Corrosion Behavior of Fe–Al Coatings Fabricated by Pack Aluminizing Method

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Received: 25 March 2016 / Revised: 25 May 2016 / Published online: 29 June 2016
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Abstract In this study, the two kinds of Fe–Al coatings were fabricated by pack aluminizing on low-carbon steel at different temperatures. The corrosion behavior of the Fe–Al coatings in artificial seawater was investigated by the electrochemical and weight loss techniques. Results show that the thickness of coating layer increases with increasing aluminizing temperature. The coatings exhibit high micro-hardness and good metallurgical bonding with the substrate. In comparison with the steel substrate, the corrosion current density I_{corr} of the Fe–Al coatings is always lower than that of substrate, about 1/38 or 1/33 after 2 h immersion, and 1/3 or 1/6 for 720 h immersion. As can be seen from the weight loss curve, the Fe–Al coatings show less loss than that of the substrate within 30-day immersion. The corrosion products formed on the surface of the coatings include oxides of Al, Mg, Fe and Ca, and pitting defect has also been found. The Fe–Al coating with higher content of Fe_2Al_5 has better corrosion resistance.

KEY WORDS: Fe–Al coatings; Corrosion; Pack aluminizing; X-ray diffraction

1 Introduction

Fe–Al intermetallic compounds are often used as the traditional engineering materials due to their low density and cost, high temperature strength and outstanding oxidation and corrosion resistance [1–11]. In recent years, many studies have been carried out and acquired great progress in the application of Fe–Al coatings prepared by different methods. Pawlowski et al. [3] researched the structure morphology of Fe–Al coating made by detonation sprayed onto carbon steel substrate. They mainly studied the formation mechanism of the coating. Zhu et al. [4] studied the high temperature wear behavior of Fe–Al coating prepared

by high-velocity arc spraying. They found that the friction coefficient of the coating decreased and the wear resistance significantly increased with increasing testing temperature. Zhu et al. [5] discussed the microstructure and corrosion resistance of Fe–Al coating synthesized by double-glow plasma surface alloying technology. They found that the corrosion resistance of the aluminized sample is much higher than that of the substrate (45 steel) in the solution. Canakci et al. [6–8] made a comprehensive research on Fe–Al intermetallic coating prepared by a novel mechanical alloying technique. They concluded that the hardness and wear resistance of the coatings decreased with increasing the milling time, but the corrosion resistance increased. In addition, there is another method to fabricate the Fe–Al coating, namely pack cementation [9–11].

The pack cementation process is an in situ chemical vapor deposition (CVD) process, which is usually used to deposit certain elements on a steel substrate [12–16]. Pack aluminizing is a common method used to form Fe–Al coatings. In a word, the method is putting the steel surrounded with the cement into the sealed oven, through the

Available online at <http://link.springer.com/journal/40195>

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process of heating, holding and diffusion annealing, to achieve aluminized surface. Moreover, the main concerned about is the high temperature oxidation [11, 14, 16] and corrosion [17, 18] resistance. The aqueous corrosion properties of the Fe–Al coatings at room temperature were also studied, which are prepared by other methods but not pack aluminizing [5, 19–21]. Typically, Zhu *et al.* [5] studied the corrosion properties of Fe–Al coatings in Na₂S solution and Na₂SO₄ + NaCl solution prepared by double-glow plasma surface alloying technology. One of the possible applications for the Fe–Al coatings is in the ocean. The artificial seawater is mostly used to simulate the real ocean environment to study the corrosion performance [21–23] of different materials. The electrochemical [5, 22, 24–27] and conventional weight loss techniques [28, 29] are usually used to characterize the corrosion behavior.

The aim of this paper is to investigate the corrosion behavior of the Fe–Al coatings in artificial seawater using electrochemical and weight loss techniques, which were prepared by pack aluminizing on low-carbon steel.

2 Experimental

2.1 Materials and Methods

The selected substrate was Q235 low-carbon steel. Its nominal composition is given in Table 1. The steel samples were cut into a dimension of 10 mm × 10 mm × 2 mm, grounded with SiC paper from 120 to 600 grades and then polished with alumina powder (0.5 μm) to obtain the surface roughness *Rz* (DIN) of 5, degreased with organic solvent and finally rinsed in distilled water.

An in-pack method was employed to aluminize the samples in a tube furnace. The chemicals used for the pack cement were the analytical purity powders of Al (200 grids), Al₂O₃ (300 grids) and AlCl₃ (anhydrous) as catalytic agent. Two different temperatures were used to acquire good coating. Table 2 displays the each aluminizing parameters. The process of pack aluminizing can be briefly described as follows. The samples were hidden in the cement, which were rushed into an alumina crucible. The crucible was sealed and then dried in an oven. Afterward, the crucible was loaded into a tube furnace, heated to

Table 2 Chemical composition (wt%) of packs with different aluminizing parameters

Materials	Al	Al ₂ O ₃	AlCl ₃	Temperature (°C)	Time (h)
Condition 1	8.0	87.0	5.0	650	20
Condition 2	8.0	87.0	5.0	750	20

the setting temperatures and held for 20 h, at the end slowly cooled with the furnace.

The solution for all the electrochemical tests was the artificial seawater, which composition is shown in Table 3 according to GB/T 17848-1999 (China) [30]. The samples were immersed in the solution for 2, 12, 24, 72, 120, 240, 480 and 720 h. The solution was refreshed every seven days during the whole experiment.

2.2 Corrosion Measurements

Polarization curves were used to investigate the corrosion behavior of the Fe–Al coatings. All the tests were conducted in a three-electrode system. The samples, used as the working electrode, were embedded in epoxy resin with an exposed working area of 1 cm². Pt electrode was used as the counter electrode, while the saturated calomel electrode (SCE) as the reference electrode. Polarization measurement of the samples was conducted at the applied potential within the −500 to +500 mV range versus open circuit potential. All the experiments were performed by the CHI604D (Chenhua, Shanghai, China)-type electrochemical workstation at room temperature.

According to GB 7901-1999 (China), the standard weight loss test was carried out [31]. In these experiments, the samples were immersed in artificial seawater at room temperature for 30 days. At 3, 5, 10, 20 and 30 days, the samples were fetched from the solution. Corrosion products were cleaned out by ultrasonic, mechanical or chemical. Before and after tests, the samples were weighed by means of a digital balance with a precision of 0.0001 g. Three parallel for each sample was weighted three times to obtain the accurate result.

2.3 Surface Characterization

The phase identification was carried out by X-ray diffraction (XRD) with CuK_α radiation (D/Max-RA, Rigaku, Japan). The microstructure as well as the element content distribution of the coatings layer was investigated by scanning electron microscopy (SEM) and its supporting energy-dispersive X-ray spectroscopy (S-3400II, Hitachi, Japan), respectively. The micro-hardness of the coatings layer and substrate along the cross section was evaluated by the Vickers micro-hardness Meter (HNV-G20,

Table 1 Chemical composition of Q235 low-carbon steel (wt%)

C	Mn	Si	S	P	Fe
0.14–0.22	0.30–0.65	0.30	≤0.050	0.045	Bal.

Table 3 Chemical composition of the artificial seawater (g/L)

NaCl	MgCl ₂ ·6H ₂ O	Na ₂ SO ₄	CaCl ₂	KCl	NaHCO ₃	KBr	SrCl ₂ ·6H ₂ O	NaF	H ₃ BO ₃
24.530	11.110	4.090	1.160	0.700	0.200	0.100	0.042	0.003	0.027

Shimadzu, Japan). The loading force was 980 mN, and the holding time was 10 s. The five points were measured for each section. The morphology and chemical composition of the corrosion products on the coatings surface were tested again by SEM and energy-dispersive spectroscopy (EDS).

3 Results and Discussion

3.1 Microstructure

Figure 1 illustrates the XRD patterns of the prepared Fe–Al coatings by pack aluminizing at different temperatures.

Fig. 1 XRD patterns of the Fe–Al coatings fabricated at: **a** Condition 1, **b** Condition 2

The result shows that the FeAl₃ and Fe₂Al₅ are the main phases and also semiquantitatively inferred that coating fabricated at 750 °C is rich in Fe₂Al₅. The phase of FeAl₃ just covers the surface as inward Al diffusion.

The cross-sectional morphologies and the element content distribution (Fe, Al) from the coatings to the substrate are shown in Figs. 2 and 3, respectively. Results show that the thickness of the coating layer increased with increasing aluminizing temperature. There are no obvious defects, such as pores and cracks (Fig. 2) to be observed. It can also be inferred that the coatings were formed mainly through the inward Al diffusion [32]. The content distributions of Fe and Al are stable at the beginning, and then, the Al gradually reduced to zero at the direction of the substrate (Fig. 3). A certain diffusion zone at the interface exists, which indicates that the metallurgical bonding formed between the coating and substrate. In addition, the EDS analysis of the coatings surface was also carried out. The Al content in the coating fabricated at 650 °C (73.02 at.%) is slightly more than the coating fabricated at 750 °C (72.49 at.%). Based on the lever rule from the Fe–Al phase diagram [33], the coating fabricated at 750 °C contained more Fe₂Al₅ phase than that fabricated at 650 °C. It is consistent with the XRD result. There is a little discrepancy compared with the previous work of Xiang and Datta [34]. They concluded that phases on the coating of alloy steels at 650 °C for 8 h by pack aluminizing are Fe₁₄Al₈₆ and FeAl₃. That is probably because the Al contained the pack cement, and the holding time for aluminizing are not sufficient and long to make the Al diffuse into the substrate, so the Al is enriched in the coating surface. To a certain extent, it probably related to the composition of the substrate. It also can be known that the temperature affects the

Fig. 2 SEM morphologies on the cross-section of Fe–Al coatings fabricated at: **a** Condition 1, **b** Condition 2

Fig. 3 EDS results of content distribution of Fe–Al coatings fabricated at: **a** Condition 1, **b** Condition 2

Fig. 4 Morphologies of micro-hardness indentation of Fe–Al coatings fabricated at: **a** Condition 1, **b** Condition 2, **c** Q235 steel

Fig. 5 Polarization curves of different materials immersed for: **a** 2 h, **b** 720 h

thickness, but not the microstructure of the coatings. Xiang and Datta [11] have studied the relationship between the pack chemistry and aluminum coating formation on alloy steel and got the similar conclusion.

The micro-hardness of the coating fabricated at 650 °C is 820 HV, which is a bit higher than that of the coating

fabricated at 750 °C (740 HV). As a contrast, the micro-hardness of the coatings is higher than that of substrate (110 HV). The typical morphology of indentation is shown in Fig. 4. The diagonal length and size of the indentation both illustrated that the coatings possess higher hardness.

3.2 Polarization Curves

Figure 5a, b shows the polarization curves obtained from the samples of the substrate and the Fe–Al coatings, which are immersed in artificial seawater for 2 and 720 h, respectively. It can be seen that the corrosion current density I_{corr} of the two coatings is always lower than that of the substrate at the same potential and the coating fabricated at 750 °C has the minimum I_{corr} .

The anodic slope β_a , cathodic slope β_c , polarization resistance R_p and corrosion current density I_{corr} can be deduced from the curves. Tables 4 and 5 reveal the values of β_a , β_c , R_p and I_{corr} obtained after 2- and 720-h immersion in the artificial seawater, respectively. The I_{corr} of the Fe–Al coatings is about 1/38 or 1/33 of that of the substrate for 2-h immersion (Table 4). And after immersing for 720 h, the I_{corr} of the Fe–Al coatings is still lower than that of substrate, about 1/3 or 1/6 (Table 5).

Clearly, it is worth noting that the point P on the blue curve in Fig. 5a, I_{corr} suddenly increased along with the rise

Table 4 Electrochemical parameters of different Fe–Al coatings obtained after 2-h immersion

Materials	β_a (V/dec)	β_c (V/dec)	R_p (ohm)	I_{corr} (A/cm ²)
Q235	0.174	0.151	832	4.232×10^{-5}
Condition 1	0.120	0.244	31,760	1.100×10^{-6}
Condition 2	0.272	0.225	42,828	1.250×10^{-6}

Table 5 Electrochemical parameters of different Fe–Al coatings obtained after 720-h immersion

Materials	β_a (V/dec)	β_c (V/dec)	R_p (Ω)	I_{corr} (A/cm ²)
Q235	0.452	0.121	242	1.713×10^{-4}
Condition 1	0.244	0.178	848	5.275×10^{-5}
Condition 2	0.266	0.160	1542	2.821×10^{-5}

in potential, which is defined as the breakdown potential E_b . It implies that the formed passive film has been destroyed. The existence of point P had also been found in other research [27].

Figure 6a, b expresses the I_{corr} and R_p of the substrate and Fe–Al coatings at certain period after immersion. It shows that the I_{corr} of the Fe–Al coatings is always lower than that of the substrate, while the R_p values are higher, namely that the larger the R_p , the smaller the I_{corr} . It indicates that the coatings have excellent corrosion resistance as compared to substrate.

3.3 Weight Loss Test

The weight loss curves of different materials are indicated in Fig. 7 after 30-day immersion. As shown in Fig. 7, the weight loss of the substrate is more obvious than that of the Fe–Al coatings in the initial stage. Afterward, it rises and then declines. However, the whole weight loss of the substrate is still higher than that of the Fe–Al coatings. There is a significant difference between the substrate and Fe–Al coatings on the curve. In simple words, the weight loss of Fe–Al coatings is less and appears to be negative value in the later, indicating that the increased Fe–Al coatings weight did not decrease. That is because the corrosion products attached firmly in the later period of immersion, which leads to the increase in weight and the decrease in corrosion rate. Dong *et al.* [21] studied the corrosion behavior of cold-sprayed aluminum coating in seawater and found the physical shielding effect of the corrosion products on the coating surface, namely hinder the medium diffusion to reduce the corrosion rate. It is consistent with the above conclusion. The corrosion products were retained on the coatings surface after the experiment to investigate the morphology and composition.

Table 6 lists for the EDS results of corrosion products of different Fe–Al coatings, respectively. According to the

Fig. 6 Corrosion current density I_{corr} **a** and polarization resistance R_p **b** of different materials

results, the corrosion products of coatings include oxides of Al, Mg, Fe and Ca. Ca and Mg are mainly through hydrolyzed to form $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ and finally deposited on the coatings surface as precipitation. Al is mainly used to form the passive film. The main chemical reactions occurred are as follows:

Fig. 7 Weight loss curves of different materials after 30-day immersion

Table 6 EDS results of the corrosion products of the different Fe–Al coatings (at.%)

Materials	Fe	Al	Mg	Ca	O
Condition 1	13.20	19.76	7.90	0.29	58.85
Condition 2	16.80	25.37	5.38	0.52	51.93

Since the activity of Al is stronger than that of Fe, the passive film formed preferentially, then is the reaction of aqueous with Fe and finally exists in a form of the oxide on the coatings surface. These reactions with aqueous solution occurred at the original defects, namely in situ pitting. This is the autocatalytic process inside the occluded cell. There are a lot of Cl^- ions in the artificial seawater solution. When the concentration of metal ions increased in the pits, the Cl^- ions began to enter the pits, surrounding and dissolving the metal ions, which maintained the charge stable. The typical reactions are as the following:

Pitting formation can be found on the morphology of corrosion products surface (Fig. 8). The increase and accumulation of the corrosion products on the coatings surface prevent the Cl^- infiltration and thus lead to the increase in the coatings weight in the later stage (Fig. 7).

From the above data, it can be known that the aluminized coating can improve the corrosion resistance of the substrate. The Fe–Al coating fabricated at 750 °C, containing more Fe_2Al_5 phase has a better performance, namely the lower corrosion current density, higher polarization resistance and less weight loss compared with the coating fabricated at 650 °C. It may be due to the strong ability to form a passive film, which is proved by the potential change suddenly at point P on the polarization curve (Fig. 5a).

4 Conclusions

- 1 The Fe–Al intermetallic coatings on the Q235 steel can be fabricated via pack aluminizing. The phases of the surface coatings are composed of FeAl_3 and Fe_2Al_5 with different contents, and the surface coatings exhibit

Fig. 8 Morphologies of the corrosion products on Fe–Al coating surface fabricated at: **a** Condition 1, **b** Condition 2

high micro-hardness and good metallurgical bonding with the substrate.

2. The Fe–Al coatings exhibit better corrosion resistance than the Q235 steel substrate due to the passive film formation. The coating fabricated at 750 °C possesses lower corrosion current density, higher polarization resistance and less weight loss.

Acknowledgments This work is supported by the Foundation of Jiangsu Key Laboratory of Advanced Structural Materials and Application Technology (No. ASMA 201403) and Cooperative Innovation Fund of Jiangsu Province (No. BY 2014004-09).

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