

Effect of Pressure Changes on the Oxidation Rate of Aluminium in the Temperature Range 323-673 K

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This paper describes some experiments on the oxidation of evaporated aluminium films in the temperature range 323-673 K. The kinetics were followed by measuring the rate of increase in resistance as the film was consumed by oxidation. The effect of suddenly altering the oxygen pressure on the oxidation rate was studied as a function of time and oxidation temperature. In the pressure range studied (*ca.* 1×10^3 - 30×10^3 N m⁻² of oxygen), pressure increases were always associated with rate increases and pressure decreases with rate decreases. The effect of the pressure change on the reaction speed was found to diminish somewhat as the oxidation progressed, and also decreased with temperature. These results have been interpreted in terms of a modified Mott-Cabrera theory.

The oxidation of metals, particularly the low temperature reaction (say less than 600 K) where the oxide growth often conforms to an approximately logarithmic rate law, has been the subject of a very large number of theoretical treatments. In recent years, there has been an increasing recognition of the fact that kinetic data alone are insufficient to distinguish between the various reaction mechanisms which have been suggested and treated theoretically. This recognition has come about because the results of rate experiments are difficult to reproduce, especially at low temperatures, and depend markedly on such factors as surface preparation, the presence of impurities and the orientation of the metal substrate. In addition, it is often difficult to distinguish between two different, but phenomenologically similar, mathematical representations of the rate results.

In some ways, the oxidation of aluminium below a temperature of about 625 K is ideal for testing low temperature oxidation theories. This is because the only oxide formed is amorphous Al₂O₃ which, lacking any significant crystal structure, approximates the ideal plane parallel-sided oxide film most commonly assumed in oxidation theories. Published work, some of which is summarized in ref. (1), indicates that the amorphous oxide is *n*-type and grows at the oxygen/oxide interface by metal transport.

The work of Boggio and Plumb² has shown that the direct logarithmic rate law, observed at room temperature, can be interpreted in terms of the Mott-Cabrera theory modified to include the effects of space charge. This theory also accounts for their Volta potential measurements and the pressure dependence studies of Kirk and Huber.^{3, 4} Above 623 K, Dignam *et al.*⁵ have interpreted their kinetic measurements using the Mott-Cabrera theory. The intermediate temperature range has received little attention. Some field experiments¹ carried out between 323 and 673 K suggest that the rate determining step is ion transport. Dickens *et al.*⁶ have shown that the presence of atomic oxygen does not alter the oxidation rate. This implies that the rate determining step is not the dissociation of oxygen.

The work described in this paper was undertaken because a knowledge of the

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pressure dependence of an oxidation reaction can be useful in evaluating the reaction mechanism.⁷ The effects of rapidly altering the pressure during the course of the reaction were investigated, since this technique is valuable when the pressure effects are time dependent.

EXPERIMENTAL

The technique by which a measure of the oxidation rate was obtained has been described previously,¹ and depends on the fact that the resistance along a thin aluminium film increases during oxidation as the very conductive metal is replaced by the highly resistive oxide.

The thin aluminium films were prepared by evaporation of 99.999 % pure aluminium onto glass slides at room temperature in a vacuum of about 10^{-3} N m⁻². The thickness of the films was dictated by the temperature of the planned experiment, the thinnest films being used at the lowest temperatures. The thickness of the films was generally 20-30 nm.

The oxygen, which had an initial purity of 99.95 % (high purity dry O₂, Commonwealth Industrial Gases), was further purified by successively passing it through a trap immersed in a dry ice/acetone slush bath, and containing molecular sieves with a 0.4 nm pore diameter (Union Carbide), then Ascarite to remove CO₂, and activated silica gel before being finally stored ready for use in a large glass bulb.

Resistance measurements were made with a Wheatstone bridge, and in order to minimize unwanted Seebeck electro-motive forces, the contacts and all electrical leads to the film were of aluminium. Pressure measurements were made with a mercury manometer isolated from the vacuum system by a cold trap. The furnace temperature, which was controlled automatically, was measured with a Gold Line thermometer, and found to fluctuate by up to 1.5 K during pressure changes.

The experimental procedure was to evaporate the sample assembly (film and contacts) in an Edwards 12E6 coating unit, and then transfer it to the vacuum system in which the resistance measurements were made. The system was evacuated to a pressure of 10^{-4} N m⁻² and the temperature raised to the required value, after which an initial decrease in the film resistance occurred which was due to the sintering of the film. The film resistance usually stabilized after about 1 h.

For the kinetic runs, about 6×10^4 N m⁻² of oxygen was admitted, and the increase in resistance was followed as a function of time. The temperature of the system usually required several minutes to reach a steady value following the admission of gas, so that readings taken during the first 5 min were less reliable than later readings. The runs were continued for periods varying between $1\frac{1}{2}$ and 8 h. Measurements were made between 373 and 673 K. Below this temperature range, the resistance against time plots were discontinuous because the metal films had to be so thin.

The effect of oxygen pressure on the oxidation rate, at a given temperature, was investigated by measuring the change caused by a sudden pressure increase or decrease. In the pressure dependence experiments, the film resistance was allowed to stabilize and 1.3×10^3 N m⁻² of oxygen was admitted. The run was commenced $\frac{1}{2}$ -1 $\frac{1}{2}$ h after the admission of oxygen. The oxidation rate was followed for 5-15 min before the pressure was suddenly raised to around 2.7×10^4 N m⁻² and the rate was again followed for a similar period of time before the pressure was suddenly reduced to around the original value. Alternate pressure increases and decreases were continued throughout the run which usually lasted for 2-3 h. In general, the time taken for pressure readings to become steady following a sharp change in pressure was not more than 30 s. It can be seen that with this technique, uncertainties inherent in the use of different samples with irreproducible surfaces are largely avoided. However, the effect of pressure changes during the initial stages of oxidation could not be readily observed.

RESULTS

KINETICS

If it is assumed that the evaporated aluminium film can be regarded as a thin isotropic metal sheet which oxidizes on one surface only, and obeys Ohm's law, then

it is simply shown that the film resistance R and the oxide thickness x are related by the equation

$$x = \frac{\phi \rho l}{w} \left(\frac{1}{R_0} - \frac{1}{R} \right), \quad (1)$$

where ϕ is the thickness of oxide derived from unit thickness of metal, ρ 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_0 is the resistance of the film prior to oxidation.

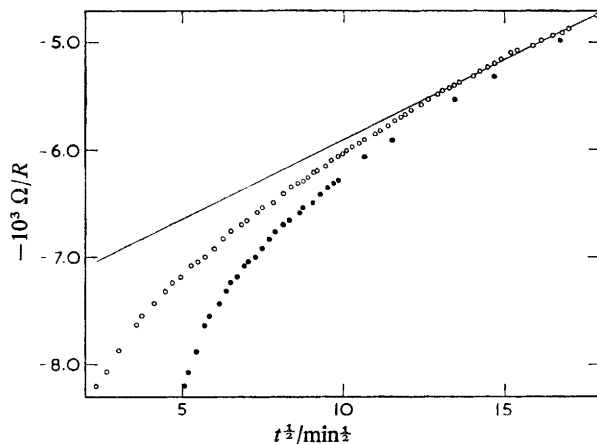


FIG. 1.—Fit of kinetic results at 558 K to the parabolic equation, $x = k_p^{1/2}(t + t_0)^{1/2}$, where t_0 is a constant: \circ , assuming $t_0 = 0$; \bullet , assuming $t_0 = 20$ min. The straight line is to show the deviation of the experimental results from linearity at short times.

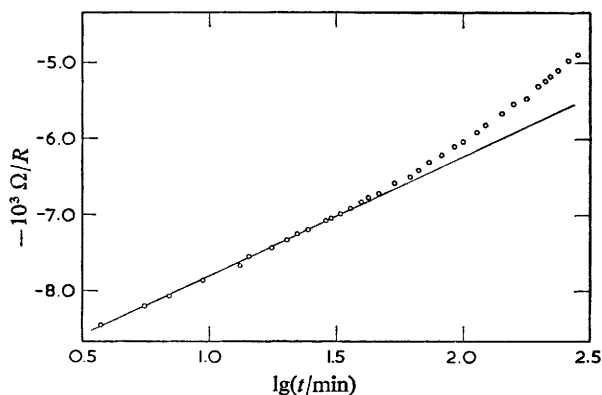


FIG. 2.—Fit of kinetic results at 558 K to the direct logarithmic equation. The conductance ($1/R$) is plotted against the logarithm of time. The straight line is to show the deviation of the experimental results from linearity at long times.

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.⁸ From this equation, it is apparent that the oxide thickness is proportional to $-1/R$, and so the applicability of a particular rate equation can be tested by plotting $-1/R$ against the appropriate function of time (t). The results obtained in the kinetic runs were tested in this way for the linear ($x \propto t$),

parabolic ($x^2 \propto t$) and direct logarithmic ($x \propto \lg t$) rate laws. Over the temperature range investigated, the resistance against time measurements could not be fitted to any one of these three laws. This is shown for the parabolic and direct logarithmic laws in fig. 1 and 2, where the results for 558 K are plotted.

The applicability of the inverse logarithmic law

$$1/x = k_1 - k_2 \lg t, \quad (2)$$

where k_1 and k_2 are constants, was also tested. Combining eqn (1) and (2), we obtain

$$(1/R_0 - 1/R)^{-1} = \frac{\phi \rho l k_1}{w} - \frac{\phi \rho l k_2}{w} \lg t. \quad (3)$$

In order to find whether the results fitted this equation, values of $1/R_0$ were required. These were obtained by back extrapolating the $-1/R$ against t plot to $t = 0$. Using these values of $1/R_0$, the results were plotted according to eqn (3), and were found to diverge appreciably from a straight line.

Thus, the results could not be fitted to any of the common oxidation rate laws. However, for low temperatures or short times, the direct logarithmic law best described the reaction kinetics. Conversely, at high temperatures or large oxide thicknesses, the results gave a better approximation to the parabolic rate law.

PRESSURE DEPENDENCE STUDIES

A typical $-1/R$ against t plot is shown in fig. 3. It can be seen that a pressure increase is always followed by a rate increase, and a pressure decrease by a rate decrease. Oxidation rates just before and just after the pressure changes were evaluated from such plots by a least squares method; over a short period of time, the plots were approximately linear.

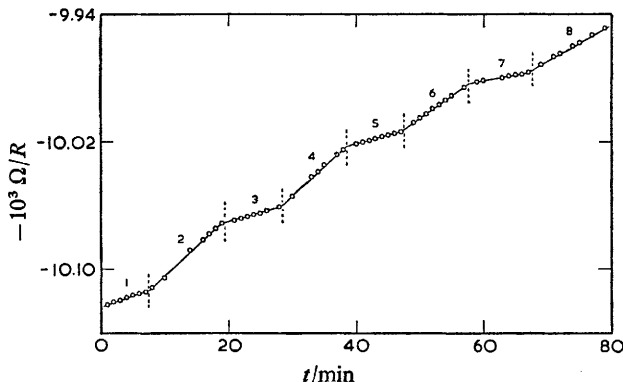


FIG. 3.—A $-1/R$ against t plot for the oxidation of aluminium at 323 K, showing the effect of changes in pressure on the oxidation rate. Numbers on the graph correspond to the following pressures in N m^{-2} : 1, 320; 2, 2506; 3, 165; 4, 2650; 5, 141; 6, 2560; 7, 107; 8, 2560.

It was assumed that the dependence of oxidation rate upon oxygen pressure (P) could be represented by an empirical equation of the form

$$\mathcal{R} = dx/dt = k'f(x)P^n \quad (4)$$

where k' is the pressure independent rate constant, $f(x)$ denotes the functional dependence of the rate upon the oxide thickness, and n is the exponent of the pressure dependence. It can be shown from eqn (4) that if the pressure is suddenly changed

from P_1 to P_2 , the corresponding change in oxidation rate from \mathcal{R}_1 to \mathcal{R}_2 can be used to calculate n from

$$n = \lg(\mathcal{R}_1/\mathcal{R}_2)/\lg(P_1/P_2). \quad (5)$$

The parameter n was found to have the following three characteristics.

(i) At any given temperature, n values corresponding to reductions in pressure were equal to those corresponding to pressure increases. For example, at an oxidation temperature of 374 K, successive n values for pressure increases were 0.48, 0.49, 0.52, 0.45, 0.41, 0.43, 0.44, with an average of 0.46 (± 0.04). The corresponding figures for decreases in pressure were 0.55, 0.64, 0.50, 0.46, 0.44, 0.39, 0.27, also giving an average of 0.46 (± 0.12). These figures show that n values cannot be determined with any great accuracy by this technique, since large errors exist in the rate measurements. Large standard deviations have also been reported for the empirical parameter n determined from manometric measurements of the oxidation rate (see, for example, the study by Anderson and Clark of the oxidation of sodium⁹).

(ii) At any given oxidation temperature, n values decreased slowly during oxidation. This is demonstrated in fig. 4 which shows the change in n values with time for an oxidation temperature of 374 K. In addition, the ratio of the n values determined during the first and the last pressure increases in each run was determined for seventeen experiments carried out in the temperature range. The average ratio was found to be 1.24, with a standard deviation of 0.11. Since the variation in n with time is small, some experiments in which the rate of oxidation was temporarily accelerated by exposing the metal to a higher oxygen pressure ($9.3 \times 10^4 \text{ N m}^{-2}$) were carried out. In one experiment at 545 K, the average of 12 n values before exposure was 0.17 which decreased to an average of 0.12 for 4 pressure changes after 38 min at the higher oxygen pressure. In another experiment at the same temperature, the average n value decreased from 0.29 to 0.15 after 1 h exposure to the higher oxygen pressure. That this effect was a function of oxide growth, and not of time alone was established by reducing the oxygen pressure to 0.1 N m^{-2} for 1 h over a sample oxidizing at 425 K. No variation, within the limits of experimental error, was observed in the n values before and after the reduction in pressure was effected.

To our knowledge, a change in the value of n with oxide thickness (or time) has not been reported before. Whatever reaction mechanism is proposed must be shown to be consistent with this observation.

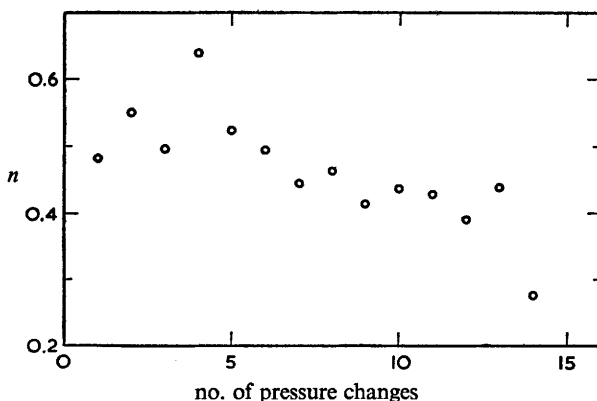


FIG. 4.—The variation in the parameter n as a function of the number of pressure changes for an oxidation reaction at 374 K.

(iii) The magnitude of n decreases with increasing temperature of oxidation. This is shown in fig. 5. The average n values were obtained from between 4 and 18 measurements, the mean number of measurements being 10.

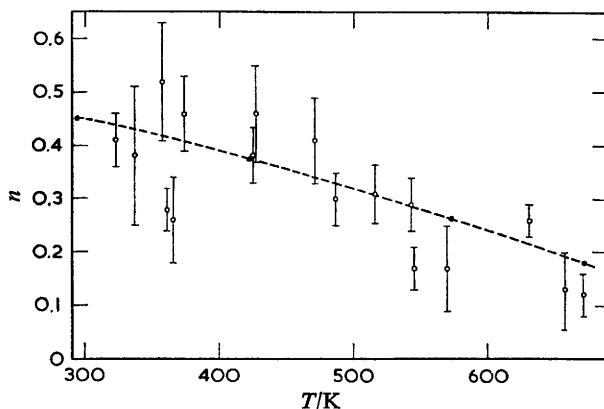


FIG. 5.—The variation in the parameter n as a function of oxidation temperature. The error bars correspond to one standard deviation. The broken line is drawn through the points ● calculated on the basis of the theory presented in the text, and using the oxide thicknesses measured by Hass.¹⁵

From these results, it can be seen that the method of studying the pressure dependence of an oxidation reaction, by observing the effect on the rate of sudden pressure changes, yields more information than it is possible to obtain from conventional static pressure studies.

DISCUSSION

KINETICS

The results are interpreted in terms of the growth of amorphous oxide only, since electron microscopic examination of the oxide films revealed insignificant quantities of $\gamma\text{-Al}_2\text{O}_3$ within the time span and temperature range of the experiments.¹⁰ It has already been established¹ that ion transport controls the rate of growth of amorphous alumina below 670 K, and since the Mott-Cabrera theory of oxidation kinetics,¹¹ or a derivative of it, has been applied to this system, we have attempted to fit the results reported here to that theory. In its original form, the theory supposed that the slow step in the reaction mechanism was the movement of ions across the oxide/metal phase boundary. This movement could not take place without the aid of a strong electric field (F) associated with a constant potential (V) established across the oxide by oxygen ions adsorbed at the oxygen/oxide interface. As the oxide increases in thickness, the field diminishes, until it is too weak to pull any more ions into solution from the metal, and oxide growth virtually ceases.

For the general case, where the rate determining step may be ion transport across the oxide/metal interface, or across the oxide itself, the growth equation is⁵

$$dx/dt = 2A \sinh(B/x), \quad (6)$$

with $A = n_1 \Omega v a \exp(-U/kT)$ and $B = z e a V / 2kT$, where n_1 is the concentration of diffusing ions, Ω is the volume of oxide created per metal ion, v is the frequency of vibration of the diffusing ion, U is the energy barrier to diffusion, z is the valence of the ion, and a is the distance moved by the ion in travelling from site to site; e , k and T have their usual significance.

Although the results of Dignam *et al.*⁵ for the formation of amorphous alumina above 623 K could not, in common with our results, be fitted to any of the usual rate laws, they found that eqn (6) provided a satisfactory representation of their measurements. We have also found that our results can be described by eqn (6), but this equation is not physically realistic since it implies that the reaction rate is independent of pressure, contrary to our experimental findings. It is clear therefore, that eqn (6) must be modified to take account of the observed pressure dependence. Grimley¹² has proposed a modification of the Mott-Cabrera theory which would introduce a pressure dependent term into the rate equation. According to Grimley, the effect of altering the pressure is to change the concentration of charged surface species. This brings about a change in the electric field which assists ion transport. Such a mechanism would be consistent with our observation that the rate changes caused by altering the pressure were practically instantaneous. The rapid response to the pressure change suggests that the adjustment in the oxidizing system has taken place at the oxygen/oxide interface, rather than in the bulk of the oxide.

Grimley's approach may be introduced as follows. Suppose that oxygen adsorbs on the surface and is ionized as in eqn (7),



where the reaction describes the situation at the gas/oxide interface. Assuming the surface coverage to be small, an equilibrium equation

$$K = [\text{O}_2^-(ads)]/P[e] \quad (8)$$

may be written. Treating the system as a parallel plate capacitor, and supposing that electrons are distributed across the oxide according to the Boltzmann distribution law, we have

$$V = [\text{O}_2^-(ads)]ex/\epsilon \quad (9)$$

$$[e] = [e]_0 \exp(-eV/kT), \quad (10)$$

where ϵ is the permittivity of the oxide, and $[e]_0$ is the electron concentration at the oxide/metal interface.

Combining eqn (8), (9) and (10) we obtain

$$V = \frac{exKP[e]_0 \exp(-eV/kT)}{\epsilon}. \quad (11)$$

When $eV/kT \gg 1$, the left hand side of eqn (11) may be considered constant, and equal to an average value of V , \bar{V} . In this way, an expression for V is obtained which may be substituted into eqn (6) to give the growth law

$$dx/dt = A[(B'x)^{za/2x} - (B'x)^{-za/2x}] \quad (12)$$

where $B' = eKP[e]_0/\bar{V}\epsilon$.

By integrating this equation, and substituting eqn (1), which relates the oxide thickness to the film resistance, the fit of our results to the modified Mott-Cabrera growth equation could be tested. In the calculations, it was assumed that the diffusing aluminium ion was trivalent. Two values for a are reported in the literature. They are 0.5¹³ and 0.7 nm.¹¹ An average value of 0.6 nm was used here.

There are certain practical difficulties in carrying out the calculations, the most important of these being that the integration had to be performed numerically. In addition, there are several unknown parameters in eqn (1) and (12). These are the resistivity of the evaporated aluminium film, which is known to depend on film thickness, and to differ considerably from the value for the bulk metal;¹⁴ the thickness

of the oxide film prior to the experiment; and the magnitude of the quantities A and B' .

In carrying out the integration, reasonable values for the film resistivity and initial oxide thickness were chosen. The parameters A and B' were allowed to vary in such a way that the fit of the results to the growth equation was optimized. It was found that a good fit could be obtained over the temperature range investigated, by a suitable choice of A and B' , but these two parameters were sensitive to the values chosen for the resistivity and initial oxide film thickness. One example, for the results at 558 K, is shown in fig. 6. However, the uncertainties of the technique (e.g., variability of film resistivity with the conditions of film deposition) were such that the magnitudes of A and B' varied considerably for runs at the same temperature. Thus, while we can show that our kinetic measurements are consistent with the modified Mott-Cabrera growth equation, and do not fit the usual oxidation rate laws, we cannot determine any kinetic parameters. This is a basic weakness of the resistance method for following oxidation kinetics of evaporated metal films.

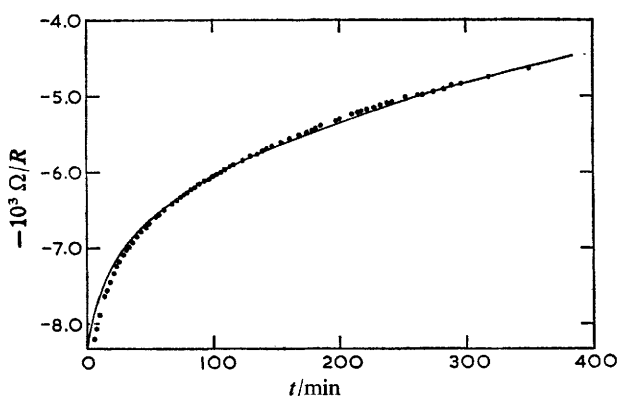


FIG. 6.—The kinetic results at 558 K. The curve was calculated using eqn (12) and the method described in the text. The parameters A and B' are given the values $2.36 \times 10^{-16} \text{ m s}^{-1}$ and $2.69 \times 10^{-7} \text{ m}$ respectively.

PRESSURE DEPENDENCE

If our model of the oxidizing system is correct, the pressure dependence of the oxidation rate will be given by the growth eqn (12). However, this equation is too complex for ready comparison with the experimental results. Accordingly, a simpler and more approximate form of eqn (12) was derived which could be used for this purpose. In deriving eqn (12), we assumed that $eV/kT \gg 1$, or $exF/kT \gg 1$. We now make the more drastic assumption that $ezaF/2kT \gg 1$. This is less likely to be valid since $za/2$ will usually be less than x . The assumption is equivalent to ignoring the backwards movement of ions in the electric field, as originally assumed by Mott and Cabrera.¹¹ Under these conditions, the pressure dependent growth equation, eqn (12), reduces to

$$dx/dt = A(B'x)^{za/2x}. \quad (13)$$

The applicability of this equation to our kinetic results was tested in the manner described earlier, and it was found that it provided a fit almost as good as that obtained with the more complete eqn (12). Furthermore, for the same parameters (metal resistivity, initial oxide thickness, etc.), the optimum values of A and B' were very

similar to those obtained using eqn (12). As expected, the disparity between the two sets of A and B' values increased with increasing oxide thickness (temperature of oxidation). For example, the results at 558 K yielded two sets of A and B' values which were virtually identical, but at 658 K, the approximation caused A to increase by 7 % and B' to decrease by 16 %. Thus, the importance of the second term in eqn (12), which has been omitted in eqn (13), becomes greater as the temperature of oxidation is increased. Eqn (13) may be rewritten

$$\frac{dx}{dt} = A \left\{ \frac{\exp K[e]_0}{V_E} \right\}^{za/2x} P^{za/2x}. \quad (14)$$

By comparison with the eqn (4), it can be seen that the exponent of the pressure dependence n is given by

$$n = za/2x. \quad (15)$$

Thus the theory predicts that n decreases with oxide thickness, in agreement with the experimental finding. Because we do not observe the initial rapid period of oxide growth in our experiments, but only make measurements in the region of oxidation where the oxide thickness changes relatively slowly, it is not surprising that the reduction in n with time which we find is small.

Before attempting to calculate n values and compare them with the experimental figures, it should be noted that the actual expression obtained for n depends on the identity of the predominant field-creating ion. The above expression, $n = za/2x$, is applicable when $O_2^-(ads)$ is the ion responsible for producing the electric field. Table 1 lists the other possibilities, and gives the corresponding expressions for n . To predict the numerical value of n , three parameters are required; these are z , a and x . We have already assumed that $z = 3$ for the diffusing aluminium ion, and taken an average value of a from the literature of 0.6 nm. Unfortunately it is more difficult to obtain the oxide thickness, since this cannot be directly measured by the resistance technique. Therefore, the ellipsometrically determined values of Hass,¹⁵ for oxide thicknesses following 2 h oxidation in air, were used. Since the most rapid oxide growth is complete in about the first hour, and experimental measurements of n were not made until after at least 30 min of oxidation, the experimental value of n should be relatively constant. For this reason, the use of oxide thicknesses measured after 2 h of oxidation should not introduce a large error into the calculated values of n . Using the figures of Hass, the calculated values of n , expected for O^- or O_2^{2-} as the field-creating ion, are compared with the experimental values in fig. 5. Considering the approximations and errors involved, the agreement is quite good. Further, the agreement is significantly worse if predominance of O_2^- or O^{2-} is assumed.

TABLE 1.—POSSIBLE SURFACE SPECIES AND THE CORRESPONDING EXPRESSIONS FOR n

predominant field-creating ion	expected expression for n
$O_2^-(ads)$	$za/2x$
$O_2^{2-}(ads)$	$za/4x$
$O^-(ads)$	$za/4x$
$O^{2-}(ads)$	$za/8x$

There has been much debate as to the nature of adsorbed oxygen on oxide surfaces. E.s.r. measurements at room temperature on various oxides, not including amorphous alumina, have suggested that both the paramagnetic species O_2^- and O^- may be present.¹⁶ Winter¹⁷ has argued from energy considerations that O^- should form on oxide surfaces, and Boggio⁴ has interpreted the results of Kirk and Huber,³ for

the room temperature oxidation of aluminium, in terms of this species. Our results are also consistent with this possibility.

In another account of the pressure dependence of the aluminium+oxygen reaction, Gulbransen and Wysong¹⁸ found the oxidation rate at 773 K to be virtually independent of pressure. Pressure independence is to be expected on the basis of the theory presented here, because greater oxide thicknesses are encountered at the higher temperatures. However, some care must be exercised in applying this theory to the oxidation of aluminium at 773 K, since the analysis becomes invalid for thicker oxides. In addition, the oxide formed at 773 K would contain an appreciable fraction of $\gamma\text{-Al}_2\text{O}_3$.⁵

CONCLUSIONS

The Mott-Cabrera theory has been modified using the approach of Grimley. By carrying out this modification, the rate law is altered and includes a pressure dependent term. Although the resistance method for following oxidation kinetics is limited, it has been shown that the results obtained in this study are consistent with the modified Mott-Cabrera rate law in the temperature range 373-673 K, and do not conform with the commonly observed growth equations.

Oxide growth on evaporated aluminium films has been found to be pressure dependent in the temperature range 323-673 K for pressures between 1.2×10^3 and $27.0 \times 10^3 \text{ N m}^{-2}$. Pressure increases and decreases cause corresponding changes in oxidation rate. The effect of a sudden pressure change on the oxidation rate diminished slowly during the course of the reaction, and, for a fixed period of oxidation became progressively less important as the reaction temperature was increased. The magnitude of the observed pressure effect is in rough agreement with the predictions of the theory.

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