

Electrochemical corrosion behavior of Ni-P, AlCrN and Ni-P-AlCrN multilayer composite coatings used on grounding grids

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Abstract. In this work, single NiP alloy, we use cathodic arc ion plating and electroless plating, AlCrN and NiP-AlCrN multilayer composite coatings were sedimented from the teeth outwards Q235 carbon steel. It is surface appearances of the coating that were inspected by using scanning electron microscope method (SEM) and the crystal structure, which was researched by the diffraction of X-ray (XRD). The electrochemical corrosion behaviors were evaluated by electrochemical polarization tests with electrochemical impedance spectrum (EIS). The results of EIS displayed that the impedance increased in the order Q235 < AlCrN coating < NiP alloy < NiP-AlCrN composite coating. The corroded surfaces of coated samples were covered by some pitting while the surface of Q235 was totally destroyed.

Keywords: Grounding grids, Ni-P alloy coating, AlCrN, Electrochemical corrosion.

1. Introduction

The grounding grids are the most important protective equipment in substations for preventing the damage of lightning, static electricity and fault current [1]. Most of the grounding grids materials are made of steel or galvanized steel which have been proved to be easily corroded in the soil [2-3]. Copper has also been used as the grounding grids in newly building 500KV substations due to its excellent electrical conductivity and high corrosion resistance in soil compared with steels. However, Cu is susceptible to the acid soil and its corrosion products will pollute the underground water [4-5].

Electroless nickel plating (Ni-P) due to its unique chemical properties, which have extensively been used in more and more industrial fields [6]. It can be divided into three types: first type is low phosphorous (P :1–3 wt.%), second type is medium phosphorous (P :4–7 wt.%) ,The third type is high phosphorous (>7 wt.% P) alloy coating[7]. High phosphorus electroless nickel-phosphorus alloy plating have been widely used for their high resistance of wear and corrosion, enhanced micro-hardness and excellent ply uniformity of the coating [8]. Compared with the low carbon steel, high phosphorous Ni-P alloy coating exhibit better corrosion resistance and has been used to substitute galvanized steel to produce the corrosion-resistant component in different industry fields.

AlCrN has become the focus of hard coating research , which is because of its excellent properties such as outstanding wear-resistant properties, high hardness and excellent oxidation resistance in recent years [9-10]. As a state of the art hard coating, some results are promising in behavior of the oxidation [11-12], the performance of cutting and fatigue applications in bearing [13] about the coating of AlCrN ,which have been reported. However, little research is focused on the electrochemical corrosion behavior of arc ion plating AlCrN coating.

In this paper, we try to deposit single alloy of the Ni-P, AlCrN layer and Ni-P-AlCrN multilayer mixed into the coating on carbon steel and investigate their electrochemical corrosion behavior systemically. The research result will be helpful to develop a new protective coating for the grounding grids materials.

2. Experiment

2.1 The lining-up sample

The samples, which were used in the present work, which were prepared via electro-discharge machine obtained from the traditional grounding grids carbon steel Q235 ($S \leq 0.050$, $Si \leq 0.30$, $P \leq 0.045$, $Mn: 0.30 \sim 0.65$, $C: 0.14 \sim 0.22\%$). The substrates, with a dimension of 10×10 mm, were mechanically ground by SiC abrasive paper and polished to a mirror surface. Ni-P alloy coating was prepared at nearly 90°C by Corning industrial process with pH 4.7, which were make-up of nickel sulfate, sodium hypophosphite, lactic acid, caustic soda. AlCrN coating were deposited onto Q235 plate and Ni-P coated Q235 substrate in N_2 ambient at a cathodic arc plating system of the home-made vacuum. Prior to deposition process, the samples in acetone, which were ultrasonically cleaned and alcoholic solutions, and then the samples in the substrate holder, which were fixed and etched in Ar glow discharge plasma. Cr ion bombardment was executed in Ar ambient to further clean up any contamination. On the 800 V substrate surface negative bias at 0.02 Pa. After bombardment then etching, N_2 gases were fed into the chamber and kept at a fixed pressure of 3.3 Pa at -150 V bias. The deposition time is about 60 min and the ply of the AlCrN coating, which is approximately $2\ \mu\text{m}$. More detailed AlCrN deposition parameters, which are showed in table 1.

Table 1. The AlCrN coating deposition parameters

Parameters	Value
Target materials	Cr(99.99%)
Voltage of substrate bias (-V)	Bombarding: 800, deposition: -150
Gases of working	Ar, N_2
Pressure of base (Pa)	7.0×10^{-3}
Pressure of working (Pa)	3.3
Current of arc (A)	70 A
Temperature of substrate ($^\circ\text{C}$)	300°C
Speed of rotation (rpm)	4
Time of deposition (min)	60

2.2 Characterization

The surface morphology of four Q235 (A) samples prepared, the pure Ni-P alloy (B), AlCrN (C) and Ni-P-AlCrN composite coating (D) have been observed by scanning electron microscope. The analyses of coatings used semi-quantitative compositional were promoted by using the spectrometer analysis of energy-dispersive (EDS). The diffraction of X-ray (XRD) has been employed to obtain the structure on phase of the as-prepared four samples. The tests of electrochemical polarization were carried out using an electrochemical workstation (CHR660d, China). All electrochemical experiments at room temperature, which were carried out in the aqueous solutions of aerated 3.5wt. %NaCl. Before the polarization test, the sample was immersed into the solution underway for about an hour, which were used to determine the steady-state corrosion potential (E_{corr}). The polarization of electrochemical scanning from -1.5 V to 0.4 V with the scanning speed of 1 mV/s. we calculating the corrosion current density (I_{corr}) and corrosion current density (E_{corr}), and then it can evaluate the corrosion properties of the coatings. Furthermore, the electrochemical impedance spectroscopy (EIS) have been promoted in 3.5 wt.% sodium chloride by setting the device within the frequency range was situated between 0.01 Hz and 105 Hz, and the corrosion resistance of the coatings and the Q235 substrate, which were evaluated by using an amplitude of $\pm 5\text{mV}$. It adopted a three-electrode potentiostatic mode and a reference electrode was make-up of the reference electrode of a saturated calomel (SCE). Finally, the acquired spectra were analyzed and modeled with the Ziew program. The surface appearances of the samples after electrochemical tests also were studied by SEM.

3. Result and discussion

3.1 Surface appearances and compositions

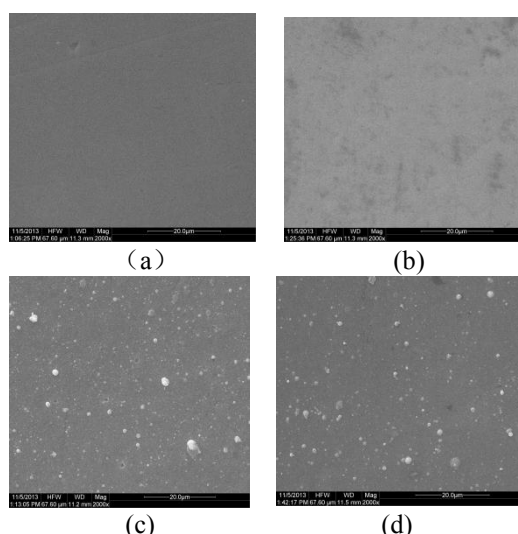


Fig.1. Surface appearances of the samples: (a) Q235 steel, (b) single NiP coating, (c) single AlCrN coating, (d) Ni-P-AlCrN multilayer composite coating

We scanned electron microscope obtain Secondary electron images of the four samples, which are shown in Fig.1. Q235 and Ni-P coating samples revealed smooth surface, no obvious particle contamination could be observed, while the AlCrN and Ni-P-AlCrN composite coatings exhibited serious particles contamination and holes in the surface, which is the typical character of the cathodic arc ion-plating. The particles are formed by the molten droplet from lower melting point AlCr target and the holes observed in the surface of sample C, D are attributed to the exfoliation of the big AlCr particles. The composition of the as-prepared samples was shown in table 2. The P content of sample B is about 11.1 wt.% which indicates the as-deposited Ni-P coating is a high phosphorous coating[14]. The content of Cr, Al, N of AlCrN and Ni-P-AlCrN coatings are similar. The difference of the two coatings is that single AlCrN revealed 24.98 wt.% Fe resulting from the effect of the Q235 substrate, while there is no Fe could be detected in NiP-AlCrN multilayer composite coating due to the thick Ni-P underlayer. The more composition details of the samples, which were shown on table2.

Table 2 Chemical composition of sample A, B, C, D (at.%).

Sample	Fe	Ni	P	Cr	Al	N
A	100					
B	1.32	79.53	19.15			
C	24.98			6.35	30.25	38.42
D		17.77	1.58	8.95	33.10	38.60

3.2 XRD study

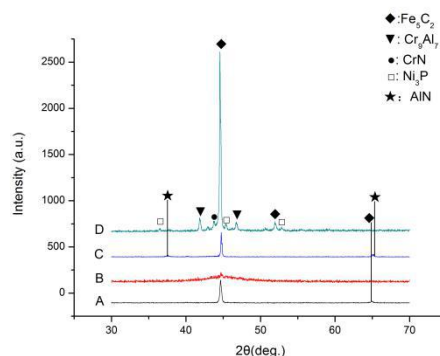


Fig. 2. The XRD pattern of the four samples

Fig. 2 showed the XRD pattern of the four samples. The diffraction peaks originating from the Fe_5C_2 phase has been perceived in all samples, because of the penetration depth of X-R-D is larger than the coatings ply. According to the XRD analysis in as-deposited Ni-P coatings, there is only broad diffraction peak of Fe_5C_2 , no other obvious diffraction peak could be observed, which indicates that Ni-P coating is an amorphous typical structure. From the diffraction pattern of AlCrN coating deposited on Q235 substrate it can be seen that the coating contains the AlN phase. In NiP-AlCrN composite coating, there exist Cr_9Al_7 , CrN, Ni_3P , which is quite different from that in sample C. The existence of Ni_3P indicates that the amorphous NiP coating partially crystallized during the process of AlCrN deposition at 300°C . Furthermore, the new phase Cr_9Al_7 phase could be observed resulting from the particle contamination of AlCrN coating.

3.3 Polarization curves

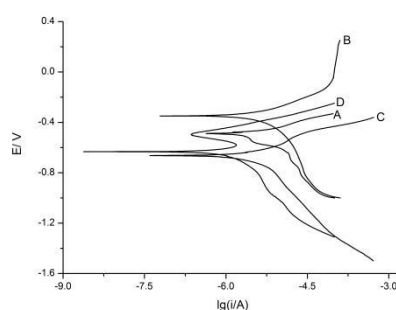


Fig. 3. Potentiodynamic polarization curves of Q235, NiP, AlCrN and NiP-AlCrN coatings in 3.5 wt.% NaCl aqueous solutions.

Table 3 Corrosion properties for the Q235, Ni-P, AlCrN and Ni-P-AlCrN coatings

Materials	Q235	Ni-P	AlCrN	Ni-P-AlCrN
$E_{\text{corr}}(\text{V})$	-0.4886	-0.3405	-0.664	-0.630
$i_{\text{corr}}(\text{A}/\text{cm}^2)$	-5.983	-5.384	-5.596	-6.030

The potential of corrosion and density of current were located in a corrosive medium, which can afford information about reaction processes of the ongoing corrosion. Potentiodynamic measurements were performed in chloride solutions of the 3.5 wt.% NaCl aqueous sodium, At the same time we can obtain a range of potential polarization curves and current density as shown in Fig. 3. We use Tafel extrapolation method, which can obtained corrosion potential and corrosion current density, Above part as shown in Table 3. It is clear seen that the corrosion potential (E_{corr}) of the Ni-P coating (-0.3405V) was higher than that, which were the corrosion potential (E_{corr}) of the AlCrN (-0.664 V) and Ni-P-AlCrN (-0.630V) coatings. The traditional grounding grids

materials Q235 showed higher corrosion potential in comparison with the other two coated substrates. Passivation area has been observed in the anode polarization curve of Ni-P-AlCrN coated sample. According to corrosion potential, the Ni-P coating with the highest corrosion potential shows the resistance of excellent corrosion, which was in simulated seawater environment. It was that corrosion current density is an important parameter for evaluating corrosion reaction kinetics. Generally, we used measured by polarization can obtain a fact, which was the rate of corrosion is proportional to the current density of corrosion. In these samples, the current density of corrosion of pure Ni-P coating is the lowest, which were indicated that Ni-P alloy coating has better corrosion resistance than AlCrN and Q235. Although the current density of corrosion of the AlCrN coating is lower than that of Ni-P alloy, it also shows better corrosion resistance compared to Q235.

3.4 Electrochemical impedance

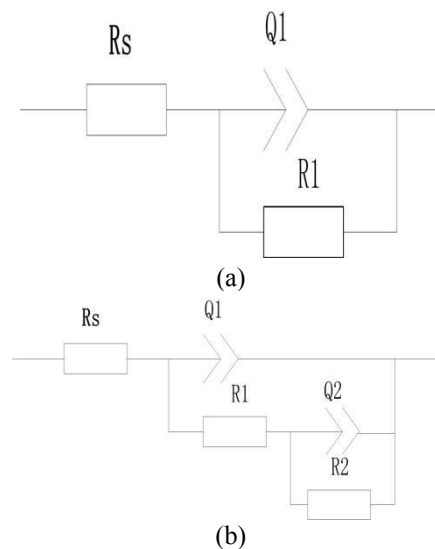
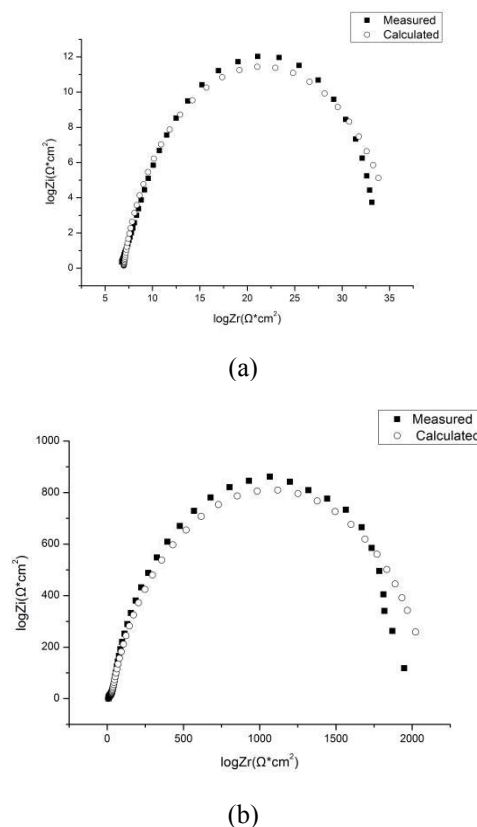
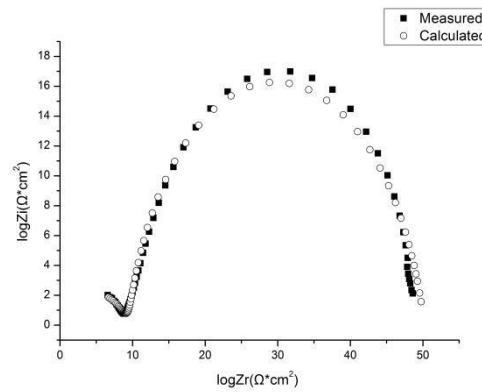
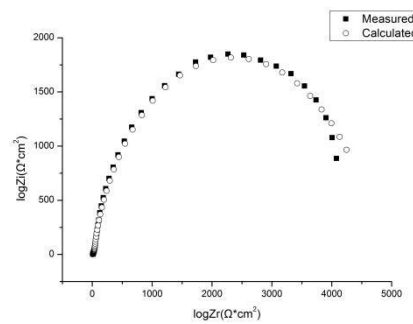


Fig. 4. Equivalent circuit employed to analyze the data; (a) Q235, (b) coated samples B, C and D.





(c)



(d)

Fig. 5. Nyquist impedance spectra in 3% NaCl solution for (a) Q235, (b) Ni-P, (c) AlCrN, (d) Ni-P-AlCrN.

Table 4 Equivalent circuit data

Samples	Q_1	$R_1(\Omega \cdot \text{cm}^2)$	Q_2	$R_2(\Omega \cdot \text{cm}^2)$	Chi-squared
A	1.194E-3	28			1.283E-3
B	3.041E-3	36.64	7.864E-4	2082	1.360E-3
C	5.139E-7	9.632	7.287E-4	40.83	7.332E-4
D	1.286E-4	111.7	7.038E-5	4688	4.782E-4

The corrosion characteristics of four samples were analyzed by Nyquist impedance spectroscopy. Different types of electrode and electrolyte interfaces with what instead several equivalent circuit models, which can obtain experimental data by using simulation. However, Most of the data are consistent with the minimum chi square value of the coating, which can obtain with the equivalent circuit of an electrical by 2 time constants, it is shown in Fig 4. For the Q235 substrate, the most suitable model was shown in Fig. 5. To get a better fitting result, considering the factor of surface inhomogeneity and a factor of possible diffusion, a phase element of more general constant (Q), which was not rigid capacitive element. The following equation represent the capacity element ;

$$Z_Q = \frac{1}{Y_0} (j\omega)^{-n} \quad (1)$$

Where Q is Y_0 constant, $(\sqrt{-1})$ imaginary unit is j, the (1 rad/s) of the sine wave angular frequency is ω , which can express as $\omega = 2\pi f$, Hz is f frequency ; the value of n was between 0 and 1.

As shown in Fig.5, The impedance diagram had a good agreement with the data of experimental and the results of simulation. We take a circuit elements on the basis of the fitting result ,which are shown in Table 4. EIS data provide the following information, which about the coating properties .R1 in the coating samples represents the resistance of the pores of the coating and R2 represent that the polatization resistance of the compact coating. The value of R1 is smaller compared to that of R2 and it indicates that the overall corrosion protection of the carbon substrate depend on the value of R2.

The resistance of the compact coating (R2) of the Ni-P coating ,which was higher than that of the AlCrN coating suggests that sample B have better corrosion resistance than sample C, which is in consistent well with the result of the polarization curve. The resistance (R1) obtained in Q235 substrate is 28 which is less than the value of R2 in sample B, C and D. It could be concluded that the corrosion resistant properties of the carbon steel could be significantly enhanced by the AlCrN and NiP coatings. Moreover, sample D with a Ni-P-CrAlN composite coating revealed much higher resistance than the pure NiP and CrAlN coated samples, which the composite coating significantly improves corrosion resistance.

3.5 SEM study after electrochemical tests

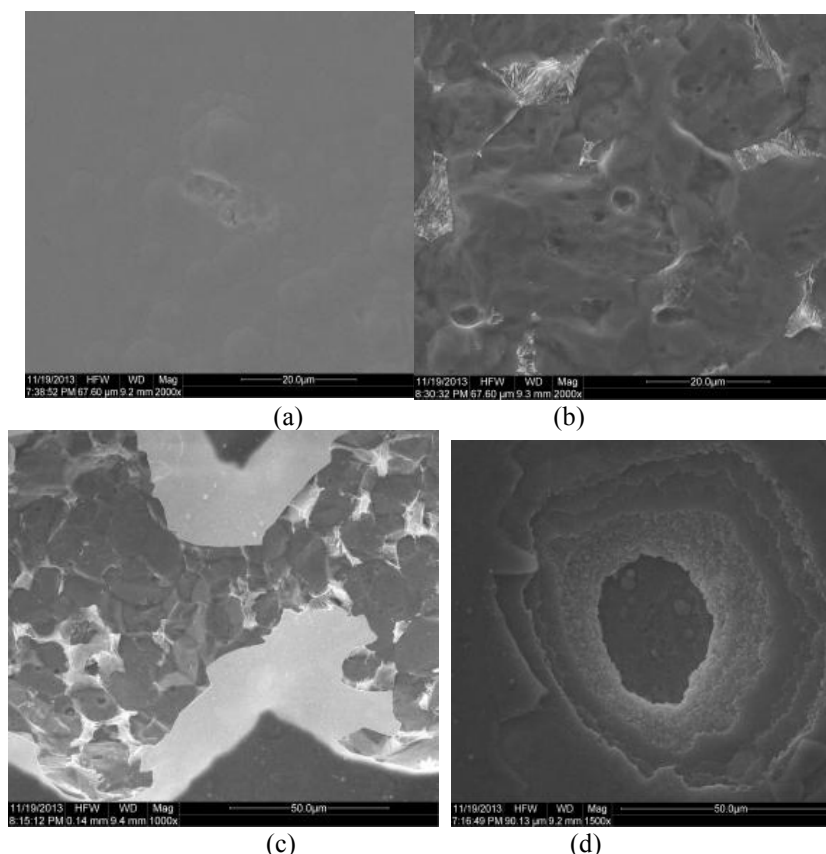


Fig. 6. Appearances of the corroded surface after testing

SEM has been applied to observe the corroded surface as shown in Fig.6. According to Fig. 6(a), the surface of Q235 has been totally corroded especially in the grain boundary. For other three coated samples, the surface retained just with some pitting. Obviously the pitting density of the three samples increased in the order of $B < D < C$, while the diameter of pitting revealed opposite order. Fig.6(b), (c) and (d) revealed the appearances of the pitting in sample B, C and D, it could be observed that pitting in sample C and D already penetrated through the AlCrN coating while the depth of pitting in sample B is lower, which indicate that the depth propagation of pitting have been prevented by Ni-P coating. The pitting shape of sample B, C and D are very similar. Ni-P-AlCrN composite coating revealed circular pattern appearances and the circle diameter decreased as the depth increased. It suggests that the outer AlCrN coating on the top of Ni-P alloy with dense

structure can act as barrier to prevent the corrosive medium penetrating to the inner NiP alloy coating, which was the principal consideration of the highest corrosion resistance in sample D.

4. Conclusion

The behavior of Q235 have corrosion, single Ni-P alloy, AlCrN layer and Ni-P-AlCrN multilayer composite coating have been inspected by the tests of electrochemical polarization and the spectroscopy of electrochemical impedance (EIS) in this paper. The Ni-P alloy, AlCrN layer can increase the Q235 corrosion resistance significantly. Ni-P-AlCrN composite coating reveal the highest impedance due to the outer AlCrN layer which conduct barrier ,which used to prevent the corrosive medium penetrating to the inner Ni-P coating. The corroded surface of NiP, AlCrN and Ni-P-AlCrN is covered by some pitting and the density of pitting increased in the order of AlCrN> NiP-AlCrN>NiP alloy. This result is very helpful to develop the new protective coating for the ground grids.

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