

INFLUENCE OF ZINC IMPURITIES ON THE OXIDATION BEHAVIOUR OF ALUMINIUM THIN FILMS

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ABSTRACT

The influence of zinc impurities on the oxidation rate of aluminium thin films has been studied from conductivity measurements at room temperature. It is found that the presence of zinc in aluminium changes the oxide growth rate of aluminium from an asymptotic to a logarithmic one.

INTRODUCTION

THE interaction of oxygen with aluminium thin films at low temperatures has been studied by different authors using a variety of techniques.¹⁻⁷ However, only a few studies have been made on the influence of impurities on the oxidation of metallic thin films. In this paper, a preliminary study is reported on the influence of zinc as an impurity in the oxidation behaviour of aluminium thin films under laboratory conditions. With different percentages of zinc in aluminium, the rate of oxidation is noted. Studies of this type can give a better understanding of the often complex mechanism of oxidation and help to find ways of improving oxidation resistance of metal films by alloying.

EXPERIMENTAL

Aluminium (99.9%) thin films with zinc (99.9%) impurities are prepared by the method of simultaneous evaporation of the elements from a single tungsten boat.⁸ The film is deposited on glass slides under a vacuum of the order of 10^{-5} torr. To get metal films of different weight percentage of impurity, different amounts of the impurities are taken with a fixed quantity of aluminium. In each case the rate of evaporation is also maintained almost constant, so that the impurity present in the metal film is proportional to the amount taken for evaporation.⁹ The exact weight percentage of zinc was estimated from atomic absorption method. These thin films are allowed to oxidize under the laboratory conditions at $\sim 30^\circ\text{C}$. The percentage of impurity is varied from 1 to 30%. From the conductivity change, the rate of oxidation is noted for about two to three months. In the case of aluminium thin films, the oxide thickness can be assumed to be proportional to the negative of the reciprocal of resistance of the film.^{4,10} Hence, for each case the applicability of a particular rate equation is tested by plotting $(1/R)$ against the appropriate time⁴,

oxidation was found to proceed by the diffusion of interstitial cations⁷ and the growth follows an asymptotic law of the form,

$$x = x_1 [1 - A \exp(-Bt)], \quad (1)$$

where x is the thickness of the oxide at time t and x_1 is a constant depending on the oxide thickness. The oxidation ceases after a certain period of time determined by the constants A and B .

When zinc was introduced into the aluminium film, the growth rate changed to a logarithmic one and a plot of $(1/R)$ (where R is in Ω) against $\log t$ (t is in minutes) gives straight lines as in figure 1. The rate of oxidation of the mixture was very much greater than that of aluminium. In the case of aluminium alone, the oxidation comes to an end within an hour, whereas in Al-Zn system the oxidation continued even after two months.

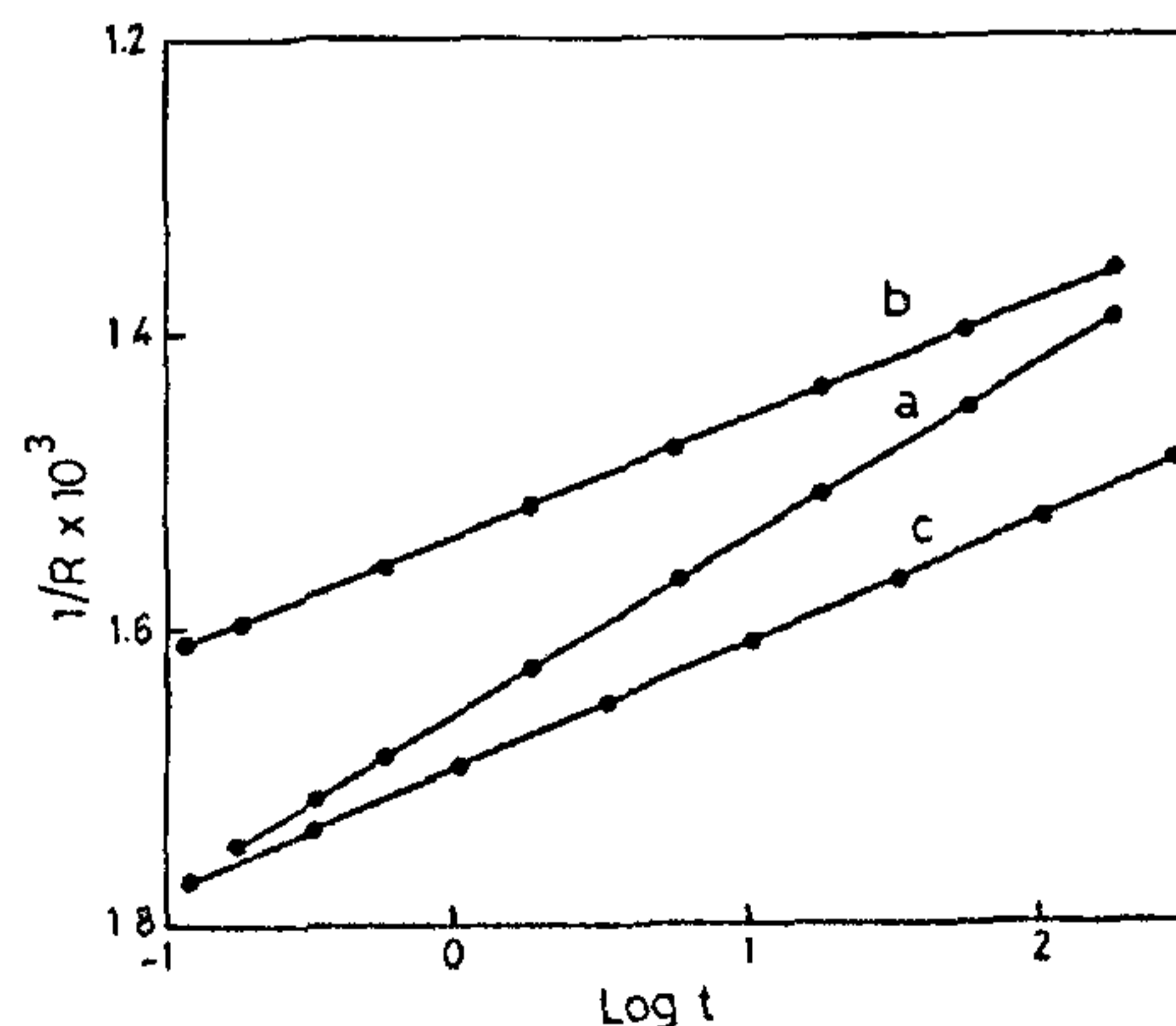


Figure 1. $(1/R)$ versus $\log t$ curve for the oxidation of aluminium with different weight percentages of zinc impurity: (a) 5.4%, (b) 16%, (c) (20)%.

RESULTS AND DISCUSSION

In the case of aluminium at room temperature, the

Aluminium oxide being an *n*-type oxide having excess cations, the introduction of elements of lower valency like zinc may be expected to increase the lattice defects in the oxide.¹¹ The increase in the lattice defect can enhance the rate of oxidation. Hence, the oxide thickness can reach a constant value more rapidly than in the case of pure aluminium. These rules based on valency alone are not enough to explain the present observation of oxidation continuing for long periods. Though the atomic radius of Zn is larger than that of aluminium, the lattice parameters favour its migration into the matrix as substitutional impurity. In fact, zinc can form solid solution with aluminium and at low temperatures zinc atoms can cluster together and form precipitates. At room temperature such clusters could not be observed from a study of surface structure using high power optical microscope. The surface of Al-Zn thin film was etched using suitable etchants and the etch pattern showed no clusters. Only the surface was found to be susceptible to the attack of etchant with prolonged oxidation. Figure 2 presents the etch pattern of Al-Zn system at the beginning of oxidation.



Figure 2 Etch pattern obtained for Al-Zn system at the beginning of oxidation ($\times 120$) (etchant used: alcoholic solution of sodium hydroxide).

Since atoms of zinc have larger radius, it requires larger energy for diffusion. Hence, at a constant temperature, the number of diffusing ions will be reduced in the Al-Zn system. In expression (1), for the oxide growth of aluminium, the constants *A* and *B*

among other factors depend upon the diffusion of ions. Thus, the introduction of zinc in aluminium, can considerably decrease the rate constants. When this happens the oxide growth takes place slowly and for short periods, the growth seems to be logarithmic. In addition to this, the introduction of zinc can modify the electric field set up across the metal-oxide, thus hindering the diffusion of cations. This can also reduce the rate constants and can lead to continued oxidation. Thus, the ionic size of the impurity and the modified electric field, across the metal oxide structure may be the two factors responsible for the change in the kinetics of the oxide growth.

The present results thus show that the addition of zinc does not improve the oxidation resistance of aluminium, but it prolongs the period of oxidation thus changing the oxide growth kinetics of aluminium from an asymptotic to a logarithmic scale.

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