

Theory of Metal Oxidation

Literature: A. T. Fromhold "Theory of Metal Oxidation", North Holland Publishing Company, Amsterdam (1976). Signatur an der Bibliothek der Uni Graz: I 466591

Early Diffusion Theories:

1. Tammann Pilling Bedworth parabolic law:

For many metals it was found that the increase in oxide thickness is proportional to the square root of time. $L(t) \sim t^{1/2}$

Assumptions for TPB parabolic law:

1. Growth occurs by uncharged particles
2. The diffusion coefficient D is independent of the concentration C
3. The concentrations $C(0)$ and $C(L)$ in the interface regions (metal - oxide and oxide - gas, respectively) are independent of the film thickness L
4. Film growth is a steady state phenomenon

If $L(t) \sim t^{1/2}$ then the atomic diffusion rate of atoms (assumption 1) through the oxide film should be inversely proportional to the thickness of the existing oxide: diffusion rate $\sim 1/L(t)$

The particle current J is according to Fick's first law:

$$J = -D \frac{\partial C}{\partial x}$$

If there is no buildup of the concentration with time (assumption 4) we can write $\frac{\partial C}{\partial t} = 0$ and

with Fick's second law $\frac{\partial J}{\partial x} = -\frac{\partial C}{\partial t} = 0$ we see that J is independent of the position x in the

film. Therefore Fick's first law reduces to:

$$\frac{\partial C(x)}{\partial x} = -\frac{J}{D} = \text{const.}$$

Integration gives $C(x) - C(0) = - (J/D)x$ and for the interface $x = L$ we get:

$$J = D[C(0) - C(L)] / L$$

The growth rate can be written as $\frac{dL(t)}{dt} = \frac{k}{L(t)}$ if we recall that the diffusion rate is proportional to $1/L(t)$. The constant k will involve the concentrations $C(0)$ and $C(L)$ (assumption 3) and the diffusion coefficient and the volume of oxide R formed with each atom that diffuses through the film. So we can write $k = RD[C(0) - C(L)]$.

In summary we get the following equation for the rate of oxidation:

$$RJ = \frac{dL(t)}{dt} = \frac{RD[C(0) - C(L)]}{L(t)}$$

With separation of the variables and fixed boundary concentrations (assumption 3) and a constant diffusion coefficient (assumption 2) we can do the integration yielding a parabolic growth law:

$$L(t)^2 - L(0)^2 = 2 k t, \text{ with } k = RD[C(0) - C(L)].$$

2. Wagner Theory:

Wagner based his theory on the assumption that metal oxidation proceeds mainly via diffusion of charged particles. He based his theory on the well known theoretical treatment of ionic diffusion in electrolytes developed earlier by Nernst and Debye. Wagner's theory is based essentially on the linear diffusion equation for charged particles:

$$J = -D \frac{\partial C}{\partial x} + \mu EC \quad (1)$$

E is the electric field and μ is the mobility, which is related to the diffusion coefficient by the Einstein relation $Z e D = \mu k T$. Z is the valence of the diffusing particle, e is the electronic charge, k is the Boltzmann constant and T is the temperature. Within the Wagner theory the concentration C refers to the concentration of the diffusing charged defect instead of the ionic concentration of the lattice.

Wagner assumed that a neutral oxide evolves during growth. This requires that the number of equivalents of positively charged cations moving through the oxide in unit time has to be equal to the number of equivalents of negatively charged anions and electrons moving through the film in unit time. This assumption can be used to eliminate the electric field from the three transport equations for the three species. According to Wagner the transport rate in equivalents per unit time for cations (N_1) equals the transport rate in equivalents per unit time for anions (N_2) plus the transport rate in equivalents per unit time for electrons (N_3). This

notation for the three different species (1, 2, 3 for cations, anions and electrons, respectively) will be used throughout this manuscript. A more general criterion is the requirement that the total charge transported through the film at each point in time is zero:

$$\sum_{s=1}^r Z_s e J_s = 0 \quad (2)$$

This is the so called coupled currents condition, which is used in all theories on metal oxidation. This can now be put into the linear diffusion equation (1) for all three species:

$$Z_1 e J_1 + Z_2 e J_2 + Z_3 e J_3 = 0$$

$$Z_1 e \left(-D_1 \frac{dC_1}{dx} + \mu_1 E C_1 \right) + Z_2 e \left(-D_2 \frac{dC_2}{dx} + \mu_2 E C_2 \right) + Z_3 e \left(-D_3 \frac{dC_3}{dx} + \mu_3 E C_3 \right) = 0$$

This equation leads the electric field E,

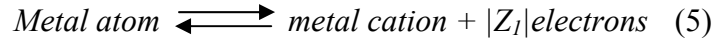
$$E = \frac{Z_1 D_1 \frac{dC_1}{dx} + Z_2 D_2 \frac{dC_2}{dx} + Z_3 D_3 \frac{dC_3}{dx}}{Z_1 \mu_1 C_1 + Z_2 \mu_2 C_2 + Z_3 \mu_3 C_3} \quad (3)$$

which can again be substituted into the linear diffusion equation to give the equations for the currents J_s .

$$J_s = -D_s \frac{dC_s}{dx} + \mu_s C_s \left[\frac{\frac{d}{dx} (Z_1 D_1 C_1 + Z_2 D_2 C_2 + Z_3 D_3 C_3)}{Z_1 \mu_1 C_1 + Z_2 \mu_2 C_2 + Z_3 \mu_3 C_3} \right] \quad (4)$$

It can be seen from this equation that we actually have a system of three coupled transport equations, where each equation contains all three concentrations of the three transported species. Wagner proposed that a number of local chemical reactions take place continuously in each element of volume of the oxide, with the reactions in each element of volume considered to be near enough to equilibrium to utilize the equations of equilibrium thermodynamics. As gradients do exist in the growing oxides the concentrations of the various species are considered to vary with position. Therefore Wagner considered the equilibrium relations to be local relations, which is the basis of modern non-equilibrium thermodynamics. It is assumed that neutral metal atoms and neutral nonmetal atoms do react to form neutral oxide in a way that the Gibbs – Duhem relation from equilibrium

thermodynamics is applicable. In addition, in each volume element of oxide the neutral metal atoms are considered to decompose into cations and electrons, and neutral nonmetal atoms are considered to combine with electrons to form anions. Both chemical reactions are taken to be in equilibrium in each volume element, and they are independent in the sense that each of the corresponding equations of chemical equilibrium is considered to be valid. This means that the reaction of metal atoms can be written as:



The corresponding equation of equilibrium in terms of chemical potentials is:

$$u_1 + |Z_1| u_3 = u_{Me} \quad (6)$$

The corresponding equation for anions is: $u_2 = u_x + |Z_2| u_3$. Now one can relate the chemical potentials of the charged and neutral species and differentiate the result which leads to:

$$|Z_2| du_1 + |Z_1| du_2 = |Z_2| du_{Me} + |Z_1| du_x \quad (7)$$

Wagner further assumed that the oxide lattice is made up of neutral metal atoms and neutral nonmetal atoms which are in equilibrium in each volume element. Therefore the Gibbs – Duhem relation holds for each volume element:

$$C_{Me} du_{Me} + C_x du_x = 0 \quad (8)$$

C_{Me} and C_x are the concentrations of the neutral metal atoms and nonmetal atoms, respectively, in the oxide lattice. The ratio of the neutral species in this lattice is inversely proportional to the ratio of the valences leading to $C_{Me}/C_x = |Z_2|/|Z_1|$, which can be substituted in the equation (8) above to yield:

$$|Z_2| du_{Me} + |Z_1| du_x = 0 \quad (9)$$

Equation (9) substituted into (7) leads to:

$$|Z_2| du_1 + |Z_1| du_2 = 0 \quad (10)$$

Now we have 5 chemical potentials that are related to each other via three independent relations which can be written as follows:

$$du_x = - |Z_2/Z_1| du_{Me} \quad (11)$$

$$du_2 = - |Z_2/Z_1| du_1 \quad (12)$$

$$du_1 + |Z_1| du_3 = du_{Me} \quad (13)$$

This set of equations enabled Wagner to solve the coupled diffusion equations. But one has to keep in mind that Wagner used quite a lot of assumptions to get there. These assumptions are:

1. Local chemical reactions occurring between various charged and neutral species at each point in the oxide film.
2. These chemical reactions are close enough to equilibrium in each elemental volume so that the usual equations of chemical equilibrium can be employed.

Now we consider the case of cations (species 1 with $Z_1 = |Z_1|$) and electrons (species 3 with $Z_3 = -1$) as the only two moving species:

The electric field from equation (3) is then

$$E(x) = \frac{Z_1 D_1 \frac{dC_1}{dx} + Z_3 D_3 \frac{dC_3}{dx}}{Z_1 \mu_1 C_1 + Z_3 \mu_3 C_3} \quad (14)$$

Defining the partial electrical conductivity of a species s as

$$\sigma_s(x) \equiv Z_s e \mu_s C_s(x) \quad (15)$$

with the total electrical conductivity at position x given by

$$\sigma_T(x) = \sigma_1(x) + \sigma_3(x) \quad (16)$$

and using the Einstein relation ($Z e D = \mu k_B T$) for the two species we can convert the field to:

$$E(x) = k_B T \sigma_T^{-1} \left[\mu_1 \frac{dC_1}{dx} + \mu_3 \frac{dC_3}{dx} \right] \quad (17)$$

Substitution of equation (17) into the linear diffusion equation (1) for the cation species gives:

$$J_1 = \frac{-k_B T \mu_1 C_1}{Z_1 e} \left(\frac{1}{C_1} \frac{dC_1}{dx} - \frac{Z_1 e}{\sigma_T} \left[\mu_1 \frac{dC_1}{dx} + \mu_3 \frac{dC_3}{dx} \right] \right) \quad (18)$$

Using the definition from equation (15) to eliminate μ_1 and μ_3 in (18) we get:

$$J_1 = \frac{-k_B T \sigma_1}{(Z_1 e)^2} \left(\frac{1}{C_1} \frac{dC_1}{dx} - \frac{1}{\sigma_T} \left[\frac{\sigma_1}{C_1} \frac{dC_1}{dx} + \frac{Z_1 \sigma_3}{Z_3 C_3} \frac{dC_3}{dx} \right] \right) \quad (19)$$

The standard expression for the chemical potential of a species s is:

$$u_s(x) = u_s^0 + k_B T \ln C_s(x) \quad (20)$$

In equation (20) u_s^0 is a constant and we assume a unit activity coefficient, so that we can write:

$$\frac{du_s(x)}{dx} = \frac{k_B T}{C_s} \frac{dC_s}{dx} \quad (21)$$

We define the transport number t for species s as

$$t_s \equiv \frac{\sigma_s(x)}{\sigma_T(x)} \quad (22)$$

With this definition we have for the present system $t_1 + t_3 = 1$. Now we substitute equations (21) and (22) into equation (19):

$$J_1 = \frac{-t_1 \sigma_T}{(Z_1 e)^2} \left(\frac{du_1}{dx} - \left[t_1 \frac{du_1}{dx} + \frac{Z_1 t_3}{Z_3} \frac{du_3}{dx} \right] \right) \quad (23)$$

By using $Z_1 = |Z_1|$, $Z_3 = -1$ and $t_1 + t_3 = 1$ we can combine the terms involving $\frac{du_1}{dx}$ to get:

$$J_1 = \frac{-t_1 t_3 \sigma_T}{(Z_1 e)^2} \frac{d(u_1 + |Z_1| u_3)}{dx} \quad (24)$$

With the assumption of local chemical equilibrium between cations, electrons and neutral species we can use equations (5) and (6) and equation (24) becomes:

$$J_1 = \frac{-t_1 t_3 \sigma_T}{(Z_1 e)^2} \frac{du_{Me}}{dx} \quad (25)$$

Within the Wagner theory there is no way to calculate t_1 , t_3 , σ_T and $u_{Me}(x)$. Wagner pointed out that all these quantities are position dependent. However, if the ionic current J_1 does not lead to a local change in the concentration of cations within the film, then J_1 and the product $t_1 t_3 \sigma_T (du_{Me}/dx)$ must be independent of the position x . In this case the integral of J_1 from $x = 0$ to $x = L$ is simply $J_1 L$, so that equation (25) can be formally written as:

$$J_1 = \gamma_1 / L \quad (26)$$

Where

$$\gamma_1 = - \left(\frac{1}{Z_1 e} \right)^2 \int_0^L t_1(x) t_3(x) \sigma_T(x) \left(\frac{du_{Me}(x)}{dx} \right) dx \quad (27)$$

Equation (26) from Wagner's theory only gives a parabolic growth law if γ_1 is independent of L . As the x dependent quantities in equation (27) cannot be computed within Wagner's theory one cannot draw any conclusions about the actual reaction mechanism from this theory. Wagner's theory can also be formulated for growth by diffusing anions and electrons (species 2 and 3, respectively) leading to a similar equation for γ_2 :

$$\gamma_2 = - \left(\frac{-1}{Z_2 e} \right)^2 \int_0^L t_2(x) t_3(x) \sigma_T(x) \left(\frac{du_x(x)}{dx} \right) dx \quad (28)$$

And finally one can use Wagner's theory for oxide growth via cation, anion and electron diffusion. Following a similar deduction one can get to the final rate equation for this case:

$$\frac{dL(t)}{dt} = -\frac{R_1}{(Z_1 e)^2 L(t)} \int_0^{L(t)} [t_1(x) + t_2(x)] t_3(x) \sigma_T(x) \left(\frac{du_{Me}(x)}{dx} \right) dx \quad (29)$$

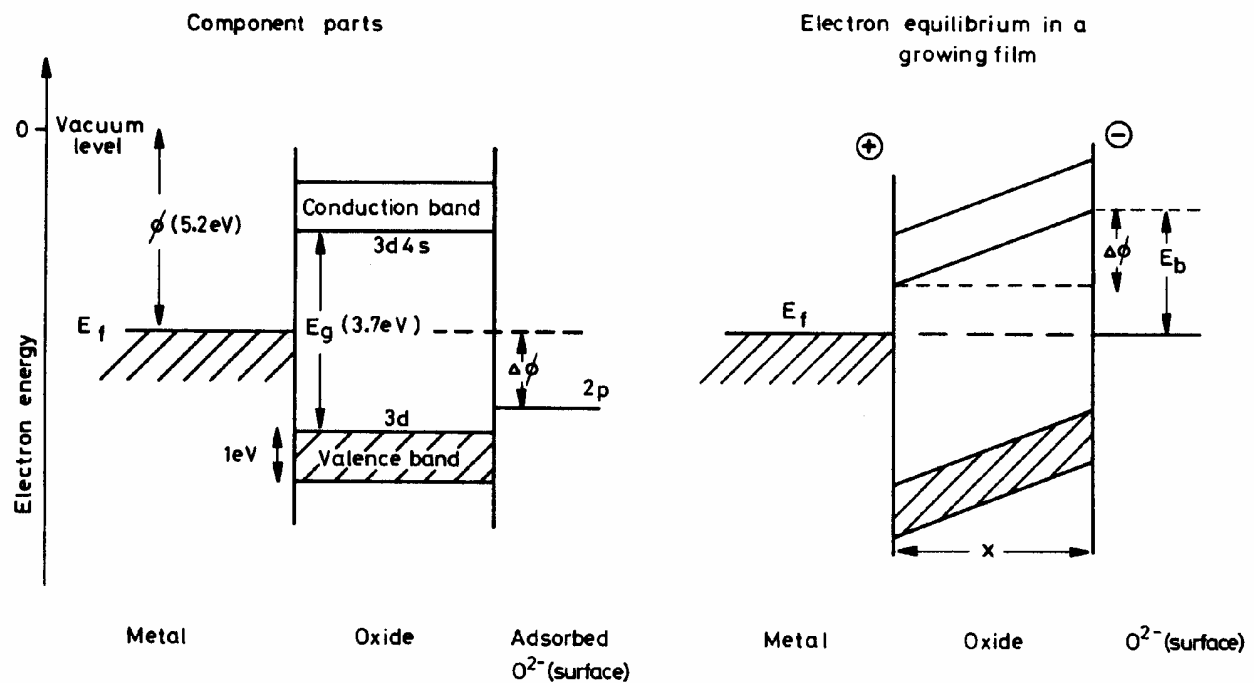
R_1 is the volume of oxide formed per particle of species 1 which is transported from $x = 0$ to $x = L$.

While the theory of Wagner is limited, as it cannot help to elucidate the mechanism of a specific oxidation process, it is still important as it is the simplest theory that takes diffusion of charged particles into account. Therefore Wagner's theory is the basis for more sophisticated theories of metal oxidation.

Cabrera and Mott Theory:

(Lit.: A. Atkinson, Rev. Mod. Phys. 57 (2) (1985) 437)

The theory of Cabrera and Mott is valid for thin films, but there are several extensions for thicker oxide films. The first assumption of the Cabrera Mott model is that electrons can pass freely from the metal to the oxide surface to ionise oxygen atoms. This establishes a uniform field within the oxide, which leads to a shift in the Fermi level of the oxide, as shown in the figure:



The so called Mott potential E_b (V_M) can be calculated as $E_b = 1/e (\Phi_M - \Phi_{Ox})$. This potential drives the slow ionic transport across the oxide film. The electrons continue to cross the film to maintain zero electrical current. The electrons are assumed to pass through the film via tunnelling within the Cabrera Mott model. This assumption restricts the model to thin films. To extend the model to thicker films one can assume electron transport via thermionic emission or via semiconducting oxides.

In order to calculate the potential one assumes that the adsorbed layer of ions is in equilibrium with the gas. This layer of adsorbed ions provides the surface charge and the voltage across the film $\Delta\Phi$. The electron transfer and adsorption reaction can therefore be written as:



As this reaction is assumed to be in equilibrium we can formulate the equilibrium constant:

$$K = \frac{a(O^{2-})}{a(O_2)^{1/2} a(e)^2} \quad (1)$$

K is of course related to the standard free energy change from equilibrium thermodynamics via

$$K = \exp\left(\frac{-\Delta G^0}{kT}\right) \quad (2)$$

For a low coverage of excess O^{2-} ions on the surface we can write $a(O^{2-}) = n_0 / N_s$. Where n_0 is the number of excess oxygen ions and N_s is the total number of oxygen ions per unit area of the surface. The activity of an electron with respect to the metal Fermi energy $a(e)$ is equal to $\exp(-e\Delta\Phi / kT)$. Taking this and the equations (1) and (2) into account one obtains for n_0 :

$$n_0 = N_s a(O_2)^{1/2} \exp\left[-\frac{\Delta G^0 + 2e\Delta\Phi}{kT}\right] \quad (3)$$

The oxide film and the surface charges can be regarded as a simple capacitor, which leads to another expression for n_0 :

$$n_0 = \frac{\varepsilon\varepsilon_0\Delta\Phi}{2eX} \quad (4)$$

with X being the thickness of the oxide film. Now we can solve equations (3) and (4) to get an expression for the Mott potential $\Delta\Phi$.

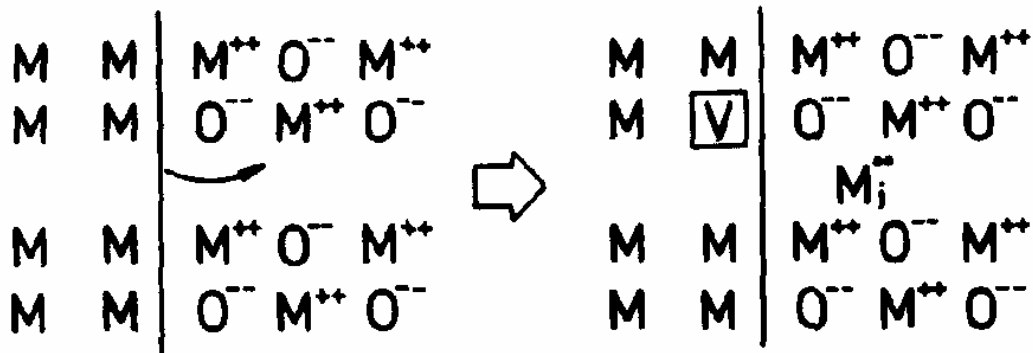
$$\frac{2e\Delta\Phi}{kT} + \ln\left[\frac{2e\Delta\Phi}{kT}\right] = -\frac{\Delta G^0}{kT} + \ln\left[\frac{4e^2 N_s a(O_2)^{1/2} X}{kT\epsilon\epsilon_0}\right] \quad (5)$$

Normally $e\Delta\Phi / kT$ will be much larger than 1. Therefore the second term in equation (5) is negligible and equation (5) reduces to:

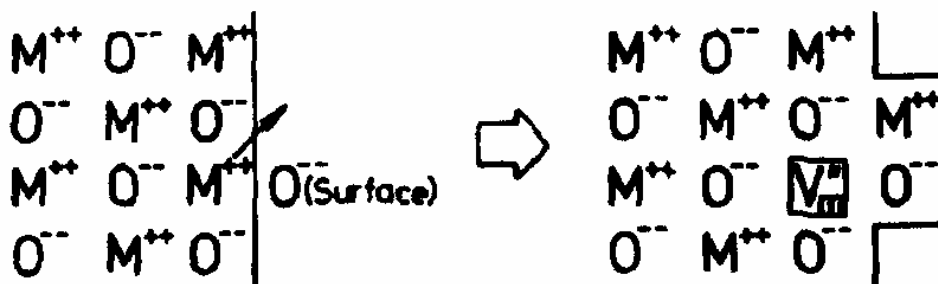
$$\Delta\Phi = -\frac{\Delta G^0}{2e} + \frac{kT}{2e} \ln\left[\frac{4e^2 N_s a(O_2)^{1/2} X}{kT\epsilon\epsilon_0}\right] \quad (6)$$

To calculate the oxidation rate Cabrera and Mott assumed that the rate controlling step is the injection of a defect into the oxide at the metal oxide or at the oxide gas interface. The two processes are shown in the figure:

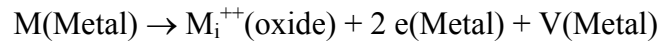
(a) Defect injection at the metal/oxide interface



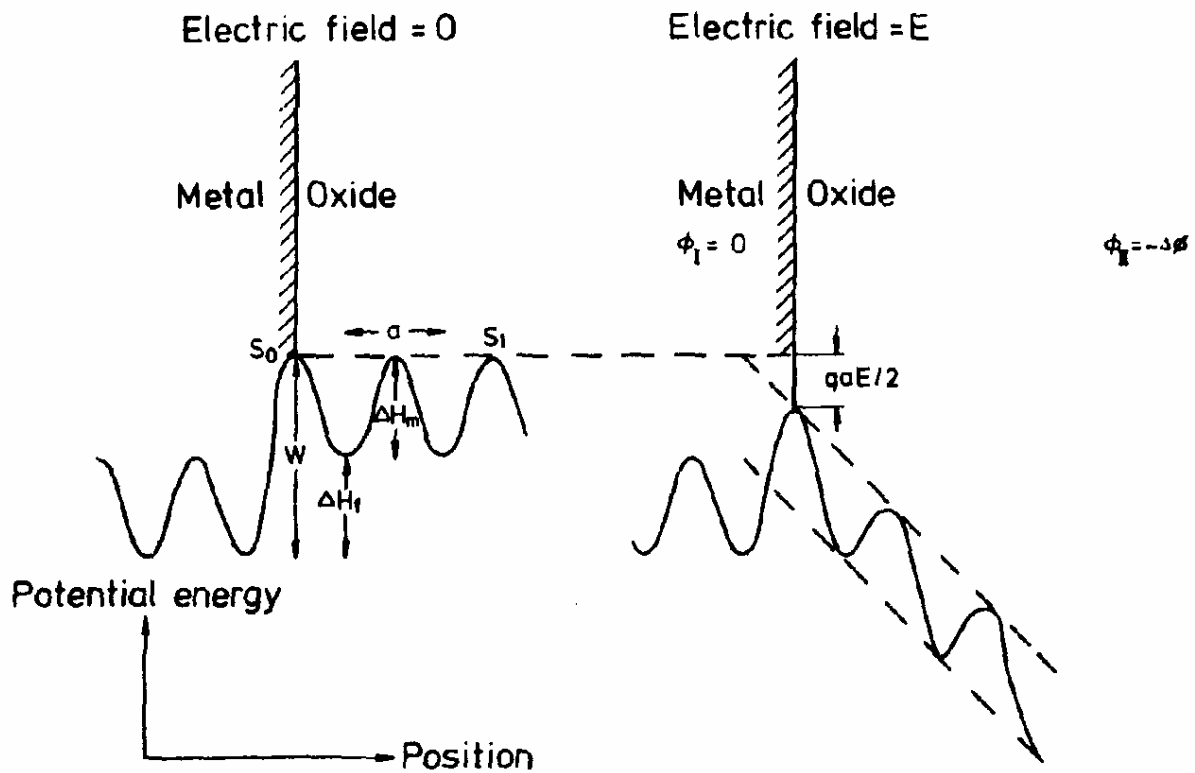
(b) Defect injection at the oxide/oxygen interface



For case (a) we can write the chemical reaction as follows:



The potential energy of the metal as it moves across the interface is shown in the next figure:



The activation energy for the jump from the metal into the oxide film (W) is greater than the activation energy for subsequent jumps within the oxide film (ΔH_m). Therefore the energy change of the chemical reaction is $W - \Delta H_m$ (the energy of incorporation of the defect). Under the influence of the electric field the activation energies are reduced by $qa\Delta\Phi/2X$. The chemical reaction is assumed to be far from equilibrium (in contrast to the assumption in the Wagner theory), as the barrier for the jump in the reverse direction is large, as long as the field E is in place. With this assumption one can write the oxide growth rate as:

$$\frac{dX}{dt} = av \exp\left(\frac{-W}{kT}\right) \exp\left(\frac{qa\Delta\Phi}{2kTX}\right) \quad (7)$$

where ν is the vibrational frequency of the atoms at the interface. With two definitions ($X_1 = qa\Delta\Phi / 2kT$ and $D_i = a^2 \nu \exp(-W / kT)$) equation (7) can be transformed into equation (8):

$$\frac{dX}{dt} = \frac{D_i}{a} \exp\left(\frac{X_1}{X}\right) \quad (8)$$

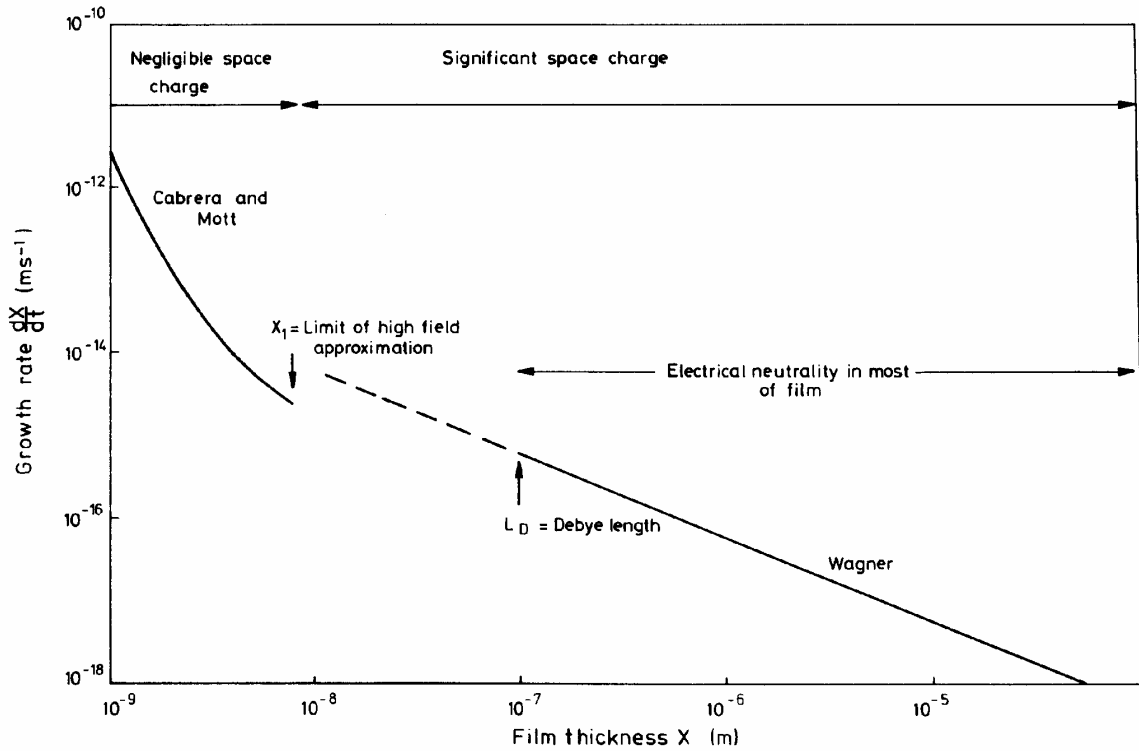
X_1 is the upper limit of oxide thickness where our assumptions are valid. If the saddle point S_0 of the interface jump is the same as the saddle point for subsequent jumps W is related to the activation energy for diffusion in the oxide film. In principle there are several theoretical prediction, which could be verified by experiments:

- The growth rate as a function of time
- The growth rate as a function of oxygen activity
- The magnitude of the growth rate in terms of independently measurable parameters
- The magnitude of the electric field in the growing film
- The response to an externally applied electric field
- The migration of tracer atoms in the growing film

As the macroscopic growth of an oxide film can also be influenced by a number of processes not considered within the framework of a theory, one finds quite often discrepancies between theory and experiment. And especially in the Cabrera Mott theory many quantities cannot be measured independently, which makes it impossible to get quantitative data by using the Cabrera Mott model. More recently V. P. Parkhutik (J. Phys. D: Appl. Phys. **25** (1992) 256) formulated a more general version of the Cabrera Mott model, in an effort to get more quantitative data and therefore more insight into the mechanism of the oxidation process.

An example for a quantitative solution for the system of NiO formation is given in the following figure. As one can see there is a thickness range where neither Cabrera Mott nor Wagner can describe the growth rate quantitatively. In the next chapter it will be shown that the Cabrera Mott model can be used for a qualitative prediction of alloy oxidation. The predictive power of this model was verified using several different alloy systems.

There were also several attempts to divide the overall oxidation reaction into more basic steps in order to find a mechanism that leads to a more general theory of oxidation. For example

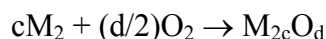
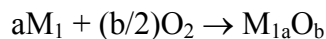


Baily and Ritchie (Oxidation of Metals **30** (1988) 405 and 419) introduced nine steps for the overall oxidation reaction with 3 steps without charge transfer and 6 steps with charge transfer. But in summary one ends up with too many parameters, which cannot be measured independently again.

Extension of the Cabrera Mott model to alloy oxidation:

(Lit.: R. Schennach, S. Promreuk, D. G. Naugle, D. L. Cocks, Oxidation of Metals **55** (5/6) (2001) 523)

Let us consider a binary alloy M_1M_2 . The oxidation process for this alloy can be divided into two reactions:



The reaction at the oxide gas interface are the cathodic reactions $(b/2)O_2 + (2b/a)e \rightarrow bO^{2-}$ and $(d/2)O_2 + (2d/c)e \rightarrow dO^{2-}$ and the reactions at the alloy oxide interface are the anodic reactions $M_1 \rightarrow M_1^{2b/a+} + (2b/a)e$ and $M_2 \rightarrow M_2^{2d/c+} + (2d/c)e$ for a binary alloy. Now we

assume that the Cabrera Mott potential for the alloy is the sum of the Cabrera Mott potentials for the two metallic components:

$$\Delta\Phi = \Delta\Phi_{M1} + \Delta\Phi_{M2}$$

Using equation (6) for $\Delta\Phi$ we get for an alloy:

$$\Delta\Phi = \frac{-\Delta G_{fM_1}^0}{2be} + \frac{kT}{2be} \ln \left[\frac{(2be)^b N_s^b a(O_2)^{\frac{b}{2}} a(M_1)^a X_b}{kT \epsilon_b \epsilon_0 a(M_1^{\frac{2b}{a+}})^a} \right] + \frac{-\Delta G_{fM_2}^0}{2de} + \frac{kT}{2de} \ln \left[\frac{(2de)^d N_s^d a(O_2)^{\frac{d}{2}} a(M_2)^c X_d}{kT \epsilon_d \epsilon_0 a(M_2^{\frac{2d}{c+}})^c} \right] + \dots$$

The terms in equation the above equation are the following:

The free energies of oxide formation per mole of O^{2-} ($-\Delta G_{fM_x}^0$) for the alloy components M_1 and M_2 . The stoichiometric factors from the oxidation reactions (a, b, c and d). The oxygen, metal and metal ion activities (a_x). The number of surface O^{2-} (N_s). The oxide layer thickness (X). The absolute temperature (T). The Boltzmann constant (k). The relative dielectric constant of the two oxides (ϵ_x) and the dielectric constant in vacuum (ϵ_0).

From this equation one can qualitatively see, that the free energy of formation and the temperature are the main parameters that influence the oxidation. Of minor importance is the oxygen activity. A couple of values of $-\Delta G_{fM_x}^0$ is listed in the following table:

Oxide	$-\Delta G_f^0$ (kJ/mole O^{2-})
ZrO ₂	521.4
TiO ₂	444.8
CuO	129.7

From this table one can predict that Zr will oxidize first followed by Ti and Cu. When the binary alloys ZrCu, TiCu and ZrTi and the ternary alloy ZrCuTi are oxidized under different conditions one gets the following result, which shows that the modified Cabrera Mott model

gives a correct qualitative prediction of the order at which the components of an alloy get oxidized:

Anodic	Thermal	Plasma												
<table border="1"> <tr><td>ZrO₂</td></tr> <tr><td>Cu_xO_y TiO₂</td></tr> <tr><td>CuTiZr</td></tr> </table>	ZrO ₂	Cu _x O _y TiO ₂	CuTiZr	<table border="1"> <tr><td>ZrO₂ TiO_x</td></tr> <tr><td>Cu_xO_y</td></tr> <tr><td>CuTiZr</td></tr> </table>	ZrO ₂ TiO _x	Cu _x O _y	CuTiZr	<table border="1"> <tr><td>CuO</td></tr> <tr><td>ZrO_x TiO_x</td></tr> <tr><td>CuTiZr</td></tr> </table>	CuO	ZrO _x TiO _x	CuTiZr			
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Comparison of the resulting oxide structures on Cu-33Ti-33Zr, Cu-50Ti, Cu-50Zr and Ti-50Zr after anodic, thermal, and plasma oxidation.