Int. J. Electrochem. Sci., 11 **(2016)** 899 - 905

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Influence of Ni-Sn-P Electroless Plating on Anticorrosion Performance of CF Steel

Junyan Liao[1], *Jie Yang*[2,*], *Weijie Fan*[2], *Qingchao Li*[2], *Qian Zhang*[2], *Xiaodong Zhao*[2,3,*]

[1] Jinhua Polytechnic, Jinhua 321007, China
[2] School of Naval Architecture and Ocean Engineering, Zhejiang Ocean University, Zhoushan 316022, China
[3] Key Laboratory of Offshore Engineering Technology of Zhejiang Province, Zhoushan 316022, China
[*]E-mail: kittyangj@163.com, danielxdzhao@aliyun.com

Received: 20 October 2015 / *Accepted:* 3 December 2015 / *Published:* 1 January 2016

In this work, Ni-Sn-P electroless plating treatment was performed on surface of Crack Free(CF) steel to improve its corrosion resistance in seawater. The electrochemical properties, microstructure and phase structure of CF steel after electroless plating for different periods of time were studied by polarization curves and AC impedance test, scanning electronic microscope(SEM) and X-ray diffraction(XRD) analysis. Results showed that with a period of electroless plating process over 1h, dense and homogeneous amorphous alloy layer generated on the surface of CF steel and served as a barrier to inhibit the anodic reaction, thus the corrosion resistance was improved.

Keywords: Electroless plating, Corrosion resistance, Potentiodynamic polarization, AC impedance, Crack Free(CF) steel

1. INTRODUCTION

Compared with the conventional carbon steel, the carbon content of Crack Free(CF) steel, developed by advanced technology, has been reduced to less than 0.09%. Its welding performance and toughness have also been greatly improved. In recent years, CF steel has drawn much attention due to its advantages of low sensitive to welding cracks and moderate yield ratio [1~3]. It has been widely used for pressure pipes in the power plants and mechanical supports in coal mines. However, CF steel is only used in the environment of inland water, while its corrosion resistance greatly declined in the harsh environment of seawater. This disadvantage of CF steel is a very important factor preventing it from using as a favorable material for marine engineering, while other materials cannot replace CF steel in terms of weldability and yield ratio. Therefore, how to improve the corrosion resistance of CF steel is of great significance to the application of CF steel in marine environment.

Ni-Sn-P electroless plating is a kind of promising surface processing technology. The produced alloy coating has relatively high hardness, excellent mechanical properties and electrochemical corrosion resistance [4, 5]. In previous study, a compound reducing agent composed of sodium hypophosphite, glucose and glycine with a certain proportion was developed, with which the reduction rate of Ni-Sn-P plating solution and utilization of effective components could be greatly improved [6]. In this study, the surface of CF steel was processed by Ni-Sn-P electroless plating based on the compound reducing agent for different time, and the electrochemical properties, microstructure and phase composition of CF steel with and without treatment were studied by electrochemical polarization, AC impedance method, scanning electronic microscope and X-ray diffraction.

2. EXPERMENTAL DETAILS

2.1. Coating Preparation

The composition of CF steel used in the experiment is shown in Table 1.

Table 1. Composition of CF steel sample

element	Cr	Mn	Mo	V	C	Fe
composition	0.1%~0.3%	1.0%~1.6%	0.1%~0.3%	0.02%~0.06%	≤0.09%	bal

The pre-plated parts were machined into the size of 200mm×100 mm×2mm, and processed according to the requirements in Table 2. Samples were cleaned by water between each two operations within 2 min, and then dried and ready for use after plating.

During the plating operation, the plating solution was prepared after the complete dissolution of all ingredients weighed accurately in 1000ml distilled water. The selected reduction agent was composed of 75% sodium phosphate, 23% glucose and 2% glycine. Then the solution was heated to 85°C and adjusted with pH value of 4.5~5.5, then the plating was performed according to 4.0dm^2/l loading ratio.

Table 2. Preparation of Ni-Sn-P electroless plating

step	operation		ingredients	condition
1	pre-treatment	sanding		SiC abrasive paper, step by step to 1000#
2		alkaline cleaning	NaOH 50g/l, $Na_3PO_4 \cdot 12H_2O$ 15g/l	40°C, 2min
3		acid cleaning	dilute sulfuric acid 150ml/l, nitric acid 10ml/l	room temperature, 2min
4		activation	dilute sulfuric acid 50ml/l	30°C, 10min
5		water cleaning	distilled water	
6	plating		$NiSO_4$ 20~27 g/l, $SnCl_4$ 2~4g/l, reduction agent 16~27g/l, Sulfourea 0.0006~0. 001 g, $Na_2S_2O_3$ 2~4 g/l, Glycine 0.1~0.5g/l, Sodium acetate 10~13g/l, $C_2H_4O_2$ 6~8g/l	temperature:85~93°C pH: 4.5~5.5 time:3h
7	modification		myristic acid in ethanol solution, 22.83 g/l	time:5~6d

2.2. Electrochemical Measurements

The electrochemical properties of CF steel with electroless coating were tested with a PARSTAT 2273 electrochemical workstation, and a conventional three-electrode cell system was adopted: the saturated calomel electrode (SCE) was selected as reference electrode, platinum electrode as auxiliary electrode, the coated sample to be measured as working electrode and clean seawater from East China Sea as the electrolyte.

The frequency range for the electrochemical impedance test was 100KHz~0.01Hz, the AC disturbance potential was 10mV, and 42 points were tested. The scanning potential range for the potentiodynamic polarization test was from -0.35 to +0.25 V/SCE versus corrosion potential at a scan rate of 20 mV/min.

2.3. Morphological Characterization

Morphological characterization was completed with Zeiss Ultra 55 type scanning electronic microscope (SEM) and the component elements were analyzed by D8 Advance type X-ray diffractometer.

3. RESULTS AND DISCUSSION

3.1. Polarization measurements

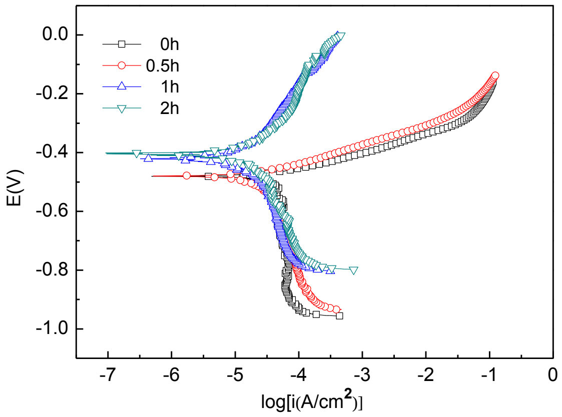

Figure 1. Potentiodynamic polarization curves of CF steel samples after electroless plating

A potentiodynamic polarization curve test was conducted on the surface of CF steel samples after electroless plating for periods of 0h, 0.5h, 1h, and 2h, respectively, shown in Fig.1.

The main shape of the polarization curves of CF steel after electroless plating for different periods had hardly changed, indicating that the reaction process of the electrodes was basically the same. Compared with the samples processed for 0h or 0.5h, anodic reaction process of the ones processed for 1h or 2h were significantly inhibited. Under the conditions of the same polarization potential, the corrosion current density of the latter was obviously decreased. The cathodic curves were nearly overlapped, showing that the cathodic reaction process were all under electrochemical control.

Furthermore, the polarization curves were fitted by the Cview software and the fitting parameters were shown in Table 3.

Table 3. Electrochemical corrosion parameters derived from polarization curves measured in Fig.1, where E_{corr} is corrosion potential, and b_a and b_c are anodic and cathodic Tafel slopes

time (h)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} (A/cm^2)	E_{corr} (V/SCE)	Corrosion Rate (mm/a)	η(%)
0	62.18	517.73	5.5675E-5	-0.4805	0.6548	--
0.5	68.26	510.02	4.8666E-5	-0.4802	0.5371	17.9
1	86.17	400.84	1.6778E-5	-0.4063	0.1873	71.3
2	94.89	386.54	1.5143E-5	-0.3980	0.1781	72.8

The results showed that after electroless plating for periods of 1h and 2h, E_{corr} of the samples shifted 0.8V towards the positive direction. Accordingly, the polarization resistance increased rapidly. As a result, the corrosion current density reduced to 1.6778E-5 A/cm^{-2} or 1.5143E-5 A/cm^{-2} from 5.5675E-5 A/cm^{-2} before the surface processing, and the inhibition rate reached to 71.3% and 72.8%, respectively. In case of 0.5h, the corrosion potential, corrosion rate and the inhibition rate of the samples changed slightly. From above, it showed that the period time for the CF steel plating had an important effect on its corrosion resistance.

3.2. Impedance measurement

Fig.2 shows the Nyquist diagram by AC impedance measurement in natural seawater of CF steel samples after electroless plating for different processing periods.

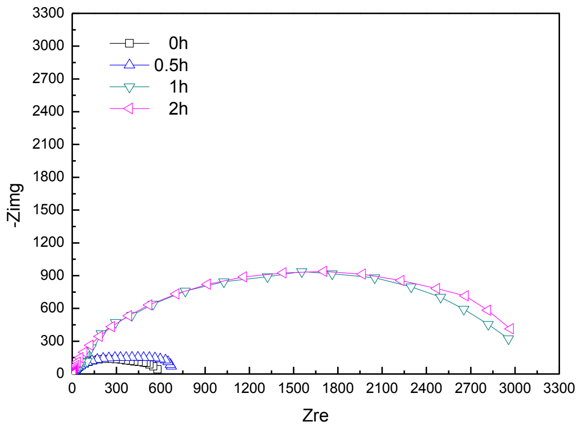

Figure 2. Nyquist diagram by AC impedance measurement of samples after electroless plating

According to the Nyquist diagram, the electrochemical impedance spectra of coating after different processing time showed the same characteristics of single capacitive loops and no inductive arcs or diffusion tails, which further indicated that the corrosion process is under the control of electrochemical reaction [7]. Compared with those of the samples with processing time of 0h or 0.5h, the capacitive loops of the ones with processing time of 1h or 2h were significantly expanded, revealing that the impedance values of corrosion reaction increased and corrosion resistance performance had been improved. The results were consistent with those obtained in polarization curve measurements.

3.3. Microscopic characterization

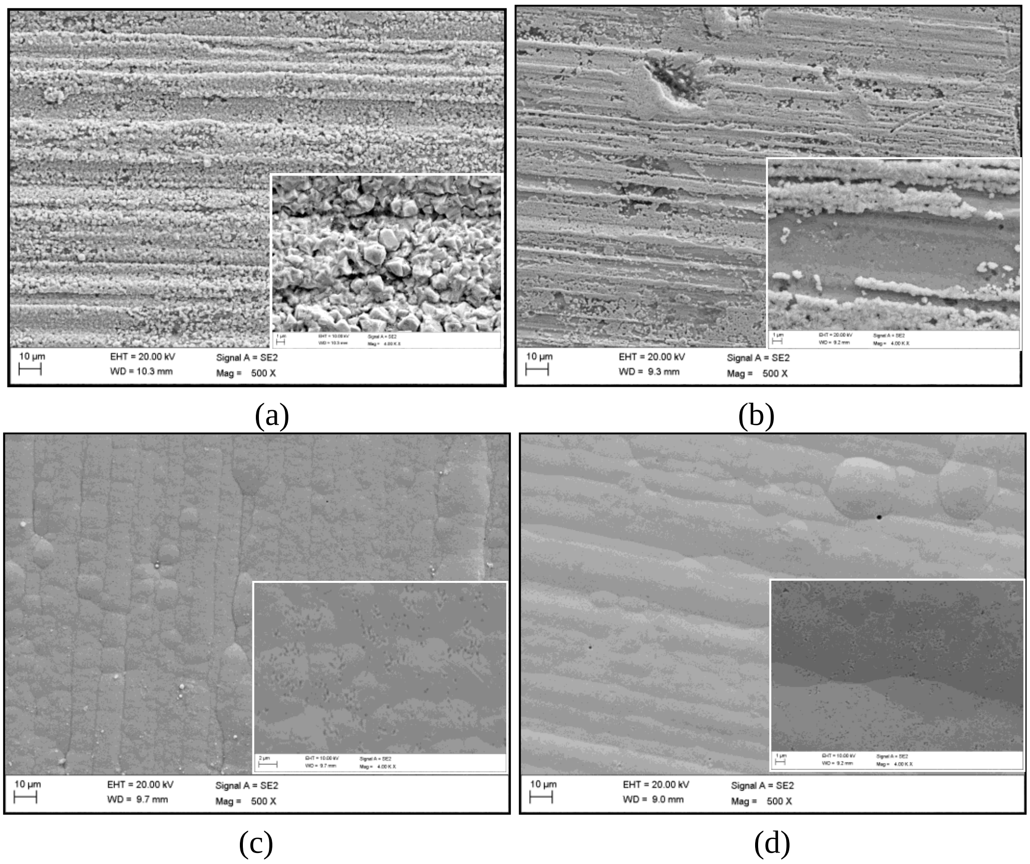

Figure 3. Morphological characterization of samples after electroless plating (a) 0h, (b) 0.5h, (c) 1h, (d) 2h

Fig.3(a) shows the surface of CF steel substrate without electroless plating. Granular and loose structure could be seen under high magnification on the surface of the steel due to the long-term exposure of steel in the air and immersion in seawater. Even the processing time lasted for 0.5h (Fig.3(b)), the coating layer was formed only in some active regions on the surface of CF steel and complete alloy coating had not been achieved, which could not protect the substrate sufficiently. When the plating time lasted for more than 1h, as shown in Fig.3(c) and Fig.3(d), dense and homogeneous alloy layer generated on the surface of CF steel and served as a barrier to prevent the substrate from directly contacting with corrosive media and at the same time to inhibit the more active Fe^{2+} ion in the anodic reaction from dissolving and diffusing to the deep of the solution. Thus the corrosion resistance of CF steel has been greatly improved [8].

The surface of the CF steel processed by Ni-Sn-P chemical plating, shown in Figure 3(c) and (d), is even and compact with only a small amount of projections. Based on the relevant literature [9], these projections resulted from imperfections as porosity, dislocation, cracks and scratches on the surface of the steel. In the plating process, such defects became the nuclei of alloy coating deposition and the coating was more likely to deposit in those areas compared with other more even areas. Taken it as a center, the coating gradually expanded to the external parts layer by layer, which gradually formed projections with the thickest coating in the center. Compared the coating in Fig.3(d) with that in Fig.3(c), the projections became less and smaller, and the coating became thicker with the increasing time for plating. As a result, all the elements in the coating distributed more homogeneously. The occurrence of local galvanic corrosion caused by different potentials was reduced.

3.4. X-ray diffraction analysis

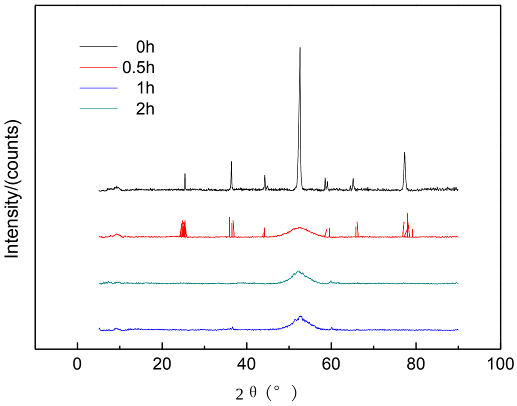

Figure 4. X-ray diffraction spectra of samples after electroless plating

As shown in Fig.4, the X-ray diffraction spectra of coating obtained by Ni-Sn-P electroless plating for one hour or two hours presented a wider single peak of fwhm (full width at half maximum), showing that the coating had a non-crystalline structure. According to analysis on relevant literature and theories [10~12], the phosphorus content has a decisive role in the crystalline structure of Ni-Sn-P coating. When phosphorus content is low or improper, the coating structure is mostly crystalline or mixed crystalline. More often, cracks and cavities appear on the coating in the heat treatment process because of the restriction of the substrate to the coating, which lead to decline of the corrosion resistance and mechanical properties of the coating [13]. However, with proper addition of phosphorus content, any defects or composition segregation caused by grain boundaries can be avoid for the amorphous structure of Ni-Sn-P coating prepared above. Thus all the elements distributed more homogeneously, avoiding the occurrence of local corrosion.

4. CONCLUSION

(1) In this study, with a period of electroless plating process over 1h, dense and homogeneous coating layer generated on the surface of CF steel. The coating served as a physical barrier on the surface of the substrate to inhibit the anodic process in the electrochemical reaction. As a result, the corrosion inhibition rate reached about 70% and the corrosion resistance was greatly improved.

(2) The amorphous structure of Ni-Sn-P coating prepared in this study diminished the occurrence of cracks and cavities resulted from the restriction of the substrate to the coating in the heat treatment process, and the distribution of elements was more homogeneous than that of the crystalline structure.

ACKNOWLEDGMENTS
This research was supported by Zhejiang Provincial Natural Science Foundation of China under Grant No. Q14D060002. The support from State Key Laboratory of Ocean Engineering (Shanghai Jiao Tong University) (Grant No.1406) and Program of Bureau of Science and Technology Department of Zhoushan(2015C41007) is also gratefully acknowledged.

References

1. Y. Zhang, H. Guo and H. Xu, *J. Iron. Steel. Res*., 24 (2012) 39.
2. H. Guo, Y. Zhang and Y. He, T. China. Weld. I., 34 (2013) 108.
3. C. Qiu, L. Lan and D. Zhao, *Mater. Sci. Forum*., (2012) 2265.
4. Y. Lin, T. Shih and S. Tien, *Scripta. mater.*, 56 (2007) 49.
5. J. Yu, T. Jing and J. Yang, *J. mater. process. tech*., 209 (2009) 14.
6. J. Yang, X. Zhao and J. Zhang, *Int. J. Electrochem. Sci.*, 10 (2015) 4523.
7. X. Fang, H. Zhou and Y. Xue, *T. Nonferr. Metal Soc.*, 25 (2015) 2594.
8. A. Aal, M. Aly, *Appl. Surf. Sci.*, 255 (2009) 6652.
9. F. Xie, T. Kraft and Y. Zuo, *Acta. Mater.*, 47 (1999) 489.
10. L. Li, W. Hu and Y. Zhang, *T. I. Met. Finish.*, 89 (2011) 95.
11. M. Paunovic, R. Arndt, *J. Electrochem. Soc*., 130 (1982) 794.
12. S. El-Rehim, M. Shaffei and N. El-Ibiari, *Met. Finish*., 94 (1996) 29.
13. S. Yang, H. Liu and S. Han, *Appl. Surf. Sci*., 271 (2013) 210.