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CHARACTERIZATION OF ELECTRODEPOSITED NICKEL-COBALT SELECTIVE BLACK COATINGS: SCANNING ELECTRON MICROSCOPIC STUDIES

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Selective black coatings are utilised for the efficient conversion of solar radiation into thermal energy. This paper describes the characterization of nickel-cobalt black coating through Scanning Electron Microscopic (SEM) studies. The microstructure of selective nickel-cobalt black coating produced from a bath containing 10 g.l^{-1} nickel sulphate, 10 g.l^{-1} cobalt sulphate and 10 g.l^{-1} ammonium acetate at 308 K at pH values of 6.2 is correlated with the optical properties (α, ε)

Keywords: Selective coatings, black nickel-cobalt, solar energy, thermal energy conversion, SEM analysis

INTRODUCTION

The future of solar thermal equipment rests on the production of systems with high efficiencies and low thermal losses. Solar selective black coatings, to suppress radiation losses in these systems, gain importance as such coatings reduce the radiation heat loss occurring at the absorber plate when it is operating at higher temperatures [1-5]. Selective coatings are characterized by high solar absorptance (α) and low thermal emittance (ε). The electrodeposition technique plays an important role for the production of selective coatings. One of the commercially electroplated solar absorber coating is black chrome, which is a favoured coating due to its high spectral selectivity and high degree of selectivity [6-8]. However, production of black chrome requires high current densities of the order of 20 A.dm^{-2} and the operating temperature is to be maintained at 293 K. This increases the cost of production. As India being a tropical country there is a need for the development of selective coating systems for operation at temperatures of 303-313 K. Hence, the authors are investigating the possibilities of different single metal and alloy coating systems for the efficient conversion of solar energy. Black cobalt [9], black nickel [10], black nickel-tin [11],black nickel-cadmium [12], black nickel-cobalt [13], black nickel-chromium [14], black nickel-phosphorous [15],black cobalt-tin [16],black cobalt cadmium [17], and black nickel-tin-cadmium [18] systems are being developed at this Institute.

An attempt was made to develop solar selective coatings with desired optical properties, high corrosion resistance and depositable at low current densities. This resulted in the evolution of a nickel - cobalt solar selective black coating [13]. This coating possesses a solar absorptance (α) of 0.92 - 0.98 and thermal emittance (ε) of 0.04. The optimised coating exhibits a very high selectivity ratio.

Scanning Electron Microscopy (SEM) is one of the powerful surface analytical techniques. In this technique the specimen surface is scanned by a high energy electron beam. During irradiation of a high energy electron beam the specimen emits a number of signals like secondary electrons, back scattered electrons, absorbed electrons, transmitted electrons, cathode luminescence, x-rays etc. Eventhough a number of signals are emitted from the surface, secondary electrons can be recorded as the mostly used signal among them. Hence in this work secondary electrons image has been taken for the studies. A scanning electron micrograph reveals informations about the specimen like surface structure, composition, topography, crystalline state, particle or grain size and shape, etc. Specimen preparation is also not much tedious for SEM studies, only requirement is that the specimen must be electrically conducting. If the specimen is not electrically conducting a thin film of conducting coating is given over the sample surface.

EXPERIMENTAL

Hull cell plating was carried out to optimize the electrolyte composition, *p*H and temperature for obtaining a high performance nickel-cobalt black coating. An electrolyte containing 10 g/l of nickel sulphate, 10g/l of cobalt sulphate and 10g/l of ammonium acetate with *p*H 6.2 at 308 K was found to produce black coating in a wide current density range of 3 to 10 $A.dm^{-2}$ [19,20].

Copper panels of 100 mm x 100 mm size were initially given pre- treatment. The pre-treatment involves mechanical polishing, degreasing with trichloroethylene, electrocleaning in alkaline solution, washing in distilled water, acid pickling with 20% sulphuric acid, washing in tap water and rinsing in distilled water. Pre-treated panels were then given an undercoating of nickel to a thickness of 10 μm using Watt's nickel bath. These panels were used as substrates for obtaining black coatings.

Nickel-Cobalt black coatings were cathodically deposited using the optimized electrolyte under optimized operating conditions. Coatings were deposited using different current densities namely 3.53 $A.dm^{-2}$, 4.70 $A.dm^{-2}$, 5.9 $A.dm^{-2}$, 7.05 $A.dm^{-2}$, 8.2 $A.dm^{-2}$, and 9.4 $A.dm^{-2}$, for different durations of time namely 5 Sec, 10 Sec., 20 Sec., 30 Sec., 40 Sec., and 50 Sec. Samples of 10mm x 10 mm size were cut from the coated panels and studied through SEM.

JEOL JSM 35 CF Scanning Electron Microscope was used to characterize the electrodeposited nickel-cobalt black coatings. The characterization was carried out to study the particle size as well as the surface structure, composition and topography of the black coatings. As the coating particles exhibited a very high contrast with respect to the background the micrographs were taken with and without conducting coating over the specimen. JEOL FINECOAT ion sputtering equipment was used to give gold conducting coating to a thickness of 10 nm over the specimen surface. The micrographs have been taken at desired magnifications. The solar absorptance (α) and thermal emittance (ε) of the coatings were measured using Alphatometer and Emissometer manufactured by M/s Devices and Services Co., USA.

RESULTS AND DISCUSSIONS

SEM studies

The scanning electron micrographs taken without gold coating on the surface, shown in Fig. 1, reveal that the particles of the black deposits are electrically semiconducting or dielectric in nature. This information is got from the very high contrast exhibited by the particles with respect to the nickel undercoated copper substrate, which is a good electrical conductor. The high contrast is due to the charge build up on the surface of the particles to some extent during the irradiation with electron beam. At the same time the

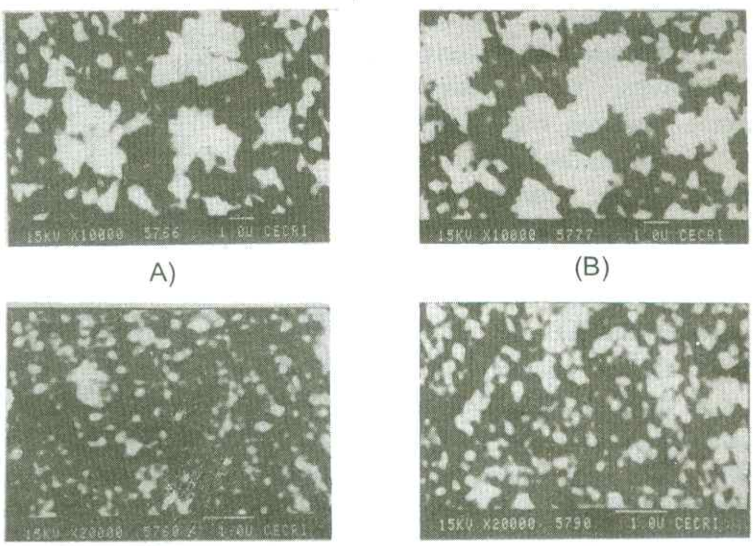


Fig. 1: SEM micrographs taken on Ni-Co black coatings deposited using (a) 3.53 $A.dm^{-2}$ for 50 sec (b) 4.7 $A.dm^{-2}$ for 50 sec (c) 5.9 $A.dm^{-2}$ for 20 sec (d) for 30 sec

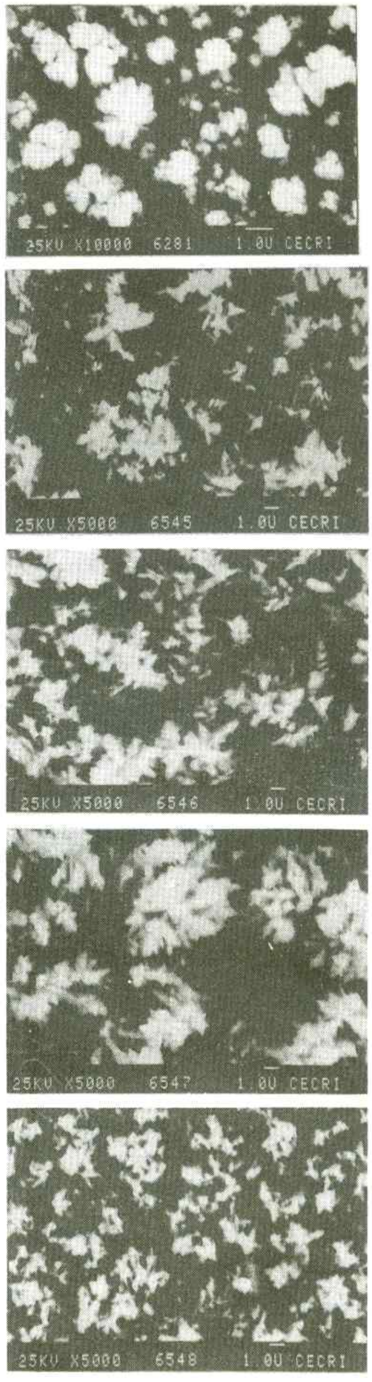
possibility of image formation of the particles in scanning electron microscopic technique reveals that the particles must have a conducting base or the particles must be semi conducting, because image formation in the case of dielectric materials without conducting coating is impossible. Hence it can be concluded that the material is either a semiconductor or a metal-dielectric cermet.

The scanning electron micrographs taken on black coating samples with conducting film of gold on the surface, shown in Fig. 2 reveal that the particles constituting the coating have highly irregular shape, micro roughness and dendritic like structure. The dendritic structure appears as conical needles or whiskers. This structure facilitates a very high surface area, which is about a few hundreds to few thousands times the area occupied by the solar absorption panel. The very high surface area facilitates very high solar absorption, while the irregular surface structure entertains optical interference between the incident and scattered beams of solar radiation. This in turn minimizes the reflection of radiation from the surface. Moreover the irregular surface structure of particles facilitates multiple scattering of radiation, hence the incident solar energy is absorbed by black coating to the greatest extent.

From this study it can be concluded that the black coating surface has textured structure. These textured surfaces appear rough and absorbing to solar energy while appearing mirror like and highly reflective to thermal energy. The dendrites absorb shorter wavelengths of solar radiation due to the geometry by the process of multiple absorption and reflection. But in the infrared region the size of dentrites plays a main role with thermal emittance. In thermal region the wavelengths associated with radiation are much longer. If the dentrite spacings are much smaller than the wavelengths then the surface appears fairly smooth and acts like a poor emitting surface. On the other hand if the dentrite spacings are comparable with the wavelengths then the surface no more appears smooth to thermal radiation and hence it exhibits high thermal emittance [21-23].

Influence of deposition time on optical properties (α, ε)

Fig. 3 shows the influence of deposition time on optical properties (α, ε) for the nickel - cobalt black coating. It could be observed that the deposition time influences both solar absorptance and thermal emittance of the coating. Thermal emittance is almost a linear function of time and to achieve minimum emittance, deposition time has to be controlled.



(A)

(B)

(C)

(D)

(E)

Fig. 2: SEM micrographs taken on Ni-Co black coatings deposited using (a) 3.53 $A.dm^{-2}$ for 30 sec (b) 8.2 $A.dm^{-2}$ for 20 sec (c) 8.2 $A.dm^{-2}$ for 40 sec (d) 8.2 $A.dm^{-2}$ for 50 sec and (e) 9.4 $A.dm^{-2}$ for 20 sec with sputtered film of gold on the surface

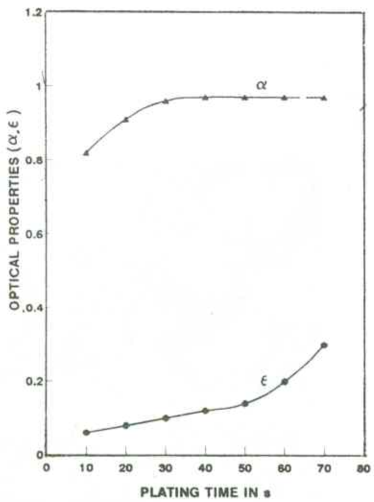


Fig. 3: Influence of plating time on optical properties (α, ε) $NiSO_4$ 10 g.l^{-1}, $CoSO_4$ 10 g.l^{-1}, CH_3COONH_4 10 g.l^{-1} at 308 K, *p*H 6.2, 4 A.dm^{-2}

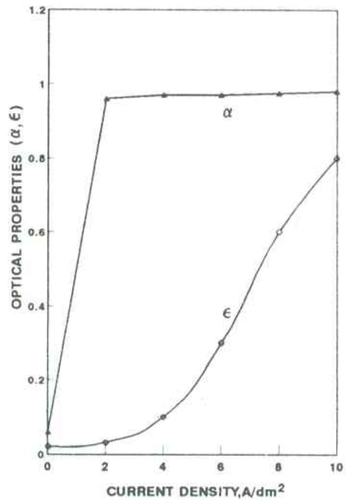


Fig. 4: Influence of current density on optical properties (α, ε) $NiSO_4$ 10 g.l^{-1}, $CoSO_4$ 10 g.l^{-1}, CH_3COONH_4 10 g.l^{-1} at 308 K, *p*H 6.2, 30 sec

Influence of current density on optical properties (α, ε)

Current density employed for the deposition of the coating has a greater influence on the optical properties of the coating as shown in the Fig. 4. Higher current densities require lesser deposition time since the coating thickness determines the optical properties. Optimized coating produced at a current density of 3.5 A.dm^{-2} for a duration of 30 seconds yields solar absorptance of 0.91 and thermal emittance 0.04.

CONCLUSION

From SEM studies it is found that the coating has been constituted by different size and shape of particles. The particles have highly textured surface. The coating materials is either semi conducting or metal-dielectric cermet nature. High degree of solar absorption in this material is due to optical interference and surface roughness. Deposition time and current density influences both the solar absorptance and thermal emittance of the coating.

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