Enhanced Interfacial Reaction of Fe–Si Alloy Sheets Hot-Dipped in Zn Melt at 460°C

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In order to understand the effect of solute Si (in the steel sheet) on the interfacial reaction between liquid Zn and solid Fe (α-Fe phase) during the hot-dip galvanizing process, a change in the interfacial microstructure between Zn coating and Fe substrate in Fe–Si alloy sheets hot-dipped in Zn melt with dipping time at 460°C was examined. In pure Fe sheet, the Fe–Zn intermetallic layers form at the interface between solid Fe and liquid Zn at an early stage of dipping and subsequently grow to approximately 60 μm in thickness after 600 s. In Fe–1Si (wt%) alloy, the thickness of Zn coating substantially increases to beyond 500 μm after 600 s and the coarse $\gamma$FeZn$_{13}$ phase with several facet planes was often observed in the Zn coating. The thickness of the Fe–1Si alloy sheets continuously decreases till 60 s and then is reduced significantly after 600 s. The thickness loss in the later stage of dipping is more significant in the Fe–Si alloy with higher Si content. These results indicate a significant Fe dissolution into liquid Zn could occur at the later stage of dipping the Fe–1Si alloy in Zn melt, which is distinguished from the interfacial reaction between pure Fe and liquid Zn. The enhanced interfacial reaction would be responsible for the decomposition of the initially formed $\gamma$FeZn$_{13}$ phase layer to liquid and FeSi phases, which can be proposed based on thermodynamic calculations of the Fe–Zn–Si ternary system.

KEY WORDS: galvanized steels; intermetallics; interfacial reaction; thermodynamic calculation; sandelin phenomenon.

1. Introduction

Hot-dip zinc (Zn) and its alloy coated galvanized steels are extensively produced for the architectural materials and the automobile industry due to their low cost and sufficient sacrificial anodic effect in atmospheric corrosion environment.1,2) The superior corrosion resistance provided by the hot-dip Zn galvanizing process is being applied to high strength multi-phase steels such as dual-phase (DP) steels with two microstructural constituents of martensite and ferrite.2–7) One of the important issues in the application of the hot-dip galvanizing process to high strength steels is a sufficient adhesiveness of the Zn coating layer on the steel sheet. It is generally known that the Fe–Zn intermetallic phase layers formed at the interface between the Zn coating and the steel sheet1) and that they are often brittle due to the difficulty of slip deformation at ambient temperature,11,12) whereby it is essential to control the formation of the Fe–Zn intermetallic phase layers. Thus, it is required to understand the interfacial reaction between steel sheet (solid Fe) and Zn melt (liquid Zn) during the hot-dip galvanizing process.13)

In order to control the Fe–Zn intermetallic phase layers formed in the hot-dip galvanized high strength steels with multi-phase microstructures, it is necessary to identify the effect of alloy elements (for high strength steels) on the interfacial reaction. In general, the multi-phase steels (DP steel or TRIP steel) contain various alloy elements. These major alloy elements are C, Mn and Si. The observations of Fe–Zn intermetallic phase layers formed on Fe–Mn–C ternary alloy sheets hot-dipped in pure Zn melt demonstrates a slight effect of Mn and C in solution (austenite stabilizer) on the interfacial reaction between solid Fe and liquid Zn.13,14) In contrast, it has been generally understood that solute Si (ferrite stabilizer) would influence the interfacial reaction in the galvanized steels. Previous studies13,15–18) have reported a significant reaction observed in the hot-dip galvanized Fe–Si alloys, whereas Lin et al.19) have noted that Si in DP steels retards the alloy reaction in hot-dip galvanizing. Thus, the influence of solute Si in solid Fe on the interfacial reaction with liquid Zn is not fully understood.

In the present study, in order to understand the effect of solute Si in the steel sheets on the interfacial reaction between liquid Zn and solid Fe (α-Fe phase) in the hot-dip galvanized steels, we have examined a change in the interfacial microstructure between Zn coating and Fe substrate in Fe–Si alloy sheets hot-dipped in Zn melt with dipping time at 460°C. The results were utilized to discuss on the
interfacial reaction between liquid Zn and solid α-Fe with Si in solution in conjunction with the calculated Fe–Zn–Si ternary phase diagram.

2. Experimental Procedure

In the present study, Fe–Si binary alloys with different Si contents of 0.2 and 1 wt.% were used. The detailed chemical compositions of the studied alloy sheets are shown in Table 1. These alloy ingots were hot-rolled and then cold-rolled to about 1 mm in thickness. The alloy sheets were used for the hot-dipping experiments.

Hot-dipping experiments were carried out using a hot-dip process simulator. Before the hot-dipping experiment, the alloy sheets were mechanically polished and then finished with buffing compounds. The alloy sheets with approximate dimensions of 200 mm × 50 mm × 1 mm were heated to 850°C for 60 s, and then cooled down to 460°C under an N₂–15 vol.% H₂ atmosphere with a dew point set to approximately −45°C. After that, these sheets were hot-dipped in a molten Zn (with a saturated solution of 0.03 wt.% Fe) bath at 460°C for different lengths of time (2 s–3 600 s), followed by rapid cooling by gas wiping. These heat profiles of the sheets were measured using K-type thermo-couples welded on the top portion of the sheet surface. Figure 1 presents the studied alloy compositions on the Fe–Si binary phase diagram and the representative thermal profile of alloy sheets during the present hot-dipping experiment (dipping for 2 s). The heating temperature (850°C) and subsequent dipping temperature (460°C) correspond to α-Fe single phase in all compositions of alloy sheets studied (Fig. 1(a)), indicating that α-Fe phase with various Si contents could be in contact with the Zn melt at 460°C.

The microstructures of the prepared samples were observed by scanning electron microscope (SEM) operating at 20 kV. The observed sample surfaces were mechanically polished and then finished using the colloidal silica. The low-magnification SEM images were utilized to measure the thickness of the Zn coating layer (including the Fe–Zn intermetallic layers) and the thickness of the Fe–Si alloy sheets. The thicknesses of the Fe–Zn intermetallic layers were measured using the high-magnification SEM images. These measurements were described in detail elsewhere. The chemical compositions were analyzed with energy dispersive X-ray spectroscopy (EDS) at 15 kV. The constituent phases of the hot-dipped samples were identified using X-ray diffraction (XRD) analysis with λ_{Kα} = 0.154 nm. In this study, the X-ray were detected from the cross section of Fe–Si alloy sheets dipped in the Zn melt.

3. Results

3.1. Changes in Thicknesses of Zn Coating and Fe–Si Alloy Sheets

Figure 2 presents the appearance of pure Fe and Fe–1Si alloy sheets hot-dipped in the Zn melt for various times. These photographs show that the alloy sheets were uniformly coated with Zn without any discernible defects,

Table 1. Compositions of the alloy studied (wt.%).

| Si | C  | Mn | P  | Al | S  | N  | O  | Fe |
|----|----|----|----|----|----|----|----|----|
| Pure Fe | 0.01 | 0.001 | <0.01 | 0.002 | 0.001 | 0.001 | 0.008 | bal. |
| Fe–0.2Si | 0.18 | 0.001 | <0.01 | 0.002 | 0.001 | 0.001 | 0.008 | bal. |
| Fe–1Si | 0.96 | <0.001 | <0.01 | 0.001 | 0.001 | 0.001 | 0.005 | bal. |

Fig. 2. Appearance of (a) pure Fe and (b) Fe-1Si alloy sheets hot-dipped in Zn melt for various times.

Fig. 1. (a) Chemical compositions of the alloys studied plotted on an Fe–Si binary phase diagram and (b) a representative thermal profile of alloy sheets to prepare the samples hot-dipped in Zn melt for 2 s.
regardless of the hot-dipping time. It is noteworthy that Fe–1Si alloy sheets dipped for longer time than 600 s exhibits a significantly thick Zn coating (Fig. 2(b)), whereas such thick Zn coating was not observed on the surface of pure Fe and Fe–0.2Si alloy sheets dipped in the Zn melt (Fig. 2(a)). Note that the dark areas on the coating surface would be an oxide film believed to be from the surface of the molten Zn.

Figure 3 shows the back-scattered electron images (BEIs) of the cross-section of the Fe–Si alloy sheets dipped in the Zn melt for 2 s and 600 s. In the early stage of dipping (2 s), all alloy sheets dipped in the Zn melt exhibit a coating thickness (corresponding to bright regions) of approximately 20 μm (Figs. 3(a)–3(c)). In the samples dipped for 600 s (Figs. 3(d)–3(f)), a trend can be observed that a thicker Zn coating is formed on the alloy sheet with higher Si content. It is evident that a significantly thick Zn coating forms on Fe–1Si alloy sheet (Fig. 3(f)), which is quite different from that of pure Fe and Fe–0.2Si sheets (Figs. 3(d), 3(e)). These results correspond well to those of previous studies on the hot-dip galvanized steels.\(^ {16,17}\) It should be noted that the thickness of the Fe–1Si alloy sheet (without the coating layer) obviously decreases after dipping in the Zn melt for 600 s (Figs. 3(c), 3(f)). The thickness loss of Fe–1Si alloy sheet by dipping is much larger than that pure Fe and Fe–0.2Si alloy sheets (Figs. 3(d)–3(f)).

Figure 4 shows variations in thicknesses of the Zn coating \((t_{Zn})\) and Fe–Si alloy sheets \((t_{Fe})\) as a function of dipping time in the Zn melt. The differences of the sheet thickness from the measured initial thickness \((\Delta t_{Fe})\) are plotted on the vertical axis of Fig. 4(b). The thickness of the Zn coating continuously increases with increasing dipping time (Fig. 4(a)). The increasing rate of the Zn coating on pure Fe sheet is similar to that on Fe–0.2Si alloy sheet, whereas a significantly high increasing rate was recognized on Fe–1Si alloy sheet hot-dipped above 60 s. The increasing rate constant was close to 1.0. In the thickness of the alloy sheets (Fig. 4(b)), the sheet thickness decreases with an increase in dipping time due to the dissolution of Fe into the Zn melt. The thickness loss of pure Fe and Fe–0.2Si alloy sheets is approximately 20 μm after dipping for 3 600 s. In Fe–1Si
alloy sheet, the thickness decreases with increasing dipping time as well and the decreasing rate is much higher than that of pure Fe and Fe–0.2Si sheets. The thickness loss is obviously pronounced at the later stage of dipping (above 60 s). This result indicates a significant dissolution of the Fe–1Si alloy sheet into the Zn melt during the dipping.

3.2. Interface between Zn Coating and Fe Substrate

Figure 5 presents XRD profiles of the alloy sheets dipped for 600 s. The diffraction peaks derived from α-Fe (bcc), η-Zn (hcp) and ζ-FeZn₁₃ phases were detected in all samples. The peaks derived from δ-FeZn₁₀ phase often overlap those derived from ζ phase. These diffractions would correspond to Fe–Si alloy sheets, solidified Zn melt in the Zn coating and Fe–Zn alloy layer, respectively. Higher peak intensities for ζ-FeZn₁₃ and δ-FeZn₁₀ phases were found in the XRD profile obtained from the Fe–1Si alloy sheet (Fig. 5(c)). In addition, a diffraction peak derived from a Fe–Si binary intermetallic phase of FeSi (B₂0 structure) was also observed in only the Fe–1Si alloy sheet (Fig. 5(c)). Note that a small peak located at approximately 38 degrees in 2θ (Fig. 5(c)) might be associated with the diffraction of ζ phase from the different X-ray (Kβ).

Figure 6 presents BEIs showing Fe–Zn intermetallic phase layers formed on Fe–Si alloy sheets hot-dipped in Zn melt at 460°C for 2 and 600 s. In all alloy sheets, various Fe–Zn intermetallic phase layers were observed at the interface between the Zn coating and the alloy sheet. The studied Fe–Si alloy sheets hot-dipped for 2 s (Figs. 6(a)–6(c)) exhibit a dual layer structure, which consists of a continuous δ-FeZn₁₀ phase layer on the solid α-Fe side and a relatively large ζ-FeZn₁₃ phase layer on the liquid Zn side (solidified η-Zn (hcp) phase observed). Note that the difference between two intermetallic phases of δ₁₀ and δ₁₃ was not identified in the present observation. The total thickness of δ-FeZn₁₀ and ζ-FeZn₁₃ phase layers is approximately 25 μm in all samples. In the pure Fe sheet, the thickness of the Fe–Zn intermetallic phase layers increases with increasing time and reaches above 60 μm after 600 s (Fig. 6(d)). The larger ζ phase layer was observed on the Fe–0.2Si alloy sheet dipped for 600 s (Fig. 6(e)). The interfacial microstructure in the Fe–1Si alloy sheet dipped for 600 s (Fig. 6(f)) is quite different from that in the other alloy sheets. A low-magnification SEM image showing an overall view of the Zn coating on the Fe–1Si alloy sheet dipped for 600 s is presented in Fig. 7. The Fe–Zn intermetallic phase layer

\[ \text{Fig. 5. XRD profiles of (a) pure Fe, (b) Fe-0.2Si and (c) Fe-1Si alloy sheets hot-dipped in Zn melt for 600 s. These profiles were measured from the cross-section of the sheet samples.} \]

\[ \text{Fig. 6. BEIs showing the Fe–Zn intermetallic layer formed on (a, d) pure Fe, (b, e) Fe-0.2Si and (c, f) Fe-1Si alloy sheets hot-dipped in Zn melt alloy for (a–c) 2 s and (d–f) 600 s.} \]

\[ \text{Fig. 7. Microstructure of the Zn coating on the Fe-1Si alloy sheet hot-dipped in Zn melt alloy for 600 s. An arrow indicates the representative region including numerous fine pores in the η phase.} \]
(δ phase) on the Fe–1Si alloy sheet exhibits a non-uniform thickness with a mean value of approximately 15 μm (Fig. 6(f)). Numerous fine pores were observed in a large part of the thick Zn coating, as indicated by the arrow in the image. The observed morphology suggests the solidified η-Zn phase (corresponding to liquid phase at 460°C), which is good agreement with high intensities of diffractions derived from η-Zn phase (Fig. 5(c)). The minute observation revealed the solidified η phase region includes fine intermetallic ζ phase with a mean size of several micrometers. Furthermore, a number of large Fe–Zn intermetallic phase with several facet planes were localized around the top surface of thick Zn coating (Fig. 7). The fine ζ phase with a mean size of several micrometers can be often observed as well (Fig. 6(f)). The XRD profile (Fig. 5(c)) indicates the intermetallic phase would be ζ-FeZn13 phase.

The mean thickness of Fe–Zn intermetallic phase layers formed at the interface between Zn coating and Fe–Si alloy sheets was quantified. The result was summarized in Fig. 8. Note that two Fe-rich intermetallic phase layers of Γ-FeZn21 and Γ-Fe2Zn10 phases were not measured since these phases were not clearly determined by present SEM observations. In pure Fe and Fe–0.2Si alloy sheets, the total thickness of Fe–Zn intermetallic phase layers continuously increases with increasing dipping time (Fig. 8(a)). The growth rate constant was approximately 0.3, which corresponds well to those of previous studies on the Fe–Zn alloy layer formed on the hot-dip galvanized steels.18 The growth rate of ζ-FeZn13 phase layer is somewhat low in all Fe–Si alloy sheets at an early stage of dipping (before 10 s), whereas the growth rate constant of ζ-FeZn13 phase layer becomes close to 0.5 after the dipping for 10 s (Fig. 8(b)). The growth kinetics of ζ phase layer on Fe–0.2Si alloy sheet was faster than that on pure Fe sheet, indicating the growth of ζ phase layer enhanced by solute Si in α-Fe phase.15 The thickness of δ-FeZn10 phase layer also increases with increasing dipping time in all Fe–Si alloy samples (Fig. 8(c)). A trend can be found that the mean thickness of δ-FeZn10 phase layer is larger on α-Fe phase with higher Si content at an early stage of dipping (before 10 s). This indicates the formation of δ-FeZn10 phase enhanced by Si in solution, which corresponds well to previous studies on the Fe–Zn intermetallic phase layer formed in the galvanized Fe–Si alloy sheets.19 The growth rate constant of δ phase layer appears approximately 0.5 in pure Fe sheet. The constant becomes smaller in the Si containing alloy sheets, indicating the retarded growth of δ phase layer after the dipping for prolonged time above 600 s.

3.3. Composition Analysis

Figure 9 presents SEM images and the corresponding concentration line profile in the Zn coating on the Fe–1Si alloy sheet hot-dipped for 60 s. The SEM observation (Fig. 9(a)) revealed a number of plate-shaped δ-FeZn13 phase and neighboring solidified regions (η-Zn) are located above δ-FeZn10 phase layer (Figs. 9(c), 9(d)). The localization of these elements indicates the formation of an intermetallic phase of FeSi detected in the Fe–1Si alloy sheet sample (Fig. 5(c)). Note that the high Fe concentration above 20% in the δ phase layer close to α-Fe phase (Fe–1Si alloy sheet) might be caused by the overlap of the composition of a multiphase.

4. Discussion

The present study investigated the interfacial reaction between solid Fe and liquid Zn in various Fe–Si binary alloy sheets hot-dipped in Zn melt, and revealed the pronounced interfacial reaction of Fe–1Si alloy sheet with the Zn melt during the dipping. The reaction results in the formation of substantially thick Zn coating and the dissolution of Fe into the Zn melt (Figs. 3 and 4). These results correspond well to the previous studies on “Sandelin” phenomenon observed in the galvanized Si containing steels.16,17 The interfacial
reaction enhanced by Si in solution is discussed utilizing the thermodynamic assessment of a Fe–Zn–Si ternary system below. Figure 10 illustrates the isothermal sections at 460°C in a Fe–Zn–Si ternary system assessed based on the thermodynamic database previously reported.27) The thermodynamic assessment presents the formation of FeSi phase in equilibrium with ζ-FeZn13 phase and liquid phase even in the Zn-rich portion of the Fe–Zn–Si ternary system (Fig. 10(b)). It is noteworthy that a composition of ζ-FeZn13 phase region (corresponding to approximately 7 at.% in a Fe–Zn binary system) changes into the three phase region of ζ-FeZn13, FeSi and liquid phases by increasing Si content (Fig. 10(b)). In order to present the phase transition quantitatively, changes in the fractions of constituent phases in a stoichiometric composition of ζ-FeZn13 phase by increasing Si content were assessed based on the calculated Fe–Zn–Si ternary phase diagram (assuming the Si content increases along the equi-Fe concentration direction, as shown in Fig. 10(b)). The result is illustrated in Fig. 11. The fraction of ζ phase remains 100% below 0.5% in Si content, whereas FeSi and liquid phases appear together with the ζ phase at high Si content above 0.5%. The fractions of both phases increase with increasing Si content. The fraction of liquid phase is more than six times higher than that of FeSi phase. The assessed phase transition indicates the decomposition of the ζ phase to FeSi and liquid phases by increasing Si content at 460°C. These assessments are supported by present observations of η-Zn phase (might be solidified during the cooling) inside the Zn coating on the Fe–1Si alloy sheet dipped above 600 s (Figs. 6 and 7(c)). Another pertinent observation is the detectable diffraction peak of FeSi phase in the Fe–1Si alloy sheet sample (Fig. 7(c)). These reasonably good agreements with the experimental results represent the decomposition of the ζ phase to FeSi and liquid phases in the Fe–1Si alloy sheets dipped for prolonged time.

Based on these findings, a possible mechanism for the enhanced interfacial reaction between liquid Zn phase and solid α-Fe phase with Si in solution is discussed below. Figure 12 presents schematics showing changes in microstructures at interface between liquid Zn and solid α-Fe with or without Si in solution during the dipping at 460°C. The reaction is considered to start with the dissolution of Fe because of the much higher diffusion rate in liquid than that in solid. Although studied Zn melt contains 0.03% Fe in solution (which reduces the driving force for the dissolution of Fe into Zn melt), the supersaturation of Fe would appear in the Zn melt close to the Fe sheet, resulting in the formation of ζ-FeZn13 phase layer (Fig. 12(a)). In case of pure Fe sheet (Figs. 12(a)–12(d)), the formation of the ζ phase is followed by the formation and growth of δ-FeZn10 phase layer through a solid-solid reaction between δ and α-Fe (pure iron substrate) phases (Figs. 12(b), 12(c)). The δ phase may grow toward both the liquid side and the substrate side after further dipping. The continuous ζ and δ intermetallic phase layers may play a role of diffusion controlling factors, resulting in the formation of multi-layered structure on the pure Fe sheets dipped in Zn melt (Fig. 12(d)). In case of the interface between liquid Zn and α-Fe with high Si content (Figs. 12(e)–12(h)), a limited solubility of Si in the ζ phase would enhance the enrichment of Si at the interface between ζ phase and Fe–Si alloy sheet accompanied by the growth of ζ phase layer. The enriched Si would lead to the formation of FeSi phase in the initially formed ζ phase layer (Fig. 12(e)), followed by the formation of liquid phase surrounding the FeSi phase (Fig. 12(f)). Further Si enrichment could facilitate an increase in the volume fraction of liquid phase close to the interface between ζ and δ phases (Figs. 12(g), 12(h)). The calculated phase diagram indicates the δ phase is not in equilibrium with the liquid phase (Fig. 10), whereby the ζ phase may form at the interface between liquid and δ phases. The newly formed ζ phase might be decomposed into FeSi and liquid phases by further Si
Fig. 11. Changes in the calculated mol fractions of constituent phases in a composition of Fe$_7$(Zn,Si)$_93$ as a function of Si content.

enrichment. The increasing liquid phase would contribute to the significant interfacial reaction (significant dissolution of Fe and coarsening of polyhedral-shaped $\zeta$ phase) observed in the Fe–1Si alloy sheet dipped for prolonged time (Fig. 7). The solid-liquid reaction is supported by the growth kinetics for the thickness of Zn coating on the Fe–1Si alloy sheet after 60 s in dipping time (Fig. 4(a)). The growth rate constant of approximately 1 indicates the reaction-controlling process, suggesting the formation of the thick Zn coating through the solid-liquid interfacial reaction.

In the aforementioned discussion on the interfacial reaction process, it may not be negligible that the $\delta$ phase layer is present on the Fe–Si alloy sheets dipped in Zn melt. The calculated phase diagram indicates Si element preferentially partition into the $\delta$ phase rather than $\zeta$ phase (Fig. 10), whereas approximately 0.5 at.% Si was detected within both $\zeta$ and $\delta$ phases (Fig. 9). One possible reason for the presence of $\delta$ phase with a small amount of Si in solution is

Fig. 10. Isothermal sections at 460°C in an Fe–Zn–Si ternary system calculated utilizing the reported thermodynamic database.

Fig. 12. Schematics showing the interfacial reaction between liquid Zn and solid $\alpha$-Fe phases: (a–d) pure Fe, (e–h) Fe–1Si alloy.
the crystallization of δ phase in the liquid phase during the following rapid cooling process (after the hot-dipping in Zn melt at 460°C), resulting in the δ phase layer observed at ambient temperature (as shown in Fig. 7). However, there is still the issue of identifying the formation mechanism of the δ phase layer in the observed interfacial reaction. Even it seems unclear whether solute Si can stabilize the δ phase. The present kinetics analysis revealed the growth of δ phase layer enhanced by solute Si in α-Fe phase at an early stage of dipping (Fig. 8(c)), which corresponds well to the previous work. In contrast, the retarded growth of δ phase layer was observed after the dipping for prolonged time above 600 s (Fig. 8(c)). To clarify the detailed mechanism of the enhanced interfacial reaction, further work is needed to better understand the phase equilibria and its related reaction among α-Fe, δ and liquid phases in the Fe–Zn–Si ternary system.

5. Summary

In present study, in order to understand the effect of solute Si (in the steel sheet) on the interfacial reaction between liquid Zn and solid Fe (α-Fe phase) in the hot-dip galvanized steels, the interfacial microstructures between Zn coating and Fe substrate in pure Fe, Fe–0.2Si and Fe–1Si (wt.%) alloy sheets hot-dipped in Zn melt for various dipping time at 460°C were observed. The observation revealed a pronounced dissolution of Fe into the Zn melt during the dipping and the formation of a significantly thick Zn coating on the Fe–1Si alloy sheet. These results correspond well to those of previous studies on “Sandelin” phenomenon observed in the galvanized Si containing steels. These interfacial reactions enhanced by solute Si in α-Fe phase would be responsible for the decomposition of the initially formed ζ-FeZn13 phase layer to liquid and FeSi phases.

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