

Corrosion Behavior of Arc Sprayed Nickel-Base Coatings

Dingyong He, Na Dong, and Jianmin Jiang

(Submitted March 12, 2007; in revised form June 11, 2007)

In this study, nickel-base cored wires were prepared by using NiCr strip to wrap metal powders of nickel (Ni), chromium (Cr), molybdenum (Mo), and chromium boron (CrB). Nickel-base coatings were prepared by electric arc spraying. Microstructures of Ni-Cr-Mo and Ni-Cr-B coatings were investigated using scanning electron microscopy (SEM), energy-dispersive analysis (EDAX), and x-ray diffraction (XRD) analysis. The coatings have a compact surface and presented a bonding strength higher than 40 MPa. Potentiodynamic polarization measurements and salt-spray test were carried out to determine the corrosion behavior of the coatings. The results showed that Ni-base coatings containing Mo (5%) or B (2-4%) had better antichlorine ion corrosion performance than that of Ni-base coatings without Mo element, and PS45 (Ni-Cr-Ti) coating. The antichlorine ion corrosion coatings could be used for resolving the corrosion protection problem of the equipment and piping contacting sour, alkali, salt liquid in petrochemical engineering applications.

Keywords arc spraying, cored wire, corrosion behavior, nickel-base coating

1. Introduction

The corrosion problem of the equipment and piping contacting sour, alkali, salt liquid in the petrochemical engineering is more and more severe, and even often causes burning and exploding. According to statistical data, one-tenth of all metal materials were scrapped because of corrosion, which causes direct economic losses in developed countries, occupying about 2 to ~4% of their gross domestic product (GDP) yearly. In China, direct economic loss from corrosion reaches more than 300 hundred millions RMB, which occupies 4% of GDP (Ref 1). Therefore, it is very important to resolve material corrosion (Ref 2). There are many means of preventing material from corroding, for example, using anticorrosion alloys, electroplating, and cathode protection, and so on. However, these processes are costly and not economical. Furthermore, most corrosion takes place at the surface of

This article is an invited paper selected from presentations at the 2007 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Global Coating Solutions, Proceedings of the 2007 International Thermal Spray Conference*, Beijing, China, May 14-16, 2007, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2007.

Dingyong He and **Jianmin Jiang**, College of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China; and **Na Dong**, The Shanghai Lincoln Electric Co., Ltd, Shanghai 201907, China. Contact e-mail: dyhe@bjut.edu.cn.

a material. It is very important to improve surface performance of equipment and parts. In many instances, using thermal spraying technology can gain good effect (Ref 3). Preventive corrosion practices all over the world prove that coating is the most effective, economic, and widely used surface technology (Ref 4).

Molybdenum and a small content of rare earth elements are added to nickel-base cored wires to improve anticorrosion performance of coating, especially antichlorine ion corrosion performance. Those studies are very important for petrochemical engineering. Therefore, this paper studied the antichlorine ion corrosion performance of nickel-base coatings by salt-spray and electrochemical corrosion tests to offer experiment data and a theoretical base for application of the coating in practice.

2. Experimental Methods and Materials

Nickel-base cored wires were prepared using 10 by 0.4 mm Ni80Cr20 strip to wrap metal powder of Ni (Ni), Cr (Cr), Mo (Mo), and chromium boron (CrB). The diameter of the wire was 2.0 mm, and filling ratio was 33 to ~35%. The composition of Ni-base coatings is shown in Table 1.

Sample substrate material was low-carbon steel Q235, and its dimensions were 25 by 16 by 5 mm. Surfaces of samples were cleaned using acetone before spraying and blasted by corundum. Spray equipment was JZY-250 arc spraying system (Beijing Jiazhiyuan Scientific & Trading Co., Ltd, China), and its technical parameters were: voltage, 28 to ~32 V; current, 180 to ~210 A; compressed air pressure, 0.4 to ~0.6 MPa; and spraying distance, 150 to ~200 mm.

The salt-spray test was carried out in salt-spray test box according to GB/T10125-88. Test conditions were: concentration of NaCl in aqueous solution, 50 ± 5 g/L; test

temperature, 35 ± 2 °C; and salt-spray rate, 0.01625 to ~ 0.0212 mL h⁻¹ cm⁻². The electrochemical corrosion test was carried out following GB/T17899-1999. Sample area was 1 cm². The corrosive aqueous solution contained 3.5% NaCl and 0.5 mol/L H₂SO₄ solution. Saturation calomel electrode (SCE) was used as reference electrode of NaCl aqueous solution. Saturation mercurous sulfate electrode (SME) was used as reference electrode of H₂SO₄ aqueous solution. Polarization measurements were performed by a computer-controlled potentiostat (PAR

M273A), using the corrosion (PAR M352/252, version 2.01) software (EG&G, Princeton Applied Research, AMETEK Inc., TN, USA). Polarization test ranged from -250 mV to 1.2 V, at a scanning rate of 2 mV/s.

Ni-Cr-Mo, Ni-Cr-Mo-Al, and Ni-Cr-B coatings are referred to as A, B, and C samples, respectively. PS45 coating was used for comparison. Microstructures of Ni-Cr-Mo and Ni-Cr-B coatings were investigated using scanning electron microscopy (SEM), energy-dispersive analysis (EDAX), and x-ray diffraction (XRD) analysis.

Table 1 Compositions of Ni-base coatings

Sample No.	Composition, wt.%						
	Cr	Mo	B	Al	Ti	RE	Ni
A1	40	5	–	–	–	–	bal
A2	21	9	–	–	–	–	bal
A3	21	5	–	–	–	–	bal
A4	21	9	–	–	–	1	bal
A5(B1)	21	5	–	–	–	1	bal
B2	21	5	–	2	–	1	bal
B3	21	5	–	4	–	1	bal
C1	40	–	6	–	–	–	bal
C2	40	–	4	–	–	–	bal
C3	40	–	2	–	–	–	bal
C4	40	–	0	–	–	–	bal
C5	14	–	6	–	–	–	bal
PS45(a)	40-45	–	–	–	≤4	–	bal

(a) PS45 is used as a base material for comparison of high NiCr alloy core wire sprayed coating

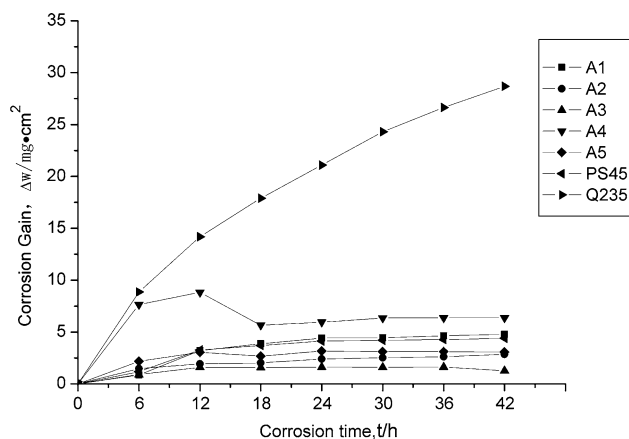


Fig. 1 Corrosion dynamic curves of samples A coatings in salt-spray test for 42 h

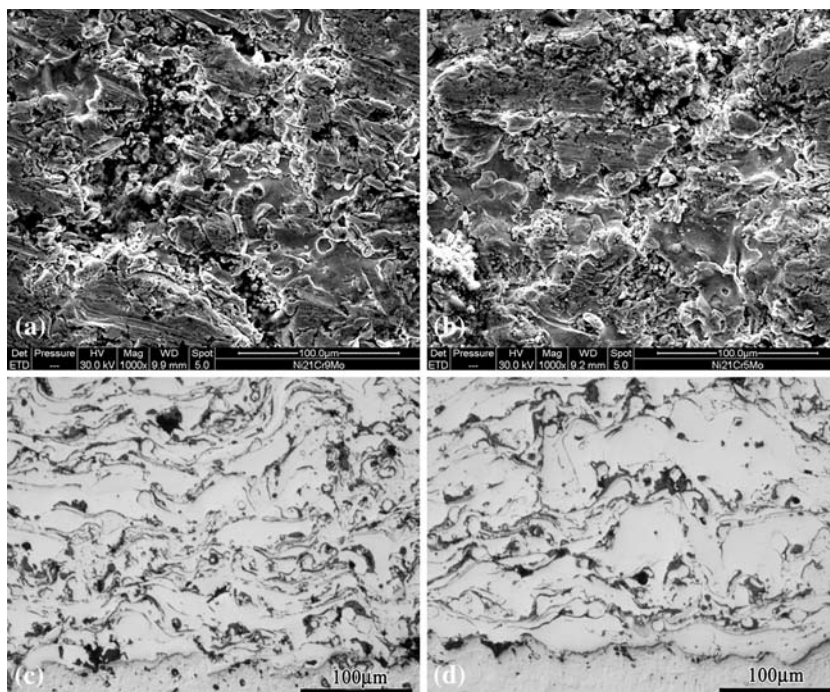


Fig. 2 SEM morphologies of samples A coatings in salt-spray test for 42 h. (a) Sample A4 coating. (b) Sample A5 coating. (c) Sample A4 coating cross section before test. (d) Sample A5 coating cross section before test

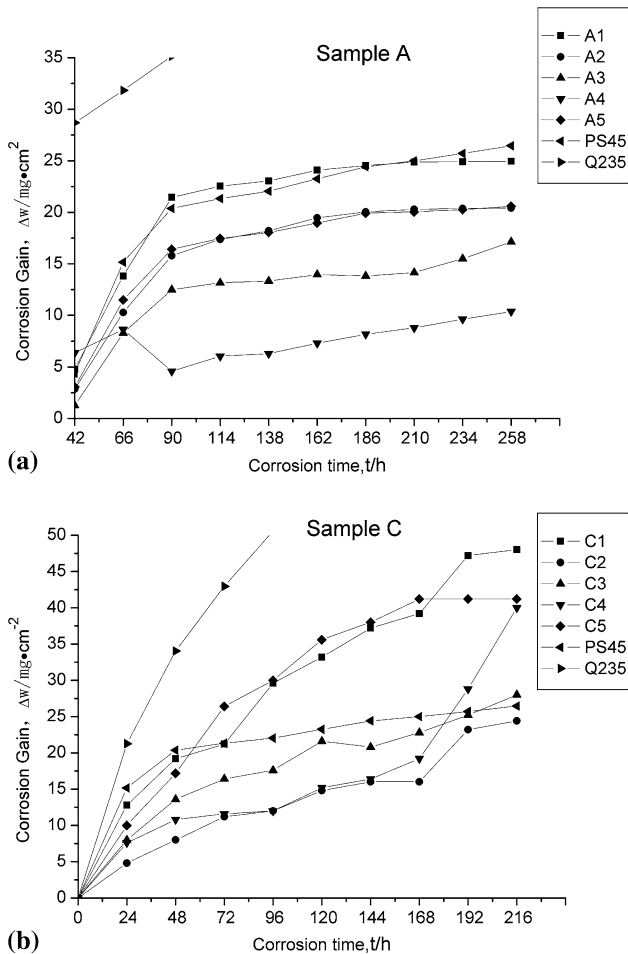


Fig. 3 Corrosion dynamic curves of samples A and C coatings in salt-spray test for 216 h. (a) Sample A coatings. (b) Sample C coatings

3. Results and Discussion

3.1 Salt-Spray Test

In an early stage of test, salt solution was continuously sprayed for 42 h. The weight of the coating sample A was tested once every 6 h. Corrosion dynamic curves of the sample A coatings in salt-spray test are shown in Fig. 1 compared with PS45 coating and Q235 steel substrate.

As can be seen in Fig. 1, the anticorrosion performance of samples sprayed coating is more than five to six times better than that of substrate material. The weight of substrate material increased almost linearly. Rust spots appeared on its surface, which show that the surface of the substrate was corrupted without protective coatings, and corrosion products were lined up on the surface. Corrosion dynamic curves of sample sprayed coatings show that coatings prevented the substrate material from corrupting. However, the corrosion dynamic curve of A4 sample fluctuates, which indicates that corrosion occurred on the substrate of A4 sample.

Corrosion of A4 coating was examined through observing surface morphologies of A4 and A5 coatings by

SEM. The results are shown in Fig. 2(a) and (b). It was seen that corrosion pit on the surface of A4 coating was deeper than that of A5 coating. The Mo content of A4 coating is 9%, more than the Mo content of A5 coating (5%), but it can be seen that the A4 coating has more porosity than the A5 coating in Fig. 2(c) and (d), which shows that too much Mo content in coatings affects the anticorrosion performance of coatings. Too much Mo in the wires, in the spraying process, can form too much molybdenum oxide in coatings, making the coating structure nonhomogeneous, presenting more porosity. So the Mo element content of coatings may as well be about 5%. Also, it is difficult for chlorine ion solution to penetrate into A5 coating to corrupt the base material. Because surface of A4 coating was porous, chlorine ion solution penetrated into hole to dissolve coating by electrode reaction. So the corrosion pit of A4 coating surface was deeper than that of A5 coating.

Because early testing showed that coatings have good anticorrosion performance, the test time was extended further. Corrosion dynamic curves of samples A and C coatings in salt-spray test lasting 216 h are shown in Fig. 3.

As can be seen in Fig. 3, the test results further proved that the above conclusion stands right throughout extending test period. Anticorrosion performance of samples with sprayed coating is better than that of the base material. The A5 Ni-base coating containing 5% Mo and a small content of rare earth elements and the A3 coating containing 5% Mo without rare earth elements present good anticorrosion performance. When the Mo content in Ni-base coating A4 was increased up to 9%, the anticorrosion performance of coating decreased.

The anticorrosion performance of coating samples containing 2 to 4% B was better than others, which shows that coatings with moderate B content have improved anticorrosion performance. On the other hand, comparing team A coatings with team C coatings shows that the antichlorine ion corrosion performance of coatings containing Mo is better than that of coatings without Mo.

Weak areas may appear on the surface of passivation film of coatings, resulting in dissolution in larding sulfide and grain boundary of carbonization as chlorine ion action in chlorine ion solution will result in dot corrosion (Ref 5). When Mo with anticorrosion and antifelt performance was added to coatings, it improved the passivation capacity of the alloy and surface film property. Therefore, coatings containing Mo have good antichlorine ion corrosion performance. When B is added to coatings, it reacts with oxygen in spraying, which reduces nickel oxide in coatings and makes the coating composition homogeneous (Ref 6). Also, B in coatings can strengthen the grain boundary and restrain nonhomogeneous composition from segregating, which reduces the porosity of coatings, and has the advantage of improving anticorrosion performance of coatings.

3.2 Electrochemical Corrosion Test

Antichlorine ion corrosion performance of coatings was also tested by electrochemical corrosion test in salt,

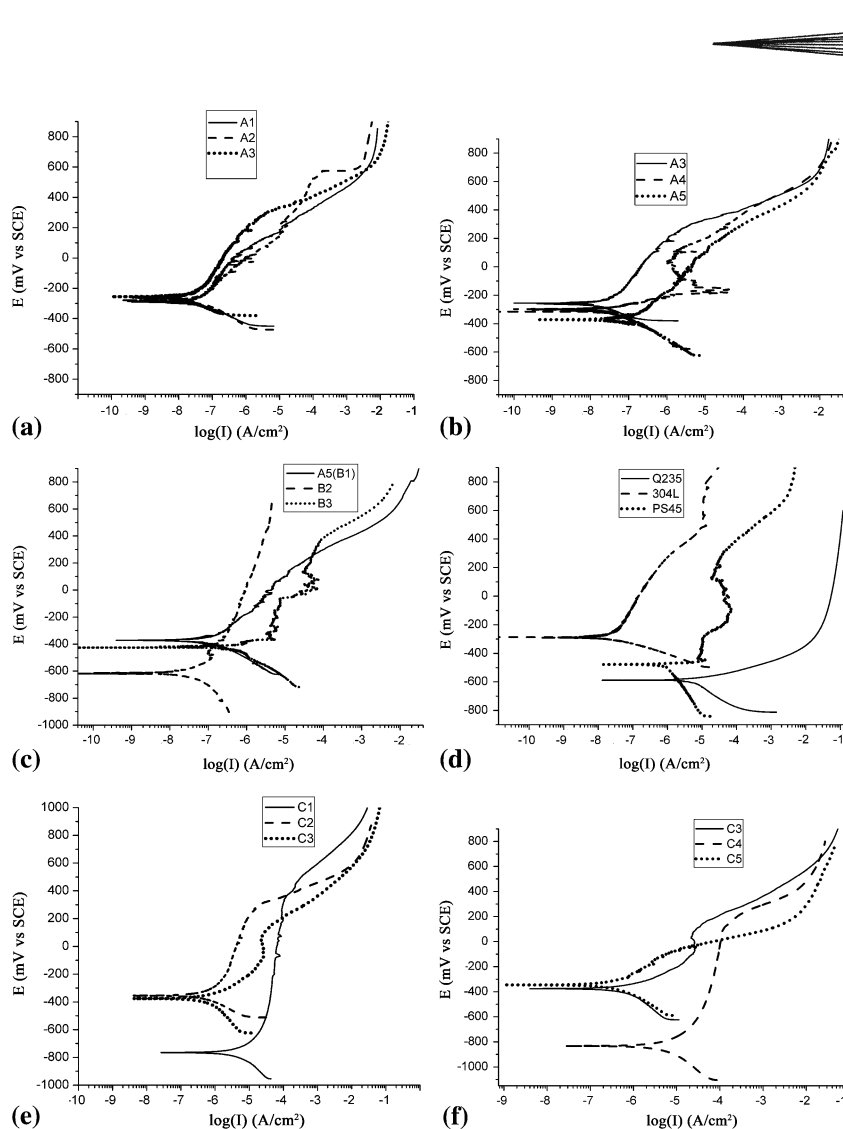


Fig. 4 Cyclic polarization curves of Ni-base coatings in 3.5 wt.% NaCl solution. (a) Sample A1, A2, and A3 coatings. (b) Sample A3, A4, and A5 coatings. (c) Sample A5, B2, and B3 coatings. (d) Sample Q235 and PS45 coatings. (e) Sample C1, C2, and C3 coatings. (f) Sample C3, C4, and C5 coatings

Table 2 Electrochemical corrosion parameter of coatings in NaCl solution

Sample	E_{corr} , mV	I_{corr} , mA/cm ²
A1	-289.5	0.03566×10^{-3}
A2	-278.2	0.038×10^{-3}
A3	-258	0.03716×10^{-3}
A4	-302.7	0.06136×10^{-3}
A5(B1)	-371.8	0.1612×10^{-3}
B2	-613.9	0.05983×10^{-3}
B3	-422	3.37×10^{-3}
C1	-765	7.558×10^{-3}
C2	-353.6	0.9495×10^{-3}
C3	-376	0.7267×10^{-3}
C4	-833.2	7.082×10^{-3}
C5	-345.2	0.4639×10^{-3}
PS45	-482.6	8.22×10^{-3}
304L	-286.4	0.02956×10^{-3}
Q235	-588.9	5.244×10^{-3}

acid solution and demonstrated using cyclic polarization behavior and the surface morphologies of coatings.

Cyclic polarization curves of the coatings in 3.5% NaCl solution are shown in Fig. 4. Electrochemical corrosion parameters of NiCrMo coatings are shown in Table 2. As can be seen from Fig. 4(a) to (d) and Table 2, the A3 coating has a low corrosion current density in the same corrosion potential and a stable polarization curve compared with other NiCrMo coatings. Corrosion current density of the substrate material rose with development of corrosion potential in the polarization curves figure. Because the surface of the substrate material has no passivation film, it cannot be protected in chlorine ion solution. The surface of the Ni-base coatings were in the active anode dissolution state in NaCl solution because of chlorine ion action. Cl^- absorption on oxidation film of the coatings made ion resistance fall (Ref 7). Also, combining

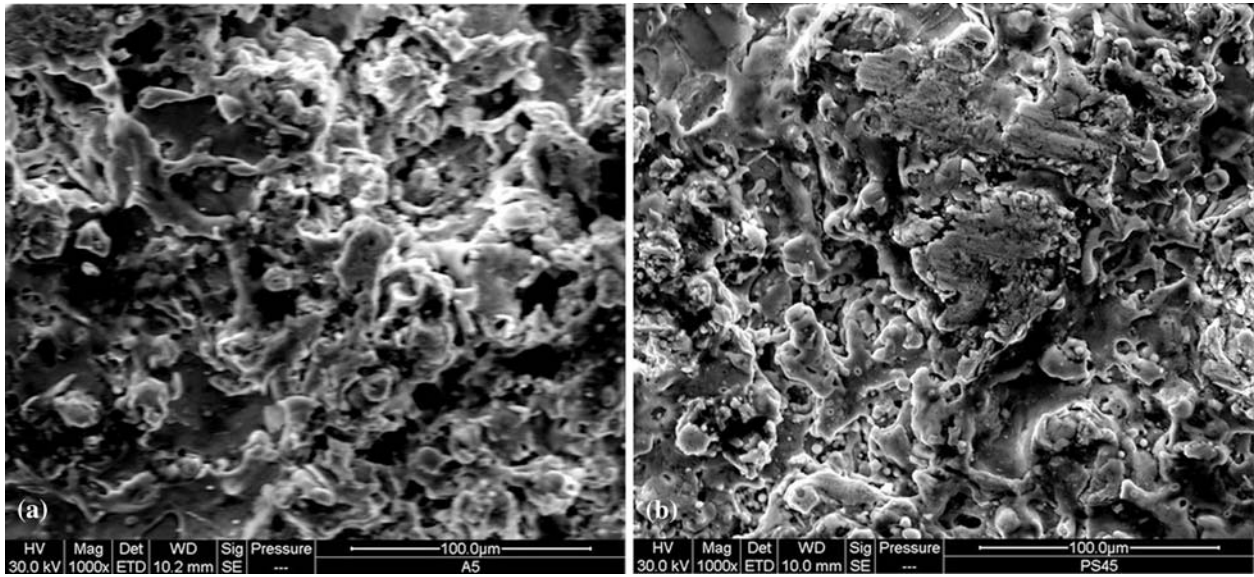


Fig. 5 SEM morphologies of the coatings after electrochemical corrosion test in 3.5% NaCl solution. (a) Sample A5 coating. (b) PS45 coating

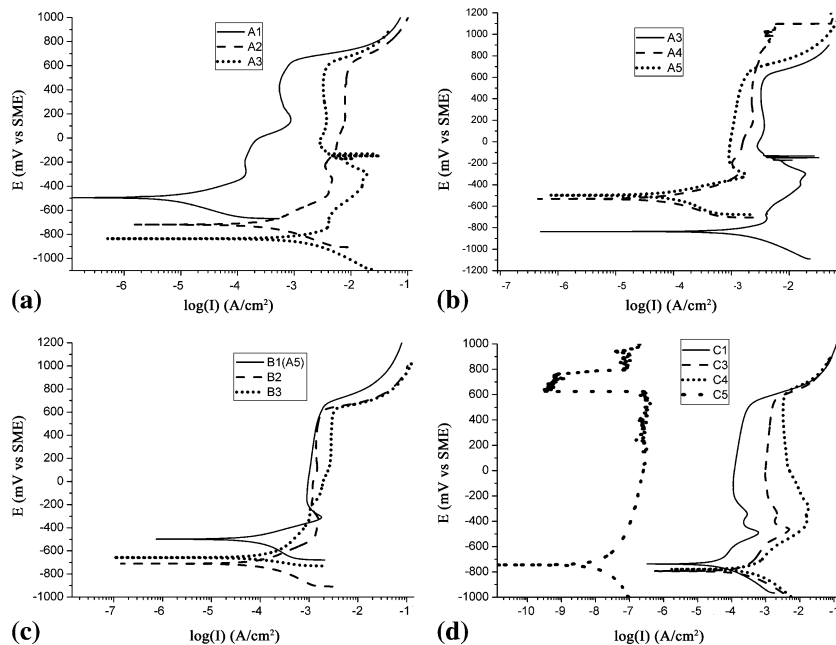


Fig. 6 Cyclic polarization curves of Ni-base coatings in 0.5 mol/L H_2SO_4 solution. (a) Sample A1, A2, and A3 coatings. (b) Sample A3, A4, and A5 coatings. (c) Sample A5, B2, and B3 coatings. (d) Sample C1, C3, C4, and C5 coatings

chlorine ion with metal ion accelerated dissolution of surface active anode products at weak area of coatings, which made corrosion current density rise rapidly, caused spot corrosion, and was unable to maintain passivation state in surface of coatings.

When coatings containing 5% Mo have a compact surface, surface weakness is less and they can maintain a more stable surface state compared with others, such as A3 and A5.

It can be seen from Fig. 4 (e), (f), and Table 2 that C2 coating has low corrosion current density in the same corrosion potential and a stable polarization curve compared with other NiCrB coatings, which shows that coatings containing moderate B element benefit for forming stable passivation film in surface of coatings.

SEM morphologies of A5 and PS45 are shown in Fig. 5. It can be seen from Fig. 5 that the surface of sample A5 coating was dissolved uniformly, which supports the

mentioned conclusion that coatings containing 5% Mo have a stable surface state. However, the surface of sample PS45 coating became nonuniform; weak areas easily appeared compared with A5 coatings.

Cyclic polarization curves of Ni-base coatings in 0.5 mol/L H_2SO_4 solution are shown in Fig. 6 and 7. It can be seen from Fig. 6 (a) to (c) and Table 3 that the A5 coating has a stable polarization curve, wide passivation area, low corrosion current density, and high corrosion potential compared with the others. When the coating surface was in acid solution, electrode reaction occurred to bring H_2 by H ion action, and the dissolution reaction product absorbed in surface of coatings at last was oxidized to become passivation film (Ref 8). Passivation film created a passivation state in the coating surfaces. However, the passivation film began to dissolve with an

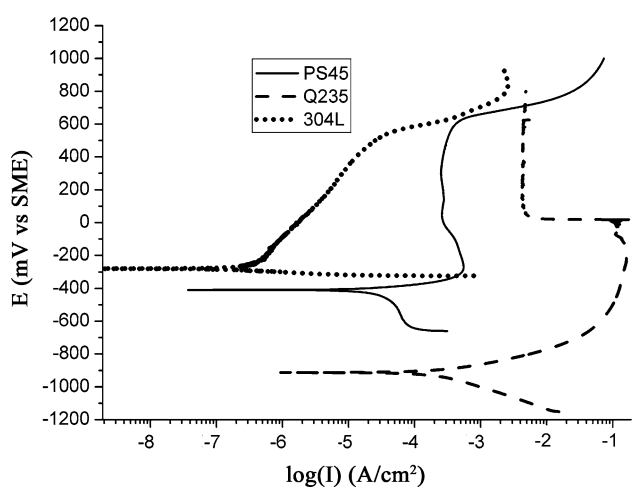


Fig. 7 Cyclic polarization curves of sample Q235 and PS45 coating in 0.5 mol/L H_2SO_4 solution

increase in potential. The coating surface was again in an active anode dissolution state. Polarization curves appeared to fluctuate because the passivation film of the surface of the coatings was broken in weak areas and dissolved, which made the corrosion current increase suddenly. Because the surface of A5 coating has fewer weak areas, electrode reaction occurred stably and forms a stable passivation film.

It can be seen from Fig. 6(d) and Table 3 that the polarization curve of the C1 coating has a stable passivation area, which shows that the surface of C1 coating that formed a stable passivation film during the electrode reaction process has fewer weak areas.

It can be seen from Fig. 7 that the polarization curve of PS45 coating sample has a relative stable passivation area, compared with Q235 sample without coating, which shows that coatings form a protective film on the surface of the substrate material and protect the substrate material from corruption to a certain extent.

Table 3 Electrochemical corrosion parameter of coatings in H_2SO_4 solution

Sample	E_{corr} , mV	I_{corr} , mA/cm ²
A1	-495.8	0.01614
A2	-718.9	0.2731
A3	-836.1	3.121
A4	-531.5	0.1233
A5(B1)	-498.2	0.06861
B2	-710.1	0.123
B3	-657.2	0.2036
C1	-736.5	0.02094
C3	-793	0.2317
C4	-779.4	0.2497
C5	-744.3	0.01772×10^{-3}
PS45	-412	0.04072
304L	-277.4	0.3452×10^{-3}
Q235	-914.3	1.038

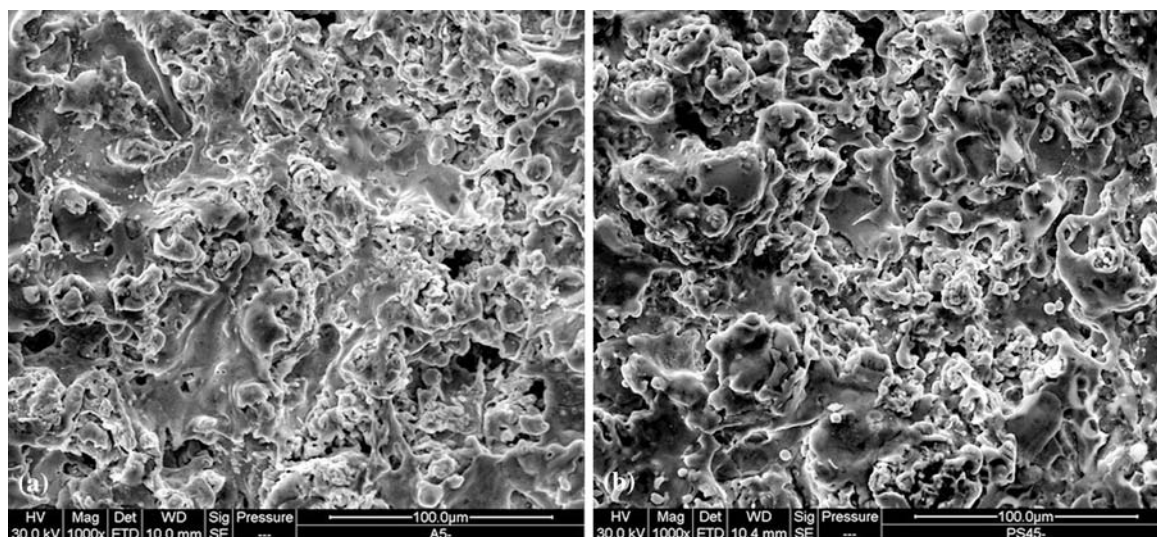


Fig. 8 SEM morphologies of the coatings after electrochemical corrosion test in 0.5 mol/L H_2SO_4 solution. (a) Sample A5 coating. (b) PS45 coating

SEM morphologies of coatings after the electrochemical corrosion test in 0.5 mol/L H₂SO₄ solution are shown in Fig. 8. It can be seen that the surface of the A5 coating was dissolved comparably to that of PS45 coating.

4. Conclusions

Nickel-base cored wires were prepared by using Ni-Cr-strip to wrap metal powders of Ni, Cr, Mo, and CrB. Nickel-base coatings were prepared by electric arc spraying. Corrosion-resistant performance of coatings was evaluated by salt-spray test and electrochemical corrosion test. The results showed that Ni-base coatings containing Mo (5 wt.%) or B (2-4 wt.%) had better antichlorine ion corrosion performance than that of Ni-base coatings without Mo and PS45 (Ni-Cr-Ti) coating. The antichlorine ion corrosion coatings could be used for resolving the corrosion protection problem of the equipment and piping contacting sour, alkali, salt liquid in petrochemical engineering applications.

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