CHARACTERIZATION OF REACTION PRODUCTS AFTER OXIDATION OF V-4Cr-4Ti AT LOW PRESSURES -- B. A. Pint and H. M. Meyer (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. Several 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 oxidation kinetics in low pressures of He to simulate higher purity He than is commercially available.

SUMMARY

There was a significant change in oxidation kinetics between 10^{-4}atm He and 10^{-3}atm He. The higher pressure results were similar to those observed in 1atm He where a surface oxide was observed. Using Auger electron spectroscopy (AES), a thicker (30-40nm) oxide was observed after 100h at 700°C in the higher He pressure whereas a thinner oxide (10-20nm) formed at the lower pressure.

PROGRESS AND STATUS

Introduction

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, Figure 1. These results suggest that an external oxide layer may be forming at the higher pressures. During exposures in 1atm He, specimens form a visible external oxide layer and retain some tensile ductility after exposure.[1] To determine if oxide layers had formed after exposures to 10^{-3} and 10^{-4}atm He, selected specimens were examined using Auger.

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 micrometering valve was used to achieve He partial pressures of either 10^{-3} or 10^{-4}atm. Oxygen content of the samples was determined by weighing before and after exposure.

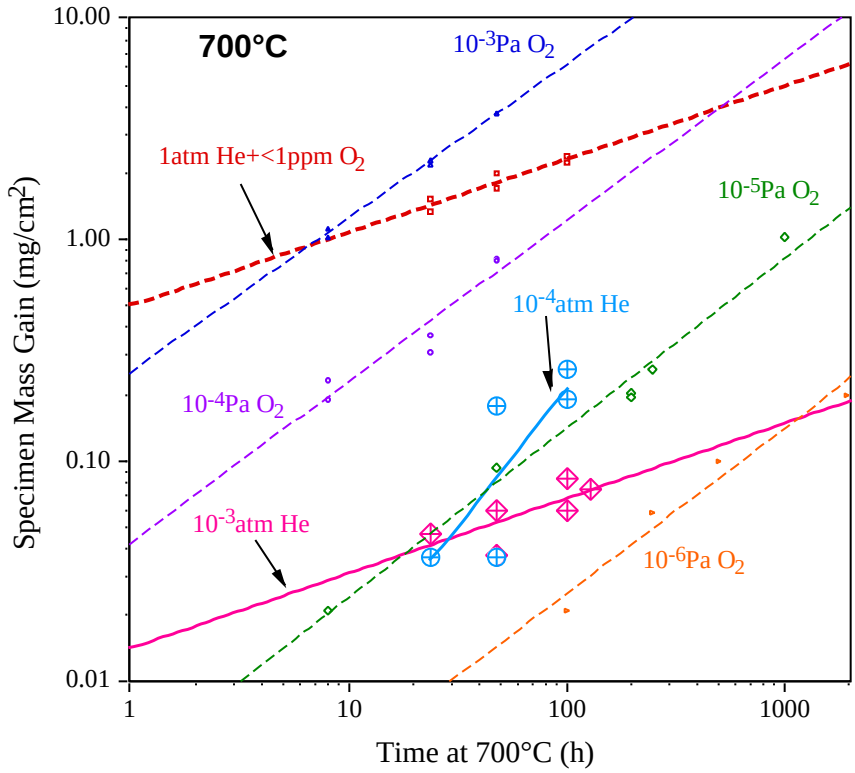

Figure 1. Log-log plot of the mass gains observed in this work at 700°C in low pressures of high purity (<1ppm O) He (solid lines). At 10^{-4}atm He, the mass gains were similar to that observed in 10^{-5}Pa O_2. At 10^{-3}atm He, the mass gains were lower and the reaction kinetics were similar to that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

Results and Discussion

Two specimens of V-4Cr-4Ti were examined by AES. Both were exposed for 100h at 700°C, one at 10^{-3}atm He and the other at 10^{-4}atm He. Both surfaces had a similar appearance with some rough and smooth areas, Figure 2. There were significant difficulties in determining the surface composition because of peak overlaps between Ti and N as well as V and O. Also, Ti, V and Cr are all difficult to differentiate because of overlap. A slow (170Å/min) sputter rate was used because of the thin surface oxide. However, a high concentration of carbon in the form of a carbide was observed on both specimens to a depth of over 200nm. There was a clear change between the graphitic carbon peak observed on the specimen surface and the carbide peak observed within the specimen. Further characterization will be required to determine the nature of this carbon enrichment near the specimen surface.

Figure 3 shows the sputter depth profiles for each specimen. For the specimen exposed at 10^{-3}atm He, the O signal became negligible at ≈35nm, Figure 3a. For the specimen exposed at 10^{-4}atm He, the O signal disappeared at ≈15nm. Therefore, a thicker oxide layer was formed in the higher He pressure. However, whether this layer was responsible for the inhibition in the rate of oxygen uptake is not certain. Further work is needed to study this mechanism. Experiments are underway for longer times at these pressures and at higher and lower He pressures. As a final

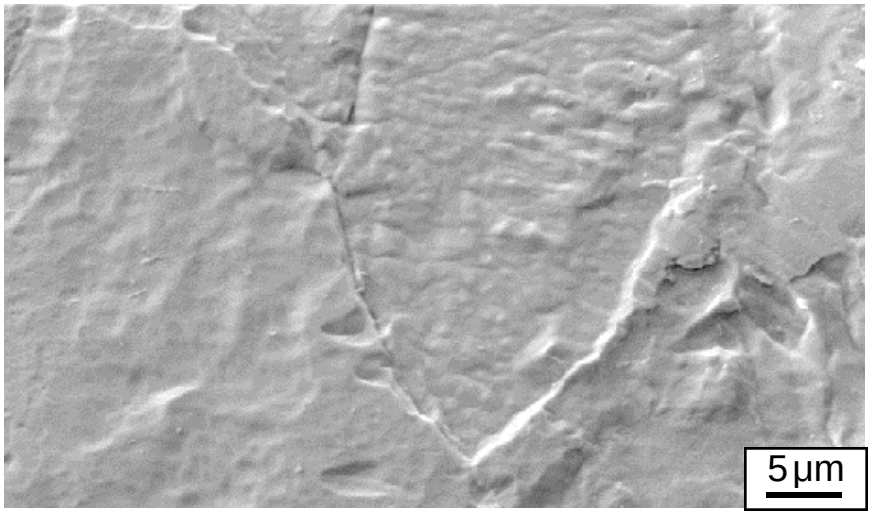

Figure 2. Secondary electron image of the specimen surface after 100h at 700°C in 10^{-3}atm He. There were smooth raised areas and rough areas observed on both specimens.

note, the formation of a surface oxide on a vanadium alloy cannot be considered a protective layer. Previous work[1] has shown that a surface oxide is not stable with vanadium and is actually a source for oxygen, which diffuses into the substrate and causes embrittlement.

REFERENCES

1. B. A. Pint and J. R. DiStefano, J. Nucl. Mater. 307-311 (2002) 560.

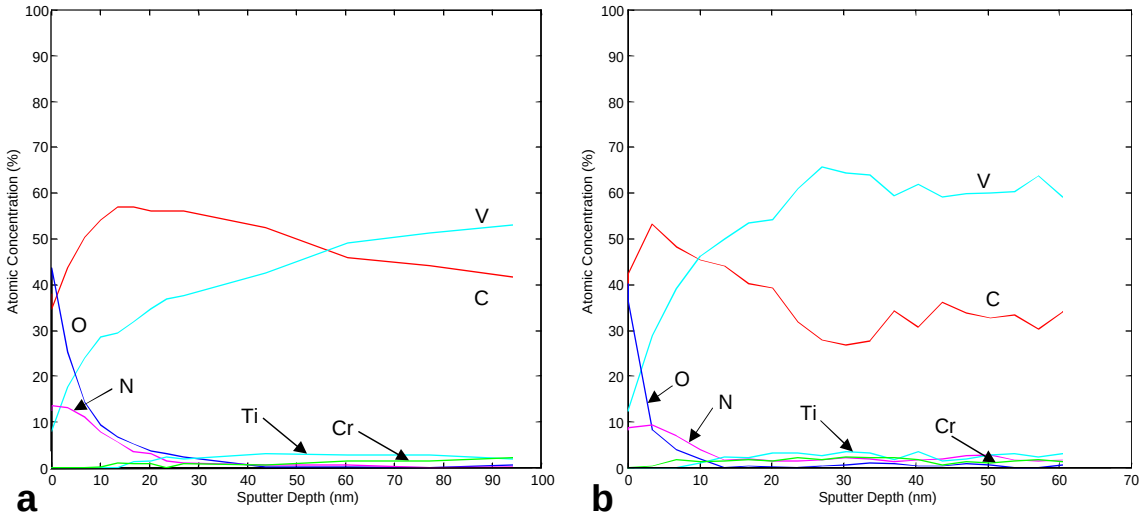

Figure 3. AES sputter depth profiles of V-4Cr-4Ti specimens exposed for 100h at 700°C in (a) 10^{-3}atm He and (b) 10^{-4}atm He.