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Evaluation of scratch resistant properties of electroless Ni-P-Al₂O₃ composite coatings

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Ni-P-Al₂O₃ composite coatings were prepared from electroless plating method on copper substrate with different contents of Al₂O₃ powder. Thus obtained composite coatings were heat treated at 400 °C for 1 h in an inert environment and subjected to scratch tests. Compared to Ni-P coating, codeposition of Al₂O₃ exhibited the nodular structure and slightly increased surface roughness of the composite coatings. Low P nickel coating with approximately 4 wt% of codeposited Al₂O₃ into the deposit was obtained with 10 g/L Al₂O₃ concentration into the plating bath. Enhanced Vickers microhardness of the composite coating was due to the synergistic effects of the precipitation hardening by Ni₃P phase and co-deposited hard Al₂O₃ particles. Furthermore, Ni-P-Al₂O₃ composite coatings have shown considerable improvement in load-bearing capacity of the coating matrix, thereby, enhancing the scratch resistant properties of the composite coating.

Key words: Electroless plating, Ni-P-Al₂O₃, Composite, Scratch testing.

Introduction

Electroless Ni-P alloy possesses an excellent mechanical, tribological and electrochemical anticorrosion properties [1-3]. In addition, electroless Ni-P coating offers better coating adhesion, uniformity in coating thickness, and is well applicable in irregularly shaped objects [4]. The formation of hard Ni₃P phase after heat treatment makes it even more attractive in the field of the protective metallic coating. Furthermore, the feasibility of the variation of phosphorus (P) content in the deposit via electroless plating plays an essential role for the desired properties of the coating such as an adjustment in hardness and variation in electrochemical anti-corrosion behavior [5].

Due to the availability of different kinds of nanoparticles and their successful codeposition along with the Ni-P alloy coating, the composite coating has gained more and more attention for improved coating properties. Several investigations have revealed that the homogeneous distribution of nanoparticles into the deposit plays an important role in the overall properties enhancement [6]. However, agglomeration of nanoparticles in the plating bath as well as into the deposit is still in the challenging phase despite the practice to use various dispersants or surfactants. Different kinds of nanoparticles such as Al₂O₃, TiO₂, SiC, PTFE, CeO₂, ZrO₂, Si₃N₄, TiC, diamond, etc., have been found to be incorporated into Ni-P coating and investigated for their effects on

material properties [7-11]. Based on the tribological point of view, codeposition of PTFE is of prime selection due to its self-lubricious nature. Studies have shown that electroless deposited Ni-P-PTFE composite coating possessed excellent anti-wear characteristics and reduced coefficient of friction [10]. However, the electroless Ni-P coating is generally subjected for the heat treatment process for stress relief, removal of hydrogen embrittlement, improvement for coating adhesion as well as to enhance the hardness of the coating. During the heat treatment process, organic PTFE molecules get melted, if the heat treatment temperature exceeds the melting point of PTFE, thereby losing the particulate properties.

An alternative choice of reinforcement in the composite coating for the tribological application falls under hard and nano-sized ceramic particles. Codeposition of hard nanoparticles such as Al_2O_3 , TiO_2 , SiC, TiC, Si_3N_4 etc. into the Ni-P coating not only improves the mechanical properties of the coating by the dispersion hardening but also enhances the tribological properties as revealed by several investigations [6, 12-13]. Among the different hard nanoparticles reinforced composite coatings, the Ni-P-Al_2O_3 coating has gained much attention due to the excellent mechanical and tribological properties. Studies have shown that incorporation of Al_2O_3 nanoparticles resulted in improvement in mechanical, tribological and electrochemical corrosion properties of Ni-P coating by electroless deposition technique [14-16].

Although several studies have been performed to investigate the effect of Al_2O_3 incorporation on the properties of the Ni-P alloy coating, still there is no adequate information available for the scratch resistance

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properties of the electroless Ni-P-Al₂O₃ composite coating. The present work, therefore, is aimed to fabricate Ni-P alloy composite coating with different contents of Al₂O₃ nanoparticles into the deposit and their effect on surface morphology, microhardness, and scratch resistant properties.

Experimental Procedure

Substrate preparation

Copper with the dimension $20 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ was used as a substrate for the electroless deposition. Prior to the electroless deposition, substrates were grounded and polished with #2000 SiC paper, washed with DI water and acetone, followed by alkaline degreasing, sensitization with SnCl₂ in HCl, and activation with PdCl₂ in HCl. After the activation process, the substrate was washed again with DI water and immediately immersed into the plating solution for electroless deposition.

Electroless deposition

Nickel sulphate was used as the source of Ni and Sodium hypophosphite was used as the reducing agent in this study. Lactic acid was used as the complexing agent while Thio-urea was used as the bath stabilizing agent. In order to obtain the low phosphorus deposit, bath pH was set to 5.6. Plating time was adjusted to 60 min at 85 ± 3 °C. A detail of composition, concentration and operating condition for the electroless deposition bath is presented in Table 1.

 Al_2O_3 nanoparticles with the concentration from 1 g/L to 10 g/L was added as composite reinforcement. The Al_2O_3 nanoparticles were ultrasonically agitated for 30 min before introducing them into the plating bath. In order to maintain the good adhesion between the substrate and the coating, initially, 10 min of the electroless

Table 1. Bath composition and operating conditions for the electroless Ni-P-Al₂O₃ composite coatings.

Composition	Concentration/ operating condition	Purpose
NiSO ₄ .6H ₂ O (g/L)	25	Ni source
Sod. Hypophosphite (g/L)	30	Reducing agent
Lactic acid (mL/L)	20	Complexing agent
Sod. Citrate (g/L)	20	Buffer
Sod. Succinate (g/L)	15	Accelerating agent
Thio-urea (mg/L)	1	Stabilizing agent
Sodium dodecyl sulphate (g/L)	0.3	Anti-pitting/ surfactant
Al ₂ O ₃ nanoparticles (g/L)	1 to 10	Ceramic composite phase
pН	5.6	
Temperature (°C)	85 ± 3	
Plating time (min)	60	

Ni-P coating was carried out and then introduced the ultrasonically agitated Al_2O_3 nanoparticles into the plating bath. After the electroless deposition, samples were cleaned by the ultrasonic method to remove loosely held particles from the surface and subjected to heat treatment in the Argon environment at 400 °C for 1h. Samples after heat treatments were labeled as HNiP, HNA11, HNA13, HNA15, and HNA110 for Ni-P, Ni-P-Al_2O_3 (1g/L), Ni-P-Al_2O_3 (3g/L), Ni-P-Al_2O_3 (5g/L), and Ni-P-Al_2O_3 (10g/L), respectively.

Characterization

The morphology and elemental composition of the coatings were observed and analyzed by scanning electron microscopy (SEM) fitted with energy dispersive X-ray spectroscopy (EDS). Surface roughness was measured by surftest surface roughness tester. Phase and crystallinity was evaluated by X-ray diffractometer (Rigaku, RINT 2200, Japan). Microhardness of the coatings was measured by Vickers microhardness tester (Buehler inc, USA) with the applied load 100 g for 10 s at ten different places on the surface and the values were averaged. Adhesion test of the coating was carried out by evaluating a scratch test using CSM revetest with Rockwell indenter in a progressive manner from 1 N to 40 N load. Friction and acoustic emission data were recorded during the test, and the scratched surface was observed by SEM.

Results and Discussion

Microstructure, surface morphology, and elemental composition

Fig. 1 shows the XRD plot of the Ni-P-Al₂O₃ composite coatings prepared from different contents of Al₂O₃ dispersion into the plating bath. After heat treatment, it led to phase transformation from amorphous Ni–P matrix to nanocrystalline structure. The crystallinity of the coating is evidenced by the higher intensity and smaller width of peaks. Furthermore, stable Ni₃P phase appeared in all the composite coatings. However, there is no peak appeared for the metastable Ni₁₂P₅ [17]. Alumina peaks were not detected in the XRD pattern which might be due to its low content and it was beyond the detection limit by XRD.

Surface morphologies of the Ni-P-Al₂O₃ composite coatings are shown in Fig. 2. Compared to Ni-P alloy, the composite coatings have shown slightly nodular structures. A significant variation in surface morphologies of the Ni-P-Al₂O₃ composite coatings can be found with the variation of alumina content in the plating bath. As the content of alumina is increased, the surface roughness of the composite coating is found to be increased as revealed by the appearance of nodular structures on the surfaces. This might be associated with the fact that the codeposition of Al₂O₃ altered the cathodic deposition process by hindering the regular grain growth of Ni-P



Fig. 1. XRD patterns of Ni-P and Ni-P-Al₂O₃ composite coatings.

matrix and stimulated the fresh nucleation sites. Hence, a deposit with a large number of smaller nodules produced in HNA15 and HNA110 samples. Surface roughness values presented in Fig. 3 for Ni-P-Al₂O₃ composite coatings well supported for this observation. Elemental composition of the Ni-P-Al₂O₃ composite coating prepared from the dispersion of 10 g/L of alumina in the plating bath measured by EDS analysis is shown in Fig. 4. From the EDS analysis, Ni-P-Al₂O₃ composite coating shows the low P in Ni-P matrix containing approx. 4 wt% of codeposited alumina. Low P electroless Ni coatings usually possess higher vickers microhardness and are better for mechanical and tribological applications[18]. Hence, it is expected to have better wear and scratch resistant properties of this type of coating, facilitated by the codeposited hard alumina nanoparticles.

Vickers microhardness

Vickers microhardness of the electroless Ni-P and Ni-P-Al₂O₃ composite coatings before and after heat treatment are shown in Fig. 5. It can be seen from the



Fig. 3. Variation of the surface roughness (R_a) of Ni-P and Ni-P-Al₂O₃ composite coatings.

plot that the hardness values of the as-plated coatings are lower than the heat-treated samples. As the Al₂O₃ content is increased, vickers microhardness is also found to be increased in both as plated and heat treated samples. Hence, it can be anticipated that the codeposited Al₂O₃ has significantly contributed to the hardness of the coatings. The increase in hardness caused by codeposited Al₂O₃ is mainly due to the dispersion hardening mechanism [19]. On the other hand, phase transformation occurs in Ni-P coating by heat treatment as the precipitated hard Ni₃P phase is responsible for increasing the hardness of the heat treated sample [20]. So, the matrix becomes harder by precipitation hardening mechanism. Hence, the overall increase in hardness of the coatings are primarily ascribed to the dispersion hardening mechanism caused by the codeposited Al₂O₃ nanoparticles and the precipitation hardening mechanism due to the formation of Ni₃P phase after heat treatment.



Fig. 2. SEM micrographs of the surface morphologies of (a) HNiP, (b) HNA11, (c) HNA13, (d) HNA15, and (e) HNA110 samples.



Fig. 4. EDS spectra and elemental analysis of HNA110 sample.



Fig. 5. Variation of the Vickers microhardness of the coatings before and after heat treatment.

Scratch test

Variation of the coefficient of friction and acoustic emission recorded during the scratch test of electroless Ni-P and Ni-P-Al₂O₃ composite coatings are shown in Fig. 6 and Fig. 7, respectively. The progressive type scratch test was carried out from 1 N to 40 N with the loading rate of 196.8 N/min using 200 µm diamond Rockwell type of indenter. Increasing the indentation load during the scratch test revealed different behaviors in the coefficient of friction. Especially, onwards 10 N of the applied load, a sudden rise in coefficient of friction is observed for different samples. Electroless Ni-P-Al₂O₃ composite coatings prepared from the dispersion of 1 g/L and 3 g/L of alumina (HNA11 and HNA13 samples) have shown a similar trend of the coefficient of friction to that of HNiP coating. However, the samples HNA15 and HNA110 have shown relatively less fluctuation of the coefficient of friction compared to other samples. This characteristic change in coefficient of friction for HNA15 and HNAl10 samples indicate the influence of codeposited



Fig. 6. Coefficient of friction measured during the progressive scratch testing.



Fig. 7. Acoustic emission signals recorded during the progressive scratch testing of different samples.

alumina to the scratch resistant performance of the coating. On the other hand, the Ni-P coating has shown the early initiation of the acoustic signal compared to other samples. However, Ni-P-Al₂O₃ composite coatings have shown the initiation of acoustic emission signals at higher loads. Hence, the presence of Al₂O₃ nanoparticles in the Ni-P matrix caused to shift the first appearance of the acoustic emission signal towards higher loads (Fig. 7).

Ni-P and Ni-P-Al₂O₃ composite coatings are relatively brittle in nature in comparison to the ductile copper substrate. Analysis of scratch resistant properties of brittle coatings on the ductile substrate can be interpreted by taking two different characteristic loads such as cohesive load (L_C) and adhesive load (L_A). A measure of the cohesive strength of the coating, usually evaluated by the appearance of the cracks in the coating, is generally referred as the cohesive load. At



Fig. 8. SEM micrographs of the scratched tracks representing the region of crack appearance (L_c) of (a) HNiP, (b) HNA11, (c) HNA13, (d) HNA15, and (e) HNA110 samples.



Fig. 9. SEM micrographs of the scratched tracks representing the region of adhesive failure (L_A) of (a) HNiP, (b) HNA11, (c) HNA13, (d) HNA15, and (e) HNA110 samples.

this point, acoustic emission signal begins to appear. However, adhesive load is influenced by several factors such as smaller regions corresponding to the coating detachment, numbers of coating failures, or formation of larger cracks [21]. The adhesive load is usually evaluated by the sudden rise of an acoustic emission signal. Hence, from the acoustic emission signals for Ni-P and Ni-P-Al₂O₃ composite coatings, the cohesive strength of the coating is found to be in the range from 3 N to 15 N. Among the prepared samples, Ni-P coating shows the lowest cohesive strength whereas the sample HNAl10 possessed the highest value of cohesive strength. This observation is also supported by the characteristic rise and fall in coefficient of friction for different samples in this range. On the other hand, a sudden change in the behavior of coefficient of friction and a sharp rise in acoustic emission signals suggest that there might be the formation of larger

cracks, or some sorts of coating defects or coating failure, which correspond to the L_A . From the analysis of acoustic emission signal, L_A can be predicted in the range from 10 N to 23 N depending on the condition of different samples. HNA15 and HNA110 samples possessed almost similar values of L_A (~20 N) indicating the higher strength against the coating failures as compared to other samples. This observation clearly suggests that the incorporated alumina nanoparticles play a vital role to strengthen the deposit. Codeposited Al_2O_3 nanoparticles distribute mainly in the grain boundaries [22] and act as a barrier to either formation of cracks or their propagation during the scratch test.

Fig. 8 shows the SEM micrographs of the worn surfaces of the coatings representing the initiation of micro-cracks at different loading during the scratch test. Ni-P coating started to produce micro-cracks at around 4 N exhibiting the earliest crack initiation among the samples. Ni-P and HNA11 samples reveal similar nature of cracks, differentiating the crack initiation loads. A significant improvement towards the resistant to crack formation can be observed for HNA13, HNA15, and HNA110 samples. The loading to which micro-cracks appeared, the density of the produced cracks, and their propagation characteristics in HNA13, HNA15, and HNA110 samples are significantly improved, demonstrating higher scratch resistant properties of the coatings as compared to Ni-P. The outcome is ascribed to the improvement in the load-bearing capacity of the composite coating. As mentioned above, Al₂O₃ nanoparticles in the coating act as the barrier to crack initiation or their propagation. As a result, the coating can withstand a higher load, and the less number of short-range micro-cracks are produced.

Similarly, Fig. 9 shows the SEM images of the region representing start-up of the adhesive failure of the coatings. It is clearly seen from the micrographs that several larger micro-cracks are produced throughout the scratched canals extending perpendicular to the scratched direction in almost all the samples. In addition, the coating detachments in some parts are also observed in this region. At the scratched region from 8 N to 12 N load, a severe coating failure is found in the Ni-P coating (Fig. 9a). The observation is well aligned with the sudden rise and fluctuation of the acoustic emission signal (see Fig. 7). However, the appearance of coating failure is observed at higher loads for the composite coatings. Although coating plow out spots have been observed at certain area, a complete detachment of the coating is not found in the sections representing L_A . It might be due to the effect of a relatively hard Ni-P-Al₂O₃ composite coating on a soft and ductile substrate. The coating is, thus, compressed into the substrate and no complete detachment of the coating observed. Furthermore, In HNA15 and HNAL10 samples, relatively less number of micro-cracks are produced as compared to other samples. Hence, from the scratch test analysis, it is revealed that the presence of alumina nanoparticles in the deposit significantly improved the scratch resistant properties of the Ni-P-Al₂O₃ composite coating.

Conclusions

Ni-P-Al₂O₃ composite coatings were prepared via electroless deposition technique. After heat treatment of the Ni-P-Al₂O₃ composite coatings, it led to phase transformation from amorphous Ni-P matrix into a nanocrystalline structure together with precipitated Ni₃P phase. Compared to Ni-P alloy, the composite coatings have shown nodular structures with slightly increased surface roughness. The overall increase in microhardness of the coatings is primarily ascribed to the dispersion hardening mechanism caused by the codeposited Al_2O_3 nanoparticles and the precipitated hardening mechanism due to the Ni₃P phase transformation after heat treatment at 400 °C. The presence of Al_2O_3 nanoparticles in the deposit significantly improved the scratch resistant properties of the Ni-P coatings.

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