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The Initial Oxidation of Manganous Oxide —Application of the Mott-Hauffe-Ilschner Mechanism

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The rate of initial oxidation of manganous oxide in air was observed by the thermogravimetric measurements in the temperature range between 380 and 675°C. The rate of this process follows direct logarithmic, inverse logarithmic and cubic rate laws successively from the very first stage. The height of the potential barrier for the electron tunneling from MnO through Mn_2O_3 was estimated to be about 0.1 eV from the results of the direct logarithmic region. The electric field strength across the oxide film in the next initial stage was estimated to be about 10^7 V/cm from the results of the inverse logarithmic region. The activation energy for the diffusion of oxygen ion in Mn_2O_3 was obtained from the results of the inverse logarithmic and cubic regions to be 1.3 and 1.2 eV, respectively. These experimental results have confirmed that the Mott-Hauffe-Ilschner mechanism can be applied to the initial oxidation of manganous oxide.

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I. Introduction

It has been known that in the initial oxidation of metals the rate of oxide film formation obeys a direct logarithmic law in some cases(1) and an inverse logarithmic law in other cases(2). Theories for the initial stage oxidation have been proposed by Cabrera and Mott(3) and Grimley and Trapnell(4). Further, Hauffe and Ilschner(5) have extended the original idea of Mott(6) and explained the initial stage of oxidation inclusively. Their theory is based on the concept that the rate of growth of a very thin oxide film is determined by the slower flow of ions or electrons in the oxide film. This situation is schematically represented in Fig. 1.

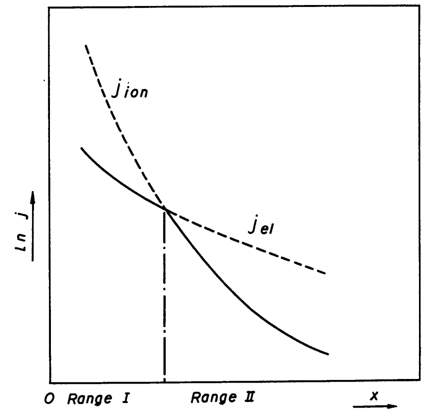

Fig. 1 Schematic representation of the rate-determining processes during the formation of very thin oxide film. (after Hauffe and Ilschner(5))

The rate of film growth in the very first stage is proportional to the probability of penetration of electrons through the oxide film to the oxide-oxygen interface by the quantum-mechanical tunnel effect(3)(5). In this process, a direct logarithmic time law is expected, and the difference between the energy levels of electrons in the metal and a conduction band in the oxide (ϕ) is considered to be of the order of 1 eV. While the rate of film growth in the next early stage is proportional to the ionic flow accelerated by the electrical double layer set up at the interfaces of the thin film(3)(5). In this process, an inverse logarithmic law is expected. The change from a direct logarithmic rate law to an inverse logarithmic one has been experimentally observed for the oxidation of aluminum with humid oxygen at room temperature(7) and for the oxidation of tantalum with oxygen at temperatures between 100 and 300°C(8).

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Thus, the mechanism and the rate of oxidation depend on the physical properties of the reacting substance and the oxide film such as the mobility of electrons, the activation energy for the migration of ions, and the height of potential barrier. Although the above theories have been regarded as being valid for the oxidation of metals or the contact of metal-oxide-oxygen, it seems that they also hold for the oxidation of a lower valent transition metal oxide-a higher valent oxide-oxygen because of the close similarity in their physical properties such as the height of potential barriers, good conductivity in the lower valent transition metal oxide and thickness.

The present investigation aims to determine experimentally whether the Mott-Hauffe-Ilschner mechanism is applicable to the oxidation of lower valent transition metal oxide.

II. Experimental

Powdered metallic manganese and Mn_3O_4 were mixed in stoichiometric ratio and the mixture is pressed to a pellet. The pellet was heated at 900 °C for 110 hr in an evacuated sealed quartz tube, followed by argon arc furnace melting. The MnO pellets were pulverized in an agate mortar in the presence of kerosene, and then the powder of equal size was obtained by the sedimentation method. X-ray and electron diffraction patterns of the powder indicated the presence of MnO only. Further, it was confirmed that the oxide has the stoichiometric composition $MnO_{1.00}$ from the weight increase of the powder after heating in air at 900 °C for 72 hr.

The electron microphotograph shows that the shape of these MnO particles is cubic. Surface area measurements by the gas adsorption method showed that the average length of the cube edge is 0.25μ. This was also confirmed by electron microscopy. Therefore, it was assumed that the powder consists of cubes having the equal edge length of 0.25μ.

About 400 mg of the powder in a fused silica basket was hung from a direct-reading type microbalance and placed in an electric furnace movable up and down. The weight increase due to the oxidation was observed at temperatures between 350 and 675 °C. The oxidation product was identified to be Mn_2O_3 by X-ray diffraction.

III. Results and Discussion

1. Data

The thickness x of the product layer and $1/x$ are plotted against log t(time) are shown in Fig. 2 and Fig. 3, respectively, and x against

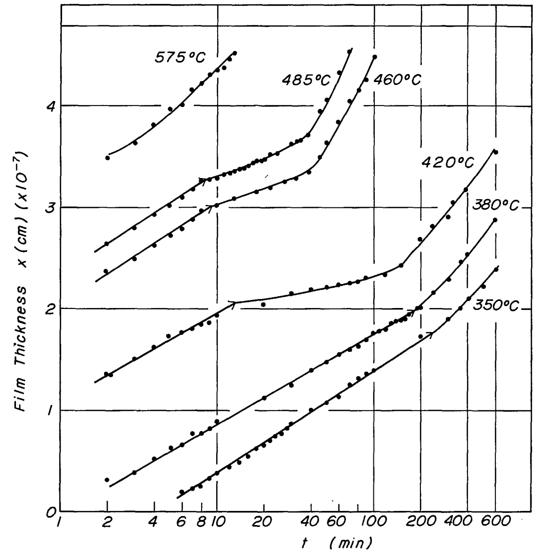

Fig. 2 Growth of Mn_2O_3 film (thickness vs log time); —•→, direct logarithmic region.

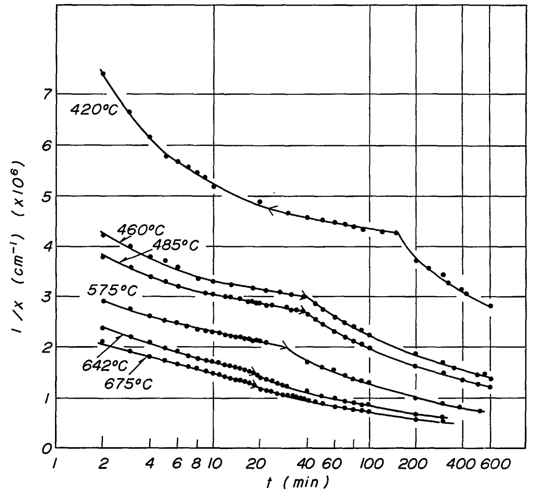

Fig. 3 Growth of Mn_2O_3 film (reciprocal thickness vs log time); ←•→, inverse logarithmic region.

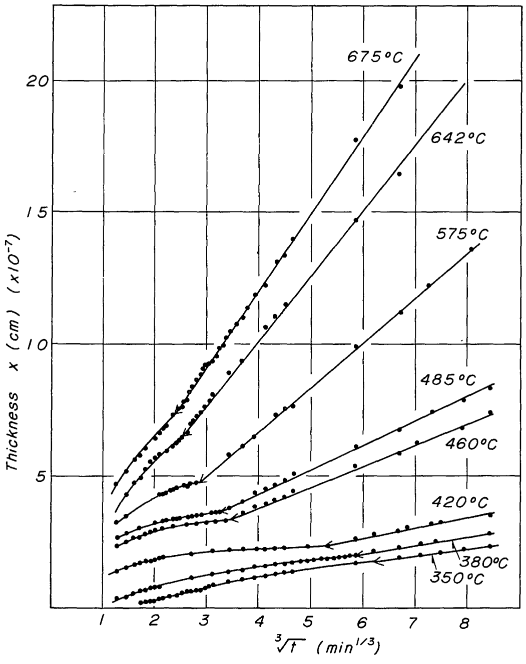

Fig. 4 Growth of Mn_2O_3 film (thickness vs cubic root of time); ←•—, cubic region.

cubic root of t in Fig. 4. x was calculated from the weight increase by the method similar to Jander's$^{(9)}$, assuming that only Mn_2O_3 is formed on the surface of MnO cube. It can be seen from these figures that the direct logarithmic, inverse logarithmic and cubic time laws can be applied in the successive ranges of temperature and time. Regions where these rate laws are known to be applicable according to Figs. 2–4 are shown in Table 1.

In general, the regions where the direct logarithmic, the inverse logarithmic and the cubic rate law are applicable are found successively from the initial stage, though the direct and inverse logarithmic regions are missing in a few higher and lower temperatures, respectively. This behavior agrees with the theory proposed by Hauffe and Ilschner for the initial oxidation of metals.

Table 1 Regions obeying the direct logarithmic, inverse logarithmic and cubic time laws.

Temp.	Direct log.	Inverse log.	Cubic
350°C	~17Å	—	17Å~
380	~20	—	20 ~
420	~21	21~24Å	24 ~
460	~30	30~34	34 ~
485	~32	32~37	37 ~
575	—	~47	47 ~
642	—	~66	66 ~
675	—	~75	75 ~

Table 2 x_0 in the direct logarithmic equation $x=x_0 \ln t-C$.

Temp.	x_0
350°C	4.3×10^{-8} cm
380	3.9
420	3.9
460	4.3
485	4.3
mean	4.2

2. The direct logarithmic range

According to the Mott-Hauffe-Ilschner mechanism$^{(5)(6)(10)}$, when the film is so thin that the electron tunneling is the rate determining process, the rate of oxidation obeys the logarithmic law: $x=x_0 \ln t-C$, where $x_0=h/4\pi\sqrt{2m\phi}$, h = Planck's constant, m = mass of electron and C is a constant. The values of x_0 obtained from the slope of very first stage in Fig. 2 are given in Table 2.

As shown in Table 2, the x_0 is nearly the same at any temperatures up to 485°C. From the average value of x_0, ϕ was found to be about 0.1 eV. This is appreciably small compared with the order of 1 eV for the oxidation of metals$^{(3)}$. This means that it is quite easier to transfer the electron from the lower valent transition metal oxide to its own higher valent oxide than the case from the metal into its oxide.

Above 575°C, the rate no longer obeys the direct logarithmic law, and the slopes of the very first stage in Fig. 2 are different from those at 485°C. It is thought that this discrepancy comes from the fact that the transfer of electrons takes place not only by the tunnel effect but also by the classical thermal activation at such high temperatures, assuming ϕ to be about 0.1 eV.

3. The inverse logarithmic range

In the range where the film thickness becomes thicker than that in the very beginning stage and the rate of the ionic transfer is rate determining, the migration of the ions is influenced by the strong electric field across the film, and the rate of the oxidation obeys the following inverse logarithmic law based on the theory of Cabrera and Mott(3)(5)(10): $x_1/x = A - \ln t$, where

$$x_1 = ZeaV/kT, \quad \text{and} \quad A = \ln\frac{1}{N^*\nu v} + \frac{W}{kT},$$

a is the jumping distance between the minimum and maximum activation barriers, Ze the charge of ions, V the potential difference due to the electrical double layer, N^* the number of ions at the oxide-oxide interface in the side of higher valent oxide, ν the frequency of oscillation, v the number of metal oxide per ion, and W the activation energy of the diffusion of oxygen ions in the higher valent oxide. Then, x_1 for each temperature is obtained from the slope of the linear part of Fig. 3 and plotted against $1/T$ in Fig. 5. These values are in the range of 1.2×10^{-6} to 2.0×10^{-6} cm, which are in good agreement with the estimation of x_1 by Cabrera and Mott(3).

Further, V and V/x (the strength of electric field) were obtained from the slope of a straight line in Fig. 5 to be about 7 V and 10^7 V/cm, respectively. These also agree with the values estimated by Cabrera and Mott(3).

Figure 6 is a plot of A against $1/T$. From the slope of the straight line in Fig. 6, W was obtained to be 1.3 eV. The diffusion constant of oxygen ion in Mn_2O_3 has not been reported up to present. However, the activation energies of the oxygen ion diffusion in the other transition metal oxides whose structures are the same as that of Mn_2O_3, e.g. c type rare-earth oxides, range from 0.9(Y_2O_3) to 2.0(Tm_2O_3) eV(11). So, the present experimental value 1.3 eV for the activation energy for the oxygen ion diffusion in Mn_2O_3 seems to be reasonable.

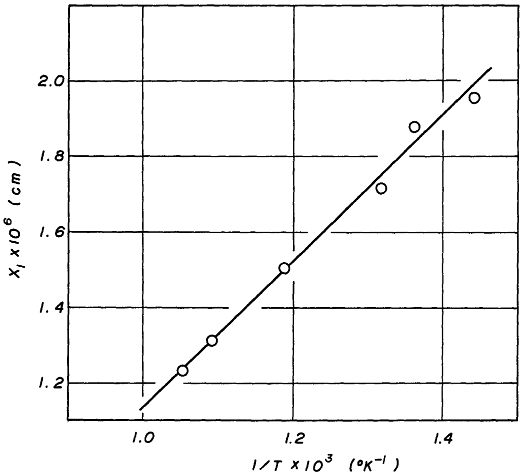

Fig. 5 Plot of x_1 (in the inverse logarithmic equation $x_1/x = A - \ln t$) against $1/T$.

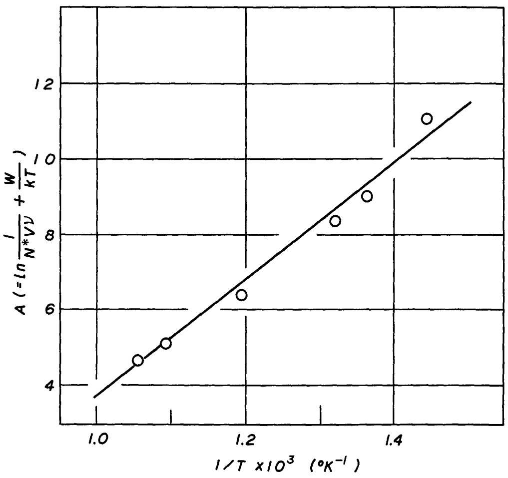

Fig. 6 Plot of A (in the inverse logarithmic equation $x_1/x = A - \ln t$) against $1/T$.

4. The cubic range

According to Cabrera and Mott(3), at low temperatures the film growth proceeds until a certain critical thickness is reached and this process obeys the inverse logarithmic law, while at higher temperatures there is no limiting thickness, and the initial rapid rate of growth in the inverse logarithmic range changes to the parabolic or the cubic type of growth due to the semi-conductive property of the film i.e. either it is n-type (parabolic) or p-type (cubic). In both cases, the film grows up to a thickness of a few hundred angstroms, and the ionic current is proportional to both strength of the electric field across the film (V/x) and the number of ionic defects per unit volume. The latter does not depend on the ambient oxygen pressure in the case of n-type semi-conducting film, but in the case of p-type it is proportional to the surface concentration of adsorbed oxygen ion σ_e whose relationship with the film thickness x is given by $\sigma_e ex/\varepsilon = V$ where ε is the dielectric constant of the oxide. Therefore, in the case of a p-type semi-conductor, the ionic current is proportional to $1/x^2$ and the rate of film growth obeys the cubic law.

In the present investigation, the film grown on the surface of MnO is Mn_2O_3 which has the crystal structure of scandium oxide type and is confirmed to be a p-type semi-conductor(12) being capable to accommodate the excess oxygen ions at interstitial sites. Therefore, it is reasonable to assume that the range of cubic law $x^3 = k_c t$ appears next to the inverse logarithmic range, where k_c is proportional to $\exp(-W/kT)$. Then, the cubic rate constants k_c were obtained from slopes of straight lines in Fig. 4. The logarithm of these constants is plotted against $1/T$ in Fig. 7. The activation energy W obtained from Fig. 7 is 1.2 eV. This agrees well with the value obtained from the results in the inverse logarithmic range.

IV. Conclusion

(1) The rate of initial oxidation of manganous oxide powder was observed in the temperature range between 380 and 675°C. The rate of this process obeys the direct logarithmic, inverse logarithmic and cubic rate law successively from the very first stage.

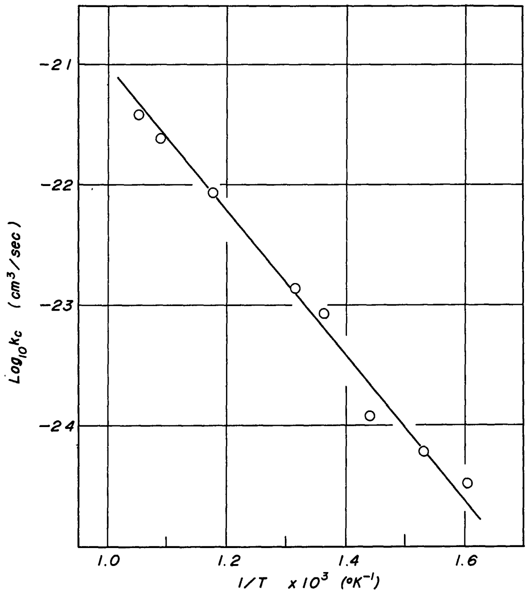

Fig. 7 Dependence of cubic rate constants on the reciprocal temperature.

(2) The height of the potential barrier for the electron tunneling from MnO through Mn_2O_3 was obtained from pre-logarithmic factors in the direct logarithmic equation and estimated to be about 0.1 eV.

(3) The electric field strength across the oxide film in the next initial stage was obtained from pre-logarithmic factors in the inverse logarithmic equation and estimated to be about 10^7 V/cm. The activation energy for the diffusion of oxygen ion in Mn_2O_3 was found to be 1.3 eV from the $1/T$ dependence of A in the equation.

(4) The activation energy for the diffusion of oxygen ion in Mn_2O_3 was also found to be 1.2 eV from $1/T$ dependence of the cubic rate constant. The fact that the cubic range appears next to the inverse logarithmic range indicates the p-type semi-conductivity of Mn_2O_3, which is consistent with the previously reported result.

(5) These experimental results lead to the conclusion that the Mott-Hauffe-Ilschner mechanism can be applied to the initial stage oxidation of manganous oxide.

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