Effect of oxide species and bath temperature on reactions in a galvanizing bath of Si-containing steel

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Reaction behavior was investigated in a galvanizing bath between Si-containing steel and molten Zn, in order to understand the influence of Si oxides and solute Si on galvanizing reactions. For the 0.2Si steel, only Mn2SiO4 formed on the surface of the substrate after reduction annealing. After galvanizing, the Fe amount in the coatings slightly increased with the rise of the bath temperature. In contrast, the Al amount at the substrate/coating interface (interfacial Al) decreased. As such behavior is similar to 0.01Si steel, it was suggested that the influence of Mn_2SiO_4 on a galvanizing reaction is small. For the 1.2Si steel, on the other hand, SiO2 formed on the surface of the substrate in addition to Mn_2SiO_4 after reduction annealing, and the galvanizing reaction was quite different from other kinds of steel. Although both the Fe in the coatings and interfacial Al were much lower below 450ºC, the Fe in the coatings increased sharply with a rise in bath temperature to more than 460ºC. As SiO_2 was detected on the coating/substrate interface, even after galvanizing at 470ºC for the 1.2Si steel, it was considered that SiO_2 exhibits a barrier effect on the reaction in the bath.

Furthermore, for the 1.2Si steel, the Fe-Zn compounds seemed to form easily compared to other kinds of steel. It was implied that the balance of stability between the Fe-Zn compounds and Fe-Al compounds was changed by the solute Si in the substrate in addition to Si oxides.

Keywords: Si-containing steel, high-strength steel, selective oxidation, galvanizing, Fe-Al compounds, Fe-Zn compounds, SiO_2, Mn_2SiO_4, reaction in the bath

INTRODUCTION

Recently, due to increased demand for automobile safety, the use of high-strength steel has become necessary in order to achieve both lightweight design and crash safety. Among the various kinds of high-strength steel available, multiphase steel, such as DP steel and TRIP steel, exhibit an excellent strength-elongation balance. In the case of cold-rolled steel, Si is an ideal element to use when producing such multiphase steel. On the other hand, galvannealed steel (GA) has been widely used for automotive bodies from the perspective of corrosion resistance. However, when Si is added to the substrate of GA, problems, such as bare spots on the coatings and a galvannealing delay, are seen. Therefore, Si-containing GA steel is quite difficult to produce.

Recent intensive investigations [1–3] have showed that Si-containing oxides (hereinafter referred to as “Si oxides”), which are formed during reduction annealing, exhibit poor wettability with molten Zn, causing bare spots. However, the mechanism for the delay of galvannealing has not yet been clarified despite that some theories [4–6] have proposed. Recently, authors [7] proposed that though Si oxides certainly can delay an alloying reaction, the galvannealing rate is still low, even for Si-oxide-free substrate in the case of high-Si steel.

To solve the mechanisms of bare spots and galvannealing delay, it is crucial to understand the galvanizing reaction in a bath between substrate with Si oxides/solute Si and molten Zn, firstly. In the case of mild steel, the following theories concerning a reaction in a galvanizing bath have been commonly proposed:

1) Fe dissolves from substrate into molten Zn immediately after dipping.
2) Dissolved Fe crystallizes into the Fe-Al compounds at the substrate/molten Zn interface at first, and then the compounds inhibit further Fe dissolution from the substrate.
3) Extra Fe forms the Fe-Zn compounds on the Fe-Al compounds.

In this study, the galvanizing reaction of Si-containing steel, especially the formation behavior of Fe-Zn/Fe-Al compounds, were focused on. The purpose of this study is to investigate the influence of Si oxides and solute Si on galvanizing behavior.

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EXPERIMENTAL

Sample preparations

The steel used as substrates in this study consisted of cold-rolled steel sheets with the chemical compositions listed in Table 1. A laboratory hot-dip galvanizing simulator was used to

Steel	C	Si	Mn
0.01Si	0.001	0.01	0.1
0.2Si	0.1	0.2	1.5
1.2Si	0.1	1.2	1.5

TAB. 1 ***Steel compositions used as substrates (mass%).***

Composizioni degli acciai utilizzati come substrato (massa%).

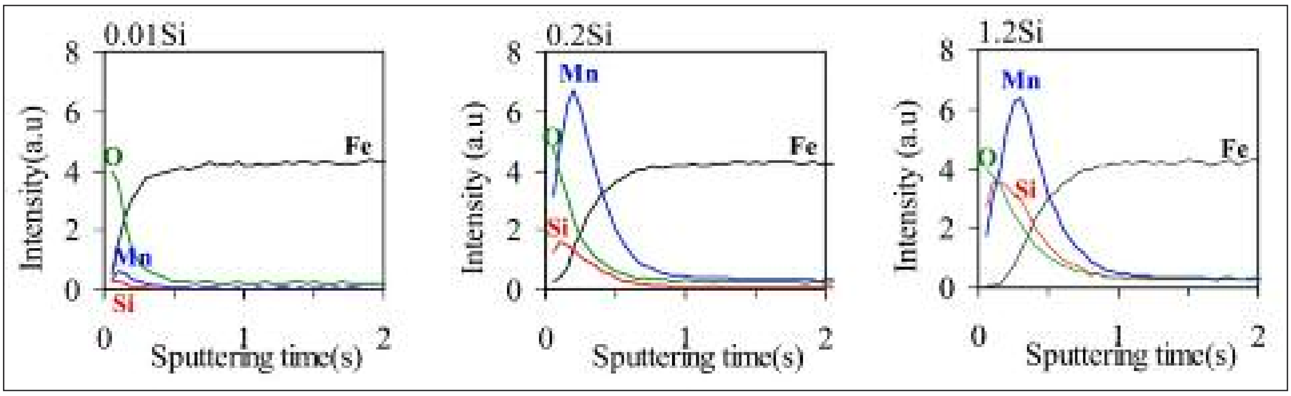

FIG. 1 ***GDS depth profiles of annealed specimens.***

Profili di profondità GDS dei provini ricotti.

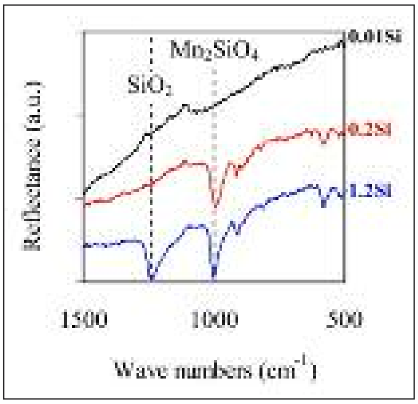

FIG. 2
FT-IR RAS spectra of annealed specimen.

Spettri FT-IR RAS dei provini ricotti.

compose the galvanizing tests. First, the substrates were annealed in a reduction atmosphere of N_2-5vol.%H_2 at 800ºC for 60 s. Then, the substrates were dipped in a Zn-0.13mass%Al-0.03mass%Fe bath for 3 s immediately after annealing. Bath temperatures were controlled to 430, 450, 460, and 470ºC, respectively. After that, annealed specimens and galvanized specimens were analyzed.

Analysis of substrates and coatings

Glow Discharge Spectroscopy (GDS) and Fourier Transform Infra-Red Spectroscopy (FT-IR) were used to analyze the surface oxides of the annealed specimens. Galvanized coatings were dissolved in a 10vol.% HCl solution containing a 0.2vol.% inhibitor. Then, the Fe amount in the coatings was measured using Inductively Coupled Plasma Spectroscopy (ICP). On the other hand, in order to expose the Fe-Al compounds at the coating/substrate interface, galvanized coatings were dissolved electrolytically at -650 mV versus an Ag/AgCl electrode in a 13mass%NH_4Cl solution. Then, the Al amounts remaining on the substrate (interfacial Al) were measured using X-ray Fluorescence Spectroscopy (XRF).

The cross-sectional microstructures of the galvanized specimens were observed by optical microscope (OM) and a Field Emission Scanning Electron Microscope (FE-SEM).

The surface morphology of the Fe-Zn compounds was observed using FE-SEM after the dissolution of the η phase in the 0.5vol%HCl solution.

FT-IR was also used to analyze the surface oxides of galvanized specimens after dissolution of the entire coating.

RESULTS

Surface analysis of annealed specimens

Figure 1 shows the GDS depth profiles of the substrates after reduction annealing. For the 0.2Si steel and 1.2Si steel, Mn and Si, and O were enriched on the surface. The Si peak height was higher for 1.2Si steel than 0.2Si steel, although the Mn peak heights were almost the same. Figure 2 shows the FT-IR RAS spectra of the specimens after annealing. Peaks at 1,000 cm^{-1} were attributed to Mn_2SiO_4, and peaks at 1,250 cm^{-1} were attributed to SiO_2 [8]. For the 0.01Si steel, no oxides were detected. For the 0.2Si steel, only Mn_2SiO_4 was detected, while both Mn_2SiO_4 and SiO_2 were detected for the 1.2Si steel.

Change of coating chemistry and microstructure

Figure 3 shows the change of the Fe in the coatings as a function of the bath temperature. It is considered that the Fe in the coatings refers to the Fe amount dissolved from substrate into the bath during dipping. For the 0.01Si steel and 0.2Si steel, the Fe in the coatings slightly increased with the rise of the bath temperature up to 460ºC. Only for the 0.01Si steel, the Fe in the coatings sharply grew at 470ºC. For the 1.2Si steel, on the other hand, the Fe in the coatings was much lower when the bath temperature was below 450ºC, but rose rapidly at more than 460ºC.

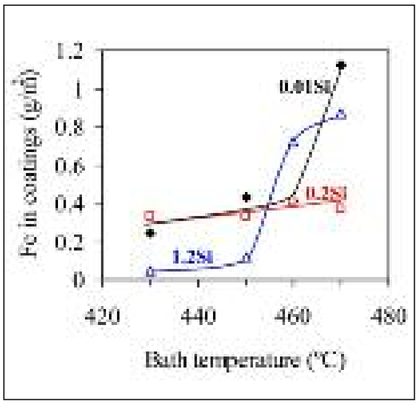

FIG. 3
Relationship between the Fe in the coatings and bath temperature.

Rapporto fra Fe nel rivestimento e temperatura del bagno.

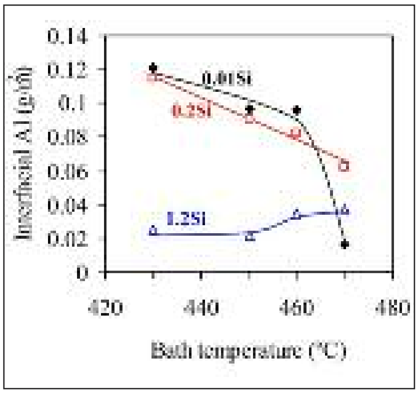

FIG. 4
Relationship between interfacial Al and bath temperature.

Rapporto fra Al interfacciale e temperatura del bagno.

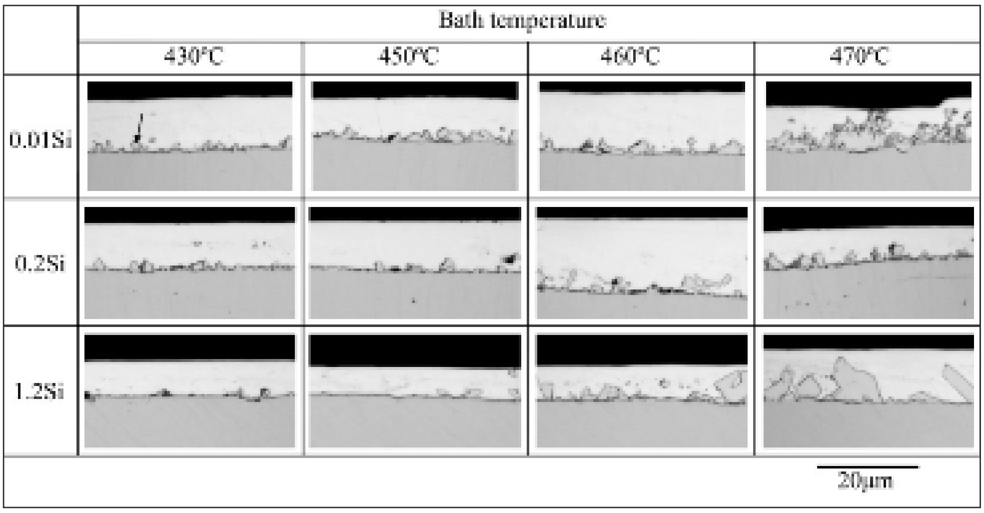

FIG. 5
Cross-sectional OM images of galvanized specimens.

Immagini al microscopio ottico della sezione trasversale di provini galvanizzati.

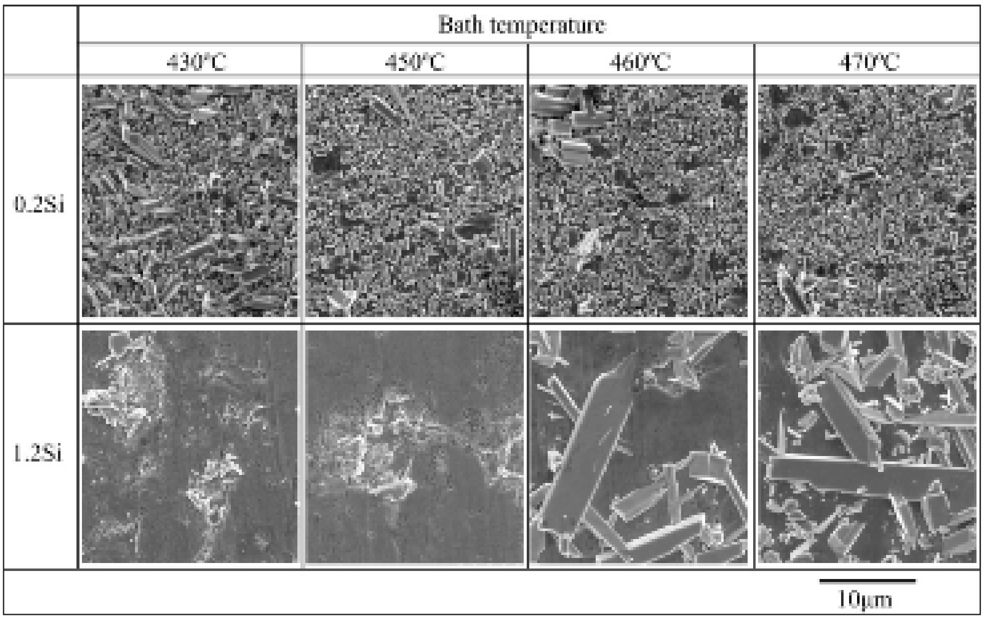

FIG. 6
Surface morphology of Fe-Zn compounds.

Morfologia superficiale di composti Fe-Zn.

Figure 4 shows the change of the interfacial Al as a function of the bath temperature. It is considered that interfacial Al refers to the Al amount contained in the Fe-Al compounds that formed in the bath during dipping. For the 0.01Si steel, interfacial Al decreased with the increase of the bath temperature, and then hardly remained at 470ºC. For the 0.2Si steel, like the 0.01Si steel, the interfacial Al declined with the rise of the bath temperature, but still existed at 470ºC–unlike 0.01Si steel. For the 1.2Si steel, however, the interfacial Al was much lower when the bath temperature was less than 450ºC, but it grew slightly at more than 460ºC–opposite to the other steel.

Figure 5 shows the cross-sectional images of the galvanized specimens as observed by OM. For the 0.01Si steel, changes of the microstructures with the increase of the bath temperature was slight–up to 460ºC–and columnar compounds at the substrate/coating interface (arrowed) were believed to be Fe-Zn compounds. (Throughout this paper, these columnar phases are considered to be Fe-Zn compounds as long as no annotation exists.) At 470ºC, the outburst structure was observed locally. For the 0.2Si steel, there seemed to be no big difference in the morphology and distribution of Fe-Zn compounds, even though the bath temperature was raised. For the 1.2Si steel, the Fe-Zn compounds were few at less than 450ºC, but coarse Fe-Zn compounds existed at more than 460ºC, in contrast.

Influence of Si oxides

Figure 6 shows the surface morphologies of the Fe-Zn compounds that were observed in the coated specimens after the dissolution of the phase. For the 0.2Si steel, the change of the morphologies of the Fe-Zn compounds with the variation of the bath temperature was not clear. For the 1.2Si steel, Fe-Zn compounds existed quite locally up to 450ºC. On the other hand, the size of the Fe-Zn compounds became coarse at more than 460ºC.

Figure 7 shows the FT-IR RAS spectra taken from the galvanized

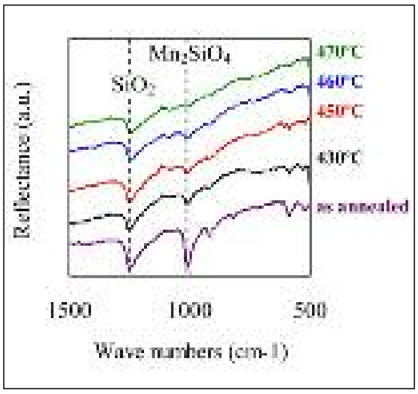

FIG. 7
FT-IR RAS spectra of galvanized 1.2Si steel after dissolution of the coatings.

Spettri FT-IR RAS dell'acciaio zincato 1.2Si dopo dissoluzione del rivestimento

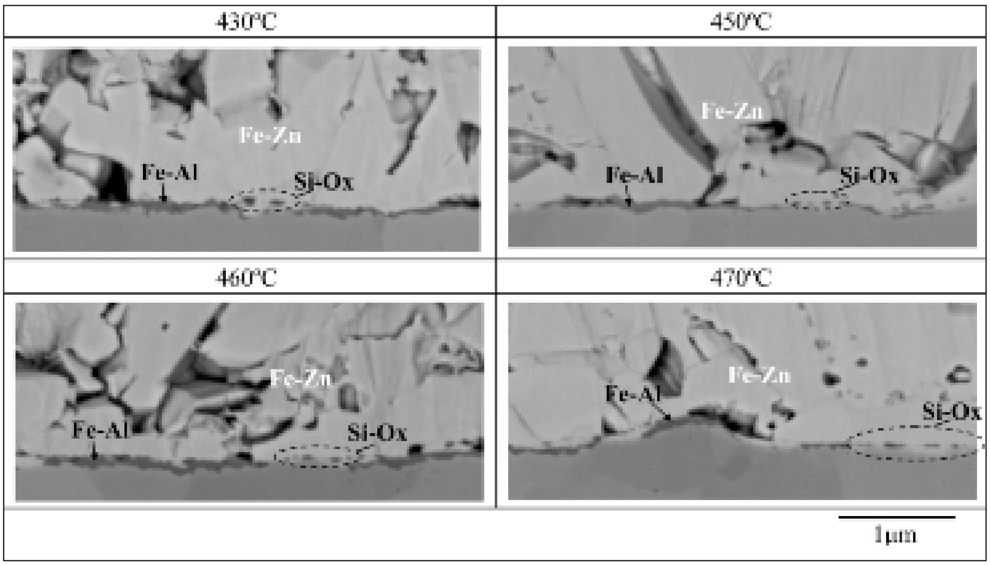

FIG. 8
Cross-sectional SEM microstructure of galvanized 0.2Si steel.
Microstruttura al SEM della sezione trasversale dell' acciaio 0.2Si galvanizzato.

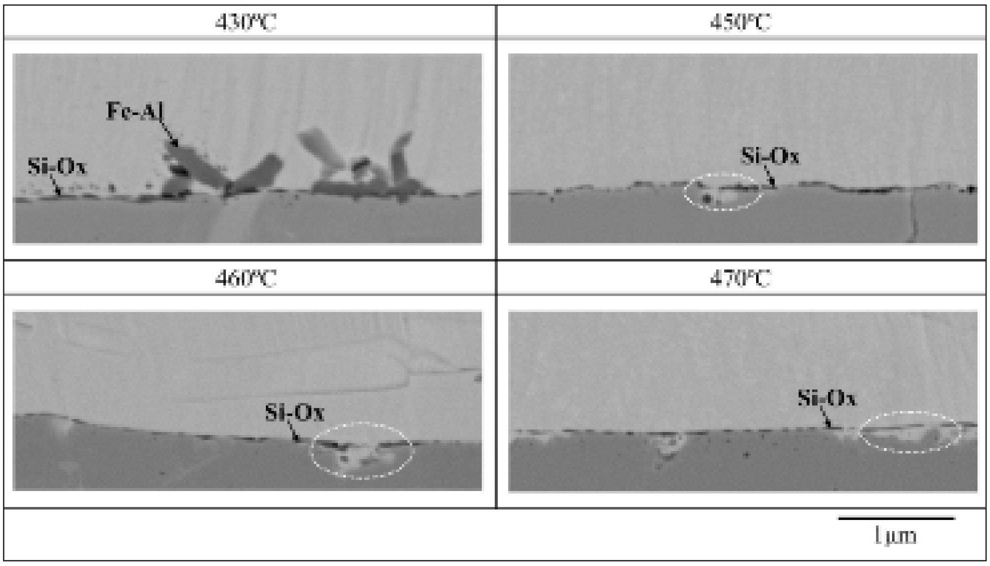

FIG. 9
Cross-sectional SEM microstructure of galvanized 1.2Si steel.
Microstruttura al SEM della sezione trasversale dell' acciaio 1.2Si galvanizzato.

1.2Si steel after the dissolution of the entire coating. For the 1.2Si steel, peaks from Si oxides were detected for the substrate galvanized at any bath temperature. The peak heights of Mn_2SiO_4 became lower with the rise of bath temperature; then there was no peak from Mn_2SiO_4 at 470ºC. However, the peak from SiO_2 still survived even after galvanizing at a bath temperature of 470ºC. Although the same analyses were performed for the 0.01Si steel and the 0.2Si steel, no peaks of Si oxides were detected at any bath temperature.

Figure 8 shows the cross-sectional SEM microstructure for the galvanized 0.2Si steel. At 430ºC, Fe-Al compounds formed at most of the substrate/coating interface. Si oxides that were captured in the Fe-Zn compounds were also observed in some areas. At 450–470ºC, the area where the Fe-Al compounds formed reduced with the increase of bath temperature. In contrast, the area where the Si oxides were captured in the Fe-Zn compounds increased. At any bath temperature, no evidence of residual Si oxides at the initial substrate/coating interface was found.

Figure 9 shows the cross-sectional SEM microstructure for the galvanized 1.2Si steel. Compared to the 0.2Si steel, the microstructure was very distinctive at a bath temperature of 430ºC; columnar Fe-Al compounds formed from the substrate/coating interface locally. Except for the area where Fe-Al compounds formed, Si oxides remained at the initial substrate/coating interface. These results corresponded to the FT-IR spectra (Fig.7). At 450–460ºC, hollow areas (circled) where Si oxides were supposed to be captured in the coatings were observed. At 470ºC, such hollow areas on the substrate were spread.

DISCUSSION

In this study, the galvanizing reaction of Si-containing steel was investigated and the following results were obtained:

1) The amount and morphology of Fe-Al/Fe-Zn compounds that formed during galvanizing changed with the variation of the bath temperature; and
2) The situation of the change differed according to the Si content in the substrate and species of Si oxides present.

The reason for such results is discussed below.

Change of stability of Fe-Al/Fe-Zn compounds

From the results of the chemical analyses, it was considered that the increase of the Fe amount that was dissolved into the bath was minimal, regardless of the bath temperature for the 0.01Si steel and 0.2Si steel (Figure 3, except for the plot of the 0.01Si steel at 470ºC). The reason for this was believed that the diffusion coefficient of the Fe in the molten Zn did not change substantially with the rise of the bath temperature from

430–470ºC. In contrast, the amount of Fe-Al compounds that formed at the substrate/coating interface when galvanizing was supposed to decrease with the increase of the bath temperature (Figure 4). The reason for this was believed to be due to the fact that Fe-Al compounds would be more stable at lower temperatures for the Zn bath composition used for galvanizing, while the relative stability of Fe-Zn compounds would become higher with the increase of the bath temperature [9].
In contrast, for the 1.2Si steel, even though the galvanizing reaction hardly occurred at a bath temperature of 430ºC and 450ºC, the Fe amount dissolved into the bath increased rapidly at more than 460ºC, and then the amounts of the Fe-Zn increased. From these results, it was supposed that the influence of Si oxides and solute Si on the galvanizing reaction was dominant for the 1.2Si steel.

Effect of species of Si oxides

For the 0.2Si steel, although Mn_2SiO_4 formed on the surface of the substrate after reduction annealing, the galvanizing reaction was similar to that of the 0.01Si steel. In other words, the influence of Mn_2SiO_4 on the galvanizing reaction was small. From the SEM microstructure (Figure 8), it was supposed that since Mn_2SiO_4 was captured into the compounds during dipping, the influence on the galvanizing reaction would become much less.
In contrast, for the 1.2Si steel, as SiO_2 survived at the surface of the substrate even after galvanizing (Figure 7), SiO_2 was believed to have a large barrier effect on the reaction between the substrate and molten Zn. Moreover, it was expected that the barrier effect would become much larger at a lower bath temperature, as the Fe in the coatings was low, below 450ºC.

Galvanizing reaction for high-Si-containing steel

For the 1.2Si steel, even though the Fe in the coatings was higher than the 0.2Si steel, at more than 460ºC, the interfacial Al was lower than the 0.2Si steel. This suggested that, for the 1.2Si steel, the stability of the Fe-Zn compounds became relatively higher when compared to the Fe-Al compounds through the following two possible hypotheses: (a) Fe solubility in molten Zn declines rapidly through the dissolution of Si into molten Zn [10], or (b) the diffusion coefficient in the Fe-Al compounds falls by containing Si [11].

CONCLUSION

In this study, the influence of Si oxides and solute Si on the galvanizing behavior of Si-containing steel was investigated. As a result, the following conclusions can be drawn:

- For the 0.01Si steel, although the Fe in the coatings slightly increased with the rise of the bath temperature, the interfacial Al decreased gradually. Then at the bath temperature of 470ºC, the interfacial Al were hardly remained and the outburst structure was observed.
- For the 0.2Si steel, although Mn_2SiO_4 formed on the surface of the substrate after reduction annealing, the galvanizing reaction was similar to that for the 0.01Si steel.
- For the 1.2Si steel, both SiO_2 and Mn_2SiO_4 formed on the surface of the substrate after reduction annealing, upon which the Fe in the coatings and interfacial Al were shown to be much smaller at a lower bath temperature. At a higher bath temperature, the Fe in the coatings sharply increased while the interfacial Al rose slightly.
- For the 1.2Si steel, the morphology of the Fe-Zn compounds and Fe-Al compounds was distinctive compared to other kinds of steel. It was suggested that the species of Si oxides present or that the solute Si in substrate contributed to such behavior.

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Abstract

Effetto delle specie di ossido e della temperatura del bagno sulle reazioni in un bagno di zincatura di acciaio contenente Si

Parole chiave: rivestimenti, acciaio

In un bagno di zincatura è stata studiata la reattività tra l'acciaio contenente Si e lo zinco fuso, al fine di comprendere l'influenza degli ossidi di Si e del Si in soluzione sulle reazioni della zincatura. Per l'acciaio 0.2Si, sulla superficie del substrato si forma solo Mn_2SiO_4 dopo ricottura riducente. Dopo la zincatura, la quantità di Fe nei rivestimenti aumenta leggermente con l'innalzamento della temperatura del bagno. Al contrario, la quantità di Al all' interfaccia substrato / rivestimento (Al interfacciale) diminuisce. Poiché tale comportamento è simile a quella dell'acciaio 0.01Si, è stato suggerito che l'influenza di Mn_2SiO_4 su una reazione di zincatura sia ridotta. Per l'acciaio 1.2Si, invece, sulla superficie del substrato si è formato SiO_2 in aggiunta a Mn_2SiO_4 dopo ricottura riducente, e la reazione di zincatura è stata molto diversa rispetto agli altri tipi di acciaio. Sebbene sia Fe nei rivestimenti sia l' Al interfacciale siano molto più bassi al di sotto dei 450 ° C, l' Fe nei rivestimenti risulta aumentato nettamente con un aumento della temperatura del bagno oltre i 460 ° C. Per l'acciaio 1.2Si l' SiO_2 è stato rilevato sull' interfaccia rivestimento / substrato, anche dopo la zincatura a 470 ° C, quindi si è ipotizzato che l' SiO_2 abbia un effetto barriera sulla reazione nel bagno.
Inoltre, per l'acciaio 1.2Si, i composti Fe-Zn sembrano essersi formati più facilmente rispetto ad altri tipi di acciaio. Ciò suggerisce che il bilancio di stabilità tra composti Fe-Zn e composti Fe-Al è stato cambiato dall' Si in soluzione nel substrato oltre agli ossidi di silicio.