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Corrosion, tensile and hardness studies of autocatalytic Nickel Coating on Al 2024

A. Sankar Kumar[1], G. Venkatachalam[1], S. Karthikeyan[2], P.A. Jeeva[1]

[1]School of Mechanical and Building Sciences, VIT University, Vellore-632 014, India.

[2]*Surface Engineering Research lab, Centre for Nanobiotechnology, VIT University, Vellore-632 014, India.

*Corresponding author (skarthikeyanphd@yahoo.co.in)

Abstract

Al 2024 is being used in aircraft industries due to its light weight and ductile nature. The autocatalytic deposition of nickel has been carried out using acetate based bath. The influences of nickel coating on tensile and flexural behaviour of aluminium are investigated using experimental methods. Potentiodynamic polarization study confirmed that the coatings offered good corrosion resistance in sea water medium. The micro hardness of the EN coated Al alloys are higher than un plated metal. SEM and XRD techniques were used to understand the surface morphology and structure of the electroless Ni-P layers.

Keywords: corrosion resistance, Electroless nickel plating, tensile, SEM

Introduction

Electroless nickel-phosphorus deposition is an established industrial practice as a protective and decorative coating in various industries due to its superior corrosion and wear resistance, excellent uniformity, wide range of thickness as well as mechanical and physical properties. Extensive research has been carried out on the characterization of the electroless nickel deposition process. Corrosion properties of electroless Ni-P deposition depend mainly on phosphorus content and the corresponding structural and mechanical state. Micro porosity, roughness and inhomogenites due to internal stress within the Ni-P deposited layer are affected by the substrate pretreatment method. It is always difficult to plate aluminium and its alloys with any metal or metallic base surface coating, either by a cathodic or electroless deposition due to the tenacious oxide layer present on aluminium. Aluminium and its alloys have high affinity for oxygen which results in a rapidly growing

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thin oxide film on freshly cleaned and etched aluminium surfaces. It is difficult to plate aluminium substrates covered with such an oxide film with good adhesion. An appropriate pre-treatment process is an essential surface conditioning step before any plating is carried out. The most satisfactory and practical method available for aluminium preparation prior to further deposition is zincating. Zincating is an electrochemical exchange reaction between zinc complexes in solution and the aluminium substrate, depositing zinc crystallites at the expense of aluminium dissolution

Brenner and Riddell first developed autocatalytic nickel deposition using a sodium hypophosphite bath [1]. There are numerous parameters affecting the electroless nickel process temperature, pH, nickel ion concentration, reducing agent concentration, the loading in the bath and agitation affect the nickel deposition rate[2-3]. Electroless nickel deposition bath is known to have a major problem of sudden bath decomposition, which results in an increase in the operating cost of the process and the generation of environmentally hazardous waste [4]. Electroless Ni-Co-P electrolyte solution containing sodium citrate and lactic acid as complexing agents in order to obtain a relatively high deposition rate [5]. The coatings can be tailored for desired properties by selecting the composition of the coating alloy, composite and metallic to suitable specific requirements [6]. Results show that Ni-P deposition is closely related to the dissolution of the zincating layer, followed by progressive nickel nucleation [7]. Another serious consequence of phosphite presence in the EN solution is its effect on the internal stress of Ni-P deposit. As the phosphite concentration increases, the internal stress becomes more tensile [8]. The tensile stress is harmful to many applications such as corrosion and memory disk. The microstructure of electroless Ni-P deposits depends on phosphorus content, as the nature of the internal stress is changed from tensile to compressive with increase in phosphorus content [9]. Stress strain relations in the plastic zone and also investigated the effective yield stress and effective stiffness of perforated sheet metals with square and hexagonal holes using Finite Element Method [10]. This gives an idea for identifying a suitable corrosion resistant coating to reduce the damage of aircraft. The developed coatings are expected to increase hardness and tensile strength [11-15]. The performance of coatings is to be screened by Vickers hardness test, Tensile strength, corrosion resistant measurement by potentiodynamic polarization and AC impedance methods [16-18]. In this paper, we have attempted to make use of nano ZnO for zincating process and then conventional EN plating has been carried out on AL 2024.The corrosion resistance of the coatings were monitored by electrochemical methods.The uniformity of the surface is a desirable factor for improvement on mechanical properties for aluminium on nickel which will be determined by micro structural analysis using SEM images.

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Experimental Procedure

Mass-gain method

The Aluminium specimen was prepared for the following dimensions: 30 mm x10.54 mm x2.02 mm. The bath for electroless plating was prepared as per the chemical composition given in table1. Prior to plating specimen, specimen was immersed in Nano ZnO/NaOH Zincating solution to remove the oxide layer followed by de-smutting (10% Nitric dip) and then cascade water dipping was done. Then the process is carried out to protect the surface to be with nickel coated. Figure 1 shows the schematic diagram of experimental setup. The initial mass of aluminium was weighed using electronic weighing machine. Then the aluminium were subjected to electroless nickel plating(35 μm). The rate of deposition was calculated using the following formula:

$$\text{The rate of deposition } (\mu m/h) = \frac{W \times 10^4}{D\,A\,T}$$

Where,

W – Weight of the deposit (g)
D – density of the deposit (g/cm^3)
T – plating duration (h)
A – Surface area of the specimen (cm^2)

Micro hardness measurements

Micro hardness measurements for aluminium on nickel (20 x 50 x 2 mm^3) were measured using Vicker's harness tester as per ASTM with a load of 100 g. A diamond shaped indentation was created on each coated aluminium at eight different locations and the mean of hardness was calculated from the diagonal of indendation on Vicker's scale using the formula.

V.H.N = (1854 x load) / d^2

where d = diagonal of the indentor

Corrosion resistance measurements

The potentiodynamic polarization study was performed on aluminium on nickel coated area of 10 mm^2 exposed surface (test electrode) in 3.5% NaCl, 40 mm^2 of platinum electrode (counter electrode) and saturated calomel as reference electrode in three electrode cell assembly[19].

Potentiodynamic polarization method

A constant quantity of 250 ml of 3.5% NaCl (sea water) solution was taken in a 250 ml beaker. The test electrode, reference electrode and the counter electrode were positioned in the electro chemical workstation (Sinsil Model 604E, USA) and the readings were recorded by shifting the potential ± 300 mV from OCP at a scan rate 10 mV.second-1 for the mildsteel.

The corrosion rate factors like E_{corr} and I_{corr}, were recorded. The reduction in E_{corr} and I_{corr} values indicated that the coatings are having good corrosion resistance than those reported earlier.

Tensile strength measurements

This measurement was carried out using tensometer as per ASTM for the tensile test.

Scanning electron microscopic studies (SEM)

The micro structural images of nickel coated aluminium were studied using SEM analyzer. The coated test electrodes were prepared for size 10 x 10 mm^2 and placed firmly on crusible to be examined for SEM images. The SEM images were portrayed by using GEMINI SUPRA 55 model with FESEM and with the magnification range of 5kx.

Results and Discussions

Stress-strain behaviour studies

The Figure 2 shows result of Ni coating affects the stress strain behavior of Aluminium. Till the elastic limit, there is no major difference in the value of yield stress. But a significant difference is visible in the stress strain curve after yield stress. This is due to the high ductility of Aluminium metals. The differences in the stress stain behaviours are insignificant from elastic limit to plastic instability. There is minor change in the values of ultimate stress and failure stress if the aluminium is coated with Nickel. Uncoated aluminium exhibits high percentage of elongation then the coated one.

Micro hardness measurements

The hardness of the electroless deposited nickel coatings determined by Vicker's hardness tester is presented in Table 2. The hardness values increased to 2 or 3 times by Nickel coating due to the precipitation of inter metallic phases (Ni_3P) appeared in XRD data. The increased hardness is claimed for precipitation hardening mechanism through the formation of Ni_3P.

Corrosion resistance studies

Potentiodynamic polarization studies

The corrosion resistance experiments were performed for hard coatings on aluminium has been done by employing current-voltage measurements using polarization studies. The coated surface was exposed to sea water medium for 5 hours and OCP was noted. The shift of Potential to more positive direction by coating indicated the corrosion resistance of the surface. Also I_{corr} has reduced by coatings shown in figure 3. The results are given in table 3.

Scanning Electron Microscopic studies

The spheres and Global structures indicate the Ni3P phase aluminium. The aggregation of Ni-P is clearly evident that through the back ground of Nodular layers Absence of pin hole clearly confirms that the coatings are exhibiting good corrosion resistance are shown in figure 4.

The figure 5 indicates corrosion of aluminium in sea water medium through the severe attack of sea water aluminium in the absence of coating.

X-Ray Diffraction Analysis

X-ray diffraction patterns, as shown in Figure 6, trace the properties of crystalline and amorphous peaks on coated hardened and coated without hardened. These patterns gradually change from sharp to very broad peaks with increasing phosphorus content as the structural composition slowly changes from crystalline to amorphous. Spectra show sharp peaks around 14°, 17°, 25°, 45°, 65°, 78° corresponding to nickel and very few diffuse diffraction peaks at (110), (220), (222), (121) planes of varying phases of nickel phosphide.

Surface roughness

Aluminium is made of fine refined surface oriented atomic species. The incorporation of Nickel increased the roughness which is evident from Ra values are given in table 4 Nickel coated on aluminium and table 5 aluminium.

Conclusion

- An engineering coating based on Nickel and aluminium was successfully developed.
- SEM studies confirms that the coatings are exhibiting good corrosion resistance.
- XRD studies revealed that the formation Ni_3P Phase.
- The coating exhibited higher hardness than aluminium both plated as well as heat treated condition at 400^{0}C.
- The enhancement of hardness due to the precipitation hardening effect by forming Ni_3P Phase.
- The Ni_3P coatings offered better corrosion resistance in sea water medium than Aluminium alloy this was confirmed by potentio dynamic polarization studies.
- Nickel phosphorus coating have significantly reduced the tensile stress of aluminium alloy validating that the incorporation of Ni-P in aluminium matrix.

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Table 1 The bath used for metallization of aluminium had the following chemicals:

Sl.No	chemical composition	weight
1.	Nickel Sulphate-0.12M	35g/L
2.	Sodium acetate-0.6M	50g/L
3.	Sodium Hypo phosphate-0.32M	28g/L
4.	pH	4.8
5.	Temperature	70^{0}C
6.	Nano ZnO for Zincating	20 g/l
7.	NaOH for Zincating	43 g/l
8.	Nitric acid for de-smutting	10%

Table 2.Micro hardness measurement

S.No	Material	Vickers Hardness Number Load:100g
1	Aluminium	200
2	Nickel	480
3	Heat treated surface	965

Table 3. Current-Potential results for the corrosion of AL 2024 in sea water medium

Coatings	**Corrosion kinetic factors**		**Tafel slopes**	
Nature of substrate	**E_{corr} (mV)**	**I_{corr} (μA.cm$^{-2)}$**	**b_a**	**b_c**
Uncoated	-680mv	1.90X10^{-4}	63	69
Coated	-642mv	6.3x10^{-5}	60	62

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Table.4. Surface roughness result for nickel coated aluminium

Sl.No	Ra(μm)
1	3.6075
2	4.5998
3	4.1662
Average	4.1245

Table.5. Surface roughness result for uncoated aluminium

Sl.No	Ra(μm)
1	0.2680
2	0.1648
3	0.1719
Average	0.2015

Legends for figure

1. Experimental apparatus of electroless nickel plating

2. Stress strain curve for aluminium with and without coated Experimental.

3. Current-Potential diagram for the corrosion of AL 2024 in sea water medium of Nickel coated aluminium & uncoated aluminium.

4. SEM image of Nickel coated Aluminium.

5. SEM image of Uncoated Aluminium.

6. XRD Patterns of electroless Nickel coated aluminium with and without hardening.

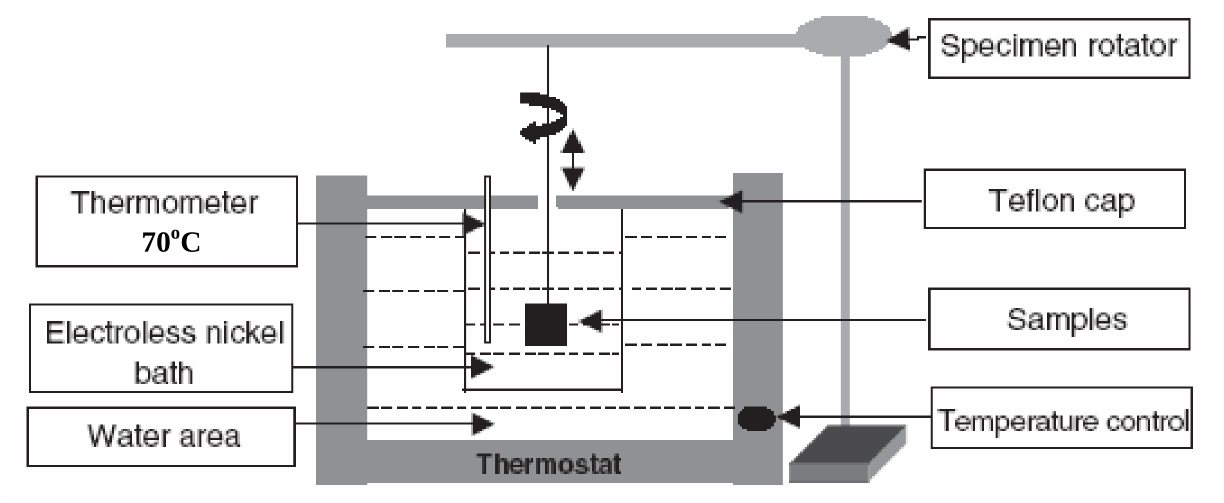

Figure 1

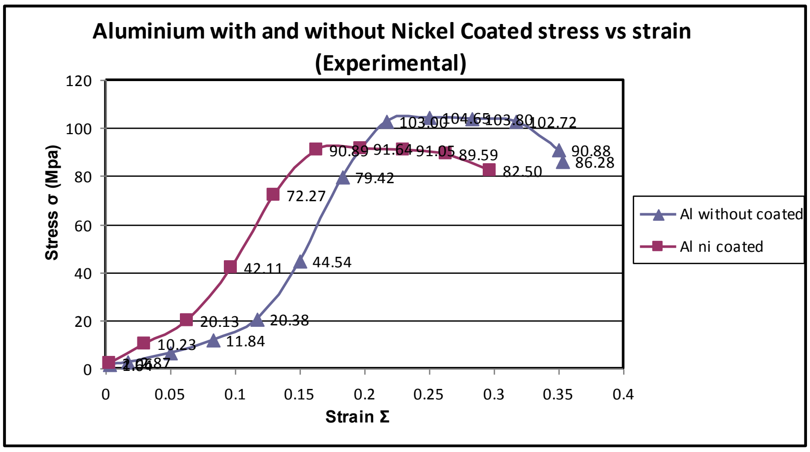

Figure 2

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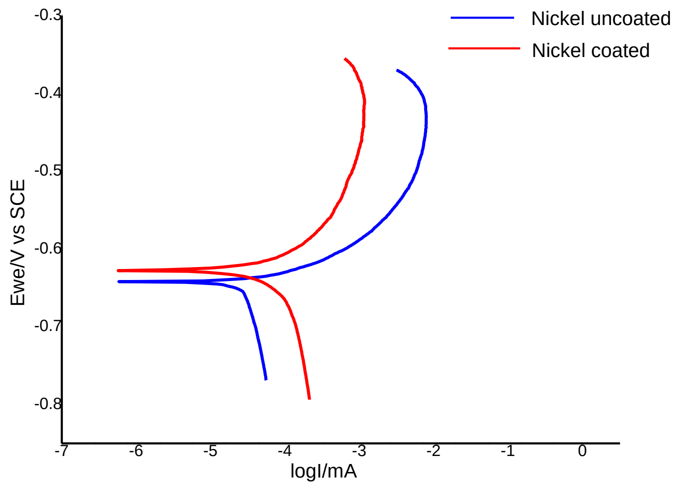

Figure 3

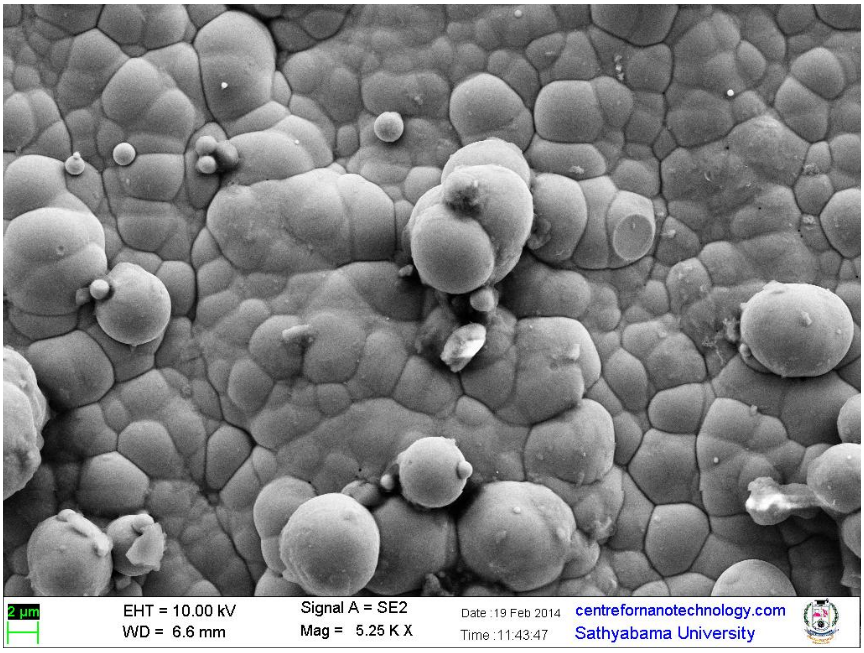

Figure 4

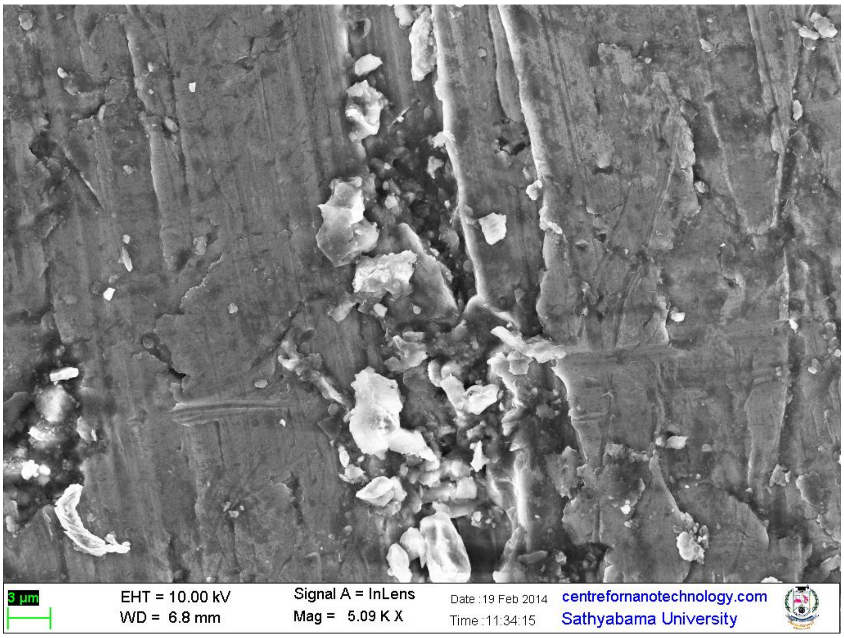

Figure 5

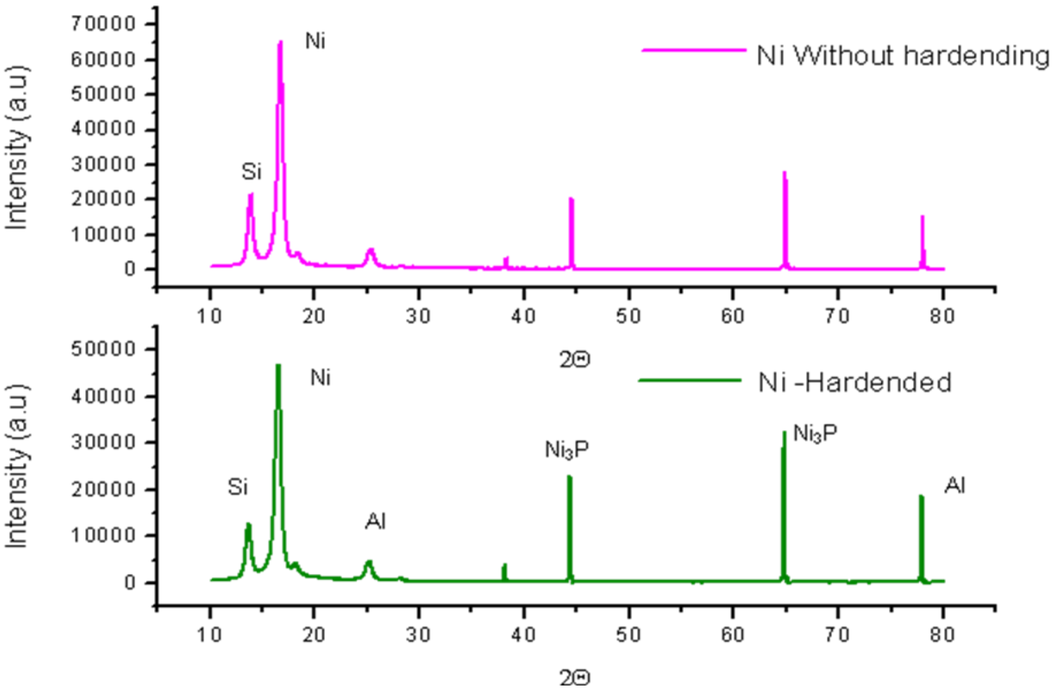

Figure 6