Formation Behavior of an Intermetallic Compound Layer during the Hot Dip Aluminizing of Cast Iron

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Hot dip aluminizing (HDA) is an effective way to improve the high temperature corrosion resistance and scaling resistance of ferrous materials. The formation of intermetallic compound layers between the two materials is a dominant factor in determining the properties of hot dip aluminized steel. The formation behavior of the intermetallic compound layer between a Si alloyed Al melt and cast iron has been investigated.

The thickness of the intermetallic compound layer was significantly reduced as a result of the increased carbon content of the cast iron matrix. The thickness of the intermetallic compound layer formed in the Al–Si–Fe three-component alloy system remains constant in the early stage of the reaction, and it becomes increasingly rough with increased reaction time. The increased roughness could be attributed to the increased Fe concentration in the Al–Si melt near the cast iron surface, which is a result of the increased inter-diffusion of Al, Si and Fe atoms with increased reaction time by which the formation, melting and spallation of the intermetallic compound layer is enhanced.

KEY WORDS: hot dip aluminizing; cast iron; intermetallic compound layer; silicon effect; carbon effect.

1. Introduction

Hot dip aluminized (HDA) carbon steels are widely used for their improved heat and corrosion resistance in various applications, including automotive exhaust systems, construction materials, and consumer electronics. To improve the physical properties of the intermetallic compound layer that is created during the interfacial reaction between the steel surface and molten Al, studies are underway to control the variables in the HDA process, such as the dipping time, the dipping temperature, and the chemical composition of the molten Al.2,3,11)

Most studies to date have attempted to understand the physical and mechanical properties of the intermetallic compound layer as well as its formation behavior when Al–Si alloy below its eutectic point is hot dip aluminized onto carbon steel with a carbon content below 1.0 wt.%. However, these studies have not paid sufficient attention to the HDA of materials with high carbon content such as cast iron (2.0 wt.%C~) which is used in various ways as a component material, with the hypereutectic Al–Si alloy.

Generally, the intermetallic compound layer formed during the HDA of ferrous alloys is formed through interdiffusion between the Al, Si, and Fe atoms. The intermetallic compound layer is known to show different formation behavior depending on the presence and Si content of the Al alloy. In particular, the thickness of the intermetallic compound layer has been reported to decrease as the content of Si in the Al alloy increased,5,9) and diffusion variables such as the reaction time, temperature, and concentration are known to affect the phases of the forming layer.

This study investigates the formation behavior of the intermetallic compound layer and its dependence on the Si content of the Al alloy, the reaction time, and the temperature during the HDA of cast iron that contains more than 3 wt.%C with Al alloys containing various Si contents.

2. Experimental Procedure

The chemical composition of the cast iron used in this study is Fe–3.5C–2.4Si–1.0Mn–0.6Cr, and the specimens were machined into 20 × 70 × 10 (mm3) plates. Commercial Al was used for the pure Al, and for the Al–Si alloys, a commercial A356 alloy ingot with 7% Si content was melted at 800°C in air using an electric resistance furnace with a Kanthal wire as heating element. To produce Al–Si alloys of eutectic composition and hypereutectic composition, pure Si was added after the A356 ingot was melted, and a separate melt treatment was not performed on the melted Al alloy. The coating process consists mainly of surface polishing of cast iron, ultrasonic cleaning, drying, and immersion in Al melt to remove oxide on the surface and to reduce the effects of roughness on the reaction. The surface of wire cut specimen was polished to 1 μm with diamond paste, and ultrasonic cleaning was performed in methyl alcohol for 30 min, then rinsing and drying were followed before immersion in HDA melt. No separate fluxing or preheating was conducted before charging in the Al alloy melt. The maximum capacity of the electric resistance furnace used for melting the Al alloys was 25 kg, and the temperature difference between the outer part and the central part of the graphite crucible was approximately ± 5°C.
The cast iron was immersed in the Al alloy for a maximum period of 600 seconds, and the HDA specimens were cooled in air and a preheating furnace at 400°C, respectively. Specimens were etched with 10% aqueous solution of NaOH and 3% Nital solution to examine the formation behavior of the intermetallic compound layer produced by HDA, while optical microscopy and field emission scanning electron microscopy were used to observe the microstructure.

3. Results and Discussion

Figure 1 shows cross-section optical microscopic images of the microstructures of specimens that were cooled in a furnace after HDA in molten Al–Si alloys with various Si content for 180 seconds. The lower part of the cross sections were cast iron with typical A-type eutectic graphite, whereas spherical primary Al, needle-shaped eutectic Si, and primary Si were observed in the upper part, depending on the Si content of the Al alloy. In addition, residual eutectic graphite was observed in the Al alloy layer. According to the previous studies, this condition appears when the graphite in the cast iron remains because of erosion of the cast iron caused by the Al melt.1)

A coating layer formed in the interface between the Al alloy layer and the cast iron, consisting of an intermetallic compound layer that was divided into two layers. The growth direction differed, depending on the presence of Si in the Al alloy. Also, the roughness of the intermetallic compound layer was observed to increase as the Si content increased.

In general, the intermetallic compound layer formed through the reaction of molten pure Al and low carbon steel (~0.2 wt% C) is known to have an average thickness of more than 100 μm, depending on the dipping temperature and time. The thickness has been reported to increase with the dipping temperature and time.2–4) Figure 1(a) shows the specimen that was dipped in pure Al, where the intermetallic compound layer grew in the direction of the cast iron matrix, and the average total thickness was 40 μm. During the dipping process, the gray intermetallic compound layer adjacent to the cast iron interface grew in a saw-tooth shape, whereas the black intermetallic compound layer adjacent to the Al alloy interface formed in a relatively linear shape. As is appeared in Fig. 2(a), the gray layer consists of η-Fe2Al5, and the black layer consists of θ-FeAl3. Because the thickness of the gray η phase is greater than the thickness of the black θ phase, it can be concluded that the growth rate of
the intermetallic compound that is composed of the η phase is faster than the intermetallic compound layer that is composed of the θ phase. This phenomenon can be explained by the diffusion path of the η phase found in the results of the study by Yeremenko, which found that the orthorhombic structure of the η phase has 30% vacancy in the c-axis direction and this vacancy becomes the diffusion path that increases the growth rate of the η phase formed by the diffusion of Al. 5)

The intermetallic compound layer formed by the inter-diffusion of Fe and Al has been known to show varying growth behaviors depending on the melt conditions to which the Fe matrix structure is exposed, including the density, volume, and melting temperature of the molten Al alloy bath. 5) According to recent reports, the carbon content of the Fe matrix also has an influence. 6) In the case of the two-component intermetallic compound system formed by the inter-diffusion of Fe and Al, this phenomenon is believed to be the result of the decreased diffusion rate caused by the presence of interstitial atoms, such as carbon. This effect can also be predicted from the result of another study, which showed that although the diffusion of Al atoms in an austenite phase Fe matrix structure is 20 times higher than the diffusion in the ferrite phase, the actual reaction with Al occurs much faster in the ferrite phase in which the carbon content is low. 7) Thus, the average thickness of the intermetallic compound layer in this study is believed to have decreased relative to those observed in other studies because of the higher carbon content present in cast iron.

Figures 1(b)–1(d) show the cross-sectional microstructure observed by optical microscopy of the specimens that formed intermetallic compound layers after undergoing HDA for 180 seconds in molten baths with alloy Si contents of 7%, 12%, and 17%, respectively. The intermetallic compound that forms the coating layer was divided into two layers, as in the case of dipping in pure Al; however, the locations of the formation of the black and gray layers were reversed from those observed in the case of pure Al. According to the studies conducted so far, the formation of the τ1–τ11 phase in the intermetallic compound layer depends on its Al, Si, and Fe contents. 8, 9) The results of the SEM/EDS analyses that were performed to evaluate the phases and components of the intermetallic compound layers are shown in Fig. 2 and Table 1. Figure 2(a) shows the results of the HDA specimen, in which HDA was performed in pure Al melt. As observed in Fig. 1(a), the intermetallic compound layer formed between the pure Al coating layer in the upper part and the cast iron in the lower part. EDS point analysis of the components of the intermetallic compound layer shows, based on the dotted line, that the θ phase occurred in the layer adjacent to the pure Al coating layer and that the η phase occurred in the layer adjacent to the cast iron. In the intermetallic compound layer formed after HDA of cast iron in the Al–12%Si alloy melt (Fig. 2(b)), with reference to the dotted line, the layer adjacent to the Al–12%Si coating layer consisted of the τ phase, while the layer adjacent to the cast iron consisted of the η phase or the τ11 phase. Within the layer adjacent to the cast iron, the τ1 phase with relatively low Al content and high Si and Fe content formed in an irregular band shape. Similar observations were made in other reports; the gray layer adjacent to the Al interface is composed of τ2–Fe2Al11Si, while the black layer is either η–Fe2Al3 or τ11–Fe2Al3Si, moreover, the τ1–Fe2Al3Si phase is precipitated in the black layer. 8, 10) The presence of the τ1 phase in a layer consisting of η or τ11 is believed to be caused by the solubility limit of Si. 11) That limit for the η phase is known to be approximately 1.5–7.5%, and the Si content for the τ11 phase is approximately 9–11%. Therefore, Si diffuses to the η phase vacancies and forms the τ11 phase, while the area with locally high Si content forms the τ1 phase. The phase fraction in these intermetallic compound layers has been reported to be affected by the dipping temperature and the temperature of the heat treatment. 11)

The intermetallic compound layer adjacent to the cast iron interface was observed to form in a linear shape, unlike the intermetallic compound layer that formed by the reaction in the pure molten Al bath. This phenomenon is thought to be a result of the ferritization of the matrix structure because of the increase in the amount of Si, which is a ferrite stabilizing element, and the aforementioned decrease in the growth rate because of the reduction of vacancy in the η phase. 13) The thickness of the intermetallic compound layer that consisted of the η phase appeared to decrease when Si was added to the Al melt comparing with dipping in pure Al melt. This decrease is thought to be a result of the reduction of the growth rate as the diffusion path of the η–Fe2Al3Si phase was reduced by the diffusion of Si, so that the intermetallic compound layer of the η–Fe2Al3 phase grew slowly during the reaction with Si alloyed Al melt. Meanwhile, the intermetallic compound layer (τ2+τ11) that formed adjacent to the Al–Si alloy interface was observed to decrease in thickness and increase in roughness

| Phase                  | Element | Atomic % |
|-----------------------|---------|-----------|
| Al K                  | 74.59   |
| Si K                  | 25.41   |
| Fe K                  | 69.35   |
| Si K                  | 2.27    |
| Fe K                  | 28.39   |
| Al K                  | 68.97   |
| Si K                  | 12.19   |
| Fe K                  | 18.83   |
| Al K                  | 52.35   |
| Si K                  | 15.57   |
| Fe K                  | 32.09   |
| Al K                  | 66.81   |
| Si K                  | 3       |
| Fe K                  | 30.19   |

* τ11: Al21.5–46Fe36.528Si15.16.511*
as the Si content increased (Fig. 1). The thickness and roughness of the intermetallic compound layer are shown in Figs. 3 and 4, respectively. The intermetallic compound layer formed by the reaction with the Al–7%Si alloy melt had a reduced thickness compared to the layer formed by the reaction with pure Al melt (Figs. 3(a), 3(b), 4). The intermetallic compound layer formed by HDA of the same duration after increasing the Si content of the Al alloy to 12% and 17% showed a continuous reduction of the thickness, but the roughness increased significantly (Figs. 3(c), 3(d), 4). Thus, the decrease in the thickness of the intermetallic compound layer ($\tau_5+\tau_1$) with increasing Si content in the Al alloy may be attributed to the melting of the intermetallic compound layer following the increase of Si diffusion in case of the $\tau_5$ formed in the Al alloy side. The increase in roughness is attributed to the increase of the Fe concentration between the Al–Si alloy melt and the intermetallic compound layer interface.

According to El-Mahallawy et al., the melting point of intermetallic compound layer is reduced with the Si content of the intermetallic compound layer, resulting in its dissolution in the Al–Si alloy molten bath.\textsuperscript{9,14} and this melting phenomenon can also be verified by the phase diagram of the three-component system shown in Fig. 5. The dotted line represents the distribution of phases that can be formed during the reaction of the Al–Si alloy and the Fe used in this study, where the $\eta$, $\theta$ and $\alpha$ phases that can appear in the Fe–Al two-component system and the $\tau$ phase that can appear in the Fe–Al–Si three-component system may be formed. In particular, the area indicated by a thick line represents the region where the liquid can exist at 800°C, depending on the content of Al, Si and Fe, and the region where the liquid + $\theta$ phase exists is found to increase as the Al and Si contents increase and the Fe content decreases.

Because the distribution of the liquid region in the three-component phase diagram occurs in the upper part of the $\tau_5$ phase, which is the area of increased Si content, the overall thickness may have decreased because the growth rate of the intermetallic compound layer decreased when it melted in the Al–Si alloy melt as the Si content of the Al–Si alloy increased.

Figures 6 and 7 show the results of the formation of the intermetallic compound layer in Al–Si melt with the same Si content and varying reaction times and temperatures; conditions were varied to investigate the formation behavior of the intermetallic compound layer and its dependence on Fe concentration.

Figure 6 shows the FE-SEM images that show the dependence of the formation behavior of the intermetallic compound layer on the reaction times in melt of the same
Si content. Generally, the diffusion rate is affected by the atomic concentration that is adjacent to the interface. Assuming a sufficient concentration for the diffusion of Al and Si atoms in the conditions of this study, the intermetallic compound layer is expected to maintain steady thickness, even if the reaction time increases, because of the melting phenomenon caused by the diffusion of Al and Si atoms. Meanwhile the thickness of the intermetallic compound layer as a function of the reaction time can be expressed as $y^2 = kt$, where $y$ refers to the thickness of the intermetallic compound layer, $k$ refers to the reaction rate, and $t$ refers to the reaction time. The thickness of the intermetallic compound layer is found to be dependent on the time when the reaction rate is constant. However, it was observed that the intermetallic compound layer formed at a relatively uniform thickness from the beginning of the reaction to a reaction time of 120 sec (Figs. 6(a)–6(c)), but the roughness significantly increased when the reaction time was greater than 120 sec (Figs. 6(d)–6(e)). This phenomenon can be explained by the growth rate of the intermetallic compound layer, which is slower than or equal to the melting rate until 120 sec, whereas the growth rate of the intermetallic compound layer becomes faster than the melting rate because of the increase in the Fe concentration adjacent to the cast iron interface once the reaction time passes 180 sec. This is thought to be caused by the formation of an intermetallic compound layer and the occurrence of melting as the interdiffusion rate between the Al, Si, and Fe atoms increases with the increase in reaction time and the intermetallic compound layer cracking resulting in the increase in the concentration of Fe in the Al–Si alloy adjacent to the cast iron interface. The isolated particles of intermetallic compound layer detached from growing one are observed in Fig. 7(c).

Figure 7 shows a cross-sectional optical microscopic image of the microstructure, showing the dependence of the formation behavior of the intermetallic compound layer on the reaction temperature and the increased layer formation rate as the reaction temperature increases. This result is attributed to the increase in the reaction rate. Generally, the reaction rate is highly dependent on the temperature, which means that the reaction rate increases as the temperature increases. The increase in the inter-diffusion rate between the Al, Si, and Fe atoms because of the increase in temperature causes the increase of the Fe concentration in the melt at the interface thereby the formation rate and roughness of the intermetallic compound may increase, even with the same reaction time.

Therefore, melting of the intermetallic compound layer must occur in order for the intermetallic compound layer to grow in uniform thickness. For melting to occur, the Fe concentration in the Al alloy melt must be unsaturated. Nevertheless, if a Fe saturation region is formed because of such an increase in the Fe concentration, the $\theta$+liquid region is reduced as shown in the phase diagram of three-component system in Fig. 5, causing a significant growth of the intermetallic compound layer. The intermetallic compound layer is expected to form with a non-uniform composition, and the region with partially low Fe content may exhibit non-uniform roughness because of melting.
4. Conclusion

(1) The thickness of the intermetallic compound layer formed from HDA of cast iron was significantly less than the previously reported thickness of the intermetallic compound layer. This reduction was caused by the high carbon content present in the cast iron matrix.

(2) The thickness of the Al–Si–Fe three-component system intermetallic compound layer remained constant when the reaction time was short, but the roughness significantly increased when the reaction time increased. This is thought to be caused by the formation of an intermetallic compound layer and the occurrence of melting as the inter-diffusion rate between the Al, Si, and Fe atoms increased with the increase in reaction time and the breakdown of the intermetallic compound layer, which resulted in an increase in the concentration of Fe in the Al–Si alloy adjacent to the cast iron interface.

(3) The thickness of the intermetallic compound layer decreased as the Si content in the Al alloy melt increased. This phenomenon may be a result of the reduction in thickness caused by melting of the intermetallic compound layer (\tau_2).

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