OXIDATION OF V-4Cr-4Ti AT LOW PRESSURES -- B. A. Pint and J. R. DiStefano (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 He environments from 1atm down to 10^{-4} atm in order to determine oxidation kinetics and effects on mechanical properties. At 10^{-4} atm He, the reaction kinetics were nearly linear at 700°C. However, at 10^{-3} atm He, the specimen mass gains were lower and followed a sub-parabolic rate, very similar to the behavior observed in 1atm of He. These results suggest that an external oxide layer may be forming at the higher pressures. During exposures in 1 atm He, specimens form an external oxide layer and retain some tensile ductility after exposure. To confirm an earlier result, specimens with various exposure times (and thus oxygen levels) were annealed for 2000h at 700°C. The ductility of those specimens which had an external oxide before annealing was reduced to zero, illustrating that a surface oxide on V-4Cr-4Ti is a source of oxygen for further 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. For testing in He at 76,000Pa (1 atm), the high vacuum valve was closed after pumpdown followed by the introduction of He. Excess gas pressure was removed through an oil bubbler. A micrometering valve was used to achieve He partial pressures of 10^{-3} or 10^{-4}atm. Oxygen content was determined by weighing the samples before and after exposure. A power law was then used to fit the data at each pressure and temperature:

$$\Delta M = k \cdot t^{1/n}$$

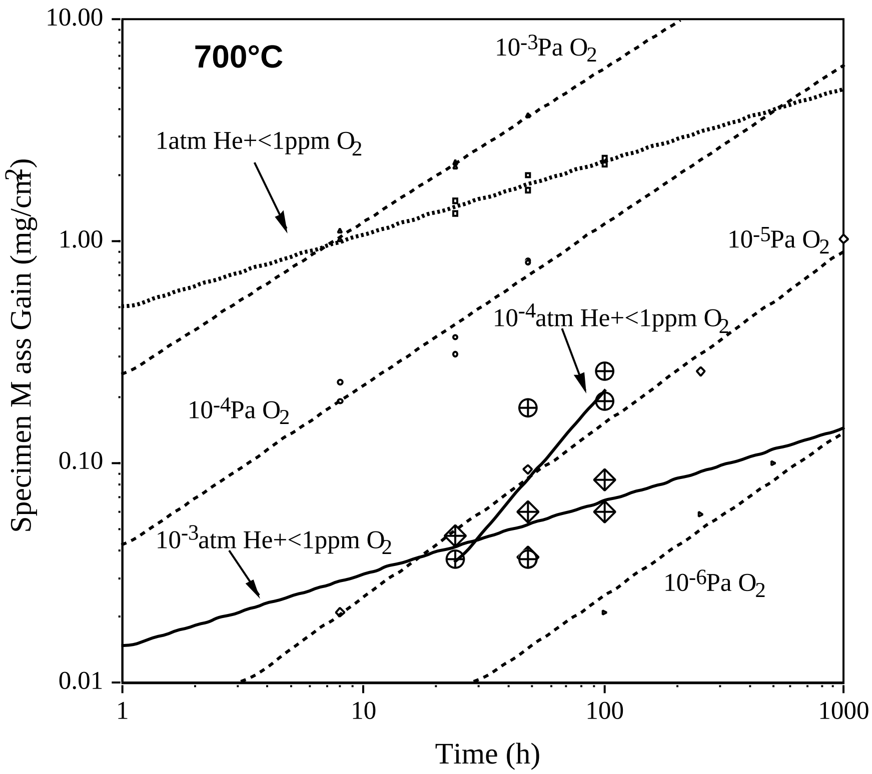
where M is mass, k and n are constants and t is time. For linear reaction kinetics, n=1 and for parabolic, n=2.

Results and Discussion

Reaction Kinetics in He at700°C

The reaction kinetics of V-4Cr-4Ti at 600° and 700°C were previously determined at oxygen partial pressures from 10^{-3}-10^{-6}Pa (10^{-5}-10^{-8}Torr) and at 1atm of high purity He[1-2]. In general, the results in oxygen showed a linear relationship between pressure and reaction rate and a nearly linear relationship with time at 10^{-4}-10^{-6}Pa (10^{-6}-10^{-8}Torr), but deviations were observed at 10^{-3}Pa. The linear-parabolic behavior (n=1.4) 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 mass increases exceeded 0.5–2% and room temperature tensile ductility was reduced to zero. In 1atm He, a similar phenomenon was observed with very high mass gains combined with the formation of a surface oxide which resulted in an n value of 3.0. These results are plotted for reference in Figure 1 (dashed lines).

The high mass gains in 1atm He are not surprising because, even with high purity (≈1ppm O_2) He, the oxygen pressure would be ≈10^{-1}Pa. In a He-cooled fusion reactor, the He pressure would be even higher but, with purification, the O_2 pressure could be lower. In order to simulate that environment, the He pressure was dropped to levels of 10^{-3} and 10^{-4}atm in an attempt to achieve



$$\Delta M = k \cdot t^{1/n}$$

Figure 1. Log-log plot of the mass gains observed in this work at 700°C in low pressures of high purity (<1ppm O) He (solid lines). At 10^{-4}atm He, the mass gains were similar to that observed in 10^{-5}Pa O_2. At 10^{-3}atm He, the mass gains were lower and the reaction kinetics were similar to that observed in 1 atm He.

oxygen pressures of ≈10^{-4} and 10^{-5}Pa, respectively. The mass gain results for 5 tests at each pressure are shown in Figure 1 with the a power law fit of the data (solid lines). At 10^{-4}atm He, the data fell near the previous results for 10^{-5}Pa O_2 which corresponds very well to the predicted oxygen level in the gas. The n value was 0.8. At 10^{-3}atm He, the mass gain values were lower and n was 3.0, identical to the value at 1 atm He. This suggests that at the higher pressure there may have been oxide film formation which inhibited oxygen uptake or that there was a change in the rate of oxygen adsorption due to the higher He pressure. Characterization of the specimens is being conducted along with additional experiments at longer times and different He pressures.

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 exposure to oxygen can significantly lower this value. As observed above, the formation of an external oxide layer can significantly change the reaction kinetics. For Fe- or Ni-base alloys, an external oxide is termed protective if it limits further reaction. However, in the case of refractory metals like vanadium, the oxide needs to prevent embrittlement of the alloy in order to be considered protective. Previous work[2] indicated that annealing for 2000h at 700°C reduced the ductility of specimens with a surface oxide from 10% total elongation at 25°C to 0%. To confirm this observation, a series of specimens were oxidized to create a range of added oxygen levels up to ≈10,000ppm. The higher oxygen levels were achieved by exposure at 600°C in 1 atm He where a surface oxide was formed. Half of the specimens were fractured after exposure and the other half were annealed for 2000h at 700°C. Figure 2 shows the room temperature ductility results for this set of specimens. For control, a specimen with no added oxygen and one with a low level of added oxygen (136ppm) also were annealed for 2000h at 700°C. Compared to the unannealed results, the specimens with little or no added oxygen showed only a small loss in ductility after annealing. However, the specimens which formed surface oxides all showed severe embrittlement after annealing, Figure 2. Because of the high solubility of oxygen in vanadium, it is likely that during the 700°C anneal the surface oxide dissolved, providing a source for additional oxygen to embrittle the specimen. In fact, the specimens were lighter in color after the anneal, indicating a change in the surface oxide thickness. These results indicate that the surface oxide on vanadium is not protective and that a change in oxidation kinetics as a result of surface oxide formation should not be interpreted as an improvement in performance. During prolonged high temperature exposure, even in the absence of further oxygen uptake, the presence of a surface oxide provides a source for oxygen which can embrittle the underlying substrate. Further experimental work in this area may include varying the surface area to volume ratio to test model predictions for the critical oxygen levels needed to embrittle specimens with different geometries.

REFERENCES

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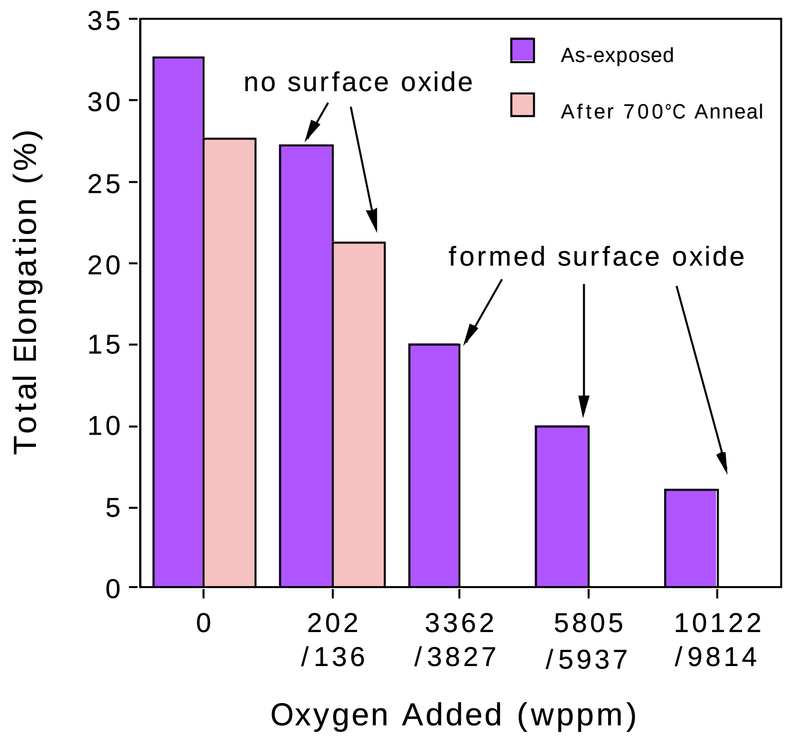

Figure 2. Total elongation at room temperature as a function of added oxygen with and without annealing for 2000h at 700°C. Specimens which formed a surface oxide and were annealed were severely embrittled.