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FIELD ION MICROSCOPY AND ATOM PROBE MICROANALYSIS OF VANADIUM

T.J. GODFREY, R.P. SETNA and G.D.W. SMITH

Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, GB-Oxford OX1 3PH, Great-Britain

Abstract: FIM specimens of vanadium have been prepared by electropolishing in a mixture of methanol and concentrated sulphuric acid (6:1) at a voltage of 6.5 V (d.c.). Imaging in Ne-He mixtures at 40-55 K produced good quality micrographs. The evaporation field in the presence of neon was 40 V/nm. Oxidation of previously field evaporated specimens was carried out in air at 1 atmosphere and temperatures of 298, 373 and 473 K. Atom probe analysis through the oxide films showed that the predominant oxide formed at all three temperatures was V_2O_3 . There were indications that a transition layer (corresponding to the suboxide V_9O) formed in the region between the main outer oxide film and the metallic substrate. In addition, the bulk metal (which was in the form of fine drawn, 0.1 mm dia. wire) contained approximately 1% oxygen. In one specimen, a high angle grain boundary was observed. This was decorated with brightly imaging impurity atoms. Atom probe analysis revealed enhanced concentrations of carbon and oxygen in the boundary region.

1 - INTRODUCTION

Vanadium and vanadium-based alloys are of interest as possible fuel cladding materials in fast breeder reactors, and as potential envelope materials in fusion reactors. In such environments, oxidation resistance is of the greatest importance. The oxidation of vanadium is somewhat unusual, both because of the wide range of oxide phases which is known to exist, and because formation of the oxide film is accompanied by appreciable dissolution of oxygen in the underlying metal [1]. The uptake of oxygen, and of other impurity atoms such as carbon and nitrogen, is also known to affect the mechanical properties of vanadium [2,3,4]. In this paper, we report the use of field ion microscopy (FIM) and atom probe microanalysis (AP) to study the oxide-metal interface in this system. Segregation of various impurity elements to a high angle grain boundary has also been observed. To the best of our knowledge, this is the first such study of vanadium which has been reported, although FIM images of this metal have been obtained previously by Melmed et al.[5]

2 - EXPERIMENTAL

The vanadium metal was purchased from the Materials Research Corporation, U.S.A. The starting material was nominally 99.98% pure, the major impurities being carbon (112 ppm), oxygen (57 ppm) and iron (20 ppm). This material had been drawn into wire of 0.1 mm diameter. FIM specimens were successfully prepared by electropolishing in a mixture of methanol and concentrated sulphuric acid (6 parts to 1, by volume). Specimens were polished at room temperature, the most suitable voltage being 6.5 V (d.c.). This solution of methanol and sulphuric acid has been previously used for the preparation of thin foils of vanadium alloys for transmission electron microscopy [6]. Field ion imaging was carried out in an ultra-high vacuum FIM/AP system, with the specimen held at 40-55 K, and using a range of neon-helium gas mixtures. Best results were obtained with Ne 10-20% He. The evaporation field at 43 K, and in the presence of the image gas, was estimated to be about 40 V/nm (taking the BIV as 36 V/nm).

Oxidation of previously field evaporated specimens was carried out in air at 1 atmosphere pressure, and at temperatures of 298, 373 and 473 K. AP analysis through the oxide layers was carried out using voltage pulsing. This produced somewhat irregular field evaporation behaviour, but on a number of occasions it was possible to section through the oxide-metal interface in a controllable manner. Composition changes in the region of the interface were represented using "ladder diagrams" (see below).

For the specimen in which a high angle grain boundary was observed, mass spectra were obtained using a probe aperture diameter of approximately 2 nm, the aperture being centred first on the boundary, and then on a region approximately 2 nm away from the interface.

3 - RESULTS AND DISCUSSION

A field ion micrograph of a field evaporated vanadium specimen is shown in figure 1. The micrograph was recorded at 8 kV, with a specimen temperature of 43 K, and using a Ne-He gas mixture. A (110) pole is located near to the centre of the image, and a high-angle grain boundary, decorated with brightly-imaging impurity atoms, can be seen lying obliquely across the field of view. The variation in regional image brightness for vanadium seems to be less than for certain other b.c.c. elements, such as tungsten and molybdenum. Also, there were no signs of bright zone-line

decorations under the imaging conditions used. Oxidised specimens showed much less regular image contrast, and after the oxide layers had been removed by field evaporation, the metallic substrate still exhibited a somewhat irregular, spotty appearance.

AP mass spectra obtained from the oxide layer on a specimen heated in air for 1 hour at 473 K, and from the underlying metallic substrate of the same specimen, are shown in figures 2a and 2b respectively. Spectra from oxide films showed many complex ions, mainly oxide and hydroxide species of vanadium, in a variety of different charge states. The predominant charge state for the metal was the 2+ species.

In order to investigate the nature of the metal-oxide interface in more detail, AP analyses through the oxide films were represented in the form of ladder diagrams, in which the collection of an oxygen atom is shown as a vertical step, while the collection of a vanadium atom is shown as an increment along the horizontal axis of the diagram. Data obtained after oxidation for 24 hours at 298 K, 1 hour at 373 K, and 1 hour at 473 K are illustrated in figures 3-5 respectively. From the slopes of the resulting curves, the oxygen-to-metal ratios of individual regions of the films can be calculated. In each case, from the initial slope of the curve, the oxygen:metal ratio in the outer region of the oxide film was found to be about 1.5:1, corresponding to an oxide composition of V_2O_3 . This is in good agreement with conclusions based on other, less direct, experimental techniques such as electron diffraction [7]. There is also some evidence of a transition region, several atoms layers thick, and situated beneath the outer oxide layer, where the average oxygen concentration is approximately 10 atomic percent. If this is indeed a distinct phase, it would appear to correspond to the formation of the alpha-prime suboxide, V_9O , which is reported to have a stable existence only below about 775 K [8]. Immediately beneath the oxide layer, the metallic vanadium substrate was found to contain approximately 1 atomic percent of oxygen. These observations are best illustrated in figure 5 (oxidation at 473 K for 1 hour). Here the ladder diagram has been divided into three regions.

- Region I: Corresponds to the formation of the surface oxide, V_2O_3 .
Region II: Corresponds to the transition region, approximately V_9O .
Region III: Corresponds to the substrate metal containing approximately 1% dissolved oxygen.

Specimens oxidised at all three temperatures, (298, 373 and 473 K) showed closely similar overall patterns of behaviour, although the oxide films formed at the highest temperature were appreciably thicker than those formed at lower temperatures. Non-oxidised samples showed lower solute contents in the substrate than oxidised ones (approximately 0.2 at.% each of carbon, nitrogen and oxygen).

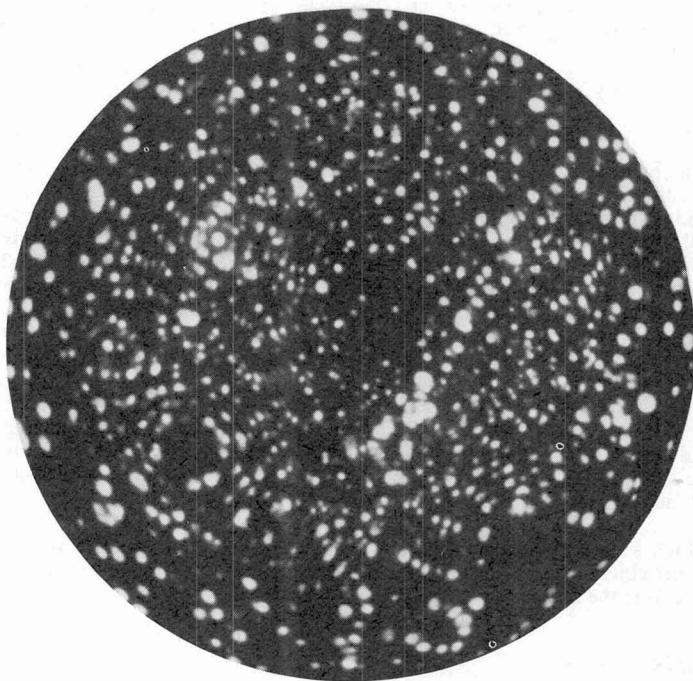


Figure 1. Field ion micrograph of vanadium showing a high angle grain boundary, decorated with brightly imaging impurity atoms.

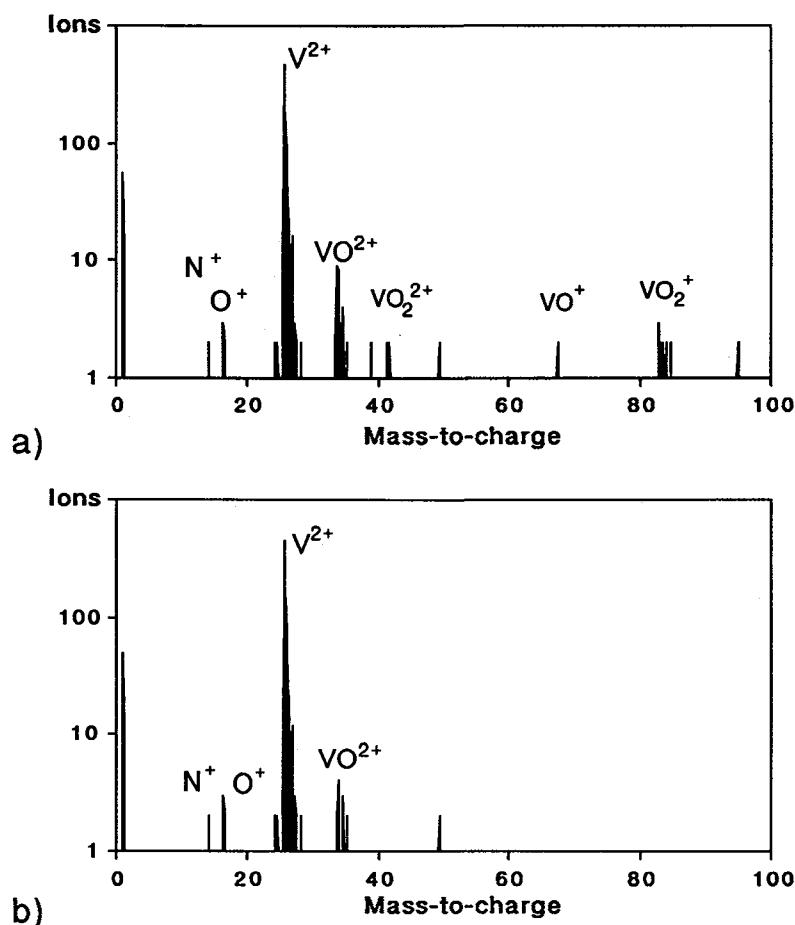


Figure 2. AP mass spectra from a specimen heated in air for 1 hour at 473K: a) oxide layer and b) metallic substrate.

One as-prepared specimen, which had not been subjected to an oxidation treatment, was found to contain a high angle grain boundary in the apex region, as shown in figure 1. Atom probe analyses were recorded with the probe hole aperture centred on the interface, and with the aperture displaced by approximately 2 nm to one side. The spectra obtained from the boundary and from the nearby matrix, are shown in figures 6a and 6b respectively, and the results are tabulated below. It is clear that the boundary is enriched in both oxygen and carbon compared to the surrounding matrix.

TABLE: ANALYSIS OF VANADIUM GRAIN BOUNDARY

Analysis position	Compositon (at% \pm 1 s.d.)			
	V	C	N	O
Centred on boundary	94	3.4 ± 0.6	0.3 ± 0.2	2.3 ± 0.5
2nm from boundary	98	1.6 ± 0.4	0.20 ± 0.15	0.20 ± 0.15

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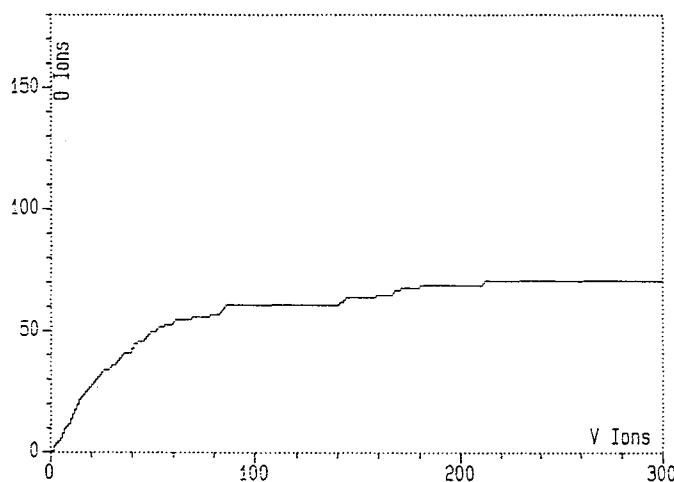


Figure 3. Ladder diagram for vanadium specimen oxidised for 24 hours at 298 K.

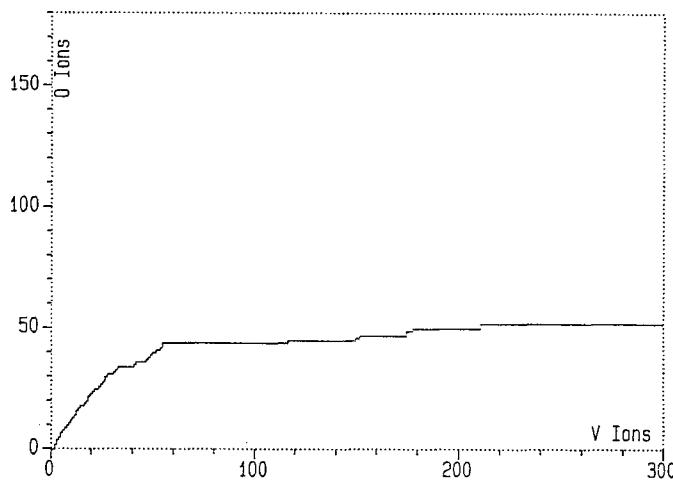


Figure 4. Ladder diagram for vanadium specimen oxidised for 1 hour at 373 K.

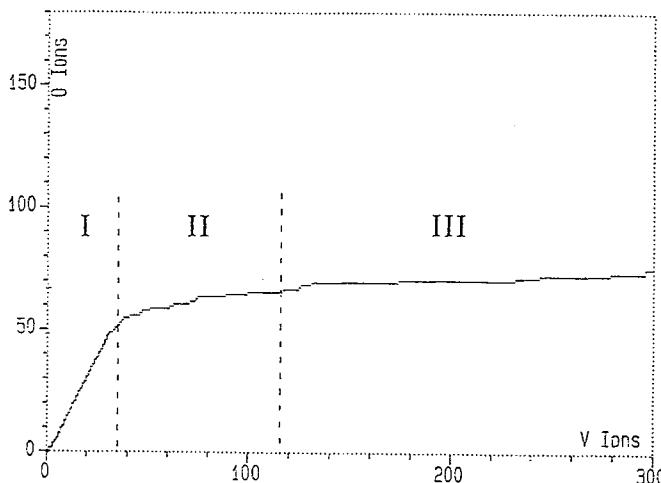


Figure 5. Ladder diagram for vanadium specimen oxidised for 1 hour at 473 K.

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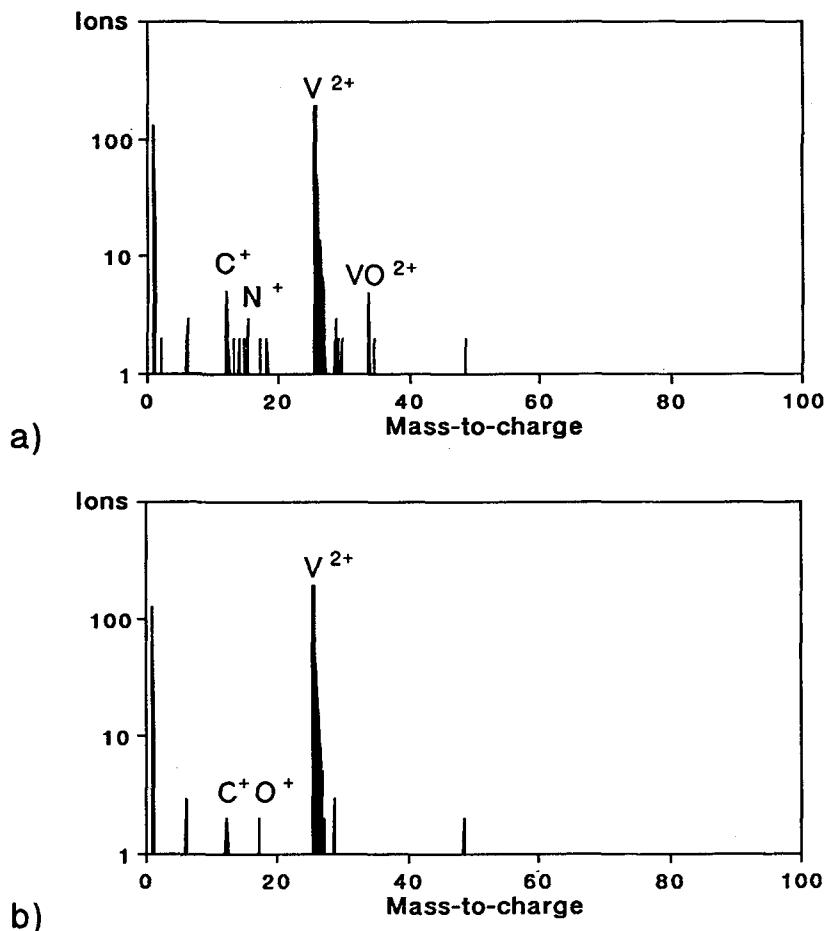


Figure 6. AP mass spectra from the grain boundary in a vanadium specimen: a) on the boundary, b) 2 nm to one side of the boundary region.