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High emittance black nickel coating on copper substrate for space applications

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ABSTRACT

Black nickel, an alloy coating of zinc and nickel, is obtained on copper substrate by pulse electrodeposition from a modified Fishlock bath containing nickel sulphate, nickel ammonium sulphate, zinc sulphate and ammonium thiocyanate. A nickel undercoat of 4–5 μm thickness is obtained using Watts bath to increase the corrosion resistance and adhesion of the black nickel coating. The effect of bath composition, temperature, solution pH, current density and plating time on the coating appearance and corresponding infra-red emittance of the coating is investigated systematically. Process parameters are optimized to develop a high emittance space worthy black nickel coating to improve the heat radiation characteristics. The effect of the chemistry of the plating bath on the coating composition was studied using energy dispersive X-ray analysis (EDAX) of the coatings. The 5–6 μm thick uniform jet black zinc–nickel alloy coating obtained with optimized process exhibited an emittance of 0.83 and an absorbance of 0.92. The zinc to nickel ratio of black nickel coatings showing high emittance and appealing appearance was found to be in the range 2.3–2.4.

1. Introduction

Black coatings on metallic substrates are widely used for numerous applications; for example, as decorative coatings, as solar absorption coatings in solar panels, as antireflective coatings in optical instruments etc [1–6]. Among the various available black coatings, black nickel coating obtained by electrodeposition method has attracted the interest of researchers since it was introduced by Tabor [7] in the late 1950s. Since then a large number of black nickel electroplating solutions based on nickel salts, containing salts of zinc, copper, cobalt or molybdenum and usually some sulphur compounds, such as sulphite, thiosulphate or thiocyanate have been reported [8–13]. A variety of other techniques such as chemical conversation, thermal oxidation of metallic films, sputtering, spray pyrolysis and electroless deposition have also been reported in literature [14–17]. Most of these earlier researches are concentrated in the development of selective solar collectors or solar absorbers exhibiting high absorbance in the range of solar spectrum and low emittance in the infrared range of radiation [18–24]. It has been reported that there is a strong relationship between the optical properties of black nickel coating and its thickness. The coating exhibits solar absorber property only in a narrow range of thickness and with increase in thickness, the coating behavior changes from a solar absorber coating (high absorbance and low emittance) to a flat absorber coating (high absorbance and high emittance) [21]. The objective of the present work is to develop an electroplating process which produces a substantially thick durable black nickel electrodeposit which is uniform in colour and exhibits an emissivity of more than 0.80.

High emittance coatings play an important role in passive thermal control of spacecraft. These coatings are predominantly applied on internal packages of spacecraft to improve their heat radiation characteristics. In a spacecraft, the electronic packages that are in operation may become too hot due to large heat dissipation while other standby may have the tendency to get colder. High emittance coating helps in minimizing the temperature gradient between the operational and standby components by improving their heat radiation characteristics (i.e., IR emissivity). To the best of our knowledge, research on the use of black nickel coating for high emittance application is limited in the literature.

In the present work, the authors have used a modified Fishlock bath composed of nickel sulphate, nickel ammonium sulphate, zinc sulphate and ammonium thiocyanate to electrodeposit flat absorber black zinc–nickel alloy coating on copper substrates. An undercoat of 4–5 μm nickel is given using Watts bath to increase the corrosion resistance and adhesion of the subsequent black nickel

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coating. Black nickel as well as the nickel undercoat plating is carried out by pulse electrodeposition using cathodic square wave pulses with complete current cut-off during the intervals of pulses. The effect of bath composition (giving emphasis to the concentration of SCN^-, Zn^{2+} and Ni^{2+}), temperature, solution pH, current density and plating time on the coating appearance and IR emittance of the coating are investigated systematically. The effect of the chemistry of the plating bath on the coating composition was studied using energy dispersive X-ray analysis (EDAX) of the coatings. This was done to identify any relationship between the emittance value and the ratio of zinc to nickel content in the coating. The main objective of this work is to optimize the process parameters to develop high emissivity space worthy black nickel coating to improve the heat radiation characteristics of the substrate surface.

2. Experimental

Black nickel coating with a base coat of nickel was obtained on flat square copper specimens with dimension of 40 mm × 40 mm × 10 mm. Prior to electrodeposition of nickel undercoat, copper substrate was subjected to a series of pre-cleaning procedures as described below.

1. Solvent degreasing using trichloroethylene in an ultrasonic bath for 5–10 min at room temperature (25 ± 5 °C).
2. Alkaline electrocleaning in a solution containing sodium carbonate (150 g/l), tri sodium ortho-phosphate (120 g/l), sodium hydroxide (60 g/l) and sodium lauryl sulphate (1 g/l) operating at a temperature of 60 ± 5 °C. The electrocleaning was done in two steps. Initially the substrate was made the cathode for 1–3 min followed by another 5–10 sec as anode. A current density of 15 mA/cm^2 was used for the whole process. After electrocleaning, the substrate was thoroughly rinsed with water.
3. Acid cleaning in a solution of sulphuric acid (650 ml/l), hydrofluoric acid (40%, 1 ml/l) and nitric acid (70%, 250 ml/l) operating at room temperature (25 ± 5 °C) for 30–60 sec. This was followed by rinsing in water.

Nickel coating of 4–5 μm thickness was done on the pre-cleaned copper substrates using Watt's nickel bath consisting of nickel sulphate, nickel chloride, boric acid and sodium lauryl sulphate. A modified Fishlock bath containing nickel sulphate, nickel ammonium sulphate, zinc sulphate and sodium thiocyanate was used to obtain a 5–6 μm thick black nickel coating over the nickel undercoat. Both nickel and black nickel electrodeposition were carried out using square wave pulsed DC, with 10% duty cycle. Samples were prepared at different average current densities at an on-time of 0.1 ms and an off-time of 0.9 ms with standard nickel of 99.99% purity as the anode. All electrolytes used in this study were prepared by adding the appropriate amounts of laboratory grade chemicals to de-mineralized water. After plating, the samples were immediately rinsed in running water and dried in hot air. The optimized coatings were characterized by scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDAX). The surface morphology and coating composition was studied by scanning electron microscopy (Leica S 440 I, USA) equipped with energy dispersive spectroscopy facilities (Oxford Instruments, INCA X-Max, U.K.). SEM was operated at a voltage of 20 kV and a secondary electron detector was used. X-ray diffraction study was carried out using a Philips X'pert-Pro instrument (PANalytical, The Netherlands) at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5406 Å) in the range of 40–100° and 0.008° step size.

3. Results and discussions

The present studies were undertaken to develop a high emittance Zn–Ni alloy coating on copper substrate for spacecraft thermal control applications. Process optimization was carried out by investigating the influence of nickel undercoat and various operating parameters viz bath composition, temperature, solution pH, current density and plating time on the coating appearance and IR emittance of the coating.

3.1. Optimization of nickel plating parameters

An undercoat of nickel plating is recommended for black nickel plating not only to increase the corrosion resistance but also to improve the adhesion of the coating. It was observed that when black nickel coating was obtained directly over the cleaned copper substrate, it exhibited poor adhesion especially at the edges. Samples with nickel undercoat were prepared at different average current densities (from 60 mA/cm^2 to 6 mA/cm^2) while keeping the solution composition and other operating parameters such as pH of the electrolyte, duty cycle and temperature constant. The process time was varied in accordance with the average current densities so as to obtain a nickel coating thickness of 4–5 μm on all the samples. The samples were subsequently coated with black nickel plating and the effect of current density variation employed in the formation of nickel undercoat on the appearance of the final black nickel plating as well as its emittance value was studied. An average current density of 6 mA/cm^2 for nickel undercoat resulted in a uniform black nickel coating with maximum IR emittance. Table 1 shows the finalized process parameters and bath composition for nickel undercoat.

3.2. Optimization of black nickel plating parameters

The optimization studies of black nickel plating were carried out in two steps. Initially, the bath composition was kept fixed and the operating parameters such as current density, plating time and solution temperature were individually varied to obtain uniform coating with optimum emissivity. To start with, the solution composition was maintained as 75 g/l nickel sulphate, 45 g/l nickel ammonium sulphate, 36 g/l zinc sulphate, 15 g/l ammonium thiocyanate and 0.5 g/l sodium lauryl sulphate. After finalizing average current density, solution temperature and plating time, the chemistry of plating bath was varied and the effect of solution pH and concentration of ammonium thiocyanate, zinc sulphate, nickel sulphate and nickel ammonium sulphate on coating properties were studied. In Table 2, the various operating parameters and electrolyte concentrations used in the present work for black nickel plating are consolidated. The optimized value for each parameter is given in parenthesis.

In the present study, the process parameters were optimized taking into consideration the emissivity of the coating, its appearance and process time to obtain the desirable coating. It was a general observation that the optical properties of black nickel coating have a strong relationship with the thickness of the coating. Emittance value of the coating increases with increase in thickness but beyond a certain thickness there is no substantial improvement in the emittance. Further, increase in thickness also affects the appearance of the coating. At higher thickness the coating tends to be powdery/non-adherent. This is evident in the study of effect of plating time on emissivity. It is observed that a coating thickness in the range of 5–6 μm, is ideal. Hence optimization of current density and plating time is carried out in combination so as to obtain the optimum thickness in a reasonable time.

3.2.1. Effect of type of current

Electrodeposition of black nickel coating was carried out for 45 min using both DC power supply and pulsed DC power supply with 10% duty cycle at two different current densities; 3 and

Table 1
Finalized parameters for the preparation of nickel undercoat.

Electrolyte composition	
$NiSO_4 \cdot 7H_2O$	300 g/l
$NiCl_2 \cdot 6H_2O$	45 g/l
Boric acid	45 g/l
Sodium Lauryl Sulphate (SLS)	0.25 g/l
Process parameters	
pH	3.0
Temperature	60 ± 2 °C
Average current density	6 mA/cm^2
Pulse on-time	0.1 ms
Pulse off-time	0.9 ms
Plating time	40 min