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Corrosion Resistance and Microhardness of Double Layer Coatings of Aluminium Alloy

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Abstract:
The anodized aluminium oxide and double layer of anodized aluminium oxide with electroless Ni-P coating on 6061 aluminium alloy substrate were prepared for corrosion resistance and microhardness. The corrosion resistance of the Anodized Aluminium Oxide (AAO) layer and double layer of anodized aluminium oxide with Ni-P coatings were compared by electrochemical impedance spectroscopy studies in 3.5 wt.% NaCl solution. A comparative study based on corrosion resistance and hardness was achieved. Compared with corrosion studies, it was found that the anodized aluminium oxide coating shows a high resistance of corrosion than the double layer of anodized aluminium oxide with Ni-P coating. Microhardness found anodized aluminium oxide with Ni-P was shows more than anodized aluminium oxide layer due to filled Ni-P into anodized aluminium oxide. The results indicate that the anodized aluminium oxide coating can be a better corrosion protection on aluminium alloys than double layer of anodized anodizing aluminium oxide with electroless Ni-P coatings.

Keywords: Anodized aluminium oxide, Electroless Ni-P coating, Corrosion resistance, Aluminium alloys, Electrochemical impedance spectroscopy

1. Introduction

Aluminum and its alloys are increasingly used in many fields due to their physical properties such as low density, high specific strength, thermal and electrical conductivities that make them suitable for various applications [1, 2]. Aluminium is a very reactive metal and Aluminum alloys coated with surface composite films that have good wear-resistance and self-lubrication properties are desired for such applications [3, 4]. Sulphuric acid is the most widely used among all the various anodizing process available commercially. The nature of the anodic coating was a amorphous. Anodizing process has been widely adopted in industry to improve the properties of aluminium and its alloys, as it allows the growth of an alumina film on the aluminium substrate with excellent corrosion resistance and mechanical characteristics [5]. Anodized aluminium oxide has a duplex structure consisting of inner barrier layer and the outer porous layer. The barrier layer is very thin and dense. The outer porous layer is a much thicker, porous oxide that has a close-packed hexagonal cells structure [6-8]. The anodized aluminum oxide layer consists of open pores that can be filled with a conducting material by electrochemical deposition such as electroless nickel plating to increase its micro harness and determine the corrosion resistance.

Ni-P alloys are very useful in automobiles, aviation, printing, chemical industrial machine, and other fields. They are used especially to plate cylinders, pistons, revolving shafts, compressors, rollers machine, and shaping molds [9-12]. Ni-P coatings exhibit high hardness and excellent machineability such as protective or decorative coatings in many industries, including petroleum, chemical, plastic, optics, printing, mining, aerospace, nuclear, automotive, electronics, computer, textile, paper, and food. The electroless nickel method was developed by Mandich and Krulik [13]. Electroless nickel plating is a chemical reduction process in a solution to reduce metallic ion to the metal state by using a reducing agent. Electroless nickel is used to protect the metals like aluminum, magnesium, titanium, copper and steel from corrosion [14].

In this present study, the electroless plating on anodized aluminium oxide surface deposited on Al 6061 alloy in order to find its the corrosion-resistant and microhardness of the coating. The comparision of corrosion resistance of the anodized aluminium oxide coating and electroless nickel plating were studied by Electrochemical Impedance Spectroscopy (EIS). Microhardness of coatings was evaluated using a Vickers microhardness tester.

2. Experimental Methods

Aluminium alloy 6061 sample with size of 30x30x0.1 mm were taken and polished mechanically to obtain smooth surfaces. The chemical composition of AA6061 is Al-97.9%, Mg-1.0%, Si-0.6%, Cu-0.25% and Cr-0.25%. Samples were then pre-cleaned by trichloroethylene for 10 min and degreased in aqueous mixed sodium carbonate, trisodium orthophosphate and sodium metasilicate solution for 10 min at 60 °C. In order to neutralize the surface, the samples are immersed in a sulphuric acid,

hydrofluoric acid and nitric acid solution for 2 min at room temperature. Anodizing experiment is carried out in a 15% H_2SO_4 bath under 16 V for 30 min at room temperature to obtain an anodic coating of approximately 18-20 μm thickness. The aluminium alloy sheet was used as anode and a lead used as cathode. All the chemicals used were of laboratory chemicals and de-mineralized water was used throughout. The AAO substrate then was subjected to sensitization and activation prior to electroless nickel plating. Sensitization and activation process were carried out by a solution containing tin chloride and palladium chloride. Then the specimens were put into the electroless nickel plating solutions after activation process. Nickel sulphate is used for nickel source, sodium hypophosphite is used as reducing agent in electroless nickel plating. The formulation of the activation process and electroless nickel plating is given in table 1. The pH of the solution was adjusted by adding 15% ammonia and 15% H2SO4. The thickness of the anodic coating was measured using Fisher isoscope thickness meter equipped with principle of eddy current. The average thickness of 10 measuring points was taken on both sides. The thickness of the AAO + electroless Ni-P coating layer was determined from the amount of deposited material and material density by using the equation given below. W1 was the before electroless Ni-P and W2 was the after electroless Ni-P coating. W1 and W2 were measured using an analytical balance with the precision of 0.0001g. The density (ρ) of electroless Ni-P coating was 8.9 g/cm^3. A was the total surface of the samples.

$$\delta = \frac{W2-W1}{\rho.A} \times 10^{-4}$$

The corrosion resistance of the coating was evaluated by EIS and it was performed in a conventional three electrode cell using a computer-controlled potentiostat /galvanostat (Autolab PGSTAT 302N potentiosat from Eco-chemie, Netherlands). Platinum electrode was used as the counter electrode, Ag/AgCl, 3M KCl as the reference electrode and the AAO and AAO + electroless Ni-P coated sample with an exposed area of 1 cm^2 as working electrode (WE). All experiments were performed in 3.5 wt.% NaCl solution at room temperature.

Before each EIS studies, the electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time up to 30 min to attain a stable state. EIS measurements were carried out using AC signals at the amplitude of 10 mV and measurement frequency range from 100 kHz-10 mHz at the stable OCP. Fresh solution and fresh samples were used after each sweep.

Microhardness of the AAO and AAO + electroless Ni-P coatings were evaluated using a Vickers microhardness tester, Wolpert Wilson Instruments, Germany. It was measured using a diamond indenter at a 50 gf load for 10 s. Five measurements were taken on each plated coatings and the values were then averaged.

3. Result and discussion

3.1. Effect of Current Density and Thickness

In the initial stages of anodizing, a small barrier layer formed during the process on aluminium surface at lower current density. After this barrier layer a thicker pores are formed owing to the increasing current density. Then a porous oxide layer formation is achieved and current density value is remaining constant in time. Temperature was increased at the time of anodizing due to it's a significant current density increase.

The thickness of the barrier layer was around 1-2% of the total AAO layer formed. The growth of the aluminium anodic oxide layer is formed from the bottom of the pores layer where the barrier layer is coated. The AAO coating thickness was around 18μm. However, the oxide layer thickness will not continue to increase because of the dissolution rate. This thickness of the layer provides the resistance of the total systems. After anodized aluminium oxide coating, the sensitization process involves a bigger role to obtain Ni-P coating by electroless method. The porous oxide layers of the anodic coating were completely filled with Ni-P electrolessly at a high aspect ratio. The Ni-P coating thickness was around 10 μm for 45 mins on anodic coating of the aluminium samples.

3.2. Corrosion Studies by Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) method is used to investigate the corrosion resistance of AAO and AAO + electroless Ni-P coating double layer on aluminium 6061 alloy. Figure 1 shows Nyquist plot of the AAO in 3.5 % NaCl solution for 30 min. Only one capacitive loop is found at high frequency side. The impedance values are calculated using by the diameters of capacitance. From the table 1 shows that the Rp value of AAO was 4.55 x 10^7 Ω and CPE value was 3.49 x 10^{-7}. The Figure 1 results indicates that the porous layer has a high conductivity of the electrolytic solution inside the pores [15,16]. The electrolyte of anodic coating can easily penetrate through the porous layer to attack barrier layer. Parameter Rp represents corrosion resistance of the aluminum substrate and parameter Constant Phase Element (CPE) corresponds to the double layer capacitance of the substrate. From figure 1 it can be seen that the resistance of the porous layer increases while capacitance of the porous layer decreases because of porous layers become more resistant. Electrolyte may be absorbed into the pores in the anodic film when anodized samples are immersed into solution [17, 18]. It is clear that the Rp value increases and the CPE value decrease. Figure 2 shows that the Bode plot (Modulus and phase angle) of AAO and AAO + electroless Ni-P coating of EIS for the AAO immersed in 3.5 wt.% NaCl solutions.

Figure 3 shows Nyquist plot of the AAO + Ni-P coatings in 3.5% NaCl solution at their respective open circuit potentials. It can be seen that the resistance decreases significantly with the decrease in diameter and compare to the anodic coating in figure 1. The semi circle diameter indicates the corrosion resistance of AAO+ Ni-P coatings. The high frequency capacitance loop was indicated charge transfer resistance and the low frequency inductive loop was attributed to the corrosion resistance of Ni-P

coating. Rp value of AAO + Ni-P was 9.4 x10^3 and CPE value was 3.14 x 10^{-5} than the anodic coating because of the Ni-P filled in the porous layer of the AAO coating.

3.3. Hardness

In general, the microhardness of the coatings is relative not only to microstructures but to chemical compositions. Table 2 shows that the hardness of the anodizing was found at 123 VHN and AAO+ Ni-P was found at 650 VHN. In addition, Ni-P is a hard coating and the higher metal content in the coatings is also helpful to improve the microhardness. AAO was less hardness than double layer AAO+ Ni-P coating due to its metal dense. Surface morphology of the coatings is given in Figure 4.

4. Conclusion

The AAO and electroless Ni-P coatings on aluminium 6061 alloy substrate were successfully prepared using sulphuric acid and nickel sulphate bath. The microhardness and corrosion resistance of the AAO and AAO + Ni-P coatings were found and compared. Based on the experimental studies, the following conclusion can be drawn.

- The AAO coating can be obtained directly by sulphuric acid on aluminium alloys.
- The AAO and electroless Ni-P coatings can be obtained by sensitization and activation process. Tin chloride and palladium chloride were played a activation processes.
- The hardness of AAO and electroless Ni-P coatings have superior than AAO.
- Corrosion resistance of the AAO showed much better than the AAO and electroless Ni-P coatings due to its porous oxide layer.

5. References

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Annexture

Sl. No.	Baths	Bath Composition and conditions
1	Anodizing	Sulphuric Acid : 15 % Temperature : $25 \pm 5\,°C$ Time : 20 – 50 min Voltage : 16 – 18 V
2	Senzitization	$SnCl_2$: 10 g / L HCl : 10 ml /L Temperature : $25 \pm 5\,°C$ Time : 2 – 3 min
3	Activation	$PdCl_2$: 1 g / L HCl : 10 ml / L Temperature : $25 \pm 5\,°C$ Time : 1-2 min
4	Electroless Ni-P	Nickel Sulphate : 30 g / L Sodium Hypoposphite : 10 g / L Sodium Citrate : 10 g / L Sodium Acetate : 5 g / L Thiourea : 1 mg / L Temperature : $82 \pm 2\,°C$ Time : 45 min pH : 4.8 ± 0.2

Table 1: Bath compositions and conditions of AAO and AAO + electroless Ni-P coating on aluminium 6061 alloys.

Coatings	Rs (Ω)	CPE (F)	Rp (Ω)
AAO	572.37	3.49×10^{-7}	4.56×10^{7}
AAO+Ni-P	5.4794	3.14×10^{-5}	9417.6

Table 2: EIS studies of AAO and AAO+ Ni-P coatings immersed in 3.5 wt.% NaCl solutions
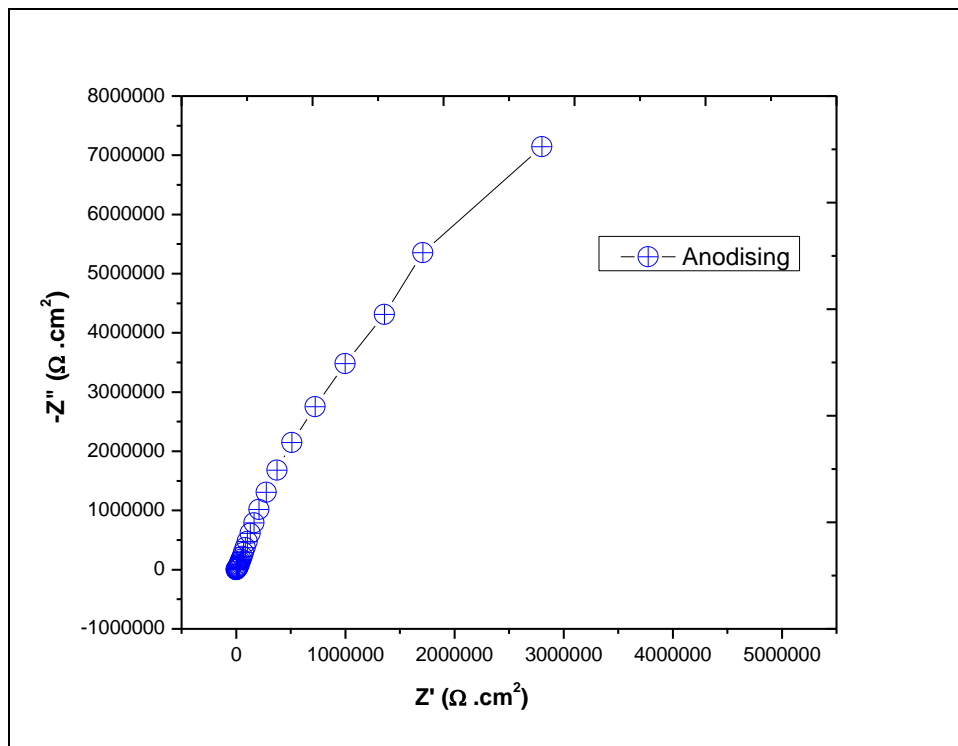

Figure 1: Nyqust plot of EIS for the anodic coating immersed in 3.5 wt.% NaCl solutions
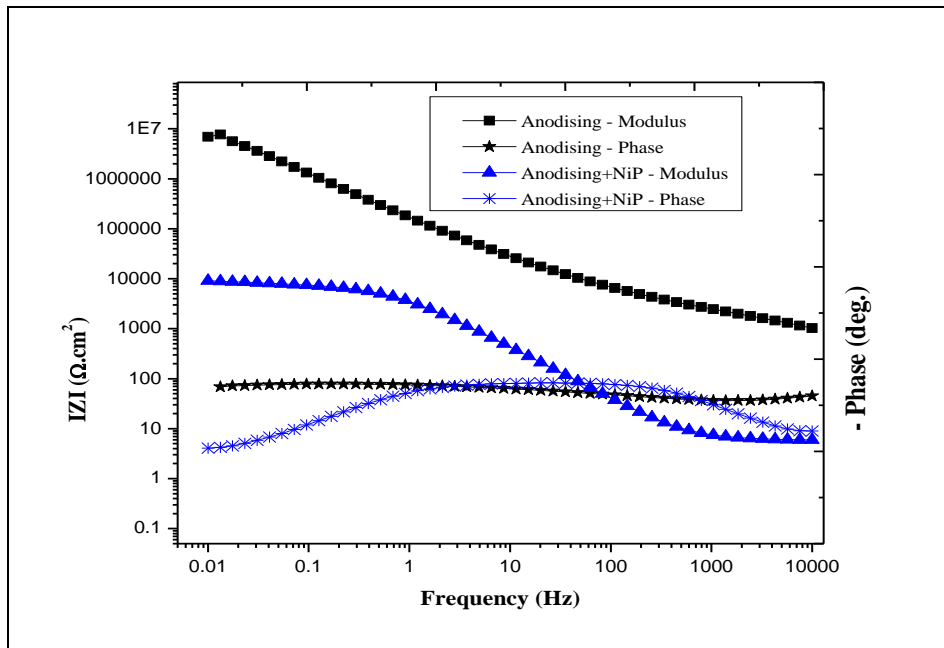
Figure 2: Bot plot (Modulus and phase angle) of EIS for the AAO immersed in 3.5 wt.% NaCl solutions

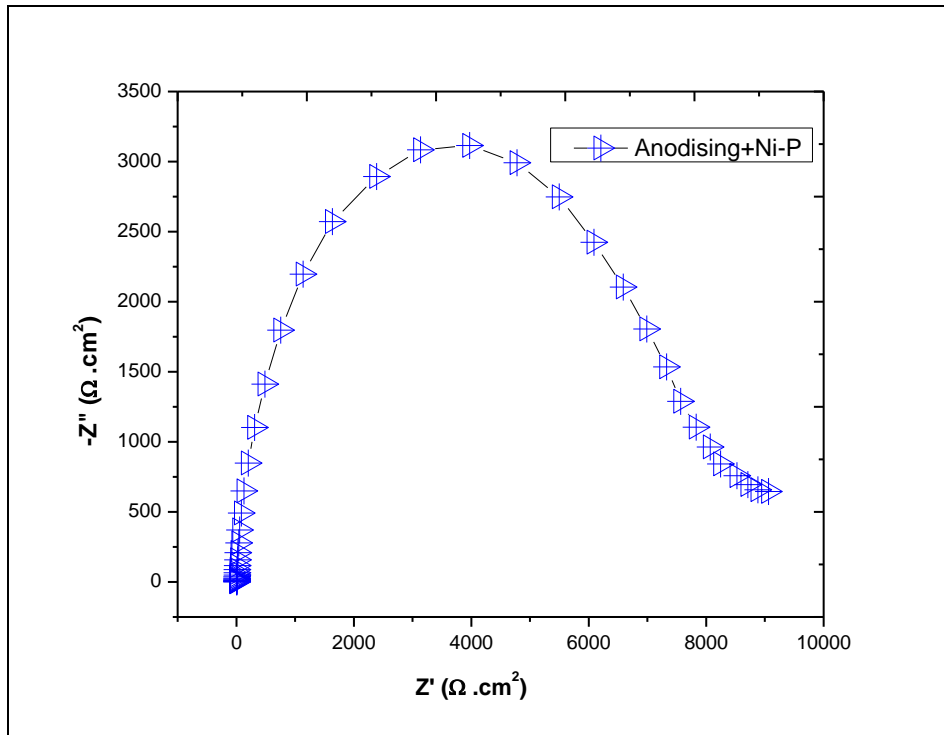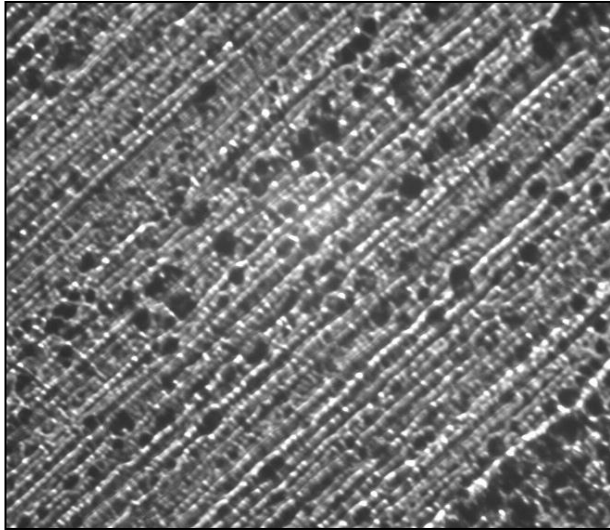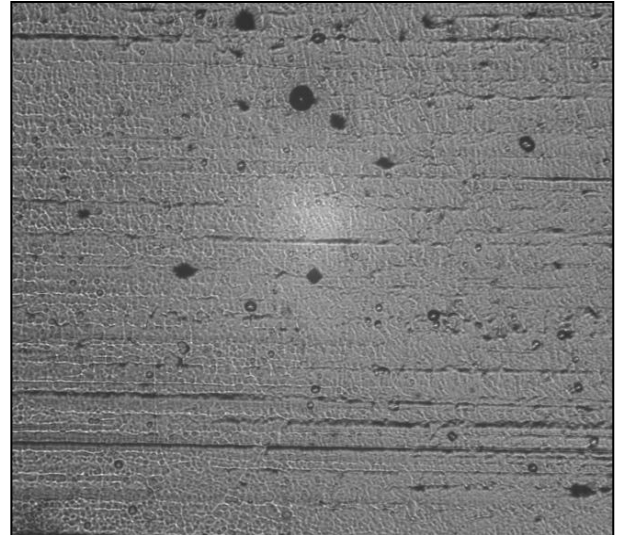*Figure 3: Nyqust plot of EIS for the anodic coating plus Ni-P immersed in 3.5 wt.% NaCl solutions*

(a)   (b)

Figure 4: Surface morphology of A) AAO and B) AAO + Ni-P coatings