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Galvanic Corrosion Behavior of Electroless Nickel Coating in Al-Zubare Harbor-Water

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Abstract

Electrode potentials in AL-Zubare harbor water (South -Gas Company), of 23.88 ohm-cm at 20°C were reported for 26 metals and alloys including values for electroless nickels that signify a greater passivity than steel. The large potential difference between steel and electroless nickel predicts severe galvanic corrosion, which was confirmed by weight loss data for coupled steel and electroless nickel electrodes immersed in AL-Zubare Harbor water (South -Gas Company, 23.88 ohm-cm at 20°C) .Changes in the phosphorous content in the range of 7.10 to 12.45 percent had only a slight effect on the electrode potential of electroless nickel.

This study indicates the beneficial use of electroless nickel coating is more passive than other (metals and alloys) and that galvanic corrosion of active metals such as steel can be severe .

Keywords: - Corrosion, Electoless Nickel Coating, Potential Plating.

الخلاصة

سجلت قيم الجهد الكهربائي المقاس في مياه ميناء الزبير (الخاص بشركة غاز الجنوب ذو المقاومة الكهربائية 23.88 أوم – سم بدرجة حرارة 20 مئوية) لــ (26) معدن وسبيكة بضمنها الطلاء بالنيكل اللاكهربائي والذي دل على خمولية أكثر من الفولاذ. كان فرق الجهد الكهربائي الأكبر بين الفولاذ والنيكل اللاكهربائي ينبئ بشدة التآكل الكلفاني والذي تم أستخراج قيمه من البيانات الخاصة بفقدان الوزن لمزدوج أقطاب الفولاذ والنيكل اللاكهربائي المغمورة في مياه ميناء الزبير. أن تغيير نسبة المحتوى الفسفوري ضمن المدى (7.1 إلى 12.45 %) كان له تأثير قليل نسبياً على مقدار الجهد الكهربائي لقطب النيكل. تشير الدراسة إلى فائدة استخدام طريقة الطلاء بالنيكل اللاكهربائي لكونه أكثر خمولية من بعض المعادن والسبائك وان التآكل الكلفاني شديد للمعادن الفعالة مثل الفولاذ.

1-Introduction:

Galvanic corrosion results when two different metals in electric contact are immersed in an electrolyte. The potential or voltage difference between the metals causes a current to flow, usually increasing corrosion of the most active metal [1] .Corrosion of steel (usually a weight loss) is directly proportional to the current flow (I) to the cathode, which is related to the potential difference (E)between the two metals by ohms law:

$$I = E/R \quad \ldots\ldots\ldots\ldots (1)$$

where R is the resistance of the cell. Current will continue to flow in a galvanic cell and the anode will continue to corrode only as long as potential difference is large enough and the resistance is small enough to support the above reaction [2].

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The potential of metals is a measure of the energy stored in it by the refinement of its ore and is indicative of its tendency to corrode. However, the environment also affects the potential of a metal, depending on the temperature, acidity, salt content and other factors [3].

A limited number of metals can be deposited by chemical reduction rather than by electrical reduction. The basic reaction is:

$M^{2+} + 2e^- \rightarrow M$……………..(2)

The deposits produced by nickel electroless plating are uniform in thickness compared to electrodeposits, which vary in thickness. It is also possible to plate onto non-metallic surfaces, for example plastics and ceramics. Chemicals need to be added to the bath continually to replace materials as they are used up. This leads to a build up of breakdown products in the bath, which reduces its efficiency. [4, 5].

2. Experimental Work:

2.1 Materials:

2.1.1 Substrate

The materials used are low carbon steel. The chemical composition is shown in Table (1) which is done in the specialized Institute of Engineering Industrials and compared with the composition of the DIN standard.

2.1.2 Surface preparation

All the samples were subjected to the following pre-treatment and plating procedure:-

1. Ultrasonic cleaning in industrial cleaning solution at 60 °C for 30 min.
2. Rinsing with tap water at room temperature for 2 min.
3. Cleaning in 20 vol. % H_2SO_4 at room temperature for 30 s.
4. Rinsing by immersion in de-ionized water at room temperature for 2 min.
5. Cleaning in 5 vol. % H_2SO_4 at room temperature for 30 s.
6. Rinsing by immersion in de-ionized water at room temperature for 2 min.
7. Electrocleaning in 40 g/l potassium carbonate solution at room temperature for 30 s. The current density applied was 0.5 A/ cm^2 . In order to provide a better scrubbing action on the surface of the specimens during electrocleaning, periodic starts and stops were introduced (5 s on and 1 s off).
8. Rinsing by immersion in de-ionized water at room temperature for 30 s.
9.Electroless nickel coating process.
10. Rinsing by immersion in 60 °C water for 1 min.

2.2. Electroless nickel phosphorus bath

In order to completely monitor and control the coating parameters such as bath pH, temperature, agitation factors, and chemical composition during the coating process which are shown in Fig.(1). Table (2-A) shows some of the general properties of electroless nickel coatings. A list of the components used in the electroless nickel technique is shown in Table (2-B) [6].

2.3 Potential measurements:

A galvanic series of 26 different metals and alloys were developed by measuring their open circuit potential in AL-Zubare harbor water (South -Gas Company , 23.88 ohm-cm at 20^{o}C), in order to compare the galvanic corrosion behavior of electroless nickel and other metals. The measurements were made in accordance with ASTM Standard G-71 [7].Many specimens were the standard, threaded electrodes used for electrochemical corrosion testing. Specimens were prepared by cutting a sample of the metals sheet, soldering it to a lead wire and cementing it in a glass holder with epoxy. The electroless nickel coatings contained 11.5 percent phosphorous. Some electroless nickel coatings samples were heat at 190 and 400^o C to compare their potentials with that of unheated electroless nickel.

Each metal and alloy were degreased and pickled before testing. After immersion in AL-Zubare Harbor water (South -Gas Company, 23.88 ohm -cm at 20^{o}C) and potential measurement, specimens were cleaned and examined for corrosion. Although corrosion was not quantified, the more active metals obviously had been attacked by the seawater. The potential of the metals and alloys were referenced to a fused silver chloride electrode while measurements were made using an electronic millivolt meter with input impedance of 10^3 ohms and an accuracy of ±0.02 percent. Such a high impedance meter was necessary to avoid polarizing the electrodes and changing their potentials. Potentials were determined two or three times daily for eight days until a steady state was reached. The last two or three reading for each electrode were recorded as the open circuit potential.

The potential data are summarized in Tables (4, 5, 6, 7), which represents a galvanic series in AL-Zubare Harbor water (South -Gas Company , 23.88 ohm -cm at 20^{o}C), phosphorous content, heat treatment for electroless nickel coatings and galvanic corrosion for steel and electroless nickel coatings.

3. Results and Discussion:

3.1 Effect of Potential Measurements:

The potential data are summarized in Table (4), which represents a galvanic series in AL-Zubare Harbor water (South -Gas Company, 23.88 ohm-cm at 20^{o}C), beginning with the most active (magnesium and zinc) and ending with the most passive (platinum and graphite).The relationship of the potential of electroless nickel coatings and steel (-205 vs.-657 mV).

Results with the galvanic series in natural seawater confirmed the stability of the test method [8].

3.2 Effect of Heat Treatment:

Less surprising were the shifts in potentials to -235mV after baking at 190 ^{o}C and -285mV after hardening at 400 ^{o}C as shown in Table (5). The -80 mV shift from -205 mV for the hardened coating, may be due to the transformation into microcrystalline nickel.

3.3 Effect of Phosphorous content:

It appears that phosphorous content in electroless nickel coatings may affect the galvanic potential 0.4 l of the coating. For example, the deposit containing 12.45 percent phosphorus had potential about 29mV more negative than the coating 11.6 percent phosphorous and different potentials for others as shown in Table(5). It is apparent that all electroless nickel coatings are more passive than steel in AL-Zubare Harbor water (South -Gas Company, 23.88 ohm-cm at 20^{o}C), the potential of electroless nickel coatings is about 348 mV more positive than steel and 452 mV than aluminum. This difference is more than enough to initiate and sustain galvanic corrosion in AL-Zubare Harbor water (South -Gas Company , 23.88 ohm-cm at 20^{o}C).

3.4 Effect of galvanic measurements:

The result confirms that galvanic corrosion in AL-Zubare Harbor water (South -Gas Company, 23.88 ohm-cm at 20^{o}C) can be severe for steel coupled to electroless nickel coating. As shown in Table (7) the corrosion rate of steel increases from 250 micrometer/year to 660 or 690 micrometer/year when connection is made to electroless nickel coatings.

The weight loss of the steel panel coupled to electroless nickel coatings with a phosphorus content of 11.5 percent was slightly less than that of the steel coupled to the low-phosphorus deposit as shown in Table (7).

Galvanic corrosion is especially severe in AL-Zubare Harbor water (South -Gas Company, 23.88 ohm-cm at 20^{o}C) because of its high salt content and electrical conductivity. In other, more resistant environments in which potential differences are smaller, the amount of galvanic corrosion can be slight.

4. Conclusions:

The data in this paper show that electroless nickel coatings in AL-Zubare Harbor water (South-Gas Company, 23.88 ohm-cm at 20^{o}C) are:

- more passive than others
- galvanic corrosion of active metals such as steel can be severe.
- it can be found that there is a marginal increase in potential may be due to the transformation into microcrystalline nickel.

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Table (1) Chemical composition of carbon steel (in Wt %).

Element	Specialized Institute of Engineering Industries values	(DIN Standard)
C%	0.178	≤ 0.2
Si%	0.006	≤ 0.55
Mn%	0.309	≤ 1.5
P%	0.0001	0.03
S%	0.022	0.05
Cr%	-	-
Mo%	-	-
Ni%	-	-
Cu%	-	-
V%	-	-
Fe%	Pure	pure

Table (2-A) General properties of nickel electroless coatings[4].

Properties	Value
Phosphorus Content	5-15% wt.
Specific Gravity	7.75 to 8.25 g/cc
Hardness (as plated)	45 to 50 Rc
Hardness (heat-treated)	60 to 70 Rc
Ductility	Will pass 180° bend test
Color	Bright deposit resembling polished stainless steel

Table (2-B) Nickel electroless coatings bath and their function [4].

Component	Function
Nickel Ion	Source of Metal
Hypophosphite	Reducing Agent
Complexants	Stabilizes the solution
Accelerators	Activate Hypophosphite
Buffers	Controlling pH (longer term)
pH regulators	Regulates the pH of the solution
Stabilizer	Prevents solution breakdown
Wetting agents	Increases wettability of surfaces

Table (3). Properties of electroless Nickel based coatings [4].

	Coating System			
Property	**Ni–3P**	**Ni–8P**	**Ni-11P**	
Composition range: balance nickel	3–4 %P	6–9 %P	11–12 %P	
Structure◦	M–c	m–c–a	A	
Internal stress (MPa)	−10	C40	−20	
Final melting point (_C)	1275	1000	880	
Density (gm/cm3)	8_6	8_1	7_8	
Coefficient of thermal				
Expansion (mm/m-_C)	12_4	13_0	12_0	
Electrical resistivity (mW-cm)	30	75	100	
Thermal conductivity (W/cm-K)	0_6	0_05	0_08	
Specific heat (J/kg-K)	1000	ND	460	
Magnetic coercivity (A/m)	10000	110	0	
Tensile strength (MPa)	300	900	800	
Ductility (%)	0_7	0_7	1_5	
Modulus of elasticity (GPa)	130	100–120	170	
Hardness as-deposited .HV100)	700	600	530	
Hardness heat-treated .HV100)	960	1000	1050	

Table (4) Galvanic series in Al-Zubare Harbor Water.

Magnesium	-1465
Zinc and zinc plating	-980
Hard coat anodizing	-695
Cadmium plating	-688
Mild steel	-657
5Cr steel	-557
Tin	-405
Watts nickel plating	-410
Tin-silver solder	-390
Antimony	-336
Lead	-340
Hardened electroless nickel coating	-287
Silver plating	-268
Baked electroless nickel coating	-236
Sulfamate nickel plating	-214
Electroless nickel coating	-205
Hard chromium	-187
Copper	-170
304 stainless steel	-117
316 stainless steel	-28
Monel 400	+20
Inconel 600	+119
Titanium	+15
Tantalum	+155
Platinum	+218
Graphite	+223

Table (5) Heat Treatment.

Process	Potential (mV vs. AgCl)
Baking at 190C	-236
Hardening 400C	-286

Table (6) Effect of Phosphorus Content on Galvanic Potential in Al-Zubare Harbor water.

Phosphorus Content %,	Potential (mV vs. AgCl)
7.10	-230
7.70	-268
9.15	-252
9.4	-233
10.40	-223
10.65	-240
10.80	-205
11.50	-220
11.75	-201
12.45	-230

Table (7) Galvanic Corrosion of Electroless Nickel and Steel Couples.

Metal	Potential (mV vs. AgCl)	Corrosion Rate, (μm/yr) Uncouple	Couple
Couple A			
Steel	- 636	252	692
Electroless Nickel (9.15%)	- 212	5.4	0.008
Couple B			
Steel	- 638	252	661
Electroless Nickel (11.5%)	- 202	2.4	0.007

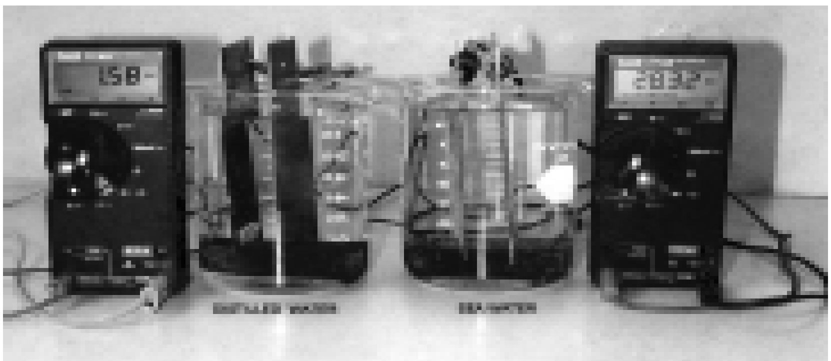

Figure (1): Effect of AL-Zubare harbor water (South -Gas company, 23.88 ohm-cm at 20^{o}C) on galvanic corrosion.