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ABSTRACT

LOW TEMPERATURE OXIDATION KINETICS OF SINGLE-CRYSTAL ZINC

BY

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The oxidation of single-crystal zinc has been studied in the temperature range 100° - 206° C and found to follow logarithmic kinetics. The reaction rate on the prism (1010) plane was found to be 2 to 2.5 times higher than on the basal (0001) plane. Oxidation on the basal plane was found to proceed in two stages, whereas that on the prism plane was found to proceed in a single, stage. No dependence of the kinetics on the oxygen pressure was found in the range 0.8mm-2.4mm Hg. Anisotropy of oxidation rate is attributed to anistropy in the metal work function. Two-stage oxidation behavior on the basal plane was found to coincide with a change of orientation of the oxide with respect to the underlying metal lattice. The rate-determining step is believed to be electron release from the base metal into the conduction bands of the oxide, limited by the potential difference and associated field strength of the space-charge layer. A significantly lower oxidation rate was found for polycrystalline zinc, in agreement with other studies. This lower rate is attributed to the effect of grain boundaries and other imperfections.

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LOW TEMPERATURE OXIDATION KINETICS OF SINGLE CRYSTAL ZINC

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1. INTRODUCTION

Although metallic oxidation is one of the commonest chemical reactions and a leading cause of deterioration and failure of metals, it remains today one of the most poorly understood reactions. The general term "oxidation" may refer to several reactions between metals and oxidizing agents; in this study, however, it refers to direct reaction between gaseous oxygen and solid metal to form an oxide. In this sense, most metals oxidize in air at ordinary temperatures, the reaction rate increasing with temperature.

The difficulty in understanding oxidation of metals results from the structural complexity of polycrystalline aggregates: crystallites of varying size; surfaces having various crystallographic orientations, sometimes random, sometimes preferred; defects and dislocations within the crystallites; grain boundaries; and myriad impurity possibilities. In principle, it should be possible to relate the bulk-metal properties to some suitable average over the contributions from such structural elements. In a first approximation, these contributions could be assumed independent and hence separable.

Both theoretical and practical application of this principle requires experimental data showing the magnitudes of the individual contributions. Such data would result from systematic,

analytical evaluation of the oxidation in well-characterized systems. It would seem almost trite to say that efforts to understand oxidation phenomena without such information would be little more than useless philosophic exercises. Nevertheless, no such data exists nor even evidence of attempts to obtain it. The literature on oxidation is full of theoretical and experimental treatments of (frequently precise) measurements on metals only vaguely characterized with respect to the above-mentioned factors.

Comparison of results from two different metals cannot be fruitful since they will differ in too many relevant variables. These differences can be minimized only by systematic study of a single system through exploitation of crystal symmetry. Measurement of oxidation anisotropy in near-perfect single crystals would be followed by similar measurements on crystals containing controlled imperfection concentrations. Thus with the minimum of differences between data sets, the individual contributions to bulk oxidation can be evaluated.

This research is part of such a systematic study of the oxidation kinetics of zinc, and centers on the reaction anisotropy and comparison with polycrystalline material. Later phases, building on the results of this study, will focus on the contributions of various defects to the reaction as well as oxidation in other systems. Zinc was selected for the following reasons:

> -- it is available in relatively high purity, easily crystallized in any orientation and shape, and the resulting crystals are strain-free and readily

prepared for study;

- -- it oxidizes at moderate temperatures to give an adherent oxide layer of fairly simple structure;
- -- zinc oxide probably is as well-understood as any
 oxide;
- -- much experience with zinc has been accumulated in this Laboratory by Professor C. T. Wei and his students.

Single crystals of zinc have been oxidized in two principal directions, parallel and perpendicular to the hexagonal axis, and the rate of oxidation has been determined gravimetrically. Polvcrvstalline samples also have been studied for comparison both with the single crystal results as well as earlier studies of polycrystalline material.

II. BACKGROUND

A. Oxidation in metals (1)

A metal oxide may form either as an adherent and continuous layer on the metal surface or as a discontinuous, nonadherent scale. Whether the oxide layer is adherent often is determined by the Pilling-Bedworth (2) criterion that the oxide will be adherent when the ratio of the oxide molar volume to that of the metal is greater than 1. In the case of zinc this ratio is about 1.75, indicating an adherent oxide film. The continuity or porosity of the initially formed oxide determines the amount of further reaction of the metal with the oxidizing gas. If this layer is compact and adherent, further reaction is difficult and the metal is considered to be oxidation resistant. On the other hand, if the initial layer is porous or spalls off, fresh metal surfaces are exposed and the reaction continues. The condition of the metal surface also influences the reaction rate. It has been found, for example, that abraded metal surfaces oxidize more rapidly than well-polished ones, indicating probable complex interaction of surface imperfections (3). The temperature of reaction, internal stresses, and the texture or crystallographic orientation of the surface as well as the partial pressure of oxygen, all may influence the oxidation rate, and the over-all process, although expressed by a simple chemical equation, actually

is quite complex. The elementary chemical equation will not indicate the actual steps by which the oxidation proceeds, such as diffusion and phase-boundary reactions in the oxide layer. To understand the reaction as a whole, it is necessary to consider several partial processes, the slowest of which, as usual, determines the reaction rate.

1. Phase boundary reactions. It is believed that the gas (oxygen) molecules initially are chemi-sorbed on the metal surface, followed by electron exchange between metal atoms and gas molecules and splitting of the molecules into atoms. The metal is transferred to the oxide film in the form of separated ions and electrons at the metal/oxide interface. Subsequent reaction then takes place between the reactants with the formation of the oxide and initiation of the oxide lattice.

2. Diffusion. After formation of an initial oxide lattice, further reaction between metal and gas occurs by transport of metal ions and electrons through the oxide layer to the chemi-sorption interface. Transport of oxygen ions through the oxide, although Possible in principle, is unlikely in view of the much larger size of the oxygen ion. Most theories of metal oxidation have assumed diffusion of metal ions into the oxide layer to be part of the basic mechanism, a concept advanced by Wagner (4).

3. Space charge effects. At low temperatures the migration mechanism is complicated by the appearance of chemical and electrical Potential gradients. The temperature dependence of electron mobility

both in metals and semi-conducting oxides is much smaller than the ionic mobility. As a result, the ion flux is not quite compensated by the electron flux resulting in an electrical potential gradient and an electric field. This is known as the space charge effect.

Two additional factors are significant in the formation, structure and composition of the oxide.

4. Thermodynamic stability of the possible oxides at various temperatures.

5. Relative structures of the oxide and metal, which affects the registry and adhesion between the two lattices. When the two structures are similar and the lattice parameters of the two are not very much different a coherent growth is possible.

Several different forms of oxidation kinetics have been Observed:

1. At high temperatures (ranging from 2/3 the melting point to the melting point) a parabolic rate law,

$$x^2 = kt, \qquad (1)$$

is observed, where x is the thickness or weight of the oxide formed at time t and k is the rate constant.

2. Sometimes at intermediate temperatures a cubic rate law,

$$x^{3} = kt, \qquad (2)$$

is observed.

3. A linear rate law,

$$x = kt, (3)$$

is also observed, sometimes at intermediate temperatures.

4. At low temperatures a reciprocal logarithmic rate law,

$$1/x = A - B \ln t$$
, (4)

or a normal logarithmic rate law,

$$x = k \log(t/\tau + 1),$$
 (5)

is observed. In the above k, τ and A,B are constants.

The initial chemi-sorption of oxygen molecules presumably proceeds by electron transfer to the oxide and decomposition of the gas molecules into atoms. The chemi-sorbed atoms can infiltrate the oxide only when there are vacant sites in it or when the oxide lattice has interstitial positions to accommodate them. Thus the migration mechanism is related closely to the nature of the defects in the lattice and the presence of chemical potential difference between the metal/oxide and oxide/gas interfaces.

ZnO is a metal-excess n-type semiconductor (5). Various lattice defects may form in ZnO in the following four ways:

$$Zn0 = Zn\dot{o} + \theta + \frac{1}{2}0_2(g),$$
 (6)

where o represents an interstitial position and · the amount
of positive charge associated with a cation and 0 an electron in
interstitial position. Here a conduction electron is bound to a
lattice zinc ion in an interstitial position according to

$$Zn\ddot{o} + \theta = Zn\dot{o},$$
 (7)

or

$$Zn0 = Zn\ddot{o} + 2\theta + \frac{1}{2}0_{2}(g),$$
 (8)

or

Null =
$$0^{\Box} + \theta + \frac{1}{2} 0_2(g)$$
, (9)

Here denotes a vacancy and • the amount of charge associated with it. In reaction (9) the excess electron is captured by an oxygen ion vacancy according to

$$0\Box + \theta = 0\Box^{*}, \qquad (10)$$

or

Null =
$$0 \square + 2\theta + \frac{1}{2}0_2(g)$$
, (11)

where "null" denotes a perfect stoichiometric crystal.

Of these, the second reaction is believed to be dominant (6, 7, 8) and is represented by Fig. 1. This is an idealized representation of the defect structure of ZnO and shows the Presence of anti-Schottky type defects (anions and cations in interstitial positions). The ratio of monovalent to divalent zinc ions increases as temperature is increased.

According to equation (6) above,

$$x_{Zno} \cdot x_{\theta} \cdot p_{0_2}^{\frac{1}{2}} = K \text{ or } x_{Zno} \cdot x_{\theta} = K p_{0_2}^{-\frac{1}{2}},$$
 (12)

where x_{Zno} stands for the mole fraction of mono-valent zinc ions in interstitial sites, and θ for the mole fraction of electrons. Since $x_{\theta} = x_{Zno}$, it follows that

$$x_{\theta} = x_{Zno} = K p_{0_2}^{-\frac{1}{4}},$$
 (13)



Figure 1. Idealized defect structure of ZnO

showing the conductivity depends on the reciprocal of $p_{0_2}^{\ddagger}$. According to equation (8) above, similarly,

$$x_{\theta}^{2} \cdot x_{Z n \ddot{o}} = K p_{0_{2}}^{-\frac{1}{2}}, \qquad (14)$$

or, since $x_{\theta} = 2x_{Zn\ddot{\theta}}$,

$$x_{\theta} = 2x_{Zn\ddot{o}} = K p_{0_2}^{-1/6}$$
 (15)

Thus the conductivity depends on the reciprocal of $p_{0_2}^{1/6}$.

Conductivity experiments by Baumbach and Wagner (9) confirm the above dependence as it was found in their experiments that the conductivity was of the order of $p_{0_2}^{-1/4.5}$ to $p_{0_2}^{-1/5}$. It is interesting to note that the rate constant for the oxidation of z inc at high temperatures depends on $p_{0_2(i)}^{-1/6}$, where $p_{0_2(i)}$ is the initial partial pressure of oxygen, which also can be derived from Wagner's theory.

The preceding treatment rests on the assumption that thermodynamic equilibrium exists between the ionic lattice defects, electrons, holes and the oxygen atmosphere. This may be true at reasonably high temperatures when the rates of migration of the above entities in and out of the crystal lattice are equal. At low temperatures, however, the migrations of ions is too slow to balance the incoming ions. Thus changes in the defect concentration take place and lead to more complex phenomena as described below.

A low temperature should lead to a change in defect concentration. Hence at low temperatures, while the chemisorption of the oxygen ions causes an electron transfer from the metal to oxide,

there is no balancing current of ionic defects in the opposite direction. This produces a difference in charge between the metal/oxide and oxide/gas interfaces. This so-called space charge effect, which is associated with a certain filed strength, limits the movement of electrons in the oxide. In other words, when chemisorption takes place, electron exchange becomes less and, at a certain thickness of oxide (100-1000A), practically stops. The excess charge becomes localized either at the chemi-sorption interface or near (5-10A) the surface of the oxide. This charge layer is referred to as the space charge boundary layer. Thus the phenomena at the chemi-sorption interface are similar to those at the metal/oxide boundary layer and form barriers to charge flow. It is evident that the electric fields which are set up in the **space** charge boundary layers cause practically unobservable ion flow only when a chemical potential gradient is present. Whether this chemical potential gradient predominates over the space charge induced electric potential gradient determines the nature of the **rate law obeyed by the oxidation process and is of basic significance** in low temperature oxidation.

Theoretical discussions of the oxidation kinetics of metals have been given by Wagner (10), Mott (11), Cabrera and Mott (12), Uhlig (13), Fromhold (14, 15, 16, 17, 18, 19), and Tammann and Koster (20). Wagner's theory applies to the cases of high tem-Perature oxidation when diffusional effects of ions and electrons Play a dominant role in the oxidation process. Fromhold has studied extensively the methods of solving the diffusion equations for the transfer of metal ions through the oxide. Mott has given

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a theoretical explanation for very thin (40A) oxide film growth. Cabrera and Mott modified the original Mott theory to explain thick oxide growth and arrived at an inverse logarithmic equation (4) above. They also derived the parabolic rate law (1). Uhlig has given a mathematically simple but plausible theory of the logarithmic kinetics as well as the parabolic kinetics for the case of copper, including an explanation for the two-stage oxidation behavior. Nwoko and Uhlig (21) applied the original Uhlig theory to the logarithmic kinetics of zinc oxidation. In the following, brief accounts of the above theories will be given, as the basic ideas contained in them will be some guide lines for the formulation of a theoretical explanation of the results of the present study.

B. Theory

1. Wagner's theory of high-temperature oxidation (4). According to Wagner, the principle of electric charge neutrality can be assumed at high temperatures because of equilibrium between the cation, anion and electron currents in the oxide. Thus the effects of the space charge boundary layer can be neglected and the terms containing the electric field associated with this may be dropped from the transport equations. If the diffusion coefficient D_j of particle j is written in terms of the partial conductivity k_j by using the Einstein relationship (23), then the transport rates of the cations, anions and electrons j_1 , j_2 and j_3 in moles of anions, cations and electrons per unit area **Per** second can be written as

$$j_1 = -\frac{K_1}{z_1 F^2} \frac{\partial \eta_1}{\partial x}, \qquad (16)$$

$$j_2 = -\frac{K_2}{|z_2|F^2} \frac{\partial \eta_2}{\partial x} , \qquad (17)$$

$$i_3 = -\frac{K_3}{z_3 F^2} \frac{\partial \eta_3}{\partial x} , \qquad (18)$$

where z_j is the charge on the particular entity j (j = 1,2,3 for anions, cations and electrons respectively), F is the Faraday, and η_j the electrochemical potential equal to the sum of the chemical potential and electrical potential; $\mu_J + z_3FV$, where is the chemical potential; Z_3 is -1.

Thus the transport rates in equivalents per unit area per second are given by

$$J_{1} - z_{1}j_{1} = -\frac{K_{1}}{z_{1}F^{2}}\frac{\partial \mu_{1}}{\partial x} - \frac{K_{1}}{F}\frac{\partial v}{\partial x},$$
 (19)

$$J_{2} = |Z_{2}| j_{2} = -\frac{K_{1}}{z_{2}F^{2}} \frac{\partial \mu_{2}}{\partial x} + \frac{K_{2}}{F} \frac{\partial v}{\partial x}, \qquad (20)$$

$$J_3 = j_3 = -\frac{K_3}{F^2}\frac{\partial^{\mu}3}{\partial x} + \frac{K_3}{F}\frac{\partial v}{\partial x}.$$
 (21)

Constant ite often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the electron velocity is much **i**te often, at high temperatures, the anions in oxidation are those **i**te oxygen, which due to their large size cannot travel at rates **comparable** to those of electrons or cations). Thus the condition **i**tion **i**tic often, at high temperatures, the electron velocity is much **condition** J₁ = J₃, gives

$$J_{1}\left(\frac{1}{K_{1}}+\frac{1}{K_{3}}\right) = -\frac{1}{z_{1}F^{2}}\left(\frac{\partial \mu_{1}}{\partial x}+z_{1}\frac{\partial \mu_{3}}{\partial x}\right) . \qquad (22)$$

Since the metal consists of the totality of the cations and electrons we can put

$$\mu_{\text{metal}} = \mu_1 + z_1 \mu_3,$$
 (23)

thus obtaining

$$\frac{\partial \mu_{me}}{\partial x} = \frac{\partial \mu_1}{\partial x} + z_1 \frac{\partial \mu_3}{\partial x} . \qquad (24)$$

From this it follows that

$$J_{1} \cdot \frac{K_{1} + K_{3}}{K_{1} \cdot K_{3}} = -\frac{1}{z_{1} F^{2}} \frac{\partial \mu_{e}}{\partial x}, \qquad (25)$$

from which

$$J_{1} \cdot dx = -\frac{K_{1}K_{3}}{K_{1}+K_{3}} \cdot \frac{1}{z_{1}F^{2}} d\mu_{me}, \qquad (26)$$

which on integration yields

$$J_{1} \cdot \Delta x = -\frac{1}{z_{1}F^{2}} \int_{\mu_{me}(i)}^{\mu_{me}(a)} \frac{K_{1}K_{3}}{K_{1}+K_{3}} d\mu_{me}$$
(27)

where

 $\mu_{me}^{(i)}$ = chemical potential at metal/oxide boundary $\mu_{me}^{(a)}$ = chemical potential at oxide/gas boundary.

Thus

$$J_{1} = \frac{1}{z_{1}F^{2}\Delta x} \int_{\mu_{me}}^{\mu_{me}(i)} \frac{K_{1}K_{3}}{K_{1}+K_{3}} d\mu_{me} .$$
(28)

The total amount of equivalents of oxidation product per unit Area, q, per second is

$$d(n/q) = J_1 + |J_2| = \frac{k}{\Delta x},$$
 (29)

by a calculation formula similar to that for J1,

$$|J_{2}| = \frac{K_{2}}{z_{2}F^{2}} \frac{\partial \mu_{2}}{\partial x} + |\frac{K_{2}}{F} \frac{\partial v}{\partial x}|,$$

$$|J_{2}| = \frac{K_{2}}{z_{2}F^{2}} \frac{\partial \mu_{2}}{\partial x}$$

$$|J_{2}| dx = \frac{1}{|z_{2}|F^{2}} \int_{\mu_{me}}^{\mu_{me}(i)} \text{etc.},$$
(30)

and finally

or

$$\frac{dn}{dt} = \frac{q}{\Delta x} \frac{1}{z_1 F^2} \int_{\mu_{me}}^{\mu_{me}} {}^{(i)} \frac{K_1 + K_3}{K_1 + K_2 + K_3} d\mu_{me}$$
$$= \frac{q}{\Delta x} \int_{\mu_{me}}^{\mu_x} {}^{(a)} \frac{K_1 + K_2}{K_1 + K_2 + K_3}, \qquad (31)$$

where x refers to non-metal ions.

If the partial conductivities are replaced by the total

$$\frac{dn}{dt} = \frac{q}{\Delta x} \frac{1}{|z_2|F^2} \int_{\mu_x^{(i)}}^{\mu_x^{(a)}} (t_1 + t_2) t_3 K d\mu_2$$
(32)

where t's stand for the transport numbers of the entities.

The above equation has the same form as a chemical rate Quation. The quantity in brackets is independent of time and Can be identified with the rate constant. This was called by Wagner as the Rational scaling constant.

Wagner's theory can be applied to the case of zinc oxidaton bo obtain the rate constant k in terms of oxygen partial ŢTESSU :: le a ca 32 (j **:** Ċ: 1 1

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pressure p_0 as below. 2 We consider the equation

$$Zn0 = Zn\ddot{o} + 2\theta + \frac{1}{2}0_2(g)$$
 (33)

to lead to defect formation in ZnO. As already shown, in such a case,

$$x_{Zn\ddot{o}} = K p_{0_2}^{-1/6}$$
 (Eqn. 15)

us ing the Wagner rate constant in terms of transport numbers t_j (j = 1,2,3 for anions, cations and electrons)

$$K = \frac{1}{z_2 F^2} \int_{\mu_x}^{\mu_x(a)} t_3(t_1 + t_2) x \, d\mu_x, \qquad (34)$$

where x is the total conductivity.

Now
$$t_3(t_1 + t_2) = t_3(1 - t_3)$$
 since $t_1 + t_2 + t_3 = 1$
 \tilde{t}_3 since t_3 is small and t_3^2 can be neglected
in comparison with t_3 .

A Lso from eqn (1.18) we see that there are two electrons corresponding to every divalent zinc ion in an interstitial position. Thus

$$t_3 = \frac{1}{2} t_{z_n}$$

Since $|z_2| = 2$, we find

$$K = \frac{1}{4F^2} \int_{\mu_x}^{\mu_x(a)} t_z x d\mu_x.$$

The chemical potential μ_x can be replaced by RT ln p_{0_2} where p_{0_2} is the oxygen partial pressure. Thus

$$K = \frac{RT t_{z_n}}{4F^2} \int_{\substack{p_0(i) \\ p_0(i) \\ 2}}^{p_0(a)} x d\ln p_0$$

-1/6Since $x \sim p_0$ as shown (eqn. 15) above,

$$K = \frac{RT t_{z_n}}{4F^2} \int_{p_{0_2}(i)}^{p_{0_2}(a)} p_{0_2}^{-1/6} d\ln p_{0_2},$$

which on carrying out the integration yields

$$K = \frac{3RT t_{z_n}}{2F^2} \left[\frac{1}{\frac{1/6}{p_{0_2}(i)}} - \frac{1}{\frac{1}{p_{0_2}(a)}} \right].$$
 (35)

P O_2 at oxide/gas interface is much larger than $p_{0_2}^{1/6}$ at metal/ **ide** interface. Thus

$$K_{\alpha} p_{0_{2}}^{-1/6}(i),$$

icating that K is independent of oxygen partial pressure.

The parabolic rate law also can be derived from Wagner's theory, but the derivation is not included here since it is in-Luded in the theory of Cabrera and Mott (below).

2. Mott's theory (11). Mott uses Wagner's principle of Charge neutrality, but postulates a new mechanism. If electrons to pass through the oxide layer, Mott proposes that thermionic Chission from the metal into the conduction bands of the oxide wist occur. The rate at which the electrons pass through the oxide is given by

(Constant)e<sup>-
$$\phi/kT$$</sup>,

where ϕ is the work function of the metal, k the Boltzmann constant, and T is the absolute temperature. Quantum 'tunneling' makes it possible for the electrons to pass through the oxide with little or no activation energy. Mott calculates the limiting thickness for this to be 40A.

The number of electrons passing through a thickness of oxide film x is given by

where x₀ corresponds to the initial thickness at which electron emission begins and A is a constant. The rate of growth of the film, dx/dt, can be calculated as follows:

Since $x \cdot Area = volume of oxide, if \Omega is the volume of <math>x \cdot Area = volume of oxide$, if $x \cdot Area$, if $x \cdot Area = volume of oxid$

number of ions =
$$\frac{(x)(Area)}{\Omega}$$

Thus the number of ions passing per unit area is x/Ω . Hence the **target of passage of ions per unit area**

= ion current = $\frac{1}{\Omega} \frac{dx}{dt}$, $\frac{dx}{dt} = \Omega$ (ion current).

or

Since the ion current and electron current are assumed equal,

$$\frac{dx}{dt} = \Omega \quad (e \ lectron \ current)$$
$$= \Omega \ A \ e^{-x/x} 0$$

 \mathbf{I} ntegrating between \mathbf{x}_0 and \mathbf{x} and simplifying, one obtains

$$x = x_0 \ln \left(\frac{\Omega A t}{x_0} + 1\right)$$

which is the logarithmic rate law.

In the above equation $x_0 = \frac{h}{4\pi \sqrt{2m\phi}}$ obtained by a quantum mechanical calculation of the tunnel effect, with m as the electron mass, h the Planck's constant and ϕ the work function which is of the order of 1 ev (11). A is a constant of the order of 10^{22} cm⁻² sec⁻¹. Mott's value of the rate constant calculated from the above theory was found to agree within an order of magnitude with Vernon's experimental value (3). It is clear from the above that the rate constant x_0 is independent of temperature, which is not borne out by experiment.

3. Cabrera-Mott theory (12). In this treatment Wagner's theory is applied to obtain the parabolic rate law $x^2 = 2At$ and to evaluate the constant A. To calculate A it is assumed that the dissolved metal atoms (in cases where an n-type semiconducting vide is formed, as in the case of zinc) are almost completely dissociated into ions in interstitial positions and electrons. A is given by $A = 2\Omega D_i n$, where Ω is the volume of oxide formed Per metal ion, D_i is the diffusion coefficient of the interstitial ions and n is the concentration of dissolved atoms at the metal/ very thick oxide, as it is derived on the assumption that the con-Centration of electrons n_e is equal to the concentration of ions n_i , which is not true for thin oxide films. Thus the above value is not true for a thickness less than x_0 , the thickness of the electrical double layer found in thin films. Mott has shown

that $x_0 = (KkT/8_{fm}ne^2)^{\frac{1}{2}}$, where K is the dielectric constant of the oxide, n is the electron density and e, the electronic charge. For oxide thicknesses less than x_0 and when $n_e \neq n_i$, the space charge has very little effect. Consequently the motions of the ions and electrons can be considered separately. In metals and semiconductors, electron mobility is greater than ion mobility and the electrons can pass freely through the film and set up a potential difference between the metal and the absorbed layer of oxygen. In such a case, $A = \Omega v_i \vee n_i$, where n_i is the concentration of metalions and v, is their mobility and V = potential difference across the space **charge layer.** A parabolic law is again obtained, but the rate is different since the value of A is different in this case. It is seen that parabolic rate laws are obeyed when $x \ll x_0$ and $\gg x_0$. In the transition region at x of the order of x_0 , a parabolic rate law is not obtained.

For thick films Mott has applied his own theory of semi-Conductors (23). Excess metal is imagined to be dissolved by an ide either interstitially with the excess ion going into an interstitial position and electron moving round in the lattice, as an F-center where an anion is missing and is replaced by an lectron. At a temperature at which the oxide is in thermodymanic uilibrium with its oxide and at which the ions are sufficiently bile, complete dissociation of the metal into ions and electrons is assumed (Fig. 2). At the interface between the metal and oxide, the situation is presumed to be as shown in Fig. 2. The process of dissolving the metal ion is transference of the ion at P into the oxide at an interstitial position. The energy required being



F 1 gure 2. Conduction bands in oxide in contact with metal.

 W_i , the heat of solution of the ion. One also should consider the energy ϕ required to remove the electron from the metal into the oxide, the work function of the metal modified by its contact with the oxide. Thus the heat of solution of the metal ion in the oxide is $W_i + \phi - \epsilon$ where ϵ is the binding energy between an electron and an interstitial position. When ϵ is smaller than W_i or ϕ by several multiples of kT, the dissociation is complete, as assumed here. The concentration of interstitial ions at the interface, $n_i(0) = N_i \exp(-W_i/kT)$ (12) where $N_i =$ number of interstitial positions in the oxide per unit volume. The concentration of electrons at the interface is denoted by ne(0) which is given by the equation

$$n_{o}(0) = N_{o} \exp(-\phi/kT)$$
 (36)

where N_e is the number of electrons per unit volume given quantum mechanically by

$$N_{e} = 2(2\pi m kT/h^{2})^{3/2}$$

If the concentrations of the electrons and interstitial ions at a distance x from the interface are $n_e(x)$ and $n_i(x)$ respectively, given by

$$n_{e}(x) = N_{e} \exp(-\phi/kT)$$
$$n_{i}(x) = N_{i} \exp(-W_{i}/kT),$$

the product $n_i(x)n_e(x)$ is constant. At large values of x, $n_i(x)$ and $n_e(x)$ are equal and can be denoted by n, and

$$n^{2} = N_{i}N_{e} \exp\left(\frac{W_{i} + \phi}{kT}\right),$$

so that

$$n = \sqrt{N_i N_e} \exp\left(-\frac{W_0^+ \phi}{2kT}\right)$$
(37)

At intermediate positions,

$$n_i(x) = n \exp(-ev/kT),$$

 $n_e(x) = n \exp(ev/kT),$

where v is the electrostatic potential given by Poisson's equation

$$\frac{d^{2}\mathbf{v}}{dx} = 4\pi e/k\{n_{i}(x) - n_{e}(x)\}$$
$$= \frac{8\pi n}{K} \sinh\left(\frac{e\mathbf{v}}{kT}\right)$$
(38)

where K is the dielectric constant of the oxide. When x is large and v small, this leads to

$$\frac{d^2 \mathbf{v}}{d \mathbf{x}^2} = \mathbf{v} / \mathbf{x}_0^2, \tag{39}$$

Where

$$x_0 = \frac{KkT}{8\pi m_e^2} \cdot \frac{1}{8}$$

Thus the treatments for $x \ll x_0$ and $x \gg x_0$ differ.

The current carried by electrons (in units of e) is given by

$$\mathbf{j}_{e} = -\mathbf{D}_{e} \frac{\partial \mathbf{n}_{e}}{\partial \mathbf{x}} + \mathbf{F} \mathbf{n}_{e} \mathbf{v}_{e},$$

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and the ionic current is given by

$$j_{i} = -D_{i} \frac{\partial^{n} i}{\partial x} - F n_{i} v_{i},$$

In the steady state,

$$j_e = -j_i = j$$
,

and thus

$$j\left[\frac{1}{n_{e}v_{e}} + \frac{1}{n_{i}v_{i}}\right] = -\frac{kT}{e}\frac{\partial}{\partial x}\ln(n_{e}n_{i})$$
(40)

For $x \gg x_0$, $n_i(x) = n_e(x) = n(x)$ and $j = -2D_i \frac{\partial n_i}{\partial x}$ by adding the equations for ion and electron currents. Writing $\frac{\partial n_i}{\partial x}$ as n(0) - n(x) = n(x), we get

$$j_x = -2D_i[n(0) - n(x)]$$

from which one obtains $\frac{dx}{dt} = \frac{A}{x}$ as in Mott's theory. Integration **Of** this equation leads to the parabolic rate law

$$x^2 = 2At$$
.

Caberera and Mott further describe mechanisms for thin and very thin films, arriving at a parabolic rate law with a different value of A and a reciprocal logarithmic rate law which has not been observed in the case of zinc.

4. Uhlig's theory (13). Mott's analysis holds for films as thick as 40A and gives a rate constant independent of temperature, which is not borne out by experiment. Uhlig's theory, however, applies to oxide thicknesses to 1000A. The fact that the reaction mechanism for thin film formation is largely controlled by processes e the s iate or ing: :ate (ieren: tifiz :: la ia ti **r**ta :: ī is is 2 at the metal/oxide interface rather than at the oxide/gas interface or by diffusion through the oxide is evident from the following:

a. In the case of cubic metals anisotropy in the oxidation rate (one crystallographic face oxidizing at a substantially different rate from another) cannot be due to differing rates of diffusion, since diffusion in cubic metals is isotropic.

b. Discontinuity in the activation energy for oxidation at lattice transformation temperature cannot be due to processes in the oxide/gas interface and must have something to do with the metal/oxide interface.

c. Discontinuity in the activation energy for oxidation at the Curie temperature (eg. Cr - Fe alloys (25)) cannot, likewise, be due to processes near the oxide/gas interface.

Uhlig postulates a mechanism in which the oxidation rate is controlled by electron emission from the metal into the conduction bands of the oxide.

Mott favored the slow escape of metal ions from the metal into the oxide lattice as the controlling step in several reactions producing thin films and electron emission as the controlling step in insulator type films below 40A. Convincing evidence is available to show that slow electron emission indeed is the controlling step up to several thousand angstroms. This comes from an empirical relationship proposed by Rideal-Jones (26) who showed that for Platinum Carbon, and Tungsten oxidation the activation energy $\Delta E = \phi_0 - K$, where ϕ_0 is the work function of the metal and k is a constant = 3.6 eV = $\phi_a + \phi_c$, with ϕ_a equal to the energy of absorption and ϕ_{a} equal to the electron affinity of adsorbed oxygen. When ϕ_0 equals K, there is no activation needed for the reaction. When ϕ_0 is greater than K, the reaction is delayed and more oxygen reaches the surface of the metal than can react. This means that oxygen can chemisorb on the metal for which it has a certain affinity and can remain there before metal ions leave their lattice positions to initiate reaction. The Rideal-Jones equation can be applied to all cases where non-volatile oxides are formed according to the logarithmic equation. Thus this equation can be expected to hold whenever the reaction is controlled by electron flow. This also may explain why the oxidation rate varies with crystal face , since the work function also varies with the crystal face . The equation also explains the change in activation energy during transformation, since the work function changes from structure to structure; the same is true for the variation of the oxidation rate above and below the Curie temperature.

In semi-conducting oxides with filled energy bands and relatively few electrons excited into the conduction bands, excess charge associates mainly with lattice imperfections (impurity centers or vacancies). Negative charge of this kind exists as so called 'trapped' electrons. In the same way, trapped vacancies or holds may exist. In view of the restricted number of sites for trapped electrons, the space charge in oxide layers extends into the oxide for several thousands angstroms. Volta potential (contact potential) measurements on copper and zinc (27, 13) bear out this fact.

viet a psitiv 1 decre i port at lat ::e:-a of the żą ès: iers; Lê exce 5 **:**:: 51<u>7</u> . **.** . ٩ 14 ï An initial positive charge layer is built up in the oxide when a metal is first oxidized because of the rapid escape of positive ions from the metal into the oxide. As the oxide grows, a decrease of the positive space charge takes place because of a portion of the electrons escaping into the oxide being trapped at lattice imperfections. Eventually the oxide may acquire an over-all negative charge, depending on the final equilibrium state of the electric charge.

To calculate the oxidation rate, consider first the excess charge in the growing oxide film of total thickness y is uniformly distributed in the oxide volume. This corresponds to uniform defect density at which the electrons or positive holes are bound. When the thickness reaches a certain value ℓ_{2} let us assume that the excess charge in the film creates an electric field at the metal surface which is compensated by the positive charge field resulting from the escape of excess metal ions into the oxide, i.e., it results from the electron 'sink' at lattice vacancies formed at the oxide surface. Thus when $y = \ell_{2}$, the electric field is zero (Fermi levels in the oxide and metal are equal).

If n is the density of trapped electrons in the oxide and -e is the charge on an electron, then the potential V at the metal/oxide interface is given by Poisson's equation

$$\frac{d^2 v}{d y^2} = \frac{4\pi n e}{\varepsilon}$$
(41)

where c is the dielectric constant of the oxide. Integrating,

$$\frac{\mathrm{d}V}{\mathrm{d}y} = \frac{4\pi\mathrm{n}\mathrm{e}}{\mathrm{e}} \, \mathrm{y} + \mathrm{C}_1.$$

Since the field is zero when $y = \ell$,

$$C_1 = -\frac{4\pi ne}{\epsilon} \ell$$

Thus

$$\mathbf{v} = \frac{4\pi ne}{\varepsilon} \frac{\mathbf{y}^2}{2} - \frac{4\pi ne}{\varepsilon} \boldsymbol{\ell} \mathbf{y}$$
$$= -\frac{4\pi ne}{\varepsilon} [\boldsymbol{\ell}\mathbf{y} - \frac{\mathbf{y}^2}{2}] + C_2. \tag{42}$$

The potential at the metal surface is $-(\phi - V)$ for y = 0, where e_{ϕ} is the energy for transferring an electron to the metal surface. V is in general numerically equal to the potential difference between the metal/oxide and oxide/gas interfaces, whenever the diffusion of ions toward the metal is negligible. Thus

$$C_2 = -(\phi - V) \tag{43}$$

For space-charge layers very much less than ℓ , y^2 can be neglected. Hence

$$V = -\frac{4\pi n e}{\epsilon} (\ell y) - (\phi - V)$$
(44)

The rate of oxide growth dy/dt is proportional to the rate of escape of metal ions, which in turn is controlled by the rate of electron escape. The electron current across a metal/semiconductor boundary is given by

$$i = A' \exp(-e_{\phi}/kT) (\exp ev'/kT - 1)$$
 (23), (45)

where A' is a constant, ϕ the work function of the metal modified by contact with the oxide, V' the applied voltage across the metal/oxide interface. V' is of the order of a volt and

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$$i = A' \exp\{-(\phi - v')/kT\}.$$
 (46)

Since the rate of film growth is proportional to i, it can be written

$$\frac{dy}{dt} = \beta I,$$

where β is another constant. Put

$$v' = v - (4\pi ne/\epsilon) ly$$

Then

$$\frac{dy}{dt} = A \exp \frac{-e_{\phi} + e_{v} - \frac{4\pi n e^{2} ly}{\epsilon}}{kT} \quad (A = \beta A'). \quad (47)$$

Integrating from 0 to 2,

$$y = \frac{\epsilon kT}{4\pi n e^2 \ell} \ell n \left[\left(\frac{4\pi n e^2 \ell A}{\epsilon kT} \exp \frac{-e(\phi - v)}{kT} \right) t + 1 \right]$$
$$= k_0 \ell n (t/\tau + 1), \qquad (48)$$

where

$$k_0 = \frac{\epsilon kT}{4\pi ne^2}$$
,

and

$$\tau = \frac{c kT}{4\pi ne^2 LA} \exp \frac{e(\phi - v)}{kT} = \frac{k_0}{A} \exp \frac{e(\phi - v)}{kT}.$$
 (49)

The above equation applies only to a limited film thickness adjacent to the metal. At the stage of oxidation where the existing interface electric field and oxide structure are no longer conducive to filling all available sites for trapped electrons, the available

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sites become only partially filled. Hence the excess charge residing farther away is no longer uniform, but is influenced by the potential existing at any point in the film. In such a case the density of positive charge is $n_1 \exp(ev/kT)$ and the density of negative charge is $n_2 \exp(ev/kT)$, so that the net excess of negative charge is

$$n = n_0 \{ \exp(\frac{ev}{kT}) - \exp(-\frac{ev}{kT}) \}.$$

If ev << kT,

If this value of n is substituted into Poisson's equation and V is assumed to be zero when the field is zero and $V = C_1^{\dagger}$ at Y = 0(Y =distance into the diffuse oxide layer), then

$$V = C_{1}^{*} \exp(-\frac{2Y}{x_{0}}),$$

n = $\frac{2n_{0}eC_{1}^{*}}{kT} \exp(-\frac{2Y}{x_{0}})$ with $x_{0} = (\frac{\epsilon kT}{2\pi n_{0}e^{2}})^{\frac{1}{2}}.$

C¹ is the potential at the metal/oxide layer at which the transition to diffuse layer begins (at thickness L).

If we now consider the potential at the metal/oxide boundary produced by the diffuse charge, potential V must become more negative with increased total thickness of oxide, y, following an equation identical with the above, except for change in sign in the exponent and where C_1' is replaced by C_0 , the potential at y = 0. For simplicity assume y = 0 at L. Then

$$C_0 = -\frac{4\pi me \ell L}{\epsilon} - (\phi - V),$$
$$V = C_0 \exp(\frac{2Y}{x_0}),$$

Thus

$$\frac{dy}{dt} = A \exp \frac{C_0 e \exp \frac{2Y}{2x_0}}{kT}.$$
(50)

It is justifiable to assume that $y \ll x_0^2$ and write

$$\exp(\frac{2Y}{x_0}) = 1 + \frac{2Y}{x_0}.$$

Then integration of (50) yields

$$y = \frac{x_0}{2} (\frac{kT}{-C_0 e}) \ln \left[\left\{ (\frac{2A}{x_0} \cdot \frac{-C_0 e}{kT}) \exp \frac{C_0 e}{kT} \right\} t + 1 \right]$$

= $k_0^* \ln (t/\tau^* + 1)$ (51)

which is the logarithmic rate law for the second stage. Here

$$k_0' = \frac{x_0}{2} \left(\frac{-kT}{C_0 e} \right),$$
 (52)

and

$$\tau' = \frac{x_0}{2A} \left(\frac{kT}{-C_0 e}\right) \exp\left(\frac{-C_0 e}{kT}\right) = \frac{k_0}{A} .$$
 (53)

Fromhold's treatment. Fromhold's treatments are all aimed at improving the mathematical methods of solving the diffusion equations in the case of high-temperature oxidation and the solution of Poisson's equation in the case of low-temperature oxidation. His results for low-temperature oxidation, although derived rigorously, appear to be the same as those derived by Uhlig by less complex methods. As Fromhold's treatments add nothing new to the baic (will no to re și cie C.T.E.): a 787] تقأ 3 <u>n</u> (<u>ا:</u>: Зę . 32 ċ k t ÷ 2 basic concepts of Mott and others, his mathematical treatments will not be discussed here (refs. 14, 15, 16, 17, 18, 19).

C. Zinc-Oxidation Work

1. Tammann and Koster (26). These workers were the first to report that a logarithmic rate law is obeyed by the oxidation process in zinc.

2. Vernon, Akeroyd and Stroud (3) studied the oxidation kinetics of polycrystalline zinc in the temperature range 25°-225°C by a gravimetric method which consisted of weighing the sheets at various times after start and confirmed that the logarithmic rate law is obeyed in this temperature range, while a parabolic rate law is obeyed above 250°C. They found that the kinetics depended on the nature of the specimen surface (whether abraded or polished). Although self-consistent results were obtained, they could not be reproduced very well. A nucleation-and-growth type theory was proposed to explain the logarithmic kinetics.

3. Raether (28) studied the nature of the oxide formed by oxidizing single-crystal specimens and obtaining electron diffraction patterns of the oxide. By a comparison of the patterns obtained with the base metal and the oxide, he deduced that while pseudomorphic strains were absent, the oxide grew with its prism planes parallel to the basal planes in the base metal.

4. Moore and Lee (29) studied the parabolic kinetics of zinc oxidation by a volumetric method (i.e., calculated the weight of oxide formed from the volume of oxygen reacted at any instant) and in order to apply Wagner's theory to the oxidation process and

obtain a theoretical value for the rate constant used the values of the diffusion coefficient of Zn in ZnO determined by Moore and Williams (30). The calculated values of the rate constant were found to agree with the experimental values.

5. Gensch and Hauffe (31) oxidized zinc alloys with aluminium and lithium and found that at high temperatures (where the parabolic rate law is applicable) the higher-valent metal aluminium reduced the oxidation rate while the lower-valent metal lithium had the opposite effect.

6. Nwoko and Uhlig (21) studied the oxidation of polycrystalline zinc in the range 125°-206°C and found again that the logarithmic rate law is observed. They also added the new fact that zinc oxidizes in two stages at all these temperatures, with the second stage starting at about 100 min after initiation and having about twice the rate of the first stage. They explained the results by the earlier Uhlig theory. Another significant result was that the oxidation rate was found to be unaffected by the oxygen pressure (pressures used: 0.2mm, 0.35mm and 0.7mm Hg).

III. EXPERIMENTAL AND RESULTS

The oxidation rates on the basal (0001) and prism (1010) planes of single crystal zinc were measured by following gravimetrically the increase in weight of the samples with time at the required temperature in an atmosphere of oxygen by using a sensitive electrobalance. Polycrystalline samples were also studied by the same method. The temperature range was $100^{\circ}-206^{\circ}$ C. Rate constants and activation energies were calculated. The orientation relationships between oxide and underlying metal were established by Laue diffraction technique.

A. Apparatus

Figs. 3(a) and 3(b) show the features of the apparatus consisting of (1) the Cahn RG vacuum electrobalance, (2) Mass panel and mass recorder, (3) Furnace, (4) Temperature controller and recorder, (5) Reaction tube, (6) Vacuum system, (7) Pirani gage, (8) McLeod gage, (9) Gas-handling system and (10) needle valve.

Details of the above are given in the following:

1. Cahn RG Vacuum Electrobalance. This is a device for measuring masses and mass changes very accurately to one tenth of a microgram. The balance operates satisfactorily under high vacuum and provides a method of continuous measurement and recording of weight changes in the sample. Because of the high sensitivity of

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Figure 3(a). Showing Front View of Apparatus.

- 1. Main manifold 13. Gas Bubbler 2. Cold Trap 14. Specimen 3. Liquid N₂ Dewar 15. Reaction Tube 4. Cold Trap 16. Gas Tower 5. Liquid N₂ Dewar 17. Split Muffle Furnace 6. 18. 'Drierite' Tower Tiltable McLeod Gage 7. Pirani Gage 19. Needle Valve 8. Oil Diffusion Pump 20. To Mechanical Pump 9. 'Drierite' Tower 21. To Cahn Mass Panel and Mass Recorder 10. Cahn RG Vacuum Electrobalance 22. To Main manifold 11. Glass Fiber 23. To Bridge Circuit 12. Chromel-alume1 Thermocouple 24. Cooling water
 - 25. To Temperature Controller
 - 26. To Gas Supply



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Figure 3(b). Showing Oblique Side View of Apparatus (Numbers have the Same Significance as in Figure 3(a)).

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the balance, small and conveniently shaped samples can be employed, thus reducing the probability of surface contamination. The balance required little maintenance. Measurement of weight by the balance is based on the null balance principle. Fig. 4 explains the principle of operation. When the weight of the sample changes, the beam deflects. A flag of metal attached to the front end of the beam moves with it, causing a change in the amount of light incident on a photo-tube. The photo-tube current is amplified in a servo-amplifier and the amplified current is fed into a coil attached to the beam placed in a magnetic field. Current in the coil produces a motor effect causing an opposing torque and restores the beam to its equilibrium position. Thus the change in electromagnetic force is proportional to the change in sample weight. The torque on the beam is proportional to the current and a measure of the current is therefore a measure of the change in sample weight. The beam itself thus is always in equilibrium since the total torque on it is zero. The restoring torque is sufficiently powerful and fast to keep the beam locked in position even when the sample weight changes continuously. The balancing current or voltage is fed into the mass panel and thence to a mass recorder for recording the weight as a function of time. Further details of the theory of operation of the balance can be found in reference (32).

Specimens can be suspended either from loop A which is deisgned to measure weight changes of 200 mg or loop B designed to measure weight changes up to lgm. Loop C is for counter-weights.

Figure 4. Principle of Operation of Cahn RG Electrobalance.



The balance was enclosed in a vacuum chamber with a 4" O-ring sealed metal plate secured to the chamber by metal springs. The bottle was mounted horizontally on a common vacuum rack on which other parts of the appartus were also mounted. The bottle had three downward-projecting ground-glass standard taper joints for attaching the reaction tube, the glass envelope for covering suspensions from loop B and another envelope for covering suspensions from loop C. The central envelope was connected to the vacuum system and only loop A was used for measuring sample weight changes.

The electrical output from the balance and the thermocouple output are fed into terminals mounted on the metal cover plate, which in turn are connected to the mass panel and temperature recorder respectively.

2. Mass panel and mass recorder. The mass panel is a switch box used for calibration and actual measurement of sample weight. It is provided with the mass-range dial with which to adjust the required range of mass to be measured, the mass dial for measuring the weight, and the recorder range dial to select the correct output to the recorder to keep the pen in the range of the chart for a maximum increase in weight. The mass panel obtains its input from the balance and feeds a signal to the recorder.

The mass recorder used was a 10mv, Speedomax H type recorder, with chart speeds adjustable at 60"/hr and 10"/hr. The slower speed was used throughout. The recorder was mounted on a rack along with the temperature recorder.

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3. Furnace. Heat supply to the sample was provided by means of a split-muffle tube electric furnace, with non-inductively wound heating coils surrounding the reaction tube. The furnace had a cylindrical bore 10" long x $1\frac{1}{2}$ " diameter, having a power rating of 1200 watts and usable up to 1100° C. The temperature profile of the furnace was found to be flat about 1" to either side of the specimen position.

4. Temperature controller and recorder. A Variac was used to control the temperature of the furnace and that of the specimen. The performance of the Variac was checked over a period of 24 hours, during which the temperature variation was found to be less than $\pm 1^{\circ}$. Since the duration of a reaction run was about 8 hrs., the temperature was controlled very well within the above limits.

A Brown potentiometer was used to measure and record the temperature of the specimen using a chromel-alumel thermocouple suspended near the specimen inside the reaction tube. The thermocouple was checked against a standard Leeds and Northrup potentiometer with satisfactory results.

5. Reaction tube. A Vycor glass tube 1" I.D x 1 m long was used as the reaction tube in which the specimens were oxidized in an oxygen atmosphere. The tube is provided with a ground-glass standard taper joint to fit the extreme left projection from the vacuum chamber and the bottom of the tube is provided with a ground-glass joint for attaching the glass tube leading from the gas inlet valve. The small bore of the tube, although limiting the specimen size, had the advantage of the gas and specimen being raise syste уż Nic Conne the c æcha ina) a'ii Œ35, is ₀₈ ;asse the ; üsed <u> 1</u>]3 ¥ith ić_{zi} The : ttro, ^{of} ti raised to the required temperature in a short time.

6. Vacuum system. The vacuum system was a typical glass system with liquid nitrogen traps, single-stage oil diffusion pump and a mechanical pump. A second cold trap connected to the main manifold served to trap mercury vapor from the McLeod guage. Connected to the center of the main manifold is a stopcock from the oxygen supply tube. This tube was connected to a second mechanical pump for evacuating the gas supply system.

7. Pirani gage. A Pirani gage was used to measure the final vacuum in the system after evacuation. The gage was calibrated by using a standard McLeod gage.

8. McLeod gage. A tilting type McLeod gage was used to measure the pressure of the oxygen during a reaction run. The gage is capable of reading pressures from 0.01 mm to 15 mm Hg.

9. Gas handling system. Oxygen from the container was passed through a metering system and then over 'Drierite' to dry the oxygen before storage in the glass supply tube. The oxygen used was 99.5% pure in the initial experiments and 99.98% pure oxygen was used in final experiments. No difference was observed with these two grades of oxygen.

10. Needle valve. An Edwards needle valve was used for admitting controlled amounts of oxygen into the reaction tube. The inlet side of the valve was connected to the supply tube through a stopcock. The outlet side was connected to the bottom of the glass tube covering the bottom of the reaction tube.

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B. Calibration of the Balance

Before installing the balance in the vacuum bottle, its performance was compared with that of a Mettler analytical balance with good agreement. To check the ability of the recorder to record continuous weight changes, a simple kinetic experiment was performed in which a small grain of 'Drierite' was placed on loop A and the gain of weight of the sample due to absorption of atmospheric moisture was recorded. The total gain in weight in 5 hours was determined from the recorder trace and the percentage gain in weight calculated. The same experiment was repeated with the Mettler balance by weighing the Drierite sample initially and after 5 hours. The % increase in weight measured with the Mettler balance was compared with the results from the electrobalance with good agreement.

These procedures were repeated after installing the balance in the vacuum system, with satisfactory results.

The performance of the balance in vacuum was also checked by suspending a known weight into the reaction tube by means of a long thin Pyrex glass fiber and comparing the weights registered in vacuum and in air. The normal weight and the weight in vacuum did not show any difference. The same experiment was repeated at an elevated temperature $(250^{\circ}C)$, again with satisfactory results. The balance was then finally calibrated with counter weights and a small platinum wire loop attached to the glass fiber on loop A (serving as specimen hanger in all experiments). Blank runs were made to see if the balance registered any change in weight

1 81.) ini tha 5 57 .e: to : ... Ì:: 13 •1. . ••• 4 5 ste . · P la: 0ť in vacuum at elevated temperatures. No such change was noted, except for an initial loss in weight due to evaporation of moisture and absorbed gases on the surface of the sample. It was established that a period of 2 minutes was quite sufficient for this purpose in an actual experiment.

The laboratory lights were always kept on during a run, as switching the lights off tended to shift the recorder pen to the left, although by a very small amount. The balance was calibrated to read mass changes up to 0.02 mg for a full scale deflection of the recorder pen. Thus the sensitivity of the measurement was 0.002 mg for a tenth of the recorder range, and 0.0002 mg per small division of the chart.

C. Specimens

 Single Crystal preparation. Zinc single crystals were prepared using a modified Bridgman method developed in this Laboratory by K. Chyung and C. T. Wei (33), from 99.99 + purity zinc of the following specifications: 99.99+% Zn,

> 0.0009 % Pb, 0.0028 % Fe, 0.0018 % Cd.

A seed prepared by the usual Bridgman method is welded to a zinc sheet of the desired shape. This assembly is placed in a graphite crucible and the empty surrounding space packed with a mixture of 1 part graphite powder and 99 parts zirconia powder to minimize lateral thermal gradients. The crucible is placed at the junction of two tube furnaces, the lower of which can be maintained at a

temperature below the melting point of zinc while the upper furnace can be maintained at a higher temperature to provide the required temperature gradient throughout the cooling program. Furnace temperatures are controlled by a precision Brown potentiometer. The temperatures of the lower and upper furnaces determined by trial experiments were 350° and 450°C respectively. The position of the junction of the seed and stock is critical: only a small part of the seed may extend into the high-temperature region of the upper furnace. Fig. 5 shows the essential features of the furnace and charge setup.

After the furnaces are raised to the set temperatures, a soaking period (about 3½ hrs.) is started. At the end of the soaking period the assembly is cooled at a programmed rate, during which crystallization begins and a grain nucleates and proceeds slowly up to the top of the stock. The solid assembly then can be removed by first shaking out the insulating powder and picking up the crystal carefully with a pair of tweezers or shaking it out slowly onto a soft cushion. The seed can be cut off by acid sawing and reused. The grown crystal has the same orientation as the seed. There are no moving mechanisms in this method as there are in the normal Bridgman method, and moreover single crystals of any desired shape can be grown in a relatively short time. Each crystal grown was 15cm x 1cm x 3mm in size (Fig. 6).

2. Orientation checks. After removing the seed, each crystal was washed thoroughly and etched with dilute hydrochloric acid to reveal any grain boundaries. A small piece also was examined metallographically at low magnification to observe any

Figure 5. Furnace Set Up for Single Crystal Preparation (Schematic).


Figure 6. 'As Grown' Cyrstal With Seed Cut Out.



Figure 7. Overlay of Back Reflection Pattern From Basally Oriented Crystal. Figure 8. Overlay of Back Reflection Pattern From Prism Oriented Crystal. small grain structure. Orientations of both seed and crystal were checked by the back-reflection Laue technique. It was established that the orientation of the crystal was the same as that of the seed in each case. Since the basal plane is easy to check, with hexagonal symmetry of the patterns, no elaborate measurements were necessary. A seed was cut from a basally oriented seed such that the new seed had the (1010) prism orientation. Two such seeds were sufficient to obtain all crystals needed for the present study. Figs. 7 and 8 show overlays of the Laue back reflection patterns of two typical crystals, one in each orientation.

3. Preparation of experimental samples. Samples required for the kinetic experiments were prepared by thinning down the grown crystal in 10N hydrochloric acid to 0.05-0.1mm. The thinned sheet was cut along lines parallel to its breadth by etching with 12Nnitric acid to obtain small rectangular specimens about 1 cm^2 in area. A small hole (0.05mm dia.) was etched with nitric acid at one end of each sample for suspension from the specimen hanger in the reaction tube. Every reasonable precaution was taken to avoid straining the crystals. The samples were washed with distilled water, and TransistAR-grade acetone and finally dried in a slow stream of cool, dry air. Each sample was prepared immediately before introduction into the reaction tube in order to avoid possible contamination during storage.

4. Specimen characterization. Each of the specimens used was $0.75 \text{mm} \times 1 \text{cm} \times 0.05 \text{mm}$, to give a total surface area of approximately 1.5 cm² (including both sides). Each specimen was confirmed

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to be a single crystal by chemical polishing and metallographic examination. Fig. 9 is a typical specimen photomicrograph, and shows no grain boundaries at this magnification. The presence of large grains is not possible because of the small size of the samples. Back reflection Laue patterns also were recorded using copper white radiation as a further check on crystallographic orientation and perfection.

Orientations were checked by using stereographic projections of the patterns from two typical samples, one of each orientation. After having established the orientation corresponding to a particular pattern, the orientation corresponding to the pattern of another sample immediately could be checked by bringing the indexed pattern and the test pattern into a single projection and noting the match between them. The basal plane could be quickly checked by inspection by measuring hexagonal symmetry around the central spot. Figs. 10 and 11 show the back reflection patterns from two typical specimens, one in each orientation.

Dislocation densities in the samples were estimated approximately by observing the dislocation-etch-pit patterns of two typical specimens. The following, developed by Vreeland et al (34) describes the polishing and etching solutions and times employed: Chemical polishing solutions:

P-1	160 g Cr0 ₃
	20 g Na ₂ S0 ₄
	500 ml distilled water.
P-2	Equal parts of 30% H ₂ 0 and 16N HNO ₃ .
P-3	160 g CrO ₃ + 500 ml distilled water.

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Figure 9. Photomicrograph of Typical Specimen, Showing Absence of Grain Boundaries (x 100). Figure 10. Overlay of Back Reflection Pattern from Basally Oriented Specimen. Figure 11. Overlay of Back Reflection Pattern From Prism Oriented Specimen. Specimen is dipped in P-1 for 20 to 100 sec with mild agatation process accelerated by dipping in P-2 occasionally, rinsed in distilled water and dried in air stream.

Etching solution E:

One part of 1 g Hg $(NO_3)_2$ 1 mil 16N HNO₃ 500 ml distilled water

in two parts of distilled water.

Etching procedure:

1. specimen dipped in P-1, 5-6 sec.

- 2. specimen dipped in P-1, 5-6 sec, withmild agitation.
- 3. specimen dipped in P-3, 2-3 sec.
- 4. specimen rinsed in running water.
- 5. specimen rinsed in distilled water.

6. specimen dried in air stream.

Dislocation etch pits on the basal plane were produced by etching with the following solutions for polishing and etching, after Rosenbaum (3⁵):

> Etching solution: 1.5 ml of 48% HBr in 25 ml ethanol Time of etching: 5 sec with mild agitation. The surface is subsequently washed in ethanol and dried in stream of air.

Chemical polish: Equal values of 70% HNO_3 and 30% H_2O_2 . Figs. 12,13 show etch pit patterns of two typical samples, one of each orientation. By counting the etch pits and knowing the magnification it was possible to estimate the dislocation density. The number of dislocations on the prism plane in an area of $0.01mm^2$

Figure 12. Dislocation Etch-pits on the Basal (0001) Plane.



Figure 13. Dislocation Etch-pits on the Prism $(10\overline{1}0)$ Plane.

•



or 10^{-4} cm² were about 50, thus giving a dislocation density of the order of 10^{5} /cm². The number for the same area on a basal plane was about 75, giving the same order of dislocation density. These values are in agreement with those obtained by Chyung and Wei (33) who prepared single crystals of zinc by the same method.

In the case of polycrystalline samples, a texture check was made by cold-rolling a pure zinc sheet with 75% reduction. The specimen, prepared by acid cutting, lcm x 5cm in size, was mounted in a goniometer with its rolling direction normal to the x-ray beam and a transmission pin-hole pattern was obtained using copper Kradiation. The procedure was repeated with the rolling direction rotated 10° , 20° and 60° to the X-ray beam. A texture determination procedure was also applied to sheets before rolling (Figs. 14, 15).

A polycrystalline rolled sample also was prepared for metallographic examination and grain-size determination. A photomicrograph was obtained for estimation of grain boundary area and metal area (Fig. 16).

D. Procedure

Immediately after specimen preparation, it was hung on the platinum-wire hangar attached to the glass fiber on loop A. The reaction tube was fixed in place, the gas inlet tube attached at the bottom, and the furnace closed. With the stopcock leading from the gas tower closed, the needle-valve was opened and evacuation started with the mechanical pump. When the pressure fell to about 50 microns, the diffusion pump was started after filling the dewars around the cold traps with liquid nitrogen. After attainment of the

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Figure 14. Transmission Pin-hole Pattern of Rolled Zinc
(75% Reduction) X-ray Beam at 10<sup>0</sup> to the Rolling
Direction, Showing No Evidence of Preferred
Orientation.
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Figure 16. Transmission Pin-hole Pattern of Rolled Zinc (75% Reduction) with X-ray Beam at 20⁰ to Rolling Direction, Showing No Evidence of Preferred Orientation.



Figure 16. Photomicrograph of Rolled Specimen (75% Reduction) Showing No Elongated Crystals (x 400).



final vacuum (measured by the Pirani gage), the furnace was switched on and the specimen brought to the desired temperature. After soaking at this temperature for about twenty minutes to remove moisture and adsorbed gases, the gas-tower stopcock was opened and the needlevalve slowly opened to let in a small amount of oxygen into the reaction tube. The oxygen pressure was checked by means of the McLeod gage and adjustments of the needle-valve made to obtain the required oxygen pressure. The balance and mass recorder were simultaneously switched on and the increase in mass continuously recorded. The mass dial reading was noted on the chart at start. The constancy of the set temperature was verified at frequent intervals throughout a run and also by recording for fairly long intervals.

Experiments were carried out at 100°, 148° and 206°C for each orientation. In order to assess reproducibility of the results, three experiments were conducted on each orientation at each temperature. Experiments were carried out at different oxygen pressures to examine the effect of oxygen pressure on the oxidation rate. Since it was found in preliminary experiments that the oxidation rate did not vary over the range 0.8mm, 1.6mm and 2.4mm Hg pressures of oxygen, the final experiments all were conducted at 0.8mm Hg oxygen pressure.

Similar experiments were conducted on polycrystalline zinc sheets prepared in the same manner as the single crystal specimens. However, these experiments were at 125° , 175° and 206° C in order to compare the results with those of Nwoko and Uhlig (21).

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E. Kinetic Data

1. Single crystals. Figs. 17 and 18 are the plots of the weight of ZnO formed in mg/cm² against log (time in minutes) and show the reproducibility of the results at 100° , 148° and 206° C, for the basal and prism planes. The figures also show that the oxidation rate is not significantly affected by the oxygen partial pressure in the range 0.8mm-2.4mm Hg.

Figs. 19 and 20 are the straight plots of the weight of ZnO formed against time in minutes for the basal and prism planes at all experimental temperatures.

Figs. 21 and 22 are the plots of ZnO formed in mg/cm² against log (time in minutes) and show the relative oxidation rates at different temperatures for the basal and prism planes. It is seen that the basal plane shows a two stage oxidation behavior, with the second-stage starting at about 60 minutes after initiation of the reaction. The prism plane is seen to oxidize only in a single stage.

The slope of each part of a semi-log plot gives the rate constant for that stage in mg/cm². The first stage rate constant and the second-stage rate constant are denoted by k_{\perp} and k'_{\perp} for the basal plane, and the rate constant on the prism plane by k_{\parallel} .

Figs. 23, 24 and 25 are semi-log plots. Each of these shows the amount of anisotropy between the prism and basal planes at each temperature.

Fig. 26 shows plots of log k against the reciprocal of the absolute temperature T, for each stage on the basal plane and the single stage on the prism plane. From these plots the activation

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Figure 17. Plots of Weight of ZnO (mg/cm²) Against log (time(minutes)) for the Basal (0001) Plane Showing Reproducibility of Data.



Figure 18. Plots of Weights of ZnO (mg/cm²) Formed Against log(time in minutes) for the Prism (1010) Plane, Showing Reproducibility of Data.



Figure 19. Plots of Weights of ZnO (mg/cm²) Formed Against Time in Minutes for the Basal (0001) Plane.



Weight of ZnO formed (mg/cm² $\times 10^3$)

Figure 20. Plots of Weights of ZnO (mg/cm^2) Formed Against Time in Minutes for the Prism (1010) Plane.





Figure 21. Plots of Weight of ZnO (mg/cm²) Formed Against log (time in minutes) Showing Relative Oxidation Rates at Various Temperatures for the Basal (0001) Plane.



(COLX ${}^$

Figure 22. Plots of Weight of Zinc Oxide (mg/cm²) Formed Against log (time in minutes) Showing Relative Oxidation Rates at Various Temperatures for the Prism (1010) Plane.



Weight of ZnO formed (mg/cm²X IO^3)

Time (min.)

Figure 23. Showing Amount of Anisotropy in Oxidation Rate at 100° C Between the Basal (0001) and Prism (1010) Planes.


Figure 24. Showing Amount of Anisotropy in Oxidation Rate at 148° C Between Basal (0001) and Prims (1010) Planes.



Figure 25. Showing Amount of Anisotropy in Oxidation Rate at 206° C Between Basal (0001) and Prism (1010) Planes.



Weight of ZnO formed (mg/cm² XIO³)

Figure 26. Plots of Log K Against 1/T for Calculation of Activation Energies of Oxidation.



energy for each stage can be calculated, as explained in the next section. The activation energy is denoted by ΔE_{\parallel} for the prism plane and by ΔE_{\perp} , ΔE_{\perp} for the first and second stages on the basal plane.

2. Poly-crystalline specimens. Fig. 27 shows semi-logarithmic plots of the increase in weight in mg/cm² against time in minutes for polycrystalline samples. Polycrystal oxidation also is logarithmic and to process two stages, with the second stage starting about 100-140 mts. after initiation of reaction. A comparison of the plots for single crystals shows that the rate of oxidation of polycrystalline samples is lower than that of the single crystal at each experimental temperature. The start of second stage in the case of polycrystalline samples is found to take place much later than in the case of single crystals. The values of the constant are also higher. A plot of log k against 1/T for calculation of the activation energies was not made as the rate constants were the same as those obtained by Nwoko and Uhlig (21).

F. <u>Reduction</u> of Data

The rate constants at each temperature and for each stage is the slope of the corresponding semi-log plot and is expressed in mg/cm². The value of τ is obtained by extrapolating the first part of the plot to the time axis and noting the time corresponding to it in minutes. Similarly the value of τ ' is the time corresponding to the breakaway point in cases where these is a second stage. Table (1) shows the experimental values of the rate constants at the experimental temperatures for the basal and prism planes the

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Figure 27. Plots of Weight of ZnO (mg/cm<sup>2</sup>) Against log
(time in minutes) for Polycrystalline Material
at Various Temperatures.
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Table 1. Values of Oxidation Rate Constants and τ and τ' for the Basal (0001) and Prism (1010) Planes at Various Temperatures.

allographic	Q	Reaction	Rate Consta	nt mg/cm ² x10 ³	ر ۲۰	
uo	Temp e rature (^C C)	k (1010)	k (0001)	k'(0001)	(u1m)	(m1n)
~	100	1.4			7.0	
	148	2.52			7.0	
	206	4.46			7.5	
	100		0.85	1.005	9.5	60
	148		1.25	1.68	9.5	70
	206		2.0	2.68	7	60

values of τ and τ' . Table (2) shows the values of the same quantities for polycrystalline samples.

The activation energies were estimated by plotting log k against the reciprocal of the absolute temperature (1/T). The slope of such a plot is $\Delta E/2.3R$, where ΔE is the activation energy per mole and R is the gas constant (cal./mol.). Thus the activation energy is obtained by multiplying the slope by 2.303R. Table (3) shows the values of the activation energies for oxidation on the prism planes, the stages on the basal planes and those for the polycrystalline samples.

In the case of the polycrystalline samples the average grain diameter was estimated by measuring the diameters of 25 grains with a grain-size ocular and obtaining an average. The number of grains in the inscribed circle of Fig. 16 is 8.

> Thus the total grain area is = $8 \times \frac{\pi}{4} (2 \times 10^{-3})^2$ = 2.512 x 10⁻⁵ cm².

Grain boundary area = Total area of circle - total grain area

$$cm^{2}.$$

$$= \frac{\pi}{4} \left(\frac{2.5 \text{ cm}}{400}\right)^{2} - 2.512 \text{ x } 10^{-5}$$

$$= (3.06 \text{ x } 10^{-5} - 2.512 \text{ x } 10^{-5}) \text{ cm}^{2}$$

$$= 0.548 \text{ x } 10^{-5} \text{ cm}^{2}.$$

These values will be used in the next chapter.

Table 2. Values of Oxidation Rate Constants and τ and τ' for Polycrystalline Material.

π) (min)	150	100	2 100
(mi	S	S	3.
constant (mg/cm x k ¹ poly	0.6	1.4	2.9
keaction kate (k poly	0.2	0.44	0.95
emperature (C)	125	157	206

Orientation	Activation En (AE)	ergy (cal/mol)	Activation Er	iergy eV/mol
	I Stage	II Stage	I Stage	II Stage
Polycrystalline	7860	8040	~ 0.34	~ 0.35
Basal Plane	3120	3350	0.135	0.143
Prism Plane	3820	,	0.161	ı

IV. DISCUSSION

Our results show that the oxidation of pure single crystal zinc in the temperature range 100° -206°C follows a logarithmic rate law

$$W = K \log(t/\tau + 1),$$
 (54)

where W is the weight of zinc oxide per unit area formed at time t, and τ is a constant having the dimension of time equal to the intercept of the W vs. log t line on the time axis. K is the rate constant expressed in the same units as W and equal to the slope of the W vs. log t line. A second stage of oxidation exhibited by the basal plane is described by a similar equation

$$W - W' = K' \log(t/\tau' + 1),$$
 (55)

where W is the weight of oxide per unit area at times $t > \tau'$ and W' is the weight of oxide per unit area at $t = \tau'$. K' is the second-stage rate constant. τ' is the time corresponding to the onset of the second stage.

The results also indicate that the prism plane rate in this **temperature range** is 2 to 2.5 times higher than that of the first **stage** on the basal plane and 1.4 to 1.7 times that of the second **stage.** There is thus a marked anisotropy in the oxidation rate.

At the outset we examine the accuracy of the measurements. Oxygen pressure was measured by a tilting McLeod gage calibrated for the range 0.01-15mm Hg, with an accuracy of about 20%. The "true" oxygen pressure is not critical, however, since the oxidation rate was found to be independent of it in the range used (0.8mm-2.4mm Hg), in agreement with the observation of Nwoko and Uhlig (21) in a lower pressure range.

The final vacuum in the system was measured by means of a pirani gage which had been calibrated against a standard McLeod gage. The lowest pressure at which the samples were degassed was of the order of 10^{-6} mm Hg, which was satisfactory since no evidence of either gas adsorption or metal evaporation was found at this pressure and the temperature range used.

Moisture was removed from all oxygen admitted using Drierite. **Possible** contamination of the zinc by mercury vapor from the McLeod **gage** was effectively prevented by using a liquid nitrogen trap be**tween** the gage and vacuum system.

The accuracy of the rate constants depends on that with which weight changes in the specimen could be measured. An accuracy of 0.1% can be expected for these, as the measuring device used has been found to have a high degree of precision up to a tenth of a microgram (32). Degassing of adsorbed gases by the specimens should be considered as absent in these experiments as the samples used were small.

Also, possible contamination of the specimens was prevented **by** preparing a specimen just before introduction into the reaction **cube**.

We next consider the influence of slight amounts of cadmium, iron and lead present as impurities (Ref. specification, Ch. III) on the oxidation rate. An investigation of the effect of alloying elements on the oxidation rate of zinc has been carried out by Gensh and Hauffe (31), who found that a zinc-lithium alloy oxidized faster than zinc, while a zinc-aluminum alloy oxidized much slower. The effect of alloying metals can be understood from the following. From the lattice-defect equations of Chapter II, we can consider the effect of introducing Li_20 and Al_20_3 as examples of metal oxides containing ions of lower and higher valence, respectively. The addition of Li^+ ions in the form of Li_20

$$\text{Li}_{2}^{0} = 2\text{Li}\dot{o}(2n) + 22n\dot{o} + \frac{1}{2}0_{2}(g),$$
 (56)

[where the blackened circle indicates substitution, and metal in parentheses indicates the substituted metal] decreases the concentration of free electrons and increases that of the zinc ions in interstitial positions. The addition of A1³⁺ ions

$$A1_{2}0_{3} = 2A1\dot{o}(Zn) + 2\theta + 2Zn0 + \frac{1}{2}0_{2}(g)$$
 (57)

increases the concentration of free electrons and decreases that of zinc ions in interstitial lattice positions. Hauffe (1) has shown that on the basis of the above equations, a zinc-lithium alloy should oxidize faster than zinc, and a zinc-aluminum alloy must oxidize slower, which agrees with the experimental results of Gensch and Hauffe. However, the above explanation is for the results of hightemperature oxidation (390°C). Assuming that it is true at lower temperatures, the presence of Cd²⁺, Pb²⁺ ions can be inferred to have no significant effect on the oxidation rate. A similar conclusion probably holds for iron.

The oxygen used initially was 99.5% pure, but repetition of one of the experiments with 99.98% pure oxygen did not produce any difference in the results within experimental error.

In terms of a possible rate-controlling step in the oxidation, we may consider two alternative mechanisms:

> diffusion of metal ions via the lattice defects of the oxide.

and

(2) electron transfer from the metal into the conduction bands of the oxide controlled by the potential difference across the space-charge layer.

For the sake of argument, we assume initially that process (1) is the slow step in the oxidation. It is possible to make an order of magnitude calculation of the rate constant by combining the self-diffusion data for zinc in single-crystal zinc oxide of Moore and Williams (30) together with Wagner's expression for the rate constant (4). The temperature dependence of the diffusion $Coefficient D_{Zn}^{*}$ of zinc in zinc oxide is given by (30)

$$D_{Zn}^{*} = 1.3 \times 10^{-5} \exp(-43,500 \pm 11,000/RT) \operatorname{cm}^{2}/\operatorname{sec}$$
 (58)

Although this applies only to the range $1000^{\circ}-1200^{\circ}C$, it will be assumed, for simplicity and for want of low-temperature data, that it can be extended to $206^{\circ}C$, and the result used to make an orderof-magnitude calculation. Taking the activation energy for selfdiffusion to be 54,500 cal/mole, we obtain

$$D_{z_n^{\star}}^{206^{\circ}C} \sim 1.3 \times 10^{-27} \text{ cm}^2/\text{sec.}$$

From Wagner's theory applied to zinc, the rate constant is given by

$$K = (1 + Z_{Zn}) C_{equ} D_{Zn}^{*} \left\{ 1 - \frac{C_{Zno}^{(a)}}{C_{Zno}^{(i)}} \right\} (1)$$
(58)

Since $Z_{Zn} = 2$, and $C_{Zn\ddot{o}}(i) >> C_{Zn\ddot{o}}(a)$,

$$K - 3 C_{equil} D_{Zn}^{*},$$

$$K' = \frac{K}{C_{equil}} \Rightarrow 3D_{Zn}^{*} cm^{2}/sec.$$

Assuming

$$x^{2} = K't$$

x ~ 10^{-11.5} cm for t = 400 minutes,
= 1.82x10⁻¹⁸ mg/cm²,

which clearly is not in agreement with tht total weight-gain for either polycrystalline or both faces of zinc, even if D_{Zn}^{\star} is several orders of magnitude in error due to the unjustified extrapolation of eqn. (58) to 206°C.

Thus the diffusion-controlled mechanism does not appear plausible in this temperature range.

Uhlig (13) has given a simple theory of logarithmic kinetics assuming the gradual escape of electrons into the oxide layer, limited by the presence of a potential difference across the space charge layer as the controlling step. Assuming this mechanism, the rate constant is calculated, according to Uhlig, as

$$K_{o} = \frac{K_{1}}{2.3} = \frac{e}{4\pi n \ell e^{2}} \text{ where}$$

$$\epsilon = \text{dielectric constant of } Zn0 \cong 10 \quad (5)$$

$$k = \text{Boltzmann constant} = 1.38 \times 10^{-16} \text{ erg/deg. K}$$

$$T = \text{Abs. Temp. n} = \text{density fo charge in uniform layer}$$

$$e = \text{electronic charge} = 4.8 \times 10^{-10} \text{ esu.}$$

$$\frac{(n\ell)}{n} = \frac{0.31 \times 10^{13}}{2 \times 10^{17}} \cong 0.16 \times 10^{-4} \text{ cm}$$
Taking the sensity of ZnO as 5.47 g/cm³ = 5.47 \times 10^{3} \text{ mg/cm}^{3}
$$\epsilon = 87.52 \times 10^{-3} \text{ mg/cm}^{2}.$$

Nwoko and Uhlig's value for $n\ell$ is thus unreasonable, since the value of ℓ or W calculated (as above) from ($n\ell$) is far beyond the value of ℓ or W corresponding to the onset of the second stage. We therefore take 10^{12} as a reasonable value for $n\ell$ in the single crystal at 106° C, on the basis of the results of low temperature conductivity and Hall effect measurements of Harrison (36). With this value, at 206° C,

$$K_{1} = 2.3x_{0} = 2.3 \frac{10x1.38x10^{-16}x480}{4x3.14x10^{3}x23x10^{-20}} \text{ cm}$$

= $(\frac{10x1.38x10^{-16}x480}{4x3.14x10^{3}x23x10^{-20}})x5.47x10^{3} \text{ mg/cm}^{2}$ (density of Zno
= $5.47x10^{3} \text{ mg/cm}^{3}$)
= $2.9x10^{-3} \text{ mg/cm}^{2}$.

The experimental value $2.1 \times 10^{-3} \text{ mg/cm}^2$ is in good agreement with this. Since the value of nl at 157° C is about twice that 206° C (21), we take the value of nl at 148° C for the single crystal as 2x10¹², obtaining at 148°C

$$K_{1} = 2.3K_{0} = 2.3 \frac{1.38 \times 10^{-16} \times 420}{2 \times 12.56 \times 10^{-8} \times 23} \text{ cm}$$

= 2.3 x $\frac{1.38 \times 10^{-16} \times 420}{2 \times 12.56 \times 10^{-8} \times 23} \times 5.47 \times 10^{3} \text{ mg/cm}^{2}$
= 1.26x10⁻³ mg/cm².

The experimental value K_1 at this temperature is $1.25 \times 10^{-3} \text{ mg/cm}^2$. The agreement between calculated and experimental values is quite good.

The Uhlig theory agrees well with the experimental data for single cyrstal basal planes, and it appears reasonable to assume that electron transfer from the metal to the oxide controlled by the uniform space charge field is the rate-determining step. Uhlig's theory cannot be applied in its entirety to the present case, however, since Uhlig explains the appearance of a second stage in the polycrystalline material by assuming a second space charge layer in which the potential at any point is not a constant (as in the first space charge layer), but depends on its position coordinate. By making this assumption Uhlig arrives at a second equation which is supposed to correspond to the kinetics of the second stage. This interpretation appears to be inconsistent with the experimental results of this study. Moreover, if Uhlig's explanation for the second stage were true, it is not clear why no second stage occurs for the prism plane. Also, Uhlig's original theory was developed to explain experimental results for copper oxidation. Whether all his calculations fit zinc is not clear. Uhlig calculated the values

of L (thickness of oxide at onset of second stage) for copper at 150° , 175° , 225° as 600 Å, 990 Å and 1720 Å (13) whereas the experimental values were 360 Å, 750 Å and 1540 Å. The agreement is not good and this is explained by Nwoko and Uhlig as a result of approximations made in the calculations. A criticism based on a more physically correct solution of Poisson's equation by Uhlig's theory has been given by Fromhold (14).

On the basis of an examination of the oxide formed on the basal plane, we attribute the second stage to a simpler and entirely different phenomenon. We suggest that on the basal plane the initial oxide layer formed in the first stage of oxidation is epitaxial.

Finch and Quarrell (37) have reported the same conclusion based on their electron diffraction experiments. The ZnO lattice has essentially the same hexagonal structure as the underlying zinc lattice. The lattice parameter a_{2n}^{\dagger} for zinc is 2.66 Å and that for zinc oxide is 3.24Å (5,5(a)). In order for the initial oxide film to grow epitaxially on the basal plane of zinc, a $\frac{3.24-2.66}{2.66} \times 100 = +28\%$ of a must exist, with an associated high misfit energy. The oxide will tend to release this energy at some stage in the oxidation process through a change of relative orientation. Space-charge fields established in the new orientation will be different from that in the initial orientation and thus a different rate of oxidation will result. $E_{\mathbf{V}}$ idence of such an orientation change is found in our transmission Laue photographs of the oxide at various times. Fig.28 is a transmission Laue picture of the specimen after 30 minutes. There is no d ifference in the symmetry of spot-pattern of the oxide and metal. Fig. 29 is a similar picture after 60 minutes, and shows the presence

Figure 28. Transmission Laue Pattern of Oxidized Specimen 30 Minutes after Start.



Figure 29. Transmission Laue Pattern of Oxidized Specimen 60 Minutes after Start.



of a new set of weak spots of a different symmetry than that of Fig. 28. Fig. 30 corresponds to the end of the experiment, where the spot-pattern of this new second symmetry has become stronger, indicating the further formation of oxide of the new orientation. In Figs. 31, 32, 33 these patterns have been traced out to more clearly identify the relevant features. The symmetry of the second spot-pattern confirms approximately to that of prism orientation (Cf. Figs. 32, 33). Raether (28) has studied the oxide formed on single-crystal zinc surfaces by electron diffraction and found that the oxide formed at high temperatures on the basal planes had its prism planes parallel to them.

Figs. 34, 35 are similar diffraction patterns at the beginning and end of the reaction on the prism plane showing no evidence of any change in orientation of oxide on the plane. This is consistent with the fact that the prism plane did not show a second stage, in the oxidation kinetics. Since the lattice parameter C_{Zn} of zinc is 4.94 Å and that of ZnO is 5.19 Å (5,5(a)), the mis-registry is only $\frac{5.19-4.94}{4.94} \times 100 \cong 5.3\%$ of C_{Zn} , and high misfit energies are not associated with epitaxial growth. A second stage would not be expected.

Coming now to the anisotropy exhibited by the rate constant, we seek an explanation for this fact in the metal work function. The role of the metal work function in causing anisotropy in oxidation rate has been discussed by Uhlig (13). Since the ratecontrolling step in the reaction is the passage of electrons from metal to oxide, the work function can be expected to have some influence on the reaction rate.

Figure 30. Transmission Laue Pattern of Oxidized Specimen at the End of Experiment.



Figure 31. Tracing of Transmission Pattern (28) Explaining the Pattern.



Spots of hexagonal symmetry due to initial oxide (at about 30 minutes) surrounding spots of same symmetry due to underlying (X-ray beam exactly along hexagonal axis). metal

Figure 32. Tracing of Figure 29 Explaining the Pattern.



Spots in very approximate hexagonal symmetry (due to X-ray beam slightly inclined to hexagonal axis) due both to underlying metal and oxide forming to hexagonal axis)

Figure 33. Tracing of Figure 30 Explaining the Pattern.


Figure 34. Transmission Laue Pattern of Specimen in Prism Orientation Before Oxidation.



Figure 35. Transmission Laue Pattern of Oxidized Prism Oriented Specimen, Showing no New Symmetry Spots.



Work function changes have been associated with such phenomena as the change in activation energy at the $\alpha \rightarrow \gamma$ transformation temperature of iron (38), discontinuities in the activation energy above and below the Curie temperature in Cr-Fe alloys (39). The direct relationship between activation energy of oxidation and the oxidation rate constant is given by the empirical equation of Rideal-Jones (26):

$$\Delta E = \phi_0 - K$$

where $\Delta E = Activation$ energy

 $= \phi_a + \phi_c$ $\cong 3.6 \text{ ev.}$

The above equation has been found to hold very well in the case of **Oxidation** of platinum, carbon and tungsten and metals which form non-**Volat**ile oxides (21).

The fact that the work function of almost all metals changes with crystallographic orientation is well established, and a list of values of work functions on various crystallographic plane of many metals is given by Michaelson (40). Anisotropy in the oxidation rates of ccpper, nickel and iron has been found by several workers (41, 42, 43) and explained on the above basis by Uhlig (13). It may be reasonable to assume that anisotropy in zinc oxidation rate results from a difference in work function between the two crystallographic planes. On the basis of the Rideal-Jones equation and from experimental values of the activation energies, it is possible to make an estimate of the work function on the prism plane, which has not been measured by direct methods. The work function on the basal plane of zinc is 4.26 eV (44) obtained by photo-electric measurements. Take $E_{\parallel}^{\dagger} = 0.135$ ev (Table 1) we get, from the Rideal-Jones equation,

$$\phi_{0} = 3.735 \text{ ev.}$$

Thus the modification of the work function due to contact with oxide is 4.26 - 3.735 = 0.525 ev. Similarly for the prism plane, with $\Delta E_{\perp} = 0.16$ ev,

$$\phi_0 = 3.76 \text{ ev.}$$

Assuming that the modification of work function for the prism plane is the same in magnitude, but opposite in sign, the work function for the prism plane should be 3.76 - 0.52 = 3.23 ev. A rough estimate of the work function for polycrystalline material is 3.23 + 4.262 ev = 3.733 ev, which agrees well with the value 3.74 ev listed by Michaelson. Some values of work functions from Michaleson's Tables are reproduced in Table 4. The lower value of work function of the prism plane is consistent with the higher oxidation rate.

It should be mentioned here that the amount of modification of the work function in the case of single crystals is about a factor of 10 larger than that for polycrystalline material (which is 0.05 ev an 'arbitrary estimate') given by Nwoko and Uhlig. The actual modification in the case of polycrystalline zinc may not be as low Table 4.Values of Photoelectric Work Functions for Different
Crystallographic Planes or Allotropic Forms of Some
Metals. (From Ref. 40)

Element	Crystallógraphíc Plane or Allotropíc Form	Photo-electric Work Function (e.V)	Mean Value for polycrystalline Material (e.V)
Copper	(111)	4.86	L ., ,
	(100)	5.61	4.4/
Iron	б	4.48 4.77	26 7
	۶	4.23	00. .
Silver	111	4.75	00 7
	100	4.81	4 0
Tungsten	(111)	4.39	
	(110)	4.68	4.5
	(001)	4.56	
Zinc	(0001)	4.26	3.74

as this, as its calculation by (21) is made on the basis that the polycrystalline sheet had a work function of 4.00 eV on any average, instead of 3.74 eV listed by Michaelson (40), on the basis of several accurate measurements.

The independence of the oxidation rate on the oxygen partial pressure in the range 0.8-2.4mm Hg can be explained from Wagner's expression for the rate constant. This has already been done in Chapter II. This independence can also be explained from the nature of the mechanism assumed for the oxidation process. Since electron transfer does not depend on the partial pressure of oxygen, rate constant is not expected to be dependent on it. Also Uhlig's expressions for the first stage and second-stage rate constants do not involve any parameter depending on oxygen partial pressure.

An attempt can be made to correlate the relative rates on the single crystal with the relative surface areas exposed by the single cyrstal and polycrystal to oxidation.

From the values presented in the last chapter,

$$\frac{\text{grain bound dry area}}{\text{total grain area}} = \frac{0.548 \times 10^{-5}}{2.512 \times 10^{-5}} = 21.8\%$$

At 206° C, from table (1),

$$K_{\parallel} = 2.54 \times 10^{-3} \text{ mg/cm}^2$$
$$K_{\perp} = 4.46 \times 10^{-3} \text{ mg/cm}^2$$

Taking two of the three principal directions in the basal planes, and one in the prism plane, an average value of the rate constant is

$$\frac{2K + K}{3} = 4.15 \times 10^{-3} \text{ mg/cm}^2.$$

But since the maximum value of the rate constant on a polycyrstalline sample at 206° C is $3x10^{-3}$ mg/cm², the decrease due to the presence of grain boundaries is

$$(4.15 - 3)x10^{-3} = 0.15x10^{-3} mg/cm^2$$

and the percentage decrease is

$$\frac{1.15}{4.15} \times 100 = 27.8\%.$$

This compares well with the ratio of the grain boundary and grain area, 21.8%, particularly since the effect of other imperfections has not been considered in the above estimate.

The result of this work that polycrystalline material of fine grain size oxidizes much slower than single cyrstals may find application in protective zinc coatings which should be preferably have a fine grain structure for high oxidation resistance.

We now turn to certain results of other workers and show that the present study can explain them. Vernon et al (3) observed that the oxidation rate showed a maximum at 130°C, which was not observed by Nwoko and Uhlig (21). Vernon's zinc sheets could be thought to have had all kinds of orientations (also explaining irreproducibility of their data), and the sheet used at 130°C may have accidentally had a predominantly prism orientation (not unlikely in view of Sachs' (45) work), thus giving a higher rate of oxidation than any observed by them.

Nwoko and Uhlig (21) observed a two-stage process on all their samples. Their sheets were "textured by the normal rolling process so that the (0001) face lay in large part parallel to the surface". It is not clear whether they conducted any experiments to verify this statement. Although, in principle, the predominant slip plane in a hexagonal metal is (0001), it is found that the texture depends on the c/a ratio. When the c/a ratio exceeds that for ideal close-packing 1.66 (c/a for zinc is about 1.86), the basal plane texture is not present. As explained in the last chapter, sheets rolled in this Laboratory with as much as 75% reduction did not show any preferred orientation. The value of 4.0 eV assumed on the basis of the basal plane texture for the work function of polycrystalline zinc and the value of the modification of the work function (0.05 eV) are both questionable. However, if they did have the basal texture, then their observation of the two stage process is consistent with ours for the basal plane.

V. SUMMARY

The oxidation kinetics of single-crystal zinc has been measured in the range 100° -206°C in two principal directions, parallel and perpendicular to the hexogonal axis. The prism (1010) plane oxidizes in a single stage and the basal (0001) plane oxidizes in two stages, with the second stage being faster. Marked anisotropy is found in the reaction rate, with the prism plane rate being 2-2.5 times higher than that of the I-stage and 1.4-1.7 times higher than the second. The second stage on the prism plane appears to be due to a change in orientation in the initial epitaxial oxide layer formed about 1 hour after the initiation of reaction. The anisotropy is explained by taking into consideration the workfunction differences between the basal and prism planes. A rough estimate of the work function on the prism plane, not thus far measured by direct methods, is made and is found to give an average value of 3.73 e.V. for polycrystalline zinc, in agreement with a well established average experimental value.

The rate-determining step is assumed to be electron release from the base metal into the conduction bands of the oxide. Uhlig's theory, which also assumes the above mechanism is applied to calculate the rate constants which are found to agree well with those on the basal planes.

An effort to correlate the relative areas of grain boundaries and metal grains with the relative oxidation rates on polycrystalline and single crystal material has been found to give a good fit between the two.

The importance of the work lies in the fact that new data have been added to those existing on zinc oxidation; the possibility of arriving at physical properties from chemical kinetic measurements is made clear; the second stage is explained on a different basis than any existing to explain two stage processes; the role of grain boundaries and inperfections in reducing reaction rate is determined; the sample Uhlig theory is extended and found valid for single cyrstals of zinc (and possibly for Cu); the fact that polycrystalline material oxidizes much slower than single crystals may be used in oxidation resistant zinc coatings by making the coatings fine grained.

The possibility of arriving at average properties of bulk materials from individual crystalline properties is shown.

The work may be extended to the study of effect of dislocation concentrations and alloying elements on the oxidation rate. The oxidation rates on the pyramidal planes can also be measured as an extension of the present study.

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