

CHAPTER I

INTRODUCTION

The pioneering work of G. Tamman, W.Köster, N.B.Pilling and R.E.Bedworth laid the foundation towards identification of a system which will behave in a manner of self destruction or self protection with respect to time under the action of any oxidising environment. The Pilling-Bedworth ratio defined the criteria for protective film formation and for nonprotective film formation. Metals which destroy themselves during oxidation at a faster rate should normally have a low volume ratio. The other group of metals which progressively tarnish at a diminishing rate is identified to have this volume ratio greater than unity. Various kinetic rate laws and mechanisms have been experimentally observed and theoretically predicted for the second group of metals undergoing oxidation reactions.

For a system like copper, whose volume ratio is greater than unity, has been found to obey a parabolic law of oxidation at high enough temperature by a large number of investigators including N.B.Pilling and R.E.Bedworth. Copper has been found to form a tenacious, adherent thin film over the metal surface which is formed in a very short time thus isolating the metal from the direct contact of the attacking atmosphere. Once, the isolation of the two reactants has taken place, to sustain the

process of growth, it was realised that one has to identify the driving force and the proper species that can migrate under the action of driving force. C.Wagner identified the driving force as originating due to chemical potential gradient for high temperature oxidation reaction and deduced the most important parabolic rate equation which was verified for copper oxidation at 1000°C. The migrating species were identified to be charged copper ions which diffuses through the tarnished layer, being the easy path for diffusion and the energy of diffusion being provided by the higher value of temperature prevalent in the system.

The existence of another type of driving force due to creation of oppositely charged species at the metal/oxide and oxide/gas interface by the availability of electrons from the metal, something of the type of a charged condenser was envisaged by N.F.Mott and N.Cabrera. Under such type of driving force, Mott theoretically deduced a reciprocal logarithmic law. The flux of the migrating species was thought to be exponentially dependent on the driving force. The field strength was assumed to be of very high order (for a film of 50 Å thickness, the field may be of the order of 10^7 V/cm.). On progressive growth of the film, it was envisaged that the flux of the migrating species gradually changed over to direct dependance on the field strength which led to the formulation of Mott's parabolic equation. N.F.Mott derived a cubic equation also for a system where the field strength was inversely dependent on the thickness

of the growing film, a possible case which can occur only under certain restrictive conditions.

Once the metal surface and the atmosphere of the reacting gas has been isolated by the growing film, for further growth process to be sustained in a particular fashion, the nature of the driving force as stated above needs further examination. As soon as the two reacting interfaces are separated by a film of considerable thickness, one has to consider the reactions occurring at both the interfaces independently. A large number of reactions and equilibrium can be thought of at these two interfaces. But the major drawback lies in the proper identification of these equilibria and to define them quantitatively. Of course this does not exclude the application of some simplified assumptions at the two reaction interfaces which may be expected to be valid and lead to a particular solution of a mathematical model giving rise to a particular growth law.

C. Wagner's assumption included the interfacial reactions to be at equilibrium, which may not be unreasonable, because at higher temperatures all the reactions must proceed at a pretty fast rate to reach an equilibrium state. Regarding the distance or film thickness over which the migrating species have to move, he assumed it to be much greater than the narrow zone at the two interfaces which develop certain space charge due to interaction at these interfaces.

It is very likely that unless the temperature is sufficiently high, the assumption of equilibrium at the two interfaces may not

be any more valid, or it may so happen that the path over which the ions have to move is not very much greater than the space charge zones or the available thermal energy may not be sufficient enough to cause the movement of ions or diffusion of ions through the lattice of the oxide.

Anyone or all of the three conditions mentioned above may prevail at low temperatures when the studies are confined to thin film range.

It is no wonder that studies conducted on copper in the intermediate temperature ranges have shown a large number of variations, and in true sense C.Wagner's parabolic rate law was not found to be obeyed. Similar experiences have also been gained from this laboratory, on tarnishing studies of silver in different halogen atmospheres at low temperatures in the thin film range.

The causative factor of the driving force i.e., the electrochemical potential gradient or the chemical potential gradient also may or may not exist at low temperatures. If Mott's assumption of uniform distribution of defects between the metal/oxide interface and the oxide/gas interface is taken to be granted, it is imperative that a disturbing factor must upset this condition before unequal distribution of defects at the two interfaces sets in. This factor may be a temperature dependent function so that the rate of formation of the defects and their destruction may differ widely with the variation in temperature. So under certain restricted conditions of experimentation prevailing at low temperatures and in the thin film range,

investigators have agreed that, perhaps Mott's assumptions are valid and, therefore the question of detecting Wagner's mechanism does not arise.

Mott's reciprocal logarithmic law has been found to be a peculiar process where the rate of growth ceases beyond a certain thickness value. Here the driving force, i.e., the field decreases with increase of film thickness and finally reaches a value which cannot further lower the activation barrier necessary for the process and results in stopping of the further growth.

The causative factor for the creation of the field in Mott's equation arises due to tunneling of electrons to the outer interface forming negatively charged oxygen ions leaving behind positively charged metal ions thereby forming a condenser. The tunneled electron may be available in plenty upto a certain thickness for a system resulting a constant voltage across the interfaces. Mott also assumed that the voltage remains constant during the film growth. As the temperature is increased, the rate law is also found to change which may be due to growth of thickness or availability of more electrons due to thermoionic emission. So the barrier of reciprocal logarithmic law does not any more hinder the process. In general, a logarithmic law is observed under such conditions.

H.H.Uhlig has analysed the space charge effect of the electron availability at the outer interface and has proposed a double logarithmic law whose experimental verifications are of

grave doubts and whose theoretical assumptions have also been highly criticized by A.T.Fromhold.

At higher temperature, the electron availability at the outer interface becomes plenty and as such, it is likely that the availability of electron will no longer be the rate controlling step and under such conditions, direct dependence of the migrating species due to the electrical potential gradient may give rise to Mott's parabolic equation shifting the rate controlling step to be governed by the reaction at one of the interfaces.

In the application of Mott's parabolic and reciprocal logarithmic laws, the major difficulties had been the proper identification of the rate controlling step as the determined activation energies are not quantities to be identified for a particular process which have been understood through experimentation other than oxidation kinetic studies. This has been very easy for verification of Wagner's equation where the activation energy for diffusion was independently measured and agreed upon with the kinetic data. Mott's parabolic law is expected to be valid within a strictly restricted stipulated conditions. Although indirect evidences of obedience of such a parabolic law exists, but varied views on observance of cubic or other type of rate laws have also been reported by a large number of investigators.

Therefore, the only approach to the identification of the rate controlling step is through studies of a large number of variables which are supposed to influence the growth rate.

Even Mott's reciprocal logarithmic law makes evaluation of different parameters difficult because the form of equation is rather a complex one. Previous work from this laboratory tried to evaluate reciprocal logarithmic law by putting more importance to the rising part of the growth curve because of limited availability of data on limiting thickness values. The analysis were partial in a sense that the limiting parts were not predictable.

Work reported here contains an analysis based on the limiting part of the rate curve which has been extended to verify the rising part of the kinetic data also.

The first part of the work comprises of oxidation studies in the low temperature range ($5^{\circ}\text{C} - 45^{\circ}\text{C}$) to confirm some of the earlier published work and to have a keen insight into the theory of low temperature oxidation resulting limiting thickness pertaining to the hypothesis formulated by N.F.Mott. The effect brought about by the presence of small amount of alloying elements in copper were also considered to have a clear idea about the nature of various parameters of Mott's equation and to identify the nature of the migrating species. The effect of humid reaction atmosphere was also undertaken at room temperature, which is of more practical importance to predict the behaviour of protection caused by the products of reaction. With the increase of temperature, a change over of the rate controlling step and ultimately the kinetic law obeyed is expected to change. So at intermediate temperature ($75^{\circ}\text{C} - 100^{\circ}\text{C}$) oxidation characteristics were studied for pure copper, copper-lithium and

copper-chromium alloys. This gave an idea of the activation energy and therefore the mechanism of the process.

With further increase of temperatures (110°C - 175°C), the equilibrium of the different reactions at the two phase boundaries were supposed to get influenced resulting a further change over in the rate law. The calculated activation energies helped in identifying the mechanism of growth process and gave a proper understanding of the different equilibrium reactions occurring at the two reaction interfaces. The contribution of each of the earlier proposed mechanisms could also be judged providing further information relating to the exact rate controlling step leading to observed rate laws.

Since oxidation processes are controlled by electron flow and ion migration, the effect of an applied external current was undertaken to estimate the extent of its influence over the rate laws operating at 175°C .

The effect of oxygen pressure was taken up to have an idea about the changes brought about at the reaction interfaces due to increased or decreased oxygen concentration on the oxide surface helping to suggest a proper mechanism of the reactions encountered at the experimental temperature range.

The electrometric technique which is an established method for accurate determination of the thickness of Cu_2O layer on copper in the thin film range was also employed in the present study.