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Surface oxidation of ferrochromium thin films

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Oxidation kinetics of ferrochromium (Cr 72 wt %, Fe 28 wt %) films of different thicknesses were followed at room temperature in the laboratory atmosphere by noting the conductivity of vacuum-deposited films as a function of time for a period of 150 minutes. A logarithmic oxidation growth with two different rate constants is obtained. X-ray diffraction analysis of 50 nm thick films at various temperatures indicated a solid solution of chromium and iron–chromium oxides. A decrease of lattice spacing observed with temperature increase is attributed to composition/structural changes near the metal–oxide interface. Microstructures of these film surfaces reveal the formation of bluish green crystals of Cr_2O_3 at 773 K.

1. Introduction

Most metals tend to form oxides in oxidizing atmospheres and this tendency increases with temperature. The reaction rates in most cases are affected by the form in which the reaction products are formed. One way to understand the oxidation behaviour of alloys is to measure their oxidation kinetics [1–4]. The oxidation properties of Fe–Cr alloys rich in chromium have been the subject of considerable study because of their excellent resistance to corrosion. These alloys are known to form continuous layers of scales of Cr_2O_3 during oxidation in air [5]. The scales include small amounts of complex oxides whose composition depends on the nature of the minor elements in the alloy. The present study deals with the oxidation behaviour of ferrochromium thin films of different thicknesses. The oxidation kinetics of the alloys oxidized at room temperature in the laboratory atmosphere exhibited a two-stage logarithmic rate law for films having initial resistances in the range 100 to 700 ohms (6 nm to 0.5 nm thick). Investigations were also made on 50 nm thick films at different temperatures using X-ray diffraction. Optical microscopic studies of 10 and 50 nm ferrochromium thin films have also been investigated at different temperatures.

2. Experimental details

The alloy films with the composition Cr 72 wt %, Fe 28 wt % are prepared on glass substrates under a vacuum of 10^{-5} torr using tungsten baskets. The rate of oxidation was monitored by noting the resistance, R, of the film as a function of time. Pre-evaporated aluminium electrodes were used for electrical contacts. Oxidation is carried out by admitting air into the vacuum chamber. The experiment is repeated for films in the range 0.5 to 6 nm thick. X-ray diffraction (XRD) experiments were carried out for films of different thickness of 50 nm or more. The oxidation studies were carried out in the laboratory atmosphere after annealing the samples for 2 h at 303, 473, 673 and 773 K. These films were investigated using an X-ray diffractometer (Philips Model 1701) in the range 2θ from 20° to 60° with Co K_α radiation. Optical morphology of 10 and 50 nm films oxidized at these temperatures after twelve months is photographed using a Leitz Ortholux microscope.

3. Results and discussions

3.1. Oxidation kinetics

When a film surface is exposed to an atmosphere containing oxygen, the oxygen will be absorbed and results in the formation of one or more monolayers of oxides, i.e., cations from the metal probably arrange themselves in an appropriate fashion to form an oxide layer. The rate of oxide thickening depends on factors such as the rate at which the cations in the metal detach themselves from neighbours, the rate at which the anions can be formed from molecules of non-metal or the rate of arrival of anions at the metallic surface. To obtain the kinetics of oxidation of vacuum-deposited films it is necessary to consider the rate equation which can be applied to the oxidation process [6]

$$x^n = Kt$$

where x is the film thickness ($x \propto 1/R$, where R is the film resistance in ohms) at time t and K is the rate constant. The resistance of oxidized film is attributed to the resistance of the alloy film and that of the oxide film. Plots of $\log(1/R)$ against $\log(t)$ for films of initial resistance ranging from 700 to 100 ohms (corresponding to 0.5 to 6 nm thickness) are shown in Fig. 1. The plots indicate that for ferrochromium thin films the oxidation reaction proceeds logarithmically with different rate constants in the regions PQ and QR. As the thickness of the film increases the time for reaching saturation of oxidation decreases and the knee point Q (Fig. 1a) shifts towards the right. Also, the rate

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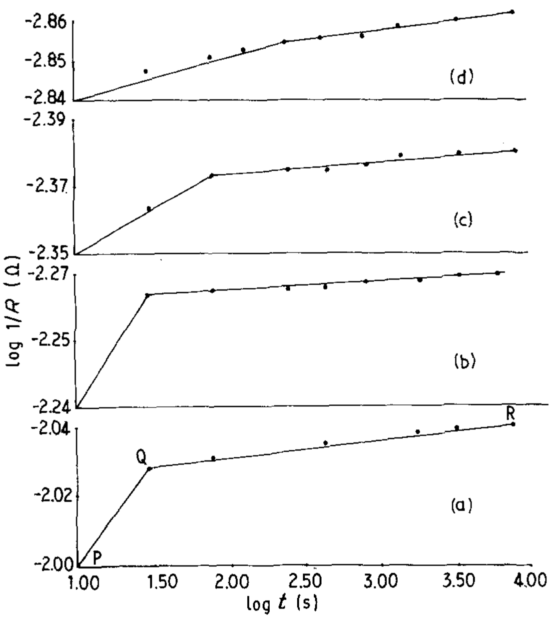

Figure 1 Plot of log(1/R) against log(t) for ferrochromium thin films with initial resistance (a) 102, (b) 174, (c) 228 and (d) 698 ohms.

constants become closer and closer as thickness decreases.

Fig. 2 shows the variation of growth rate in the region PQ and knee point Q as a function of film thickness. As a first approximation, the growth rate can be considered to be directly proportional to the number of atoms participating in the oxidation process. As the film thickness increases, this number increases exponentially and reaches a saturation value with the formation of a few atomic layers. Hence, the growth rate also increases with film thickness, exponentially at first, until it reaches a constant value. Further, as the thickness increases from zero to a few atomic layers the formation time for the protective oxide layer decreases and hence the time to reach the point Q decreases. For very thin films (Fig. 1d), this protective cover is not very effective and hence the two growths are equal.

The corrosion resistance of Fe–Cr alloys depends on the selective oxidation of the constituents. The simple example is Fe–Cr alloys with higher Cr content. Caplan and Cohen showed that for iron alloys with Cr content greater than 13% the protective oxide formed is Cr_2O_3 with little dissolved Fe_2O_3 [7]. For ferrochromium films the initial oxidation proceeds with the formation of Fe_2O_3 and Cr_2O_3. Multilayer oxide formations occur around 3.25 nm (Fig. 2) corresponding to the formation of Fe_2O_3 and Cr_2O_3. After saturation, the protective oxide scale Cr_2O_3 covers the surface. In the region PQ, chromium and iron ions are active for oxidation forming Cr_2O_3 and Fe_2O_3. As the oxide layer thickens it becomes increasingly difficult for these cations to move towards (or anions inwards) sufficiently quickly. Also the minor elements get dispersed in the alloy as the oxide film grows. Hence the rate changes beyond Q.

3.2. X-ray diffraction analysis

Fig. 3 shows the X-ray diffraction scan of ferrochromium thin films on glass substrates subsequently annealed for 2 h at 303, 473, 673 and 773 K. The X-ray data are compared with ASTM card file data and reference spectra of powder samples of Fe_2O_3 and Fe_3O_4 [8]. The XRD analysis of thin films is usually different from that of randomly oriented power samples. In thin films the number of observable peaks is likely to be small or the intensity may differ from that of powders [9]. The XRD scan at 303, 473 and 673 K gave only two peaks which are attributed to Cr_2O_3 and Fe_2O_3. Additional peaks appear at 773 K showing the formation of iron–chromium oxides. As the temperature increases from 303 to 673 K oxidation proceeds discontinuously forming Cr_2O_3 and Fe_2O_3. At 773 K mixed spinel oxide $FeCr_2O_4$ is formed.

When a metal is heated in an oxidizing environment fast oxidation occurs initially and is replaced by a stable oxide. Annealing increases the cations at the metal–oxide interface and anions at the oxide–gas interface to segregate into the film which may lead to structural or compositional changes at the metal–oxide interface. Annealing causes rearrangement of the film which results in the formation of oxide grain boundaries which are an easy path for ion migration, promoting oxide islands and results in the speedy

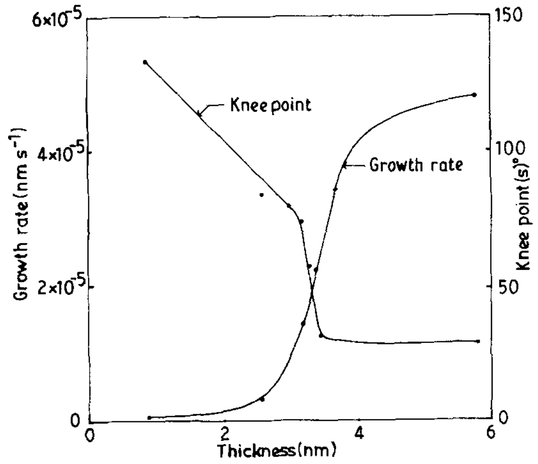

Figure 2 Variation of growth rate and knee point with film thickness.

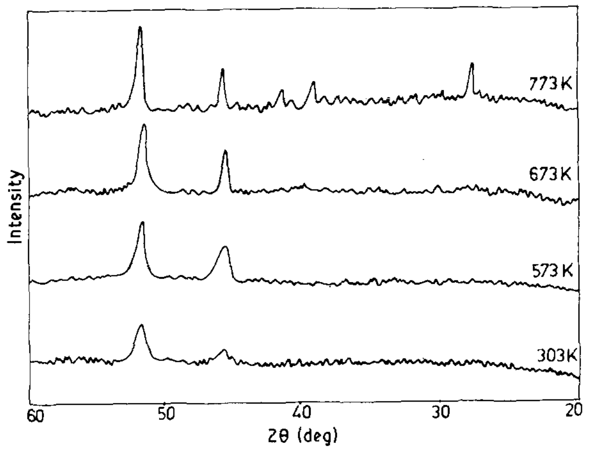

Figure 3 XRD scan of ferrochromium films (50 nm) oxidized at 303, 473, 673 and 773 K.

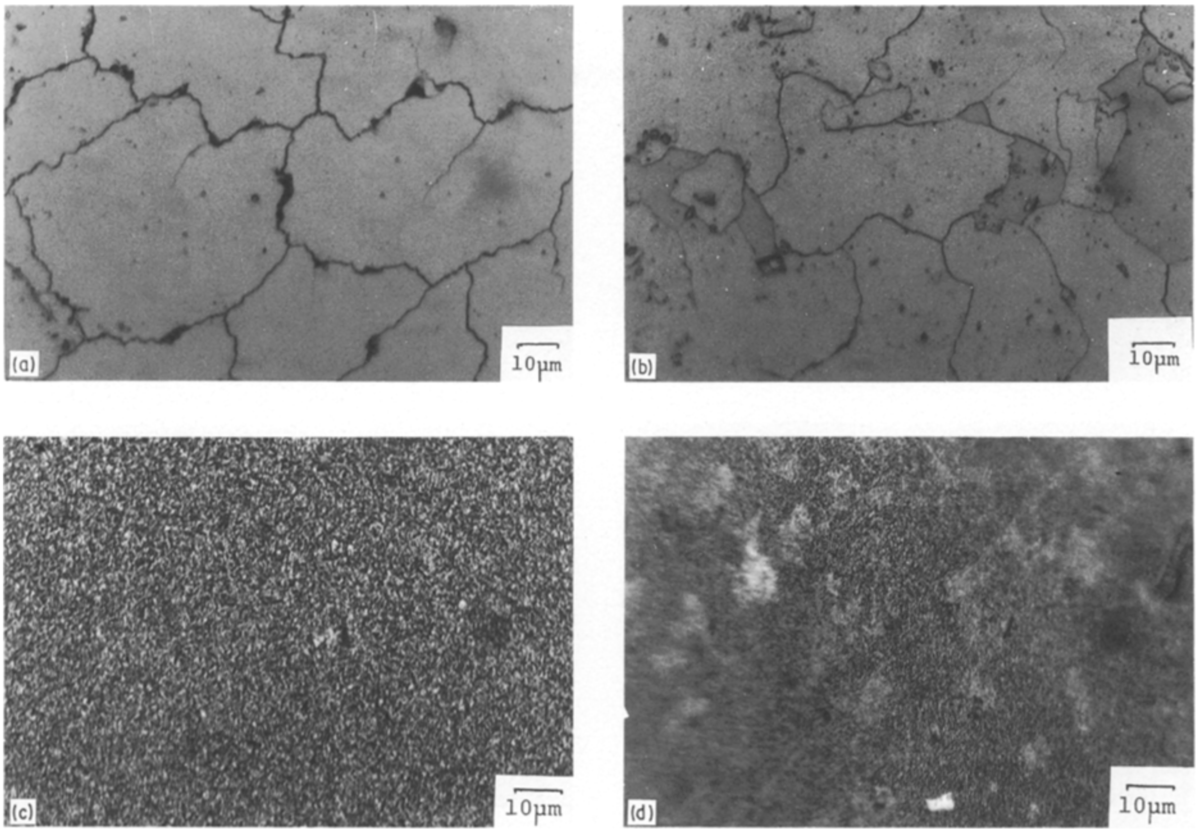

Figure 4 Surface morphology of 10 nm thick ferrochromium films at (a) 303, (b) 473, (c) 673 and (d) 773 K.

formation of oxides at higher temperature. The gradual decrease of *d* spacing observed for peaks corresponding to Cr_2O_3 and Fe_2O_3 ($2\theta \approx 52°$ and 46°) as the temperature increases is attributed to these changes occurring at the metal–oxide interface. At 303 and 473 K the peaks are broad, indicating the amorphous nature of the oxides formed. The presence of $FeCr_2O_4$ could not be detected at low temperatures. Annealing tests carried out at these temperatures using Raman spectroscopy indicate the presence of $FeCr_2O_4$ at low temperatures. Also, the film is amorphous at 303 K and begins to crystallize at about 773 K [10]. The intensity increase observed for Cr_2O_3 with temperature can be explained in terms of its crystallization.

TABLE I X-ray diffraction data and identification of oxides of ferrochromium thin films at different temperatures

Temperature (K)	Lattice spacing (nm)	Identification
303	0.205	Cr_2O_3
	0.230	Fe_2O_3
473	0.204	Cr_2O_3
	0.229	Fe_2O_3
673	0.203	Cr_2O_3
	0.228	Fe_2O_3
773	0.203	Cr_2O_3
	0.228	Fe_2O_3
	0.251	$FeCr_2O_4$
	0.269	Fe_2O_3
	0.367	Cr_2O_3

3.3. Oxide morphology

Studies of the microstructure of vacuum-deposited thin films in relation to the nucleation and growth have been reported by several authors [11, 12]. Thin film formation occurs by the nucleation and growth of small three-dimensional islands which may coalesce by impingement and necking. During the growth process, structural transformation, which may not occur in the bulk, may occur in thin films because of the physical dimension and geometrical shape of the films. The crystallite size is expected to increase with temperature, rate of deposition, velocity of vapour atoms, smoothness of the surface, etc.

The growth and development of surface structure of ferrochromium thin films at 303, 473, 673 and 773 K for films of about 10 and 50 nm thickness are shown in Figs 4 and 5. A network pattern with dark spots is observed for 10 nm thick films at 303 and 473 K. The mirror finish of these films changes to a brown–grey colour after twelve months of oxidation. At 673 K a greenish tint is visible in the brown background indicating the presence of Cr_2O_3 and Fe_2O_3. At 773 K mixed colours of green, red and brown are observed. Some regions show a reddish-orange tint indicating the formation of $FeCr_2O_4$. The as-deposited films (50 nm) were grey in colour and then changed to light brown after twelve months of oxidation in the laboratory atmosphere. For the heat-treated samples colour changes are observed as the temperature increases. At 773 K the intensity of bluish-green colour increases, probably due to the increase of oxide growth of microcrystallites confirming the crystalline nature of the alloy at higher temperature.

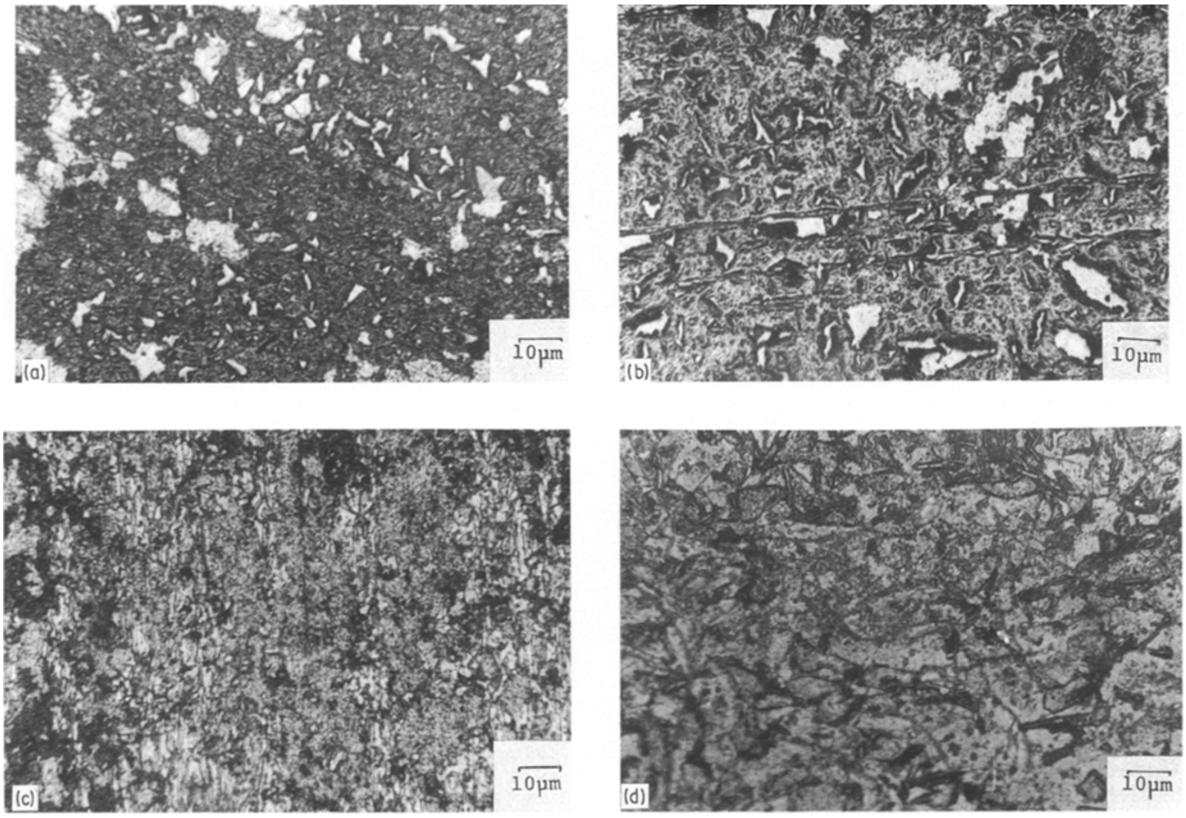

Figure 5 Surface morphology of 50 nm thick ferrochromium films at (a) 303, (b) 473, (c) 673 and (d) 773 K.

4. Conclusion

A logarithmic oxidation growth with two different rate constants is obtained for ferrochromium thin films. A decrease of lattice spacing observed for 50 nm films at various temperatures is attributed to the compositional/structural changes near metal–oxide interface. Optical micrographs of 10 and 50 nm films indicate crystallization at 773 K.

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