J Appl Electrochem (2010) 40:333–339
DOI 10.1007/s10800-009-9980-5

ORIGINAL PAPER

Studies on black electroless nickel coatings on titanium alloys for spacecraft thermal control applications

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Received: 24 December 2008 / Accepted: 17 August 2009 / Published online: 27 August 2009

Abstract A process of blackening of electroless nickel coating is investigated to produce ultra black coating on titanium alloys with higher optical properties. Process optimization was carried out by investigating the influence of various operating conditions, namely, processing time of etching solutions, thickness of electroless nickel deposit, temperature of blackening solutions, and pH of electroless nickel solution on the physico-optical properties of the black coating. It was observed that an optimum thickness of 35 + 5 μm of electroless nickel is required to achieve the ultra high optical properties after blackening. Energy dispersive X-ray spectroscopy studies suggested that films containing ~7% phosphorous are good for further blackening. Scanning electron and optical microscopic studies confirmed that the surface morphology played the major role to get the ultra high optical properties. The environmental tests, namely, humidity, corrosion resistance, thermal cycling, thermo vacuum performance, and thermal stability tests were used to evaluate the space worthiness of the coating. Optical properties of the coating were measured before and after each environmental test to ascertain its stability. The blackened electroless nickel provides higher optical properties in the order of ~0.85; this coating has good adhesion, uniformity, and stability in adverse space conditions. Hence, these coatings were extremely suitable for spacecraft thermal control applications.

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Keywords Electroless nickel plating · Ultra blackening · Thermal control · Solar absorptance and infrared emittance

List of symbols

ε_{IR} Infrared emittance
$\propto_S$ Solar absorptance
P Phosphorous content by weight

1 Introduction

Titanium is a metal of great interest in the aerospace industry, because of its combination of good mechanical properties, low density, and operability in a number of special forming processes. Titanium is recognized for its high strength-to-weight ratio. It is a light, however, strong metal with low density. Titanium can be alloyed with other elements such as iron, aluminum, vanadium, molybdenum, etc., to produce strong lightweight alloys for aerospace. The two most useful properties of the metal are corrosion resistance and the highest strength-to-weight ratio of any metal. Further its ability to withstand fairly high temperatures has focused attention on its increased use in the aerospace and allied fields; however, full utilization of titanium in the aerospace industries is prevented by its tendency to gall and seize and its severe reactivity to atmospheric oxygen at elevated temperatures. In order to overcome these limitations and meet some functional requirements, suitable surface treatment of titanium is of utmost importance [1].

Titanium alloys are difficult to plate with adherent metal coatings because they form a tenacious, passive oxide film quickly. The oxide film may be removed by various etching procedures, but the oxide film reforms so rapidly that it is difficult to accomplish any coating before the film reforms to block access of the plated atoms to the surface. If the plating is accomplished over the oxide film, a layer of metal can be deposited, but the layer is not sufficiently adherent for most purposes [2].

There is therefore a continuing need for a method of coating metals such as electroless nickel onto titanium, particularly on its alloys. The present investigation reports a study of blackening of titanium alloys with higher optical properties for spacecraft applications.

2 Experimental

2.1 Materials and methods

Test specimens of titanium alloy 6 Al-4 V (Al, 5.5–6.75; V, 3.5–4.5; Fe, 0.30 maximum, H_2, 0.0125 maximum, all percent by weight) of the size 30 × 30 × 0.1 mm were used. The following sequences of operations were carried out as per our previous publications [3–5]. All chemicals were laboratory grade, and de-mineralized water was used throughout.

(1) Solvent cleaning with ultrasonic agitation and vapor degreasing using methyl ethyl ketone ($CH_3COC_2H_5$) for 10 min.
(2) Descaling in a solution containing sodium hydroxide (NaOH), 500 g L^{-1} and copper sulfate penta hydrate ($CuSO_4 \cdot 5H_2O$), 100 g L^{-1} at 363 K for 15–20 min. Water rinse.
(3) Acid pickling in a solution of 275 mL L^{-1} of 70% nitric acid and 225 mL L^{-1} of 40% hydrofluoric acid for 20–30 s. Water rinse.
(4) Immersion zincating in a solution containing sodium dichromate ($Na_2Cr_2O_7$), 100 g L^{-1}, hydrofluoric acid (40%), 65 mL L^{-1}, zinc sulfate penta hydrate ($ZnSO_4 \cdot 5H_2O$), 12 g L^{-1}, pH 2.0 ± 0.2; temperature 388–393 K; time 3–4 min. Water rinse.
(5) Stripping for the first zincate layer in acid pickling solution as formulated in step 4 for 45–60 s. Water rinse.
(6) Rezincating by immersion for 5–6 min as per step 6. Water rinse.
(7) Electroless nickel plating in a solution containing nickel sulfate hexa hydrate ($NiSO_4 \cdot 6H_2O$), 30 g L^{-1}, sodium hypophosphite (NaH_2PO_2), 10 g L^{-1}, tri sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), 12.5 g L^{-1}, sodium acetate (CH_3COONa), 5 g L^{-1}, thio urea (NH_2CSNH_2), 1 mg L^{-1}, pH, 4.5–5.0; temperature, 388–396 K; continuous agitation and filtration; time, 75–90 min to get adequate higher thickness, 35 ± 5 μm for further blackening.
(8) Blackening of electroless nickel was carried out by immersing in Nitric acid (9 M) for 30–50 s at room temperature.
(9) After blackening, the test specimens were rinsed quickly and thoroughly with water.

The pH was adjusted upward by addition of dilute ammonia and downward by the addition of dilute sulfuric acid. Continuous filtration of plating solution and mechanical agitation of job is mandatory to obtain good electroless nickel deposits and blackening thereafter.

2.2 Instrumentation and measurement techniques

The surface morphology of coatings has been investigated by a scanning electron microscope. The morphological studies and the elemental analysis of the black nickel coating were carried out with ZEISS EV050 scanning electron microscope, Germany. This electron microscope was equipped with an energy dispersive X-ray spectroscopic micro analyzer, Oxford Instruments Analytical, UK. Oxygen was detected in the "windowless" mode of EDX detector.

Adhesion of electroless nickel was evaluated by a heat quench test. The specimens were heated to 423 K for 1 h and quenched in cold water.

The thickness of electroless nickel plating was examined under a graduated scale optical microscope after microsectioning and metallographically polishing the cross section of the test coupons.

The microhardness of the coating was measured with a Shimadzu Micro hardness tester Model HMV 2000, Kyoto, Japan, using a diamond indenter. Vickers Hardness numbers were obtained by averaging five measurements on each specimen with a load of 50 gf for 10 s indentation.

The optical properties, namely, solar absorptance and infrared emittance of the black anodic film, were measured using a solar reflectometer version 50, model SSR-ER and an emissometer model RD1, respectively, from Devices and Services Co. (USA). Both these instruments provide an average value of solar absorptance and infrared emittance digitally over the entire solar and infrared regions.

The corrosion resistance studies were carried out by immersion of test specimens in 5% sodium chloride solution at pH 7.0. After 7 days of immersion, the film was carefully examined for discoloration or formation of any corrosion spots on the surface.

3 Results and discussions

3.1 Mechanism of film formation

Titanium has high affinity for oxygen; hence, there is an oxide film always present on the metal surface. The speed of formation of the oxide is such that if the film is removed, it reforms immediately regardless of the surface preparation process. This permanent oxide film interferes with the formation of the metallic bond between the titanium substrate and the metal deposit. Reoxidization of the titanium must be prevented during that period of time between the removal of the oxide and the beginning of the deposition process. The oxide film was replaced by a simple immersion deposit of zinc on titanium [6].

3.2 Mechanism of alloy zincating

In zincate treatment, the surface film of the oxide on titanium is removed by dissolution in hydrofluoric acid and a zinc film is deposited. The principal chemical reaction can be characterized as follows in the anodic dissolution of titanium and titanium oxide [7]:

$$Ti^0 + 6HF \rightarrow H_2[TiF_6] + 2H_2\uparrow + 4e^-, \quad (1)$$

and the cathodic deposition of zinc:

$$Zn^2 + 2e^- \rightarrow Zn^0. \quad (2)$$

The zincate layer acts as a good base and activator for subsequent electroless nickel deposition. Dissolution of the zinc film occurs when the zincated titanium substrate is immersed in the electroless nickel-plating bath. Then nickel is reduced and deposited into the electroless nickel deposit [7].

3.3 Mechanism of electroless nickel plating

The principle redox reaction in the electroless nickel solution is the reduction of nickel ion to nickel metal and oxidation of hypophosphite ion to phosphite ion and phosphorus. As this reaction can take place at the catalytic surface, dehydrogenation of reactant is therefore proposed as the first step of the reaction mechanism [8]:

$$H_2PO_2^- + H_2O \rightarrow 2H^+ + HPO_3^{2-} + H^-. \quad (3)$$

The hydride ions so formed react with nickel ion, and a charge transfer occurs resulting in the deposition of nickel metal.

$$Ni^{2+} + 2H^- \rightarrow Ni^0 + H_2. \quad (4)$$

The overall reactions can thus be written as:

$$2H_2PO_2^- + Ni^{2+} + 2H_2O \rightarrow 2HPO_3^{2-} + Ni^0 + 4H^+ + H_2\uparrow + 4e^-. \quad (5)$$

The side reaction of the above equation can dominate when the concentration of nickel in solution falls or the level of hypophosphite ion increases. The rate of co-decomposition of phosphorous with nickel was controlled by varying the bath constituents [9]. Due to the presence of phosphorous contents, the electroless nickel deposit is easy to etch by the oxidizing acids to obtain the ultra black surface. The blackening of electroless nickel deposit is obtained when the deposit is dipped in a nitric acid solution (9 M). The blackening results from hole formation visible first on the boundaries between the different nodules and then on the whole deposit surface, as seen by SEM [10]. This structure produced by selective etching traps the light and is capable of absorbing over 99% light in solar region (300–2000 nm) [11].

3.4 Morphological studies

In this study, the autocatalytic electroless nickel–phosphorous deposits with P content 5–7% were considered for further blackening. The surface morphology plays a crucial role in obtaining the high solar absorptance coating. The scanning electron micrograph of etched electro-nickel–phosphorous given in Fig. 1 shows *stalagmite-like* structure. The morphology of electroless nickel depends on the phosphorous content. The coating with low phosphorous (<4% P) produces a pronounced *crater* morphology and with high phosphorous (5–7%) a *stalagmite-like* morphology. Nickel–phosphorous alloys with lower phosphorous (<4% P) contents are etched more completely, with larger crater formation as large portions of the alloy are dissolved, while as the P content increases, it is more difficult for large swaths of Ni–P to be etched; hence, narrow sharper features are observed. With low phosphorous alloys, for a given unit volume, more Ni–P is etched away than unetched giving large craters as shown in Fig. 2 and thin short stalagmites, whereas, for high phosphorous alloys (5–7% P), less Ni–P is etched away than left and the result is larger, broader stalagmites and thinner craters [12].

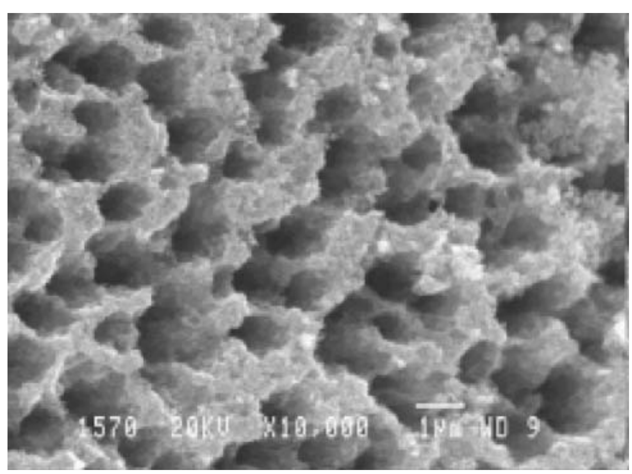


Fig. 1 SEM image of black electroless nickel coating with high P ($\sim$7% P) content

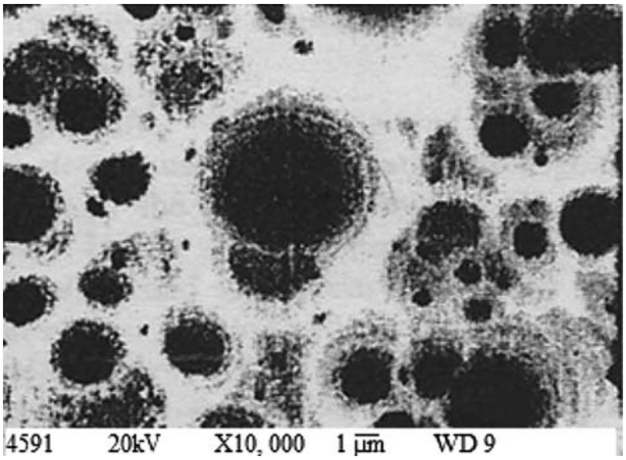


Fig. 2 SEM image of black electroless nickel with low P (<4% P) content

The high solar absorptance value of present coatings is associated with unique surface morphology consisting of a dense array of microscopic, conical pores perpendicular to the surface. This structure produced by selective etching of nickel–phosphorous acts as light traps and is capable of absorbing 99% light in solar region (300–2300 nm). The pore diameter, pore depth, and pore spacing range from a fraction of micrometer to a few micrometers or about a fraction to several wavelengths of light. Consequently, the pores trap any incident light in wide spectral range. The black color of nickel–phosphorous coating is due to this unique surface morphology as well to the formation of nickel oxides (NiO, Ni_2O_3) and some nickel phosphate [13, 14].

The EDX spectral studies of electroless nickel coating obtained under optimal conditions before and after blackening confirmed 93.25% nickel and 6.75% P by weight for pre-etched coating and 90.05% nickel, 5.75% P, and 4.20% oxygen by weight for blackened coating. The etched electroless nickel showed lower nickel and phosphorous contents [4, 5].

Cross-sectional views of the electroless nickel coating were studied at micrometer scale and evaluated under 700× were presented in Fig. 3. The electroless nickel as obtained shows very uniform deposition. The coating after etching shows a peak to trough height of 6–7 µm, with the top layer of nickel–phosphorous black oxide being ~0.7 µm. However, the thickness of this top layer in excess of 1.0 µm is powdery and non-adherent.

3.5 Process optimization

Process optimization was carried out by the investigation of the influence of the process parameters on the physico-optical properties of the coating.

3.5.1 *Effect of blackening time on optical properties*

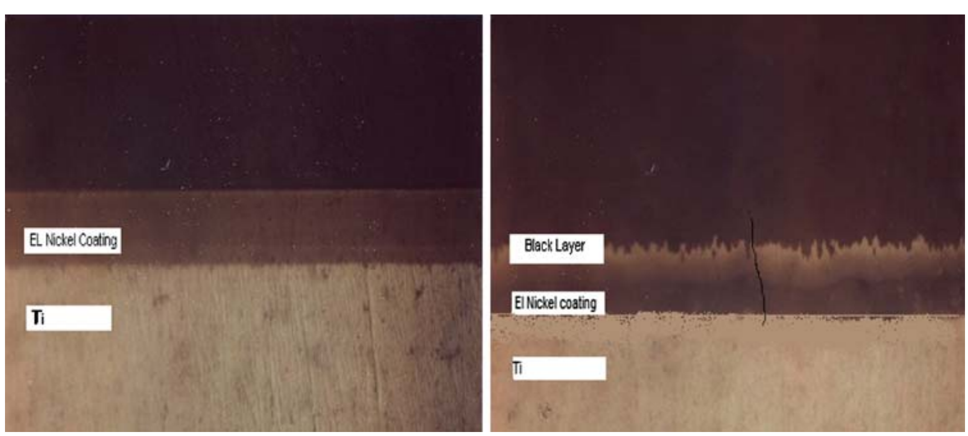
As very strong acid solution is employed for blackening of electroless nickel, the etching time is a very important parameter to control the quality of resultant coating. The etching time significantly affects the appearance, uniformity, and optical properties of electroless nickel black coating and, therefore, has to be monitored carefully. The optimum etching time for nitric acid is 15–75 s.

Lower etching time results into incomplete non-uniform blackening of electroless nickel with high solar optical properties value. And the etching beyond the given range results into excessive etching of the coating with peeling from the edges and powdery deposits. The effect of etching time on optical properties value of nickel black coating is shown in Fig. 4.

3.5.2 *Effect of thickness of electroless nickel deposit on optical properties*

The thickness of electroless nickel coating plays an important role in achieving good low optical properties black coating after etching. Sufficient thickness of electroless

Fig. 3 Cross section of an electroless nickel sample obtained under ×700 before and after etching



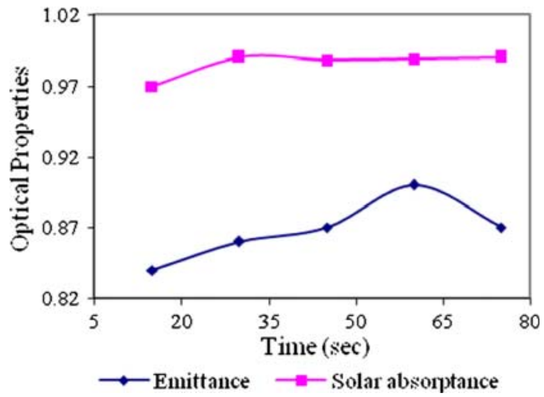


Fig. 4 Effect of blackening time on optical properties

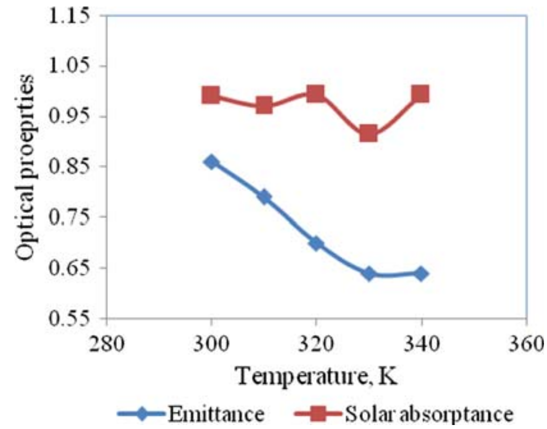


Fig. 6 Effect of temperature on optical properties

nickel coating is required as significant amount of coating is etched out during etching or blackening process. A non-uniform black coating is formed with electroless nickel thickness below 15 μm. A thickness of 35 ± 5 μm of electroless nickel is required to achieve the ultra high optical properties after etching.

Thickness reduction after etching of electroless nickel under optimum conditions was noticed. About 5 μm average thickness of electroless nickel is reduced after etching with nitric acid. It may, however, be noted that the etching process is not uniform, microscopically, formation of notches and valley with average height of notches ∼6.5 μm is observed by etching with nitric acid. The thickness of electroless nickel should be sufficient to take care of average thickness reduction and selective etching, i.e., notches formation during etching.

The effect of thickness on optical properties is shown in Fig. 5. Emittance is a surface phenomenon and it increases with the thickness of nickel coating. However, no much variation in solar absorptance was noticed with thickness variation.

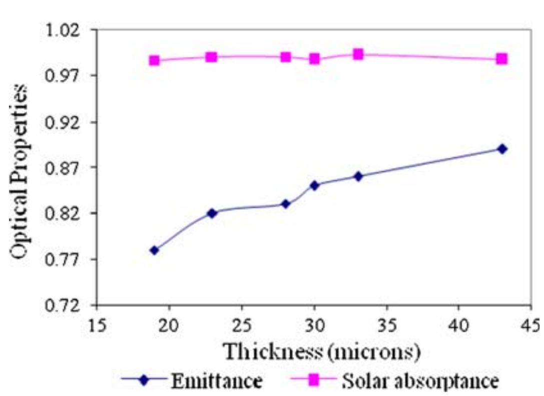


Fig. 5 Effect of thickness on optical properties

3.5.3 Effect of temperature of etching solution on optical properties

The operating temperature of etching solutions is very sensitive to obtain the quality blackened electroless nickel surface. Etching experiments with different etching solutions were conducted at the wide operating temperature range of 303 to 333 K. The influence of operating temperature on the solar optical properties of the resultant coating is shown in Fig. 6. At the low operating temperature, the etching rate of coating is slow and the solar optical properties of resultant coating are high. As the operating temperature of etching solution increases, the process time to obtain low solar optical properties coating decreases. However, at higher temperatures, the rate of etching becomes too high to control the process. The excessive etching results into powdery deposits.

A moderate etching temperature has to be selected to achieve uniform blackening of the coating. However, for the current study, blackening was carried out at room temperature.

3.5.4 Effect of pH of electroless nickel solution on optical properties

The pH of solution should be regulated to obtain the most favorable conditions. Phosphorous contents of electroless nickel influence the etching behavior and properties of resultant black nickel coating. Higher phosphorous coatings are not suitable for blackening due to their high resistance to etching solutions. As the phosphorous contents increases, the electroless nickel coating requires higher concentration of oxidizing acids for etching. When the phosphorous contents in the electroless nickel coating exceeds 11% P, it becomes extremely difficult to etch the coating even with higher concentrations of oxidizing acids. In general, lower the initial phosphorous content (<4% P) in the electroless

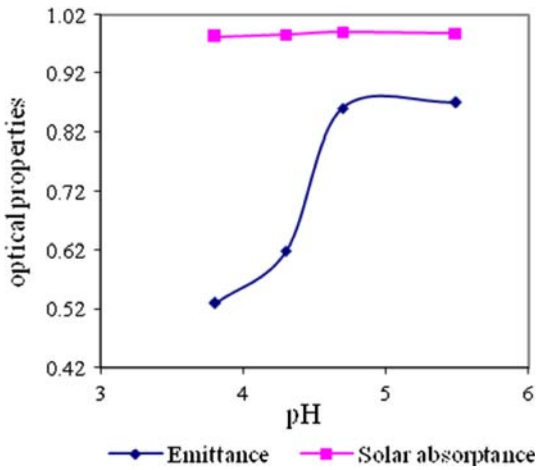


Fig. 7 Effect of pH on optical properties

nickel, the greater the extent of the etching and lower the optical properties of the resulting surface.

The phosphorous contents of the electroless nickel deposits in turn depend on the pH value of the plating solution. Hence, the pH of the solution should be carefully regulated to obtain the most favorable results. At high pH, phosphorous content decreases, but the solution may decompose and at low pH value phosphorous contents are higher and the resultant coating has high stress [12]. The influence of electroless nickel-plating solution pH in the range of 4.0 to 5.5 on the optical properties of subsequently etched black coating process was investigated. The results are shown in Fig. 7. As expected, the coatings obtained from the bath with pH < 4.0 are totally etched away during blackening because of the lower P content (<4%). Good blackening was obtained in the pH range of 4 to 5. At pH 4.0, though the solar absorptance was high, however, infrared emittance of black coating was lower (0.65), and at pH 5.5 and above the electroless nickel-plating solution starts decomposing. The optimum results were obtained at a solution pH value of 4.7. Hence pH 4.7 was optimized.

4 Testing and evaluation

The black electroless nickel coatings obtained from the optimized bath were examined visually under 4× magnification for any degradation in physical appearance before and after environmental stability tests. The coatings were perfectly uniform with no defects such as cracks or patches. After visual inspection, the plated specimens were subjected to the following evaluation tests.

4.1 Adhesion test

Adhesion of black electroless nickel was evaluated by a heat quench test. The specimen was heated to 478 K for 1 h and quenched in cold water. No blisters, cracks, or discoloration were observed. The adhesion test on testing specimens after humidity, thermal cycling, and thermo vacuum performance tests, but no degradation of any kind was noticed.

4.2 Thickness measurement

Coating thickness was measured by micro sectioning. The test samples were mounted using a resin and hardener in a 5:1 ratio, curing for 4–5 h at room temperature and polishing. The thickness of nickel was measured on a graduated scale under 480×. The average thickness of electroless nickel was found to be 35 ± 5 µm.

4.3 Microhardness measurement

The microhardness of electroless nickel was measured using a diamond indenter at a 50-gf load. The Vickers microhardness values of black electroless nickel are ~450 VHN.

4.4 Measurement of optical properties

The optical properties, namely, solar reflectance and infrared emittance of the electroless nickel black coating, were measured using a solar reflectometer version 50, model SSR-ER and an emissometer model RDI, respectively, from Devices and Services Co. (USA). Both these instruments provide an average value of solar absorptance and infrared emittance digitally over the entire solar and infrared regions.

4.5 Humidity test

This test was designed to check the effect of humidity and higher Indian shore temperature, which is likely to be encountered at launch site (this also shows the corrosion resistance of the launch site). The test was conducted in a thermostatically controlled humidity chamber for 96 h. The relative humidity in the chamber was maintained at $95 \pm 5\%$ at 323 K. After the test, the specimens were examined under 4× magnification and their optical properties were measured. No degradation in optical properties or physical appearance was observed.

4.6 Thermal cycling

A satellite in orbit undergoes extreme temperatures due to direct sun load on one side and cold deep space on the other side. This test is designed to evaluate the cycling temperature on the coating, which is likely to be encountered throughout the life span of the spacecraft. Five samples of electroless nickel specimens were subjected to

Table 1 Change in optical properties of black electroless nickel coatings on titanium alloys before and after environmental tests

S. no.	Tests	Test conditions	Before testing		After testing		$\Delta_{\alpha s}$	$\Delta\varepsilon_{IR}$
			α_S	ε_{IR}	α_S	ε_{IR}		
1	Humidity	R.H.: 95 ± 0.5% T: 323 ± 1 K Time: 48 h	0.993	0.85	0.993	0.85	0.000	0.00
2	Thermal cycling	228–358 K 100 cycles	0.992	0.86	0.992	0.86	0.000	0.00
3	Thermo vacuum	228–358 K Vacuum 10^{-5} Torr 10 cycles	0.993	0.86	0.993	0.86	0.000	0.00

Note: Values are for the coating obtained from optimized bath

this test. A total of 100 cycles was applied a cycle consists of lowering the temperature to 228 K with a dwell time of 5 min and raising the temperature to 358 K with a dwell time of 5 min. After thermal cycling, the specimens were examined under 4× magnification. No degradation was observed.

4.7 Thermo vacuum performance test

This test is designed to examine the effect of cycling temperature in the space environment (vacuum) on the coating. The test was conducted in a thermostatically controlled vacuum soak chamber. The test consists of lowering the temperature to 228 K with a dwell time of 2 h and raising the temperature to 358 K with a dwell time of 2 h. Ten hot and cold soaks were applied, and a vacuum below 10^{-5} Torr was maintained inside the chamber during the test. No degradation was observed.

Table 1 shows the changes in thermo-optical properties before and after environmental exposures.

5 Conclusions

A process of ultra black electroless nickel black coating with higher optical properties on titanium is described. The higher optical properties especially the higher solar absorptance of the coatings is associated with unique surface morphology and formation of nickel oxides (NiO, Ni_2O_3) and nickel phosphides. SEM results showed that the surface morphology consisting of a dense array of microscopic, conical pores perpendicular to the surface. This structure produced by selective etch acts as light traps and is capable of absorbing over 99% light in solar region. The coating has good adhesion, uniformity, and stability in adverse space conditions. Hence, these surfaces are extremely suitable for spacecraft thermal control applications. Moreover, these surfaces are extremely suitable in improving the absorptance of thermal detectors and to minimize the effect of stray and scattered light in optical instruments and sensors.

Acknowledgments The authors are grateful to D. R. Bhandari [Deputy Director (retired), Mechanical Systems] and Dr. Badarinarayana (Group Director, Thermal Systems) for their constant encouragement during the study. Thanks are also due to Y. Subba Rao, JRF, for his cooperation.

References

1. Wilson DH (1982) Cleaning and finishing of reactive and refractory alloys, vol 5, 9th ed. Metal Handbook. American Society for Metals, pp 650–668
2. Lozano-Morales A, Bonifas A, Inman M, Miller P, Taylor EJ (2008) J Appl Surf Finish 3(4):168
3. Sharma AK, Bhojaraj H (1992) Met Finish 90(7):23
4. Saxena V, Uma Rani R, Sharma AK (2006) Galvanotechnik 97(1):827
5. Saxena V, Uma Rani R, Sharma AK (2006) Surf Coat Technol 201(3–4):855
6. Thurlow KP (1989) Trans Inst Met Finish 67(3):82
7. Simon J et al (1990) Met Finish 88(10):23
8. Hung A (1988) Plat Surf Finish 75(1):62
9. Henry J (1990) Plat Surf Finish 88(10):15
10. Papini M (1986) Sol Energy Mater 13:233
11. Johnson CE (1980) Met Finish 78:21
12. Brown RJC, Brewer PJ, Milton MJT (2002) J Mater Chem 12:2749
13. Kumar SN, Malhotra LK, Chopra KL (1980) Sol Energy Mater 3:519
14. Wicerzbicka M, Malecki A (1999) J Therm Anal Calorim 55:981