Int. J. Bio-Inorg. Hybr. Nanomater., 6(1): 37-41, Spring 2017

Investigation of phosphor percent and distribution on surface properties in alumina nanotube substrate

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Received: 29 January 2017; Accepted: 4 March 2017

ABSTRACT: Electroless composite coatings used for achieving of high hardness, lubrication properties, non-stick surface, abrasive coating applications that by impregnation of soft and hard particles into Ni matrix. Electroless Nickel-phosphorous coatings properties and performance is greatly affected by the amount of phosphorus in them. The phosphor in this coating usually varies from 1 to 13 percent. In this project we investigated effect of phosphor percent and distribution of it in alumina nanotube substrate. In this study we investigate effect of phosphor percent in distribution on substrate and our results suggest that the surfaces of Ni-P coatings are very complex in character, with a variety of features, which affect the function of the part in different ways.

Keywords: *Anodizing; Alumina nanotube; Electroless composite; Lubrication; Ni-P coatings*

INTRODUCTION

Among different metallic coatings, the Nickel–phosphorous coating has attracted special attention due to their good wear resistance, great corrosion resistance, high electrical conductivity and low internal stress (Talu, *et al.*, 2014, Chockalingam, *et al.*, 2016, Pan, *et al.*, 2016). In general, the Nickel–phosphorous coating can be prepared by electroless and electrolytical plating, respectively, which have respective advantages and disadvantages. For instance, compared with the electrolytically plated coatings, the electroless coatings are less porous and more uniform without hydrogen embrittlement, which lead to a better corrosion resistance (Talu, *et al.*, 2014). Extensive work has been done on electroless Ni–P deposition (Chockalingam, *et al.*, 2016, Pan, *et al.*, 2016, Murugan, *et al.*, 2016, Hu, *et al.*, 2016) but research on electrolytic deposition is scarce. Electrolytic deposition has been of interest to industries because it boasts faster deposition rate and requires lesser maintenance of the electrolytic bath. Studies based on electrochemical and weight loss tests have been done to explain the change in corrosion behavior due to bath temperature (Hu, *et al.*, 2016), applied potential, phosphorous (P) content (Gao, *et al.*, 2017, Arulvel, *et al.*, 2017) and grain size (Gao, *et al.*, 2017). Although Ni–P is reported to be more corrosion resistant than pure Ni, it has been largely studied without much comparison to the latter. The enhanced corro-

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sion resistance of amorphous Ni–P lies in its homogeneity and absence of defects such as grain boundaries, which serve as preferential corrosion paths (Talu, *et al.*, 2014, Chockalingam, *et al.*, 2016). Ni–P coating could also be utilized for improving the damping capability of the vibrating structure. It is well known that when compared to electroplated coating, electroless method produces uniform thickness throughout the material.

MATERIALS AND METHOD

Alumina nanotube synthesis

In this project alumina nanotube was synthesized by anodizing method. Electrolyte bath is prepared by sulfuric and succinic acid in 185 gr/lit and 20 gr/lit respectively. The substrate material was 1050 aluminum alloy (AA). Its chemical composition in weight percent is: <0.40%Fe, <0.25%Si, <0.07%Zn, <0.05%Cu, <0.05%Mg, <0.05%Ti, <0.05%Mn and Al accounts for the remainder. The preparation process principally involved three successive steps: pre-treatment of the surface, anodization and functionalization by incorporation of PTFE particles inside the porous anodic films. All chemicals used were analytical graded and aqueous electrolyte solutions were prepared using deionized water. Before anodization, the surface was pretreated according to the European Space Agency (ESA) standard (ECSS-Q-ST-70-03C (Pan, *et al.*, 2016)) for space applications (Murugan, *et al.*, 2016). The aluminum sheet (45 mm × 37 mm × 0.5 mm) was degreased with ethanol and etched in mixed aqueous Na_2CO_3(6.2 g/L) and Na_3PO_4(12.5 g/L) solution for 5 min at 93 ± 2 °C. Then, the sheet was neutralized in aqueous HNO_3(50%, v/v) for 3 min at room temperature. Samples were rinsed with distilled water after each step. The anodization was performed in an electrochemical cell, where the aluminum sheet was used as anode and a lead plate as counter-electrode. The anodization was run for a given duration (in the range 30–45 min, usually for 34 min) in the galvanostatic mode (1.2 < Ja< 1.5 A/dm^2, typically 1.4 ± 0.1 A/dm2) using a phosphoric acid solution (0.4 M) thermally regulated (15 < T < 35°C, typically at 20°C). To increase the anodic pore diameter, the sheet was then soaked in a cell containing a phosphoric acid solution (5 wt.%) from 0 to 30 min thermally regulated at 30°C (Arulvel, *et al.*, 2017).

Ni-P electroless process

The electrochemically promoted electroless plating procedure of the Nickel-phosphorous coating is as follows: Firstly, the Ti sheets were polished using SiC sandpaper with different finer roughness (200, 400, 800, 1200, and 1500 grit) and then degreased in an alkali cleaner composed of NaOH 50 g/L, Na_2CO_3 20 g/L, Na3PO4 20 g/L and sulphonic acid 2 g/L at 80°C for 10 min. After that, in order to remove the oxides and scales from the Ti surface, the samples were picked in a solution composed of HNO_3 400 g/L and HF 50 g/L at room temperature (about 25°C) for 3 min, and then activated in the solution with 35 g/L $NaBF_4$ and 50 g/L $NaNO_3$ at 80°C for 10 min. Finally, the electrochemically promoted electroless deposition of Nickel–phosphorous coatings was carried out in a typical sulfate bath. After each step, the titanium substrates were washed thoroughly by deionized water. The compositions of the bath and experimental operating conditions are listed in Table 1.

RESULTS AND DISCUSSION

The deposition of Ni-P on alumina substrate applied. Substrate non-activated is used for process. Fig. 1

Table 1. Bath composition

S. No.	Ni-P bath composition	
1	$NiSO_4.6H_2O \rightarrow$ 25 g/l,	Nickel Sulfate Hexahydrate
2	$C_6H_5Na_3O_7.2H_2O \rightarrow$ 30 g/l,	Sodium Citrate
3	$(NH_4)_2.SO_4 \rightarrow$ 15 g/l,	Ammonium Sulfate
4	$NaH_2.PO_2.H_2O \rightarrow$ 20 g/l,	Sodium Hypophosphite
5	$Pb.(NO_2)_2 \rightarrow$ 1 ml,	Lead Nitrate

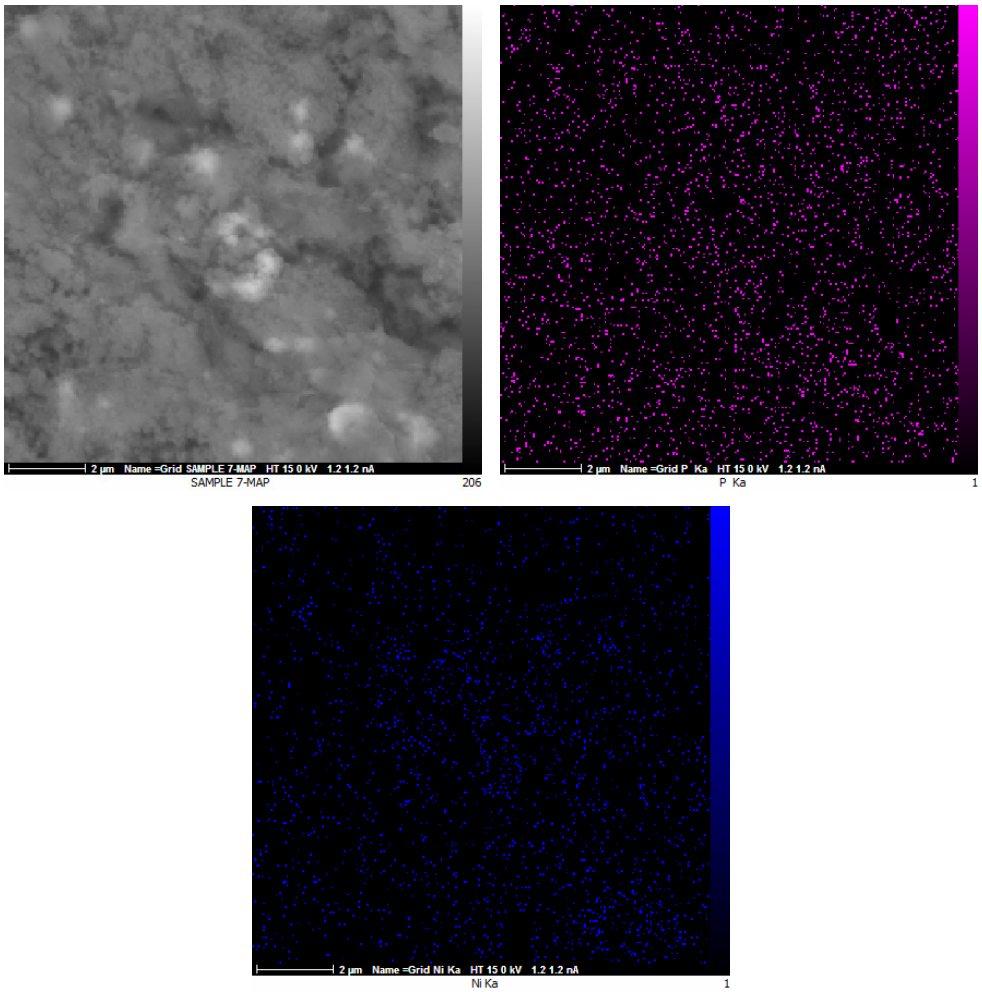

Fig. 1. MAP analysis of Ni-P distribution on alumina nanotube in 20 minutes, violet is P and blue is Nickel particles

shows the Ni-P deposition on alumina nanotubes in different time. Deposition started in preferential sites on substrate that this process is dependent on surface topography. After nucleation step growth is started on these sites. By continuation of this process particles convert to islands, islands grew and in final produce film of Ni-P. Ni diameter is 2.48 angstrom and the sites are estimated to be less than 30 angstrom in diameter (Arulvel, *et al.*, 2017). The number of activation sites per unit surface area σ was different for different substrates. In this process the value of σ is about $4/\mu^2$ in 4 second, $10/\mu^2$ in 10 second, $15/\mu^2$ in 15 second and $25/\mu^2$ in 60 second. Figs. 1 and 2 show distribution of Ni and P on alumina nanotube substrate in 10 and 20 minutes in electroless bath. As shown in these Figures by increase of process time increased density of P and Ni on substrate. The coating film thicknesses of the Ni–P are 21.9 ± 1.1. The lateral surface of the Ni–P specimen has a uniform, dense microstructure. When the heat-treatment temperature was increased to 500ºC, the structure became crystalline, and new peaks corresponding to crystalline FCC Ni and Ni_3P appeared. This behavior can be attributed to the crystallization of pure Nickel followed by the precipitation of Nickel phosphide (Ni_3P) from the supersaturated Nickel-phosphorous solid solution. The onset of the allotropic transformation of the Ni-P alloy occurred between 400°C and 500°C. Studies of similar systems have concluded that crystalline Ni-P alloys are denser than microcrystalline and amorphous alloys of the same chemical composition and that the transition from amorphous to crystalline structure is accompanied by a volume contraction. When the coating was treated at 400°C an amorphous structure with a few crystals formed was observed; these crystals are associated with the initial formation of the Ni_3P spe-

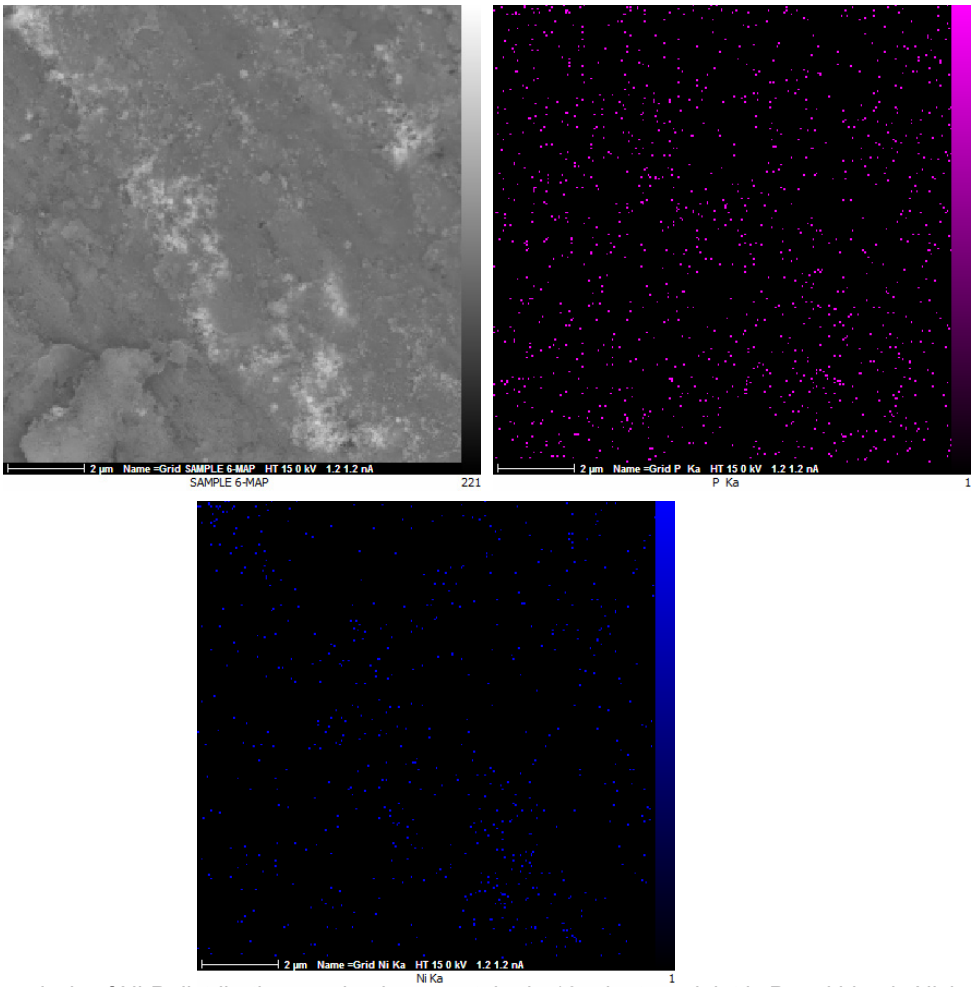

Fig. 2. MAP analysis of Ni-P distribution on alumina nanotube in 10 minutes, violet is P and blue is Nickel particles

cies that in Figs. 1 and 2 distributions of heat-treated samples is shown. The results showed that the Ni-P coatings (10.6 at% P) that were thermally treated at 500°C possessed the best surface finish. Nickel and Phosphor distribution is that Ni_3P distribution.

CONCLUSIONS

1. The operating temperature of the electroless platin Nickel–phosphorous coating on alumina substrate is decreased to 40-60°C due to the electrochemical promotion. The uniform and compact Nickel–phosphorous coatings show typical amorphous structure with phosphorous content of 6-8 wt.%.
2. Both the phosphorus content and thickness increase as the temperature increases. With the current density increasing, the phosphorus content in the coating decreases and the coating thickness increases.
3. When the applied current density increases, the value of E_{corr} moves 17 positively and the value of i^{corr} decreases. The Ni–P coating prepared with a current density of 1.1 A dm-2 at 55°C has the best corrosion resistance. With further increasing the deposited current density to 1.5 A dm-2, the value of i_{corr} increases significantly.

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