KINETICS AND MECHANISM OF THIN HALIDE FILM GROWTH ON SILVER AT LOW TEMPERATURES

Thesis submitted in partial fulfilment
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DOCTOR OF PHILOSOPHY

IN

METALLURGICAL ENGINEERING

BY

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C E R T I F I C A T E

This is to certify that the thesis entitled "Kinetics and mechanism of thin halide film growth on silver at low temperatures" being submitted by Sri Subir Kumar Bose for Ph. D. degree, is a record of bonafide research carried out by him for about five years, in the Metallurgical Engineering Department at the Indian Institute of Technology, Kharagpur, India under my guidance and supervision. In my opinion, the work fulfils the requirements for which it is being submitted.

The work incorporated in this thesis has not been submitted to any other University or Institute for the award of a degree or a diploma.

29/11/71

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PREFACE

Tarnishing reactions of many metals in variety of atmospheres are now fairly well understood phenomena. This knowledge has come through accumulations of experimental facts and theoretical developments. On occasions, experimental observations of new kinetic patterns of tarnishing have provided impetus to the development of theories consistent with the experimental findings. In certain cases, theoretical developments have preceeded the experimental verifications of such theories.

The pioneering experimental works of G.Tammann, and N.B.Pilling and R.E.Bedworth led to the development of the famous parabolic growth law of C.Wagner for high temperature oxidation of metals. But this law was inadequate in explaining the various other rate laws observed by different workers under widely different conditions of temperature of tarnishing, pressure of the attacking gas and the thickness of the tarnished layer. A purely theoretical approach of generalised nature was later on developed by N.F.Mott and N.Cabrera embracing Wagner's mechanism only as a special case. The outcomes of this analysis were a reciprocal logarithmic law, a cubic law and a parabolic law which can be experimentally expected under different sets of conditions. This theory had many simplifications and simplifying assumptions which were not always justifiable and, consequently, some modified and more generalised theories with less restrictions and simplifications were proposed by K.Hauffe, T.B.Grimley and B.M.W.Trapnell, and A.T.Fromhold.

In certain systems under certain experimental conditions the above proposed rate laws were also not adequate, leading to the formulation of different theories by U.R.Evans, C.Wagner, I.M.Ritchie and G.L.Hunt, H.H.Uhlig, and E.C.William and P.C.S. Hayfield which could explain the individuality of many systems.

The experimental and theoretical works of different research schools like Max-Planck Institute, Cambridge University, M.I.T. and Westinghouse Research Laboratory have enriched the knowledge of tarnishing reactions to the present level.

There exists still certain gap in the knowledge of kinetics studies of tarnishing reactions for certain systems and verifications of certain theoretical relations. This discrepancy is more often encountered during tarnishing studies at low temperatures and in the thin film range. There are not many systems which can be fruitfully studied for throwing more light on the oxidation behaviour. Tarnishing of silver in halogen atmospheres has many features which give a scope for low temperature investigation and examination of the developed theories.

In this investigation, silver halide film growth has been studied near room temperatures and in the thinner film range.

For the silver-chlorine system, a cubic to parabolic transition, which is not reported so far, has been observed here providing experimental verification of Mott's cubic law.

In the silver-bromine system also, a cubic law has been found to be obeyed in the similar temperature range which has never been reported before.

For the silver-iodine system, a parabolic law has been observed althrough the temperature and pressure range studied conforming to Wagner's mechanism.

Pressure dependence studies reveal that observed pressure relation during tarnishing is influenced to a great extent by the thickness of the film.

Kinetics of growth of halide films as influenced by alloy additions, moisture content of the atmosphere and prior deformation of the sample have also been included in this work.

An analysis of the possibility of change over in tarnishing laws in thin film range has been presented.