INFORMATICS JOURNALS
The Journal of Electrochemical Society of India, Volume 74, Issue (7&8), October – December 2025; pp. 221–227
ISSN (Print) : 0013-466X
ISSN (Online) : xxxx-xxxx
DOI: 10.18311/JESCI/2025/55409

Electroless Nickel Coatings for Enhanced Wear Resistance of Ti-6Al-4V Alloys

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Abstract

Titanium and its alloys are mainly used for strategic applications such as aircraft and space programs due to their high strength-to-lightweight ratio. A suitable surface treatment process is necessary to further enhance its mechanical and tribological properties. In the present study, an attempt has been made to deposit a uniform and adherent Electroless Nickel (EN) coating on difficult-to-plate titanium alloys such as Ti6Al4V substrates using RoHS compliant EN plating bath. Process parameters were optimised to obtain a thickness of about 24 µm at a pH 5.1 at a temperature of 87°C for 2 h. Deposits were characterised for their morphology and composition using a field emission scanning electron microscope and energy dispersive X-ray analyser, respectively. The as-plated coating exhibited nodular morphology with about 8 wt.% phosphorus codeposited in the Ni matrix. X-Ray Diffraction (XRD) studies were carried out on both as-plated and heat-treated (400°C, 1 h) Ni-P deposits. A thermal quench test was carried out on an EN-coated Ti alloy substrate to assess coating adhesion. There were no signs of blisters or peeling of the coating, indicating excellent adhesion to the substrate. Microhardness measurements were made on both as-plated and heat-treated coatings. Heat-treated coatings exhibited a higher microhardness of 980 HV_{50} gf compared to 550 HV_{50} gf microhardness in the as-plated coating. The tribological properties of as-plated and heat-treated coatings were determined. The heat-treated coatings exhibited 40% reduction in the coefficient of friction compared to as-plated coatings with improved wear performance. The above studies showed that the appropriate pre-treatment followed resulted in obtaining an adherent and uniform electroless Ni-P coating on difficult to plate Ti-6Al-4V alloy using RoHS compliant electroless nickel bath.

Keywords: Adhesion, Electroless Nickel, Microhardness, Ti-6Al-4V, Wear

1. Introduction

Titanium (Ti) and its alloys have emerged as critical materials in the aerospace industry due to their unique combination of high strength-to-weight ratio and operability in a number of special forming processes. Titanium alloys are recognised for their excellent corrosion resistance and biocompatibility, making them a preferred material in fields ranging from aerospace to biomedical engineering. Among these alloys, Ti6Al4V is one of the most widely used, offering superior fatigue resistance and the ability to withstand cyclic loading, making it particularly suitable for critical components in the aircraft and aerospace sectors[1].

A primary drawback of Ti alloys is their low surface hardness and poor wear resistance, which persist despite their high mechanical strength. Consequently, employing an appropriate surface treatment is crucial to developing a coating that provides superior wear resistance. It is necessary that the developed coating provide a uniform, hard coating that is easy to apply, even to complex geometries. There are many coating methods, such as vacuum-based deposition methods, plasma-based methods, electrodeposition, and electroless plating. Vacuum and plasma-based deposition methods are line-of-sight processes. Among aqueous-based methods, such as in electrodeposition, an external power source is required for plating. Apart from that, the deposition depends mainly on the current density lines and always results in a non-uniform coating over complex geometries. Hence, another machining operation is mandatory to achieve uniform thickness before utilising it for functional application. In the case of electroless

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plating, a chemical reduction process, a uniform coating, irrespective of the component's size or shape, can be achieved. It is possible to deposit a variety of metals, such as nickel, copper, zinc, cobalt, gold, platinum, *etc*., on metallic and non-metallic components, including plastics and carbon-based composites[2,3]. Among them, the EN plating process is widely used in the aerospace, electronics, and automotive industries due to its unique properties, such as excellent hardness, wear and abrasion resistance, and improved corrosion resistance. Depending on the reducing agent used, it is possible to obtain an electroless nickel coating codeposited with either Phosphorus (P) or Boron (B). Electroless Ni-P coatings are preferred for their excellent corrosion resistance in mild acids and alkalines, as well as in harsh seawater. Also, heat-treated electroless nickel coatings exhibit excellent microhardness and are widely used for wear- and abrasion-resistant applications. The microhardness of electroless Ni-P coating (450-550 HV_{100} gf) is considerably higher compared to that of bulk nickel (100-150 HV_{100} gf) and electrodeposited nickel (250-350 HV_{100} gf)[4,5]. Also, due to their good solderability and thermal conductivity, these coatings find applications in microelectronics and EMI shielding. EN coating is mainly deposited on Ti alloy substrates as a solar absorber coating for space applications[6]. A novel pretreatment process, with a single process step, has been implemented to obtain adherent EN coating on Ti-6Al-4V substrate with improved wear resistance[7]. Ultrasonically assisted EN plating has been carried out on a Ti alloy, and the detailed growth mechanism of the EN coating has been provided. Tribological properties have also been reported for the EN-Ti alloy system[8]. It has been reported in the literature that electroless Ni-P coatings are susceptible to severe adhesive wear against plain carbon steel under dry sliding contact because the low interfacial and high surface free energies of these materials produce highly compatible surfaces[9]. Controlled heat treatment eliminates severe wear by inducing crystallisation of amorphous nickel into hard nickel phosphide, which is incompatible with steel[10].

In electroless nickel plating, toxic heavy metals such as cadmium and lead are specifically used as bath stabilisers and brighteners. Usage of those elements in plating baths is of major concern as per environmental regulations. The focus of the RoHS (Restriction of Hazardous Substances) directive is the restriction of the use of hazardous substances. With increasing environmental concerns, there is a necessity for using RoHS-compliant baths for electroless Ni coating. Not much information is available on the published open literature, except in a US Patent reported in which sulphur-containing compounds were used as bath stabilisers and brighteners in place of toxic heavy metals[11]. However, RoHS-compliant commercial electroless nickel formulations are available on the market today. To the best of our knowledge, we did not find any literature available in the open domain exploring RoHS-compliant EN baths for surface treatment of Ti alloys to enhance the properties. In the present study, an electroless nickel-based acidic bath was used to deposit a uniform and adherent Ni-P coating on Ti alloy (Ti-6Al-4V) substrate by optimising the process parameters. The obtained coating is characterised by its composition, morphology, thickness, adhesion, and tribological properties.

2. Experimental

2.1 Sample Preparation

Titanium alloy (Ti6Al4V) specimens (2.4 cm X 2.4 cm X 0.02 cm) were used as substrates for the deposition of Ni-P alloy films. Specimens were scrubbed using 600-200 grade emery papers to remove the passive oxide layer, followed by polishing with 0.5 µm alumina to obtain smooth and uniform surface. Then the specimens were rinsed with running water, followed by deionised water. Then the specimens were cleaned ultrasonically in acetone for about 8 min. These specimens were immersed in a mild alkaline solution containing sodium carbonate, sodium hydroxide, and trisodium phosphate at 85°C for about 13 min, followed by rinsing in running water and deionised water. Further, the substrate was subjected to acid pickling in HF-HCl solution at room temperature for 2 min. with continuous stirring. After rinsing in DI water, the specimens were immersed in HCl-H_2SO_4 acidic solution (continuous stirring) for 65 min. to form a hydride conversion layer (hydrogenating treatment). Then these specimens were rinsed with running water and DI water, followed by Ni strike using Woods nickel bath for 1 min. by passing 1.3 A current. The pictorial representation of the above pre-treatment steps is shown in Figure 1. Then the specimens were immersed in an acidic electroless nickel plating bath (pH 5) containing proprietary lead- and cadmium-free stabilisers, utilising nickel sulphate and sodium hypophosphite as the nickel source and reducing agent, respectively, to deposit a Ni-P coating. The electroless Ni solution contained in a 500 ml glass beaker was kept in a constant temperature water bath

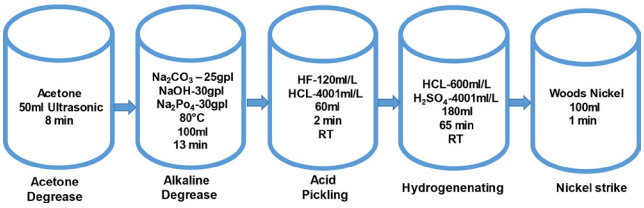


Figure 1. Steps involved in the pre-treatment process for Ti-6Al-4V alloy for depositing electroless Ni-P coating.

(Siskin Julabo VPC model) at 84±3 °C. All the specimens were plated for 2 hrs with a deposition rate of ~ 12 µm/hr. After plating, the samples were again rinsed in running water and DI water, dried and kept for characterisation.

2.2 SEM, XRD and Optical Studies

Field Emission Scanning Electron Microscopy (FESEM, Supra 40 VP (Carl Zeiss)) was used to analyse the surface morphology. SEM with EDX (Energy Dispersive X-ray analysis, Oxford Instruments Analytical, UK) attachment was used to determine the elemental composition of the deposits. X-ray Diffraction (XRD) measurements of the deposits were made in as-plated and heat-treated conditions with a Rigaku D/mx 2200 powder diffractometer using Cu K_α radiation. Cross-section of the deposits were analysed by using an optical microscope (Olympus SZ61).

2.3 Adhesion Test

The adhesion properties of the EN coatings were assessed using a heat quench test as per ASTM B571 – 97. The coated Ti alloy specimens were heated to a temperature of 250°C and maintained at this temperature for 1 hour. Subsequently, the samples were rapidly quenched in cold water to evaluate the adhesion characteristics of the coating.

2.4 Microhardness

Microhardness measurements were made on both as-plated and heat-treated electroless nickel coatings. Heat treatment was carried out on some of the specimens, which were heat-treated for 1 hour at a temperature of 400°C in a muffle furnace. To prevent the oxidation of the coating, a paste of proprietary mixture was uniformly applied on the coated specimens, dried and wrapped in a nickel foil and introduced into the furnace when the required temperature was attained. Heat treatment lasted for 1 h, and the samples were cooled to room temperature in the furnace itself. Wilson Hardness Tester (Buehler make, Model VH1102) was used to measure microhardness of both coatings by employing a load of 50gf. Five readings were taken on each deposit, and the values were then averaged.

2.5 Tribological Studies

The wear resistance of the samples was assessed using a reciprocating wear tester (Rtec Instruments, Model MFT2000A). The test employed a ϕ6.35 mm hardened steel ball as the counter surface, with a load of 5 N applied on each sample. Each test was conducted for a duration of 30 min, with a stroke length set at 10 mm/s. The total sliding distance for each 30 min test was calculated to be 60 m. The wear resistance was evaluated on an electroless nickel-deposited Ti alloy substrate (24 mm × 24 mm × 2 mm) in as-plated and heat-treated conditions.

3. Results and Discussion

3.1 SEM and EDX Analysis

Elemental composition was analysed for electroless nickel deposited Ti-6Al-4V substrate using FESEM attached with EDX. Corresponding EDX spectra obtained for the Ti alloy substrate and electroless Ni-P coating are shown in Figure 2. It was found that the Ti alloy substrate contains Al: 5.6 wt.%, V: 4.4 wt.% with a balance Ti which is similar to Ti-6Al-4V alloy. The as-plated Ni-P coating contains 8.3 wt.% P with a balance Ni as evident from EDX spectra. The characteristic peaks of Ti, Al, and V corresponding to the Ti alloy substrate and Ni and P corresponding to the EN coating were observed.

Figure 3 shows the SEM micrographs obtained for the surface of the as-plated electroless Ni-P coating. The surface morphology of electroless Ni-P coating showed the spherical nodular structure with fine nodules. The agglomerated nodules are of the size about 2-4 µm in size. This growth pattern is typical for electroless Ni-P coatings and is influenced by factors such as deposition parameters, bath composition and substrate characteristics[12].

The microstructure of the electroless Ni-P alloy cross-sectioned along the thickness direction is shown in Figure 4. From the optical micrograph, it is evident that the deposited electroless nickel coating is uniform and adherent to the Ti alloy substrate without any cracks or voids. Also, there is no porosity observed within the thickness of the electroless nickel deposit.

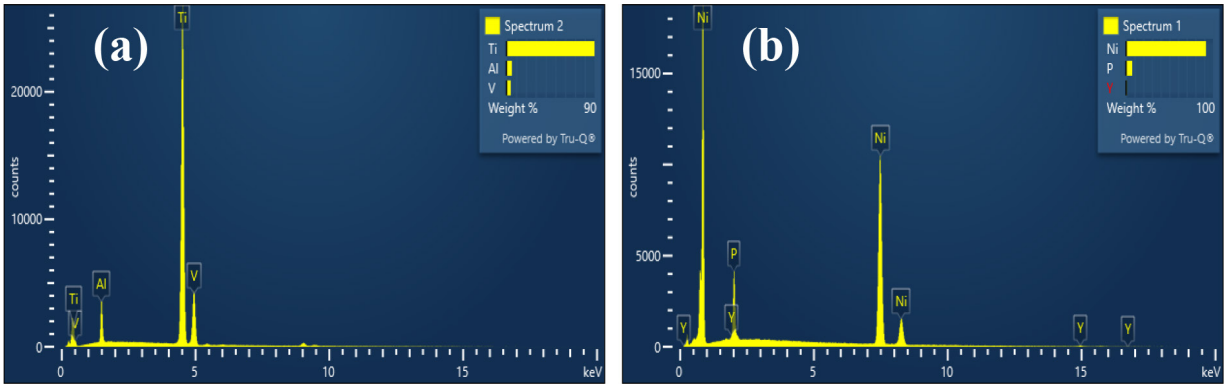


Figure 2. EDX spectra obtained for **(a)** Ti-6Al-4V substrate **(b)** As-deposited electroless nickel coating.

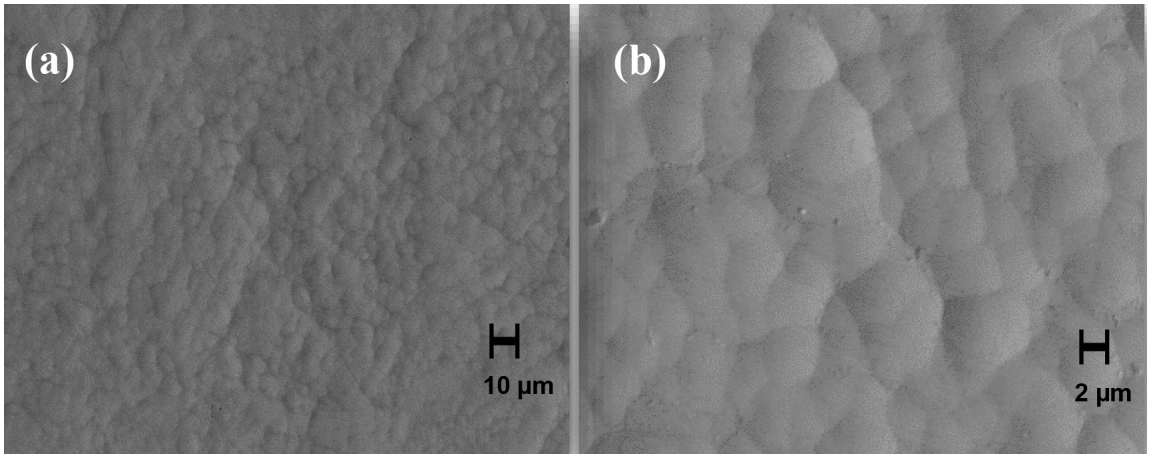


Figure 3. SEM micrographs of as-plated electroless nickel coating at **(a)** 500 X **(b)** 15,000 X.

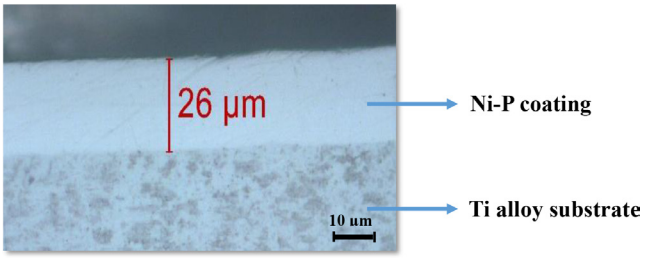


Figure 4. Optical micrograph obtained for the cross-section of electroless nickel coating.

3.2 XRD Analysis

The X-ray diffraction patterns of the as-deposited and heat-treated electroless Ni-P deposited Ti alloy substrates were shown in Figure 5. From Figure 5a, it is evident that only a single, broad peak around a 2θ value of 45° is seen for the as-deposited Ni-P coating. The peak broadening can be attributed to the amorphous nature of the deposit. It has been reported in the literature that the electroless nickel deposits having >7 wt.% phosphorus are amorphous in the as-deposited form13. Figure 5b shows the diffraction pattern obtained for a heat treated (400°C, 1 h) deposit. It is evident that after heat treatment, sharp peaks arising from bcc nickel phosphide and fcc nickel are present.

3.3 Adhesion Test

The heat quench test is a rigorous method used to simulate the thermal stresses that a coated material might encounter in practical applications. The surface images of the EN coated Ti alloy substrate before and after the test are shown in Figure 6. The absence of defects such as blisters or cracks and delamination of the coating shows that the EN coating is adherent to the Ti alloy substrate. No tarnishing of the coating surface was observed after the test. From this, it can be concluded that the pretreatment procedure followed for the Ti alloy substrate before

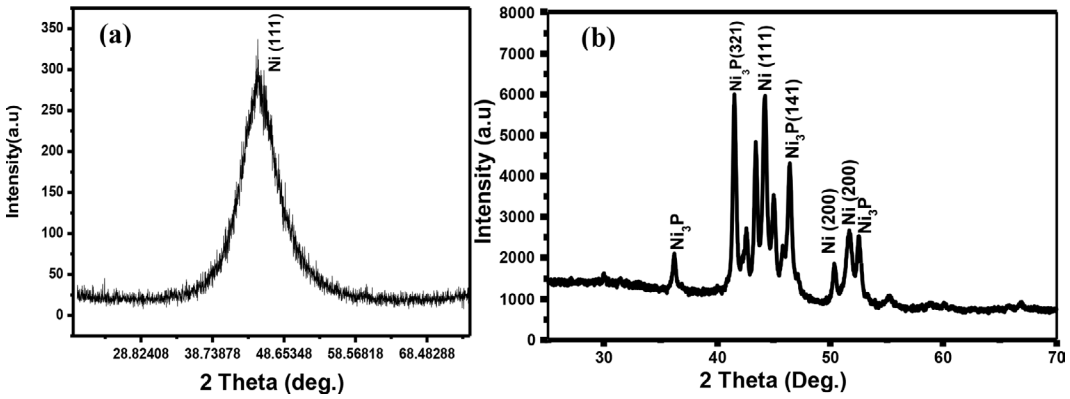


Figure 5. X-ray diffraction patterns obtained for as-plated and heat-treated electroless Ni-P coatings deposited on Ti alloy substrates.

electroless nickel plating is excellent, which resulted in coating adherence when it is subjected to thermal cycling.

3.4 Microhardness

Microhardness measurements were made on surfaces of both as-plated and heat-treated electroless Ni-P deposits, along with Ti-6Al-4V substrate for comparison, and the obtained values are given in Table 1. Surface hardness obtained for the as-plated electroless Ni-P deposit is about 550 $HV_{50\ gf}$. Heat-treated electroless Ni-P deposit is about 985 $HV_{50\ gf}$. Whereas in the case of the Ti alloy substrate, the surface hardness is about 460 $HV_{50\ gf}$. About 31% increase in hardness is noticed in the case of the as-plated Ni-P coating compared to the Ti alloy substrate. This clearly indicates that the Ti alloy substrate is softer than the deposited EN coating. From this, it is evident that the stress required to trigger shear banding in the amorphous state is higher to produce dislocation movement, which is responsible for the improved hardness of as-plated Ni-P coatings. About 54% increase in hardness is observed upon heat treatment of Ni-P coating compared to the as-plated coating. The enhanced surface hardness is due to the precipitation of very hard intermetallic particles of Nickel Phosphide (Ni_3P) and its distribution in a crystalline nickel matrix when the as-plated coating is subjected to heat treatment[14].

3.5 Reciprocating Wear Test

The wear resistance test using the reciprocating method is crucial for evaluating the durability and performance of materials under sliding contact conditions. In this method, materials are subject to repetitive motion, providing insights into their longevity and suitability for various applications. By measuring parameters such as the coefficient of friction and material height loss, this test helps in assessing the effectiveness of surface treatments in enhancing wear resistance.

Table 1. Surface hardness values of Ti-6Al-4V substrate and electroless Ni-P coating in as-plated and heat-treated condition (400 °C/1 h)

Type of Coating/ Substrate	Microhardness ($VHN_{50\ gf}$)*	
	As-deposited	Heat Treated (400°C/1 h)
Ni-P	600 ± 5	980 ± 3
Ti-6Al-4V	350 ± 4	

*Average of five indentations.

The Coefficient of Friction (CoF) and height loss due to wear of Ti alloy substrate, as-plated and heat-treated Ni-P coatings, are tabulated and are given in Table 2. The bare Ti alloy substrate exhibited a CoF value of 0.42 with a height loss of 0.004 mm (4 μm). In the case of as-plated Ni-P coating, there is a slight decrease in CoF value (0.32) and not much change is seen in height loss value (0.005 mm). This suggests that the as-plated electroless nickel coating provides a protective layer that reduces friction, though it may not significantly reduce the material loss under the tested conditions. The CoF value obtained for heat-treated Ni-P is about 0.29 with a height loss of 0.002 mm (2 μm). This remarkable performance can be attributed to the heat treatment process, which induces crystallisation and the formation of hard phases within the nickel-phosphorus coating. The crystallised coating not only lowers the CoF but also enhances the overall hardness and wear resistance of the surface.

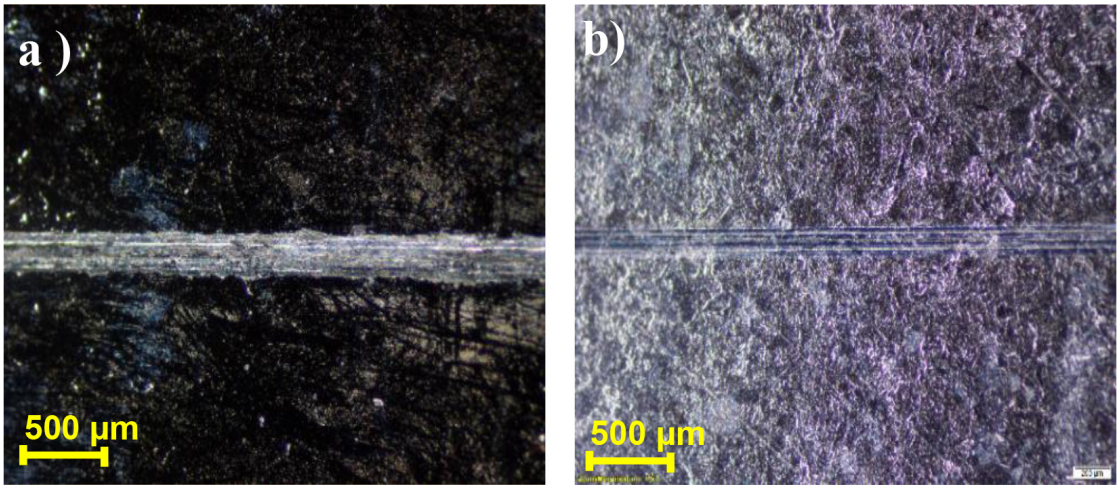


Figure 6. Optical micrographs of wear track patterns of electroless nickel-coated Ti alloy substrate **(a)** As-plated and **(b)** Heat-treated condition.

Table 2. Coefficient of friction values obtained for as-plated and heat-treated electroless Ni-P coatings

Type of Coating	Coefficient of Friction (CoF)
As-plated Ni-P	0.322 ± 0.02
Heat-treated Ni-P	0.189 ± 0.01

The optical micrographs of the wear-tested electroless nickel-coated Ti alloy substrate in as-plated and heat-treated conditions are shown in Figure 6 (a, b). From the figure, it is evident that the scratch width formed due to wear on the as-plated EN coating is greater than heat treated EN coating. There is almost 50% reduction in the scratch width on the wear scratch formed on heat treated Ni-P coating after the wear test. The presence of torn patches and, in some places, detachment of material is seen in as-plated EN coating (Figure 6a). Hence, adhesive wear appears to be the most likely mechanism during the wear process in as-plated EN coating. This sort of morphological feature, commonly called 'prows', is reported for adhesive wear failure of electroless Ni-P coatings[5,15]. Figure 6b exhibits the wear track pattern of heat-treated EN coating. In contrast to the as-plated EN coating, the wear scratch of the heat-treated deposit exhibits a bright and smooth finish with fine grooves along the sliding direction. From the above, it is evident that as-plated EN deposits exhibited severe adhesive wear; however, the Ni-P coating in heat-treated conditions showed the presence of hard Ni_3P phase, which plays a dominant role in determining the wear mechanism in preventing mutual solubility between two mating surfaces.

4. Conclusion

Electroless Ni-P coating has been successfully deposited on difficult-to-plate Ti-6Al-4V substrate using a RoHS-compliant electroless nickel plating bath. About 26 µm thick Ni-P coating deposited on a Ti alloy substrate in a plating duration of 2 h. Pre-treatment process parameters were optimised to get an adherent coating with uniform thickness. As-deposited Ni-P coating exhibited an amorphous structure and crystalline peaks seen after heat treatment. The deposit has a qualified heat quench test exhibiting good adhesion established at the interface between the Ti alloy substrate and EN coating. Heat-treated coatings showed enhanced hardness compared to as-plated electroless Ni-P coatings. Improved wear resistance with low coefficient of friction values was obtained for heat-treated EN coatings compared to as-plated coatings. These coatings may find applications in aerospace and other industrial applications as a replacement for toxic hard chrome coatings.

5. Acknowledgments

The authors are grateful to the Director, CSIR-NAL, and the Head of SED for their constant support and encouragement throughout this work. The authors thank Mr. Ganesh for his assistance during experimentation, Mr. M. Muniprakash for the wear studies, Mr. Siju for the SEM analysis and Mr G. Srinivas for XRD analysis. We also acknowledge CSIR (U-8-846) for the financial support.

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