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Flat Absorber Phosphorous Black Nickel Coatings for Space Applications

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A new process of flat absorber black nickel alloy coating was developed on stainless steel by electrodeposition from a bath containing nickel, zinc and ammonium sulphates; thiocyanate and sodium hypophosphite for space applications. Coating process was optimized by investigating the effects of plating parameters, *viz* concentration of bath constituents, current density, temperature, pH and plating time on the optical properties of the black deposits. Energy dispersive X-ray spectroscopy showed the inclusion of about 6% phosphorous in the coating. The scanning electron microscopy studies revealed the amorphous nature of the coating. The corrosion resistance of the coatings was evaluated by the electrochemical impedance spectroscopy (EIS) and linear polarization (LP) techniques. The results revealed that, phosphorous addition confers better corrosion resistance in comparison to conventional black nickel coatings. The black nickel coating obtained from hypophosphite bath provides high solar absorptance (α_s) and infrared emittance (ε_{IR}) of the order of 0.93. Environmental stability to space applications was established by the humidity and thermal cycling tests.

KEY WORDS: Phosphorous black nickel alloy; Electrochemical impedance spectroscopy; Linear polarization; Solar absorptance; Infrared emittance

1. Introduction

Black nickel coatings comprising nickel–zinc oxide/sulphide complex were introduced by Tabor[1] in the late 1950s. Many researchers have reported black nickel coatings prepared by chemical conversion of zinc coated substrate[2–4] or by electrodeposition from a plating bath containing nickel and zinc salts[5,6]. The black nickel plating is a well-known commercial process that has been found numerous applications because of their excellent optical properties. However, unsatisfactory corrosion resistance of black nickel coating limits its use in aggressive climates[7]. The present work describes the electrolytic deposition of black nickel coatings on stainless steel 316 from the bath containing Ni, Zn and ammonium sulphates; thiocyanate and sodium hypophosphite. The plating process aims to modify the bath composition by the addition of sodium hypophosphite and to optimize the operating conditions to obtain coatings of superior optical properties and corrosion resistance. The improvement in the corrosion resistance of the coating was evaluated by electrochemical impedance spectroscopy (EIS) and linear polarization (LP) techniques. The results were compared with the conventional black nickel plating obtained from a plating solution that does not contain sodium hypophosphite.

2. Experimental

2.1 Sample preparation

Circular test specimens of stainless steel alloy 316 (16% Cr, 10% Ni, 2% Mo and 0.1% C, and balance iron by wt%) of 5 cm diameter and 0.4 cm thickness were used. All the chemicals used were of laboratory reagent grade, and de-mineralized water was used throughout.

Bare stainless steel 316 alloy coupons were sub-

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jected to solvent cleaning with ultrasonic agitation using trichloroethylene at 25 °C for 15 min, followed by anodic electrolytic cleaning in a solution of sulphuric acid (SG 1.84, 600–700 mL/L) using DC power supply at a voltage of 10 V for 60 s. Stainless steel 316 electrode was used as cathode and anode was the working electrode itself. After rinsing with de-mineralized water the coupons were subjected to nickel strike using a solution of 225–275 g/L of nickel chloride and 84–88 mL/L of hydrochloric acid (35 %, V/V) at a current density of 30 mA/cm^2, at 25 °C, and the coupons were then rinsed with de-mineralized water.

After pre-treatment steps as listed above, the coupons were processed for conventional black nickel plating as cited in literature[8] as well as for the present phosphorous black nickel coating. Phosphorous black coating was obtained from a bath containing 75 g/L nickel sulphate hexa hydrate ($NiSO_4 \cdot 6H_2O$), 30 g/L zinc sulphate ($ZnSO_4$), 30 g/L ammonium sulphate $(NH_4)_2SO_4$, 37.5 g/L sodium thiocyanate (NaSCN) and 37.5 g/L sodium hypophosphite (NaH_2PO_2), operating at pH 4.8–5.2, current density 5 mA/cm^2, bath temperature 25–30 °C, for 15 min. Standard nickel was used as the anode. It was followed by rinsing with de-mineralized water, dipping in hot water for few seconds and air drying.

The pH of the plating solution was adjusted upward with the addition of dilute ammonium hydroxide and downward by the addition of dilute sulphuric acid. Continuous filtration of the plating solution and mechanical agitation of the job is mandatory to obtain good black deposits.

2.2 Characterization of the coating

The surface morphology and elemental analysis of the coating were examined using a scanning electron microscope attached with energy dispersive X-ray analyzer (EDXA, Model Leica S440i and INCA X–sight, respectively, from Leica, Cambridge Oxford instruments, UK). This instrument was operated at a voltage of 20 kV with probe current 100 pA and filament current 2.70 A.

Adhesion of the coating was evaluated by heat quench test. The specimens were heated to 200 °C for 1 h and quenched in water at room temperature. The test specimens were then examined visually with a magnification of 4X for any degradation in physical appearance like blisters, cracks or discoloration.

Optical properties of the coatings, *viz* solar absorptance and infrared emittance were measured by using a Solar Reflectometer version 50, Model SSR–ER and Emissometer Model RD1, respectively, from Devices and Services, USA. Both these instruments provide an average value of solar absorptance and infrared emittance digitally over the entire solar and infrared regions.

EIS and linear polarization measurements were performed using an Autolab PGSTAT 302N potentiostat system with FRA2 (frequency response analyser) module, which was driven by NOVA 1.4 software from Eco-chemie, Netherlands. The measurements were performed using a conventional three-electrode set up where the test sample with approximately 1 cm^2 exposed surface area was placed in the corrosive medium[9]. The platinum electrode was used as counter electrode and the Ag/AgCl, 3 mol/L KCl electrode was used as reference electrode. Prior to EIS measurements, samples were immersed in the corrosive medium (3.5% sodium chloride, pH 6.0) for about 15 min in order to establish the steady state condition. Both electrochemical impedance spectroscopy and linear polarization measurements were performed in open atmospheric conditions.

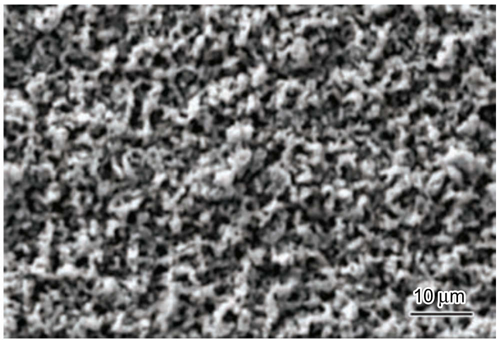

Fig. 1 SEM image of phosphorous black nickel coating

3. Results and Discussion

Surface morphology plays a crucial role in determining the optical property of the coating. Surface morphology of the coating as observed by scanning electron microscopy (SEM) shown in Fig. 1 revealed the presence of rough, irregular dark particles distributed in the lighter matrix. The dark particles are metal sulphides. The elemental composition of black coating obtained from EDXA indicates the co-deposition of Ni, Zn, S and P. The composition of phosphorous black nickel coating is summarized in Table 1. The black colour of the coating is attributed to the deposition of sulphide particles along with Ni–Zn alloy. Though, faint gray colour in Ni–Zn alloy coating can be obtained without co-deposition of S[10], deep black colour are produced with the co-deposition of sulphides. Metal sulphides, *viz* NiS, ZnS were reported to be responsible for black colouration of the coating[11]. The deposition of S requires the electrochemical reduction of S, combined with SCN^- ion, at the cathode. Since SCN^- ion is negatively charged

Table 1 Elemental composition of phosphorous black nickel coating (wt%)

O	P	S	Ni	Zn
23.38	6.24	7.94	11.92	50.52