Chapter IV

OXIDATION OF ALUMINIUM AT ROOM TEMPERATURE

4-1 Introduction 115
4-2 Kinetics of oxidation 116
4-3 Effect of an electric field on the oxidation of aluminium 124
4-4 Influence of magnesium on the oxidation of aluminium 140
4-5 Effect of zinc on the oxidation of aluminium thin films 154
4-6 Conclusion 162
OXIDATION OF ALUMINIUM AT ROOM TEMPERATURE

4-1 Introduction

A proper understanding of the nature of oxidation of aluminium and ways of improving its oxidation resistance is of great importance, due to its vast commercial and industrial use. The oxidation of aluminium has been the focus of both theoretical and experimental activity. The oxidation characteristics have been investigated both in the low and high-temperature regions and more sophisticated methods are being developed for the study of metal oxidation.
However, a complete knowledge of the mechanism of oxidation at low temperature is still lacking. Hence, an attempt is made to study the oxidation characteristics of aluminium thin films in the laboratory atmosphere and at room temperature (around 30°C). First, the kinetics of oxidation were investigated. Further studies were conducted by applying an electric field across the oxide and also by doping magnesium and zinc impurities.

4-2 Kinetics of oxidation

In the low temperature region, though a few rate experiments were done, different results have been obtained by different workers. For aluminium, there are inferences that oxygen is chemisorbed even at -183°C\textsuperscript{10}. At room temperature and one atmosphere pressure, oxygen reacts with aluminium to give oxide films of about 40Å thick. This has been studied theoretically by Mott\textsuperscript{11,12} who has suggested a logarithmic growth in terms of a slow process of electron tunnelling. Later, it has been interpreted in terms of a process of field induced cation migration through the oxide film giving an
inverse logarithmic growth law\textsuperscript{13,14}. In the case of evaporated aluminium films at low pressure of $10^{-3}$ to $10^{-2}$ torr at 20°C, a change over from place exchange to electron tunnelling has been observed by Eley and Wilkinson\textsuperscript{15} at an oxide thickness of 6 Å. A second change over at a thickness of 10 Å, to the inverse logarithmic law by cation migration has been suggested. The work of Boggio and Flumb\textsuperscript{16} has shown that the direct logarithmic law observed for thin evaporated films can be interpreted in terms of the Mott-Cabrera theory modified to include space-charge effects.

4-2.1 Experimental details

The experiment was carried out on pure Indal aluminium films of thickness about 100 Å. The film was deposited on a glass slide by evaporating the specimen from a tungsten basket under a vacuum of about $10^{-5}$ torr as described in sections 3-2 through 3-5. The film is exposed to laboratory atmosphere and the rate of oxidation was studied from the rate of change of resistance as explained in section 3-7.1
4-2.2 Results and discussion

For films of thickness of the order of 20 Angstroms, a random variation of resistance with oxidation was found to occur. But for films of thickness about 100 Angstroms, the conductivity decreased with time and within one hour attained a constant value. The conductivity $\sigma$ at any time $t$ can be represented as

$$\sigma = A \exp(-Bt) + \sigma_1$$  \hspace{1cm} (4.1)

where $\sigma_1$ is the constant value of conductivity, $A$ and $B$ are constants. The validity of equation 4.1 is well illustrated by a plot of $\log (\sigma - \sigma_1)$ vs. $t$ (figure 4-1). The constants $A$ and $B$ depend on the thickness of the film as well as on the evaporating conditions of the film.

The conductivity change can be related to the oxide growth in the following manner. If it is assumed that the evaporated aluminium can be regarded as thin isotropic metal sheet which oxidized on one surface only and obeys Ohm's Law, then it follows that the film resistance $R$ and oxide thickness $x$ are
FIG 4-1A LOG $(\sigma - \sigma_t)$ vs TIME GRAPH. INITIAL RESISTANCE OF THE SAMPLES ARE (a) 41.5 $\Omega$, (b) 43 $\Omega$, (c) 85.5 $\Omega$
FIG 4-1B LOG (\(\sigma - \sigma_i\)) vs TIME GRAPH. INITIAL RESISTANCE OF THE SAMPLES ARE (a) 35 \(\Omega\), (b) 60 \(\Omega\), (c) 30 \(\Omega\)
related by the equation

\[ x = \frac{\phi P L}{w} \left( \frac{1}{R_o} - \frac{1}{R} \right) \]  

(4.2)

\( \phi \) is the thickness of oxide derived from unit thickness of metal, \( P \) is the resistivity of the metal film, \( L \) is the length of the film between the contacts, \( w \) is the width of the film and \( R_o \) is the resistance of the film prior to oxidation. In deriving this equation it has been assumed that the resistivity of the oxide is very much larger than that of the metal, a condition which is certainly met by amorphous alumina and aluminium\(^{17}\). From this equation, it is clear that the oxide thickness is proportional to \(- (1/R)\), i.e.,

\[ x \propto - \frac{1}{R} \]  

(4.3)

so that equation 4.1 gets modified as

\[ x = x_i \left\{ 1 - A' \exp(-Bt) \right\} \]  

(4.4)

where \( A' \) is a new constant taking the proportionality by the oxygen diffusion of concern, and at low temperature, grain boundaries provide easy
constant of equation (4.3) also into account. Equation (4.4) shows that the oxide film thickness obeys an asymptotic growth rate, and the time taken to grow to the limiting thickness of the oxide film depends on the constants $A'$ and $B$. After this characteristic time, the growth of the oxide stops.

An asymptotic growth rate for oxidation of metals has been proposed by Evans, where the reaction is controlled by the diffusion of ions through pores which get healed up or blocked as oxidation progresses. Except for certain aluminium alloys as asymptotic growth is not observed for bulk materials. In the present case the growth rate can be explained on a similar line as proposed by Evans. The aluminium film is deposited on glass substrates (i.e., an amorphous substrate) kept at room temperature. Hence, we may expect a polycrystalline film with crystal axes randomly oriented with respect to the substrate.

The oxidation of aluminium is mainly controlled by the outward diffusion of cations, and at low temperature, grain boundaries provide easy
paths of diffusion for these cations. As oxidation proceeds, the oxide formed blocks these grain boundaries. Depending upon the amount of oxygen consumed, these easy paths of diffusion get blocked giving rise to an asymptotic growth resembling the one proposed by Evans.

The rate of oxidation of thin films is determined by several factors such as structure and microstructure of the metal film and its oxide, the nature of the substrate surface and the environmental factors. Further, it is difficult to deposit thin films under the same evaporating conditions. Hence, no two films formed at different times can be expected to have the same structure, and hence the same oxidation rate. Also, the number of grain boundaries, the grain size and the number of adsorbed species can vary for different films. All these factors can change the rate constants $A'$ and $B$ of equation (4.4) which explains the change of slopes of the curves for different films (figure 4-1).
4-3 Effect of an electric field on the oxidation of aluminium

The mechanism of oxidation of metals cannot be fully understood from the study of kinetics alone, since different mechanisms can result in the same rate law $^{21,22}$. Hence to understand more about the nature of oxidation, it is necessary to carry out additional experiments. For aluminium in the temperature range between 50 and 400°C, a detailed investigation of the mechanism of oxidation has been carried out from the influence of an applied electric field $^8$ and also from the effect of the pressure changes of oxygen $^7$. At room temperature such a detailed study is still lacking, though a few experiments were done $^{15,16}$. Hence the reaction mechanism of oxidation for aluminium at room temperature is studied from the influence of an applied field across the growing oxide layer.

4-3.1 Experimental details

The experiment was carried out on evaporated aluminium thin films the thickness of which ranged between 100 to 500 Å. The film was kept either at
a positive or at a negative potential with respect to
the ground using a circuit arrangement shown in
figure 3-6. A capacitive field was developed across
the metal-metal oxide structure, as the metal was
oxidised, and the magnitude and direction of the field
depended on the potential applied to the film. For a
potential of 200V the voltage across the metal-oxide
was \(1.2 \pm 0.1\) volt. In a particular experiment, the
field was kept constant. At regular intervals, the
field was switched on and off, and the rate of oxida-
tion was noted both in the presence and absence of
the field. Thus a comparison for the rate of oxidation
with and without an applied field was made for the same
metal film. The experiment was repeated for different
field strengths corresponding to an applied voltage
30 to 200 volts. The experiment was repeated revers-
ing the direction of the field. To check that the
results were not due to the effect of the current
passing through the film, the experiment was repeated
for different values of current ranging from 25 \(\mu\) A to
3 mA. Also keeping the film at earths potential and
passing current at regular intervals, the rate of
oxidation with and without the passage of current was
compared.
4-3.2 Results and discussion

In general, a negative potential has an accelerating effect (figure 4-2) and a positive potential has a retarding effect (figure 4-3) on the oxidation rate of aluminium irrespective of the film thickness (the thickness of the metal film varied from 100 to 500 Å). When the metal film is at a negative potential, the direction of the field is such as to assist only the flow of positively charged cations from the metal-metal oxide interface, and it can neither assist the diffusion of negatively charged electron from the metal-metal oxide interface nor the flow of negatively charged oxygen ions through the oxygen-oxide interface. Thus, if the rate-controlling factor of the oxidation mechanism is the flow of metal ions, an increase in the rate of oxidation can be expected when we apply a negative potential to the film. By the same argument we can say that the application of a positive potential can decrease rate of diffusion of cations and hence the rate of oxidation. Thus, the observed results can be explained based on the fact that the rate of oxidation is controlled by the flow of cations from the metal to the oxide surface.
FIG 4-2A COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING NEGATIVE POTENTIALS OF (a) 170V, (b) 150V, (c) 200V. MINUS SIGN INDICATES THE PERIOD OF APPLICATION OF NEGATIVE POTENTIAL
FIG 4-2B COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING NEGATIVE POTENTIALS OF (a) 100V (b) 120V (c) 70V. MINUS SIGN INDICATES THE PERIOD OF APPLICATION OF NEGATIVE POTENTIAL
FIG 4-3A COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING POSITIVE POTENTIALS OF (a) 175V, (b) 200V, (c) 120V. PLUS SIGN INDICATES THE PERIOD OF APPLICATION OF POSITIVE POTENTIAL
FIG 4-3B COMPARISON OF OXIDATION WITH AND WITHOUT APPLYING POSITIVE POTENTIALS OF (a) 150V, (b) 100V. PLUS SIGN INDICATES THE PERIOD OF APPLICATION OF POSITIVE POTENTIAL
The same results were obtained by keeping the potential a constant and decreasing the current from 3 mA to 25 μA (figure 4.4). No change in the rate of oxidation could be observed when the film was at ground potential and a current was allowed to pass through the film at regular intervals (figure 4.5). Thus, it was made clear that observed change in the rate of oxidation was due to the presence of electric field and not due to the flow of current.

For a low temperature region, Cabrera and Mott have postulated a theory based upon field-assisted ion transport. The Mott-Cabrera rate expression is

$$\tau = \frac{dx}{dt} = N \Omega \nu \exp\left(\frac{-W}{kT}\right) \exp\left(\frac{qaf}{kT}\right)$$

where $N$ is the number of atoms in the kink sites at the oxide-metal interface, $\Omega$ is the volume of oxide formed per metal ion, $\nu$ is the frequency of vibration of the metal atoms, $W$ is the energy barrier to the movement of a metal ion from a kink site at the oxide-metal interface into an interstitial position in the oxide, $q$ is the charge on a diffusing ion, $a$ is the distance from the bottom of the potential energy well of a kink site metal atom to the top of the energy well.
FIG 4-4A EFFECT OF ELECTRIC FIELD ON THE OXIDATION CURVES OF ALUMINIUM AT LOW CURRENT VALUES (≈25μA). MINUS SIGN INDICATES THE PERIOD OF APPLICATION OF AN APPLIED NEGATIVE POTENTIAL OF 200V
FIG 4-4B EFFECT OF ELECTRIC FIELD ON THE OXIDATION CURVES OF ALUMINIUM AT LOW CURRENT VALUES (~25 μA). PLUS SIGN INDICATES THE PERIOD OF APPLICATION OF AN APPLIED POSITIVE POTENTIAL OF 200V
FIG 4-5 COMPARISON OF OXIDATION RATE WITH AND WITHOUT PASSING A CURRENT OF 3 mA THROUGH THE FILM KEPT AT ZERO POTENTIAL. 'i' INDICATES THE PERIOD OF PASSAGE OF CURRENT
barrier between the kink site and an interstitial position in the oxide and $F$ is the electric field strength at the oxide metal interface. In the experimental situation, when we apply an external electric field of intensity $F_e$ across the oxide layer having natural field $F_0$, the field across the oxide becomes,

$$ F = F_0 \pm F_e \quad (4.6) $$

the sign depends on the sense of applied field. Equation (4.5) now becomes,

$$ \tau_\pm = N \alpha \nu \exp \left( -\frac{W}{kT} \right) \exp \left[ q a (F_0 \pm F_e)/kT \right] $$

$$ = \tau_0 \exp (\pm q a F_e/kT) \quad (4.7) $$

where $\tau_0$ is the rate of oxide growth with no external field. Thus for the field which aids oxidation, we have

$$ \gamma_+ = \frac{\tau_+}{\tau_0} = \exp (q a F_e / kT) \quad (4.8) $$

and for the field which opposes oxidation process

$$ \gamma_- = \frac{\tau_-}{\tau_0} = \exp (-q a F_e / kT) \quad (4.9) $$

In our experiment, we have changed the field $F_e$ by changing the applied potential $E$, and for aluminium
a negative potential aids the oxidation process while a positive potential reduces it. As the strength of the applied field, $F_0$ is proportional to $E$, and also from equations (4.8) and (4.9) we have

$$\log \gamma \propto |E|$$

(4.10)

where $\gamma = \gamma_+ \text{ or } 1/\gamma_-$ for an applied potential $-E$ or $+E$, respectively.

Observations were taken for different values of $E$ in the range 30 to 200 volts. An approximate measure of the ratio $\gamma_+$ or $(\gamma_-)^{-1}$ for different potentials and hence for different field strengths was estimated using the same method adopted by Hunt and Ritchie. In the oxidation-time graphs of figures 4-2 and 4-3, the ratio maximum slope to minimum slope was calculated for adjacent line segments. In a particular run, the ratios varied slightly, but within the limits of experimental error, no time dependence could be observed. In a particular run the average value of $\gamma$ was found out, similarly for the same potential the mean value of $\gamma$ was found for different runs. The ratios thus determined at different field strengths corresponding to applied potentials in the
range 50 to 200V are given in table 4-1. A graph is plotted with log $\gamma$ vs $|E|$ (figure 4-6). The straight line nature of the graph within the limits of experimental errors shows the validity of equation (4.10). It may be due to the logarithmic variation of $\gamma$ with $E$, we were not able to observe any change in the rate of oxidation below a particular potential. In the present experimental set up for fields corresponding to an applied potential less than $\pm$ 50V, no change in the rate of oxidation was observed. At this field strength $\gamma$ reaches a value about 1.3 $\pm$ 0.2. Hence below $\pm$ 50 V the value of $\gamma$ is still lower so that it becomes difficult to detect it experimentally.

Thus, at room temperature, oxide growth on evaporated aluminium films has been found to proceed by metal transport. The variation of the ratio in rates of oxidation with an applied field is found to be in agreement with the predictions of the Mott-Cabrera theory.
Table 4-1  Variation of $\gamma$ with electric field.

<table>
<thead>
<tr>
<th>Applied potential</th>
<th>$\gamma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>E</td>
</tr>
<tr>
<td>200</td>
<td>$2.3 \pm 0.4$</td>
</tr>
<tr>
<td>175</td>
<td>$2.1 \pm 0.3$</td>
</tr>
<tr>
<td>150</td>
<td>$1.9 \pm 0.2$</td>
</tr>
<tr>
<td>120</td>
<td>$1.8 \pm 0.2$</td>
</tr>
<tr>
<td>100</td>
<td>$1.6 \pm 0.2$</td>
</tr>
<tr>
<td>70</td>
<td>$1.4 \pm 0.2$</td>
</tr>
<tr>
<td>50</td>
<td>$1.3 \pm 0.2$</td>
</tr>
</tbody>
</table>

* Average value of $\gamma_+$ and $(\gamma_-)^{-1}$ is taken as.
FIG 4-6 LOGγ vs E GRAPH
Influence of magnesium on the oxidation of aluminium.

The study of mechanism of oxidation of aluminium-magnesium alloys has been of theoretical interest since the two pure metals follow different rate laws and fall under two different groups according to the classification of Billing and Bedworth. Earlier, studies were conducted on bulk samples and gave evidence for the presence of a duplex structure, an inner thin and continuous layer consisting of alumina or magnesium aluminate and a thick outer layer of porous magnesium oxide. The oxidation was controlled by the diffusion of magnesium ions through the magnesium aluminate. Oxidation of dilute Al-Mg alloy thin films has also been carried out by Ritchie et al. in the temperature range 200-500°C. The formation of MgO at low temperature and conversion to the spinal MgAl₂O₄ at high temperature has been suggested. In the present work the influence of magnesium on aluminium thin films at room temperature was investigated from kinetic measurements, etching and also by studying the surface morphology of the oxidized films.
4-4.1 Experimental details

As in the previous cases, the studies were conducted on evaporated specimens of thickness about 100 Å. Weighed samples of aluminium and magnesium were evaporated from a single tungsten basket. Due to the difference in the evaporation rates of the two elements there is generally a slight variation in the ratios of the weights of two samples in the film. The correct weight percentage of magnesium impurity in the specimen was determined by atomic absorption method. The specimen so prepared was transferred to a separate glass jar with a time delay of 1 to 2 minutes and the specimen was allowed to oxidize in a dust free atmosphere. The rate of oxidation was followed by noting the rate of change of the resistance with time. Using a low power microscope (magnification \( \sim 270 \)) the nature of surface oxides formed were examined at different times of oxidation. The experiment was conducted for different films containing different weight percentages of magnesium ranging from 0 to 15%. The etching action with oxidation time has also been noted both for pure
aluminium films and films with magnesium impurity. The different etchants used in this case were hydrochloric acid, nitric acid and sodium hydroxide, all sufficiently diluted with ethyl alcohol.

4.4.2 Results and discussion

With the presence of magnesium the asymptotic form of oxide growth changed to a power law of the form,

\[ x^n = kt \]  \hspace{1cm} (4.11)

where \( x \) is the oxide thickness at a time \( t \) and \( k \) and \( n \) are constants. Since the oxide thickness \( x \) is proportional to \(-1/R\), \( R \) being the resistance of film,

\[ (\frac{1}{R})^n \propto t \]  \hspace{1cm} (4.12)

Thus a plot of log \( 1/R \) versus log \( t \) gave straight lines as in figure 4-7. This transition of the growth law indicates an increase in the rate of oxidation. After several days of exposure of the film to air, a surface structure as shown in figure 4-8, was found to develop gradually, where as no
FIG 4-7A LOG \( \frac{1}{R} \) vs LOG \( t \) PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.% OF MAGNESIUM: (a) 5 wt.%  (b) 1.5 wt.%  (c) 3 wt.\%
FIG 4-7B LOG $1/R$ vs LOG $t$ PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.% OF MAGNESIUM:
(a) 10 wt.% (b) 12 wt.%
FIG 4-7C LOG $1/R$ vs LOG$t$ PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.% OF MAGNESIUM: (a) 7.5 wt.% (b) 15 wt.%
surface structures were visible for oxidized pure aluminium films, when viewed under the same magnification. Also, it was found that with higher percentages of magnesium, the oxide pattern grew and spread more rapidly than that in the case of aluminium films with lower percentages.

On etching the aluminium thin films, etch patterns as shown in figure 4-9, were obtained. The etch pattern could be obtained only if the films were etched within 15 or 30 minutes of oxidation. With further oxidation, the oxidized surface was not attacked by the etchant, indicating the growth of a stable oxide film. The same results were obtained for all the etchants used. When magnesium was introduced, the etch pattern could be obtained for much longer periods of oxidations (even for one or two days of oxidation, figure 4-10, 11, 12). When the magnesium content was low (about 0 to 10 wt.% of magnesium), the etch patterns for aluminium (magnesium) thin films during the initial period of oxidation were similar to that obtained for pure aluminium.
In the oxidation of aluminium(magnesium) thin films, the possible reactions are

\[ \text{Mg} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgO} \]  \hspace{1cm} (4.14)

\[ 2\text{Al} + \frac{3}{2} \text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \]  \hspace{1cm} (4.15)

\[ \text{Mg} + 2\text{Al} + 2\text{O}_2 \rightarrow \text{MgAl}_2\text{O}_4 \]  \hspace{1cm} (4.16)

\[ 3\text{Mg} + 4\text{Al}_2\text{O}_3(\text{amorph}) \rightarrow 3\text{MgAl}_2\text{O}_4 + 2\text{Al} \]  \hspace{1cm} (4.17)

\[ 3\text{Mg} + 2\text{Al}_2\text{O}_3(\text{amorph}) \rightarrow 3\text{MgO} + 2\text{Al} \]  \hspace{1cm} (4.18)

Thermodynamically, the possible reaction is that which produces maximum decrease in the free energy change. Hence, under conditions favourable for the attainment of thermodynamic equilibrium, that is under high temperature and for long periods of oxidation of thick films the stable oxide is the spinel MgAl₂O₄. But at low temperatures, the kinetics of the reaction determine which oxide is to be formed at the alloy surface.

The similarity in the etch patterns of pure aluminium and aluminium magnesium films for the initial periods of oxidation indicates that even
in the presence of magnesium the initially formed oxide is Al$_2$O$_3$ as in the case of pure aluminium. But the continued etching action suggests that the reaction does not stop with the formation of a stable Al$_2$O$_3$ layer as with pure aluminium. Most probably, the magnesium ions may be diffusing out of the Al$_2$O$_3$ layer. When higher quantities of magnesium are introduced, this diffusion of magnesium ions to the surface can take place very quickly, so that it becomes difficult to trace the initial formation of Al$_2$O$_3$ layer with etching.

Although the chemical potential gradient of reaction (4-14) is greater than that of reaction (4-15) due to the slow diffusion of magnesium through the oxide, for short periods of oxidation Al$_2$O$_3$ is formed on the surface. If the system is exposed to the oxidizing environment for sufficiently long periods, magnesium ions may diffuse out through the oxide and form a separate oxide phase, most probably MgO$^{27,28}$ at the Al$_2$O$_3$-oxygen interface. This gives rise to the surface oxide structure as in figure 4-8. When the magnesium content increases, the surface gets covered by
MgO layer rapidly. The diffusion of magnesium through the amorphous alumina may be responsible for the change in oxide growth kinetic also. Thus, the development of MgO over the initially formed Al₂O₃ layer may be responsible for all these observed changes.

4-5 **Effect of zinc on the oxidation of aluminium thin films**

A study of the oxidation characteristic of aluminium by introducing zinc as an impurity was also done at room temperature. The influence was studied with kinetic measurements and etching studies as carried out in the case of aluminium (magnesium) thin films. The preparation of specimen and method of study were as same as discussed in section 4-4.1. The weight percentage of the impurity was varied from 0 to 20%. Each time the exact weight percentage of zinc present in the aluminium films was confirmed by atomic absorption. In each case the rate of oxidation was measured from rate of change of resistance. The applicability of rate equation was tested by the usual method of plotting \(-1/R\) against the appropriate function of time.
4-5.1 Results and Discussion

When zinc was introduced in the aluminium film, no marked change in the growth kinetics could be observed. However, the time of oxidation was very much greater than that of aluminium. For the case of aluminium alone, the oxidation ceased within one hour, whereas for Al(Zn) system the oxidation continued even after a period of two months. Due to this, the asymptotic form of oxide growth seemed to be a logarithmic one. For the time of observation and a plot of \(-1/R\) against \(\log t\) gave straight lines as in figure 4-13. As in the case of any other material, there was a change in the rate of oxidation during the initial period of oxidation.

When aluminium films containing different weight percentages of zinc were etched using alcoholic solutions of hydrochloric acid, nitric acid and sodium hydroxide in all the three cases, action of etchant decreased with oxidation time (figure 4-14). After one or two days etch patterns were not obtained indicating that the oxide film formed was protective as in the case of pure aluminium.
FIG 4-13A \( I/R \) vs \( \log t \) PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.\% OF ZINC: (a) 1 wt.% (b) 2.5 wt.\%
FIG 4-13B  I/R VS LOG t PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.% OF ZINC: (a) 5.4 wt.% (b) 7.5 wt.%
FIG 4-13C I/R vs Log t PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.% OF ZINC: (a) 9 wt.% (b) 13 wt.%. 
FIG 4-13D  I/R vs LOGt PLOT FOR ALUMINIUM FILMS WITH DIFFERENT wt.% OF ZINC: (a) 16 wt.% (b) 20 wt%
Aluminiun oxide being an n type oxide having excess cations the introduction of elements of lower valency like zinc are expected to increase the lattice defects in the oxide. The increase in the lattice defect can enhance the rate of oxidation. Hence, an oxide film of sufficient thickness to prevent further oxidation, may be expected to form sooner in the presence of zinc than in the case of pure aluminium. In the observed oxidation of long periods some other factors may be responsible. One probable cause can be the size difference of the zinc atoms. For zinc, the atomic radius is larger than that of aluminium. However, considering the lattice parameters of aluminium, it can go into the aluminium matrix as a substitutional impurity. Because of the larger size the zinc ions may require larger energy for diffusion. So at a constant temperature the number of diffusing ions will be reduced in the aluminium-zinc system compared to pure aluminium samples. In expression (4-4) 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 lower the rate constants. When this happens the oxide growth takes place slowly and for short periods, the growth seems to be logarithmic. Thus, the decrease in the number of diffusing ions at any time and the difficulty in distinguishing the two rate laws (asymptotic and logarithmic) under limited time interval can be responsible for the observed logarithmic growth of oxide layer. Further, the introduction of zinc impurity can also modify the electric field set up across the metal oxides, thus sometimes hindering the diffusion of cations. This can also reduce the rate constants and can lead to slow oxidation in a prolonged period. Thus at low temperature such as room temperature the size effect and the modified electric field across the metal oxide structure seems to have more influence than that due to valency difference.

4-6 Conclusion

Aluminium was found to oxidize following an asymptotic growth rate and has been explained as due to the blockage of grain boundaries present in the polycrystalline films as oxidation proceeded. Hence,
the rate of oxidation should fall exponentially with time, and from equation (4.4) this rate can be written as

\[ r_o = \frac{d\alpha}{dt} = \alpha_1 \Lambda B \exp(-Bt) \]  

(4.19)

For a small interval of time, as a first approximation, \( r_o \) can be considered to be a constant. Within this small interval of time, when the rate of oxidation was compared with and without applying the field, the ratio of two rates agreed with the predictions of the Cabrera-Mott theory. Also, from the sense of the applied field and its influence on the rate of oxidation, diffusion of cations was found to be the controlling factor of oxidation. Hence, it can be concluded that the main mechanism of oxidation of aluminium is the field-assisted diffusion of cations through the grain boundaries.

The presence of magnesium impurities in aluminium changes the rate of oxidation from an asymptotic to a power law. Also, new surface oxide patterns were found to develop. These oxide patterns grew rapidly as the percentages of magnesium was
also increased. All these observed changes may be due to the development of a new oxide layer MgO by the diffusion of magnesium ions through the initially formed Al$_2$O$_3$ layer.

The presence of zinc (0 to 20wt.% of zinc in aluminium) also changed the oxidation kinetic to a logarithmic one. The change in the rate law may be due to the lowering of the rate constants, A' and B of equation (4.4) because of the slow diffusion of zinc ions which require larger diffusion energy.
REFERENCES

1. N D Long and A R Williams
   Phys Rev Letters 34 (1975) 531

2. J Harris and G S Painter
   Phys Rev Letters 36 (1976) 151

3. S A Flodstrom, R Z Bachrach, R S Bauer and
   S B M Hagstrom
   Phys Rev Letters 37 (1976) 1282

4. S A Flodstrom, L G Petersson and S B M Hagstrom
   J Vac Sci Tech 13 (1976) 230

5. K Y Yu, J N Miller, W E Spicer, N D Long and
   A R Williams

6. A M Bradshaw, P Hofmann and W Wyrobisch
   Surface Sci 62 (1977) 269

7. G L Hunt and I M Ritchie
   J Chem Soc Faraday Transactions 68 (1972) 1413

8. G L Hunt and I M Ritchie
   Oxid Met 2 (1970) 361

9. I M Ritchie
   Thin Solid Films 34 (1976) 83

10. M A H Lanyon and B M W Trapnell
11. N F Mott  
Trans Faraday Soc 35 (1939) 1175

12. N F Mott  
Trans Faraday Soc 36 (1940) 1

13. N F Mott  
Trans Faraday Soc 43 (1947) 429

14. N Cabrera and N F Mott  
Rep Prog Phys 12 (1949) 163

15. D D Eley and P R Wilkinson  

16. J E Bogio and R C Plumb  
J Chem Phys 44 (1966) 1081

17. J C Fisher and I Giaever  
J Appl Phys 32 (1961) 172

18. U R Evans  
The Corrosion and oxidation of metals  
(Edwin Arnold, London 1960)

19. J R Anderson and B G Baker  
Chemisorptions and reactions on metallic films  

20. S R Pollack  
Materials Sc Engg 2 (1969) 249

21. W J Moore  
Phil Mag 43 (1952) 688
22. I M Ritchie and G L Hunt
   Surface Sci 15 (1969) 524

23. N B Pilling and R E Bedworth
   J Inst Metals 22 (1923) 529

24. L De Brouckere
   J Inst Metals 71 (1945) 131

25. R A Hine and R D Guminski
   J Inst Metals 89 (1960-61) 417

26. W W Smeltzer

27. I M Ritchie, J V Sanders and P L Weickhardt
   Oxid Met 2 (1971) 91

28. D R Spalding, J W Edington and R E Villagrana
   Phil Mag 20 (1969) 1203