OXIDATION OF V-4Cr-4Ti AT LOW PRESSURES -- B. A. Pint, J. R. DiStefano, 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 and argon at 400-700°C. Recent emphasis has been on determining kinetics of oxidation at 600-700°C.

SUMMARY

Specimens of V-4Cr-4Ti have been exposed to low pressure oxygen and high purity helium and argon environments to determine oxidation kinetics. 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 $\leq 10^{-5}$Pa. Higher oxygen partial pressures and lower temperatures can result in external film formation and parabolic kinetics. Internal oxidation resulting in oxygen concentrations >2000wppm 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 2000h 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.

PROGRESS AND STATUS

Experimental Procedure

All of the experiments were conducted on V-4Cr-4Ti (Heat#832665). Prior to exposure, the specimens were annealed at 1050°C to produce a uniform grain size. Specimens were 0.76mm thick tensile specimens. 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 76,000Pa (1 atm), the pumping system was closed and excess gas pressure was removed through an oil bubbler. Oxygen content was determined by weighing the samples before and after exposure. 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.

Results and Discussion

Reaction Kinetics 600°-700°C

The reaction kinetics of V-4Cr-4Ti at 600° and 700°C were previously determined[1] at oxygen

partial pressures from 10^{-3}-10^{-6}Pa (10^{-5}-10^{-8}Torr). Similar experiments to these conducted at 700°C were repeated at 10^{-6}Pa (10^{-8}Torr) for 100, 250 and 500 h using material with the same thermo-mechanical history as that used to obtain the data at 10^{-4}-10^{-5}Pa. Mass gain data are shown in Table I. The mass gains of the new data set at 10^{-6}Pa averaged about 10X less than that at 10^{-5}Pa and 100X less than at 10^{-4}Pa which is in agreement with the linear pressure relation on reaction rate that has been proposed for high temperature/low pressure oxidation where a significant surface film does not form. These data fit a nearly linear relationship with time (n=1.02). The previous data set[1] had a value of n=2.85 but included specimens that had received a different thermo-mechanical treatment. No further investigation of why these materials behaved differently has been conducted.

Mass gain results from tests at 600° and 700°C in helium at 76,000Pa (1 atm) or argon (10 Pa) are also reported in Table I. Data from tests in pure helium (<0.1vppm oxygen) had n values of 1.39 at 600°C and 3.02 at 700°C. These deviations from linear behavior are similar to observations in tests conducted in vacuum with high (10^{-3}Pa) oxygen pressures[1] and have been observed when the mass gains are extremely high. A linear rate is associated with a reaction limited by a surface reaction such as oxygen absorption. However, when the mass gain becomes very high and the near-surface region becomes saturated with oxygen, the rate limiting step may switch to another process such as diffusion in the metal, which would result in a parabolic relationship (n=2). Values of n between 1 and 2 suggest a time period when there is a change in the rate controlling mechanism. Thus, when the mass gains become very high, it is not surprising to observe parabolic kinetics. However, when the mass gains are high, the material is usually already embrittled and subsequent oxidation behavior is of less interest. Of more technological importance are the periods where the oxygen uptake is relatively low and the material retains

Table I. Oxidation data for V-4Cr-4Ti at low pressure and in high purity helium*.

Temp.	Pressure (Pa)	Time (h)	Mass Gain (mg/cm^2)	Rate of Mass Gain (mg/cm^2h)	Ave. Mass Gain Rate Normalized to 10^{-3}Pa	Ave. Mass Gain Rate Normalized to 10^{-4}Pa	power law fit (n)
Vacuum:							
700°C	10^{-6}	100	0.021	2.1×10^{-4}	0.002	0.012	1.02
		250	0.058	2.3×10^{-4}			
		500	0.100	2.0×10^{-4}			
Helium*							
600°C	7.6×10^{4}	24	0.69	2.9×10^{-2}	0.97	2	1.39
		48	1.1	2.3×10^{-2}	0.86	1.6	
		100	1.9	1.9×10^{-2}			
700°C	7.6×10^{4}	24	1.4	6.0×10^{-2}	0.67	3.1	3.02
		48	1.9	3.9×10^{-2}	0.49	2	
		100	2.3	2.3×10^{-2}			
Argon							
600°C	10	100	0.06	1.3×10^{-3}		1.7	
700°C	10	100	2.9	2.9×10^{-2}		1.5	

* research grade He with <0.1vppm oxygen

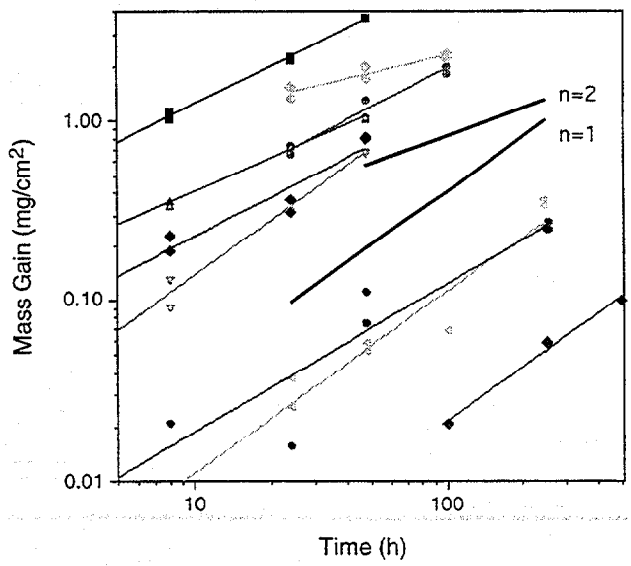

Figure 1. Log-log plot of the mass gains observed in this work at 600° (open symbols) and 700°C (closed symbols) in He and in oxygen pressures of 10^{-3}-10^{-6}Pa. At lower oxygen pressures, the data fit a linear relationship (n=1) whereas at higher pressures the value of n increased.

some ductility. During these periods, the oxidation reaction tends to follow linear kinetics. This distinction is illustrated in Figure 1 using data from Table I and from previously reported data for V-4Cr-4Ti[1].

The mass gains after 100h in helium were similar to those obtained in low pressure (10Pa) argon which contained 10vppm O_2. Mass gains were similar to those obtained at oxygen partial pressures of 10^{-3}-10^{-4}Pa (10^{-5}-10^{-6}Torr) in vacuum. In the low pressure argon tests, the oxygen partial pressure was ~$4x10^{-4}$Pa (4x 10^{-6}Torr). In pure helium at 1atm, the oxygen concentration would have to be in the 1-10vppb range for its partial pressure of oxygen to be in that same range; otherwise the volume of helium present had some type of shielding effect that reduced the oxidation rate, as has been reported for Nb-1Zr.[2]

Mechanical Properties

As previously reported,[3] sub-size sheet tensile specimens (SS-3) of unoxidized, annealed V-4 Cr-4 Ti have a room temperature elongation of ~30%, but internal oxidation can significantly lower this value. Post-oxidation, tensile data at room temperature and 600°C are reported in Table II. Although elongation was initially lower at 600°C (9-13%), values as low as 2-5% uniform elongation were obtained after oxidation. Furthermore, the room temperature tensile data indicated that internal oxidation was more important to embrittling V-4Cr-4Ti than the oxide scale since samples with a surface oxide retained significant ductility (~10% elongation) for total mass gains up to ~6000wppm oxygen, whereas samples with no visible surface oxide had little ductility (~2% elongation) after mass increases of ~2000wppm oxygen. However, although the surface film may not initially contribute to tensile embrittlement, over time it is a source of oxygen for further internal oxidation to occur. For example, two samples exposed to He picked up 2944 and

Table II. Mechanical properties at 25° and 600°C of V-4Cr-4Ti after exposure

Temp.	Pressure (Pa)	Time (h)		Oxygen Content (wppm)	Surface Oxide	Yield Strength (MPa)	Ultimate Strength (MPa)	Elong-ation (%)	Total Elong. (%)
No anneal						Properties at 25°C			
700°C	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°C	10^{-5}	242		1896*		468	572	0.7	2
600°C	10^{5}(He)	100	☆	2944*	Visible	458	523	7	10
		48	☆	5805	Visible	387	457	8	10
600°C	10(Ar)	100		13314	Visible	413	417	0.2	0.2
700°C	10(Ar)	100		15879	Visible	broke on loading			
Annealed for 2000h at 700°C in vacuum						Properties at 25°C			
600°C	10^{5}(He)	100	☆	3827	Visible†	broke on loading			
700°C	10^{5}(He)	24		8282	Visible†	broke on loading			
		100		11836	Visible†		422	0	
700°C	10(Ar)	100		15638	Visible†		422	0	
No anneal						Properties at 600°C			
	no exposure					272	394	9	15
700°C	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°C	10^{-5}	242		2082*		370	424	2	7
600°C	10^{5}(He)	100		3153*	Visible	284	408	5	8
		48		5937	Visible	298	371	5	6

* different heat of V-4Cr-4Ti which relatively higher mass gains
† after annealing, the surface oxide was no longer visible

5805 wppm oxygen, respectively (marked by stars in Table II), and both contained a visible surface oxide. When tensile tested at room temperature, total elongation of either sample was 10%. Another sample with 3827wppm oxygen (marked by a star in Table II) also had a visible surface oxide; but it was subsequently heat treated for 2000h at 700°C in static argon. This heat treatment was conducted in order to examine if the surface oxide layer was truly protective, i.e prevented oxygen embrittlement of the alloy. Because of the high solubility of oxygen in vanadium, it is possible that this anneal would allow the surface oxide to react with the alloy to further internally oxidize the sample. 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 8382wppm indicate that the formation of a surface oxide does not represent a long-term protective state for V-4Cr-4Ti. During prolonged high temperature exposure even in the absence of further oxidation, the presence of a surface oxide provides a source for oxygen which can embrittle the underlying substrate.

Considering both the oxidation and mechanical properties data, these results indicate that V-4Cr-4Ti, after relatively short exposures to oxidizing environments containing oxygen partial pressures of $\geq 10^{-4}$Pa at 600°-700°C, picked up sufficient oxygen (either internally or as a scale) to significantly reduce the tensile ductility. Thus, even though n values greater than 1 were observed under these conditions the material already contained enough oxygen to be embrittled. The conditions where low mass gains were observed, and the V-4Cr-4Ti specimens were not severely embrittled, showed linear kinetics. However, one area of concern is that all of the tensile data in this study used 0.76mm thick, SS-3 specimens. For a fixed exposure time, temperature and pressure, an increase in specimen thickness would reduce the amount of oxygen uptake, because the surface area to volume ratio would decrease and the oxidation rate per unit surface area should be constant. In contrast, a specimen geometry with a higher surface area to volume ratio should result in a higher oxygen concentration given the same oxidation conditions. Thus, extrapolating the present data to another design geometry and wall thickness represents a modification in the surface area to volume ratio that has not yet been considered experimentally. Future work should examine the effect of specimen thickness on the oxidation kinetics to provide more reliable predictions for fusion reactor applications.

As a final note, it has been argued that a purification system in conjunction with a recirculating inert gas can reduce the oxygen partial pressure in the gas many orders of magnitude to levels comparable with or better than ultra high vacuum systems can produce. However, to date high vacuum has been the system of choice for protecting refractory metal/alloys at high temperature, and there is little, if any, experimental evidence that has been reported attesting to successful operation of a niobium, tantalum or vanadium system in a recirculating gas for long times at the temperatures of interest.

REFERENCES

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