Characterization of Electroless Ni-P and Ni-P/Al₂O₃ Composite Coating on Al6061 Alloy

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Abstract. Aluminum and its alloy have a light density with good properties of stiffness and corrosion resistance. Although it has a good property, aluminum alloy still vulnerable to wear and corroded. A possible solution to protect the aluminum product from wear and corrosion is by applying coating such as nickel-phosphorus (Ni-P) coating onto its surface. Co-deposition of alumina (Al₂O₃) particles into Ni-P coating is expected to improve the wear resistance of the Ni-P coating layer. This study investigated the Ni-P and Ni-P/Al₂O₃ composite coating on Al 6061 alloy via electroless coating by varying the agitation speed and amount of Al₂O₃. The characterization of coatings includes morphology, coating thickness, hardness and wear properties were investigated by using field emission scanning electron microscopy (FESEM), optical microscope, Vicker microhardness and pin-on-disc tribometer. The agitation improved the adherence of alumina particles to the substrate. The increment amount of alumina in Ni-P/Al₂O₃ composite coating showed a decrement in percentage of nickel and phosphorus present in the coating but improved the hardness of the coating. The wear rate and coefficient of friction of the Ni-P/Al₂O₃ composite coating were lower than Ni-P coating.

1. Introduction
Electroless nickel plating on aluminum and many of its alloys is applied with a view to improve the surface hardness, corrosion protection and wear resistance. Aluminum and its alloy are considered a difficult substrate to be coated by autocatalytic nickel deposition. This is due to the other metals (e.g.) nickel does not adhere onto new formed aluminum oxide film. In order to create a suitable (oxide-free) aluminum surface for nickel deposition and adherent nickel coating, different pre-treatments for aluminum were developed. Most of these pre-treatments involve chemical dissolution of the aluminum oxide film and formation of an immersion deposit of another metal such as zinc and tin. Zinc immersion remained commonly used due to the fact that it can be adjusted to a large variety of aluminum alloys. The pre-treatment process involved many procedure and process parameter depending on aluminum alloy used.

The requirement towards uniformity of metal coatings and their characteristics such as hardness, resistance against corrosion, wear hardness, coefficient of friction etc., are constantly increasing. The properties of Ni-P can be improved by co-deposition with hard particles (e.g. SiC, WC, Al₂O₃) and dry lubricant (e.g. PTFE, MoS₂, graphite). The major challenges with the co-deposition of particles are the achievement of a high level of co-deposition, and the agglomeration of particles suspended in the electrolytes. Currently, research on electroless Ni-P coating is mostly focused on the effect of
surfactant, pH, or reducing agents toward electroless Ni-P coating [1-4]. However, the agitation (stirring speed) during the coating process also one of the factors that might affect the properties of Ni-P coating. In this project, effect of agitation toward electroless Ni-P coating was studied. Researchers have reported that the addition of SiC improved [5] tribological behavior, while the others indicate worsening of wear behavior after introduction of SiC particles in Ni-P coating. However, Karthikeyan & Vijayaraghavan [6] have found that the hardness and wear resistance of steel substrate have improved by incorporation of Al₂O₃ in electroless nickel. Aluminium and alumina particles were selected as aluminum has higher strength and alumina particles can improve the wear resistance of Ni-P coating. In this study, Al₂O₃ particles with different amount were co-deposited in electroless coating and its surface morphology were characterized. Hardness and wear resistance for both Ni-P coatings and Ni-P/Al₂O₃ were compared.

2. Experimental Procedure

Al 6061 alloy with a size of 40 mm x 20 mm x 1 mm was used as the substrate. Alumina (99.98%) having particle sizes in the range 0.33 μm to 13.35 μm supplied by SkySpring Nanomaterials was used as the reinforcement material. The average alumina particles size was 4.02 μm. The aluminum sheets were ground using SiC abrasive papers with grit of 400, 600, 800, 1200 and 2000 and followed by polishing using diamond suspension of 0.6 and 0.1 μm. The polished specimens were immersed in an ultrasonic bath containing acetone to ensure oil and dirt-free surface. Then the samples were immersed in a mixture of sodium carbonate and sodium phosphate dodecahydrate. After that, the samples were immersed in a mixture of sulphuric acid, phosphoric acid and propionic acid for 2 minutes at 65°C. For each step, the samples were washed and rinsed with distilled water. In order for chemical activation of the surface, the zincating pre-treatment was executed by dipping and stirring of samples into zincating bath for 1 min. The deposition of a uniform Zn layer at the Al surface requires double process of zincating process within a short time to avoid the formation of rough surfaces. Between the two zincating processes, Al substrates were dipped in 50% volume of nitric acid for 1 minute.

After zincating process, the Al substrates immediately immersed in the electroless nickel bath solution that was pre-heated at 89°C containing 8 g/L Al₂O₃ with different agitation speed. The agitation of electroless nickel coating process was carried out at different stirring speed 200, 250 and 300 rpm. Next, to produce Ni-P/Al₂O₃ composite coatings, different amount of Al₂O₃ particles (4 g/L, 6 g/L, 8 g/L) were added to the bath and kept in suspension by magnetic stirring and air bubbling. The composition of the composite electroless nickel solution is shown in Table 1. The zincate layer on the surface might become less activated if the substrate exposed longer time before immersed in electroless bath. Therefore, the nickel deposition might not occur on the substrate. Thus, electroless nickel process was prepared beforehand. The surface morphology and surface characterization of NiP/Al₂O₃ coatings were done by FESEM (LEO SUPRA 35VP) equipped with EDX spectrum analysis. The microhardness of the coatings was measured using Vicker microhardness Tester. The wear resistance of the coatings was determined by Ducon TR-20 pin-on-disc tester at sliding speed of 0.5 m/s, load of 3 kg and sliding distance of 1000 m. The specific wear rate is calculated based on Equation 1.1 (Karthikeyan & Ramamoorthy 2014).

\[
Specific \ Wear \ Rate = \frac{W}{DL} \ k g \ N^{-1} m^{-1}
\]  

(Eq. 1.1)

Where, \( W \) = mass loss of sample, \( D \) = sliding distance and \( L \) = load.
Table 1. Composition of electroless nickel solution

| Function       | Chemical used                  | Composition   |
|----------------|--------------------------------|---------------|
| Source of Nickel | Nickel (II) sulphate heptahydrate | 0.1 mol      |
| Reducing Agent   | Sodium hypophosphite            | 0.35 mol      |
| Complex Agent    | Glycine                         | 0.09 mol      |
|                  | Lactic acid                     | 0.40 mol      |
|                  | Propionic acid                  | 0.02 mol      |
| Stabilizer       | Copper (II) sulphate            | 4 ppm         |
|                  | Lead (II) acetate trihydrate    | 2 ppm         |
| Surfactant       | Cetyl trimethylammonium bromide (CTAB) | 0.3 g   |
| Alumina          | Al₂O₃                           | 4, 6, 8 g/L   |

3. Results and Discussion

3.1 Determining agitation for the electrolysis process

Figure 1 shows the morphology of Ni-P/Al₂O₃ composite coating with different agitations. These coatings produced different size of nodules with similar shape. Similar observation has been reported by Sen et al. [7], which different size of nodules of Ni-CeO₂ is formed with different agitation. Figure 2 shows the cross-section images of Ni-P with alumina particles coating layer at different agitation speed. The coating layers for 200 rpm, 250 rpm and 300 rpm had almost the same thickness which was about 18 µm. The changes in the agitation of electroless nickel coating process did not show a significant influence on the thickness of coating layers. The samples were further analyzed using EDX. The EDX analysis in Figure 3 showed the increasing of nickel content by decreasing agitation. The lower amount of nickel content was detected in a coating that used agitation of 300 rpm. About 58.24 wt% of nickel were found in the coating with agitation of 300 rpm, while 82.25 wt% and 85.03 wt% of nickel were detected in coating with agitation of 250 rpm and 200 rpm, respectively. Bulasara et al. [8] also found that the higher agitation resulted in decreasing amount of nickel deposited in the coating. In addition, higher agitation would result in the decrease of deposition rate as nickel does not have enough time to be deposited onto the surface. Moonir-Vaghefi & Saatchi [9] also reported that higher agitation would cause the decrease of coating hardness. Based on the result, it can be concluded that the agitation that applied in an electroless nickel coating process not only maintain the temperature and improving the stability of the electroless nickel bath solution, but also influences the nickel deposited in the Ni-P with alumina particles coating layer. Thus, agitation for 200 rpm was used as it has the highest amount of nickel deposited.

3.2 Hardness

The hardness of Ni-P/Al₂O₃ composite coating was measured using Vicker micro hardness indenter. Seven measurements were done on the surface of the coating layer and the average value of microhardness of each sample was calculated and plotted in Figure 4. From the figure, the hardness of composite coating was increased to 90.2 HV with the addition of 4 g/L of alumina particles. Then, the hardness of composite coating showed an increasing trend with higher composition of alumina particles. The high hardness achieved with the addition of 8 g/L which recorded a hardness value of 95
HV. The improvement of the hardness of Ni-P/Al₂O₃ composite coating compared with binary Ni-P coating is due to alumina particles which were added in the coating process. As the alumina is one of the hard particles that used for wear resistance [10], this results in the improvement of the hardness of the coating layer. Alumina hard particles act as a barrier to plastic deformation of Ni–P matrix under the load [11]. As the higher amount of alumina particles added during the coating process, it produces a higher composition of alumina particles in coating layer. This result shows the similar trends with electroless Ni-P/WC composite coating that coated on steel [12]. They found that the hardness of Ni-P/WC composite coating on steel increases with an increment of WC composition. Meanwhile, in this research, increases of alumina particle composition used from 4 to 8 g/L during electroless nickel coating resulted in the increment of hardness of Ni-P/Al₂O₃ composite coating. Thus, sample with the highest hardness (8 g/L alumina) was used to evaluate the wear behaviour of Ni-P and Ni-P/Al₂O₃.

Figure 1. SEM morphology of Ni-P/Al₂O₃ coating layer with agitation of (a) 200 rpm, (b) 250 rpm, and (c) 300 rpm
Figure 2. Thickness of Ni-P/Al₂O₃ coating with agitation of (a) 200 rpm, (b) 250 rpm and (c) 300 rpm

Figure 3. EDX analysis of Ni-P/Al₂O₃ coating with different agitation (a) 200 rpm, (b) 250 rpm, (c) 300 rpm
3.3 Wear behavior

Wear test was performed to evaluate the Ni-P and Ni-P/Al₂O₃ composite coating performance on Al 6061 aluminium substrate at sliding speed of 0.5 m/s, sliding distance of 1000 m and at an applied load of 30 N. Figure 5 shows the wear rate of Ni-P/Al₂O₃ composite coating which was lower than Ni-P coating. This was due to the alumina particles acted as abrasive for the wearing toward the Ni-P coating. Alirezaei et al. [11] showed that the existence of hard alumina particles became a barrier to plastic deformation of Ni–P matrix under the load. Thus, the Ni-P/Al₂O₃ composite coating has lower wear rate. Devaraju et al. [13] have found that during wear process, the Al₂O₃ particles were released on the wear surface. Mahmoud et al. [14] and Tjong et al. [15] also found that both Al₂O₃ and boron nitride (BN) particles enhances the wear resistance.

4. Conclusion

The Ni-P/Al₂O₃ composite coating was successfully developed on the surface of Al 6061 alloy. The morphology of Ni-P/Al₂O₃ composite coating depends on the amount of alumina particle deposited.
The hardness of Ni-P/Al₂O₃ composite coating was improved with the increasing of alumina particles. The highest hardness of Ni-P/Al₂O₃ composite coating was 95 HV with containing 8 g/L of alumina particles. The wear rate of the Ni-P/Al₂O₃ composite coating was lower than Ni-P coating.

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References
[1] Afroukhteh, S, Dehghanian C and Emamy M 2012 Progress in Natural Science: Materials International 22 p 480–487.
[2] Chuang Y C, Chung S T, Chiu, S Y, Li C Y and Tsai W T 2013 Thin Solid Films 529 p 322–326.
[3] Dinakaran R, Arumugam A, Elansezhiyan R, 2013, Advance in Tribology 2013 p 304–308.
[4] Karthikeyan S and Ramamoorthy B 2014 Applied Surface Science 307 p 654–660.
[5] Malfiatti C F, Veit H M, Santos C B, Metzner M, Hololeczek H and Bonino J P 2009 Tribology Letters, 36 p 165–173.
[6] Karthikeyan S and Vijayaraghavan L 2016 International Journal of Materials, Mechanics and Manufacturing 4 p 106-110.
[7] Sen R, Das S and Das, K 2011 Surface and Coatings Technology 205 p 3847–3855.
[8] Bulsara V K, Thakuria H, Uppaluri R and Purkait M K 2011 Journal of Materials Processing Technology 211 p 1488–1499.
[9] Moonir-Vaghefi S M and Saatchi A 1997 Metal finishing p 102–106.
[10] Sahoo P and Das S K 2011 Materials and Design 32 1760–1775.
[11] Alirezaei S, Monirvaghefi S M, Salehi M, Saatchi A 2004 Surface and Coatings Technology 184 p 170–175.
[12] Hamid Z A, El Badry S A and Aal A A 2007 Surface and Coatings Technology 201 p 5948–5953.
[13] Devaraju A, Kumar A and Kumaraswamy A 2013 Materials and Design 51 p 331–341.
[14] Mahmoud E R I, Takashi M, Shibayanagi T, Ikeuchi K 2010 Wear 268 p 1111–1121.
[15] Tjong S C, Lau K C and Wu S Q 1999 Metallurgical and Materials Transactions A 30 p 2551–2555.