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Development of ZnO incorporated composite Ni–ZnO–P alloy coating

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Abstract

The process of electroless nickel phosphorus (EN) plating has become an inevitable technology in various industrial fields due to its excellent corrosion and wear resistance characters. Incorporation of Zn in EN plate has great impact on the chemical composition and properties of the plate. This paper focuses on significant improvement of the plate by incorporation with ZnO as a composite in the EN plate. In the present study, ZnO was selected for the composite plating by virtue of its properties like semiconductivity (band gap of 3.37 eV), piezoelectric property and biocompatibility. ZnO incorporated plate was obtained using a standard EN bath dispersed with ZnO. The plate was evaluated based on the results of porosity test, hardness and thickness measurements, OCP measurements and polarization studies. The composite plate corresponding to 0.50 g/l of ZnO in the bath showed excellent mechanical as well as electrochemical characteristics. The effect of incorporation of ZnO and the influence of its concentration on the plating characteristics are briefly discussed in this paper.

Keywords: Zinc oxide; Electroless plating; Nickel plating; Composite nickel coating; Nickel phosphorous coating

1. Introduction

Composite electroless nickel phosphorus (EN) coatings have potential applications in the aerospace industries. Composite EN coatings are regenerative, meaning that their properties are maintained even if some portions of the coating are removed during use. This feature results from the uniform manner with which the particles are dispersed throughout the entire plated layer. Co-deposition of the particles within EN coatings can dramatically enhance the existing characteristics and even add entirely new properties. For example, crystalline Ni–Cu–P deposits show better corrosion resistance characteristics compared to Ni–P plates [1]. The presence of W in Ni–P plates causes increase in the layer hardness up to 30% and better corrosion resistance [2]. Wear resistance can be increased by incorporation of diamond in Ni–P plates [3]. The Ni–P alloy deposit containing 2.5% TiO_2 nanometer powder has the co-efficient of friction some seven times higher than that of the pure Ni–P deposit [4,5]. Ni–P–carbon nanotube composites have wear resistance about 1000 times as high as that of pure Ni–P plating [6]. The present study focuses on incorporation of ZnO as a composite for significant improvement of the Ni–P plate.

ZnO was selected as the composite by virtue of its properties like semiconductivity (band gap of 3.37 eV), piezoelectric properties and also its biocompatibility[7]. Alkaline baths are advantageous for Zn coating as evidenced in literature. Valova et al. [8] have studied about incorporation of zinc in a partially oxidised state in nickel coating. It has also been reported that zinc incorporation causes a reduction in the phosphorus content and the deposition rate [9]. Zinc deposition in Ni–P plates inhibits the nickel discharge and as a consequence its catalytic activity on hypophosphate oxidation [10]. The Ni–Zn–P coatings have high corrosion resistance and better electrochemical properties [12,13]. Moreover, these plates are seemed to possess more noble characteristics than the Ni–P plates when we compare the electrochemical properties of Ni–Zn–P alloys [11]. High corrosion resistance tendency of nanometer size $Zn_3(PO_4)_2$, $ZnSnO_3$ and $ZnSiO_3$ has been recently reported [14,15]. However, there has not been any work on ZnO composite electroless Ni–P plating reported. The present study explores

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the process of incorporation of ZnO as a composite in EN plate for significant improvement of the plate.

2. Experimental

The mild steel coupons used in the present study has the composition Fe+C—0.189%, Si—0.03%, Ni—0.14%, Al—0.3%, Sn—0.17%, Mn—0.53, P—0.04, G—2.7, Cu—0.04% and Ti—0.006% and has the dimension of $4\times1\times0.2$ cm^3. Using emery paper up to 4/0 grade polished all the specimens. The specimens were then cleaned using 5% NaOH solution followed by 3% HCl each for 1 min, and then rinsed with distilled water. The specimens were activated using a solution of $SnCl_2$ 10 g/l and HCl (37%) 40 ml/l. The specimens containing adsorbed Sn^{2+} were placed in a nucleating solution having composition of $PdCl_2$ (0.1–1 g/l) and HCl (37%) (5–10 ml/l).

The hardness of the plate sample was tested using a Shimmadzu HMV 2000 hardness tester (as per ASTM E-38489) for Vicker's hardness number. The test load was 100 gf and the indentation time was 12 s. Thickness of the plate was measured using a Microtester Electrophysik (Germany). The deposition potential (E_d) of the specimens were recorded during the course of electroless plating, with respect to a saturated calomel electrode. Polarization studies were carried out using a standard potentiostat. Saturated calomel electrode was the reference electrode. The chemicals used for this study were of analytical grade. Zinc oxide used for the study was of Fischer make.

3. Results and discussion

3.1. Effect of ZnO incorporation

Only a very few baths containing zinc or Zn salts for EN plate are available in literature, due to the inhibitive effect of zinc on the nickel discharge [9,10]. As evident from literature, the alkaline baths are superior as for as the plates with zinc additives are concerned [8,9]. In this context, a suitable alkaline bath was selected for the present work also. The composition of the bath is listed below. The cleaned and activated coupons were immersed in the bath containing the required quantity of ZnO. The bath was agitated using a mechanical stirrer during the course of plating.

Chemicals	Compositions, g/l
Nickel sulphate	30
Sodium hypophosphite	10
Sodium citrate	84
NH_4Cl	50
pH=8–10	
Temperature=90 °C	
Time=3.5 h	

All ZnO incorporated plates showed better mechanical as well as electrochemical properties during preliminary studies. However, change in concentration of ZnO has significant effect in yielding good plating properties. Hence, the concentration of ZnO was optimized based on the plating properties.

3.2. Physical characteristics of the plate

The zinc oxide incorporated plates, generally have bright appearance. Analyzing different area of the plate using mechanical and electrochemical tests ensured the uniformity of ZnO dispersion in the plate. The adherence of the plate was also good. Prying with a sharp blade did not cause lift off the coating indicating good adhesion. As the concentration of the ZnO in the plates increases, the adherence was found to decrease.

The porosity of the plates was tested using Ferroxyl reagent. The reagent was prepared using 25 g of potassium ferricyanide and 15 g of NaCl in 1 l of distilled water. The plated coupons were immersed in the solution at 25 °C for 30 s. After rinsing and drying, the specimens were examined for appearance of blue spots which forms at pore sites. The uniform blue spots were few in number indicating less porosity of the plate.

3.3. Standardization of ZnO incorporation

3.3.1. Optimization of concentration of ZnO in the plate

The concentration of ZnO has significant influence on improving the characteristics of the Ni–ZnO–P plate. The influence of ZnO concentration has high impact in altering the Vicker hardness number of the plate. In the as plated state, the hardness of Ni–P–ZnO coating was found in the range of 350–400 VHN, which is comparable with the hardness of normal EN plate which is in the range of 420 under a load of 100 gf. The high hardness value is due to the uniformity and homogeneity of the plate. The hardness of the uncoated mild steel sample was found to be 252 VHN, which was substantially lower than that of the coated samples. The hardness value varies with the amount of ZnO incorporation. It was found that the hardness of the plate increases corresponding to addition of zinc oxide only up to 0.5 g/l in the bath and further addition of ZnO causes decrease in hardness value (Fig. 1). This indicates that higher concentration of ZnO incorporation has detrimental effect on the plate. This is in accordance with other available literature [9,10]. High ZnO content causes more micro-level segregation of the composite rather than each composite particle covered by the electroless plate.

3.3.2. Thickness

The adherence of the plate was strong and prying with a sharp blade did not cause lift off the coating indicating good adhesion. Thickness of different ZnO incorporated plates is compared in Fig. 1. Thickness of the plates is in the range of