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A FIM atom probe study of vanadium oxidation

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Abstract. Vanadium specimens have been prepared and imaged for the first time in the field ion microscope. The composition of oxide films formed on vanadium at temperatures between 290 and 473 K has been determined by atom probe microanalysis. It is shown that the outer oxide film has a composition close to V_2O_3 in this temperature range, and that an intermediate layer of suboxide of composition approximately V_9O forms between the outer oxide and the metallic substrate. Appreciable solubility of oxygen in the vanadium metal matrix is also observed.

The oxidation behaviour of vanadium is of interest both because of the wide range of oxide phase known to exist, and because the formation of the oxide film is accompanied by appreciable dissolution of oxygen in the underlying metal [1]. We have used field ion microscopy (FIM) and atom probe (AP) microanalysis to study the oxide–metal interface in this system on the atomic scale.

To the best of our knowledge, vanadium had never previously been imaged in the FIM. We successfully prepared specimens by electropolishing vanadium wire of diameter 0.1 mm in a mixture of methanol and concentrated sulphuric acid (six parts to one by volume) at a voltage of 6.5 V. This solution had been used previously for the preparation of thin foils of vanadium for electron microscopy [2]. Field ion imaging was carried out in a Ne–10% He gas mixture at 40–50 K.

Oxidation of previously field-evaporated FIM specimens was carried out in air at 1 atm pressure and at temperatures of 290, 373 and 473 K. 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 (see figure 1). From the slope of the resulting curve, the oxygen : metal ratio of any region of the film can be calculated. In each case, 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 indirect deductions based on other experimental techniques [3]. However, we also find evidence of a second region, several atom layers thick, and situated beneath the outer oxide layer, where the concentration of oxygen is approximately 10 at.% This would appear to correspond to the formation of the α' suboxide phase (V_9O), which is reported to have a stable existence only below about 775 K [4].

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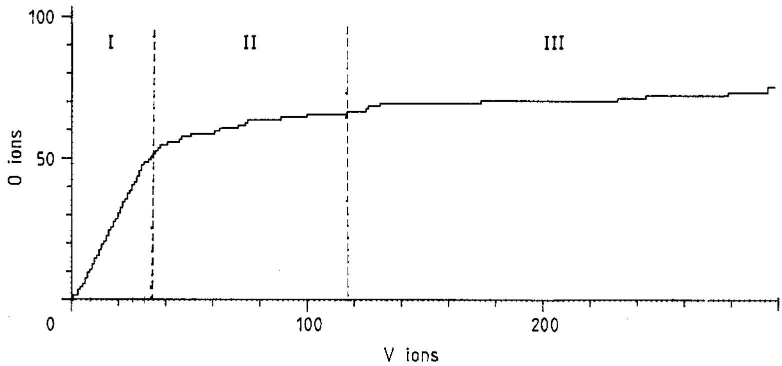

Figure 1. A 'ladder diagram' representing the composition of an oxide film formed on vanadium after exposure in air for 1 h at 473 K. Three regions of different slope are evident: I is the outer oxide (V_2O_3), II is an inner suboxide (approximately V_9O), and III is the substrate metal, which contains about 1% dissolved oxygen.

Beneath the suboxide layer, the metallic vanadium substrate was found to contain approximately 1 at.% of oxygen, irregularly distributed throughout the matrix. This concentration appeared to be independent of any oxidation treatment given to the specimens, and is believed to have been introduced into the material during its manufacture into fine wire.

We conclude that the low-temperature oxidation of vanadium is a two-stage process, involving the formation of both a stable outer oxide (V_2O_3), and suboxide (V_9O) at the metal interface.

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