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Effect of Si on growth kinetics of intermetallic compounds during reaction between solid iron and molten aluminum

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Abstract: The effect of Si on the growth kinetics of intermetallic compounds during the reaction of solid iron and molten aluminum was investigated with a scanning electron microscope coupled with an energy dispersive X-ray spectroscope, and hot-dip aluminized experiments. The results show that the intermetallic layer is composed of major Fe₂Al₅ and minor FeAl₃. The Al–Fe–Si ternary phase, τ_1/τ_9 , is formed in the Fe₂Al₅ layer. The tongue-like morphology of the Fe₂Al₅ layer becomes less distinct and disappears finally as the content of Si in aluminum bath increases. Si in the bath improves the prohibiting ability to the growth of Fe₂Al₅ and FeAl₃. When the contents of Si are 0, 0.5%, 1.0%, 1.5%, 2.0% and 3.0%, the activation energies of Fe₂Al₅ are evaluated to be 207, 186, 169, 168, 167 and 172 kJ/mol, respectively. The reduction of the activation energy might result from the lattice distortion caused by Si atom penetrating into the Fe₂Al₅ phase. When Si atom occupies the vacancy site, it blocks easy diffusion path and results in the disappearance of tongue-like morphology.

Key words: intermetallic compound; Fe-Al system; growth kinetics; activation energy; Si; hot-dip aluminizing; diffusion reaction

1 Introduction

Hot-dip aluminized and hot-dip Zn-Al alloy (Galvalume) coatings are two important methods used to improve the corrosion-resistance of steel sheet. The intermetallic layer between the iron panel and the overlay determines the quality of the coating. Fe₂Al₅ is the major phase in the aluminized and Galvalume coatings. GUO and WU [1] investigated the mechanical properties of aluminum-coated low carbon steels, the results showed that the hardness of intermetallic layer in aluminized coating is up to HV891. According to the report in Ref. [2], Fe₂Al₅ could lead coating toughness to decrease, it is easy to rupture and result in flaking of the coating. It is common to add Si into the aluminum or Zn-Al bath in order to prevent the excessive growth of alloy layer at the coating-steel interface. The reaction between the aluminum melt and the steel substrate is extremely rapid and strongly exothermic [3,4]. The reaction zone repeatedly flakes off. SELVERIAN et al [5] found that Si in the Al-Zn bath suppressed the rapid exothermic reaction between Al-Zn melt and iron panel

by forming a solid reaction layer. The solid reaction layer acts as a diffusion barrier for the reactive species, probably aluminum, and reduces the reaction rate between the bath and the iron panel by several orders of magnitude.

The purpose of this work is to study the influence of Si on the growth kinetics of intermetallic compounds during reactive diffusion between solid iron and molten aluminum. DYBKOV [6] studied the interaction of stainless steel with molten aluminum by the rotating disc method. The time dependence of the total thickness of intermetallic compound layers was described in terms of paralinear kinetics. The microstructure of aluminized coating on steel was investigated by many researchers [7-9]. They proposed that the phases were FeAl₃ near aluminum and Fe₂Al₅ near the iron panel. For Fe₂Al₅ phase, the parabolic kinetics of growth was found by DENNER and JONES [10], BOUCHE et al [11] and BOUAYAD et al [12]. YEREMENKO et al [13] and EGGELER et al [14] observed negative deviations from the parabolic law after a long time reaction. The latter confirmed that this deviation was due to the iron enrichment in the aluminum melt by dissolution.

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HEUMANN and DITTRICH [15] identified the Fe_2Al_5 phase as the major constituent of the coating and found that the growth obeyed parabolic law. QIAN and GU [16] studied the microstructure and composition of the intermetallic layer obtained by hot-dip aluminized 08F steel in molten aluminum containing 2% Si (mole fraction). The results showed that Si enriched in the interfacial layer. The comprehensive literature review about reaction diffusion between solid iron and molten aluminum is detailed in Ref. [12]. But there is no report about the effect of Si on the growth kinetics of Fe_2Al_5 .

2 Experimental

One pure aluminum and four Al–Si alloy baths were prepared, with 250 g in total for each bath. The purities of Al and Si were 99.99%. The contents of Si in Al–Si alloy baths were 0.5%, 1.0%, 1.5%, 2.0%, 3.0%, respectively. To obtain accurate compositions, Al–30%Si master alloys were used to adjust the Si content in the bath. The pure aluminum and Al–Si alloy were melted in an alumina crucible at 700–850 °C. The temperature of the molten was measured by a thermocouple in an alumina sheath immersed in the bath. The Al–Si alloy baths should be agitated and annealed for 1 h to ensure homogeneity of the Si distribution in the liquid Al.

Rectangular pure iron specimens with a purity of 99.99% were cut to the dimensions of 10 mm× 10 mm×1.5 mm and polished with 1.5 μ m-thick diamond paste. The specimens were degreased in 100–200 g/L NaOH at 80 °C for 15 s, then rinsed with water, and followed by pickling in 100–200 g/L HCl for 15 s. The specimens were rinsed again with the flowing water, then dipped in a flux bath consisting of 100 g K₂ZrF₆+100 g KCl+1 g NaF, and kept at 80 °C for 2 min. The fluxed sheets were dried and preheated at 110 °C for 2 min in a drying box. Next the sheets were hot-dip aluminized in the entire temperature range of 700–850 °C in steps of 50 °C for 30, 60, 180, 300, and 600 s, respectively. Then the sample was withdrawn and quenched into water immediately.

A JSM-6360LV scanning electron microscope (SEM) equipped with an OXFORD INCA energy dispersive X-ray spectroscope (EDS) was utilized to study the morphology and chemical compositions of various phases in coatings.

3 Results and discussion

3.1 Phase layer characterization

Figure 1(a) shows the microstructure of the cross section of the coating obtained by immersing pure iron into pure molten aluminum at 800 °C for 60 s. The intermetallic layers can be clearly identified as Fe_2Al_5

(layer adjacent to iron) and FeAl₃ (layer adjacent to aluminum) by the EDS analysis. The interface of the Fe_2Al_5 phase shows highly irregular tongue-like morphology. The boundary between FeAl₃ and the liquid phase is also irregularity orientating towards the aluminum shown in Fig. 1(b). Figure 2 shows the



Fig. 1 Microstructures of intermetallic layer obtained in pure aluminum bath at different conditions: (a) 800 °C, 60 s; (b) 800 °C, 600 s



Fig. 2 Microstructures of intermetallic layer obtained in different baths (800 °C, 60 s): (a) Al–0.5Si%; (b) Al–1Si%

microstructures of cross sections of the coating obtained by immersing pure iron in a molten aluminum with different Si contents at 800 °C for 60 s. It can be seen that the addition of Si makes the tongue-like morphology of the Fe₂Al₅ phase less distinct and disappear finally, and the thickness of Fe₂Al₅ layer decreases with increasing content of Si in molten aluminum. With the addition of Si, there are fine white particles distributing in the Fe₂Al₅ phase layer shown in Fig. 2. The results of EDS show that they are Al–Fe–Si ternary phase τ_1/τ_9 . The content of Si in the Fe₂Al₅ increases tardily with adding Si into the aluminum bath, as shown in Fig. 3.



Fig. 3 Relationship between Si content in $\mathrm{Fe_2Al_5}$ and that in bath at 800 °C

3.2 Growth kinetics of intermetallic layers

Owing to the irregularity of the interface between the intermetallic layer and the iron substrate, the mean thickness of the intermetallic layer has been used to understand and calculate the kinetic parameters of the coating. The detail of the mean thickness method was described in Ref. [12]. The mean thickness of the Fe₂Al₅ layer is plotted against square root of immersing time in Fig. 4 and a linear regression fitting is performed. It can be seen that the growth kinetics of the Fe₂Al₅ layer conforms well to a parabolic rate law expect the initial stage. This is because there is an interface control reaction at the beginning of the process [8].

The following equation can be used to fit the growth kinetic data of the Fe_2Al_5 phase:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_1}{x} \tag{1}$$

where k_1 is the parabolic coefficient in m²/s. Eq. (1) can be conveniently written in the form of Eq. (2). In other words, the thickness x is directly proportional to square root of time t.

$$x^2 = 2k_1 t \tag{2}$$

The parabolic coefficient k_1 values at different temperatures are evaluated by fitting thickness data in Eq. (2). The values of k_1 for Fe₂Al₅ at temperatures of 700–800 °C are given in Table 1.

The temperature dependence of k_1 is expressed by

$$k_1 = k_0 \exp\left(\frac{-Q}{RT}\right) \tag{3}$$

where k_0 is the pre-exponential factor, Q is the activation energy, R is the gas constant and T is the thermodynamic temperature.



Fig. 4 Relationship between mean thickness of Fe_2Al_5 and time with different Si contents at different temperatures: (a) 700 °C; (b) 750 °C; (c) 800 °C

| Temperature/°C | $k_{1}/(\mathrm{m}^{2}\cdot\mathrm{s}^{-1})$ | | | | | | | |
|----------------|--|------------------------|------------------------|------------------------|------------------------|------------------------|--|--|
| | Pure Al | 0.5% Si | 1.0% Si | 1.5% Si | 2.0% Si | 3.0% Si | | |
| 700 | 3.98×10^{-12} | 2.78×10^{-12} | 1.36×10^{-12} | 1.19×10^{-12} | 0.78×10^{-12} | 0.32×10^{-12} | | |
| 750 | 1.56×10^{-11} | 1.27×10^{-11} | 6.44×10^{-12} | 5.92×10^{-12} | 2.67×10^{-12} | 1.36×10^{-12} | | |
| 800 | 4.31×10^{-11} | 2.35×10^{-11} | 9.33×10^{-12} | 8.08×10^{-12} | 5.28×10^{-12} | 2.69×10^{-12} | | |

Table 1 Variation of parabolic rate constant k_1 with content of Si

From Eq. (2) and (3), we can get

$$2\ln(\frac{x}{\sqrt{t}}) = \frac{-Q}{RT} + \ln(\sqrt{2k_0}) \tag{4}$$

From Eq. (4), it is easy to obtain the pre-exponential factor k_0 and activation energy Q using the growth kinetic data.

Figure 5 shows the relationship between the logarithm of $x/t^{1/2}$ and the reciprocal of the temperature *T*.



Fig. 5 Relationship between $\ln(x/t^{1/2})$ and reciprocal of temperature for Fe₂Al₅ layer

The results show that the addition of small amount of Si in aluminum bath can reduce the activation energy of Fe₂Al₅. When Si content exceeds 1%, the activation energies keep almost constant. The values of the pre-exponential factor and activation energy are listed in Table 2. From Table 2 it can be seen that the pre-exponential factor decreases sharply with the increase of the Si content in aluminum bath. The effect of Si in the bath on the activation energy of Fe₂Al₅ is shown in Fig. 6.

Table 2 Effect of Si content on activation energy andpre-exponential factor for growth of Fe_2Al_5 phase

| w(Si)/% | $Q/(kJ \cdot mol^{-1})$ | $k_0/(m^2 \cdot s^{-1})$ | | | | | |
|---------|-------------------------|--------------------------|--|--|--|--|--|
| 0 | 207 | 0.55 | | | | | |
| 0.5 | 186 | 3.21×10^{-2} | | | | | |
| 1.0 | 169 | 1.84×10^{-3} | | | | | |
| 1.5 | 168 | 1.56×10^{-3} | | | | | |
| 2.0 | 167 | 0.73×10^{-3} | | | | | |
| 3.0 | 172 | 0.69×10^{-3} | | | | | |



Fig. 6 Relationship between Si content in bath and activation energy of Fe_2Al_5

Many researchers have evaluated the activation energy of Fe₂Al₅ by pure aluminum immersion test. The activation energies obtained by different authors are listed in Table 3. There are larger differences between the values available in the literatures. BOUAYAD et al [12] and HEUMANN and DITTRICH [15] reported activation energy in the range of 74-76 kJ/mol. EGGELER et al [14] and DENNER and JONES [10] found that these values were in the range of 134-155 kJ/mol. NAOI and KAJIHRARA [17] reported that activation energy was 281 kJ/mol. SHIBATA et al [18] and our work found that these values were in the range of 207-226 kJ/mol. BOUAYAD et al [12] proposed that the discrepancies observed can be explained by different experimental conditions and different methods used to determine parabolic coefficient k_1 . DENNER and JONES [10] affirmed that the activation energy increased with increasing carbon in the iron content up to 0.17%. In the present work and NAOI and KAJIHRARA's research [17], the activation energy is larger than 200 kJ/mol but that obtained by BOUAYAD et al [12] is 74.1 kJ/mol. The iron used in these experiments is almost free from carbon. So large difference between values of activation energy cannot only be caused by the purity of the metals used. BOUAYAD et al [12] found that under condition of long interaction time and high temperatures, the sapling of the intermetallic layer affected the measurement of layer thickness. The same phenomenon was found in the present work.

For the FeAl₃ layer, the growth kinetics obeys linear law after the transient stage shown in Fig. 7. It indicates

Table 3 Activation energy (Q) of Fe₂Al₅ phase without Si obtained from references

| $Q/(kJ \cdot mol^{-1})$ | 155 | 134 | 76.1 | 74.1 | 226 | 281 | 207 |
|-------------------------|-----|------|------|------|------|-------|------|
| D | [7] | [11] | [10] | [0] | [16] | F1 43 | This |
| Reference | [/] | [11] | [12] | [9] | [15] | [14] | work |



Fig. 7 Relationship between mean thickness of FeAl₃ phase and time at 800 °C

clearly the existence of an initial transient chemical reaction control period before the linear growth. Because of the irregular interface and thinner thickness of the FeAl₃ layer, it is very difficult to measure the thickness accurately, especially at a lower temperature. The diffusion activation energy for FeAl₃ is not elevated in the present work. However, experimental results show clearly that the addition of Si can reduce the growth rate of FeAl₃.

3.3 Influence of Si on growth rate of Fe₂Al₅ phase

HEUMANN and DITTRICH [15] reported that there were 30% of the vacancies along the c-axis of the Fe_2Al_5 phase with the orthorhombic structure. The crystalline defect of Fe₂Al₅ offered a rapid diffusion path along [001] direction. CHENG and WANG [3] found that the Fe_2Al_5 phase grew preferentially along the [001] direction, the *c*-axis, of the crystal structure, resulting in a non-uniform growth of Fe₂Al₅ layer and the formation of the tongue-like morphology. The Si presented in the Fe₂Al₅ phase blocked the easy diffusion path along the *c*-axis. This made the tongue-like morphology of the Fe₂Al₅ phase disappear and change to the coagulum. The growth rate and morphology of Fe₂Al₅ were controlled by the amount of Si available in the aluminum bath. It was clear that the thickness of Fe₂Al₅ layer became thinner as the content of Si in aluminum bath increased.

When Si atom penetrates into the vacancy in the Fe_2Al_5 phase, it will strain the lattice thereby making atom jump easier as the amount of strain increases, and result in the reduction of activation energy. As discussed above, the growth rate of the Fe_2Al_5 layer is reduced by the addition of Si. This means that Si in the vacancy

reduces the interdiffusion coefficient of Fe and Al in the Fe_2Al_5 phase. From the view point of atom jump, the temperature dependence of diffusion coefficient is given by

$$D_{\text{Al,Fe}}^{\text{Fe}_2\text{Al}_5} = D_0 \exp(\frac{-Q}{RT}) = \alpha a^2 v X_v \exp(\frac{\Delta S}{R}) \exp(\frac{-Q}{RT}) \quad (5)$$

where $D_{Al,Fe}^{Fe_2Al_5}$ is the interdiffusion coefficient of Fe and Al in the Fe₂Al₅ phase; D_0 is a frequency factor; α is geometry factor; a is jump length; v is vibrating frequency; X_v is vacancy concentration; ΔS is activation entropy. When Si atom occupies the vacancy of the Fe₂Al₅ phase, it will reduce the activation energy and increase activation entropy. As can be seen from Eq. (5), the main reason for the reduction of $D_{Al,Fe}^{Fe_2Al_5}$ is the reduction of the vacancy concentration.

4 Conclusions

1) Two intermetallic layers are observed in the coating obtained by interaction between solid iron and pure liquid aluminum. The major phase is Fe₂Al₅ and the other is FeAl₃. When liquid aluminum contains Si, the τ_1/τ_9 phase forms in the Fe₂Al₅ layer.

2) The growth kinetics of the intermetallic layer is determined experimentally at temperatures between 700 and 800 °C. The growth of the Fe_2Al_5 layer is controlled by diffusion reaction and obeys a parabolic law, while the $FeAl_3$ layer growth is linear and controlled by interface reaction.

3) The growth rates of the Fe_2Al_5 layer and the $FeAl_3$ layer are decreased with the increase of Si content in aluminum bath.

4) The activation energy of Fe_2Al_5 reduces with increasing Si content in bath.

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Si 对铁铝固-液扩散反应中间化合物生长动力学的影响

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摘 要:利用扫描电子显微镜-能谱仪和热浸镀铝实验研究 Si 对铁铝固-液扩散反应中间化合物生长动力学的影响。结果表明,中间层主要由 Fe₂Al₅和薄层 FeAl₃组成。当向浸镀熔体中加入硅后,在镀层的 Fe₂Al₅相中出现颗粒状的 Al-Fe-Si 三元相(τ₁/τ₉)。舌状形貌的 Fe₂Al₅层随着合金浴中 Si 含量的增加而逐步平整。合金浴中的 Si 显著抑制 Fe₂Al₅和 FeAl₃的生长。当 Si 含量为 0、0.5%、1.0%、1.5%、2.0%和 3.0%时,Fe₂Al₅相的激活能分别为 207、186、169、168、167 和 172 kJ/mol。当 Si 原子进入 Fe₂Al₅相时会引起晶格畸变,从而导致 Fe₂Al₅的扩散激活能下降。Si 原子占据空位时能够阻止扩散通道,抑制 Fe₂Al₅相的生长,从而导致舌状形貌的消失。 关键词:金属间化合物;Fe-Al 系;生长动力学;扩散激活能;Si;热浸镀铝;扩散反应

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