Solar Energy Materials and Solar Cells 174 (2018) 163–171

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Space qualification and characterization of high emittance black nickel coating on copper and stainless steel substrates

Soniya Somasundaram[a], Anju M. Pillai[a,*], A. Rajendra[a], Aravindram P.[b], P. Murali Krishna[c,*], A.K. Sharma[a]

[a] Thermal Systems Group, ISRO Satellite Centre, Vimanapura Post, Bangalore 560017, India
[b] Parts Materials and Process Group, ISRO Satellite Centre, Vimanapura Post, Bangalore 560017, India
[c] Department of Chemistry, M. S. Ramaiah Institute of Technology, Bangalore 560054, India

ARTICLE INFO

Keywords:
Coating materials
Electrodeposition
Nanoindentation
XPS
XRD

ABSTRACT

Black nickel coatings exhibiting high infrared emittance were developed on copper and stainless steel substrates by pulse electrodeposition using a modified Fishlock bath. The uniform jet black coating is intended to provide passive thermal control of spacecraft components. Space worthiness of the coating was evaluated by conducting a series of space environmental tests such as humidity, thermal stability, thermal cycling and thermo-vacuum performance tests. The thermo-optical properties namely solar absorptance (α_s) and infrared emittance (ε_{IR}) of the coatings were measured before and after each environmental test. No significant change in thermo-optical properties was observed after environmental tests showing their high stability for spacecraft thermal control applications. The coatings were characterized by cross-sectional SEM and EDX, XRD, XPS, Nanoindentation and Nano Vision analysis. X-ray diffraction pattern reveals the amorphous nature of the coating with possible presence of ZnS. XPS analysis confirms the chemical and electronic state of the elements. Average modulus and hardness of the coating was recorded using Nanoindentation method and a high resolution 3D image of the surface was generated using Nano Vision scan.

1. Introduction

Besides aesthetic purposes, metallic substrates having black finishes are desirable for many other applications [1–7]. Relatively thin black nickel coatings exhibiting high solar absorptance and low infrared emittance in particular have been used as selective absorbers or selective solar collectors for quite long time [8–13]. With increase in thickness, black nickel coating with relatively high emittance value can be produced to improve its heat radiation characteristics [14,15]. The authors have successfully developed an electroplating solution which produces a relatively thick uniform black nickel electrodeposit exhibiting an IR emittance in the range of 82–84% [16]. These coatings are predominantly intended to be applied on the internal surfaces of spacecraft electronic packages. High IR emissivity of internal surfaces of spacecraft helps in minimizing the temperature gradient between the operational and standby components. Though thin black nickel coatings have been used as selective absorbers, their long term reliability is poor. These are susceptible to discoloration when exposed to humid atmospheric conditions thereby resulting in the degradation of thermo-optical properties [17,18]. As very little is known about the stability and degradation of thick high emittance black nickel coatings when operated at high vacuum and extreme temperature conditions in space environment, authors have presented the results of these studies.

Any material or coating used in the spacecraft application needs to be qualified for its space worthiness. These materials / coatings need to be subjected to various space simulation (environmental) tests as well as accelerated aging tests prior to the implementation on actual spacecraft hardware. For spacecraft applications any change in the initial values of α_s and ε_{IR} of coating during its mission life (change in value from beginning of life to end of life) has to be considered. The space worthiness of the coating has been evaluated by conducting a series of tests such as adhesion, humidity, thermal stability, thermal cycling and thermo-vacuum performance tests [19]. Further, characterization of the coating is carried out by cross-sectional SEM and EDAX, XPS, XRD, Nanoindentation and Nano Vision analysis.

* Corresponding author.
E-mail addresses: savithrisoman@yahoo.co.in (S. Somasundaram), anjum@isac.gov.in (A.M. Pillai), rajendra@isac.gov.in (A. Rajendra), aravindr@isac.gov.in (A. P.), muralikp21@gmail.com (P.M. Krishna), aks@isac.gov.in (A.K. Sharma).

http://dx.doi.org/10.1016/j.solmat.2017.08.023
Received 12 May 2017; Accepted 17 August 2017
Available online 08 September 2017
0927-0248/

Table 1
Test conditions used for environmental tests.

Test	Conditions
Humidity	95% RH at 50 °C for 48 h
Thermal Cycling	−20 °C to 85°C, 5 min dwell time, 1500 cycles
Thermovac Cycling	−20 °C to 85°C, 2 h dwell time, 10 cycles, 10^{-5} Torr

2. Experimental

Black nickel coating of about 4–5 µm thickness was obtained by pulse electrodeposition using a modified Fishlock bath on two different substrates namely copper and stainless steel. Square wave pulsed DC with 10% duty cycle (0.1 ms on-time and 0.9 ms off-time) was used for the process. Circular block specimens of copper (6.5 cm diameter and 0.5 cm thickness) and stainless steel (5 cm diameter and 0.4 cm thickness) were employed as cathode and a soluble anode of 99.99% pure nickel was used. The electrolyte concentration and operating conditions used in the present work for preparing black nickel electrodeposits are same as optimized and published by us earlier [16]. For copper substrates, an under coat of 4–5 µm thick nickel was given to increase the corrosion resistance and also to improve the adhesion of the subsequent black nickel coating. This nickel undercoat was obtained on the precleaned copper substrates using Watt's nickel bath consisting of nickel sulphate, nickel chloride, boric acid and sodium lauryl sulphate employing the same pulse settings as that used for black nickel plating.

The pre-cleaning procedures used for copper substrates include ultrasonic solvent degreasing in trichloroethylene, 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) and acid cleaning in a solution of sulphuric acid (650 ml/l), hydrofluoric acid (40%, 1 ml/l) and nitric acid (70%, 250 ml/l). In the case of stainless steel substrates, since corrosion resistance of the substrate is not much of concern, only a flash of nickel layer to promote good adhesion of black nickel coating is sufficient. After ultrasonic solvent degreasing in trichloroethylene and anodic electrolytic cleaning in sulphuric acid solution (650 ml/l), the stainless steel substrates were subjected to activation in a solution containing nickel chloride (250 g/l) and hydrochloric acid (35.4%, 86 ml/l). This activation step carried out at a current density of 30 ASF for about 10 min using standard nickel as anode results in the formation of a very thin layer of nickel on the substrate. Subsequently, a uniform jet black colored coating of 4–5 µm was obtained using the optimized bath. After plating, the test specimen was immediately rinsed in running water and dried with hot air.

As part of the qualification plan, the plated samples were subjected to visual inspection and measurement of solar absorptance and infrared emittance in the as plated condition as well as after subjecting to humidity, thermal cycling and thermovac cycling. The test conditions used for the various environmental tests are listed in Table 1.

Visual inspection of the black nickel plated surface was performed with unaided eye as well as under a magnification of 15 X using a stereo microscope (Mantis Elite, U.K.) to ensure that the coating is continuous, smooth, uniform and free from powdery areas, loose films, breaks, scratches and other defects. The thermo-optical properties namely solar absorptance (α_S) and infrared emittance (ε_{IR}) of the black nickel coating were measured using a Solar Spectrum Reflectometer, model SSR and an emissometer, model AE, respectively (Devices and Services, USA).

Cross sectional SEM and EDX analysis of the coating was performed to visualize the nickel undercoat and the black nickel coating on the copper and stainless steel substrates. Scanning electron microscope (Leica S 440 I, USA) was operated at a voltage of 20 kV and probe current of 100 pA and the detector used was secondary electron detector. The elemental composition of the different layers of the deposit were determined in a semi quantitative way in the same scanning electron microscope which was equipped with energy dispersive x-ray spectroscopy (EDX) facilities (Oxford Instruments, INCA X-Max, U.K.). X-ray diffraction (XRD) studies were carried out using a BRUKER instrument (The Netherlands) at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5406 Å) in the range of 20–100° and 0.008° step size. In order to analyze the chemical and electronic state of the elements present in the coating, x-ray photoelectron spectroscopy was employed. XPS of black nickel coating was recorded with a SPECS spectrometer (Germany) using non-monochromatic Al Kα radiation (1486.6 eV) as an X-ray source operated at 150 W (12 kV, 12.5 mA). The binding energies reported here were referenced with C1s peak at 284.6 eV. All the survey spectra were obtained with pass energy of 70 eV and step increment of 0.5 eV, whereas individual spectra were recorded with pass energy and step increment of 40 and 0.05 eV, respectively. Successive sputtering was carried out by focused Ar^+ ion beam using IQE12/38 ion gun by applying energy of 2 keV with Ar gas pressure of 5×10^{-7} Torr for 5 and 10 min.

The Nano Indenter® G200 system was used to study the hardness and elastic modulus of the black nickel coating on copper and stainless steel substrate. A diamond Berkovich (pyramidal) tip was used for indentation studies. Measurements were done using the Continuous Stiffness Measurement (CSM) option which yields hardness and elastic modulus as a continuous function of depth into the sample. The specimens were loaded to a constant depth of 1000 nm and the maximum load was held constant for 10 s. A total of 15 indentations were performed and the average values of hardness and modulus were reported.

In order to generate a high resolution 3D image of the surface, the Agilent NanoVision option of the Nano Indenter G200 driven by NanoSuite 5.0 Professional software was used. In this method, the

Table 2
Measurement of thermo optical properties before and after environmental tests for black nickel plating over copper substrates.

Sample No	Testing Condition	Solar Absorptance (α_S)		Infrared emittance (ε_{IR})	
		Before Testing	After Testing	Before Testing	After Testing
1	**As Plated**	0.902,0.911	–	0.84,0.83	–
2	**Thermal Cycling**	0.894,0.889	0.894,0.888	0.83,0.83	0.82,0.82
3		0.877,0.876	0.876,0.876	0.81,0.81	0.81,0.80
4		0.907,0.901	0.902,0.906	0.83,0.83	0.83,0.82
5	**Humidity**	0.897,0.902	0.908,0.905	0.84,0.84	0.84,0.84
6		0.893,0.892	0.902,0.903	0.83,0.83	0.84,0.83
7	**Thermovac Cycling**	0.878,0.883	0.872,0.870	0.83,0.83	0.83,0.83
8		0.874,0.864	0.866,0.862	0.82,0.82	0.82,0.83