Effects of Si Solid Solution in Fe Substrate on the Alloying Reaction between Fe Substrate and Liquid Zn

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Effects of Si solid solution in Fe substrate on the formation of Fe–Zn intermetallic phase layers between the Fe(-Si) substrate and liquid Zn were investigated using a combinatorial technique. The formation of Fe\(_{13}\)Zn layer was promoted by Si solid solution up to 2 at.% in the Fe substrate but retarded by further solution. The formation of Fe\(_7\)Zn\(_{10}\) phase and Fe\(_3\)Zn\(_{10}\) phase was retarded by Si solid solution up to 10 at.% The rate of Fe dissolution from the Fe substrate to the liquid Zn region and the FeZn/Si contents in the \(\delta\) phase were analyzed as a function of Si content in the substrate. The results obtained suggest that the retardation of the Fe–Zn phase formation is caused by a difficulty in the nucleation of \(\delta\) phase at lower Si contents less than 3 at.% and by a decrease in the rate of Fe dissolution at higher Si contents.

KEY WORDS: galvanized/galvannealed steel; alloying reaction; intermetallic phase; Si effect; combinatorial technique.

1. Introduction

Hot-dipped galvanized/galvannealed steels are extensively used as steel sheets for automotive bodies because of good productivity, low cost and excellent corrosion resistance due to its sacrificial anodic effect.\(^1\) Fe–Al based and Fe–Zn based intermetallic phases are formed as alloying layers between the steel sheets and coating during hot-dipping and annealing.\(^2\) The mechanical properties of the steel substrate/coating layer interfaces depend on the size, types and morphologies of the Fe–Zn based intermetallic phases formed in the alloying layers.

According to the previous researches on the alloying reaction,\(^3,4\) in the case of steels coated by liquid Zn with a small amount of Al, the Fe\(_5\)Al\(_5\) intermetallic phase is firstly formed at the interface between the steel substrate and the liquid Zn coating, which phase is considered as a barrier for the reaction of Fe and Zn. Then, the Fe–Zn based intermetallic phases are formed in a way to break the Fe\(_5\)Al\(_5\) phase. In the Fe–Zn intermetallic phase layers, the Fe\(_7\)Zn\(_{10}\) phase is formed as a main phase and the Fe\(_3\)Zn\(_{10}\) and Fe\(_{13}\)Zn layers are formed on the substrate side and the coating side, respectively.

It has been apparent in recent years that the formation of a \(\delta\) phase layer is retarded by the addition of Si in steels, which is problematic in the galvanizing process of high strength steels. The retardation has been studied and possible reasons are reported.\(^5,6\) The reasons include: (1) the formation of Si oxides on the steel substrate during a recrystallization annealing in reductive atmosphere, (2) solid solution into the Fe–Al intermetallic phase to enhance the barrier effect, and (3) solid solution into the \(\delta\) phase to retard the interdiffusion of Fe and Zn. The effects of Si on the retardation of the alloying reaction are, however, not fully understood because of the following reasons: (1) the alloying reaction is related to oxidation and it is difficult to distinguish the effects of Si in the two phenomena, (2) multi-elements (Fe, C, Zn and Al etc.) are involved in the alloying reaction, and (3) the partitioning of Si into the phases present is not clarified.

The present paper aims to clarify the effects of Si on the reaction between the solid Fe and the liquid Zn, which is the fundamental reaction in the hot-dip galvanizing/galvannealing process, by designing an experiment in which the effect of oxidation on the steel substrate surface is minimized and Al is excluded in the reaction. More specifically, an Fe/Fe–Si alloy diffusion couple sample electrodeposited with Zn was prepared to investigate the effect of Si solid solution in the steel substrate on the alloying reaction during heat treatment.

2. Experimental Procedures

The Fe/Fe–Si substrate with a continuous concentration gradient of Si was prepared by a diffusion couple method using pure Fe and Fe–10 at.% Si binary alloy plates as end members. Atomic percent is used through this paper unless specified. The end members were prepared by arc melting using 4N purity of Fe and 6N purity of Si and cutting into...
plate with 1 mm × 5 mm × 20 mm in size. The surfaces of the members were ground and polished. The plates were coupled and sandwiched by metal plates, tightened with screws and heat-treated at 900°C for a period of 200 h to introduce a continuous gradient of Si content by interdiffusion in the ferrite single-phase field. The Fe/Fe–Si substrate was then treated in an acid bath with a pH of 1–2 to electrodeposit a Zn layer with 7 μm in thickness. The electrodeposited sample was heat treated for alloying at 450°C for a period between 10 s and 60 s in a salt bath, followed by water quenching.

The microstructures of the samples before and after the alloying heat treatment at 450°C were observed with field emission type scanning electron microscopes (FESEM). The samples for microstructure observations were prepared by grinding, polishing and milling with focused ion beam (FIB) for the cross sections cut at 1 mm inside from the heat treated sample surfaces. The chemical compositions of the elements in the alloying layers were analyzed using energy dispersive spectroscopy (EDS). The ZAF method was used for the quantification of the chemical compositions in EDS analysis. Electron backscattering diffraction (EBSD) patterns were used for phase identification.

3. Results and Discussions

3.1. Concentration Profile in the Fe/Fe–Si Diffusion-couple

Figure 1 shows a cross section of the Fe/Fe-10%Si diffusion-couple sample together with a Si concentration profile across the original interface of the end members. The left side was pure iron and the right side was Fe-10%Si alloy before the heat treatment at 900°C. A concentration gradient of Si is clearly seen in a range within a few hundred μm from the original interface. The diffusion distance of Si at 900°C for a period of 200 h can be estimated as 264 μm by using a reported diffusion coefficient. The distance is in good agreement with the experimental result. The wider diffusion zone observed in the silicon-poor side qualitatively indicates that the diffusion of Si is faster at lower Si contents.

3.2. Microstructures and Phase Identification of the Alloying Layers

The alloying layers were observed at different Si contents after alloying heat treatments. Figures 2 and 3 show examples of the alloying layers formed between the substrate and the liquid Zn at 450°C. The phases designated in the figures were identified by taking scanning electron micrographs, EBSD patterns and EDS concentration profiles into account. Figure 4 shows examples of EBSD patterns and EDS profiles taken at specific Si contents after milling with FIB. Clear EBSD patterns were obtained from the η-Zn (hcp) phase (Fig. 4(a)), but not from the ζ (monoclinic) type phase. Both the clearness of the patterns and the Fe/Zn concentration profiles were used to distinguish the two phases. The δ1 (hcp) type (Figs. 4(a), 4(b)) and for the ζ1 (cubic) type (Fig. 4(b)) phases were identified by their symmetries of EBSD patterns. The existence of ζ1–Fe11Zn39 phase was not identified in between the δ1 phase layer and the ζ phase.
layer in the present study.

3.3. Dependence of the Alloying Layer Formation on the Si Content in the Substrate

Figures 5 and 6 show the Fe/Zn concentration profiles across the alloying layers formed in the samples heat-treated at 450°C for 10 s and 60 s, respectively. The formation of the ζ phase is not observed in the Si free area but observed at the Si contents higher than 1.4% in the short annealing sample (Fig. 5). The thickness of the ζ phase layer shows a maximum at the Si content of 2–3%. Similar dependence of the ζ phase formation rate on the Si content was reported. 8) The thickness of the δ₁ phase layer, on the other hand, decreases monotonically with increasing the Si content (Figs. 5, 6), as reported in a previous study.4) The Γ phase layer was observed in the longer annealing sample at low Si contents but its thickness decreases with increasing the Si content (Fig. 6).

3.4. Dependence of the Amount of Fe Dissolution on the Si Content in the Substrate

It is generally recognized that the Fe–Zn intermetallic phases form in order from high to low Zn content, which allows us to consider that Fe dissolution to the liquid Zn is an important process to control the rate of alloying reaction in the beginning of the reaction. The amount of Fe dissolution was estimated from the Fe/Zn concentration profiles measured at early alloying reaction. More specifically, the amount was estimated as the integrated value of the Fe concentration in the 10 μm range on the coating side of the Fe substrate/alloying layer interface in the concentration profiles of the samples annealed at 450°C for 10 s (hatched areas in Fig. 5). Figure 7 plots the amount as a function of the Si content in the substrate together with the thickness of the alloying layers. The amount of Fe dissolution shows a peak at the Si content of around 3%. This tendency qualitatively agrees with that of the thickness of the ζ phase layer as a function of the Si content but not with that of the δ₁ phase layer, which indicates that the Fe dissolution rate is not the cause to retard the formation of δ₁ phase layer at
3.5. Dependence of the Fe Content in the δ1 Phase on the Si Content in the Substrate

A careful analysis on the Fe/Zn concentration profiles indicates that the Fe content in the δ1 phase depends on the Si content in the substrate. Figure 8 shows the Fe content range in the δ1 phase layer as a function of the Si content at different annealing times. At the shorter annealing time, the Fe content ranges from 8 to 10% in the case of Si free, but it increases to above 12% in the presence of Si in solution by more than 1%. At the longer annealing time, the Fe content ranges from 8 to 16% regardless of the Si content in the substrate. If considering that the δ1 phase nucleates at the interface between the Fe substrate and the Zn phase, the results obtained allow us to consider that the Fe content needed for the nucleation of the δ1 phase increases with increasing the Si content, and the nucleation becomes, thus, difficult.

Kainuma et al. 9) investigated the phase separation of the δ1 phase into the Zn-rich δ1k and the Fe-rich δ1p phases, and reported that the δ1 phase separates below about 550°C and the ranges of Fe contents in the two phases are 8–9% and 10.5–13%, respectively, at 450°C. By taking this report into account, the results obtained can be interpreted such that the order of nucleation is δ1p phase with a lower Fe content → the δ1k phase with a relatively high Fe content in the case of Si free substrate, while the order is vice versa in the presence of Si in the substrate.

3.6. The Effect of Si Solid Solution in the Substrate on the Formation of Fe–Zn Intermetallic Phases

The results obtained above suggest that there are two causes for the retardation of the formation of the δ1 phase by Si solid solution in the Fe substrate. The first one is that the nucleation of the δ1 phase becomes difficult by Si addition. The second is the reduction in the rate of Fe dissolution into the liquid Zn due to the increase in the Si content.

The reason why the Si solid solution in the substrate makes the nucleation of the δ1 phase difficult is discussed below. The partition of Si into the alloying layers was small regardless of the type of alloying layers and annealing time. Figure 9 shows examples of Si concentration profiles across the alloying layers. It is noted that the Si contents in the...
Fig. 6. The Fe/Zn concentration profiles across the intermetallic phase layers at different Si contents in the substrate after an alloying heat treatment at 450°C for 60 s: (a) 0.2%Si, (b) 0.4%Si, (c) 1.2%Si, (d) 2.4%Si, (e) 3.4%Si.

Fig. 7. The Effect of Si contents in the substrate on the amount of Fe dissolution and the thickness of intermetallic phase layers, estimated from the hatched areas in the Fe/Zn concentration profiles in Fig. 5, in the sample heat treated at 450°C for 10 s.

Fig. 8. The dependence of Fe content in the δ phase on the Si content in the substrate. It is noted that the maximum Fe contents are not rigid. The hatched composition ranges correspond to those for the phase regions of the δ₁p and δ₁k at 450°C in the Fe–Zn binary phase diagram, reported by Kainuma et al.7

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**Fig. 6.** The Fe/Zn concentration profiles across the intermetallic phase layers at different Si contents in the substrate after an alloying heat treatment at 450°C for 60 s: (a) 0.2%Si, (b) 0.4%Si, (c) 1.2%Si, (d) 2.4%Si, (e) 3.4%Si.

**Fig. 7.** The Effect of Si contents in the substrate on the amount of Fe dissolution and the thickness of intermetallic phase layers, estimated from the hatched areas in the Fe/Zn concentration profiles in Fig. 5, in the sample heat treated at 450°C for 10 s.

**Fig. 8.** The dependence of Fe content in the δ phase on the Si content in the substrate. It is noted that the maximum Fe contents are not rigid. The hatched composition ranges correspond to those for the phase regions of the δ₁p and δ₁k at 450°C in the Fe–Zn binary phase diagram, reported by Kainuma et al.7
alloying layers decreases with increasing annealing time, as shown in Fig. 10 where the Si contents in the δ₁ phase are plotted as a function of the Si content in the substrate at different annealing time conditions. It is seen from the figure that the reduction in the Si content with increasing annealing time is clear and becomes more apparent at higher Si contents in the substrate. These results suggest that the δ₁ phase contains supersaturated Si in the early stage of annealing and destabilized thermodynamically. This reduces the driving force for the nucleation, and is therefore one of the reasons to retard the formation of the δ₁ phase.

Parrot et al. 10) calculated the solubility of Si in δ₁ phase is 1% at 450°C. The reliability of the calculation must be, however, low according to the experimental evidence obtained in this study that the Si content decreases down to ~0.2% with annealing for 60 s. The solubility of Si in the phase is certainly below 0.2%.

4. Summary

Effects of Si solid solution in Fe substrate on the formation of Fe–Zn intermetallic phase layers between the Fe–Si substrate and liquid Zn at 450°C were investigated using a combinatorial technique. The main results obtained are as follows:

1) The formation of ζ-FeZn₁₃ layer was promoted by Si solid solution up to 2 at.% in the Fe substrate but retarded by further Si solid solution. The formation of δ₁-FeZn₁₀₋₁₅ phase and Φ-FeZn₁₀ phase was retarded by Si solid solution up to 10 at.%.

2) The amount of Fe dissolution into the liquid Zn region shows a maximum at the Si content of ~3% in the substrate.

3) The Fe content in the δ₁ phase increases by solid solution of Si into the substrate in the early stage of annealing.

4) The Si content in the δ₁ phase decreases with increasing annealing time.

5) The results obtained suggest that the retardation of the δ₁ phase formation by Si solid solution is caused a difficulty in the nucleation of δ₁ phase at Si contents less than 3 at.% and by a decrease in the rate of Fe dissolution at higher Si contents.

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