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Effect of Zincating bath additives on structural and electrochemical properties of electroless Ni-P coating on AA6061

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Electrochemical behavior of electroless nickel phosphorus (EN-P) coated aluminum 6061 alloy combination in different zincating conditions have been evaluated. The effect of the zincate additives (anionic surfactant sodium dodecyl sulfate (SDS) and copper sulfate) on structure and morphology of zincating and electroless EN-P deposition have been studied. Corrosion performance of the prepared samples was studied by polarization and electrochemical impedance spectroscopy (EIS). Scanning electron microscope (SEM), Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analysis were used for studying surface morphology and chemical composition of coatings. According to the obtained results, the zincate solution containing copper sulfate and SDS surfactant indicated the fast deposition of Zn and dense nucleation with small Zn particles at the surface. This Zn films resulted in dense and small grains of EN-P deposition with smooth surfaces.

Keywords: Al 6061 alloy; Zincate treatment; surfactant; electroless nickel phosphorus; Electrochemical behavior

1. INTRODUCTION

By development of industry aluminum and aluminum alloys have been chosen instead of steel in numerous applications because of their high strength to weight ratio where the weight of the structure is an important economic factor[1, 2]. Aluminum has also interesting properties like high reflectance ratio and low absorption, good wettability and low cost[3, 4]. However, the main issues with aluminum alloys are their low hardness and weak wear and abrasion resistances. This weakness do not allow them to be used for various engineering application, and it should be improved by using hard and wear resistant protective layer[5, 6].

Nickel and nickel alloys can be coated by electrodeposition and electroless deposition [7-10]. Among them, electroless nickel phosphorus (EN-P) coatings have been widely used in the metal finishing industry that can be used for many metal substrates, including steel, copper, nickel, aluminum and alloys[11]. It is noteworthy that EN-P coating has been considered as a corrosion and wear resistance coating in various type of applications[7]. Because of its amorphous nature and passivity, the corrosion resistances of the coatings are excellent and it has superior properties than pure nickel or chromium alloys in many environments [12, 13].

Deposition of coating on aluminum surface with general electroless and electrodeposition is very difficult because of the presence of a strong and chemically stable surface oxide film[14]. Removing the oxide layer from the surface requires special pretreatment operation to condition the surface for deposition[14]. For this reason the zincating process (or double zincate pretreatment) have been applied for aluminum coatings[15]. This coating preserve the aluminum surface from re-oxidation and dissolving in electrolyte. This process consist of deposition of a zinc layer by dipping the aluminum in zincating electrolyte. This pretreatment directly affected the final deposition quality and formation of a fine and uniformly deposited Zn layer is desirable to obtain smooth and pinhole-less plating layer with sufficient adhesivity[15-18].

There are many attempts for improvement of zincate layer properties in the recent years. For example Azumi et al.[19], reported the effects of etching of Al–Si alloy films in H2SO4 solution containing Cu^{2+} ions on double zincate pretreatment . They claimed that the etching process dramatically improved uniformity of Zn deposition and suppressed Al dissolution in the double zincate process. So the additive can improve the zincating properties. According to the author’s previous reports, surfactant in the bath improves the coating morphology and other properties of the coating such as mechanical and corrosion properties[20, 21] .

Many attempts have been made to find out the effect of surfactants on the properties of electroless and electrodeposited Ni–P coatings. However, to the best of our knowledge there is no reports about the effect of surfactant on zincating performance which directly changed the corrosion and structural performance of final EN-P coatings. Here we will try to evaluate the SDS surfactant and copper sulfate effects on zincating properties and final Electroless coating corrosion and structural performance.

2. MATERIALS AND METHODS

Aluminum 6061 alloy with 10 × 10 × 6 mm3 size have been used as substrate for coating process. The substrate firstly were by successive emery papers (numbers: 120, 500, 1000 and 2000). After thorough cleaning, the step-by-step cleaning procedure was employed prior to plating consists of ultrasonically cleaning the substrate with acetone, cleaning with ethanol, and alkaline solution pickling for 1 min in NaOH, 10 vol%, 60^0 ±2 respectively. After then, the sample were subjected to acidic pickling in of sulphuric acid (SG 1.83) 10 ml/L, hydrofluoric acid (40%) 12.5 ml/L and nitric acid (SG

1.42) 25 ml/L 25 ml/l acid nitric solution for 2-3 minutes at ambient temperature. Samples were rinsed by double distillated water after each pretreatment stage explained above.

The zincating process have been conducted as fallow: zincating by dipping the sample in bath 1, then removing the first layer by immersion the sample in 40% acid nitric solution for 10 seconds following by water washing. Finally the second zincating part has been conducted by dipping in the bath 2. The bath 1 and 2 compositions were listed in table 1 and 2. The zincating process have been conducted as fallow: zincating by dipping the sample in bath 1, then removing the first layer by immersion the sample in 40% acid nitric solution for 10 seconds following by water washing. Finally the second zincating part has been conducted by dipping in the bath 2. The bath 1 and 2 compositions were listed in table 1 and 2. In order to understand the effect of two different additives (anionic surfactant sodium dodecyl sulfate (SDS) and copper sulfate) three types of zincating bath solutions have been used in this study. The bath A and B are traditional zincating bath and the bath with copper sulfate respectively. Finally the bath C has contained both additives means SDS surfactant and copper sulfate. The amount of additive have been determined according to the previous study and authors own experiences [15, 20, 21].

After the zincating parts the samples subjected to EN-P coating. Table 3 lists the electroless bath composition and operating conditions. EN–P deposition was carried out using nickel sulfate as the source of nickel and sodium hypophosphite as the reducing agent. After EN-P deposition, the samples were washed in distilled water and ethanol. The electroless deposition carried out with the same condition for all zincated samples for evaluated effect of zincating process an EN-P coating properties. All chemicals used in this study were of analytical reagent grade.

Table 1. Chemical composition of first step zincating procedure (bath1).

(g/L)	NaOH	ZnO	Rochelle Salt	$FeCl_3$
	380	75	10	1

Table 2. Chemical composition of second step zincating procedure (bath2).

sample	NaOH	ZnO	Rochelle Salt	$FeCl_3$	$CuSO_4.5H_2O$	SDS
A	380	75	10	1	-	-
B	380	75	10	1	5	-
C	380	75	10	1	5	1

Scanning electron microscope (SEM) CamScan MV2300 equipped with energy dispersive X-ray spectroscopy (EDS) have been used for surface morphology and composition study of the electroless EN–P coatings. Phase characterization of the EN-P coatings was investigated by X-ray diffraction (XRD) using (Philips X’pert, XRD, Cu K α radiation). Electrochemical performance of the sample have been evaluated by using potentiostat/Galvanostat model 263A EG&G Princeton Applied Research and a classical three electrodes cell with a platinum electrode as counter electrode, saturated calomel electrode (SCE) as reference electrode and the samples with an exposed area of 1 cm^2 as working electrode. Simulated acidic rain solution (sulfuric acid (96%) 31.85mg/l, nitric acid (70%) 15.75mg/, sodium nitrate 21.25mg/l, ammonium sulfate 46.2 mg/l, sodium sulfate 31.95 mg/l and sodium chloride 84.85 mg/l) was used as the corrosive media in the electrochemical tests. The potentiodynamic polarization plots were recorded by using a constant voltage scan rate of 1 mVs-1. Electrochemical impedance spectroscopy (EIS) experiments were done in the frequency range of 100 KHz-10 mHz and the perturbation amplitude was 5 mV.

Table 3. Electroless bath compositions and operating conditions

Bath Compositions		Operating conditions	
Nickel sulphate (g 1^{-1})	30	pH	4.9±0.2
Sodium hypophosphite(g 1^{-1})	10	Deposition temp. (°C)	89± 2
Lactic acid (g 1^{-1})	24	Bath Vol. (ml)	250
Propionic acid (g 1^{-1})	3		

3. RESULTS AND DISCUSSION

Figure 1 shows surface morphology of sample after zincating process. Figure 1 a, b, c are obtained morphology of zincating pre-coating process from zincating bath A, B and C respectively. As it shown, by adding copper sulfate to the zincating bath, the surface covering of aluminum substrate by zinc have been increased. Table 4 illustrates the EDS analysis of different zincating coatings obtained from different bathes. According to the results, the Zn concentration increased from 41.6% in bath A to 91.6 in bath C. during zincating process, by immersion of Al substrate in zincating bath, in the surface of sample oxidation and reduction reactions occur. The reactions happened in two anodic (Al dissolution) and cathodic (Zn reduction) sites that can be listed as follow[22]:

$$Zn(OH)_4^{2-} + 2e^- = Zn + 4OH^- \qquad (1)$$

$$Al + 2H_2O = AlO_2^- + 4H^+ + 3e^- \qquad (2)$$

The summation of these two reactions is:

$$Zn(OH)_4^{2-} + 2Al = 2AlO_2^- + 3Zn + 4H_2O + 4OH^- \qquad (3)$$

As results of these reactions, the Zn deposited on the surface of aluminum substrate. Also because of high pH of solution, the aluminum has also been dissolved in electrolyte and hydrogen has been produced according the following reaction:

$$2Al + 4H_2O = 2AlO_2^- + 3H_2 + 2H^+$$

For deposition of Zn on the surface of Al, the nucleation sites is needed. If these sites increase, the final deposition would be more homogenous and uniform. Also the dissolution of aluminum is not uniform, and the surface consist of hollow and pits. For obtaining uniform Zn coating, the Zn atoms should diffused to this hole like sites. According to the EDS and SEM results, addition of copper sulfate to the zincating bath, improved the Zn uniformity and content on the surface. This effect can be explained by nucleation effect of Cu ion. The deposition of Cu on the surface of aluminum, create suitable site for Zn nucleation. Cu increase the electron transformation for reduction of Zn and increase the deposition uniformity and homogeneity. But in bath C, the results show this effect accelerated by adding surfactant. The surfactant, by increasing the surface negative charge, improve the reaction and cause double effect.

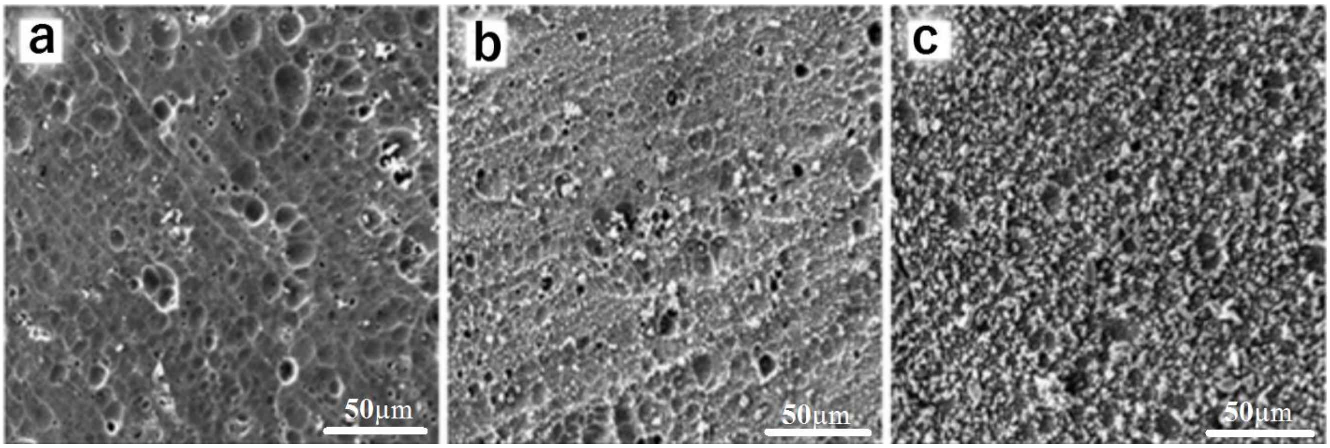

Figure 1. SEM images of the zincating coating from a) A b) B c) C bath

Table 4. EDS chemical composition analysis results for various zincating coatings.

Zincating bath type	Fe (%wt.)	O (%wt.)	Cu (%wt.)	Al (%wt.)	Zn (%wt.)
A	0.8	1.4	-	52.8	41.6
B	1.1	2.5	6.6	3.9	85.8
C	0.8	1.4	5.8	0.23	91.6

Fig. 2 depicts the surface morphology of electroless EN-P coatings on different zincating depositions. As it shown in figure 2, the sample C that pretreated by surfactant and copper sulfate additives, has very uniform and homogenous coating with significantly having more fine nodules and crystalline size. According to the fig.1.a the first sample EN-P coatings is not uniform and consist of various pits and defects. During electroless nickel coating process, by immersion the zincated sample in the electrolyte, the nickel atoms deposited on the surface with substitution reaction between Zn and Ni, and nickel nucleation site have been created by galvanic reaction. By appearing nucleation sites, the general electroless coating have been deposited on the surface. If the first nucleation layer will be uniform, the final coating then obtained significantly homogenous. Referring to the obtained zincating coatings, results confirm that there is high correlation between zincating deposition quality and final electroless coating morphology, adhesion and protective performance.

Fig.3 illustrates the microhardness results of prepared samples in different conditions. According to the results, the substrate zincating quality, directly affected the microhardness of EN-P coatings. Guojun Qi and et al.[23] reported the effect of zincating process on adhesion of EN-P coatings. They claim that, there is a significant correlation between zinc layer morphology and EN-P adhesion to Al surface. Also they concluded that in combination with the zincating process, an optimized EN-P coating is mandatory for the production of reliable and morphologically sound bumps. In another report the Guojun Qi and et al [24] showed that the obtained zincate morphology has a direct impact on the quality of EN coating and zincate solution chemistry plays main role in achieving good zincate morphologies. Jeong-Gi and his co-workers[25] investigated the effect of ultrasonic agitation during zincating process on adhesion improvement of EN-P layer. They found that the ultrasonic power during zincating increased the nucleation density of Zn particles and refined Zn particle size and as a consequence the adhesion strength of the electroless Ni layer deposited increased. Here the same trend have been observed.

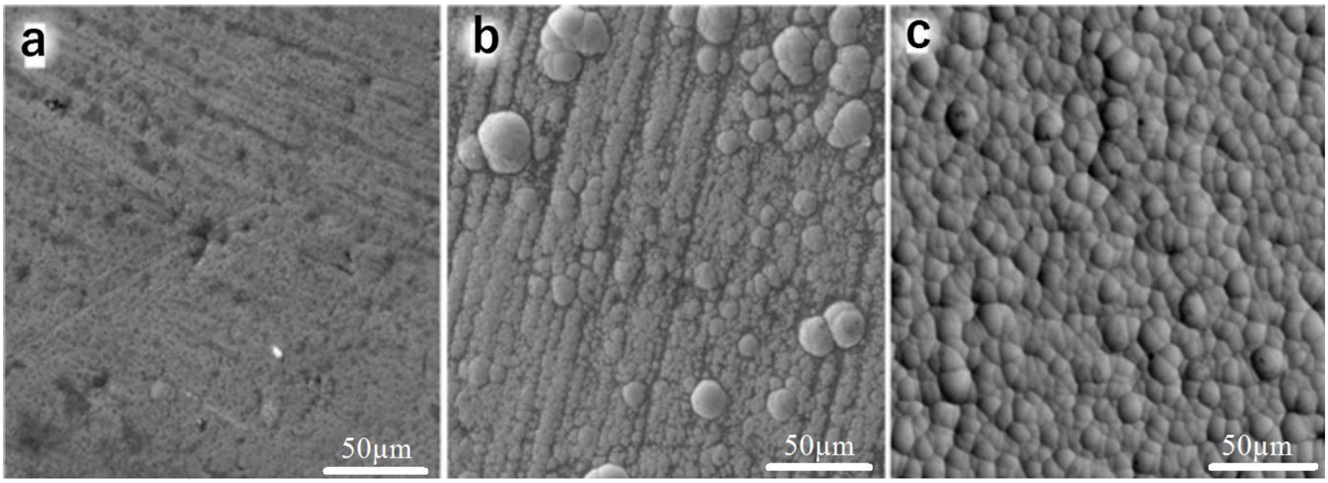

Figure 2. SEM images of the EN–P deposits in various zincating conditions from a) A b) B c) C bath.

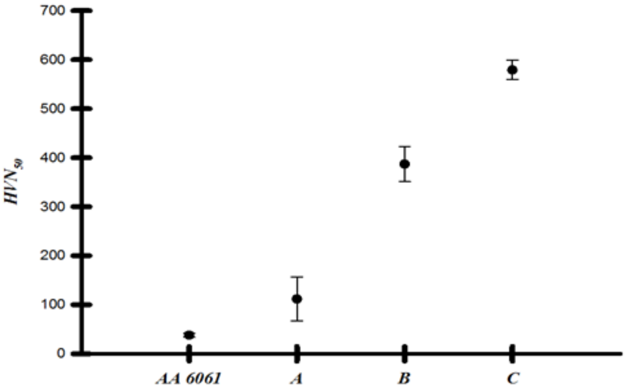

Figure 3. The microhardness of the EN-P coatings and Al substrate in various condition

Fig. 4 shows the diffraction patterns of the EN–P deposits prepared in various zincating conditions. According to the results, the coating microstructure contain mixture of nano-crystalline and amorphous structure. By improving the zincating depositions, the XRD pattern of the electroless coatings peak broaden and the peak height decreased. This is confirm that he nucleation site for electroless deposition increased by obtaining the homogenous and uniform zincating film. According to the Scherrer formula as[20]:

$$D = 0.9\ \lambda/\beta cos\theta$$

where D, λ, β , and θ are grain size, wave length, peak width, and the angle, respectively. The equation depicts the reciprocal relation of broadening of peaks (β) with grain size (D). As the XRD plot revealed the grain size of the coating decreased by improving the zincating coating homogeneity and quality and therefore microhardness of deposits increases. The zincating coating uniformity may be attributed to either dwindle in the size of the grain in electroless coating.

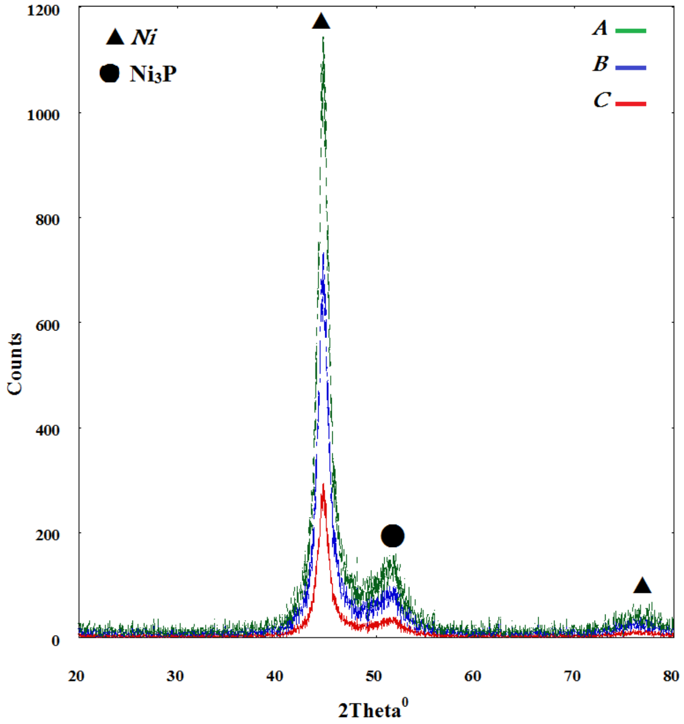

Figure 4. X-ray diffraction plots of the EN–P deposits in various zincating conditions from a) A b) B c) C bath.

Fig. 5 illustrates the obtained typical polarization curves of the EN-P coatings in different conditions. The extracted corrosion parameters for each sample are listed in Table 5. As the polarization results show, the EN-P corrosion resistant directly depends on zincating coating conditions. As we discussed the condition C for zincating coating gave the best Zn coating and also it affected the EN-P coating performance. As a result this conditions leads to decrease in corrosion rate of EN-P coatings. In the presence of surfactant and copper sulfate in zincating coating, the obtained Zn coating covered the Al surface completely with uniform microstructure. This leads to decrease the EN-P crystalline grain size as a results the coating microstructure improved its corrosion resistance. It can be interpreted that when the substitution reaction starts on the substrate surface between Ni and Zn, the Zn layer in C condition provided the very uniform sites for this reaction and with the resumption of Ni-P deposition reaction the film growth conducted very uniform without impressive defects and porosity.

In the Fig. 5 in can be found that the EN-P coatings show the large variation in the cathodic Tafel slope that can be attributed to the surface inhibition by a passive film. The sample C contain larger passive region compare with other samples. In the sample A, the passive region break down in to two parts. This may confirm that the coating contain several defects and porosity.

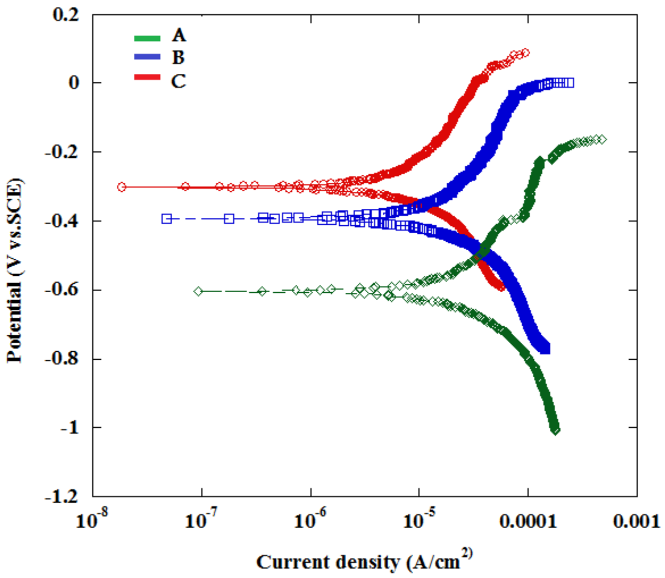

Figure 5. Potentiodynamic Polarization curves of the as-deposited Ni-P coatings.

Table 5. Values of E_{corr} and i_{corr} of EN-P coatings in simulated acidic rain solution.

Sample	$i_{corr}(\mu A/cm^2)$	$E_{corr}(mV)$	b_a(mV)	b_c(mV)
A	78	-611.32	196	75
B	50	-394.66	224	96
C	9.35	-298.64	256	105

The EIS method is a powerful technique that provides the significant information about of protecting performance of the coating. Nyquist plots of EN-P deposition that was precipitated in various conditions was illustrated in fig. 6. The equivalent circuit that was inset of Fig. 6 was used for modeling of the coating corrosion property parameters, where R_S is resistance of the solution, R_1 is the thin oxide layer between electrochemical double layer and protective coating resistance and R_2 is charge transfer resistance of the nickel coating and CPE is the constant phase element which is mainly used to explain the system heterogeneity and some distribution of the value of physical properties of the system. The electrochemical fitted parameters are listed in table 6. Electrochemical studies revealed that the EN-P coating obtained by the best zincating condition improved corrosion resistance of the coating. This effect confirm that the condition C contain lower porosity and grain boundary available for corrosion in EN-P coating. The combined results revealed that zinc nucleation sites correlate to the surface roughness, and electrochemical properties of EN-P coatings. According to the Saito and coworkers[26], the grain size of the deposited Zn, which have smaller grain size and larger nucleation density, can affect the deposition condition of EN-P, resulted in flat and smooth features. D. Takács and et al.[27] investigated the effect of pretreatment on the corrosion performance of EN-P coatings. They reported that pre-treatments affected the corrosion properties of the EN-P coatings. The same trend has also been obtained in this study. Also phase elements (CPE) decreased in different range, meaning that the coating structures changed to a denser and more homogenous film by adding the copper sulfate and surfactant that demonstrated by the dense and uniform Zn film.

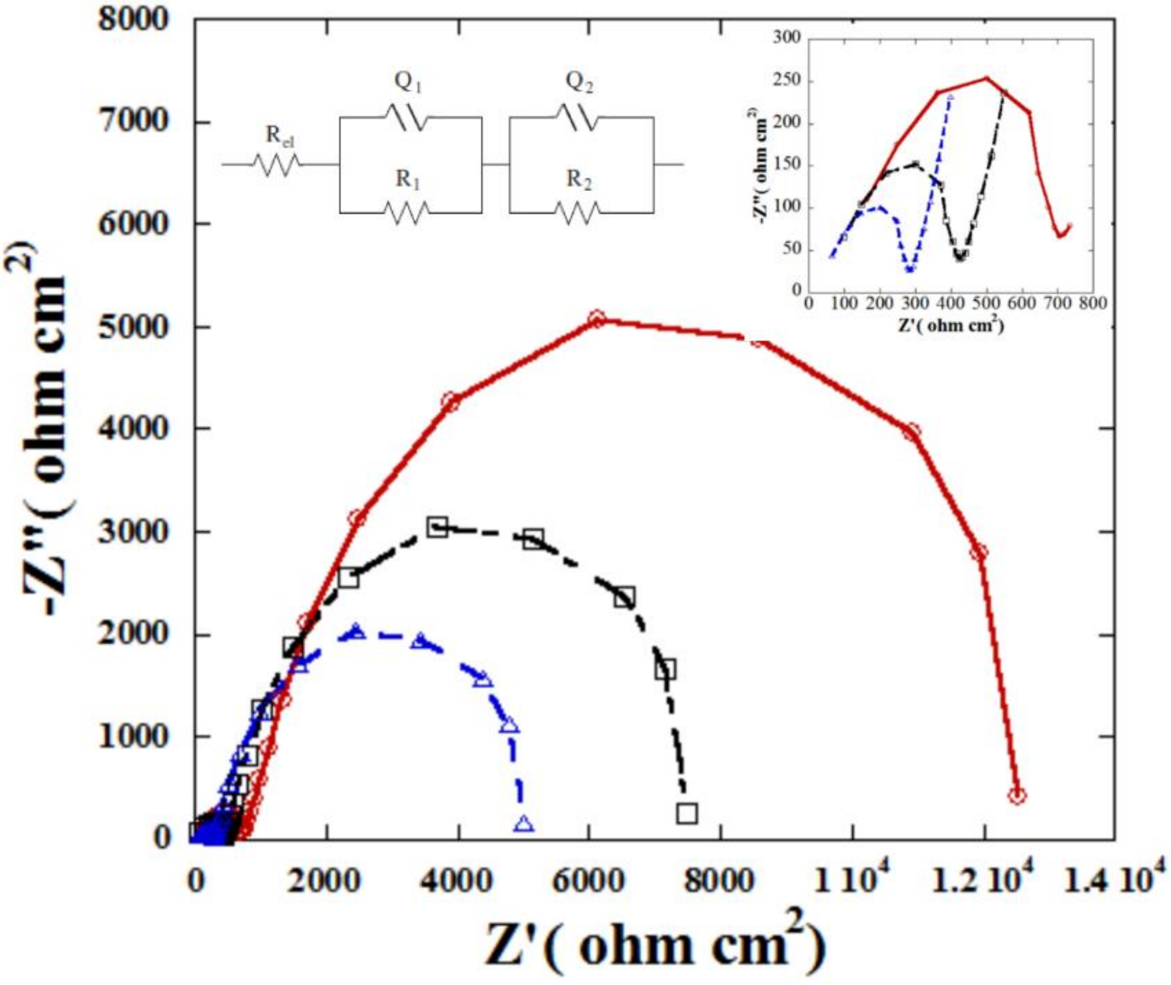

Figure 6. Equivalent circuit and Nyquist plots EN-P coatings in simulated acidic rain solution.

Table 6. Impedance parameters the EN-P coatings in simulated acidic rain solution.

Std	R_S (ohm cm^2)	CPE1-T (μF)	*CPE-P*	R1 (ohm cm^2)	CPE2-T (μF)	CPE2 -P	R2 (ohm cm^2)
A	65.32	0.96	0.812	236.1	72.36	0.936	5233
B	85.66	0.64	0.836	354.1	48.32	0.928	7849
C	185	0.29	0.928	590	38.56	0.824	13080

4. CONCLUSION

Electrochemical behavior of Al 6061 alloy coated with EN-P combination in different zincating conditions have been evaluated. The zincate solution containing copper sulfate and SDS surfactant indicated the fast deposition of Zn and dense nucleation with small Zn particles at the surface. Electrochemical studies revealed that the EN-P coating obtained by the best zincating condition, improved corrosion resistance of the coating. The combined results revealed that zinc nucleation sites correlate to the surface roughness, and electrochemical properties of EN-P coatings. According to the results it can be say that the zincate solution contain these additives is a suitable zincating treatment for Al 6061 alloy and the EN-P coating can protect aluminum alloy from corrosion in corrosive media such as acid rain.

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