Surface & Coatings Technology 228 (2013) 34–40

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effect of nickel immersion pretreatment on the corrosion performance of electroless deposited Ni–P alloys on aluminum

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ARTICLE INFO

Article history:
Received 4 February 2013
Accepted in revised form 1 April 2013
Available online 6 April 2013

Keywords:
Electroless Ni–P plating
Nickel immersion pretreatment
Corrosion
Electrochemical impedance spectroscopy

ABSTRACT

Ni–P alloys with 7 wt% to 10 wt% phosphorus were deposited by sodium hypophosphite onto industrially pure aluminum substrates after different pretreatments. Two nickel immersion pretreatments (NIPs) were tested prior to electroless Ni–P plating, and their effects on the corrosion properties of the Ni–P alloy layers were evaluated using polarization curves and electrochemical impedance spectroscopy. The surface morphology and chemical composition of the Ni–P coatings were investigated by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction analysis. Both proposed NIPs were found to improve the corrosion resistance. Thus, a double NIP method similar to the double zincate treatment method was developed. The alloy layer pretreated by this developed method showed the highest corrosion resistance, which can be mainly attributed to the high phosphorus content and low microporosity.

1. Introduction

Aluminum alloys are widely used in the spacecraft industry because of their light weight, high strength-to-weight ratio and excellent workability. However, the application of Al alloys is limited due to their undesirable properties such as low microhardness, poor corrosion and wear resistance. Thus, protective surface modification is essential to the manufacturing process of aluminum components. Amongst various surface treatment techniques, electroless nickel (EN) plating attracts considerable attention because of its advantages such as high corrosion resistance and wear resistance, high lubricity and solderability, non-magnetism, improved microhardness as well as coating thickness uniformity [1–3].

However, EN deposition onto aluminum substrate has technical limits [4–6].

Firstly, aluminum and its alloys are covered on their natural state by a tightly adhering, dense oxide film approximately 0.02 μm thick that forms upon exposure of the film to the atmosphere. Freshly exposed aluminum is rapidly covered with an oxide film in aqueous solution, which impedes the formation of a metal-to-metal bond with the deposited metal. Direct electroless deposition on aluminum usually results in unsatisfactory adhesion.

Secondly, given that the electrode potential of aluminum is very low (approximately −1.67 V), aluminum easily loses electrons. Without proper pretreatment, aluminum substrates rapidly react with metal ions in solutions. Then a loose and rough layer is produced, which affects the bonding strength between the substrate and the coatings as well as other properties of the material.

Finally, the dissolution of aluminum in acid and alkaline solutions contaminates the bath, which leads to the decomposition of the electroless deposition solution. This phenomenon is a major challenge in the application of electroless deposition.

To solve these three problems, an efficient pretreatment method similar to the well-established and commonly adopted zincate treatment should be developed. In the zincate treatment method, the surfaces of substrates are covered with zinc film by a replacement reaction of aluminum and zinc [7–9]. In the double zincate treatment method, the alloy is subjected to the conversion treatment twice. This technique remarkably increases the adhesive strength and other properties of electroless plated films onto substrates [10,11]. However, the zinc layer acts as an anode during nickel plating in humid environments and lateral etching occurs, which eventually leading to nickel layer peeling. As an alternative to the zinc immersion method, nickel immersion [6,12–14] is widely used before EN deposition.

In this study, aluminum samples were pretreated by two different nickel immersion methods. The corrosion behaviours of all coatings were measured by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [15–17] in 3.5 wt.% NaCl solution. Then we selected a pretreatment method from the first pretreatment and developed it into a double nickel immersion pretreatment (NIP) method. This developed method, which was similar to the double zincate treatment, provided better corrosion resistance than direct EN plating.

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http://dx.doi.org/10.1016/j.surfcoat.2013.04.001

2. Experimental details

2.1. Material preparation

Commercially pure aluminum samples 30 mm × 10 mm × 1.5 mm in size were used in the experiments. The samples were subjected to surface finishing by grounding them successively with sand papers (nos. 1000, 1500 and 2000) and polishing to a mirror finish. After thoroughly cleaning, the samples were degreased in acetone, cleaned with ethanol and dried in air. Then, the samples were pretreated based on the main condition parameters shown in Table 1. The aluminum substrate was activated by using 250 mL/L aqueous ammonia and 6 g/L sodium citrate. The pH values of all solutions were adjusted with aqueous ammonia. Copper sulphate and sodium thiosulphate were added to the EN bath as stabilisers.

2.2. Pretreatment and coating deposition

Five samples labelled as sample 1 to sample 5 were pretreated with five methods. The first three methods were single pretreatments, and the other two were double (nickel immersion) pretreatments. Afterwards, the samples were placed in the same EN bath for 50 min and treated as follows. For sample 1, direct electroless Ni–P plating onto the Al substrate was conducted without other pretreatment. For sample 2, No. 1 nickel immersion and electroless Ni–P deposition were performed. For sample 3, No. 2 nickel immersion and electroless Ni–P deposition was conducted. For sample 4, No. 1 nickel immersion was conducted, following by immersion in 68 wt% concentrated nitric acid for 5 s to remove the nickel film obtained in the first nickel immersion process. The sample was then cleaned with distilled water, and activation was repeated. Afterwards, No. 2 nickel immersion was performed, following by electroless Ni–P deposition. For sample 5, No. 2 nickel immersion was performed following by immersing in 68 wt% concentrated nitric acid for 5 s. The sample was then cleaned with distilled water, and activation was repeated. Afterwards, No. 2 nickel immersion was again performed, following by electroless Ni–P deposition.

2.3. Electrochemical measurements

All tests were performed by using the CHI660C electrochemical workstation (Chenhua Instrument Company). Before the tests, the surfaces were degreased with ethanol by using an ultrasonic oscillator and dried in air. The experiment was conducted by using near-neutral (pH 6.9–7.0) 3.5% NaCl solution in air at room temperature.

A conventional three-electrode setup [18] was used. The sample served as the working electrode, a saturated calomel electrode served as the reference electrode and a platinum net served as the auxiliary electrode. For each sample, the open circuit potential (OCP) was first

Table 1
Condition parameters for pretreatments and Ni–P deposition onto aluminum.

Process	pH	Solution composition	Temperature (°C)	Time (min)
Activation		250 mL/L aqueous ammonia 6 g/L sodium citrate	Room temperature	1
No. 1 nickel immersion	10–11	6 g/L sodium citrate 2 g/L nickel acetate 10 mL/L lactic acid 10 mL/L triethanolamine	Room temperature	1
No. 2 nickel immersion	9.0–9.5	13 g/L nickel sulphate 30 g/L sodium hypophosphite 40 g/L sodium citrate 30 g/L ammonium chloride	40 °C	3
EN plating	5.0	27 g/L nickel sulphate 30 g/L hypophosphite 20 g/L sodium acetate 1.2 g/L sodium citrate 31 mL/L lactic acid 3.7 mL/L propionic acid 5 mg/L copper sulphate 5 mg/L sodium thiosulphate	91 ± 1 °C	50

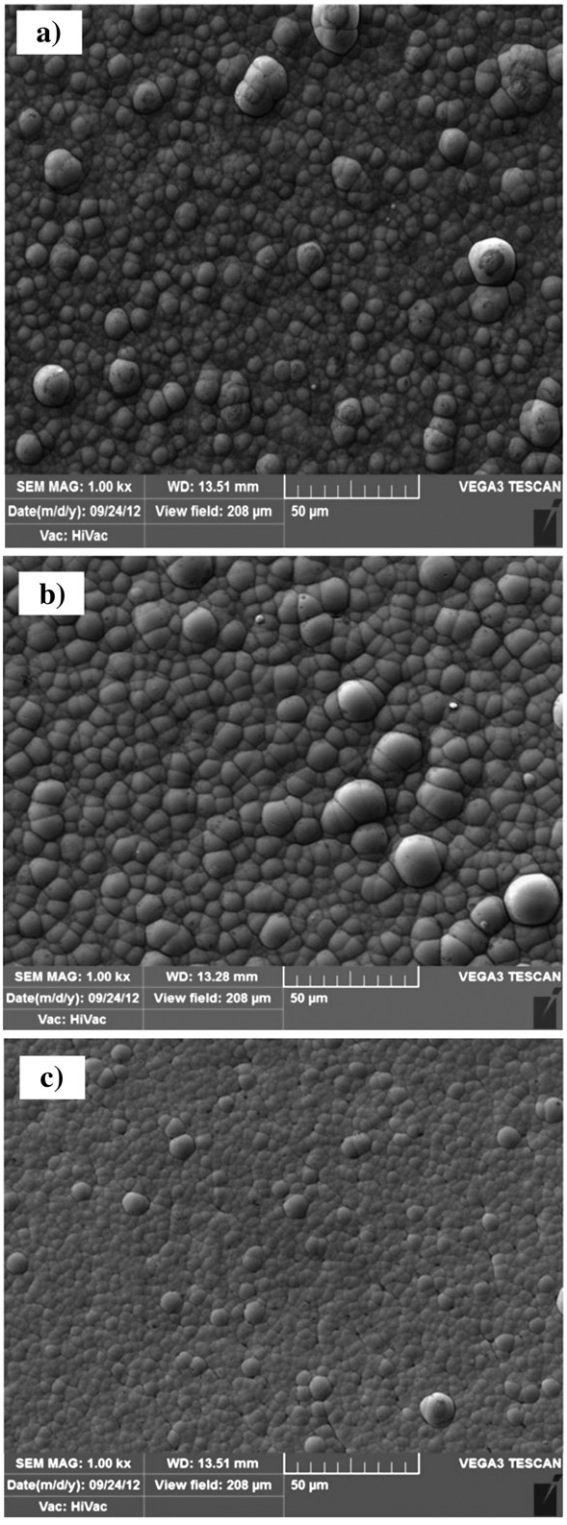

Fig. 1. SEM images of the sample surface: (a) direct EN plating onto substrate after material preparation, (b) pretreated by No. 1 and (c) pretreated by No. 2 nickel immersion.