Research Article

Hot-Dip Aluminizing of Low Carbon Steel Using Al-7Si-2Cu Alloy Baths

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Hot-dip aluminizing of low carbon steel was done in molten Al-7Si-2Cu bath at 690°C for dipping time ranging from 300 to 2400 seconds. Characterization of the intermetallics layer was done by using scanning electron microscope with energy dispersive spectroscopy. Four intermetallic phases, τ_5 -Al₇Fe₂Si, θ -FeAl₃, η -Fe₂Al₅, and τ_1 -Al₂Fe₃Si₃, were identified in the reaction layer. τ_5 -Al₇Fe₂Si phase was observed adjacent to aluminum-silicon topcoat, θ -FeAl₃ between τ_5 and η -Fe₂Al₅, η -Fe₂Al₅ adjacent to base material, and τ_1 -Al₂Fe₃Si₃ precipitates within Fe₂Al₅ layer. The average thickness of Fe₂Al₅ layer increased linearly with square root of dipping time, while for the rest of the layers such relationship was not observed. The tongue-like morphology of Fe₂Al₅ layer was more pronounced at higher dipping time. Overall intermetallic layer thickness was following parabolic relationship with dipping time.

1. Introduction

Hot-dip aluminizing is an effective and inexpensive coating process to protect steels from oxidation [1, 2]. The quality of coating depends on the properties of the intermetallics layer forming at the interface. A brittle intermetallic layer may peel off from surface during forming operations [3], which generally follows aluminizing treatment. Therefore it becomes necessary to study the formation of intermetallics layer under different conditions. Gebhardt and Obrowski [4] observed that when steel comes in contact with the molten aluminum, the major intermetallic layer formed is Fe₂Al₅. Bouché et al. [5] reported the formation of two intermetallic layers, namely, Fe₂Al₅ and FeAl₃, when solid iron is dipped in liquid aluminum over the temperature range 700°C to 900°C. They reported that the growth behaviour is initially nonparabolic which is followed by parabolic. Kinetic studies done by Bouayad et al. [6] for medium dipping times (<45 min) showed that the growth of Fe₂Al₅ layer is diffusion controlled and FeAl₃ layer growth is linear with time.

Many researchers tried to explain the observed tongue-like morphology of the intermetallic layers [5–7] and are of the opinion that the anisotropic diffusion is responsible for this growth. Springer et al. [8] investigated interdiffusion between low carbon steel and pure Al (99.99%) and Al alloy (Al-5%Si) between temperatures 600°C and 675°C and showed that growth rate of η -layer (Fe₂Al₅) is diffusion controlled and it governs overall intermetallic layer growth. Cheng and Wang [9] observed that as the silicon content in the molten bath increases, the thickness of intermetallic layer decreases as well as the interface between intermetallic layer and steel substrate becomes flat. Cheng and Wang [10] investigated the effect of nickel preplating on the formation of intermetallic layer when the mild steel is dipped in pure Al. Li et al. [11] investigated the phase constituents within the intermetallic layer formed during hot-dip aluminizing. Bhat et al. [12] discussed the effect of ZnCl₂ + NH₄Cl flux on the microstructural formation during dip aluminizing of steel with aluminum.

It is also reported that Si and Cu are the alloying elements in the aluminizing bath which are effective in restraining

FIGURE 1: Cross-sectional BSE micrographs of aluminized samples. (a) A low magnification micrograph showing morphology of the coating. (b) A magnified image from the interface showing morphology of various phases in the intermetallic layer. Chemical compositions at locations A, B, C, and D are given in Table 1.

the growth of intermetallic layer [4, 13]. Addition of Cu has an additional effect that promotes formation of cubic variant for $\text{Al}_7\text{Fe}_2\text{Si}$ [9]. Cubic variants are better than hexagonal variants because of improved ductility [14]. Also, Al-Si-Cu alloy is one of the filler metals used during dissimilar TIG welding of aluminum alloys to stainless steels [15, 16]. To the best of our knowledge there is no reported investigations on the combined effect of Si and Cu on the intermetallic layer formation during hot-dip aluminizing. In the present work an attempt has been made to study the kinetics of various intermetallic phases formed as a function of time during hot-dip aluminizing of steel with Al-7%Si-2%Cu bath at a dipping temperature of 690°C.

2. Materials and Methods

The substrate used in this experiment is a low carbon steel having the following composition (all are in wt%): C-0.24%, Si-0.29%, and Mn-0.54%. The substrate was in the form of a cold rolled strip. Coupons of dimensions 3 mm × 8 mm × 50 mm were cut, metallographically polished, and used for aluminizing. Before aluminizing samples were precleaned using 10% hydrochloric acid, followed by washing with distilled water and drying.

Samples were dipped in a melt of Aluminum-7Si-2Cu (all are in wt%). The aluminizing was conducted at 690°C temperature ($\pm 5^\circ\text{C}$) for different dipping times (300 s, 600 s, 900 s, 1500 s, and 2400 s). After dipping for predetermined time, the sample was removed and cooled rapidly in air. During melting and aluminizing, the Al melt was covered with a flux made using an eutectic mixture of zinc chloride and ammonium chloride (ratio being 3:1 by weight). The specimens were cut across the cross-section, metallographically polished, and etched using 3% nital solution. Microstructures were studied using scanning electron microscope (SEM) and the chemical composition was measured using EDS (Energy Dispersive Spectroscopy). The intermetallic layer thickness was measured over a large number of locations (>40) spread on 4 surfaces.

3. Results

Figure 1(a) shows a typical cross-sectional micrograph of the interface between the base material and Al-Si topcoat. Besides topcoat and base material, it has a continuous intermetallic layer (IML). The thickness of the intermetallic layer was varying across the length of the interface. Figure 1(b) shows a magnified image from Figure 1(a). It indicates that the IML consists of a number of intermetallic phases. Chemical compositions at various locations (A to D) in the IML was estimated, and they are given in Table 1. Using morphological information shown in Figure 1(b) and chemical composition shown in Table 1, we identify four intermetallic phases in the IML. They are at A: $\tau_5\text{-Al}_7\text{Fe}_2\text{Si}$, at B: $\theta\text{-FeAl}_3$, at C: $\eta\text{-Fe}_2\text{Al}_5$, and at D: $\tau_1\text{-Al}_2\text{Fe}_3\text{Si}_3$.

Figures 2(a) and 2(b) show IML formation at 690°C for dipping times of 300 s and 2400 s, respectively. At the initial dipping time of 300 s the thickness of total IML is in the range of 8–24.6 μm with an average value of 17.5 μm. Within the IML, ($\tau_5 + \theta$) layer formed the largest fraction. Since the thickness of $\theta\text{-FeAl}_3$ layer is very small, the thickness of $\theta\text{-FeAl}_3$ and $\tau_5\text{-Al}_7\text{Fe}_2\text{Si}$ was measured together. With increase in dipping time, the thickness of $\eta\text{-Fe}_2\text{Al}_5$ layer increased rapidly, while increase in ($\tau_5 + \theta$) layer was relatively gradual. At dipping time of 2400 s the average thickness of $\eta\text{-Fe}_2\text{Al}_5$ was more than that of ($\tau_5 + \theta$) layer.

4. Discussion

4.1. Microstructural Features. From Figures 1(a), 1(b), 2(a), and 2(b) we see that the intermetallic layer consists of four phases, namely, $\tau_5\text{-Al}_7\text{Fe}_2\text{Si}$ (with Cu), $\theta\text{-FeAl}_3$, $\eta\text{-Fe}_2\text{Al}_5$, and $\tau_1\text{-Al}_2\text{Fe}_3\text{Si}_3$. This is true for all time scales investigated. As expected near Al-Si topcoat we have τ_5 which is richer in Al compared to η (which is near steel side). Presence of $\tau_5\text{-Al}_7\text{Fe}_2\text{Si}$, $\theta\text{-FeAl}_3$, $\eta\text{-Fe}_2\text{Al}_5$, and $\tau_1\text{-Al}_2\text{Fe}_3\text{Si}_3$ is reported for the case of Al-5Si and Al-10Si bath [9]. Other phases in the Fe-Al system like Fe_3Al , FeAl which were observed by Li et al. [11] in the case of Fe-Al system were not observed.

FIGURE 2: Intermetallic layer formed between substrate and Al-Si topcoat for dipping times of (a) 300 s and (b) 2400 s at 690°C temperature.

FIGURE 3: Plots of intermetallic layer growth. (a) Variation of average thickness of η layer with dipping time. (b) Plot of η thickness with square root of dipping time.

TABLE 1: Chemical compositions (at%) at various points identified in Figure 1(b).

Location	Al	Fe	Si	Cu
A	73.81	16.89	7.72	1.58
B	74.22	22.09	3.68	—
C	69.35	27.23	3.42	—
D	43.58	25.51	30.75	—

τ_5 is the only layer which had Cu in it, which could be detected by SEM-EDS. All other phases were devoid of Cu. Song et al. [15] and Lin et al. [16] have reported partial substitution of Al by Cu in θ -FeAl₃.

Although the phase τ_1 -Al₂Fe₃Si₃ is discontinuous and embedded in η -Fe₂Al₅, we can say that the diffusion path from iron side is BCC Fe-Fe₂Al₅, τ_1 , θ , and τ_5 . It is to be noted that when Si content in Fe₂Al₅ layer increases more than 4.7

at %, τ_1 is getting precipitated in Fe₂Al₅ layer [9]. τ_5 is present very close to Al-Si-Cu topcoat. Its thickness is continuously varying. In the literature [9] Cheng and Wang have reported two variants for τ_5 , that is, $\tau_{5(c)}$ (cubic) and $\tau_{5(H)}$ (hexagonal). Hexagonal variant has a chemical formula corresponding to Al₇Fe₂Si, and cubic variant has a chemical formula corresponding to Al₇(Fe, M)₂Si, where M can be copper, cobalt, or manganese. From mechanical property point of view cubic variant is desirable than hexagonal variant [14].

4.2. Growth of Intermetallic Layers. Figures 1 and 2 indicate that the intermetallic layer is not smooth. This is also true for individual layers, namely, η -Fe₂Al₅ and ($\tau_5 + \theta$) layers. Hence thickness is measured over a relatively larger area, covering four sides of the sample. The reported thickness values are average of at least 40 readings. Figure 3(a) shows variation of η -Fe₂Al₅ layer thickness as a function of dipping time. As dipping time increases, the η -Fe₂Al₅ layer thickness

increases and the relation is a parabolic one with a fitting coefficient $R^2 = 0.97$. A plot of thickness of η -Fe₂Al₅ layer against square root of the dipping time is drawn (Figure 3(b)), and the rate constant estimated is $0.57 \mu\text{m/s}^{1/2}$. We can write kinetics of growth of η -Fe₂Al₅ as $X_{(\text{Fe}_2\text{Al}_5)} = (2kt)^{1/2}$, where X is thickness, k is rate constant, and t is dipping time. The value of rate constant is much less than in the case of a bath without silicon and copper [5]. It is assumed that at this temperature, the dissolution of the substrate in the molten bath is negligible.

With increase in dipping time the growth rate of η -Fe₂Al₅ layer is higher as compared to that of $(\tau_5 + \theta)$ layer. Therefore, at higher dipping times the tongue-like morphology or the waviness of the η -Fe₂Al₅ layer is more pronounced. The literature [5] reports that this tongue-like morphology is a result of favourable path for aluminum atoms to diffuse along c -axis of the Fe₂Al₅ orthorhombic structure.

Figure 4 shows variation of $(\tau_5 + \theta)$ layer with time, and an attempt to fit parabolic curve fitting shows very poor fitting. This may be due to various mechanisms involved in the formation of τ_5 -Al₇Fe₂Si. Literature [9] reports that (i) τ_5 can be formed by the interdiffusion of Al and Si towards steel and steel towards molten Al bath, (ii) τ_5 can be formed as a product of eutectic reaction during cooling from diffusion temperature. The report also says that τ_5 phase is a metastable phase which is forming only during fast solidification after aluminizing using high silicon baths. Also, it is reported that the θ -FeAl₃ layer follows quasilinear growth behavior with time [5].

4.3. Comparative Growth of η -Fe₂Al₅ with respect to $(\tau_5 + \theta)$. Figure 5 shows a comparison of relative growth of η -Fe₂Al₅ with respect to $(\tau_5 + \theta)$. We see that at lower dipping time $(\tau_5 + \theta)$ layer is more compared to η -Fe₂Al₅ layer. In Fe-Al system, Gibbs free energy for formation of θ is smaller than that of η . When Fe is dipped in molten Al, FeAl₃ layer forms first by interfacial reaction. Later Al diffuses through FeAl₃ layer to form Fe₂Al₅ layer. Dybkov [17] have reported that, for the formation of a second compound layer, a minimum thickness of first compound layer is essential. Bouché et al. [5] have reported that growth kinetics of η -Fe₂Al₅ is always greater than that of θ -FeAl₃, at 800°C. So at higher dipping time more of η -Fe₂Al₅ compared to θ -FeAl₃.

4.4. Overall Growth Behavior of Intermetallics. Figure 6 shows variation of total intermetallic layer (IML) thickness as a function of time. The IML thickness value is very low compared to IML formation in the case of steel-Al 8combination [5, 10, 11, 18, 19]. The values are still low compared to IML values reported by Hwang et al. [20] who has done aluminizing at 660°C using a bath of Al-9 wt% Si. It is reported [13] that the elements like Cu and Si can decrease the activity coefficient of Al in Fe so as to reduce the thickness of intermetallic layer forming at the interface. The Si in the Fe₂Al₅ occupies vacancies in the c -axis of the crystal structure and reduces diffusion of Al towards Fe side. Comparing the experimental data with the reported data we can conclude that Cu and Si can be added in a view to control

FIGURE 4: Variation of average thickness of $\tau_5 + \theta$ layer with square root of dipping time.

FIGURE 5: Relative growth of η -Fe₂Al₅ and $\theta + \tau_5$ (Al₇Fe₂Si + FeAl₃) layers as a function of dipping time.

the thickness of the intermetallic layer. The critical limit for intermetallic layers in Al-Fe dissimilar joints with respect to their mechanical properties is about $10 \mu\text{m}$ [8, 21].

5. Conclusions

Low carbon steel is hot-dip aluminized using Al-7Si-2Cu bath at 690°C for time in the range of 300 s to 2400 s. The intermetallic layer consisted of four phases, namely, τ_5 -Al₇Fe₂Si (with Cu), θ -FeAl₃, η -Fe₂Al₅, and τ_1 -Al₂Fe₃Si₃. The growth of Fe₂Al₅ layer is diffusion controlled with a parabolic rate constant of $0.57 \mu\text{m/s}^{1/2}$. The value is much less than

FIGURE 6: Polynomial fit of intermetallic growth. (a) Shows polynomial fit of total intermetallics layer as a function of dipping time; (b) shows a linear fit of total intermetallics layer thickness as a function of square root of dipping time.

that reported in the literature for Al-Si bath. The overall intermetallic growth is also parabolic in nature.

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