400°C reaching 6080 ppm after 240 h. Room temperature elongation decreased with increasing oxygen pick-up and was 8.9% after 240 h.

Table 2. Results of Oxidation of V-4Cr-4Ti at 500°C in Air

	Time (h)	Temp. (°C)	ΔW (ppm)	Y.S. (MPa)	U.T.S. (MPa)	Elong. (%)	Rate $\text{mg}/\text{cm}^2/\text{h}$
Air	12	500	2118	374	469	24.8	3.1×10^{-2}
Air	48	500	2871	402	504	18.1	1.1×10^{-2}
Air	72	500	3796	392	483	13.1	9.4×10^{-3}
Air	95	500	4373	381	477	15.3	8.2×10^{-3}
Air	240	500	6080	382	456	8.9	4.5×10^{-3}

Reduced Oxygen Pressure The oxidation of V-4Cr-4Ti was also measured at 400 and 500°C at reduced oxygen pressures of 10^{-4} and 10^{-5} Torr. Results are summarized in Table 3. If we compare oxidation rates under these conditions with those previously measured in air or at $P_{\text{O}_2} = 1 \times 10^{-6}$ Torr, discussed below (Table 4), it is interesting to note that after long times there is little difference. In air an oxide film forms on the specimen at both 400 and 500°C, although it is significantly thicker at 500°C. Overall the oxidation rate in air at 500°C was about a factor of 10 higher than at 400°C. However, the rate during the first 120 h of exposure at 400°C was about the same as during the last 135 h at 500°C. In low pressure oxygen, oxide films are not visually or microscopically apparent and the rates of oxygen uptake do not change dramatically with time. Although the limited data at reduced pressures do not yet allow reporting a rate law dependence, the data at 500°C at 10^{-4} and 10^{-5} Torr are not inconsistent with parabolic behavior, which indicates a thermal diffusion process. Since the rate in air is initially much higher, than after longer times, it appears that formation and growth of the oxide film is a factor. However, it is not readily apparent why long-term rates in air are essentially the same as those at reduced pressures where measurable oxide films do not form.

In other experiments, V-4Cr-4Ti was exposed to oxygen at 1×10^{-6} Torr at either 400 or 500°C, without and without a pre-oxidation in air at the same temperature, respectively. Results are summarized in Table 5.

Based on weight changes at 10^{-6} Torr and 500°C, pre-oxidation in air at 500°C appeared to prevent further oxidation during the subsequent low-pressure exposure for times to 100 h. Furthermore, total elongation was slightly higher with pre-oxidation than without.

At 400°C, pre-oxidation in air at 400°C was not as effective, probably because the oxide film formed during the air exposure was very thin or was not continuous after 24 h. Even so, as had been the case at 500°C, no serious loss in ductility was observed.

Table 3. Oxidation of V-4Cr-4Ti at Low Oxygen Partial Pressures

Sample No.	Conditions	Wt. Change (mg)	Rate mg/cm ² /h	Y.S. (MPa)	U.T.S. (MPa)	Elong. %
1 x 10 ⁻⁴ Torr O ₂ /400°C						
WE69	10h	.06	3.1 x 10 ⁻³	358	441	35.5
70	25h	.04	8.4 x 10 ⁻⁴	350	444	34.0
71	50h	.07	7.4 x 10 ⁻⁴	359	458	34.0
1 x 10 ⁻⁵ Torr O ₂ /400°C						
WE72	25	.03	6.3 x 10 ⁻⁴	353	436	34.0
73	50	.03	3.2 x 10 ⁻⁴	355	445	35.7
74	100	.07	3.7 x 10 ⁻⁴	359	452	33.3
1 x 10 ⁻⁴ Torr O ₂ /500°C						
WE75	10	.15	7.9 x 10 ⁻³	348	451	33.8
76	26	.31	6.3 x 10 ⁻³	364	470	28.7
77	50	.45	4.7 x 10 ⁻³	366	480	30.0
1 x 10 ⁻⁵ Torr O ₂ /500°C						
WE34	25	.38	8 x 10 ⁻³	343	454	30.0
35	50	.59	6.2 x 10 ⁻³	337	455	25.3
36	100	.79	4.2 x 10 ⁻³	344	458	24.7

Table 4. Oxidation Rates of V-4Cr-4Ti

PO ₂ Torr	Rate (mg/cm ² /h)	
	400°C	500°C
Air	5-35 x 10 ⁻⁴	5-30 x 10 ⁻³
1 x 10 ⁻⁴	7-32 x 10 ⁻⁴	5-8 x 10 ⁻³
1 x 10 ⁻⁵	3-6 x 10 ⁻⁴	4-8 x 10 ⁻³
1 x 10 ⁻⁶	7 x 10 ⁻⁴	3-8 x 10 ⁻³

Table 5. Effects of Pre-Oxidation in Air

Pre-Oxidation		Oxidation				Room Temperature Tensile Properties ^a		
Pre-Oxidation Treatment	Weight Change (ppm)	Oxygen Pressure (Torr)	Time (h)	Temp. (°C)	Weight Change (ppm) (mg/cm ² /h)	Y.S. (MPa)	U.T.S. (MPa)	Total Elong. (%)
None	—	1 x 10 ⁻⁶	48	500	1375 .005	353	449	21.5
24h/500°C	2106	1 x 10 ⁻⁶	48	500	-29 -.0001	366	460	23.8
12h/500°C	2118	—	—	—	—	374 ^b	469 ^b	24.8 ^b
12h/500°C	2210	1 x 10 ⁻⁶	48	500	-86 -.0003	358	451	23.3
24h/400°C	467	—	—	—	—	359	476	25
24h/400°C	311	1 x 10 ⁻⁶	48	400	198 .0007	363	482	21.1

a. Samples heat treated 100h/500°C in vacuum following oxidation except where noted.

b. Sample not heat treated following pre-oxidation.

Work in Progress

Experiments to determine the oxidation of the reference V-4Cr-4Ti alloy at low oxygen partial pressures are continuing to develop rate equations for the uptake of oxygen as a function of temperature and oxygen pressure. Samples from these experiments are also being used to evaluate the effect of oxygen uptake on the mechanical properties of the alloy. Large-grained material may be more susceptible to embrittlement by oxygen and, therefore, the effect of grain size is also being studied.