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THE OXIDATION OF THIN CHROMIUM FILMS*

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1. INTRODUCTION

The kinetics of growth of oxide films at temperatures below 400 °C can often be represented by a logarithmic type of growth law[1]. While this is an established experimental fact, there is no clear agreement as to the mechanism which is responsible for this behaviour. Since kinetics alone are insufficient to establish a reaction mechanism, it is necessary to carry out other mechanistic experiments. This paper describes some experiments of this type for chromium.

Essentially two lines of research were pursued. The first was to investigate the reaction mechanism by determining over a range of oxidation temperatures from 100° to 450 °C the effect on the oxidation rate of various perturbations: applying an electric field across the growing oxide layer; injecting traces of iodine into the oxygen atmosphere; and rapidly altering the oxygen pressure over the oxidizing metal. The second was to examine the structure and composition of the oxide by electron diffraction. Although chromium has one of the most protective oxides of all metals, its oxidation at low temperatures has been little studied. This particular investigation is of the oxidation of evaporated chromium films, which can be prepared reproducibly with a relatively clean surface.

2. EXPERIMENTAL

The interface at which the oxide grows, and hence the diffusing species responsible for the oxide growth, was determined by the resistance marker technique[2].

The rate of the oxidation reaction was followed by measuring the rate of increase of resistance of a thin (10–50 nm) film[3] which had been evaporated onto a soda glass substrate at 300 °C. Electrical contact to the film was made via a pair of thicker (100 nm) chromium contacts which were deposited across the ends of the thin film. The evaporations were carried out at a rate of about 2 nm s^{-1} in a conventional vacuum line at pressures of less than 10^{-6} torr. The source was an electroplated tungsten filament which had been outgassed both before and after plating. To carry out the experiments in which an electric field was established across the growing oxide layer, it was necessary to evaporate a porous platinum layer[2] across the oxide growing on the chromium film.

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The resistance along the chromium film was determined by a two-electrode technique in which the potential drop across the film was measured when a constant current of about 7 μA was passed through the film. This corresponds to a current density of between 10 and 100 A cm^{-2}. In the field experiments, it was found necessary to restrict the field current to a density of less than 10^5 A cm^{-2}. Above this value, the oxide appeared to fail.

In all experiments other than the pressure dependence experiments, the reactions were carried out in a stream of purified oxygen at atmospheric pressure. Iodine vapour to a concentration of about 0.03 mol.% could be introduced into the oxygen by passing it over iodine solid.

In the electron microscope investigation, the films were stripped from the glass using 10% hydrofluoric acid, mounted on carbon-coated copper grids and examined in a Siemens Elmiskop 102 at 100 kV.

3. RESULTS AND DISCUSSION

3.1. *Chromium films*

The metal films consisted of very small crystallites approximately 3 nm across. Diffraction patterns of unoxidized metal films gave strong rings corresponding to chromium only. Chemical analysis showed that the concentration of tungsten was less than 10^{-3} wt.%. The films were ohmic in an argon atmosphere between 25° and 400 °C and the temperature coefficient of resistance was similar to that reported previously[4].

3.2. *Marker experiments*

The resistance between a porous platinum marker film and a partially oxidized chromium film remained constant during further oxidation over the temperature range 225°–425 °C. This implies that the oxide was growing at the oxygen-oxide interface by the transport of cations or cation vacancies. When a temperature gradient was applied across the oxide, a potential developed consistent with the oxide being p type. Thus the thermally grown oxide is probably a p-type metal-deficient semiconductor; Cr_2O_3 has been reported to be of this type[1].

3.3. *Kinetics*

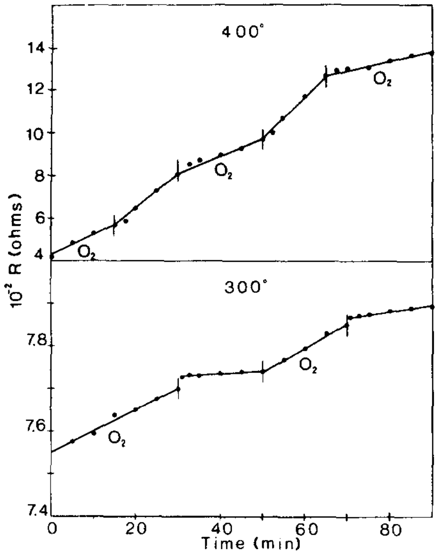
As discussed previously[5], the technique of measuring the rate of increase of resistance of a thin evaporated film is not ideal for determining the absolute kinetics of an oxidation reaction. It is good, however, for comparing the rates of reaction for two different sets of reaction conditions. When the rate of the reaction was measured as a function of temperature, it was found that there was a sharp increase in oxidation rate at about 350 °C. It is assumed that this temperature marks a logarithmic-parabolic rate law transition since it has been reported that the oxidation rate at 400 °C is parabolic, and transitions of this type have been reported for other systems[2].

3.4. *Field experiments*

In all field experiments, an increase in oxidation rate was noted when the oxygen-oxide interface was made negative with respect to the oxide-metal interface. A reversal in the polarity caused a decrease in oxidation rate. The field effect is consistent with ion transport across the growing oxide as the rate-determining step in the reaction mechanism. As the oxide thickens, the effect of the field for a constant field producing current diminishes. One explanation of this is that the oxide is growing up through the interstices of the porous platinum layer. The applied field will then only affect that portion of the oxide below the platinum, which will be a decreasing fraction of the total thickness. The rate-determining step is the same above and below 350 °C, despite the change in oxidation rate.

3.5. *Iodine doping experiments*

When iodine was introduced into the oxygen, two distinct effects were observed, as shown in Fig. 1. Below an oxidation temperature of about 350 °C, the effect of iodine was to cause an immediate sharp increase in resistance followed by a decrease in oxidation rate. Presumably the sharp increase in resistance is caused by ionization of iodine, which withdraws electrons from the metal to the oxide surface. Above an oxidation temperature of 350 °C, iodine causes an increase in oxidation rate after a short induction period. This change in the effect of iodine on the reaction rate is clearly an indication of a change in the reaction mechanism which is paralleled by an observed change in reaction rate. Since the reaction below 350 °C is probably logarithmic in type and is controlled by slow ion transport, the Mott–Cabrera mechanism which has been established for aluminium^5 may be applicable. However, the adsorbed iodine should



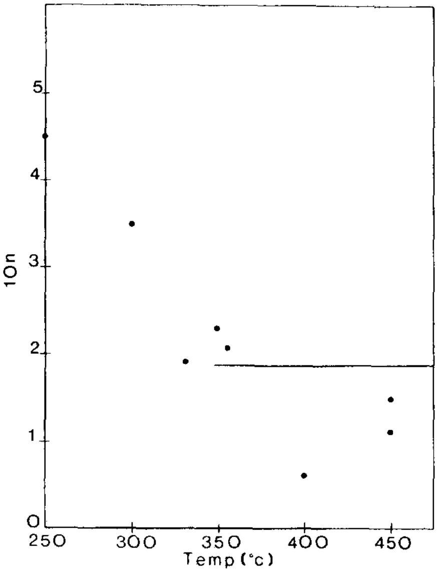


Fig. 1. The effect of iodine doping on the oxidation rate at 300 °C and 400 °C. The sections marked O_2 are oxidation in pure oxygen; the unmarked sections are for oxidation in iodine-doped oxygen.

Fig. 2. A plot of the exponent n as a function of oxidation temperature. The line is the expected pressure dependence assuming the oxidation conforms to a Wagner mechanism.

increase the field and hence the rate. The observed decrease may be due to blanketing of the surface. In the region above 350 °C, the change in rate is consistent with slow ion diffusion and Hauffe's doping rule[1].

3.6. Oxygen pressure dependence

If the oxygen pressure over the oxidizing metal is changed rapidly, there is a corresponding change in the oxidation rate. This effect may be quantified by calculating n in the equation

$$\frac{R_1}{R_2} = \left(\frac{P_1}{P_2}\right)^n$$

where R_1 and R_2 are the oxidation rates corresponding to the pressures P_1 and P_2. As with aluminium[5], n decreases during the course of the reaction, and diminishes as the temperature increases. This is shown in Fig. 2. Also included in Fig. 2 are the expected pressure dependences, calculated assuming that the Wagner theory is applicable[1], as seems likely above 350 °C. The scatter in the results is too great for the fit to be described as good.

3.7. Oxide structure

In the electron microscope, the oxide film formed at oxidation temperatures below about 300 °C appeared to be largely amorphous. The diffraction pattern consisted of diffuse rings corresponding to chromium metal and Cr_2O_3. At an oxidation temperature of 400 °C, the product layer was initially amorphous but some oxide crystals were observed to form. Chemical tests suggest that the oxide contains chromium(VI) as well as chromium(III).

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