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Effect of Annealing and Oxidation on the Microstructure Evolution of Hot-Dipped Aluminide Q345 Steel with Silicon Addition

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Abstract: Q345 steel was coated by hot dipping into molten pure aluminum and Al-Si baths. The coatings were annealed at 800 and 900 °C for 1–3 h and subsequently oxidized at 900 °C for 15 h in air. The results revealed that the thickness of the intermetallic layer increased with increasing hot-dipping time in the range of 700–750 °C, while it decreased when the hot-dipping aluminizing temperature was 800 °C. As the silicon content in the aluminum bath increased, the thickness of the intermetallic layer decreased, and the intermetallic layer/steel-substrate interface transformed from an irregular morphology into a flat morphology. The hot-dipped Al-2.5Si samples were subjected to annealing; the higher the annealing temperature and longer the annealing time, the faster the transformation of the intermediate phase in the coating. The Fe₂Al₅ phase was fully transformed into the ductile FeAl phase after the hot-dipped samples annealed at 900 °C for 3 h. When the outermost layer of Q345 steel was the FeAl phase, oxidation resistance of the oxide was the best.

Keywords: Q345 steel; hot-dipping aluminum-silicon; annealing; FeAl phase; Al₂O₃



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1. Introduction

In order to reduce room-temperature gas emissions and oil consumption, the use of bioethanol in the automotive industry is gradually increasing; bioethanol and the concentration of ethanol used as a bioadditive in gasoline has increased to about 20% in EU countries [1,2]. It is well-known that after burning bioethanol in engines, the flue gas consists of large amounts of H₂O and CO₂, which can significantly increase the reaction rate of steel in motorcycle- and automotive-exhaust-system components, resulting in the components of the exhaust system being subjected to massive oxidation and severe corrosion of steel and its alloys [3–6]. Low-alloy high-strength steels (Q345) are increasingly used in the automotive industry because of their high strength, good welding properties, and better corrosion resistance, which can save metal materials and reduce the weight of equipment. However, after long-term use of low-alloy high-strength steel in a high-temperature environment with water vapor, the steel surface can very easily form iron oxide, which seriously reduces the surface quality of the steel and limits its use in high-temperature conditions.

Hot-dipping aluminizing is an effective and inexpensive method to form a protective coating on the steel surface [7,8]. By inhibiting the rapid diffusion of aluminum atoms in Fe₂Al₅ and reducing the thickness of the alloy layer, the addition of a certain amount of silicon to the aluminum bath is beneficial to improve the quality of the coating [9–13]. The mechanism of the reduction of the intermetallic layer by the addition of silicon to the hot-dip-coated aluminum solution has been studied widely [9,10,13,14]. Heumann and Dittrich [9] stated that the reduction in the Fe₂Al₅ layer is due to the fact that silicon occupies vacant sites in the c-axis of the Fe₂Al₅ crystal structure, thus slowing down

the growth of the Fe_2Al_5 layer. In contrast, Lainer and Kurakin [13] proposed that the growth of the intermetallic compound layer can be slowed down due to the nucleation rate of the Fe-Al-Si intermetallic compound layer. Studies have shown that the high-temperature oxidation resistance of aluminized steel can be improved by using a suitable diffusion-annealing treatment to produce a phase-microstructure transformation in the coating [15–21]. The mechanism to improve the oxidation resistance of aluminized steel is the formation of a dense and stable Al_2O_3 protective layer on the surface of the aluminized layer during the oxidation process, accompanied by a phase transition from the Al-rich phase to the Fe-rich intermetallic compound in the aluminized layer. The improvement of high-temperature oxidation of low-carbon steel exposed to the ethanol combustion product by hot-dip-aluminized coating has been investigated widely [21–23]; however, there are few studies on hot-dip-aluminizing silicon of Q345 steel and its high-temperature oxidation properties. Therefore, it is important to study how to improve the high-temperature resistance of low-alloy high-strength steels in order to reduce the effect of alternative fuels on the high-temperature corrosion of low-alloy high-strength steels.

Previous studies indicated that the mechanical properties of the Fe-Al intermetallic compounds were different [24–26], in which the Fe_3Al and FeAl_2 phases show plastic characteristics, and FeAl , Fe_2Al_5 , FeAl_3 , and $\text{Fe}_4\text{Al}_{13}$ show brittle characteristics. The coatings evolved from the plastic phase had better adhesion. Therefore, the purpose of this paper is to study the effects of hot-dipping aluminizing and diffusion annealing on the evolution of the Fe-Al phase, and to explore ways of improving the high-temperature oxidation resistance of Q345 steel.

2. Experimental Materials and Methods

2.1. Experimental Materials

The substrate used in this experiment was Q345 steel plate; rectangular specimens were cut to the dimensions of 10 mm × 10 mm × 3 mm by a water-cooled cutting machine. The composition of Q345 high-strength steel is shown in Table 1. The hot-dipping Al-Si solution was prepared by pure aluminum and Al-15Si master alloy.

Table 1. Comparison of chemical composition (wt.%) of Q345 steel in this study with standard values.

Sources	Fe	Mn	S	Si	C	P
This study	Bal.	1.3	0.015	0.3	0.16	0.015
Standard	Bal.	≤1.70	≤0.035	≤0.50	≤0.20	≤0.035

2.2. Hot-Dipping Aluminizing

The samples were soaked in 15 wt.% sodium hydroxide aqueous solution at 70 °C for 3 min, and then washed with water and soaked in 15 wt.% hydrochloric acid solution for pickling for 3 min. After washing with water, the samples were treated in 200–300 g/L $\text{KCl-K}_2\text{ZrF}_6\text{-NaF}$ solution at 90 °C for 3 min with a mass ration of $\text{KCl}:\text{K}_2\text{ZrF}_6:\text{NaF}$ of 100:100:1. Then, the samples were removed and dried at 100 °C for 8 min. The hot-dipping aluminizing was carried out in a bath that was placed in a KGPS-30-8 medium-frequency induction furnace (Shenguang electric furnace, Ningbo, China) at 700, 750, and 800 °C, respectively. The working thermocouple was periodically tested against a calibrated standard thermocouple. The overall temperature accuracy was estimated to be ±5 °C. After the samples were immersed in the hot-dipping bath for 30 s and 3 min, respectively, they were quickly removed from the bath and cooled in room-temperature water.

2.3. Hot-Dipping Al-Si

The Al-Si molten bath was prepared from industrial pure Al and Al-15Si master alloy. The experiments were divided into six groups, with nominal composition of each group was Al-0.5Si, Al-1Si, Al-2.5Si, Al-5Si, Al-7.5Si, and Al-10Si, weighing 200 g in each. The hot-dip temperature was 750 °C, and the hot-dip time was 30 s.

2.4. Annealing and Oxidation

After removing the surface oxides, the hot-dipped samples were sealed in evacuated quartz tubes and placed in SK2-4-12 tubular resistance furnace (Shanghai Y-feng Electrical Furnace Co. Ltd., Shenyang, China) for diffusion annealing. The annealing temperatures were 800 °C and 900 °C, and the annealing times were 1 h, 2 h, and 3 h, respectively. The oxidation experiments were carried out in three groups: the first group of Q345 steel was hot-dipped in Al-2.5Si solution at 750 °C for 30 s and then directly oxidized in air at 900 °C for 15 h; the second group of Q345 steel was hot-dipped in Al-2.5Si solution at 750 °C for 30 s and then annealed in vacuum at 800 °C for 1 h; followed by oxidation in air at 900 °C for 15 h, and the third group of Q345 steel was hot-dipped in Al-2.5Si solution at 750 °C for 30 s and then annealed in vacuum at 900 °C for 3 h, followed by oxidation in air at 900 °C for 15 h. The three groups of samples were noted as D1, D2, and D3, respectively.

2.5. Characterization

Surface morphology, cross-sectional microstructure, and chemical composition of the coating were analyzed by a JSM-6510 Scanning Electron Microscope (SEM) (JEOL, Tokyo, Japan) equipped with Energy Dispersive X-ray Spectrometer (EDS) (Oxford Instrument, Cambridge, UK). In the observation of SEM, a focused electron beam with energy of 20 keV and working distance of 15 mm interacted with the sample in a teardrop-shape (around 1 µm deep into the sample).

3. Results and Discussion

3.1. Cross-Sectional Microstructure Analysis of Hot-Dipping Pure Aluminum

Figure 1 shows the cross-sectional microstructure of Q345 steel hot-dipped in aluminum solution at 700, 750, and 800 °C for 30 s and 3 min, respectively. It can be seen that the cross-sectional structure of the coating was divided into three different areas: external aluminum layer, intermetallic compound layer, and matrix steel. Composition of the intermetallic layer determined by EDS are listed in Table 2. The representative positions of the components of each phase determined in Figure 1 are marked with symbols a, b, c, respectively. In fact, the composition of each phase was the average of the components at five similar positions. According to the EDS results and combined with the Fe-Al phase diagram, the intermetallic compound layer consisted of two sublayers: the inner part at the metal-coating interface was the Fe_2Al_5 phase, and the composition determined by EDS point analyses was 70.9–71.9 at.% Al, 27.9–28.8 at.% Fe, and ≤ 0.6 at.% Mn. The outer part was the FeAl_3 phase, and the composition found by EDS point analyses was 75.6–75.9 at.% Al, 23.8–24.1 at.% Fe, and 0.3 at.% Mn. The Fe_2Al_5 phase was formed by reactive diffusion of iron atoms and aluminum atoms at the interface during hot dipping [4,6]. There was an irregular interface between the alloy layer and the steel matrix, which was in a tongue shape [9,10]. However, the FeAl_3 -phase layer was not so obvious until the hot-dipping temperature increased to 800 °C. In addition, it could be found that there was also a small amount of discrete-phase precipitation in the external aluminum layer. According to EDS analysis, this discrete phase was the FeAl_3 phase, which was precipitated through eutectic reaction in the solidification structure as the cooling speed was not quick enough while taking out the sample from the hot-dipping bath. Because the precipitated FeAl_3 phase was relatively small, the average Al content measured by EDS was relative higher than that in the FeAl_3 sublayer.

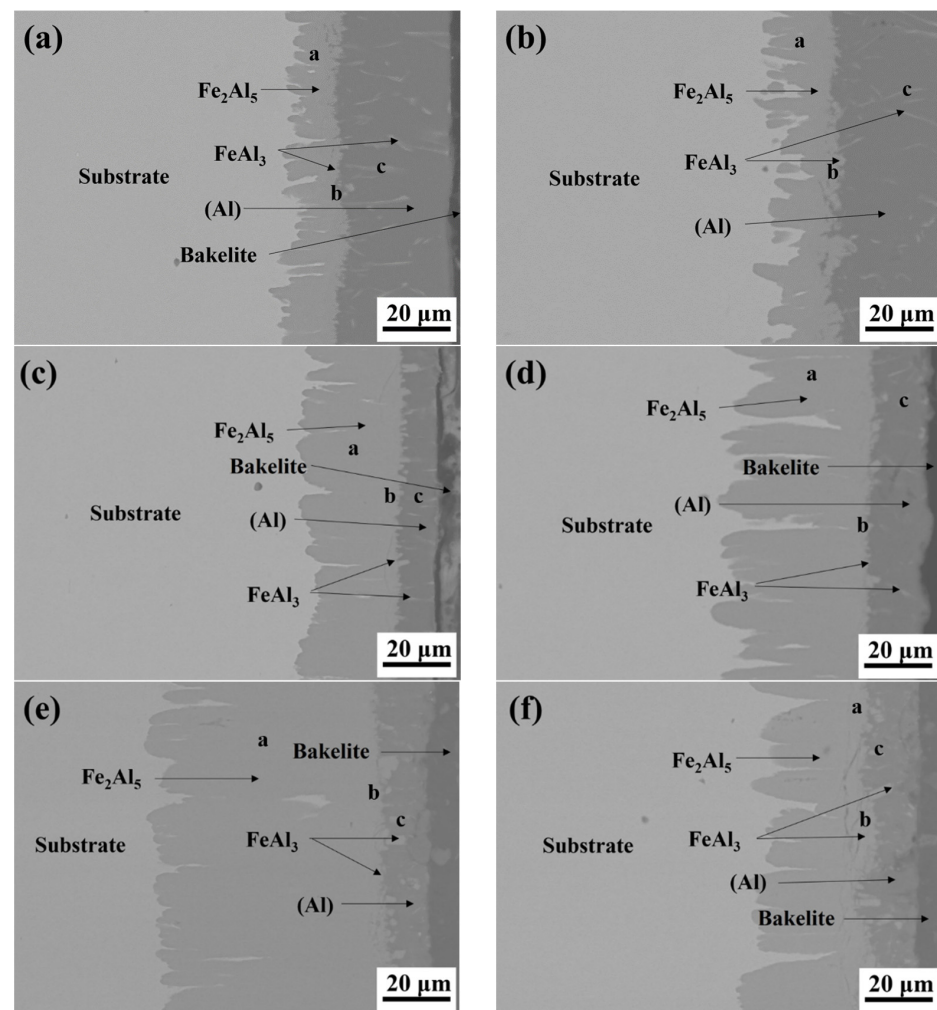


Figure 1. Cross-sectional microstructure of coating of Q345 steel hot-dipped in pure aluminum solution at 700, 750, and 800 °C for 30 s and 3 min, respectively. (a) at 700 °C for 30 s, (b) at 700 °C for 3 min, (c) at 750 °C for 30 s, (d) at 750 °C for 3 min, (e) at 800 °C for 30 s, (f) at 800 °C for 3 min.

Table 2. Phase Analysis by EDS in Figure 1 (at.%).

No.	Typical Positions	Fe	Al	Mn	Phase
(a)	a	28.2	71.2	0.6	Fe ₂ Al ₅
	b	24.2	75.3	0.5	FeAl ₃
	c	23.3	76.4	0.3	FeAl ₃
(b)	a	28.8	70.9	0.3	Fe ₂ Al ₅
	b	24.1	75.3	0.6	FeAl ₃
	c	23.4	76.1	0.5	FeAl ₃
(c)	a	28.5	71.4	0.1	Fe ₂ Al ₅
	b	24.3	75.3	0.4	FeAl ₃
	c	23.3	76.2	0.5	FeAl ₃
(d)	a	28.1	71.6	0.3	Fe ₂ Al ₅
	b	24.5	75.1	0.4	FeAl ₃
	c	23.2	76.2	0.6	FeAl ₃
(e)	a	27.9	71.9	0.2	Fe ₂ Al ₅
	b	23.8	75.9	0.3	FeAl ₃
	c	23.1	76.3	0.6	FeAl ₃
(f)	a	28.1	71.5	0.4	Fe ₂ Al ₅
	b	24.1	75.6	0.3	FeAl ₃
	c	23.1	76.5	0.4	FeAl ₃

The intermetallic layer thickness of Q345 steel hot-dipped in pure aluminum solution at 700, 750, and 800 °C for 30 s and 3 min is shown in Figure 2. Comparing Figure 1a,b, it can be found that when the hot-dip temperature was 700 °C, the external pure aluminum layer was relatively thick, while the Fe_2Al_5 phase area was relatively thin. The reason for this obvious difference was that at this temperature, the thermal diffusion was relatively slow and the fluidity of the aluminum solution was poor, resulting in a considerable part of thick pure aluminum layer still adhering to the sample when the sample was taken out after hot dipping. At the same time, it can be found that when the hot-dip temperature was 700 °C, the type and thickness of the intermetallic layer did not change significantly with the extension of hot-dip time. When the dipping time was extended from 30 s to 3 min, the thickness of the intermetallic layer increased from 17 to 20 μm .

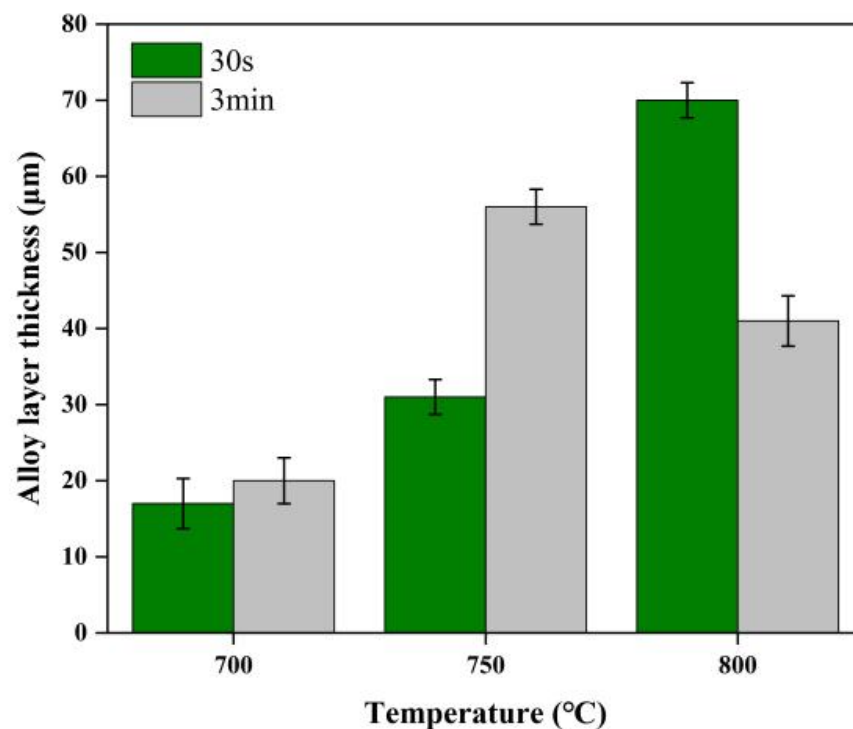


Figure 2. Thickness of intermetallic layer in the coating of Q345 steel after hot dipping at different temperature for 30 s and 3 min.

By observing Figure 1c,d, it can be found that when the hot-dip temperature was increased to 750 °C, the fluidity of aluminum solution was improved, so the external pure aluminum layer of the sample was significantly reduced compared with Figure 1a,b. At the same time, due to the increase of temperature, the diffusion of aluminum and iron was accelerated, and the intermetallic layer was obviously thickened. At 750 °C, the thickness of the intermediate alloy layer increased greatly with the extension of hot-dip time. When the dipping time was 30 s, the thickness was about 31 μm . When the dipping time was 3 min, the thickness was about 56 μm . The thickness increased by about 25 μm .

When the hot-dip temperature was raised to 800 °C, as shown in Figure 1e,f, the thickness and type of intermetallic layer changed significantly. When the dipping time was 30 s, the thickness of the intermetallic layer was about 70 μm . Compared with 750 °C, the thickness of the intermetallic layer had increased further. However, with the extension of the hot-dipping time to 3 min, the thickness of the intermetallic layer decreased. According to the results reported by Chen et al. [27], the average thickness of Fe_2Al_5 also decreased with increasing reaction time when studying the interfacial reaction between liquid aluminum and ST12 cold-roll steel sheets, though the growth of Fe_2Al_5 almost followed the parabolic law at 700, 800 and 900 °C. They had attributed the decrease in thickness into the austenitizing of the substrate (austenitizing temperature of ST12 was 935 °C). The

crystal structure of steel transformed from the body-centered cubic phase (α -Fe) into the face-centered cubic phase (γ -Fe) when the temperature of steel exceeded the austenitizing temperature. The diffusion coefficient of Al atoms in the γ -Fe phase was significantly lower than that in the α -Fe phase [28], which means that the migration of the $\text{Fe}_2\text{Al}_5/\gamma$ -Fe interface was suppressed relative to that of the $\text{Fe}_2\text{Al}_5/\alpha$ -Fe interface. Thus, the growth of Fe_2Al_5 was hindered. Yousaf et al. had also found that the intermetallic layer decreased radically or even ceased when the relative amount of α -Fe decreased substantially or when the single γ -Fe phase came in contact with the growing front of the intermetallic layer, in the temperature range 775–950 °C [29]. In the present study, as the critical temperatures for Q345 steel undergoing phase transition were $A_{c1} = 756$ °C and $A_{c3} = 900$ °C [30], the Q345 substrate was undergoing austenitizing while hot-dipping at 800 °C; thus, the migration of the $\text{Fe}_2\text{Al}_5/\gamma$ -Fe interface was suppressed. With the extension of hot-dipping time, Al atoms reacted with the Fe_2Al_5 phase to form the FeAl_3 phase, which consumed the Fe_2Al_5 phase, leading to further thinning of Fe_2Al_5 phase layer.

3.2. Effect of Si Addition in Molten Bath on Microstructure of Coating

Since Q345 steel had a moderate, flat, and uniform diffusion layer after hot dipping in pure aluminum at 750 °C for 30 s, so the temperature of hot dipping aluminum-silicon was also set to be 750 °C and the dipping time was 30 s. Figure 3 shows the cross-sectional microstructure of Q345 steel hot-dipped in different Al-Si molten pools. Phase analysis by EDS in Figure 3 is listed in Table 3. Similarly, the typical positions (a, b, c . . .) used to determine the composition of each phase were also added. It should be noted that the compositions of two ternary phases ($\text{Al}_2\text{Fe}_3\text{Si}_3$ and $\text{Al}_4\text{Fe}_{1.7}\text{Si}$) in Figure 3 are not listed in Table 3. This is mainly because their size was too small to be analyzed by EDS. These two phases were inferred by combining the phase diagram and literature, which will be discussed in detail later. Figure 4 shows the relationship between the thickness of the intermetallic layer and the silicon content. When the Si content was 0.5 at.%, the thickness of the alloy layer was about 19 μm . When the Si content was increased to 10 at.%, the thickness of the alloy layer was reduced to about 7 μm . It is also found that when the Si content was 0.5 at.%, the interface between the alloy layer and the matrix was still in a classic tongue shape, but when the Si content was increased to 2.5 at.% or above, the interface between the alloy layer and the matrix gradually changed from tongue-like to flat. These observations indicated that the Si addition in pure Al reduced the growth rate of the intermetallic layer and changed its morphology.

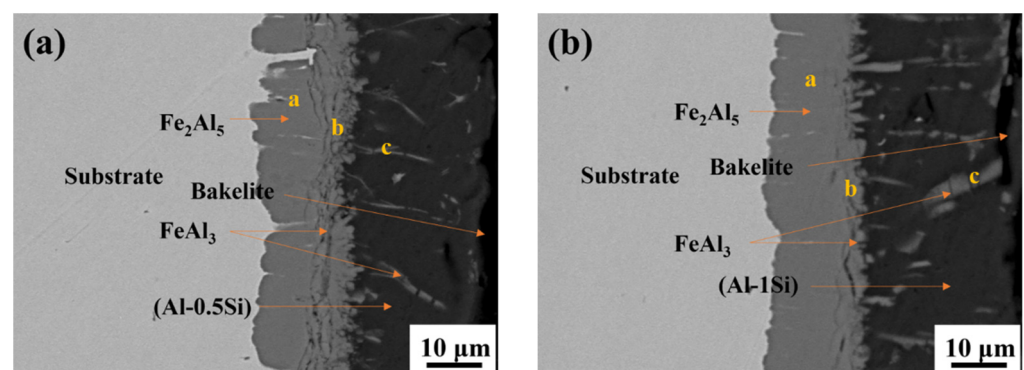


Figure 3. Cont.

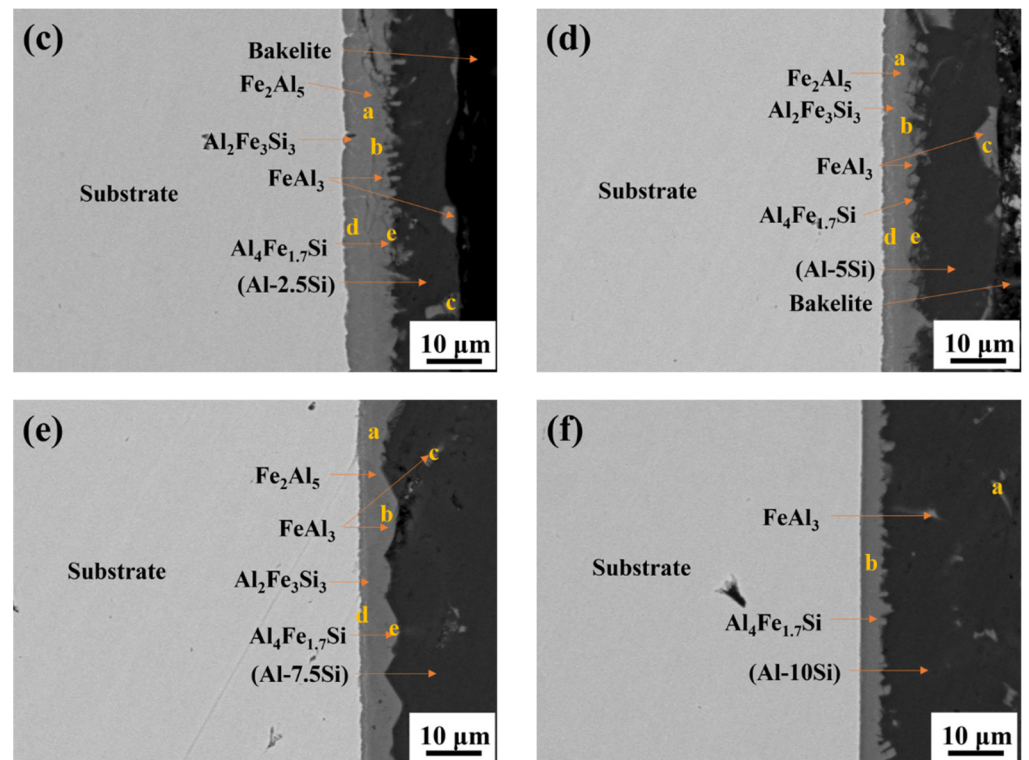


Figure 3. Cross-sectional micrographs of coatings of Q345 steel hot-dipped in baths with different Si addition at 750 °C for 30 s. (a) 0.5Si, (b) 1Si, (c) 2.5Si, (d) 5Si, (e) 7.5Si, and (f) 10Si.

Table 3. Phase analysis by EDS in Figure 3 (at.%).

No.	Typical Positions	Fe	Al	Si	Phase
(a)	a	28.1	70.5	1.4	Fe_2Al_5
	b	24.5	74.3	1.2	FeAl_3
	c	23.6	74.9	1.5	FeAl_3
(b)	a	27.3	70.6	2.1	Fe_2Al_5
	b	23.3	74.9	1.8	FeAl_3
	c	22.9	75.2	1.9	FeAl_3
(c)	a	26.5	70.4	3.1	Fe_2Al_5
	b	23.3	74.3	2.4	FeAl_3
	c	22.3	75.2	2.5	FeAl_3
(d)	a	27.7	69.1	3.2	Fe_2Al_5
	b	23.4	73.5	3.1	FeAl_3
	c	23.4	74.1	3.5	FeAl_3
(e)	a	27.6	68.2	4.2	Fe_2Al_5
	b	24.2	69.7	6.1	FeAl_3
	c	23.0	70.4	6.6	FeAl_3
(f)	a	24.1	68.6	7.3	FeAl_3

The intermetallic layer of hot-dip pure aluminum at 750 °C consisted mainly of the Fe_2Al_5 phase, while the intermetallic layer of hot-dipped Al-0.5Si consisted of the outer FeAl_3 phase layer and the inner Fe_2Al_5 phase layer. According to the Al-Si binary-phase diagram [31], the addition of Si elements can lower the melting point of the Al-Si alloy and makes the microstructure formation temperature of Al-0.5Si hot-dip coating lower than that of pure aluminum hot-dip coating. At the same time, the lower temperature during the hot dip of the Al-Si alloy slowed down the interdiffusion between the steel

substrate and the bath, resulting in a thinner alloy-layer thickness. In addition, when the Si content was added to 2.5 at.%, white granular intermetallic compounds appeared in the inner layer of the coating. The size of the white granular phase was so small that it was difficult to analyze its exact composition by EDS. According to the Al-Fe-Si ternary-phase diagram [32], at 700–800 °C, $\text{Al}_2\text{Fe}_3\text{Si}_3$ is in equilibrium with Fe_2Al_5 and FeAl_3 phases; therefore, these white intermetallic-compound phases were probably the $\text{Al}_2\text{Fe}_3\text{Si}_3$ phase. Meanwhile, a new phase layer appeared in the outer layer of coating, and this new phase was distributed between the (Al) phase and the FeAl_3 phase. By a similar analysis of the Al-Fe-Si ternary-phase diagram, it can be estimated that this intermetallic-compound phase was the $\text{Al}_4\text{Fe}_{1.7}\text{Si}$ phase. It can be seen that when the Si content was added above 2.5 at.%, the coating consisted of the $\text{Al}_4\text{Fe}_{1.7}\text{Si}$ phase, the FeAl_3 phase, the Fe_2Al_5 phase, and the $\text{Al}_2\text{Fe}_3\text{Si}_3$ phase. When the Si content was increased to 10 at.%, the coating consisted mainly of the FeAl_3 phase and the $\text{Al}_4\text{Fe}_{1.7}\text{Si}$ phase. Based on the above analysis, a plausible reason for reducing the growth rate of the intermetallic layer can be attributed to the formation of new phases due to the Si addition in molten aluminum. Meanwhile, a small amount of Si was dissolved into the Fe_2Al_5 phase, as listed in Table 3, so the reduction of the Fe_2Al_5 layer might also be due to the fact that silicon occupies vacant sites in the c-axis of the Fe_2Al_5 crystal structure, thus hindering the diffusion of Al to the interface Fe_2Al_5 /substrate.

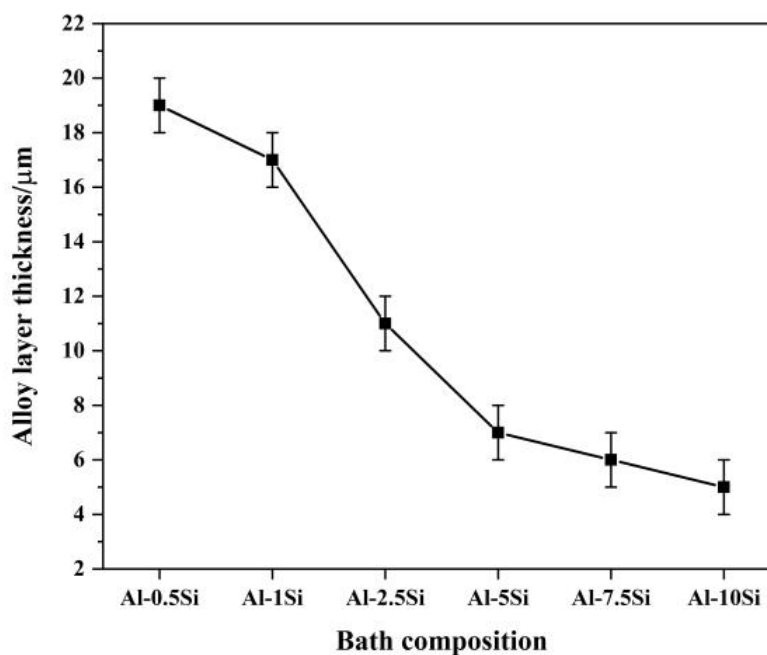


Figure 4. Relationship between intermetallic thickness of Q345 steel after hot-dip aluminum with different silicon content.

3.3. Effect of Annealing Temperature and Time on the Phase Evolution of the Coating

Since the thickness of the diffusion layer of Q345 steel was moderate, flat, and uniform after hot dipping in Al-2.5Si solution at 750 °C for 30 s, this group of samples was selected for the subsequent diffusion-annealing treatment to study the effects of annealing temperature and annealing time on the evolution of microstructure in the coating. Figure 5 shows the cross-sectional microstructures of hot-dipped samples annealed at 800 °C and 900 °C for 1, 2, and 3 h, respectively. Phase analysis by EDS in Figure 5 is listed in Table 4. The typical positions used to determine the composition of each phase were also added in Figure 5. As the composition contrast between the α -Fe phase layer and the Fe-Al phases shown in BSE was not obvious in Figure 5, EDS line profiles were supplemented to distinguish these phase boundaries. In addition, compositions of each phase were determined by point analysis of EDS, and the typical positions marked as a, b, c, and d were also added in the figure.

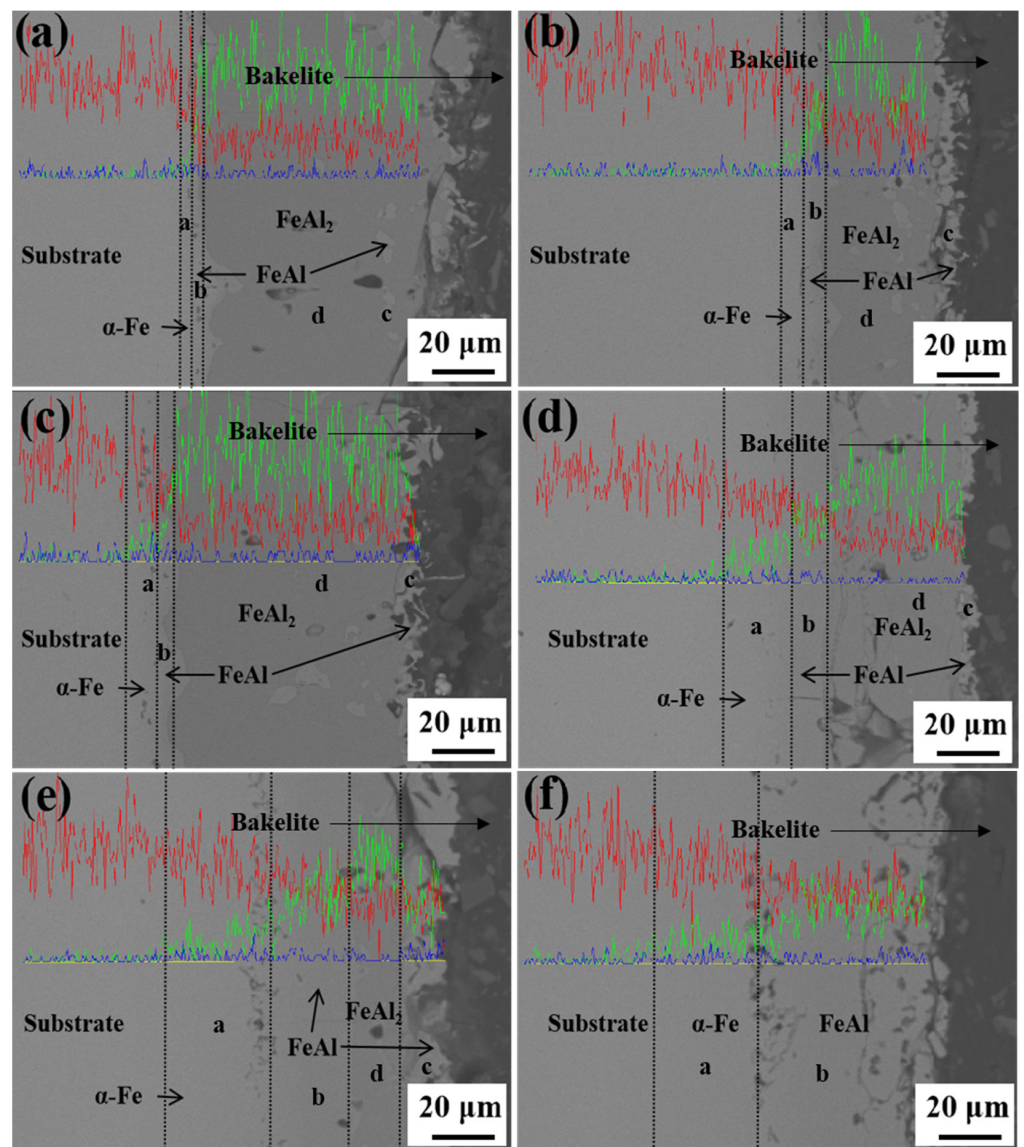


Figure 5. Cross-sectional microstructure of Q345 after hot dipping in Al-2.5Si solution and annealed at 800 °C or 900 °C for different times, and its corresponding EDS line profiles of elements Fe (red line), Al (green line), and Si (blue line) distributions across the coating layer on the steel substrate. (a) at 800 °C for 1 h, (b) at 800 °C for 22 h, (c) at 800 °C for 3 h, (d) at 900 °C for 1 h, (e) at 900 °C for 2 h, (f) at 900 °C for 3 h.

Figure 5a shows the cross-sectional microstructure of Q345 steel after being hot-dipped in Al-2.5Si solution and annealed at 800 °C for 1 h. According to the EDS results and the analysis of the Fe-Al binary-phase diagram, it is found that the gray phase in the outermost layer of the coating was the FeAl₂ phase. There was a small amount of light-gray circle areas, which were composed of the FeAl₂ phase according to the EDS analysis. This was due to the inward diffusion of Al elements and the outward diffusion of Fe elements from the matrix during annealing at 800 °C, resulting in the transformation of the Fe₂Al₅ phase in the original coating into the FeAl₂ phase. Moreover, the Fe₂Al₅ phase had a rhombohedral crystal structure with an atomic saturation concentration of only 70% [15], which allowed the inner Fe atoms to diffuse through the phase and further accelerates transformation of the external Fe₂Al₅ phase. Between the inner FeAl₂ phase layer and the substrate in Figure 5a, there were another two layers, though the color contrast was not

obvious. According to the EDS analysis, these two layers consisted of the FeAl phase and the α -Fe phase, respectively.

Figure 5b shows the cross-sectional microstructure of Q345 steel after being hot-dipped in Al-2.5Si solution and annealed at 800 °C for 2 h. The outermost light-gray region and the middle gray-circle region were composed of the FeAl phase. Compared with Figure 5a, it can be found that the thickness of the FeAl phase presented between the α -Fe phase and the FeAl₂ phase increased and the outermost region gradually changed from the FeAl₂ phase to the FeAl phase. This indicates that the rate of diffusion of Fe atoms into the outer FeAl₂ phase layer increased with time. In Figure 5c, the thickness of the FeAl phase layer between the α -Fe phase and the FeAl₂ phase further increased.

Figure 5d shows the cross-sectional microstructure of Q345 steel after being hot-dipped in Al-2.5Si solution and annealed at 900 °C for 1 h. According to the EDS analysis and its corresponding line profiles of elements Fe, Al, and Si distributions across the coating layer on the steel substrate, the outermost layer was the FeAl₂ phase, inwardly followed by the FeAl phase, the α -Fe phase, and the matrix. In Figure 5e, the outermost layer was the FeAl phase, inwardly followed by the FeAl₂ phase, the FeAl phase, the α -Fe phase, and the matrix. In Figure 5f, the FeAl₂ phase disappeared and all of them were transformed into the FeAl phase. By analyzing the experimental results in Figure 5, it is known that in order to transform the brittle Fe₂Al₅ phase in the coating into the FeAl phase with better toughness, it is better to anneal the coating at 900 °C for 3 h.

Table 4. Phase Analysis by EDS in Figure 5 (at.%).

No.	Typical Positions	Fe	Al	Si	Phase
(a)	a	74.6	22.3	3.1	α -Fe
	b	45.2	41.9	12.9	FeAl
	c	52.1	36.7	11.2	FeAl
	d	31.7	67.2	1.1	FeAl ₂
(b)	a	78.2	19.1	2.7	α -Fe
	b	46.6	45.5	7.9	FeAl
	c	46.4	47.5	6.1	FeAl
	d	30.2	67.5	2.3	FeAl ₂
(c)	a	75.2	22.1	2.7	α -Fe
	b	48.5	44.1	7.4	FeAl
	c	44.8	7.1	48.1	FeAl
	d	31.1	67.2	1.7	FeAl ₂
(d)	a	78.8	18.7	2.5	α -Fe
	b	56.9	40.4	2.7	FeAl
	c	62.3	35.6	2.1	FeAl
	d	33.8	65.5	0.7	FeAl ₂
(e)	a	78.8	18.8	2.4	α -Fe
	b	50.4	46.5	3.1	FeAl
	c	49.4	44.9	5.7	FeAl
	d	34.1	64.8	1.1	FeAl ₂
(f)	a	78.3	21.3	0.4	α -Fe
	b	52.5	46.4	1.1	FeAl

3.4. Effect of Oxidation Process on the Formation of Al₂O₃ Film

Figure 6 shows the surface morphology and cross-sectional microstructure of these three groups of samples after oxidation and the corresponding EDS line profiles of elements Fe (red line), Al (green line), O (blue line), and Si (purple line) distributions across the coating layer on the steel substrate. Compositions of each phase are listed in Table 5. In Figure 5a–c were typical positions used to determine the composition of each phase.

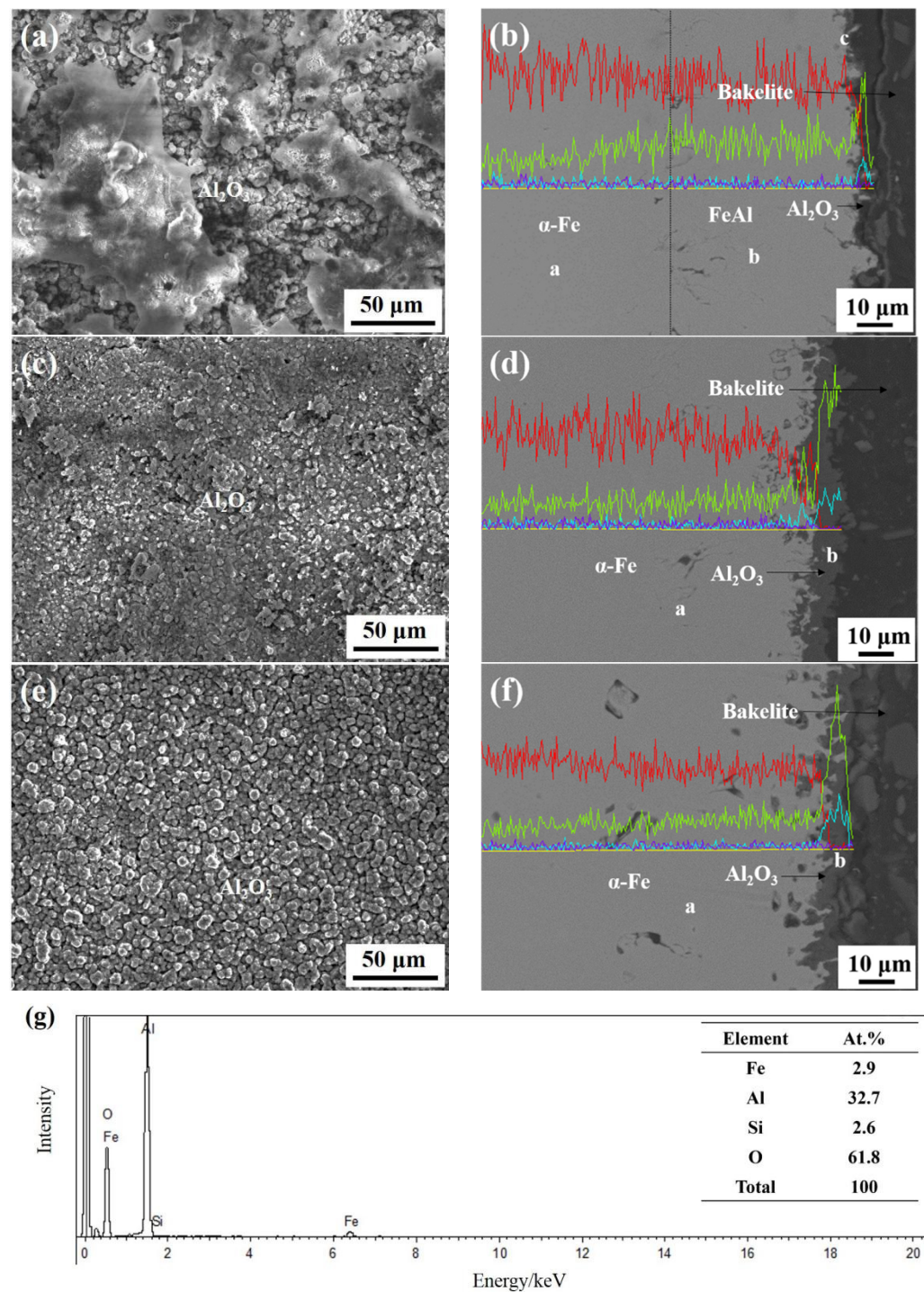


Figure 6. Surface morphology and cross-sectional microstructure of Q345 steel and its corresponding EDS line profiles of elements Fe (red line), Al (green line), O (blue line), and Si (purple line) distributions across the coating layer on the steel substrate after oxidation at 900 °C for 15 h with different preoxidation heat treatment. (a,b) Oxidation directly after hot dip in Al-2.5Si; (c,d) oxidation after hot dip in Al-2.5Si and annealing at 800 °C for 1 h; (e,f) oxidation after hot dip in Al-2.5Si and annealing at 900 °C for 3 h; and (g) the typical EDS pattern of the Al₂O₃ phase.

Table 5. Phase Analysis by EDS in Figure 6 (at.%).

No.	Typical Positions	Fe	Al	Si	O	Phase
(b)	a	76.6	22.2	1.2	-	α -Fe
	b	63.9	35.3	0.8	-	FeAl
	c	2.9	32.7	2.6	61.8	Al_2O_3
(d)	a	78.2	19.1	2.7	-	α -Fe
	b	2.6	29.2	2.8	65.4	Al_2O_3
(f)	a	72.9	24.9	2.2	-	α -Fe
	b	2.4	29.8	2.6	65.2	Al_2O_3

Figure 6a,b show the surface morphology and cross-sectional microstructure of the D1 sample after oxidation at 900 °C for 15 h in air. The phase near the matrix in the cross section contained about 76 at.% Fe, 22 at.% Al, and 1 at.% Si, which was determined to be the α -Fe phase, and the phase near the outer part in the cross section contained about 64 at.% Fe, 35 at.% Al and 1 at.% Si, which was determined to be the FeAl phase according to the Fe-Al-Si phase diagram [32]. According to the EDS pattern shown in Figure 6g, the dark-gray area was the Al_2O_3 film that formed in the surface, which had poor continuity and was not dense, with a thickness of about 4–6 μm .

Figure 6c,d show the surface morphology and cross-sectional microstructure of the D2 sample after oxidation at 900 °C in air for 15 h. From the figures, it can be found that the Al_2O_3 film on the surface of this group of samples was denser after oxidation. In the surface morphology shown in Figure 6c, Al_2O_3 was covered with particles in the outermost layer, and in the cross-sectional microstructure shown in Figure 6d, the light-gray phase contained about 74 at.% Fe, 25 at.% Al and 1 at.% Si, so this phase was the α -Fe phase. The dark-gray area was the Al_2O_3 film formed in the surface, which had good continuity and denseness and was about 6–8 μm thick.

Figure 6e,f show the surface morphology and cross-sectional organization of the D3 sample after oxidation at 900 °C for 15 h in air. It can be found that Al_2O_3 was covered in the outermost layer in the form of strips, and the light-gray phase in the cross-section contained about 77 at.% Fe, 22 at.% Al, and 1 at.% Si, which was the α -Fe phase, and the dark gray area was the Al_2O_3 film formed in the surface layer, which had better continuity and denseness than the other two groups, with a thickness of about 5~7 μm .

3.5. High-Temperature Oxidation Resistance of Al_2O_3 Film

In order to test the high-temperature oxidation resistance of the oxidized samples, Q345 steel and oxidized D1, D2, and D3 samples were placed in corundum crucibles and oxidized at 900 °C in a chamber furnace. The weight increased was recorded at regular intervals, and each sample was oxidized for a total of 63 h. Figure 7 reveals the variation of the weight gain with time. It can be seen from the Figure 7 that the oxidation weight gain of the original Q345 steel was the most obvious as the high-temperature oxidation continued, while slopes of the oxidation weight-gain curves of D1, D2, and D3 samples were relatively small, indicating that the Al_2O_3 film on the surface of the samples could play a good role in inhibiting further high-temperature oxidation and protecting the Q345 steel substrate. Among the three oxidized samples, sample D3, i.e., the sample with Al_2O_3 film prepared after annealing at 900 °C for 3 h, showed the smallest weight gain in the subsequent high-temperature oxidation. This indicates that the Al_2O_3 film formed from the FeAl phase in the outermost layer of the coating has the best resistance to high-temperature oxidation.

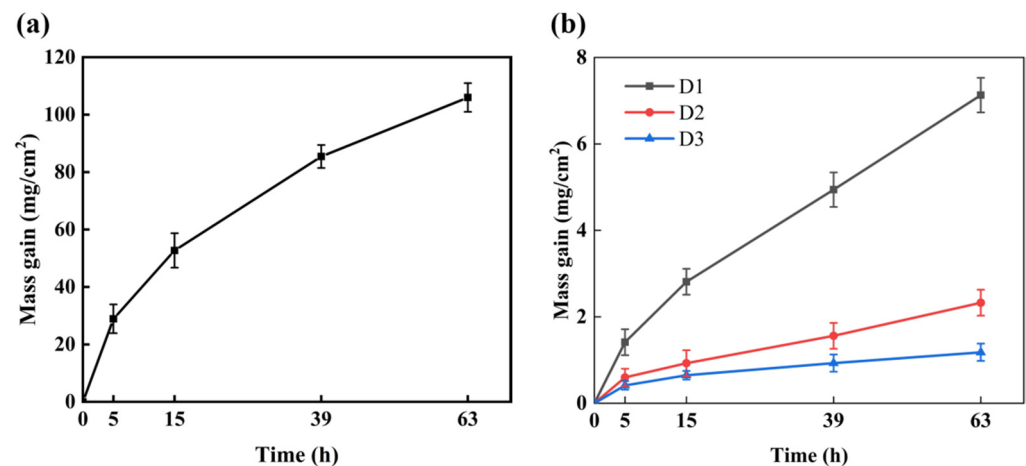


Figure 7. Relationship of weight gain of Q345 steel with oxidation time: (a) pure Q345 steel; (b) D1, D2, and D3 samples prepared by hot dipping and annealing.

4. Conclusions

The addition of silicon in aluminum baths changes the microstructure and phase constitution of the coating. The main findings of the study are as follows:

- (1) When Q345 steel was hot-dipped in pure aluminum, the intermediate phase layer was mainly composed of the Fe_2Al_5 phase. When the hot-dipping temperature was 750°C and hot-dipping time was 30 s, the interface between the intermetallic phase layer and the substrate was relatively flat.
- (2) As the silicon content in the aluminum bath increased, the thickness of the intermetallic layer decreased, and the intermetallic layer/steel-substrate interface transformed from an irregular morphology into a flat morphology.
- (3) The annealing time affected the transformation of the intermediate phase in the coating. In addition, the longer the time, the more favorable the transformation of the brittle Fe_2Al_5 phase into the FeAl phase with good toughness. When the aluminized sample was annealed at 900°C for 3 h, the intermediate phase in the diffusion layer was completely transformed into the FeAl phase.

In conclusion, the addition of Si into the aluminum bath made the thickness of the aluminizing layer decrease, and the outermost aluminized layer could be transformed into FeAl phase by annealing. This was found to be beneficial to improve the oxidation resistance of Q345 steel. Although annealing at 900°C was beneficial to promote the transformation from the Fe_2Al_5 phase to the FeAl phase, the effect of high-temperature annealing on the mechanical properties of the steel matrix should be further studied.

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