

Research Article

Effect of Processing Parameters on the Protective Quality of Electroless Nickel-Phosphorus on Cast Aluminium Alloy

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The effects of temperature, pH, and time variations on the protective amount and quality of electroless nickel (EN) deposition on cast aluminium alloy (CAA) substrates were studied. The temperature, pH, and plating time were varied while the surface condition of the substrate was kept constant in acid or alkaline bath. Within solution pH of 5.0–5.5 range, the best quality is obtained in acid solution pH of 5.2. At lower pH (5.0–5.1), good adhesion characterised the EN deposition. Within the range of plating solution pH of 7.0 to 11.5, the highest quantity and quality of EN deposition are obtained on CAA substrate in solution pH of 10.5. It is characterised with few pores and discontinuous metallic EN film. The quantity of EN deposition is time dependent, whereas the adhesion and brightness are not time controlled. The best fit models were developed from the trends of result data obtained from the experiments. The surface morphologies and the chemical composition of the coating were studied using the Jeol JSM-7600F field emission scanning electron microscope.

1. Introduction

Electroless plating is a process that does not require electricity before metal deposition is attained from the solution. Electroless plating is an established industrial practice and gained increasing significance at the present time. By such ways both pure metals and alloys can be formed on ferrous and non-ferrous materials with enhanced surface characteristics. This is accomplished by applying suitable surface pretreatment processes [1].

The nomenclature, electroless, is a bit ambiguous according to Schlesinger and Paunovic [2]. Even though no external electrodes are present, electric current is engaged. The metal coat is supplied by the metal salt in place of an anode; metal replacement is accomplished either by the addition of salt or by external looping with an anode of the matching metal of higher efficiency than the cathode. Hence, the substrate serves as the cathode, as a substitute of a cathode to reduce the metal, whereas the electrons are supplied by the reducing agent.

The rewards include uniform plating and the ability to coat nonconductive materials [3, 4]. The ease of simultaneous deposition particulate matters within a matrix of EN has given birth to the discovery and the development of new composite coatings, which can be made with crystalline and/or amorphous structure having a wide range of compositions [5, 6]. Electroless Ni-P coatings were plated on aluminium alloy surface and the effect of posttreatment was studied on the wear resistance by Rajendran et al. [7].

The bath composition for electroless Ni-P deposition contains nickel chloride and sodium hypophosphite while the temperature was maintained at $85 \pm 1^\circ\text{C}$. The solution pH was fixed between 9 and 10 by the addition of an adequate measure of ammonia solution.

The surface morphology of the EN coating was examined using a Jeol 6400 high-resolution scanning electron microscope (SEM). The phosphorus and nickel content of the EN deposits were analysed using Jeol 6400 SEM EDAX attachment [7, 8]. In a few earlier investigations [9, 10] on zincate treatment for aluminium alloy surfaces, structure of

the zinc particles and the effect due to roughening, brought by the substrate dissolving in the plating solution, were reported to affect adhesion of the electroless nickel-phosphorus (Ni-P) coating to the substrate [9–13].

Hajdu and Zabrocky [14] laudably designed surface preparation methods for EN deposition by using masking in preparation. Numerous components may need just partial coating using EN, and segment of the substrate must be guarded by masking. It is unfortunate that masking objects may discharge harmful metallic or organic contaminants into the bath.

Electroless Ni-P composite plating on 6061 Al alloy has been investigated from acidic bath [15]. Aluminium alloy 6061 shows outstanding metallurgical and mechanical properties, corrosion resistance, and workability [16–18]. EN alloy deposits, particularly nickel-phosphorus alloys, are extensively used for corrosion protection of Al and steel [15–18].

Ayoub [19] studied electroless Ni-P deposition on stainless steel and concluded that uniform, compact mixture of microstructures of amorphous and microcrystalline Ni-P coating (with 8.57 wt% P) can be effectively formed on the stainless steel substrate.

EN is well known for its hardness, abrasive wear, and corrosion resistance [7, 20–25]. Among the diverse surface engineering methods that are available for this purpose, EN coating is exceptionally accepted, especially in the electronic industry owing to its conductivity and numerous other engineering properties [15].

The effect of microstructure and plating parameters on the EN plating of AZ91D magnesium alloy were studied and reported by Ambat and Zhou [26]. In the report the early growth of electroless nickel on AZ91 and the variation of coating thickness as a function of time at constant temperature and pH were presented. The coating thickness was directly proportional to the plating time. It was inferred that both the precleaning steps and the concentration of bath components have the influence on EN coating. The consequence of these bath parameters on the EN deposition of Mg is not obtainable in the literature [26].

EN of different kinds are found to be very useful in many engineering applications for their wear and corrosion resistance characteristics. Das and Sahoo [27] studied the tribological qualities of electroless Ni-B deposition and optimization of coating factors using Taguchi supported grey relational analysis. In another report, Gadhari and Sahoo [28] explored the influence of coating factors on the microhardness of electroless Ni-P- Al_2O_3 composite coating using Taguchi analysis. In the study, four parameters, concentrations of nickel sulphate, sodium hypophosphite, and Al_2O_3 particles and annealing temperature, were considered. The optimized condition is found to yield about 20.47% enhancement in hardness of the coating in contrast to the initial condition.

Mallory and Hajdu [29] investigated the effect of bath pH and reported that the P wt% reduces with increasing solution pH from 4.0 to 5.2. Singh et al. [30] carried out electroless plating on c-Si solar cell for diverse periods of time ranging from 30 s to longer durations (1–4 min). The main interest was

to observe the effect of both immediate and the prolonged immersion on EN depositions. A pH ~7.5 controlled alkaline bath was used for EN deposition while other experimental settings were kept unchanged for all the tests.

The metallurgical properties, wear, and corrosion behaviours of aluminium alloy used in the hydraulic brake master cylinder pistons immersed in brake fluid have been studied and reported [31–35]. In understudying and providing a remedy to this menace, Ajibola et al. [10] had reported the effect of hard surface grinding and activation on EN deposition on CAA substrates in sodium hypophosphite baths. The samples were polished with different grits (60 μm –1200 μm) of emery paper prior to EN plating. The impact of polishing grits was studied on the adhesion, appearance, and quantity of EN deposition on substrates. The best yield in terms of adhesion and appearance was obtained from the activation in zincate and Palladium Chloride (PdCl_2) solutions among the six surfactants used [10]. The investigation on the effect of heat treatment for EN coating of Ni film on hollow glass beads was reported by Wang and Zhang [36]. The microstructures and component of EN film on glass beads surface were examined SEM/EDX. The report shows that the EN plating was uniform with the nickel element in the deposition being higher than 95.71 wt% fraction. Rajaguru et al. [37] reported the examination of EN deposition on PerFactory rapid prototype model made on PerFactory R05 material. The preactivation surface etching was found to have a noteworthy effect on surface and generates secure basement for finishing overlay.

It is well noted that commercially available electroless nickel baths contain important additives such as small amounts of lead, typically 0.5 ppm. Yet, there are many/different workable laboratory bath formulations that have been reported in the literature over the years. Each depends on the type and the nature of substrates (steels, cast iron, wrought Al alloy or cast Al alloy, Mg alloy, etc.). The present bath was fashioned after Winowlin Jappes [38, 39], as Al alloy is of our concerned substrate.

Most of the previous works in literature have attempted to report the EN plating of primary Al and how the plating parameters affect the properties. Some other reports have been devoted to A3000 and A7000 series of Al alloy based in hydrazine, sodium borohydride, aminoborane, and borohydride-reduced baths. These usually are examined at temperature between 85 and 90°C in pH of 4.0–5.2 and 10–12 controlled baths. However, not so much has been found reported on the use of cast Al6061 as a substrate for the EN plating in sodium-hyposphite bath. A6061 Al alloy seems to be one of the most readily available Al alloys in the metal markets in many developing countries. Thus the present study considered the effect of some other parameters such as the plating temperatures, solution pH, and the immersion time on the protective quality of EN film on cast A6061Al alloy.

2. Materials and Methods

2.1. Chemical Analyses of Aluminium Alloy Substrates. The chemical compositions of aluminium alloy substrates were determined using Atomic Absorption Spectrometer (AAS)

TABLE 1: Pretreatment and EN plating chemicals.

Baths	Media	Volume (cm ³)	Concentration (g/L or mL/L)	Immersion time (min)
Rinsing	Water	1000	—	0.5–1.0
Emulsifying	Emulsifier: kerosene + detergent solution	1000	15 ml 15 g	0.5–1.0
Alkaline cleaning	Sodium hydroxide	1000	0.4 g	0.5–1.0
Acid cleaning	Hydrochloric acid	1000	5 mL	0.5–1.0
Surfactant	PCl ₂	1000	0.0–0.12 g	0.5–0.75
Plating	Nickel chloride	3000–5000	30 g*	1–10
	Sodium hypophosphite		40 g*	
	Sodium citrate		25 g*	
	Ammonium chloride		50 g*	
	PCl ₂		0.02	
Post plating	Antitarnish chemical: potassium-dichromate solution	1000	15 g	2-3

* According to Winowlin Jappes [38].



FIGURE 1: (a) Cast aluminium alloy specimen and (b) EN plating bath line [10].

TABLE 2: AAS chemical analysis of cast aluminium alloy (CAA).

Samples	Al	Si	Mg	Fe	Mn	Cu	Zn	Cr	Ti
CAA	98.44	0.32	0.29	0.16	0.001	0.01	0.001	0.001	0.001

Thermo series 2000 Model (Table 2). The melting pot was charged with 2 kg scrap sourced from automobile brake master cylinder piston [31, 33] and melted at a temperature range of $750 \pm 50^\circ\text{C}$ in an electric furnace. The molten metal was sand cast into rod of 300 mm length by 30 mm diameter. The rods were machined on the lathe and sliced to 15 mm thickness by 25 mm diameter (Figure 1). The specimens' surfaces were sequentially grinded and polished to smoothness/fine finishing, using $60 \mu\text{m}$ – $1200 \mu\text{m}$ grits of emery paper as reported by Ajibola et al. [10].

The list of the pretreatment and EN plating chemicals is shown in Table 1. The samples were cleaned and pretreated in series of chemicals (bases and acids) to prepare the surface for good quality adhesion. Each pretreatment stage is followed by water rinsing to remove the chemical that adheres to the

surface. The surface activation is done in Palladium Chloride (PdCl_2) solution at 85°C [10] before they are finally immersed in the electroless nickel bath (Figure 1). Three parameters were varied: plating time, pH, and temperature. The time (1–10) is in minutes, temperatures (70, 75, 80, 85, 90, and 95) are in $^\circ\text{C}$, and the solution pH is of 5.0 to 6.5 (acid bath, NaOH regulated) and of 7.0 to 11.5 (alkaline bath, NH_4OH controlled). The surface condition of the substrate ($1200 \mu\text{m}$ grit polishing paper) and PdCl_2 (activation) parameters were kept constant.

The EN deposited per unit area was calculated using

$$\text{EN deposited per unit area} = \frac{\Delta W}{A_T}, \quad (1)$$

where

$$\Delta W = W_f - W_i, \quad (2)$$

where ΔW is weight of EN deposition, A_T is total surface area of substrate, t is plating time, and W_i and W_f are weights of the sample before and after immersion, respectively.

TABLE 3: Effect of plating time variation on electroless nickel deposition.

Plating time (min)	Deposition (g/mm ²)	Appearances (quality)
1	0.000177	Uniform deposits
2	0.000236	Uniform deposits
3	0.000256	Uniform deposits
4	0.000276	Uniform deposits
5	0.000284	Tendency to peel
6	0.000316	Uniform deposits
7	0.000396	Flaky, metallic
8	0.000415	Flaky
9	0.000428	Metallic
10	0.000434	Metallic

TABLE 4: EDX spectrum data for 2 min EN plating on cast Al alloy.

Element	C	O	Na	Ni	P	Al	Si	Cr	Total
Weight %	11.65	23.28	3.28	17.86	0.82	39.57	7.66	-4.10	100
Atomic %	21.27	31.92	3.13	6.67	0.58	32.18	5.98	-1.73	

After the plating process, coated surface is washed in antitarnish chemical and water rinsed to prevent unwanted stains and dried in the oven; after that, the amount of EN deposition per area and the microstructure were examined.

The substrate samples were characterised by AAS (Thermo series 2000 model). The microstructures were examined to compare the similarities and differences in the grain sizes and the structures under the microscope (Nikon-Eclipse M600 model). The surface morphology and characterisation of the coating were studied through the scanning electron microscope (Jeol JSM-7600F Microscope) with the EDX facilities attachment. Such varying parameters under which the SEM/EDX studies were performed are kV value (1.0 kV, 10.0 kV); magnifications ($\times 100$, $\times 500$, $\times 1000$, $\times 2000$, $\times 10000$, $\times 30000$); resolutions (LM, GB_HIGH); image/spectrum target size (100 nm, 1 μ m, 10 μ m, and 100 μ m); and WD (7.9, 8.0, 8.3, and 10.1 mm). These are reportedly shown on each of the micrographs.

3. Results and Discussion

Table 2 shows the chemical compositions of CAA sample used for the experiment as obtained by AAS. The average hardness (BHN) value was determined as means of identifying its behaviour under friction with respect to the composition and microstructure. With these characterisations, some reasons for the plating, wear, and corrosion resistance behaviours could be understood.

3.1. Effect of Plating Time on Electroless Nickel Deposition.

Effects of plating time variation on the amount and physical appearances of the EN deposition on CAA are presented in Tables 3–5 and Figures 2 and 3.

The effects of plating time on the amount of EN deposition on CAA are presented in SEM imagery in Figure 3.

TABLE 5: EDX spectrum data for 10 min EN plating on cast Al alloy.

Element	C	O	Na	Ni	P	Al	Si	Cr	Total
Weight %	9.50	9.31	1.47	55.79	2.28	22.08	0.44	-0.87	100
Atomic %	24.13	17.75	1.94	28.99	2.25	24.96	0.48	-0.51	

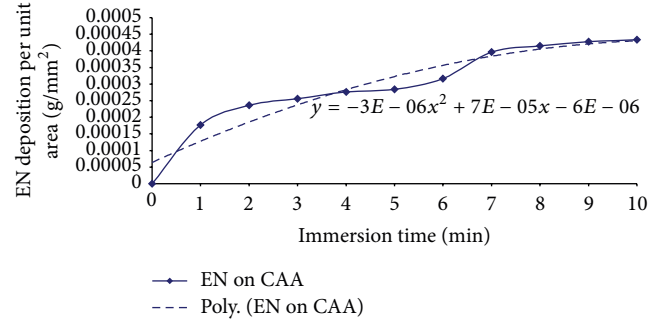


FIGURE 2: Variation of plating time on EN deposition per unit area on cast Al alloy (CAA) substrates.

Electroless nickel was deposited on CAA substrates with time varying from 1 to 10 minutes in sodium hypophosphite reduced bath. It was observed that the quantity of electroless nickel deposition per unit area is dependent on the time, whereas the adhesion and brightness are not controlled by the plating immersion time.

Figure 2 shows the effect of the variation of plating time (from 1 to 10 minutes) on EN deposition per unit area on CAA substrates. The EN deposition per unit area increases with the increasing plating time at very close and similar trends of CAA substrates. Small amounts of CAA deposition (0.000177 to 0.000434 g/mm²) were obtained per unit area of the CAA substrate. The trend of the EN deposition per unit area with respect to increasing plating time was studied using the experimental data generated from the experiment. The curve fit parameters model is of polynomial power 2 relating the EN deposition per unit area to time (minutes) presented as

$$M_{n1} = -0.000003t^2 + 0.00007t - 0.000006, \quad (3)$$

where t is plating time, $t > 0$ (minute), and M_{n1} is the EN deposition per unit area with respect to plating time on CAA in sodium hypophosphite reduced bath. About 0.000434 g maximum EN deposition per mm² area of the CAA substrate was obtained in 10 minutes. The results show that the EN deposition rate increased from 0.000177 to 0.000434 g/mm²/min for the CAA within the increasing 1 to 10 minutes plating time frame.

The microscopic outlooks of the EN films are revealed in the SEM electron images in Figure 3. The SEM image in Figure 3(a) shows the homogeneous layer of nickel-phosphorous coating similar to the results of the morphology study by Rajaguru et al. [37]. The EDX spectrum data show the chemical compositions of the characterisations of the EN deposition in Tables 4 and 5. The EDX data inferred that the

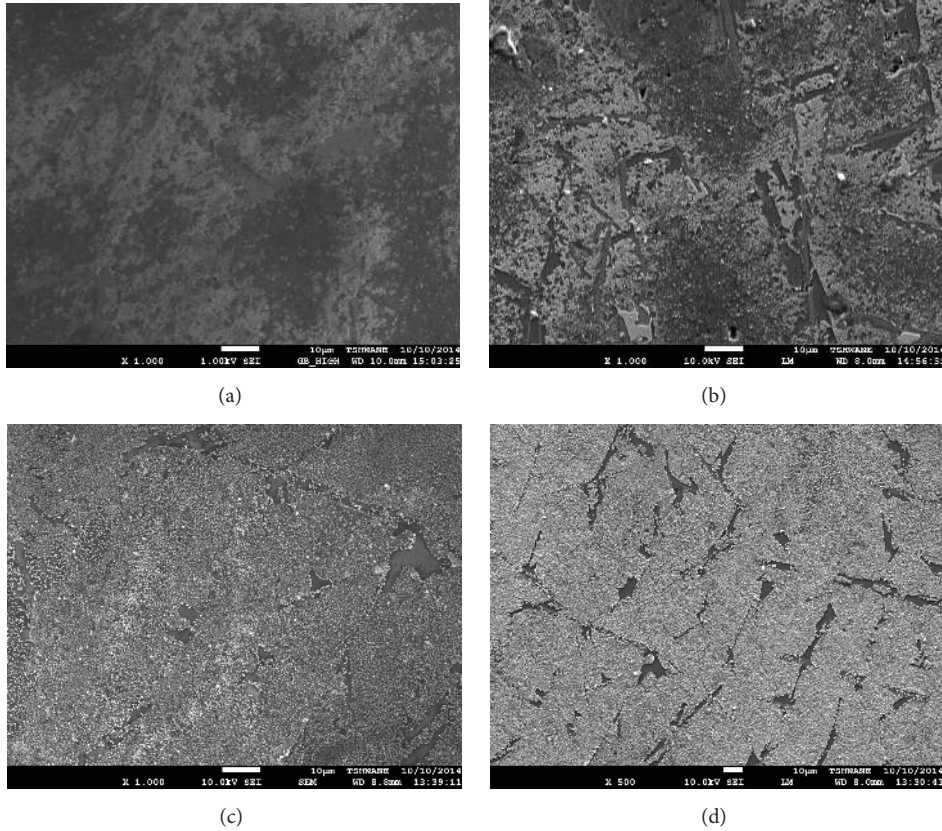


FIGURE 3: SEM images showing EN films on CAA surfaces after (a) 2, (b) 4, (c) 8, and (d) 10 minutes of immersion.

TABLE 6: Effect of plating temperature variation on electroless nickel deposition.

Temperature (°C)	Deposition (g/mm ²)	Appearances (quality)
70	0.000179	Nonmetallic, very poor
75	0.000231	Nonmetallic, peeling
80	0.000121	Metallic, peeling
85	0.000138	Metallic, uniform
90	0.000244	Metallic, flaky
95	0.000236	Metallic, peeling

EN deposition increased with the immersion. This correlates with what is presented in the weight gain measurement in Table 3 and Figure 2.

3.2. *Effect of Plating Temperature Variation on Electroless Nickel Deposition.* Effect of plating temperature variation on the quantity and appearances of the EN deposition on CAA are shown in Tables 6–9 and Figures 4 and 5.

Issues arise about the efficiency of washing off the plating bath residue on samples when, for example, the ten-minute plating EDX data presented in Table 5 shows the presence of 1.47 wt% sodium, Na. Though, the situation may partially arise from the washing off plating bath residue on EDX samples. The presence of substantial amount of wt% sodium, Na, detected and reported in the EDX data (Tables 4–8), is

TABLE 7: EDX spectrum data for 10 min EN plating on cast Al alloy at (a) 80°C.

Element	C	O	Na	Al	Si	P	Cl	Ca	Ni	Total
Weight %	13.19	13.44	1.15	0.26	0.33	4.43	0.55	0.33	66.31	100
Atomic %	33.22	25.41	1.51	0.30	0.36	4.33	0.47	0.25	34.16	

TABLE 8: EDX spectrum data for 10 min EN plating on cast Al alloy at (b) 85°C.

Element	C	O	Al	Na	P	Ni	Total
Weight %	7.60	7.86	—	1.06	3.98	79.48	100
Atomic %	23.90	18.51	—	1.74	4.84	51.01	

TABLE 9: EDX spectrum data for EN plating on cast Al alloy at (c) 90°C.

Element	C	O	Al	Si	P	S	Fe	Ni	Total
Weight %	9.75	12.82	51.23	13.53	0.60	0.27	2.39	9.40	100
Atomic %	19.22	18.97	44.94	11.41	0.46	0.20	1.01	3.79	

most likely due to the imperfections such as trapped Na-bath solution in the pores and at the interface between the EN deposit and the Al alloy substrate due to poor adhesion.

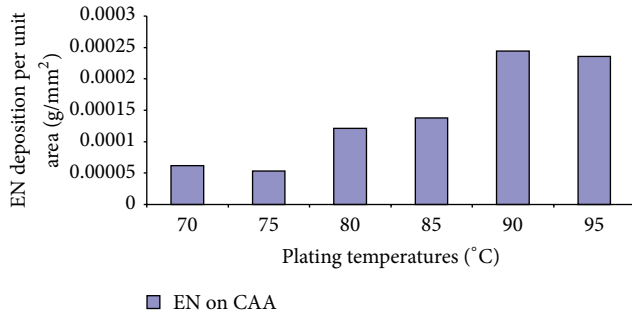


FIGURE 4: Variation of plating temperature on electroless nickel deposition per unit area on cast Al alloy (CAA) substrates.

The effects of plating temperature variation on EN deposition on CAA in acidic sodium hypophosphite reduced bath are presented in Figures 4 and 5. The qualities (morphologies such as the appearance, roughness, porosity, and film continuity) of the EN deposition on the 1200 μm grit polished CAA substrates at 80°C, 85°C, and 90°C, respectively, at microscopic level are compared in the SEM images in Figure 5. It was shown that the amount of EN deposition increased as the bath temperature increased from 80°C to 90°C. From the result, the film properties (adhesion and brightness) are dependent on the plating temperature and the best of the adhesion of EN films on CAA were in most cases obtained at temperatures higher than 80°C. The amount of EN deposition on the CAA substrates is temperature controlled as the bath temperature increased from 80 to 90°C. The highest EN nickel deposition per unit area was obtained at 90°C. There is little difference in the EN film per unit area on CAA as temperature increased from 80 to 85°C, above which there was much increase in the EN film per unit area obtained on the CAA substrate, even though, this did not bring significant improvement in the qualities of the EN deposition.

The curve fit parameters model developed is of polynomial function to power 2 relating the EN deposited to the bath temperature (°C) as in

$$M_{n1} = 4E - 05T^2 - 0.0001T + 0.0002, \quad (4)$$

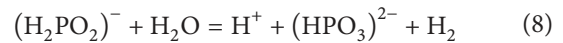
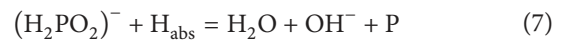
where $80 \leq T \leq 90$, T is plating bath temperature °C, and M_{n1} is the EN deposition per unit area. The EN plating requires a high amount of energy for the autocatalytic reaction to be effective. The kinetics of the reaction is temperature controlled. EN is deposited at the rates of $1.79E-05$ – $2.31E-05$ range ($\text{g}/\text{mm}^2/\text{min}$) on CAA at the temperature range of 80 to 85°C, respectively.

3.3. Effect of Solution pH on the Electroless Nickel Film. Effects of solution pH on the amount and qualities of the EN deposition on CAA substrates are in Tables 10–16 and Figures 6–8.

The function played by intermetallic particles in surface preparation of Al alloys for EN plating using double zincating method of surface activation is in a few words explained in the US Patent 5,405,646. For cleaned substrates activated in PdCl_2 and EN plated surfaces, it will be also admitted that

the heterogeneous electrochemical characteristic of the alloy (A6061 Al) surface plays a role in Palladium (Pd) activation as applied to the present study.

The amphoteric nature of aluminium makes it react with both acids and alkaline and bases. The pH of the bath was maintained by adding required quantity of liquor ammonia. A number of systems have been imagined and projected for the chemical reactions that transpire in hypophosphite reduced EN plating solutions. The most comprehensively recognized mechanism and sequence as given by R. C. Agarwala and V. Agarwala [40] are in the following:



With the sufficient amount of energy and catalysed surface, hypophosphite ions are oxidized to orthophosphite. Hydrogen gas is evolved in the process which is detrimental to the EN deposit film morphology and affects the porosity. Hence, stirring conditions are necessary to remove evolved hydrogen bubbles.

Effect of variation of solution pH on the quantity and qualities of EN deposition on 1200 μm grit polished CAA substrates at various pH and temperatures in both the acid and alkaline reduced baths are presented in Figures 6 and 7. In the acid reduced bath, the amount and quality of EN deposition were significantly affected by the level of solution pH.

The immersed substrate is very much aggressive in the plating baths. This affects the surface morphology of the CAA. EN coatings follow the surface profile of the substrate on which it is deposited. Hence, the roughness of the substrate has a profound impact on the tribological properties of the coating while the roughness of the substrate affected the film composition [3, 4]. Hence, there is significant need to zincate the CAA substrate prior to the immersion into the plating baths. The intersection zinc film between the substrate and the EN solution reduces the early alteration of the CAA substrate prior to EN deposition. The film properties such as adhesion and brightness are dependent on the pH of the plating solution. This might account for why superior adhesion was previously reported from the zincating experiment [10].

EN preferentially deposited on the stainless steel vat at 85°C and pH = 5.1 without pH regulator (Figure 7). The deposition is full bright metallic and of very high level of adhesion and continuity. Other SEM images in Figure 7 show EN deposition on 1200 μm grit polished CAA substrates at 80°C in pH = 5.2 using NaOH regulated bath. The plating comes with fairly bright deposit and good adhesion to the CAA substrate. In the pH (5.3) acid reduced baths, the deposition consists of both dull nonmetallic and bright metallic EN films on the CAA. The adhesion is poor and hence, the

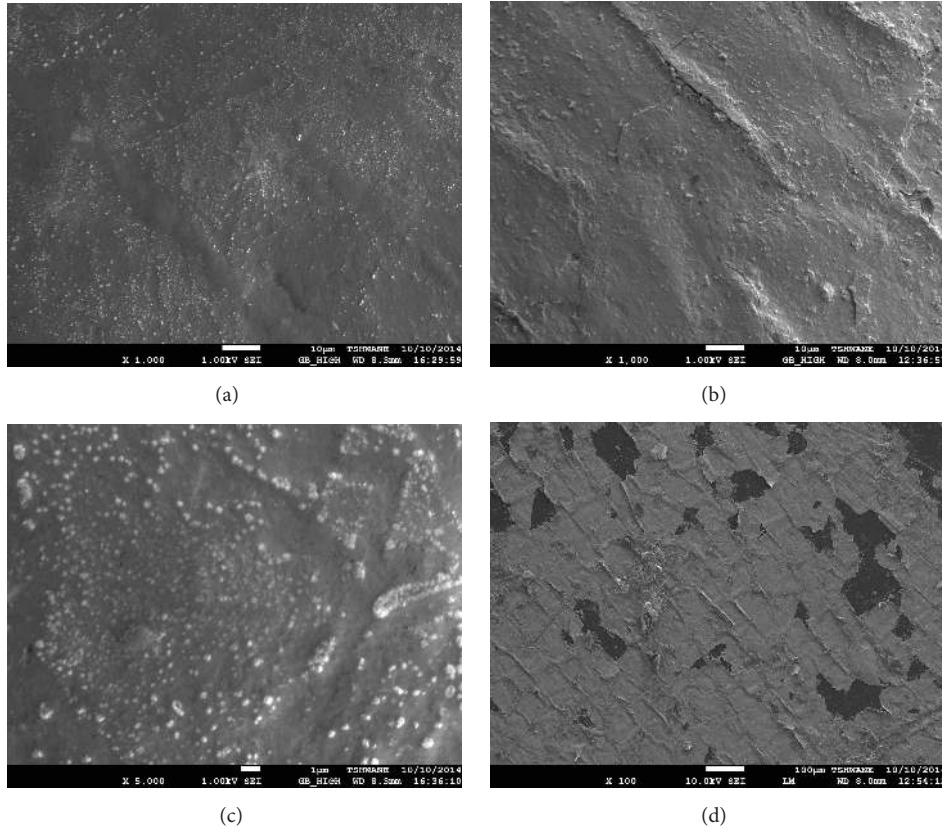


FIGURE 5: Microphotographs showing EN deposition on 1200 μm grit polished cast Al alloy (CAA) substrates at (a) 80°C, (b) 85°C, and (c) 90°C plating temperatures.

TABLE 10: Effect of solution pH variation on electroless nickel deposition.

pH	Acid bath		pH	Alkaline bath	
	Deposition (g/mm^2)	Appearances		Deposition (g/mm^2)	Appearances (quality)
5.0	0.000275	Metallic	9.0	0.000252	Flaky, metallic
5.1	0.000273	Metallic	9.5	0.000286	Metallic
5.2	0.000312	Metallic	10.0	0.000302	Metallic
5.3	0.000399	Nonmetallic,	10.1	0.000223	Poor, peeling
5.4	0.000421	Poor	10.2	0.000221	Poor
5.5	0.000443	Poor	10.3	0.000257	Flaky
6.0	0.000303	Very poor	10.4	0.000253	Metallic, peeling
6.5	0.000308	Very poor	10.5	0.000352	Metallic, bright
7.0	0.000334	Very poor	10.6	0.000229	Flaky, metallic
7.5	0.000361	Very poor	10.7	0.000376	Flaky, metallic
8.0	0.000325	Very poor ^c	11.0	0.000322	Metallic, flaky
8.5	0.000354	Poor	11.5	0.000343	Metallic, uniform

deposit is pilling. At pH = 5.4 NaOH regulated EN bath, though the EN film is fairly bright, it is not continuous and having poor adhesion on the CAA substrate. Better adhesion of EN film on CAA was obtained at pH operated between 5.1 and 5.2, while EN deposited on the plastic substrates (lining) at pH between 5.3 and 5.4 for an acid reduced EN bath run at 85°C. Different levels of poor qualities of EN film were

deposited at solution pH 5.5–8.5 range operated at diverse temperatures.

Figure 8 shows the quality of EN film on 1200 μm grit polished CAA in solution pH of 9.5, and NH_4OH regulated bath. The EN deposition forms with a little quantity of fairly poor adhered dull metallic film whereas the EN plating at pH = 10.5 and 11.0 in NH_4OH regulated bath at 85°C produced

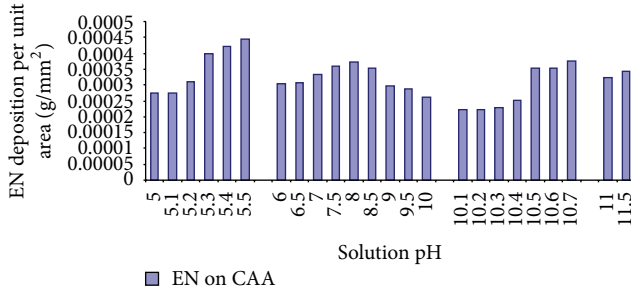


FIGURE 6: Variation of pH on electroless nickel deposition per unit area on as-received Al alloy (AAA) and cast Al alloy (CAA).

TABLE 11: EDX spectrum data for Ni-P plated CAA at pH = 5.2 NaOH regulated at 80°C.

Element	C	O	Na	Ni	P	Al	Si	Cr	Total
Weight %	8.16	7.79	1.81	67.51	1.96	9.63	4.26	-1.13	100
Atomic %	23.08	16.53	2.68	39.04	2.15	12.11	5.15	-0.74	

TABLE 12: EDX spectrum data for Ni-P plated CAA at pH = 5.3 NaOH regulated at 80°C.

Element	C	O	Na	Ni	P	Al	Si	Cr	Total
Weight %	8.73	7.36	1.65	70.94	2.31	11.41	0.31	-2.71	100
Atomic %	24.87	15.73	2.45	41.33	2.55	14.46	0.38	-1.76	

TABLE 13: EDX spectrum data for Ni-P plated CAA at pH = 5.4 NaOH regulated at 80°C.

Element	C	O	Na	Ni	P	Al	Si	Cl	Total
Weight %	6.38	9.05	0.47	61.40	1.37	18.33	2.62	0.35	100
Atomic %	17.77	18.92	0.69	34.97	1.48	22.72	3.12	0.33	

metallic Ni with fairly good adhesion as compared with what was obtained on the stainless steel substrate. At higher pH (11.5), there is preferential EN deposition on the plastic substrates (lining and stirrer) in the NH_4OH regulated bath at 85°C. In the alkaline reduced EN bath, the amount and quality of EN deposition were significantly influenced by the solution pH level. The film properties such as adhesion and brightness are dependent on the pH of the plating solution. Operating the electroless nickel bath at pH = 9.0 produces metal flakes of EN on the CAA coins substrate. The best of adhesion of EN film on CAA was obtained at pH operated within 10.5, 11.0, and 11.5, while there is full bright metallic and strongly adhered electroless nickel deposition on the plastic substrates (lining) at pH of 11.5 in an alkaline reduced bath run at 85°C. The general observation shows that solution pH

TABLE 14: EDX spectrum data for Ni-P plated CAA at pH = 10.5 NH_4OH regulated at 85°C.

Element	C	O	Na	Al	Si	P	Fe	Ni	Pd	Total
Weight %	7.33	15.84	0.48	46.29	9.27	0.73	6.74	12.42	0.91	100
Atomic %	15.13	24.56	0.51	42.57	8.19	0.58	2.99	5.25	0.21	

TABLE 15: EDX spectrum data for Ni-P plated CAA at pH = 11.0 NH_4OH regulated at 85°C.

Element	C	O	Al	Si	P	S	Cl	Ni	Zn	Total
Weight %	10.57	13.63	51.98	13.57	0.70	0.31	0.27	7.98	0.98	100
Atomic %	20.31	19.66	44.47	11.15	0.52	0.22	0.18	3.14	0.35	

has a significant influence on the appearance and adhesion of EN deposit on CAA substrate.

In Figure 6, the amount of EN deposition per unit area on CAA substrates in acid and alkaline reduced baths is reported. The pH of the bath was varied from 5.1 to 5.5 for the acid bath. The amount of EN deposition on the CAA varies with the increasing solution pH. A range of 0.000273–0.000443 g/mm² EN film was obtained. The results show that at lower values of solution pH (5.0–5.2), there is less EN deposition per unit area on the CAA substrate. Subsequently, at pH of 5.3 and above, there is greater increase in the electroless nickel deposition per unit area on CAA substrate in the acid bath. The trend of the EN deposited per unit area with respect to increasing plating solution pH was studied, using the experimental data generated from the experiment. The developed model is given as in

$$M_{n1} = 0.000000009x^2 + 0.00003x + 0.0002, \quad (9)$$

where x is solution pH, $5.0 \leq x \leq 5.5$, and M_{n1} is the EN deposition per unit area on CAA in acid sodium hypophosphite reduced baths.

In Figure 6, there is greater EN deposition per unit area on the CAA substrate in solutions of pH (9 to 11) lower than 11.5 in the alkaline bath. There was an increase in EN deposition per unit area from increasing pH from 5.0 to 5.5, above which the EN deposition per unit area reduced between 6.0 and 10.4. There was high EN deposition per unit area from increasing pH from 10.5 to 11.5 as compared with what was obtained at pH range of 10.1 to 10.4, and NH_4OH regulated solution. The quantity of EN deposition per unit area could be considered to increase with increasing solution pH for CAA substrates at pH 10.5–11.5 range regulated by NH_4OH solution. The model equation derived using MS Excel is of polynomial equation to power 2 relating the amount of EN deposited on CAA to the plating solution pH given as in

$$M_{n3} = -0.000004x^2 + 0.00005x + 0.0002, \quad (10)$$

TABLE 16: EDX spectrum data for Ni-P plated CAA at pH = 11.5 NH₄OH regulated at 85°C.

Element	C	O	Na	Al	Si	P	Ni	Total
Weight %	6.00	5.09	0.35	6.67	9.60	—	72.30	100
Atomic %	18.82	11.99	0.57	9.32	12.89	—	46.42	

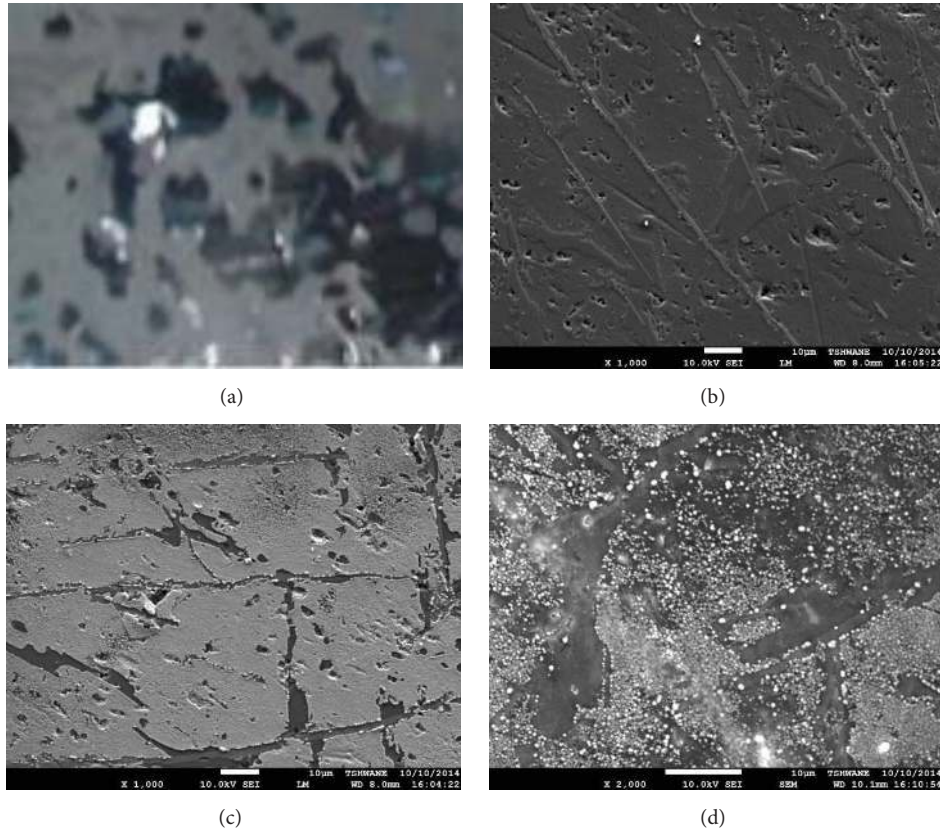


FIGURE 7: Microphotograph and SEM images showing EN deposition on (a) stainless steel at 85°C and pH = 5.1 without pH regulator and 1200 μm grit polished substrates at (b) pH (5.2), (c) pH (5.3), and (d) pH (5.4) NaOH regulated at 80°C.

where x is solution pH, $9.0 \leq x \leq 11.5$, and M_{n3} is the electroless nickel deposition per unit area with respect to plating solution pH on CAA coins in alkaline sodium hypophosphite reduced bath. The amount of deposition on the CAA varies with the increasing solution pH in which a range of 0.000252–0.000343 g/mm² EN film depositions were obtained.

In summary, Figure 6 compares the amount of EN deposition on CAA substrates in acidic and alkaline sodium hypophosphite reduced plating baths. The study shows that the EN deposition per unit area and the EN film quality such as brightness are controlled by the plating solution pH on the CAA surfaces.

The metallurgical and surface properties that characterised the cast samples used in the present study have been discussed by the authors [41, 42]. The present results also give further and better appreciation to the effective protective application of EN to solving or reducing the wear and corrosion of the cast aluminium alloy sample [43, 44].

It gives room to compare the similarities and the differences in the electroless nickel plating properties of the cast test samples available in the previous reports by Ajibola et al. [10].

4. Conclusions

The EDX data inferred that EN deposition increased with the immersion time that correlates with the experimentally derived weight gain measurement. Maximum values of 4.34×10^{-04} g/mm² and EN deposition rate of 4.34×10^{-05} g/mm²/min were obtained within the increasing 1 to 10 minutes plating time frame.

The EN plating requires a high amount of energy for the autocatalytic reaction to be effective since the kinetics of the reaction is temperature controlled. The range of EN deposition on CAA is at 1.79×10^{-05} to 2.31×10^{-05} (g/mm²/min) at 85°C. The film properties (adhesion and brightness) are dependent on the bath temperature, and the best of the

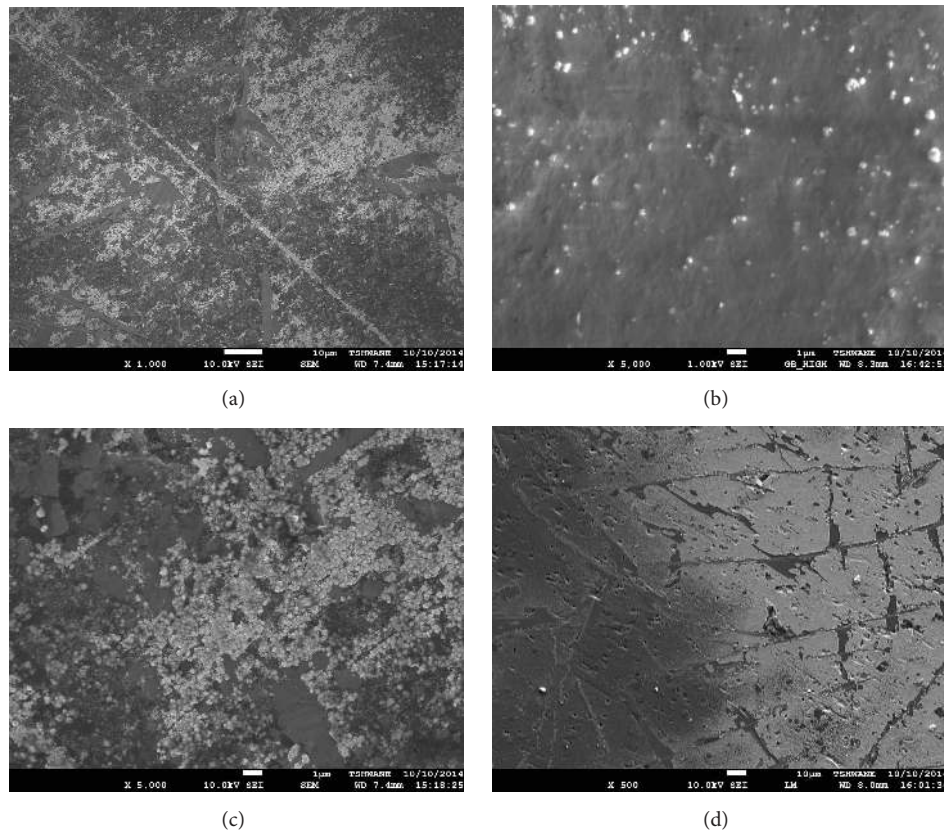


FIGURE 8: Micrographs showing deposits of (a) EN flakes on CAA surfaces at pH = 9.5, bright, metallic EN plating at (b) pH = 10.5, (c) pH = 11.0, and (d) EN on plastic stirrer in pH = 11.5 NH_4OH regulated baths at 85°C .

adhesion of EN films on CAA was in most cases obtained at temperatures higher than 80°C .

The reaction is aggressive, hence the significant need to zincate the CAA substrate prior to the immersion. The film properties (adhesion and brightness) are dependent on the pH of the plating solution. The best sets of electroless nickel plating were obtained at solution pH operated at 5.1–5.2 and 10.5–11.5 for acid and alkaline sodium hypophosphite reduced bath, respectively, being operated at 85°C .

The study shows that the amount and the quality of EN film (morphology) are mainly dependent and controlled by the plating solution pH and the operating temperature at any corresponding time.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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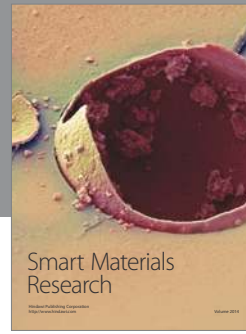
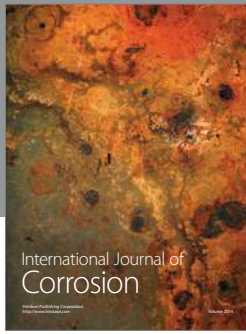
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