OXIDATION OF V-4Cr-4Ti AT LOW PRESSURES -- B. A. Pint, J. R. DiStefano, J. Bentley and L.D. Chitwood (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to assess the high temperature oxidation behavior of V-4Cr-4Ti in low oxygen pressure environments and any related effect on mechanical properties. Many reactor designs involve vanadium alloys in high temperature environments such as vacuum or helium which will contain some level of oxygen and hydrogen impurities. Testing is being conducted in vacuum with low oxygen pressures, 10^{-3}-10^{-6}Pa (10^{-5}-10^{-8}Torr), and in high-purity helium at 400-700°C. Recent emphasis has been on determining kinetics of oxidation at 600-700°C.

SUMMARY

To complement previous work on V-4Cr-4Ti at 400-500°C,[1] similar oxidation experiments were conducted at 600-700°C. In general, the rates were linear with time. However, at higher oxygen pressures, e.g. 10^{-3}Pa (10^{-5}Torr), specimen surfaces became slightly discolored indicating the formation of a surface oxide and rates were linear-parabolic. The addition of more than 1000ppm oxygen resulted in a significant loss of room temperature ductility. Annealing at 950°C was effective in improving ductility at oxygen levels below 1500ppm. With higher oxygen levels, the anneal was ineffective or further reduced ductility. High resolution analytical electron microscopy was used to examine the oxidized V-4Cr-4Ti microstructure before and after annealing at 950°C. Low ductility before annealing is attributed to fine oxide particles in the matrix inhibiting dislocation movement. Large Ti-rich oxide particles were observed at grain boundaries while the alloy matrix adjacent to the boundary was depleted in Ti.

PROGRESS AND STATUS

Experimental Procedure

All of the experiments were conducted on V-4Cr-4Ti (Heat#8326). Prior to exposure, the specimens were annealed at 1050°C to produce a uniform grain size. Low pressure exposures were conducted in an ultra high vacuum system with a base vacuum of 10^{-7}Pa (10^{-9}Torr). A leak valve is used to achieve oxygen partial pressures of 10^{-3}-10^{-6}Pa (10^{-5}-10^{-8}Torr). Specimens were 0.76mm thick tensile specimens. Oxygen content was determined by weighing the samples before and after exposure. Select samples were then annealed for 4h at 950°C in vacuum, which has been shown to restore room temperature ductility to O-loaded vanadium[1]. Mechanical properties were measured at room temperature. TEM samples were prepared in parallel near the center of the specimen using electropolishing.

Results and Discussion

Reaction Kinetics 600°-700°C

The oxidation rate of V-4Cr-4Ti was measured from 10^{-3}-10^{-5}Pa (10^{-5}-10^{-7}Torr) at 600°C and from 10^{-3}-10^{-6}Pa (10^{-5}-10^{-8}Torr) at 700°C. Results to date are summarized in Table I (mass gain data in Table I are based on either 2 or 3 test specimens). Mass gains in ppmw O are shown for

Table I. Oxidation data for V-4Cr-4Ti at low pressure.

Temp.	Pressure (Pa)	Time (h)	Mass Gain (mg/cm^2)	Rate of Mass Gain (mg/cm^2h)	Mass Gain Rate Ave. Normalized to 10^{-5}Torr	power law fit (n)	Fitted Linear Rate (mg/cm^2h)
600°C	10^{-3}	8	0.35	$4.4x10^{-2}$	1	1.63	$2.0x10^{-2}$
		24	0.73	$3.0x10^{-2}$			
		48	1.04	$2.2x10^{-2}$			
	10^{-4}	8	0.11	$1.4x10^{-2}$	0.4	0.98	$1.4x10^{-2}$
		24	0.34	$1.4x10^{-2}$			
		48	0.67	$1.4x10^{-2}$			
	10^{-5}	24	0.06	$1.3x10^{-3}$	0.04	1.00	$1.5x10^{-3}$
		48	0.11	$1.2x10^{-3}$			
		100	0.07	$6.8x10^{-4}$			
		242	0.35	$1.4x10^{-3}$			
700°C	10^{-3}	8	1.06	$1.3x10^{-1}$	1	1.44	$7.2x10^{-2}$
		24	2.22	$0.9x10^{-1}$			
		48	3.70	$0.8x10^{-1}$			
	10^{-4}	8	0.2	$2.5x10^{-2}$	0.19	1.38	$1.6x10^{-2}$
		24	0.34	$1.4x10^{-2}$			
		48	0.81	$1.7x10^{-2}$			
	10^{-5}	8	0.021	$2.6x10^{-3}$	0.016	1.23	$9.5x10^{-4}$
		24	0.016	$0.7x10^{-3}$			
		48	0.092	$1.9x10^{-3}$			
		250	0.256	$1.0x10^{-3}$			
	10^{-6}	48	0.042	$8.7x10^{-4}$	0.004	2.85	$1x10^{-4}$
		100	0.036	$3.6x10^{-4}$			
		250	0.058	$2.3x10^{-4}$			
		500	0.058	$1.2x10^{-4}$			

10^{-3} and 10^{-4}Pa in Table II. A power law was used to fit the data at each pressure and temperature where n=1 is linear reaction kinetics and n=2, parabolic. In general, the results showed near linear behavior at 10^{-4}-10^{-6}Pa (10^{-6}-10^{-8}Torr) but deviations were observed at 10^{-3}Pa. The linear-parabolic behavior at 10^{-3}Pa (10^{-5}Torr) 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 weight increases exceeded 0.5–2%. For the data at 10^{-6}Pa (10^{-8}Torr), the mass gains were so low and scattered that they are difficult to reliably interpret. In order to compare the various results, a linear rate was fitted in all cases. 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}Pa and 10^{-4}Pa the rates were less than an order of magnitude different and thus did not scale with the oxygen pressure. At 700°C, the rates at 10^{-6}Pa, averaged about 4X less than at 10^{-5}Pa, but the linear rate fit over all of the data points was almost exactly one order of magnitude lower.

No single mathematical relationship likely describes the oxidation rate over the range of temperature and pressures of interest. However, if the assumption is made that the data generated thus far fits an equation of the form:

$$r = k \bullet P_{O_2}, \text{ and } k = k_o \bullet e^{-Q/RT}$$

where:

r = rate in mg/cm^2h
k_o = constant
R = gas constant
P_{O_2} = oxygen partial pressure in Pa
T = temperature in Kelvin

then the data yields:

$$r = 4.7 \times 10^6 \bullet e^{-821/T} \bullet P_{O_2}$$

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^{-3}-10^{-6}Pa (10^{-5}-10^{-8}Torr). These levels correspond approximately to the total residual oxygen pressures in vacuum between 10^{-1}-10^{-3}Pa. Previous work indicated that at 500°C, the oxidation rate was independent of pressure at 10^{-2}-10^{-4}Pa (~4 x 10^{-3} mg/cm^2h).

Testing in helium also has been initiated at 600° and 700°C. Samples will be exposed to ultra pure (<1 ppmw O) and impure (10 ppmw O) helium to determine oxidation rates and effects on tensile properties.

Room Temperature Mechanical Properties

The room temperature tensile properties were measured as a function of oxygen pick-up by the V-4Cr-4Ti. Tests have been completed on the specimens exposed at 10^{-3} and 10^{-4}Pa at 600° and 700°C, Table II. Unexposed specimens generally have a room temperature elongation of ~30% and a yield strength of 350MPa. Most of the 10^{-3}Pa exposures at both temperatures resulted in

Table II. Room temperature mechanical properties of V-4Cr-4Ti after exposure

			No Anneal			with 950°C Anneal		
Temp.	Pressure (Pa)	Time (h)	Oxygen Content (wppm)	Yield Strength (MPa)	Elong-ation (%)	Oxygen Content (wppm)	Yield Strength (MPa)	Elong-ation (%)
600°C	10^{-4}	8	723	475	10.3	522	354	29.0
		24	1806	590	2.3	1993	383	9.1
		48	3613	520	3.6	3741	604*	0
	10^{-3}	8	1991	502	12.6	1856	394	4.3
		24	4012	402	6.0	4029	513	1.4
		48	5647	399	6.3	5793	640	0.3
700°C	10^{-4}	8	1065	421	6.6	1092	390	12.3
		24	1704	456	4.4	2005	395	2.8
		48	4466	533*	0	4381	688*	0
	10^{-3}	8	6048	343	4.2	5580	666*	0
		24	12312	219	1.2	11862	537*	0
		48	20408	broke	0†	20606	257	0.2

* no yield, ultimate strength
† broke during preparation

severe embrittlement and the 950°C anneal did not improve performance. In most cases, the anneal reduced the ductility further. This negative effect is attributed to the higher temperature anneal allowing the diffusion of oxygen throughout the specimen. For example, the oxygen uptake (1991ppm) after 8h at 600°C in 10^{-3}Pa was likely concentrated at the specimen surface, resulting in a total elongation of 12%, Table II. When a similarly exposed specimen (1856ppm O) was annealed at 950°C, thus allowing more oxygen diffusion throughout the cross-section, its ductility dropped to 4.3%. Specimens with 1000ppm of oxygen or less showed improved ductility when annealed. Further tensile testing is being completed to determine mechanical properties at 600°C.

Microstructural Characterization of V-4Cr-4Ti After Oxidation

Previous TEM work on large-grained V-4Cr-4Ti after exposure to 10^{-4}Pa at 500°C (1434ppmw O addition) and a 100h vacuum anneal at 600°C revealed a uniform matrix microstructure with ultra fine oxide precipitates.[2] At every grain boundary there was a 100-200nm denuded zone adjacent to the boundary and large precipitates along the boundary. The same TEM specimen was analyzed recently with electron energy loss spectroscopy (EELS) to examine the chemical composition of the precipitates and the matrix near the grain boundaries. A typical EELS spectrum from a large area of the specimen has clear peaks for V, Cr and Ti, Figure 1a. The grain boundary region was then mapped by energy-filtered TEM (EFTEM) imaging to produce fully quantitative maps of elemental concentrations of Ti and V, Figures 1c and 1d, respectively. This technique uses electrons with characteristic energy losses like those in regions marked 3 in Figure 1a and then adjacent regions, marked 1 and 2, as a relative background. A 'zero loss'image of the region is shown in Figure 1b. As expected, the precipitates were denuded in V and were likely TiO_x but may contain some level of N and C. Figure 1e combines the information in Figures 1c and 1d and shows the Ti/V atomic ratio generated with calculated ionization cross-sections. Analyzing a 50-pixel wide region across the boundary, Figure 1e, showed that the matrix adjacent to the boundary was depleted in Ti, Figure 1f. Away from the boundary, the Ti/V was close to the bulk composition of 0.042 and at the boundary the Ti/V ratio showed a peak. These results suggest that the majority of Ti near the boundary was incorporated into the large oxide precipitates.

Grain boundary precipitates were observed before and after annealing so their presence does not appear to affect ductility.[2] The denuded zone adjacent to the boundaries has been proposed to be an important factor in reduced ductilities observed in refractory metals.[3] However, based on these observations, the low ductility in V-4Cr-4Ti is attributed to the fine oxide particles in the matrix preventing dislocation movement. The 950°C anneal improved the room temperature alloy ductility from near 0% to 15-20% by coarsening the fine matrix oxide particles into large precipitates similar in size to those on the grain boundaries.[2] Further work is being conducted on lower O content specimens prepared under similar conditions to assess the importance of the particles and denuded zone at the alloy grain boundaries.

REFERENCES

1. J. R. DiStefano and J. H. DeVan, J. Nucl. Mater. 249 (1997) 150.
2. B. A. Pint, P. M. Rice, L.D. Chitwood, J. H. DeVan and J. R. DiStefano, DOE/ER-0313/24 (1998) 77.
3. C. T. Liu, H. Inouye, R. W. Carpenter, Met. Trans. 4 (1973) 1839.

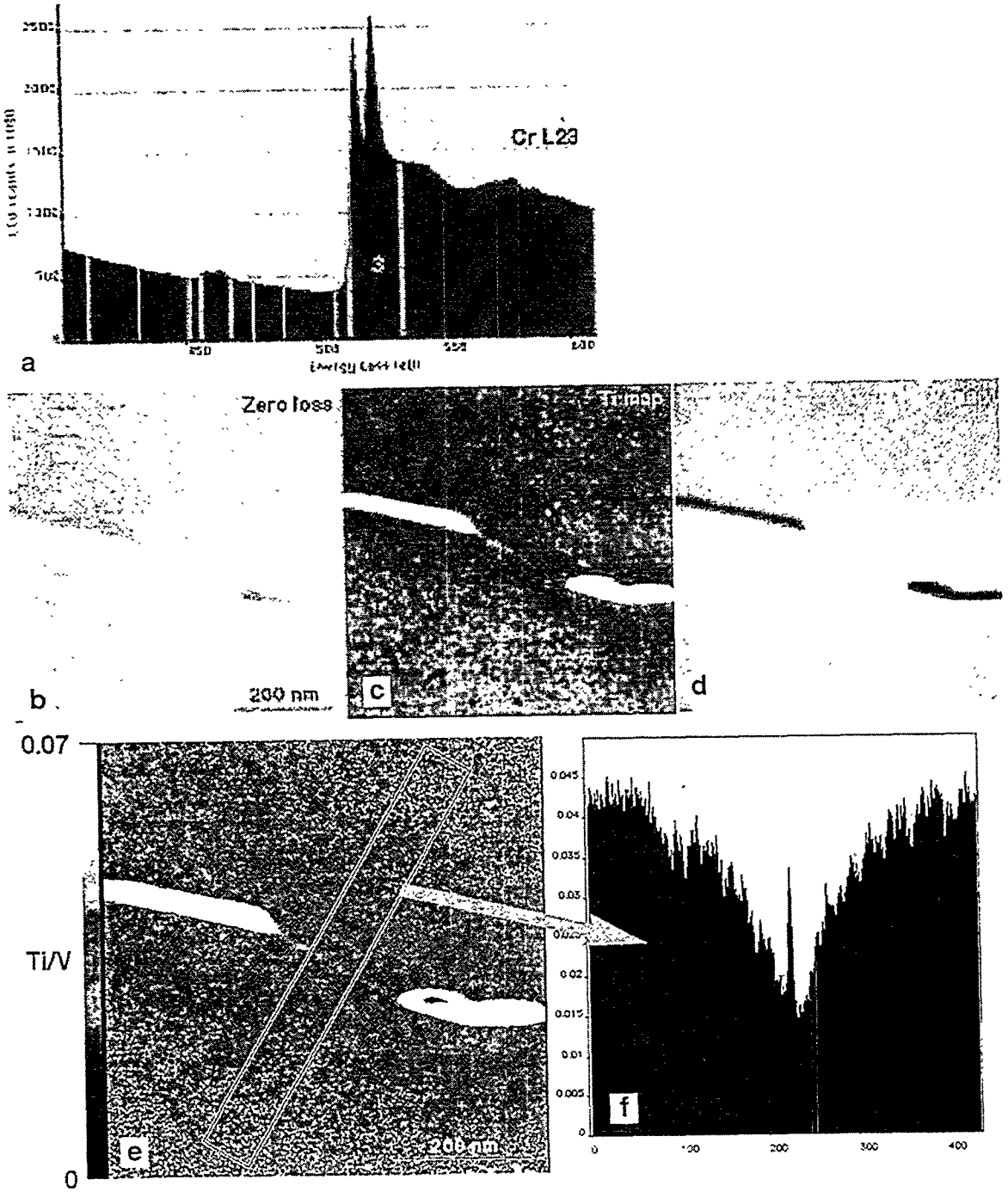

Figure 1. TEM/EELS analysis of V-4Cr-4Ti after the addition of 1434ppmw O at 500°C and annealing for 100h at 600°C. Fine oxide precipitates are observed in the matrix and larger precipitates at the grain boundary (b) which is surrounded by a precipitate denuded zone. A typical EELS spectra is shown in (a). The peak (3) and background (1&2) regions are used to construct EFTEM maps (c,d) of the region showing the particles rich in (c) Ti and denuded in (d) V. Images (c) and (d) were used to create a Ti/V distribution in (e) and analyzing a region across the boundary (box in (e)) showed that the boundary region was depleted in Ti (f).