

MICROSTRUCTURAL CHARACTERIZATION OF EXTERNAL AND INTERNAL OXIDE PRODUCTS ON V-4Cr-4Ti -- B. A. Pint, P. M. Rice, L.D. Chitwood, J. H. DeVan and J. R. DiStefano (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to assess the reaction product and microstructural changes in V-4Cr-4Ti after exposure to 1atm air and low oxygen pressures (10^{-6} Torr) at 500°C. In both cases, transmission electron microscopy (TEM) is required to observe the fine structure of the oxide scale and grain boundaries of the internally-oxidized vanadium alloys.

SUMMARY

Air oxidation of V-4Cr-4Ti at 500°C at 1atm resulted in the formation of a thin (100-150nm) external vanadium nitride layer which was identified beneath a thicker (1.5 μ m) vanadium oxide scale. This nitride layer would only be detected by high-resolution, analytical electron microscopy techniques. Subsequent tests comparing room temperature tensile properties for exposure in laboratory air, dry air and dry oxygen at 1atm showed more embrittlement in air than in O₂. Internal oxidation of coarse-grained V-4Cr-4Ti at low oxygen pressures at 500°C was followed by TEM examination. In a sample with a 1400ppmw O addition, which is sufficient to reduce the ductility to near zero, there appeared to be an oxygen denuded zone (150-250nm) near the grain boundaries with precipitates at the grain boundaries and uniform ultra-fine (<5nm) oxygen particles in the matrix. In a similar O-loaded specimen that was subsequently annealed for 4h at 950°C to restore ductility, large oxide particles were observed in the matrix and at the grain boundaries.

PROGRESS AND STATUS

Experimental Procedure

All of the experiments were conducted on V-4Cr-4Ti. Exposures at 1atm were conducted in a tube furnace at 500°C using both coupons and tensile specimens annealed at 1050°C. Experiments were conducted in both laboratory air (tube open) or in dry air or dry oxygen using endcaps on the tube and bottled gas. After exposure, samples were analyzed using scanning electron microscopy (SEM), glancing angle x-ray diffraction (GAXRD) and TEM equipped with an energy dispersive x-ray diffractometer (EDX) and an electron energy loss spectrometer (EELS).

Low pressure exposures were conducted in an ultra high vacuum system with a leak valve to achieve an oxygen partial pressure of 10^{-6} Torr. Prior to exposure the samples were annealed at 1200°C to produce a relatively large grain size. The coupons were exposed for 48h at 500°C and then annealed for 100h at 600°C to homogenize the oxygen distribution. Oxygen content was determined by weighing the samples before and after exposure. Half of the samples were then annealed for 4h at 950°C, which has been shown to restore room temperature ductility to O-loaded vanadium¹.

TEM samples were prepared in parallel (using electropolishing) near the center of the specimen and in section by a combination of mechanical thinning and precision ion milling.

Results and Discussion

Using SEM, the oxide on V-4Cr-4Ti after 200h at 500°C was observed to have blade-like grains and to be 3-4 μ m thick. GAXRD identified V₂O₅, V₆O₁₃, and V₄O₉ but no nitrides or Cr- or Ti-rich phases. Using cross-sectional TEM/EELS, four regions were identified in the reaction layer (Figure 1) with grain size, d:

(A) 0-150nm from metal; no visible crystal structure	d<5nm	VN _x layer
(B) 150-450nm from metal; very fine grains	d=10-15nm	VO _n
(C) 450-1 μ m from metal; small grains	d=50nm	VO _y
(D) >1 μ m from metal; large, faulted grains	d=250-1000nm	VO _z

The inner layer (Figure 2) was analyzed by EELS in order to determine the presence of nitrogen and the absence of any Ti enrichment (Figure 3). Some particles were observed at the metal-oxide interface but also were not enriched in Ti. No segregation was observed at oxide grain boundaries. There was a slight reduction in the O/V ratio towards the gas interface which may reflect the different oxides observed by GAXRD. Previous work had suggested a titanium nitride layer formed during air oxidation². The vanadium nitride layer observed in the present work is too thin to be detected by conventional microprobe, SEM/EDX analysis or GAXRD.

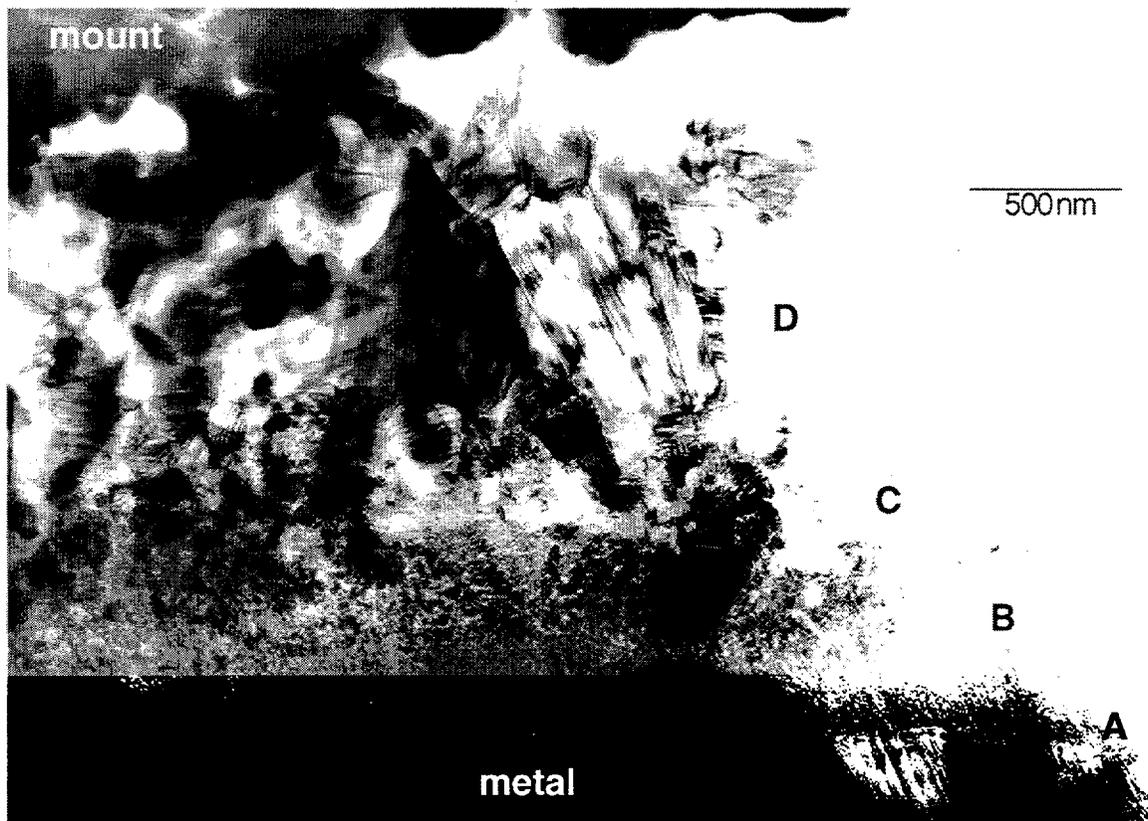


Figure 1. TEM bright field image of the external scale formed on V-4Cr-4Ti after 200h at 500°C. Four distinct layers are identified with increasing grain size. Layer A is rich in nitrogen while the others are vanadium oxide.

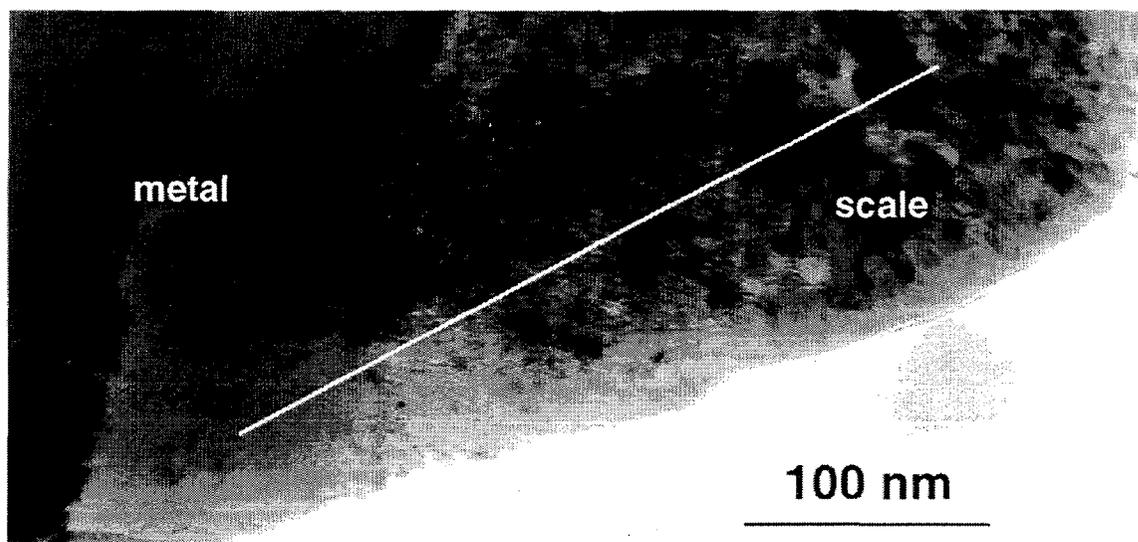


Figure 2. TEM bright field image of the external scale formed on V-4Cr-4Ti after 200h at 500°C. The line denotes where the EELS profile in Figure 3 was performed across the metal-scale interface.

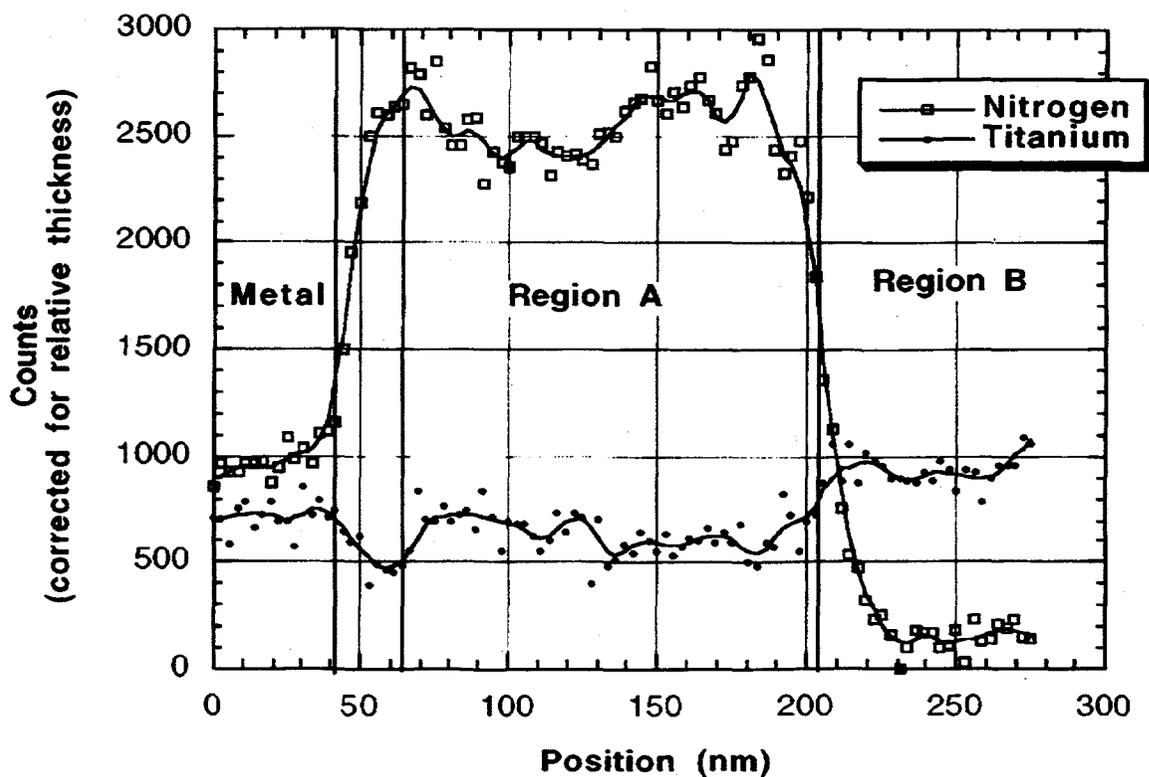


Figure 3. TEM/EELS profile along the line marked in Figure 2. The layer is clearly enriched in N but not in Ti, indicating a VN_x layer. Regions A and B correspond to the layers indicated in Figure 1.

In order to explore any possible role of this nitride layer in affecting diffusion through the external scale or changing the mechanical properties of the underlying alloy, coupons and tensile specimens were exposed in flowing dry oxygen, dry air and laboratory air. In general, there was little difference between the rate of weight gain in air and oxygen indicating that the nitride layer was neither accelerating or decelerating the rate of corrosion. Relative to changes in mechanical properties, there was slightly more embrittlement in laboratory air than in dry O₂ (Table I). Results for dry air were in between, possibly indicating a slight effect of water vapor on embrittlement.

Table I. Mechanical properties results comparing samples exposed at 500°C in 1atm of laboratory air and oxygen. The laboratory air exposure appeared to embrittle the alloy more than a comparable exposure in dry oxygen. The dry air exposure had an intermediate effect.

Oxidation Time:	Dry Oxygen		Laboratory Air		Dry Air	
	Yield Strength (MPa)	Elongation (%)	Yield Strength (MPa)	Elongation (%)	Yield Strength (MPa)	Elongation (%)
50h	338, 356	17.8, 20.3	405, 405	14.2, 14.4	355,371	17.7,18.2
200h	355, 376	11.4, 12.0	386,413	7.2, 7.7	383,395	8.3,9.5

Characterization of the vanadium alloy after exposure to a low oxygen partial pressure at 500°C (1434ppmw O addition) revealed a uniform matrix microstructure with ultra fine oxide precipitates, Figure 4. At every grain boundary there was a 100-200nm denuded zone adjacent to the boundary and precipitates along the boundary. Chemical analysis has not yet been performed on these precipitates.

After a similar oxygen addition at 10⁻⁶Torr and 500°C (1160ppmw O) followed by annealing for 4h at 950°C, the microstructure was remarkably different (Figure 5). Large TiO_x precipitates were observed in the matrix and on the boundaries. The platelets followed established crystallographic patterns in the vanadium alloy. The denuded zone appeared to be retained adjacent to the grain boundaries indicating that the fine precipitates prior to annealing at 950°C grew significantly. The 950°C anneal improves the room temperature alloy ductility from near 0% to 15-20%. Without the anneal, the fracture is predominantly intergranular. Since grain boundary precipitates are observed before and after annealing, their presence does not appear to affect ductility. The denuded zone adjacent to the boundaries has been proposed to be an important factor in the failure³ and future work will focus on characterizing the composition of this region.

REFERENCES

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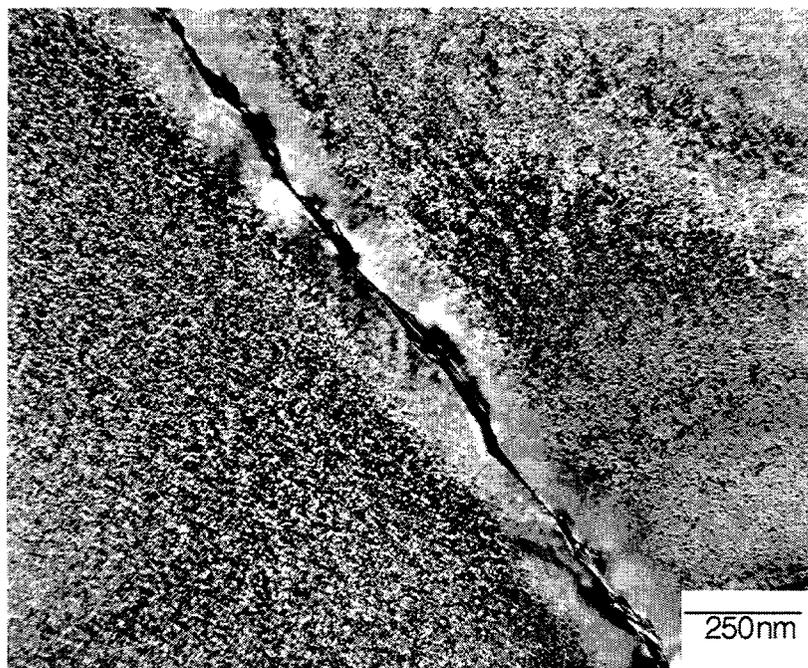


Figure 4. TEM bright field image of V-4Cr-4Ti after the addition of 1434ppmw O at 500°C and annealing for 100h at 600°C. Fine oxide precipitates are observed in the matrix and larger precipitates at the grain boundary which is surrounded by a precipitate denuded zone.

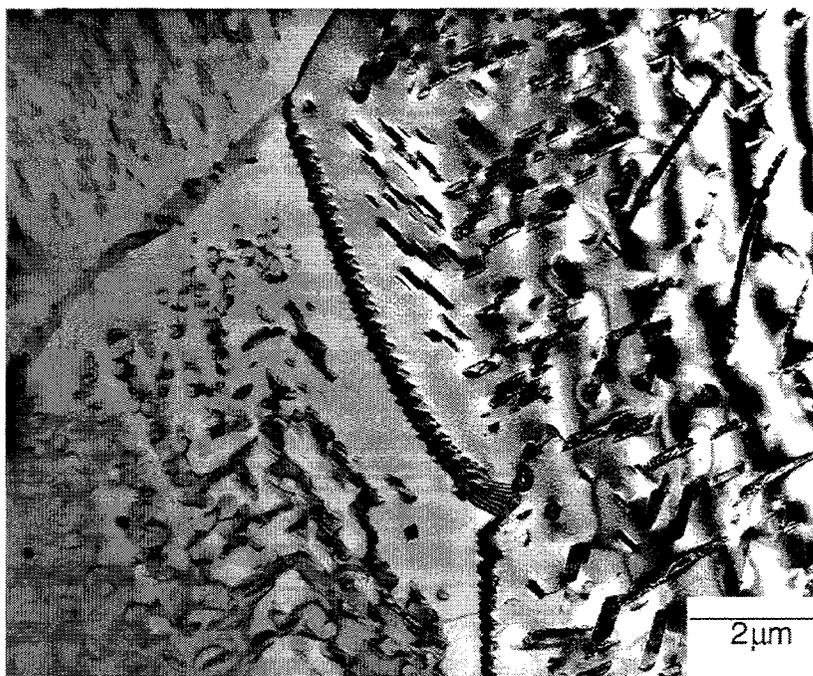


Figure 5. TEM bright field image of a similarly exposed alloy as in Figure 4 (1160ppmw O) but including a 4h at 950°C anneal. In this case, large oxide precipitates are observed.