Preparation and Corrosion Resistance of Electroless Ni-P Coating on Open-Cell Aluminum Foams

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The electroless Ni-P coatings were deposited on open-cell aluminum foams substrate by using hypophosphite as a reducing agent. Ni-strike was developed as a pre-treatment for Ni-P coatings to interlock between the substrate and coatings. Thereby, it improves the corrosion resistance of Ni-P coatings on open-cell aluminum foams substrate. The surface morphology, structure and phases of the Ni-P coatings were characterized by SEM-EDS and XRD. The corrosion behaviours of the coated and uncoated aluminum foams were evaluated by immersion test and electrochemical polarization measurement. The experimental results show that the Ni-P coatings cover the entire surface with a thickness of ~25 μ m. The coated aluminum foams have good corrosion potential and enhanced corrosion resistance compared with as-received aluminum foams.

Keywords: Open-cell Foams; Aluminum; Electroless nickel; SEM-EDS; Corrosion

1. INTRODUCTION

Recently, aluminum foams with open-cell structure receive a wide attention because they exhibit a unique combination of mechanical and functional properties due to their special cellular structure [1]. However, the applications of aluminum foams are restricted due to its relative poor corrosion resistance in humid and salty environments. Surface treatment is a proper approach to increase the corrosion resistance of aluminum and its alloy. Therefore, some surface treatment methods have been carried out on aluminum foams [2, 3]. These studies on the surface treatment of the aluminum foams were aimed to increase the mechanical and corrosion resistance properties of the aluminum foams. The ceramic coatings were formed on open-cell aluminum foams by micro-arc

oxidation to increase their mechanical strength [2]. Electrodeposited Ni-W coatings were deposited on open-cell aluminum foams, which increase both the compressive strength and energy absorption [3].

Electroless deposition can provide a protective coating for aluminum and its alloy. This technology is widely used in different industrial applications to improve the wear resistances, mechanical properties and corrosion resistance of various aluminum alloys [4-8]. A suitable surface preparation (cleaning, pickling, polishing, activation, etc.) is an essential step before any plating procedure on aluminum alloys [5-7]. Therefore, the electroless coatings can cover the complex-shaped components uniformly, such as those with holes or internal surfaces [6-8]. To date, corrosion resistance was increased by micro-arc oxidation and electroless plating on open-cell and closed-cell aluminum foams, respectively [9-11]. Nevertheless, the study on electroless coatings on open-cell aluminum foams was not yet studied and it is new to open-cell aluminum foams. Hence, in this study, the preparation and characterization of open-cell aluminum foams with electroless Ni-P (EN) coatings has been investigated in detail.

2. EXPERIMENTAL PROCEDURE

2.1 Electroless deposition procedure

Table 1. Technical process and bath composition of the Ni-strike pre-treatment and EN coating on open-cell aluminum foams.

Process* Ultrasonic Cleaning	Plating parameters and composition Acetone	Conditions 3 min at RT
Degreasing bath	Na ₂ CO ₃ - 10 g/L Na ₃ PO ₄ 12H ₂ O - 50 g/L	2 min at 65 °C
Etching bath	Conc. $H_2SO_4 - 40 \text{ ml/L}$ $H_3PO_4 - 20 \text{ ml/L}$ DM water - 40 ml/L $C_3H_6O_2 - 1 \text{ ml/L}$	2 min at 65 °C
Pre-treatment bath for Ni strike	NiSO ₄ ^{.7} H ₂ O - 28 g/L HF (40 %) - 90 ml/L H ₃ BO ₃ - 40 g/L	1 min at RT
Electroless nickel	NiSO ₄ · $6H_2O$ - 0.1 mol/L NaH ₂ PO·H ₂ O - 0.35 mol/L C ₂ H ₅ NO ₂ - 0.09 mol/L C ₃ H ₆ O ₃ - 0.40 mol/L C ₃ H ₆ O ₂ - 0.02 mol/L Stabilizer - 1 ppm	120 min at 85 °C at pH 6.00

- In between each process rinse with deionized water.

The open-cell aluminum foams were fabricated from Al-7mass%, Si-0.3mass%, Mg alloy by the infiltration method. The as-fabricated foams were cut into samples $(15 \times 10 \times 10 \text{ (all in mm)})$ and

were ultrasonically cleaned in acetone, and followed by alkaline cleaning and Ni-strike pre-treatment activating process. The nickel immersion (Ni-strike) plating solution contained hydrogen fluoride, nickel salts and boric acid. The process was kept for 1 min at room temperature. A thin film of Ni was produced on the substrate by contact reduction type reaction between substrate and nickel salt solution (Table-1). The Ni nucleus on the open-cell aluminum foams effectively produced and acts as a catalyst for the succeeding EN coatings [12]. The pre-treated sample was immersed in the electroless bath solution for EN layer. The bath composition and all operation parameters for the EN deposition are reported in Table 1.

2.2 Characterizations

The surface morphology and compositions of the EN coating was evaluated by using a scanning electron microscope (SEM, EVO@18, ZEISS) attached with energy-dispersive spectroscopy (EDS, INCA, Oxford). The phases of the EN coatings were employed to identify by X-ray diffraction (XRD, D/MAX2500PC, Cu K α). The thickness of the EN layers could also be measured on the SEM images taken on the cross-sections of some representative samples.

2.3 Corrosion test

The immersion test was carried out in a 3.5 wt.% NaCl solution. Electrochemical methods are popular because they can be carried out in a few hours. They are based on the measurement of the current as a function of the voltage applied to the test piece. The electrochemical test was carried out in a 3.5 wt.% NaCl solution (at room temperature) in a three-electrode cell using an electrochemical analyzer (Versa STAT-3, AMETEK); with a platinum plate as counter electrode and a saturated calomel electrode (SCE, +242 mV vs. SHE) as a reference electrode. Pitting corrosion potential is an important property for industrial corrosion resistance of the metal materials, and therefore, linear sweep voltammetric (LSV) tests were performed in a 3.5 wt.% NaCl solution to study the pitting behavior for both uncoated and coated open-cell aluminum foams.

3. RESULTS AND DISCUSSION

3.1 Surface morphology and compositions of the EN coatings

Fig.1 shows the optical images of the open-cell aluminum foams. It shows the porous nature of the aluminum foams. Fig.2 (a & b) shows the SEM surface morphology of EN coatings on the open-cell aluminum foams. The EN layers showed a rough surface with small grain both in lower and higher magnification. The coatings cover not only external surface but also internal surface of the open-cell foams. Fig. 2 (c) shows the cross-section of the EN coating on the foams. For many practical applications electroless nickel-phosphorus layers must have at least a 10-20 μ m thickness. In this study, the average thickness of the EN coatings is ~ 25 μ m as it can be seen from the SEM cross-section image.

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Fig.3 shows the EDS analysis of the cross section of the EN coatings. Aluminum, silicon, nickel and phosphorus elements were detected, which indicate that the coatings consist chiefly of nickel and phosphorus. Furthermore, the EDS analysis also indicates that EN coatings are uniform. The coating uniformity is also revealed from the cross-section of the SEM image and it is the special characteristic of the electroless coating than electroplating.



Figure 1. Image of the open-cell aluminum foams



Figure 2. SEM images of the coatings on the open-cell aluminum foams: (a & b) surface of the coatings and (c) cross section of the coatings.



Figure 3. Element distributions of cross-section of EN coatings on the open-cell aluminum foams from energy-dispersive spectra.

3.2 Phases of the EN coatings

Fig.4 (a & b) shows the XRD profiles of the top surface of the as-received aluminum foams and coated aluminum foams with EN coating, respectively. Fig.4 (a) indicates only the peaks of Al and Si. Fig.5 (b) indicates single wide angular range of 40° - 50° diffraction was observed, which is from the (111) diffraction of nickel ($2\theta = 44.8^{\circ}$). Generally, the phosphorus content plays an important role in determining the structure and properties of the EN coatings [6-8, 13]. The EN coatings contain high phosphorus are mainly composed of amorphous structure, and show a high anticorrosive property. On contrary, the EN coatings contain low phosphorus are mainly composed of nanocrystalline structure, and show a high mechanical property [7, 8]. The grain size (d) of the Ni can be determined from the (111) peak via the Debye-Scherrer equation [13].

$$d_{XRD} = K\lambda/\beta(\theta)\cos(\theta)$$
(1)

Where, λ is the X-ray wavelength, β is the FWHM of the (111) diffraction peak, θ is the diffraction angle and the constant K ~ 1. The average grain size is 14 nm and EDS analysis on the surface of EN coating shows phosphorus content (9-10 wt.% P, balance wt.% Ni). The present case is medium phosphorous range and it is a mixture of amorphous plus nanocrystalline phase [14].



Figure 4. X-ray diffraction pattern of open-cell aluminum foams (a) and electroless coatings on open-cell aluminum foams (b).

3.3 Immersion test result of the EN coatings

Fig.5 and Fig.6 show the corrosion morphologies of uncoated and coated aluminum foams after immerse in 3.5 wt.% NaCl solution for 100 and 300 h, respectively. Fig.5 (a & b) shows that some pits are formed on uncoated aluminum foams when exposed to a chloride media in 100h. Generally, aluminum alloy usually has low corrosion rates because its surface is covered with a protective oxide layer [15]. For aluminum foams fabricated by infiltration process, the thin oxide layers with the thickness of 100 nm protect the reaction between aluminum and chloride corrosion medium. This oxide layer contains bayerite crystal lying on a soft gelatinous hydroxide layer [16]. And an inner hard amorphous alumina layer situates between the aluminum and the gelatinous hydroxide layer [16, 17]. But when exposed to a chloride media, the pit flaws in the oxide layer are unable to be repaired immediately. Fig.5 (c) shows that the coated aluminum foams. The EDS image (Fig.5 (d)) reveals that there is no evident of base aluminum peaks on the surface, so the EN coating protect the surface effectively from chloride media in 100h.

Fig. 6 (a, b, c & d) shows corrosion morphologies (in 300h) of uncoated aluminum foams in 50 x, 500 x, 2000 x magnification and its EDS analysis, respectively. Furthermore, Fig. 6 (a', b', c' & d') shows the corrosion morphologies (in 300h) of coated aluminum foams and its EDS analysis. The oxide layers in the uncoated aluminum foams breaks down in 300h immersion and more corrosion

product forms on the surface. On the other hand, EN coating starts forming the cracks from which the corrosion is initiating and its EDS analysis shows the Al corrosion product on the coated surface.



Figure 5. Corrosion morphologies of: uncoated aluminum foams and its EDS analysis (a & b), coated aluminum foams and its EDS analysis(c & d), after immerse in 3.5 wt.% NaCl solution for 100 h.





Figure 6. Corrosion morphologies of: uncoated aluminum foams (a, b & c) and its EDS analysis (d), coated aluminum foams (a', b' & c') and its EDS analysis (d'), after immerse in 3.5 wt.% NaCl solution for 300 h.

3.4 Electrochemical behavior of the EN coatings

Fig. 7 shows the potentiodynamic polarization curves of the as-received aluminum foams and EN coated aluminum foams. Active-passive polarization behaviors were observed for the both coated and un-coated foams (Fig. 7). The polarization curve in an aqueous medium is the sum of the electrochemical reactions.

In the cathodic curve, reduction of H⁺ions:

$$3\mathrm{H}^{+} + 3\mathrm{e}^{-} \rightarrow 3/2 \mathrm{H}_{2} \tag{2}$$

In the anodic curve, oxidation of aluminum:



 $Al \to Al^{3+} + 3e^{-} \tag{3}$

Figure 7. Polarization curves of open-cell foams with and without EN coated.

From the electrochemical polarization curve (Fig. 7), the passivation parameters, i.e., zero current potential (ZCP), potential for primary passivation (E_{pp}), potential for complete passivation (E_{cp}), critical current density (I_{crit}), passive current density (I_{pass}), passive range (E_b-E_{cp}) and break-down potential (E_b) shows improvement after electroless plating (in Table-2). The critical current densities and passive current densities were determined at E_{pp} and E_{cp} , respectively. ZCP shifted towards noble direction and passive current density had improved [18]. The positive shift in the ZCP is actually a consequence of the lower corrosion rate reducing the demand for cathodic current from the reduction of dissolved oxygen. The critical current densities of passivation were not similar. This demonstrates that the mechanism of onset of passivity and passivation itself is not similar. There was a change in the passive range for uncoated compared to coated. The passive current density changes for uncoated compared to coated. This could be defective nature of the passive film formed on coated surface. The passive film get breakdown and pitting corrosion occur, as the applied anodic potential increase. Recent study showed that EN coating containing high phosphorus content reacts with electrolyte to form a layer of adsorbed hypophosphite anions [19]. This will block the supply chain of electrolyte to the electrode surface, thereby preventing the hydration of nickel. Therefore, this might to be the main mechanism of the coated foams to form a passive nickel film during electrochemical corrosion. For the as-received foams, the oxide layers play an important part in preventing the reaction between aluminum substrate and chloride corrosion medium. Therefore, the oxide layers are considered as the passive film for the un-coated foams.

In fact, there is little advantage to plot these polarization curves completely, because only the area around the corrosion potential (the dissolution potential) is useful for determining the corrosion

current. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are important parameters to evaluate the corrosion resistances of materials. This corrosion current can be measured in two ways: by the Tafel slope and by the polarization resistance [20]. In this study, these values can be derived from the Tafel region extrapolation. Compared with uncoated foams, the corrosion potential of coated foams is positively shifted from -1.521 V to -0.756 V. Moreover, the corrosion current density of coated foams is decreased from 212.14 μ A/cm² to 11.65 μ A/cm². Therefore, the EN coating can provide a good anticorrosion performance to open-cell aluminum foams.

Passivation parameters	Un-coated	EN Coated
	foams	foams
ZCP (mV vs. SCE)	-1521	-756
E_{pp} (mV vs. SCE)	-1428	-538
E_{cp} (mV vs. SCE)	-1374	-450
E_b (mV vs. SCE)	-799	+45
$E_b - E_{cp} (mV)$	575	495
I_{crit} ($\mu A/cm2$)	310.69	628.7
I_{pass} ($\mu A/cm2$)	341.37	1087.3

Table 2. Parameters obtained from polarization curves of the open-cell foams with and without EN coating in 3.5 wt.% NaCl at room temperature.

Table 3. LSV test results of the open-cell foams with and without EN coating in 3.5 wt.% NaCl at room temperature.

Sample	Pitting Potential (Vs. SCE)/mV	Passive film stability range (Vs. SCE)/mV
Un-coated	-788±10.5	565±5.6
EN Coated	+42±6.4	505±7.2

Table 3 shows the experimental results of LSV test for the EN coated open-cell aluminum foams and as-received aluminum foams. From the LSV result, the pitting corrosion potential was dramatically improved from -788 mV Vs. SCE (un-coated foams) to +42 mV Vs. SCE (EN coated foams). Furthermore, passive film stability ranges are almost same. This indicates the EN coating is beneficial for improving corrosion resistance to open-cell aluminum foams.

4. CONCLUSION

The EN coatings successfully fabricated on open-cell aluminum foams and the corrosion resistance was improved. The following conclusion can be drawn from the study:

The EN coatings cover the entire complex shaped open-cell aluminum foams uniformly. After the EN deposit, the coated foams have a lower corrosion current density and higher corrosion potential than the as-received foams. The pitting corrosion potential was dramatically improved from -788 mV to +42 mV Vs. SCE range, which also implies that the increasing anticorrosion property of the coated foams compared with un-coated foams. The present study reveals that the EN deposits on open-cell aluminum foams can extent the application of the foams in various industry fields.

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