# ELECTROLESS DEPOSITED BLACKS AND METAL PIGMENTED ANODIZED ALUMINIUM AS SOLAR SELECTIVE COATINGS


BY

**S. N. KUMAR**

**CENTRE FOR MATERIALS SCIENCE AND TECHNOLOGY**


Thesis submitted
in fulfillment of the requirements
of the degree of

**DOCTOR OF PHILOSOPHY**

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

**DECEMBER, 1983**

THESIS SUPERVISORS:

PROFESSOR K.L. CHOPRA
Head, Thin Film-Solid State
Technology Cell
Department of Physics

DR. L.K. MALHOTRA
Assistant Professor
Centre for Materials Science
and Technology

Indian Institute of Technology
New Delhi-110016, INDIA

## ACKNOWLEDGEMENTS

I am deeply grateful to Professor K.L. Chopra and Dr. L.K. Malhotra for their invaluable guidance, objective criticism, continuous encouragement and inspiration during all stages of this work.

It has been my privilege to be a member of the Thin Film Group. I have always enjoyed the intensive cooperation and helping hand of my colleagues. I wish to thank especially Drs. A. Banerjee, S. Rajagopalan and T.V. Rao for their help in AES/XPS studies. I am also thankful to Dr. Bharat Bhushan for his useful discussions during the initial stages of the work. I appreciate Drs. V. Dutta, G.B. Reddy, Miss C.S. Uma and Mr. Satyendra Kumar for their assistance in reflectance measurements. I am thankful to Mr. Harminder Singh for his help in the photographic work. I would also like to thank Mr. Sunil Kumar, Mr. A.N. Tiwari and Miss Purnima for their generous help in compiling the thesis.

Special thanks are due to Dr. R. Samuel of Mechanical Engineering Department, who introduced me to the exciting world of computer science. I also thank Dr. N.C. Mahanti of Centre for Atmospheric Sciences for his guidance during the initial stages of computations.

I would also like to record my thanks to the technical staff of IIT Delhi, in particular to Mr. V.K. Lal and Mr. D.C. Sharma for their help in scanning electron microscopy, Mr. V.D. Arora for transmission electron microscopy and to Mr. Rawat of IDDC for the cutting of samples.

The help given by Dr. S.C. Mullick of Centre of Energy Studies for carrying out some field performance tests, and by Mr. B.K. Mohanty and Mr. S. Kumar of Mechanical Engineering Department for the fabrication of solar oven is thankfully acknowledged.

I express my special thanks to Mr. V.N. Sharma who took keen interest in typing out the manuscript efficiently.

Finally, although I have deprived my son of some very joyful moments, I feel gratified that my wife and parents rendered their patience and moral support during the course of this work.

S. N. Kumar

(SUNDARAM N. KUMAR)

## ABSTRACT

The present work investigates the usefulness of solution growth techniques of electroless deposition and anodization of aluminium followed by metal pigmentation by ac electrolysis to fabricate selective absorbing surfaces for photothermal conversion of solar energy.

The technique of electroless deposition has been used to prepare nickel and molybdenum black coatings on galvanized steel and aluminium substrates. Optimized coatings have been obtained near room temperatures of deposition. By changing the deposition conditions from that of the conventional electroless deposition of metals, it has been possible to deposit both the metal and the oxide simultaneously, such that a graded composition profile of metal and oxide is obtained.

Porous anodic alumina films embedded with nickel or cobalt particles have been prepared by anodizing in an oxidizing electrolyte followed by ac electrolysis in an Ni or Co electroplating bath. The effect of various anodization parameters on the structural features and optical properties of these pigmented anodic alumina coatings has been studied. A correlation between the microstructural features and the solar selectivity of these coatings has been established. Coatings with low thermal emittance, $\approx 0.06$ (at $100^{\circ}C$), and solar absorptance $\geqslant 0.90$ have been prepared by anodizing in a phosphoric acid electrolyte. Addition of sulphuric acid increased the $\alpha_s$ and $\varepsilon$ values of the film due to the formation of a thicker and alumina rich anodic film.

A detailed microstructural characterization of the electroless deposited Ni and Mo blacks and Ni and Co pigmented anodized aluminium coatings has been carried out. The electroless nickel black coatings have a graded profile of Ni, Zn and NiO throughout the film cross section with traces of $Ni_2O_3$ and $Ni_7P_3$ also probably present in the upper layers of the films. The electroless Mo black coating has a graded composition profile of Mo, Zn and $MoO_3$ in the film. The metal pigmented anodized Al coatings contain Ni or Co particles impregnated in the porous alumina matrix. These coatings have not shown any significant degradation in their optical properties on annealing upto $250^{o}C$ in air.

The optical properties of Ni and Co pigmented anodized aluminium coatings have been analyzed in terms of the effective medium theories of Maxwell Garnett and Bruggeman. These pigmented coatings have been treated as a two-component cermet of $Ni-Al_2O_3$ and $Co-Al_2O_3$ in which the pigmenting particles occupy a significant volume fraction of the film. By taking reasonable estimates of surface roughness and particle configuration, the Bruggeman theory yielded a good agreement with the experimental curve over the solar spectrum. The infrared absorption bands, observed in the experimental curves, have been found to be due to the characteristic vibrational modes of the various molecular species present in the anodic film.

To explain the optical properties of the three-component composites of electroless nickel and molybdenum black coatings, a two-step approach to the above effective medium theories has been described. These 3-component systems have been treated on the format of a 2-component effective medium, involving two steps of computations. Using such an extension of the effective medium theories, a satisfactory agreement between the experimental and theoretical reflectances is obtained by a mixed treatment of the Maxwell Garnett and Bruggeman theories in two steps.

The electroless nickel black deposition process has been successfully used to produce large area water heating collector panels and a box type solar oven. Detailed field performance tests of these large area selective absorbers have been carried out.

CONTENTS

Page