

CHAPTER I

I N T R O D U C T I O N

Different mathematical models have been proposed to explain the kinetics and mechanism of formation of a metal oxide, sulphide or halide layer on a metal as a result of the action of oxygen, sulphur vapour or halogen gas at low or elevated temperatures. The apparently simple observation of tarnished layer or scale formation on metals by the reacting gases is complicated by the fact that the reaction product frequently appears as a compact phase which tends to isolate the metal from the attacking gas and the film can continue to thicken only if ionic species can diffuse through the barrier layer. This diffusion controlled process of oxidation at higher temperatures and for thicker films can be explained only by the mechanism suggested by Wagner. Different theories have also been put forward favouring one of the phase boundary reactions or the nucleation process as the rate determining step. Various mathematical relations have also been advanced by Evans, Mott-Cabrera, Engell-Hauffe-Ilschner, Uhlig, Grimley-Trapnell, William-Hayfield and Fromhold explaining the thin film growth on metals exposed to an attacking gas with considerations of different boundary conditions.

Various rate laws such as linear, parabolic, cubic, normal or inverse logarithmic, have been reported by many experimenters for the oxidation of metals and alloys and these have been matched either to Wagner's mechanism of thick film growth or to the theory of thin or very thin film growth at low or intermediate temperatures proposed by Mott-Cabrera or to a somewhat extended and modified form of Mott-Cabrera theory as presented by Engell, Hauffe and Ilschner or to one of the thin film mechanisms proposed by others.

In the oxidation of copper which leads to the formation of Cu_2O (p-type semiconductor - mainly hole conducting), various rate laws have been found to be operative at various temperatures by different workers and these have been fitted either to thin film or to thick film mechanism depending on the temperature, pressure of oxygen and the thickness of the scale. This is the most thoroughly studied system with the help of which almost all the available oxidation mechanisms have been verified.. At room temperature because of formation of thin films ($\sim 40 \text{ \AA}$), oxidation of copper conforms to the reciprocal logarithmic law supported by Mott-Cabrera theory as shown by Krishnamoorthy and Sircar. In contrast to this system, the tarnishing of silver in halogen atmosphere which leads to the formation of silver halide films(Frenkel type of defect - mainly ion conducting) according to the parabolic law is in agreement only with the widely established mechanism of Wagner, because different investigations so far carried out

from room temperature to high temperatures have dealt only with thicker films of halides. Hence, it is seen that the temperature and the thickness of the growing layer and the electronic and ionic characters of the scale are the deciding factors in conforming to a particular mechanism out of the many available mechanisms of film growth. The temperature and the thickness factors are not well defined and they are definitely highly dependent on the individuality of the system. Possibility of obedience to other rate laws and other mechanisms in case of thinner halide growth on silver has not been explored so far. The aim of this investigation is to examine and verify the kinetics and mechanisms of thin film growth at lower temperatures when the oxidation product is an ionic conductor.

This work covers the kinetics studies of chloride, bromide and iodide growth on silver in the thin film range under the corresponding halogen atmosphere in dry as well as in humid conditions. Lower temperature range (30° - 70°C) and lower partial pressure of halogen were selected to confine the study to the thinner film range. The study was extended to thicker growth in case of Ag/AgI/I₂ system in order to get a clear understanding of the pressure dependence relations observed in thinner film range.

Effect of cadmium as an alloying element on the kinetics of AgCl and AgI growth on silver at low temperatures was also investigated to examine the influence of defect concentration on the rate of reaction in the low thickness range.

Another metallurgical parameter such as cold deformation of silver was also included in the study to find its effect on the kinetic behaviour of AgCl and AgI growth on silver.

Estimation of thickness of the reaction product in the thinner film range has been done electrochemically by cathodic stripping of the halide films in a NaH_2PO_4 and Na_2HPO_4 buffer solution. For thicker AgI growth, weight change method has been followed using a sensitive balance.