Investigation of Corrosion Resistance in Stainless Steel 316L Alloy of Energy Separator by Electroless Plating (Ni-Zn-P)

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Abstract. The corrosion and hardness resistance of Ni-P coating is well recognized. By adding Zn, the electrochemical and mechanical properties of these coatings can be improved. In the coating procedure, two distinct periods of 1-hour and 2-hours are used. To improve the surface qualities of coating specimens, heat treatment at 400oC for one hour is performed. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive analysis (EDS) were used to analyze the deposits. The hardness values of the coated heat-treated samples exceeded 900HV when compared to the bare and as-plated samples. The Tafel extrapolation test is used to determine the voltage and corrosion current in a 3.5% NaCl solution in order to calculate the corrosion rate. Corrosion rates are reduced from 1.81 mpy in bare specimens to 0.0642 mpy in heat treated plated specimens.

1 Introduction

Cadmium, due to its superior corrosion resistance, is widely employed as an anticorrosive protective coating for steel parts utilized in energy systems, transportation, chemical equipment manufacturing, metallic constructions, and so on. [1]. However, due to metal toxicity and utilized salts, in addition to the simultaneous emission of hydrogen ions throughout the cadmiation process, cadmiated materials are prone to acid-induced brittleness [2, 3]. These are the primary reasons why, in recent decades, significant investigations and research have been conducted to identify substitutes for Cd-based anticorrosive protective coatings.

Zinc and its alloys are the most favored sacrificial layer substitutes for Cd. Zn contains a low electrodes standards potential (E0 = - 0.76 V, calculated vs. hydrogen ordinary electrode), making it appropriate for usage as a sacrificial layer for coated steel products [4]. In corrosion conditions, the variance between the normal potentials of zinc and the surface of the substrate (iron) generates the corrosion force of the protective layer, and an elevated level of this difference leads to the rapid dissolution of zinc. The dissolving rate of the protective coating was significantly lowered by alloying zinc with additional components (Ni, Co, Fe, and so on), which changed the alloy's standard electrode potential to values closer

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to the substrate [5]. The Zn-Ni alloy possesses superior anticorrosive characteristics, which are comparable to those of cadmium.Electrochemical deposit of Zn-Ni alloys is an uncommon process by definition. Despite the fact that Ni is considered more noble than Zn, co-depositing both metals resulted in a significant Zn concentration in the produced alloy. Because of the high Zn concentration, the alloy dissolution rate under corrosive medium conditions is likewise high. Ni alloy coating is typically created using two methods: electrodeposition and electroless deposition [6,7].

However electroless Ni-based coatings are increasingly being used in a wide range of applications in the chemical, food, and automotive industries, since this method may be used to create homogenous coatings with superior chemical and mechanical qualities [8,9]. Electroless Ni-based coatings have been shown to have good anti-corrosion and wear resistance capabilities .Nickel and phosphorus alloys can be formed by reducing nickel ions in the presence of sodium hypophosphite (NaH_2PO_2). The composition, temperature, and pH of the plating bath utilized determine the Ni and P concentration of the alloy coating [10, 11]. Many investigations have been conducted to better understand the deposition features of Ni-P-Zn alloy. Abdel Hamid et al. [12] discovered that combining Zn with Ni-P improved corrosion resistance in an alkaline solution (pH 9.5). In this work Ni-P-Zn alloy coatings were developed on stailess steel surfaces via electroless deposition.

Electroless coating processes are chemical reactions that have been in use for more than 70 years and have been used to improve the surface properties of carbon steel and stainless steel [13].

Electroless coating processes may be using metallic alloys (binary, ternary or quaternary). Amongst Ni electroless coats, Ni-P electroless plating is of significant category. This latter plating is commonly used in the engineering industry due to its good hardness, non-crystalline structure, good machining capabilities, high corrosion resistance, good solderbility, very good magnatic, electric properties, high wear resistance and moderate ductility. From its aqueous solutions of electroless nickel plating that use for depositing some nickel alloy onto different substrates without any external source of electric current [14]. Electroless plating differs from electro-deposition which uses direct current from an external source for nickel ions reduction in the electrolyte solution to nickel metal on the different substrates [14].

The sodium hypophosphite is the most important reducing agent which be used in this processes. It is expected that sodium hypophosphite is employed in further than 99% of all electroless plating of nickel. However there are three sorts of EN (Electroless plating of Nickel), coatings obtainable rely on the phosphorus percentage weight [15].

Limited contents of phosphorus (1 to 3% P) are good crystalline and have good wear resistance, but have a slightly lower corrosion resistance in chloride environments. Medium-contents of phosphorus (5 to 9 % P) have a lesser crystalline size but somewhat tend to remain semi-amorphous, on the other hand high- phosphorus contents (over 10 percent P) be present mostly as glass metal. Generally when the deposition of phosphorous content is high, the good corrosion resistance is achieved but the low phosphorous content exhibit bad corrosion resistance [15-16].

The ability to produce deposits with a completely uniform thickness is an extremely important characteristic in all electroless nickel applications. Electroless coating is clearly advantageous when coating complex components with critical areas or dimensions, such as ball valves or threaded parts. This significant advantage over electroplating nickel is due to the absence of current and the associated problems of current distribution. For uniform coating thickness and heat treatment have a significant effect on the corrosion resistance by calculating the corrosion current in the polarization test in a medium 3.5% NaCl solution [17].

2 2 Experimental Details

2.1 Materials Used

Shaft sample from stainless steel 316L is cut to several specimens by wire cutting machine (ACRA-W-A430 type) with dimensions 15mm diameters and 10 mm thickness with 2mm diameter of side hole to hinge in electroless Ni-Zn-P solution. Table 1 shows the chemical composition as determined by an inductively connected plasma atom emission spectrometer (ICP-AES). These samples are grinding by using silicon carbide (SiC) grinding papers (100,150,180, 220, 320, 400, 600, 800, 1000, 1200, 1500, 2000, 2500, grit size). After the processes of grinding and polishing that mentioned above the specimens need high preparation according to ASTM B 254 that used for material preparation as follow:

- Clean for 30 minutes in an ultrasonic device with acetone to remove dust, finishing compound, and any contaminations.
- An alkaline cleaning solution (60g/L NaOH+38g/L Sodium Phosphate+38g/L Carbonate of Sodium) is made to remove contaminations, grease, and any residues of oil at 65-70oC using a low voltage (3-5volt) from a (DC power supply).
- A special activation is performed on the surface of the specimen in order to break the oxide thin metal coating and increase the adhesive force between the bare surface and the thin plating. This method is used in an electro-chemical process that contains [240g/L nickel chloride (NiCl2)+126ml/L hydraulic acid (HCl)] and the specimens are linked to a power supply as anode with a voltage of 3volt for 2-4 minutes at room temperature. The cathode, on the other hand, is nickel pole. After that, the polarity is reversed for 3-5 minutes, and the specimens are rained down with purified water.

Table 1. Chemical Composition of Specimen

Element	%	Element	%
C	0.0258	S	0.0005
Si	0.509	Cr	17.61
Mn	1.04	Mo	2.35
P	0.0409	Ni	11.55
S	0.0005	Cu	0.261
Fe	Bal.		

In this work the bath composition of electroless nickel plating is Ni-Zn-P. Table 2 indicates to the bath composition and its operating conditions of Ni-Zn-P. After finishing of grinding, cleaning, polishing, and activation surface processes the solution is prepared. The specimen is hanged from the side hole inside the solution.Two different times 60 and 120minutes are chosen for coating specimens. The solution is homogenized by magnetic stirrer. The bath temperature is ranged between 85-87oC. pH of solution is controlled between 8-9 in Ni-Zn-P coating. Drops of sodium hydroxide or hydrochloric acid are added to regulate solution pH during the operation of coating.

Sodium hydroxide is added to increase pH but hydrochloric acid is added to decrease pH.The time of coating is chosen 1 and 2 hours. After the coating process is completed, the specimens are placed in a vacuum oven for 30 minutes at 50 oC to dry. For heat treatment the specimens are maintained for 1 hour at the setting temperature and allowed to be coaled. specimens are put in small cup in vacuum furnace (Electrical Tube Furnace Type MTI-(GSL1600X)) at 400oC for one hour. A scanning electron microscope was used to examine the morphology of the Ni-P alloy layer (SEM device model-TESCAN) with an EDS instrument model (X-Max), and an EDS attachment was used for qualitative elemental

chemical analysis. The X-ray difractometer (XRD) is used to examine the sample's crystallographic structure. Figure 1 shows bare and coated specimens.

Table 2. Bath and Conditions of Operation

Chemical Composition	**Concentration (g/L)**
Nickel Sulphate	25
Sodium Hypophosphite	16
Zinc Chloride	3
Ammonium Chloride	23
Sodium Citrate	35
Operating conditions	
pH	8 -9
Temperature	85-87 °C
Magnetic Stirring (RPM)	300 ± 10

Fig. 1. (a): Bare and (b) Coated Specimens

2.2 Polarization Test

The resistance of corrosion for deposited specimens is measured by computerized automated lab electrochemical system. This test is carried in electrolyte solution (3.5% sodium chloride).There are three electrode are used in this electroless plating or any another electroless plating, one of them is the electrode of working (Ni-Zn-P) deposited on stainless steel with 4.71 cm2 surface area. The second is auxiliary electrode which made from a platinum and the other is a saturated calomel electrode (SCE).The SCE electrode is used as a reference electrode and 1mV/s is used as the scan rate in this process.

2.3 Hardness Resistance

Despite the high hardness of stainless steel, electroless coating methods enhance the metal's penetrating resistance by more than half in the absence of heat treatment. More than three hardness measurements were carried out in bare metal according to the effect of a force of 300 g/cm2 and a stable duration of 15 seconds. On the other hand 50-100g/cm2 and 10s period time were carried out on the coating surface.

2.4 Measurement of Coating Thickness

A digital gage Type (TT260), is used to determine the thickness of coating for different

coating specimens at two different time of coating. The device accuracy ± 0.1 μm. In this way measurement is taken in three or four places to obtain averaged thickness but this device in some times gives non accurate readings, so that, the optical microscope and SEM are used to know the thickness in most times.

3 Results

3.1 Qualitative Analysis and Surface Morphology

Dispersive X ray microanalysis (EDAX) was used to determine the concentration and elemental distribution of the thin films, and scanning electron microscopy (SEM) was used to determine the morphology and microstructure. The surface morphology of the Ni-Zn-P coating is characterized by a spherical nodular structure (Fig. 3). Temperature was the most important parameter evaluated since it plays a critical role in electroless baths and provides a driving force for the process. Temperature between 85-87 oC were carried out because Ni-P-Zn electroless coating deposition does not occur below 65oC.The photos also indicate that the coatings are consistent and non-porous.

The morphology of the surface of the layers was observed and displayed in Figure 2 after heat treatment at 400 C for 1 hour. The heat treatment coatings have a distinct morphology than the as plated coatings. After heating, the coating became more homogeneous and crystalline, with a spherical-like structure (Figure 2).

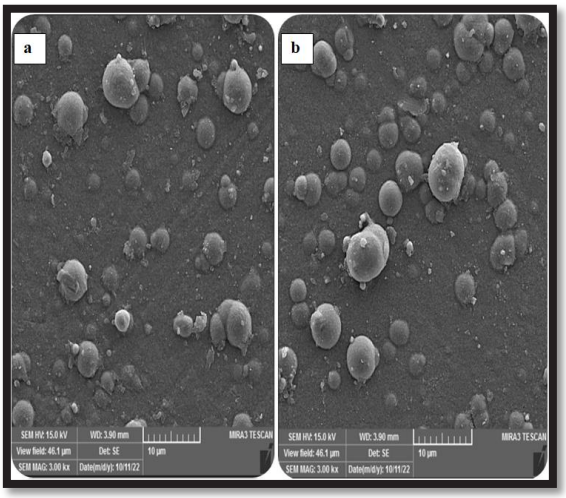

Fig. 2. SEM Images of Ni-Zn-P Plating (a): As-Plated(b):Heat Treated (400oC 1-hr.)

Figure (3. a) shows the (Ni-Zn-P) EDS chart for a one-hour time coating. This graph shows different important substances that are present on coating surfaces, including Ni, P, and Zn. Figure (3. a) shows the percentage of zinc produced by coating after one hour, which is equal to 15.77%; whereas, Figure (3. b) shows the percentage after two hours, which is equal to 18.77%.

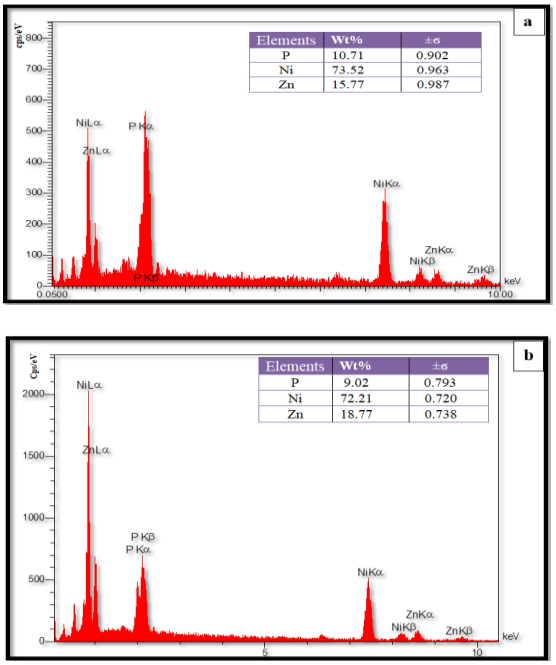

Fig. 3. EDS Chart of Coated Specimen by Ni-Zn-P at Coating Time: (a): 1-hr. (b): 2-hrs.

3.2 Phases Analysis

Figure (4.a) depicts the Ni-Zn-P plating bath's X-ray diffraction pattern as it was being plated. Randomness and the absence of crystallization are obvious, however under some circumstances and with a certain level of intensity, crystallization may be observed, and the phase may be weak. On the other hand, Figure (4. b) depicts the X-ray diffraction pattern for the Ni-Zn-P plating bath after heat treatment. The predominant phases are Ni12P5, NiZn and Ni5P2 due to increased X-ray scattering. These phases appear in the planes (400) with 100%, (101) with 45% and (428) with 55% respectively.

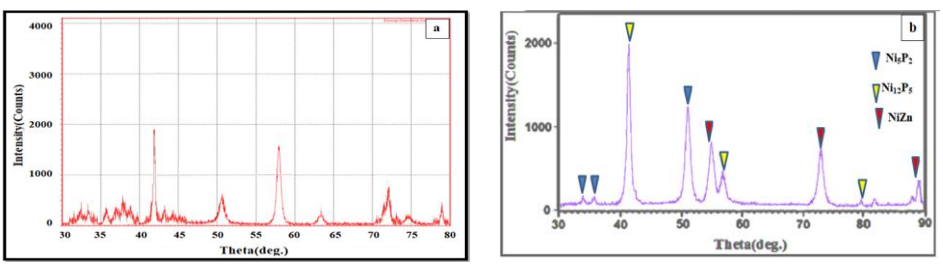

Fig. 4. XRD Pattern of (Ni-Zn-P) :(a): As Plated, (b): Heat-Treated

3.3 Resistance of Corrosion

Nickle chloride (NaCl) is the most common medium corrosion of the electrochemical tests. Electroless plating (Ni-Zn-P) can be effected by pitting corrosion in the solution. Many voids can be appear in surface coating of electroless plating (Ni-P). Pitting corrosion takes place due to the presence of halides ions such as effective chloride ions (Cl)

where these ions penetrate the voids. The electrochemical data for corrosion test such as voltage and current of corrosion can be taken from polarization curves which can be shown in Table 3. Figure 5 shows the polarization curve of bare specimen but Figures 6 and 7 display the curves of potantiodynamic polarization for electroless plating (Ni-Zn-P) at 1-hour and 2-hours coating time after heat-treatement at 400°C in (3.5% NaCl) respectively.

From these curves it is possible to obtain the corrosion potential difference as well as the corrosion current, and thus we can calculate the corrosion rate according to the equation of electrochemical corrosion where corrosion rate

$$(\text{mpy}) = \frac{0.13\ Icorr.EW}{A.\rho} \quad (1)$$

E.W= equivalent weight of coated metal (for NiZn=31.025, for Ni5P2=14.74,) calculated according to ASTM G102

A= exposed specimen area (cm2)

mpy = Corrosion rate (mils per year).

Table 3. Data of Electrochemical Corrosion.

Polarization Results in 3.5% NaCl			
Specimens	Bare	Time of Coating 1-hour	Time of Coating 2-hour
E_{corr} (mV)	-360.7	-277.7	-288.1
i_{corr} (μA/mm^2)	4.37	0.3	0.259
Corrosion rate (mpy)	1.81	0.073	0.0642
inhibitive efficiency (I.E.) **%**	-	96	96.5

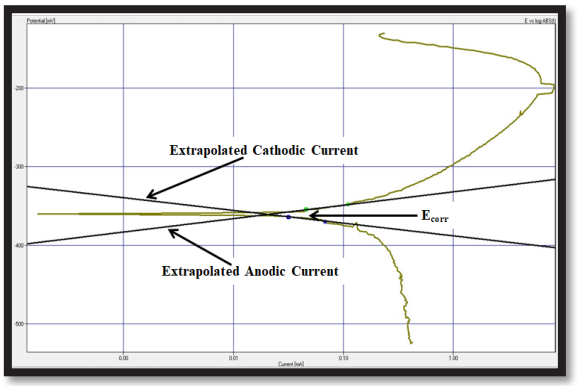

Fig. 5. Polarization Curve for Bare Specimen in 3.5%NaCl

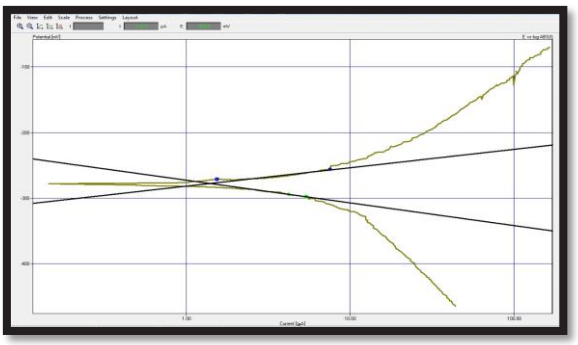

Fig. 6. Polarization Curve for Coated Specimen by Ni-Zn-P (1-hr. Coating Time)

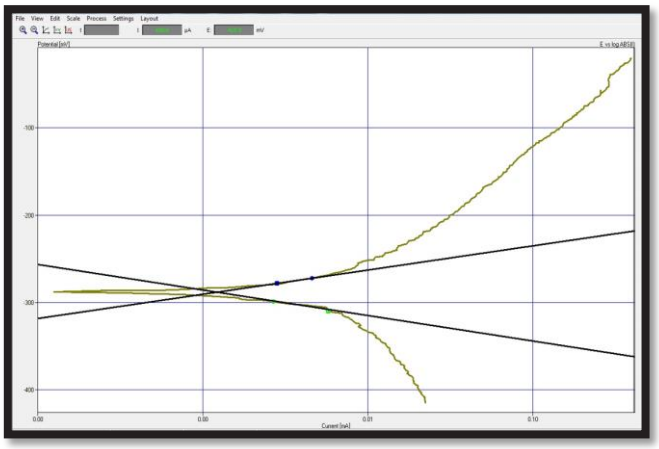

Fig. 7. Polarization Curve for Coated Specimen by Ni-Zn-P (2-hrs. Coating Time)

3.4 Test of Hardness Resistance

The micro-hardness increased from 330HV in base metal to 937HV heat treated samples. Continuing to increase the temperatures by heat treatment above a certain limit gives a negative indications of a decrease in hardness.On the other hand the coating specimens by (Ni-Zn-P) without heat treatment (as plated) have lower hardness than heat treated specimens. The hardness of as plated specimens exceed 682HV.The formation of intermetallic compound such as (NiZn,Ni5P2 and Ni12P5) after heat treatment and the redistribution of plating elements are the major important reasons for improving surface properties such as hardness. Figure 8 depicts the hardness of bare and coated specimens.

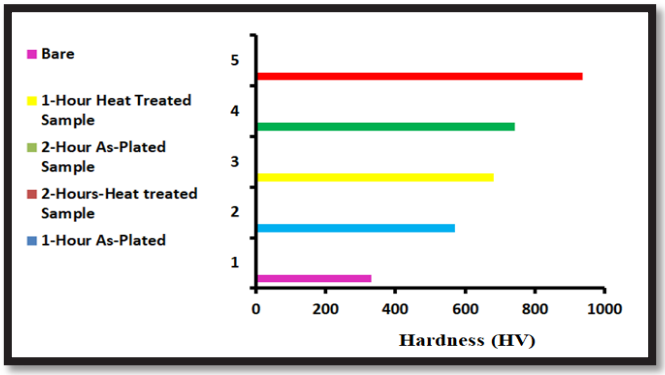

Fig. 8. Hrdness Chart for Bare and Coated Specimen

3.5 Coating Thickness

Coating thickness in electroless plating (Ni-Zn-P) has high effect on most of mechanical, electrical, and surface properties. Several different range of coating thickness that are obtained; (10-70) μm. This different depend on several parameters (time of coating, temperature of solution, type of bath, degree of agitations, the

presence of another particle). In this study two different time(60,120min.) are used. Figure 9 shows the thickness of coating by SEM image for cross section of coated specimens by(Ni-Zn-P).

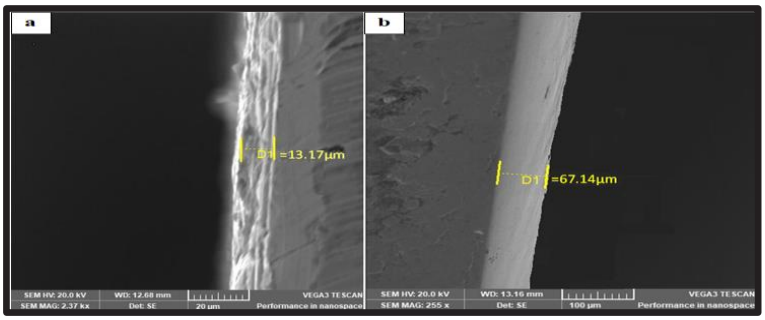

Fig. 9. SEM Images of Coating Specimens by (Ni-Zn-P) at: (a): 1-hr. Time of Coating; (b): 2-hrs time of Coating

4 Conclusion

1. Electroless plating with Ni-P as a matrix is an efficient process for coating metals or alloys that can offer an adequate homogeneous distribution on most alloys and metal substrates.
2. The additives elements metal to matrix such as Zn in low percentage give good surface properties rather than with out these elements.
3. Coating thickness is depended on time of coating so (10-30) µm in i-hour time of coating and (30-70) µm in 2-hours coating time. This different in thickness depend on several parameters (time of coating, temperature of solution, type of bath, degree of agitations.
4. Good corrosion resistance in Tafal test in 3.5%NaCl solution with compared with bare metal.
5. High increasing in hardness Vickers (HV) for coating specimens by Ni-Zn-P (2hrs.coating time-heat-treated) than bare specimens,where reached to 937HV in the coating specimens while was 330HV in bare specimen .

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