

CHAPTER - IINTRODUCTION

With the exception of Gold, no pure metal or alloy is stable in air at room temperature. This reaction between a metal and oxygen is one of the most common phenomena encountered. The interest in this line has given rise to numerous investigations and in some cases, the mechanisms are well established. There is a complexity in the number of reviews because of dearth of factual knowledge concerning processes on an atomic and sub-atomic scale involved in the oxidation and film growth. Although investigations have been reported on the low temperature study of oxidation of Copper, the influence of the metallurgical state of the metal upon its subsequent reactivity has not been given due consideration.

Equations for the increase of thickness of oxide film (x) with time (t) have been worked out on various assumptions. Many times the assumptions have been chosen to simplify the treatment. Known constants have been calculated to fit in certain data and the pattern of the curves, which are of doubtful absolute significance.

Evans* rightly comments as follows :

" There can be no question of concealing the essential mathematical character which any quantitative presentation must possess, but it would seem possible to express it in a way which is reasonably concise and which introduces no complications irrelevant to the theme and which does not hide the approximations introduced or the questions left unsettled."

Most of the common equations controlling the low temperature oxidation in the thin film range are the logarithmic, cubic and the inverse logarithmic laws. It can be shown that under certain circumstances one can be regarded as an approximation to the other. It can also be expected that the experimental data will occasionally be obtained which do not fit in any equation, in which case according to Evans, intermediate forms would be expected. For example the experimental data fitted in a logarithmic equation of the type $x = A + B \ln t$ may also be fitted in an inverse logarithmic law of the form $\frac{1}{x} = A - B \ln t$ thus complicating the theoretical discussions.

In many cases where a cubic equation has been reported, the slope of the $\log x$ vs. $\log t$ plot has not been exactly $1/3$. Also it has been observed that the cubic equation can in general be fitted equally well by a double (a two stage) logarithmic equation.

* Evans, U.R. -Oxidation of metals - A simplified quantitative discussion. Rev.Pure & App.Chem.5,1(1955).

Many investigators have suggested a logarithmic law of the type $x = k \log \left(\frac{t}{\tau} + 1 \right)$ where k and τ are constants. Here a straight line plot can be obtained only when x is plotted against $\log(t + \tau)$ except in cases where $t \gg \tau$, where the x vs. $\log t$ plot itself will yield a straight line. But this condition is usually not true in the thin film range and hence the x vs. $\log t$ curve yields two straight lines of differing slope representing a break in the curve. Such a break has been interpreted by many as a change in the mechanism in the process taking place at that thickness, or as a boundary line between the uniform and diffuse space charge regions etc.

These induced the author to undertake further systematic study of the low temperature oxidation and the thin film growth kinetics. Copper has been chosen since it offers a most promising system to study. The thin oxide films formed at low temperatures which has been confirmed to be cuprous oxide, is physically and chemically homogeneous and there exists considerable information on the semiconducting properties of this oxide. Most of the early work has been analysed on the basis of Cabrera - Mott theory, the exact nature of which has been tested only on a qualitative basis. Many investigators have used Mott's equation by integrating the same by imposing certain boundary conditions which are not always true. Hence, in the present work, the rate equations

are fitted not on the basis of $x - t$ curves, but in the differential form viz. $\frac{dx}{dt}$ vs. $\frac{1}{x}$. The errors in slope measurements could be checked by extrapolating the $x - t$ curves from the $\frac{dx}{dt} - \frac{1}{x}$ curves by numerical methods and comparing these with the experimental points thereby eliminating the boundary conditions, which are unavoidable while integrating Mott's equation.

The first part of the work consists of the studies made at room temperature to confirm some of the earlier published work and to get the growth pattern for the particular composition used. The thickness values obtained are not claimed to be absolute, due to surface roughness factor, but the trend can be taken to be correct, as the roughness factor is constant throughout. Next a parallel study was made for a high purity Copper specimen to detect whether the Nickel content in the Copper used (0.23%) had any appreciable effect. Then the effect of temperature was studied in the range of 8 - 115°C. This gave an idea about the activation energy and therefore the mechanism. The temperature effect of one set of cold worked samples was also studied under similar conditions.

Since most of the low temperature oxidation processes are controlled by electron flow and ion migration the effect of an applied external current was undertaken from which the

potential difference across the metal/oxide and the oxide/gas interface and other parameters could be calculated. The effect of oxygen pressure was taken up next to get an idea about the increase in vacancy concentration in the oxide due to increased oxygen concentration on the oxide surface.

The effect of cold working and annealing was then investigated to find out the importance of the structure or the metallurgical state of the metal and the defect concentration, on the kinetics.

A few Copper-Lithium alloys were then made and its oxidation characteristics studied to investigate the effects of blocking of defects in the oxide (Hauffe's rule).

In studying the above effects it was tried to obtain a picture of the variation of the number of cation vacancies migrating through the oxide to the metal-oxide interface which is proportional to the number of ions migrating to the oxide-gas interface.

The specimens were electrolytically polished before exposure and the thickness estimations performed by the electrometric method, as this has been found to be most accurate for thin films formed on metals.