JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 19, Paper 23 first submitted 12 March 2016
published 31 December 1969

Salt Spray Corrosion Behaviors of Arc Sprayed Al Coating on S355 Steel by Laser Remelting

Kong Dejun[*1, 3], Sheng Tianyuan[1], Wang Wenchang[2]

[1]*School of Mechanical Engineering, Changzhou University, Changzhou 213164, China;*

[2]*School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China;*

[3]*Jiangsu Key Laboratory of Materials Surface Science and Technology, Changzhou University, Changzhou 213164, China*

Corresponding author e-mail address: kong-dejun@163.com

Abstract

A layer of arc sprayed Al coating on S355 steel was remelted with a CO_2 laser, the surface-interface morphologies, distributions of chemical elements, and phases were analyzed with a SEM (scanning electron microscopy), EDS (energy dispersive spectrometer), and XRD (X-ray diffraction), respectively. The corrosion performance of Al coating before and after laser remelting was investigated with a NSS (neutral salt spray) test, and the products of salt spray corrosion were also analyzed with a XRD. The result shows that the Al coating surface by arc spraying is rougher, the interface bonding mode is a mechanical bonding, after salt spray corrosion, the surface corrosion phenomenon is obvious, and the corrosion mode is primarily composed of pitting corrosion. After laser remelting, the coating surface tends to be smooth, the interface bonding mode is mechanical bonding and metallurgical bonding, while the surface tends to roughness after salt spray corrosion, and the corrosion mode is converted into general corrosion. The corrosion potential E_{Corr} of arc sprayed Al coating by laser remelting shifts positively, showing that the corrosion resistance is enhanced.

Keywords: Arc spraying; Al coating; Laser remelting; Salt spray corrosion

1. Introduction

As a new structural steel, S355 steel is used in the manufacturing of marine platform legs, duo to high strength, ductility, and impact toughness [1, 2]. The S355 steel is serviced in the sea water for long term and easily eroded, and a strong electrochemical corrosion happens, which reduces the mechanical properties of S355 steel and shortens its service life. Because offshore platform is far away from the coast [3], it is difficult to carry out maintenance regularly, especially in the wave splashed zone, the corrosion rate is about 6 times of that under normal circumstances, therefore, there is a significance issue of processing Al coating on the S355 steel. Recently, researches on S355 steel are mainly focus on welding microstructure and mechanical properties [4-7], the investigations of laser remelting on salt spray corrosion of arc sprayed Al coating are less reported. The Al coating by arc spraying is the main method for long-term preservation [8-10], which plays a role of isolating and cathodic protection, but in the ocean environment, the corrosion resistance of Al coating decreased very fast. Laser remelting has many advantages such as high efficiency, simple process, and good environmental performance [11-13], the salt spray resistance of arc sprayed Al coating by laser remelting can be further enhanced. The effective thickness of Al coating can be controlled by laser parameters, achieving the purpose of increasing the bonding force of the Al coating-substrate. In this study, a layer of Al coating was prepared on S355 steel substrate by arc spraying, which was processed with laser remelting, forming a laser remelted layer. The corrosion resistance was discussed with salt spray corrosion test, which provide a technical support for surface modification treatment of S355 steel in ocean engineering.

2. Experimental

The experimental material was the European standard S355 structural steel with the chemical compositions (mass, %) as follows: C 0.17, Mn 0.94, Si 0.55, Mo 0.30, Cr 0.065, Ni 0.065, Zr 0.15, S 0.035, the remainder was Fe. The process of arc sprayed Al coating as follows: polishing → chemical washing → blasting → drying → arc sprayed Al coating → cooling → cleaning. Technical parameters as the following: Al wire with the diameter of 2 mm; spraying voltage of 20-30 V; spraying current of 100-200 A. The process of laser remelting was shown as follows: Al coating → chemical washing → blasting → drying → laser remelting, the Al coating on the S355 steel was remelted by a CO_2 laser with laser power of 1000-1200 W, broadband spot of 1mm×10mm, scan speed of 6-8 mm/s, lap rate of 50 %, Ar as protective gas. The NSS test was carried out according to the GB 6458-86 standard of NSS test in China, test conditions: continuous salt spraying of 3.5 ±0.5 % NaCl solution, pH of 6.5-7.2, the temperature of 30℃±1 °C. The electrochemical experiments were carried out on a PS268A type electrochemical workstation. The morphologies, chemical compositions, and phases of the Al coating after salt spray corrosion were analyzed with a JSM-6360LA type SEM, its configured EDS, and D/max2500 PC type XRD, respectively.

3. Analysis and discussion

3.1 Surface-interface morphologies and EDS analysis of arc sprayed Al coating

Fig.1 (a) shows that the Al coating surface was comparatively rough after arc spraying, there were some particles stacked on the sample surfaces, existing a few pores. The flaws generated during arc spraying, caused by Al mistes under high temperature and pressure, the coating was coated firmly and sealed well. Fig.1 (b) shows the results of EDS analysis, the mass frations (mass, %) were shown as follows: C 7.14, O 11.29, Al 71.35, Si 3.82, K 0.72, Ca 0.85, Fe 4.83; and atom fractions (at, %): C 14.14, O 16.77, Al 62.86, Si 3.42, K 0.44, Ca 0.50, Fe 2.06. The part of Al coating had been oxidized by the air, a few Fe atoms were detected, which came from the substrate. The Fe element was so active that it was easily oxidized into Fe_2O_3 with the loose structures, affecting anti-corrosion of the coating. The Si, K, and Ca were impurity elements, which came from Al wire. Fig.1 (c) shows that the Al coating with the thickness of 300 μm was formed on the substrate, the bonding interface appeared sawtooth shape, this was because that of the surface irregularities were filled by Al mists during arc spraying, and mechanical bonding was formed to improve the bonding strength effectively. Fig.1 (d) and (e) shows the EDS analysis results of point B and C, the mass fractions (mass, %) of point B were shown as follows: Fe 100; and atom fractions (at, %): Fe 100, the mass fractions (mass, %) of point C were shown as follows: Al 96.4, Fe 3.86; and atom fractions (at, %): Al 98.10, Fe 1.90, no Al element diffused into the substrate, and only a small amount of Fe element appeared in the Al coating, which was illustrated that no diffusion behavior happened during arc spraying, and it was further proofed that bonding mode was mechanical bonding between the coating and substrate.

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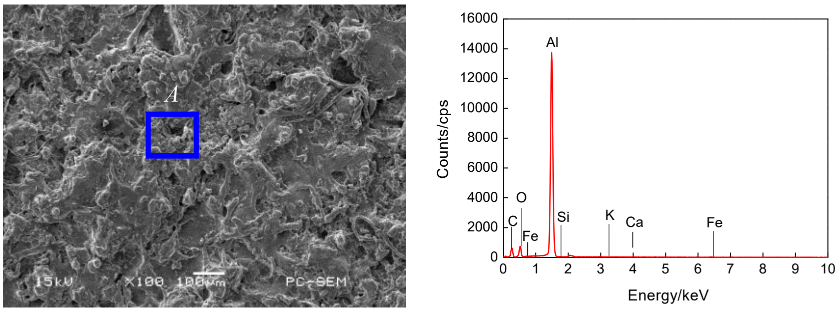
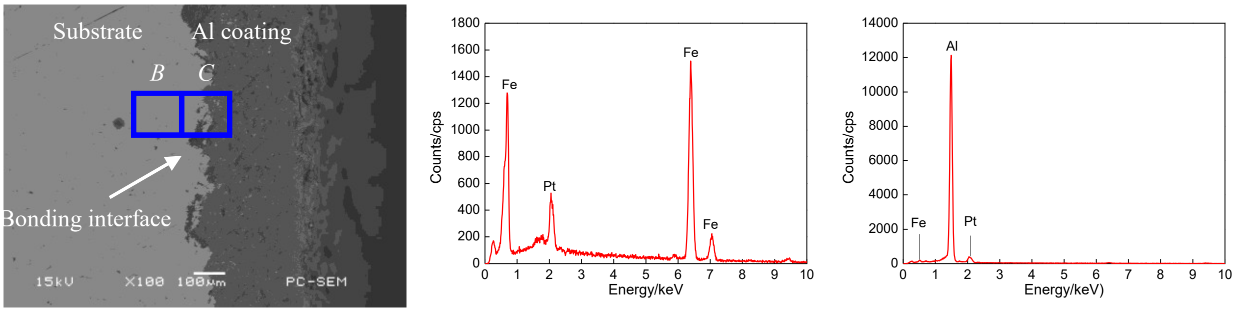


(a) Surface morphology (b) EDS analysis of point *A*



(c) Interface morphology (d) EDS analysis of point *B* (E) EDS analysis of point *C*

Fig.1 Surface morphology, EDS analysis, and interface morphology of arc sprayed Al coating

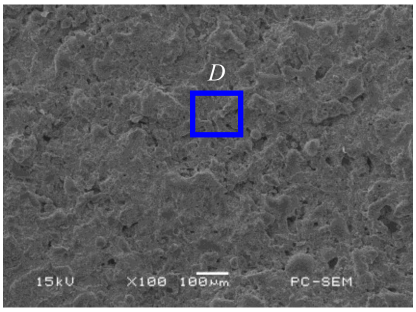
3.2 Surface-interface morphology and EDS analysis of arc sprayed Al coating by laser remelting

Fig.2 (a) shows that the coating surface roughness decreased after laser remelting, this was because that the Al of the coating surface was melted into liquid by the laser energy, during solidification, the liquid Al was distributed equally on the sample surface. Fig.2 (b) shows the results of EDS analysis of point *D*, the mass fractions (mass, %) were shown as follows: C 7.07, O 23.32, Al 58.39, Si 4.16, Fe 7.06; and atom fractions (at, %): C 13.14, O 32.51, Al 48.23, Si 3.31, Fe 2.81. The Al content by laser remeling decreased, while the O content by laser remeling increased, compared that by arc spraying. It was illustrated that the Al element was further oxidized into Al_2O_3, which reduced coating consumption rate effectively. The interface morphology by laser remelting was shown in Fig.2 (c), the Al coating was dense and flat, a small number of lateral pores existed, this was because that the Al coating became larger during laser remelting, and the Ar gas got into the coating. The Al coating rapidly cooled after laser melting [14], as the temperature decreased, the coating shrank, no liquid metal added into the pores, and the lateral pores appeared. The interface was composed of Al coating-FeAl metallurgical bonding layer-S355 steel substrate, among them, the Fe-Al metallurgical bonding layer with the thickness of about 10 μm was produced at the Al coating-substrate interface. The combination reaction occurred at the surface to form the Fe-Al metallurgical bonding layer, no cracks appeared, which was ensured that the close integration of the coating-substrate was formed. The Fe appeared in the Al coating that was closed to the bonding layer, indicating that a small number of Fe atoms got into the Al coating under the impact of Ar gas, and occurred compound reaction with Al to form Fe-Al compounds. The following reaction occurred during laser remelting:

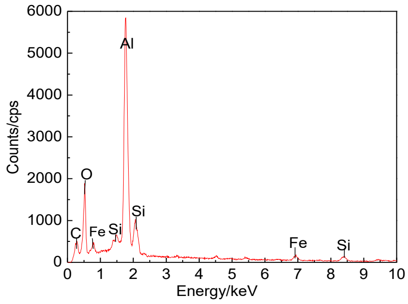
$$Fe+Al \rightarrow FeAl \qquad (1)$$

$$3Fe+Al \rightarrow Fe_3Al \qquad (2)$$

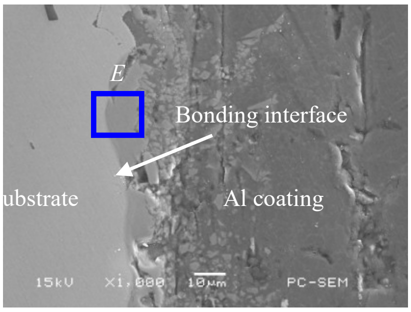
The FeAl and Fe_3Al were two relative stable phases of Fe-Al alloy at high temperature, the interatomic bonding mode were covalent bond and ionic bond, which improve the bonding performance. Fig.2 (d) shows the EDS analysis results of point *E*, the mass fractions (mass, %) were shown as follows: Al 51.34, Fe 48.66; and atom fractions (at, %): Al 68.59, Fe 31.41, the Al and Fe atoms diffused mutually, it was further proofed that the bonding mode was metallurgical bonding from the perspective of element content.



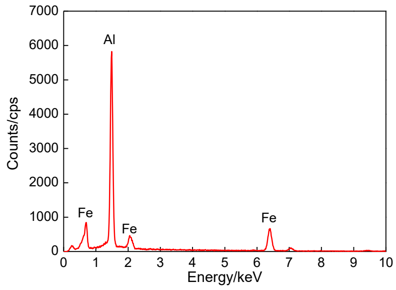
(a) Surface morphology



(b) EDS analysis of point *D*



(c) Interface morphology

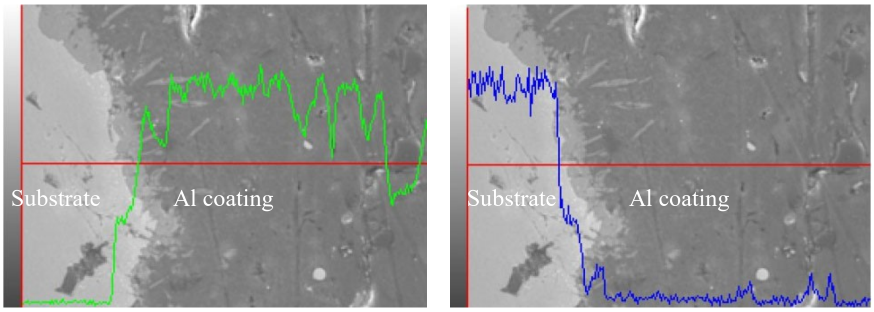


(d) EDS analysis of point *E*

Fig.2 Surface morphology, EDS analysis, and interface morphology of arc sprayed Al coating by laser remelting

3.3 Line scan analysis of arc sprayed Al coating interface by laser remelting

Fig.3 (a) shows that the Al element maintained a low content in the substrate, and began to increase at the metallurgical bonding layer closed to the substrate, the gradient increase exhibited at the bonding layer. This diffusion, gap diffusion and vacancy diffusion were coexisted, the obvious metallurgical bond appeared at the middle and the outer coating, the Al content maintained a relatively high concentration. Fig.3 (b) shows that the Fe element had high content in the substrate, and declined rapidly at the diffusion layer, the gradient of Fe element was significantly larger than that of Al element. It was illustrated that there was almost no Fe element arrived at the Al layer, no Fe_2O_3 appeared during salt spray corrosion, which was ensured the Al coating had excellent corrosion resistance.



(a) Al content (b) Fe content

Fig.3 Line scan analysis of arc sprayed Al coating interface by laser remelting

3.4 Surface-interface morphology and EDS analysis of arc sprayed Al coating after corrosion

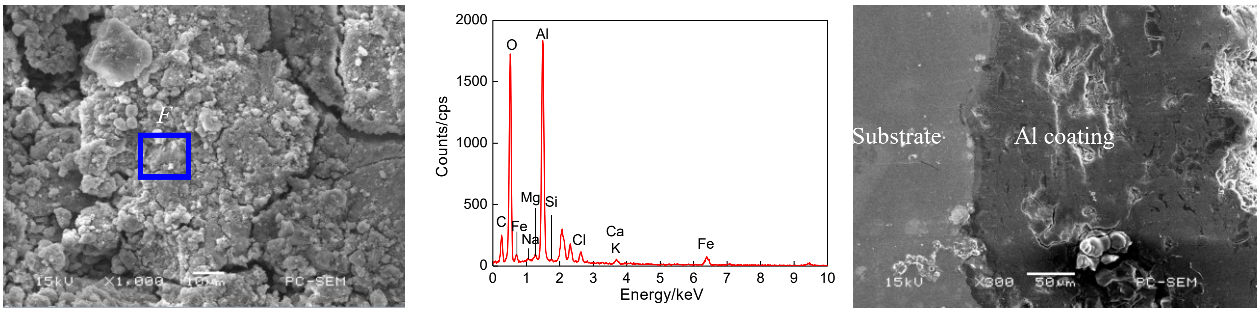
Fig.4 (a) shows that the Al coating surface became loose and occurred cracking phenomenon after salt spray corrosion. The cracking was the starting point of coating failure, the Cl^- and O^{2-} could easily penetrate into the substrate from the cracking, which could destroyed bonding performance between the coating and substrate. The corrosion phenomenon was most evident at the spraying defects, the deep etch pits and corrosion particles appeared, which was caused by the phenomenon of "occluded cell", and the following reaction occurred in occlusive area [15].

$$O_2+2H_2O+4e^-\rightarrow 4OH^- \quad (3)$$

$$Al\rightarrow Al^{3+}+3e^- \quad (4)$$

$$Al^{3+}+3H_2O\rightarrow Al(OH)_3+3H^+ \quad (5)$$

Eq.(3) shows that a large amount of H^+ generated during reaction, which improved the sensitivity of Cl^- on the Al element of, the Al^{3+} was difficult to form Al_2O_3, deepening further the pits, the mechanical bonding between the coating and substrate destroyed after the pits connecting, which could lead to the coating peeling and affected its anti-corrosion seriously. The results of EDS analysis was shown in Fig.4 (b), the mass fractions (mass, %) as follows: C 19.67, O 59.79, Mg 0.33, Al 13.40, S 1.54, Cl 1.13, Ca 0.53, Fe 3.62; and atom fractions (at, %): C 27.10, O 61.85, Mg 0.23, Al 8.22, S 0.79, Cl 0.53, Ca 0.22, Fe 1.07. The Al element on the surface severely decreased, which existed in the oxide form. The Cl and S elements came from etchant residue, the Fe content did not change, which was illustrated that the corrosion behavior occurred on the coating surface. Fig.4 (c) shows that a small number of corrosion cracks appeared, and the thickness of Al coating changed, which was illustrated that the arc sprayed Al coating had a certain of salt spray resistance.



(a) Surface morphology (b) EDS analysis of point *F* (c) Interface morphology

Fig.4 Surface morphology, EDS analysis, and interface morphology of arc sprayed Al coating after corrosion

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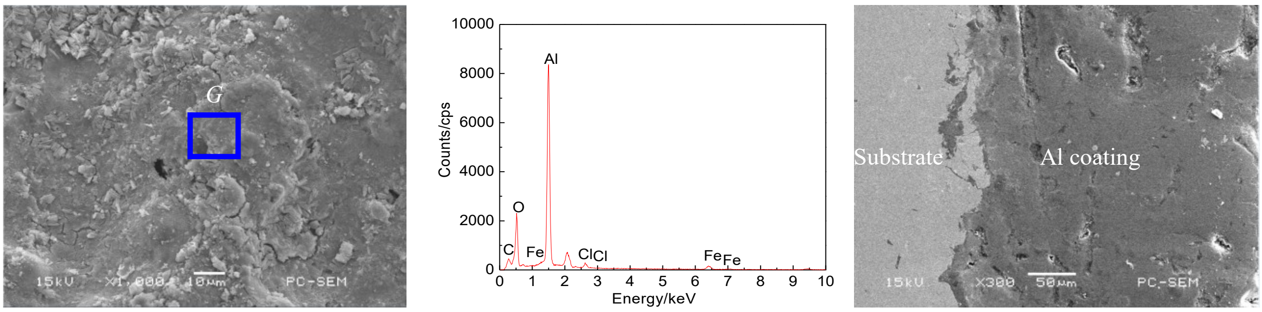
3.5 Surface-interface morphologies and EDS analysis of arc sprayed Al coating by laser remelting after corrosion

Fig.5 (a) shows that the laser remelted surface was relatively flat after corrosion, a small number of corrosion cracks appeared, and the surface porosity decreased, which came from two sources: (1) the Al coating was oxidized into Al_2O_3 after laser remelting, the structure was more compact, which was less sensitive to Cl^-, and it could avoid Al element directly dissolved into the salt spray etching solution, which reduced the consumption rate of the Al coating; (2) the following reaction occurred during corrosion.

$$Al^{3+}+3OH^- \rightarrow Al(OH)_3 \quad (6)$$

$$2Al(OH)_3 \rightarrow Al_2O_3+3H_2O \quad (7)$$

The surface Al element adsorbed on the pits, then dehydrated into Al_2O_3, which had a larger volume to fill potholes effectively and made the surface smooth. The corrosion behavior of the coating changed from pitting corrosion into general corrosion. General corrosion was a corrosion mode which was more uniform slower, in this corrosion mechanism, the corrosion behavior only happened on the coating surface, deep coating and the substrate would not be influenced, which could extend service life of the coating. Fig.5 (b) shows the results of EDS analysis, the mass fractions (mass,%) as follows: C 12.97, O 27.71, Al 49.42, Cl 1.94, Fe 7.95; and atom fraction (at, %): C 22.30, O 35.78, Al 37.84, Cl 1.13, Fe 2.94. The Al content by laser remelting decreased, but it was far higher than that by arc spraying after corrosion, which was illustrated that laser remelting could reduce the effect of Cl^- on Al coating. Fig.5 (c) shows that the metallurgical bonding mode between the coating and substrate did not destroy after corrosion, the pores generated during laser remelting did not grow up after corrosion, illustrating that salt spraying only affected the surface performance.



(a) Surface morphology (b) EDS analysis of point *G* (c) Interface morphology

Fig.5 Surface morphology, EDS analysis, and interface morphology of arc sprayed Al coating by laser remelting after corrosion

3.6 XRD analyses of Al coating by laser remelting before and after corrosion

The XRD analyses of Al coating by laser remelting before and after corrosion are shown in Fig.6. Fig.6 (a) shows that the coating surface was mainly covered by α-Al_2O_3, which was the most stable phase of alumina [16], and it had the advantages such as stable structure, high body density, high strength, and good corrosion resistance. Fig.6 (b) shows that the coating surface was also covered by α-Al_2O_3 with a lower peak, the $Al(OH)_3$ appeared at 78.12° and was amphoteric hydroxides, which could soluble in acid and alkali and had an effect on the coating corrosion resistance.

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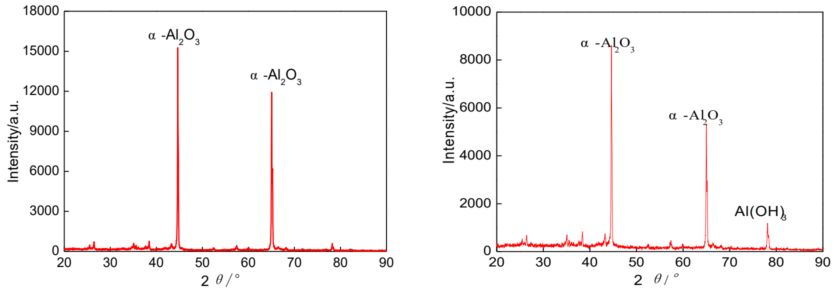

(a) Before corrosion (b) After corrosion

Fig.6 XRD analysis of arc sprayed Al coating by laser remelting before and after corrosion

3.7 Electrochemical test

The polarization curves of Al coating by laser remelting in NaCl solution were shown in Fig.7. The corrosion potential E_{Corr} of the Al coating by arc spraying was -1100 mV, while that by laser remelting was -1000 mV, the corrosion potential moved forward after laser remelting, showing the corrosion resistance had enhanced. The corrosion of Al coating in 3.5 % NaCl solution was a process of Al dissolution and reduction of dissolved oxygen. The following reaction occurred during electrochemical corrosion [17].

$$Al \rightarrow Al^{3+} + 3e^- \quad (8)$$

$$O_2 + 4H_2O + 6e^- \rightarrow 6OH^- + H_2 \quad (9)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (10)$$

$$2Al_2(OH)_3 \rightarrow Al_2O_3 \cdot H_2O \quad (11)$$

The high passivity normally associated with Al came from the highly adherent barrier oxide of Al_2O_3 that formed on the surface. In aqueous environments, this protective oxide was formed with a certain thickness, and as long as there was the O element, which continued to repassivate when the flaws were formed.

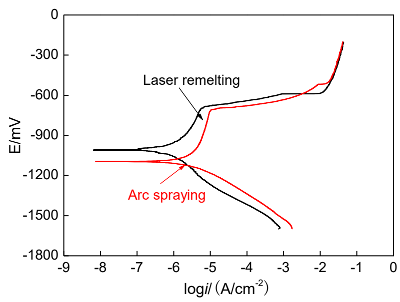

Fig.7 Polarization curves of arc sprayed Al coating by laser remelting in 3.5 % NaCl solution

4. Conclusions

(1) The Al coating surface by arc spraying was rough, the interface binding mode is a mechanical bonding, and the corrosion behavior is pitting corrosion and cracking corrosion after salt spray corrosion.

(2) The Al coating surface by laser remelting becomes smoother, a small number of longitudinal gaps appear at the interface, the interface binding mode is mechanical and metallurgical bonding, and the corrosion behavior changes into general corrosion.

(3) The salt spray corrosion product is $Al(OH)_3$ with a smaller degree of crystallinity, which is illustrated that the corrosion resistance capability of arc sprayed Al coating is improved after laser remelting.

(4) The corrosion potential of Al coating by arc spraying and laser remelting is -1100 mV and -1000 mV respectively, which is illustrated that the corrosion resistance enhanced after laser remelting

Acknowledgment

Financial support for this research by the Key Research and Development Project of Jiangsu Province (Industry) (BE2016052) is gratefully acknowledged.

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