Effect of Si/Mn Ratio on Galvannealing Behavior of Si-added Steel

Mai MIYATA,* Yusuke FUSHIWAKI, Yoshitsugu SUZUKI, Hideki NAGANO and Yasunobu NAGATAKI
Steel Research Laboratory, JFE Steel Corporation, 1 Kokan-cho, Fukuyama, Hiroshima, 721-8510 Japan.

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The influence of the Si/Mn ratio on the galvannealing behavior of 1.5 wt% Si − 1.5~2.5 wt% Mn-added steel in the Fe oxidation-reduction process was investigated. The Si/Mn ratio of the steel affected the formation of Si-containing oxides during the annealing process. The amount of SiO_2 formed on the steel surface decreased with as the Si/Mn ratio decreased, while the amount of Mn_2SiO_4 increased. In addition, the internal oxide formed in a relatively narrow area near the surface in the lower Si/Mn ratio sample, which indicated that the content of solute Si near the surface was lower in the lower Si/Mn ratio sample. The galvannealing reaction was accelerated by decreasing the Si/Mn ratio of the steel. The species and morphology of the Si-containing oxides determined the galvannealing behavior of the Si-added steel. The Si-containing selective surface oxide affected the formation of the initial Fe–Zn intermetallic compounds (IMC) during hot-dipping in molten Zn. The formation of SiO_2 was suppressed in the sample with the lower Si/Mn ratio, which resulted in accelerated Fe–Zn IMC formation. On the other hand, solute Si in the steel affected the growth of the Fe–Zn IMC during heating in the galvannealing process. The content of solute Si was assumed to be lower in the lower Si/Mn ratio sample, which resulted in acceleration of Fe–Zn IMC growth.

KEY WORDS: Si-added steel; hot-dip galvanizing; galvannealing behavior; Si-containing oxide.

1. Introduction

In recent years, demands for automotive body weight reduction have increased. Advanced high strength steel (AHSS) is widely used in the automotive industry to reduce body weight while securing collision safety. In addition, the need for high strength hot-dip galvannealed steels to secure high corrosion resistance is also increasing. Among many strengthening elements added to steel, Si is an attractive element, as it increases the hardness of the steel without deteriorating ductility.1) However, Si has negative effects on the surface properties of galvannealed steel.

One problem is that Si causes surface defects. Because Si forms oxide at a lower oxygen potential than Fe, Si is selectively oxidized on the steel surface during recrystallization annealing, in which the oxygen potential is suppressed to a lower level to prevent Fe oxidation prior to hot-dipping in molten Zn.2,3) Since the Si-containing oxide formed on the steel surface has poor wettability with molten Zn, it deteriorates the wettability of the steel with molten Zn and causes surface defects such as bare spots which are not coated by zinc.3,4) The Fe oxidation-reduction process is one solution for manufacturing Si-added high strength galvannealed steel. In that process, the steel is heated in an oxidation atmosphere prior to recrystallization annealing to form an Fe oxide layer on the steel surface, and the Fe oxide is then reduced in the subsequent recrystallization annealing process. Since the reduced Fe on the steel surface has good wettability with molten Zn, formation of surface defects is suppressed.

Another problem caused by Si is delay of the galvannealing reaction, but the mechanism of this phenomenon has not been clarified. Many studies have been carried out to elucidate the mechanism, and some possibilities have been proposed, such as the action of the Si-containing oxide on the steel surface or the effect of solute Si in the steel.6–13) However, most previous studies focused on the influence of the Si content in the steel. Si is often added to steel together with Mn, which is also an attractive element for hardening steel. Mn easily forms a complex oxide with Si, which can be expected to affect galvannealing behavior.14,15) In addition to this issue, there have also been few studies on the galvannealing behavior in the Fe oxidation-reduction process. Therefore, in the present report, the effect of Si/Mn ratio on the galvannealing behavior of Si-added steel in the Fe oxidation-reduction process was studied to investigate the possibility of controlling the galvannealing behavior of Si-added steel by means of the steel composition.

2. Experimental Procedure

1.5 wt% Si-added steel samples with Mn contents from 1.5 wt% to 2.5 wt% were prepared in the laboratory. The chemical compositions of the steels are shown in Table 1. In the following, these steels are called 1.0Si/Mn, 0.75Si/Mn and 0.6Si/Mn according to the mass ratio of Si/Mn ratio in the steel. The steel was cold-rolled to a thickness of 1.0 mm...
and cut to dimensions of 70 mm × 180 mm. The samples were then ultrasonically cleaned in ethanol and pickled in 5 wt% HCl to remove the lubricant used in cold rolling.

The samples were heat-treated and galvanized in a hot-dip process simulator (Rhesca). Oxidation treatment was carried out in an atmosphere of 0.1 vol% O2−N2. The samples were heated at a rate of 10°C·s−1 at 800°C or 830°C and cooled to room temperature by N2 gas. For comparison, some samples were prepared without oxidation treatment. Annealing was carried out in a 10 vol% H2−N2 atmosphere at 850°C for 20 s. The samples were cooled to 460°C by N2 gas after annealing and then hot-dipped in molten Zn containing 0.130 wt% Al for 1 s. The galvanized samples were heat-treated in the air to cause the galvannealing reaction.

The galvannealing temperature used here were 520°C and 540°C, as η-phase (FeZn13) is stable below 530°C, which may cause a difference in the galvannealing behavior. The samples were heated to the galvannealing temperature in 10 s and kept at that temperature for 3 s to 30 s.

The amount of oxide was measured by the inert gas fusion infrared absorption method. Two test pieces were cut from an oxidized sample, and one was pickled to remove the Fe oxide. The difference in the amount of oxygen of the two test pieces was defined as the amount of Fe oxide of the sample. The amount of oxygen of the pickled piece was defined as the amount of internal oxide.

The surface and cross section of the samples were observed by scanning electron microscopy (SEM). Attenuated total reflection Fourier transformation infrared spectroscopy (ATR-FTIR) was used to identify the Si-containing oxide at the Fe oxide/steel interface of the oxidized samples and on the surface of the annealed samples. The area of the absorption peak was used for evaluation of the amount of the oxide, as it is proportional to the amount of the oxide on the steel surface. For cross-sectional observation, the sample was prepared by a focused ion beam (FIB) technique. The angle of the cross section was 45° tilted toward the surface. An electron probe micro analyzer (EPMA) was used to investigate the elemental distribution. To measure elemental distribution in the depth direction of the steel in a wide area, radiofrequency glow discharge optical emission spectrometry (RF-GD-OES) was used. The size of the sputtered area was 4 mm² in diameter, and the power output was 35 W. Measurement of each sample was performed sequentially.

For the observation of the initial Fe–Zn intermetallic compounds, the η-phase (Zn) of the coating was electrochemically dissolved in methanol containing 4 wt% methyl 2-hydroxybezoate, 1 wt% salicylic acid and 10 wt% KI. The coating of the galvannealed samples was dissolved in 5 vol% HCl, and the Fe content was measured by inductively coupled plasma spectroscopy (ICP).

3. Results

3.1. Oxidation Behavior of Si-added Steel

A different Fe oxidation temperature was applied to each sample to control the amount of oxide, as the amount of Fe oxide has a large effect on the galvannealing behavior of the steel in the Fe oxidation-reduction process. Figure 1 shows the amount of external Fe oxide and internal Si-containing oxide of the oxidized samples. The amounts of Fe oxide and internal oxide were almost the same in each sample. The scale of Si-added steel is composed of two layers, the Si-containing oxide on the steel itself and an outer Fe oxide layer. The Si-containing oxide was identified by FT-IR. Figure 2 shows that all samples had absorption peaks at around 1 000 cm⁻¹ and 500 cm⁻¹, which belong to Fe2SiO4 and Fe oxide, respectively.

3.2. Effect of Si/Mn Ratio on Si Oxidation during Annealing

The selective Si-containing oxide on the steel surface was identified by ATR-FTIR. Figure 3 shows the ATR-FTIR spectra of the annealed 1.0Si/Mn samples with oxidation and without oxidation treatment. The absorption peak at around 1 240 cm⁻¹ belongs to SiO2, and those at 1 000, 920, 590 and 520 cm⁻¹ belong to Mn2SiO4. The peak area of the ATR-FTIR spectra was used for the amount of the surface oxide. The absorption peaks of 1 240 cm⁻¹ and 1 000 cm⁻¹ were used for semi-quantification of SiO2 and Mn2SiO4.

Table 1. Chemical composition of steel (wt%).

| Steel   | C    | Si  | Mn  | P   | S   |
|---------|------|-----|-----|-----|-----|
| 1.0Si/Mn | 0.121| 1.45| 1.52| 0.010| 0.0006|
| 0.75Si/Mn| 0.121| 1.48| 2.02| 0.011| 0.0006|
| 0.6Si/Mn | 0.122| 1.47| 2.51| 0.011| 0.0010|

Fig. 1. Oxidation behavior of 1.5 wt% Si-added steel.

Fig. 2. ATR-FTIR spectra of oxidized samples.
respectively. Figure 4 shows the results. The results for the samples without oxidation are also shown as a comparison. The amount of SiO$_2$ increased with increasing Si/Mn ratio, while the amount of Mn$_2$SiO$_4$ decreased. Although the amount of oxide was lower in the samples with oxidation than in those without oxidation, the tendency was almost the same in the samples with and without oxidation.

Figure 5 shows the cross-sectional SEM back scattering electron images of annealed samples of 0.6Si/Mn and 1.0Si/Mn. There was an Fe layer on the surface of the steel, and a thin intermittent Si-containing oxide had formed just beneath the Fe layer. Si-containing oxides also formed along the steel grain boundaries and inside the grains. In the 1.0Si/Mn sample, the internal Si-containing oxide mostly formed along the grain boundaries. From the SEM image in Fig. 5(b), it can be seen that the Si-containing oxide show two different contrasts, light gray and dark gray. The light gray contrast corresponds to Mn$_2$SiO$_4$, and the dark gray contrast corresponds to SiO$_2$. Most of the internal oxide inside the grain seems to consist of a Mn$_2$SiO$_4$ core with a SiO$_2$ shell. In the 0.6Si/Mn sample, internal Si-containing oxides with a light gray contrast and dark gray contrast can also be observed in Fig. 5(d). However, the amount of the dark gray area was small compared with that in the 1.0Si/Mn sample. Furthermore, the size of the steel grain near the surface was smaller than that of the 1.0Si/Mn sample. As a result, the density of the internal oxide near the surface was larger in the 0.6Si/Mn sample.

Figures 6 and 7 are the results of element intensity mapping of annealed samples obtained from almost the same area as the SEM image. Both Si and Mn exist along the grain boundaries, and the intensity of both elements is low in the area around internal oxidation. The intensity of Mn is higher near the surface, while the intensity of Si is higher...
both near the surface and in deeper areas.

Since the cross-sectional observation was limited to a very local area, the element distribution in the depth direction was measured by RF-GD-OES. Figure 8 shows the RF-GD-OES profiles of the annealed samples. Si had two peaks in all the samples. One was at the surface, which
corresponded to selective oxidation, and the other was just beneath the surface, which corresponded to internal oxidation. The Si peak at the surface became higher with increasing Si/Mn ratio. On the other hand, the second peak became lower and broader with increasing Si/Mn ratio. The height of the Si peak corresponds to the amount of Si-containing oxide, and the Si peak position corresponds to the position where the Si-containing oxide forms. Therefore, these results indicate that the amount of Si-containing oxide near the surface was larger in the 0.6Si/Mn sample and the Si-containing oxide formed in a deeper area in the 1.0Si/Mn steel.

3.3. Effect of Si/Mn Ratio on Galvannealing Behavior

In order to investigate the influence of the Si-containing oxide on galvannealing behavior, the morphology of the Fe–Zn intermetallic compounds (IMC) was observed. Figure 9 shows the SEM images of the initial Fe–Zn IMC formed during hot-dipping in molten Zn. In the 1.0Si/Mn sample, there was a large area that was not covered by the Fe–Zn IMC, but as the Si/Mn ratio decreased, the number of Fe–Zn IMC increased and uncovered area decreased.

Figure 10 shows the galvannealing behavior of the samples heat-treated at 520°C and 540°C for 15 s. At both temperatures, the amount of Fe in the coating decreased with increasing Si/Mn ratio. For a detailed investigation of the growth behavior of the Fe–Zn IMC, the 0.6Si/Mn and 1.0Si/Mn samples were galvannealed for different times at 520°C and 540°C. Figure 11 shows the results. The Fe

![Fig. 9. SEM images of initial Fe–Zn IMC. (a) 1.0Si/Mn, (b) 0.75Si/Mn, (c) 0.6Si/Mn.](image)

![Fig. 10. Effect of Si/Mn ratio on galvannealing behavior of 1.5 wt% Si-added steel.](image)

![Fig. 11. Effect of galvannealing time on galvannealing reaction of different Si/Mn samples. (a) at 520°C, (b) at 540°C.](image)
content in the coating increased with increasing galvannealing time in both Si/Mn samples. However, the reaction rate of the 0.6Si/Mn sample was much higher than that of the 1.0Si/Mn sample. The difference between the amounts of Fe in the coatings of the samples became larger with increasing time, and the difference was especially large at 520°C. At both temperatures, all the Fe–Zn IMC formed on the surface was identified as $\delta$-phase (FeZn10). Figure 12 shows SEM images of the Fe–Zn IMC morphology during the galvannealing reaction at 540°C. In the 0.6Si/Mn sample, fine Fe–Zn IMC completely covered the surface, and this fine IMC seemed to grow uniformly. On the other hand, in the 1.0Si/Mn sample, there were many coarse IMC grains, and the coarse grains remained for long time.

4. Discussion

4.1. Effect of Si/Mn Ratio on Si Selective Oxidation and Internal Oxidation

Fe oxidation, which has a large effect on galvannealing behavior in the Fe oxidation-reduction process, was controlled by the oxidation temperature. The amounts of Fe oxide and internal Si-containing oxide were almost the same in all samples. Therefore, the influence of the oxidation treatment on the samples can be neglected in this investigation.

In the annealing process, Si/Mn ratio has a large effect on the formation of the Si-containing oxide. With increasing Si/Mn ratio, the amount of Mn$_2$SiO$_4$ selective oxidation decreased, while the amount of SiO$_2$ increased. The internal oxide was mainly composed of Mn$_2$SiO$_4$ near the surface region and became SiO$_2$ at deeper positions in both the 1.0Si/Mn and 0.6Si/Mn samples (Figs. 6 and 7). The internal oxide density of the 0.6Si/Mn sample near the surface was larger than that of the 1.0Si/Mn sample (Fig. 5). The results explained above are summarized in Fig. 13.

Si-containing oxide formation has been investigated extensively under various conditions. Suzuki et al. investigated the selective oxidation behavior of 1.0 wt% Si-added steel by thermodynamic calculation and showed that the results of the calculation were in good agreement with experimental data. The stable Si-containing oxide species was influenced by both the Si/Mn ratio of the steel and the oxygen potential. Under a constant oxygen potential (log$P_{O2}$/atm < −19), SiO$_2$ is stable in higher Si/Mn ratio steel while Mn$_3$SiO$_4$ or MnSiO$_3$ is stable in lower Si/Mn ratio steel. Under a constant Si/Mn ratio ($-2 < \log((Si/mass\%)/(Mn/mass\%)) < 0$), Mn$_3$SiO$_4$ or MnSiO$_3$ is stable at a higher or lower oxygen potential, and SiO$_2$ is stable in the medium oxygen potential range. Although the Si content of the steel in this experiment is different from that in the investigation by Suzuki et al., the selective oxidation behavior on the surface can be explained, qualitatively by using their results. In the case of the 1.0Si/Mn sample with an annealing dew point of $-35$°C, the Si-containing oxide which forms initially on the steel surface is SiO$_2$. As solute Si is consumed by the oxidation reaction, the Si/Mn ratio of the steel around the SiO$_2$ becomes relatively lower. Mn$_2$SiO$_4$ formation occurs when Si/Mn ratio becomes low enough to reach the stable Mn$_2$SiO$_4$ condition. The initial Si-containing oxide on the surface of the 0.6Si/Mn sample is also SiO$_2$. However, Si/Mn ratio decreases more rapidly in the 0.6Si/Mn sample than in the 1.0Si/Mn sample. Therefore, the amount of Mn$_3$SiO$_4$ is larger in the 0.6Si/Mn sample, while the amount of SiO$_2$ is larger in the 1.0Si/Mn sample.

In the case of internal oxidation, the results of this experiment were more complicated. It is well known that the equilibrium oxygen potential of SiO$_2$ is lower than that of Mn$_3$SiO$_4$. Although the actual oxygen potential in the steel cannot be measured, the oxygen potential inside of the steel is lower than that at the surface, and the oxygen potential decreases with depth. Therefore, Mn$_3$SiO$_4$ formed relatively near the surface, and SiO$_2$ formed at deeper positions. The density of the internal oxide cannot be explained from the oxygen potential. The grain size of the steel near the surface was smaller in the 0.6Si/Mn sample than in the 1.0Si/Mn sample. The internal oxide mainly formed at the grain boundary, whereby the oxygen potential is higher than inside the grain. Therefore, since the grain size of the steel near the surface was smaller in the 0.6Si/Mn sample, a larger amount of internal oxide formed near the surface in Fig. 12. SEM images of Fe–Zn IMC galvannealed with different galvannealing times at 540°C. (Online version in color.)
the 0.6Si/Mn sample. In this experiment, Si/Mn ratio also affected the structure of the steel, which in turn affected the formation of the internal oxide. As a result, it was found that the content of solute Si in the area with the internal oxide was lower than that in the higher Si/Mn ratio sample.

4.2. Effect of Si/Mn Ratio on Initial Fe–Zn Reaction and Galvannealing Reaction

Although it is known that Si addition suppresses the galvannealing reaction, the mechanism has not been clarified so far. Some possibilities have been suggested. One is the influence of Si selective oxidation on the steel surface. That is, the Si-containing oxide that forms on the steel surface may inhibit the contact between the molten Zn and the steel, which would delay the galvannealing reaction of Si-added steel. Another possible mechanism involves solute Si in the steel. Solute Si in the steel may stabilize the Fe$_2$Al$_5$ inhibition layer or delay the diffusion of Fe and Zn in the Fe–Zn IMC. In this investigation, the galvannealing behavior of Si-added steel will be discussed in two processes, namely, the formation of the initial Fe–Zn IMC during hot-dipping in molten Zn, and the growth behavior of the Fe–Zn IMC during the subsequent galvannealing heat treatment.

Figure 14 summarizes the results of the galvannealing behavior and the surface condition after annealing. The number of initial Fe–Zn IMC was small in the higher Si/Mn ratio sample and increased as Si/Mn ratio decreased (Fig. 9). The initial Fe–Zn IMC corresponds to the reactivity of the steel surface. In this experiment, the reactivity of the steel surface was determined by the Si-containing oxide that formed on the steel surface during annealing. SiO$_2$ and Mn$_2$SiO$_4$ formed on the steel surface, and the amounts of those Si-containing oxides varied depending on the Si/Mn ratio of the steel (Fig. 4). SiO$_2$ is known to form a thin amorphous layer which has a strong barrier effect on atomic diffusion. On the other hand, Mn$_2$SiO$_4$ tends to form a granular oxide which is expected to have a poor barrier effect on atomic diffusion. Therefore, it is assumed that the initial Fe–Zn IMC formed more easily on the surface with Mn$_2$SiO$_4$ than on the surface with SiO$_2$. The initial Fe–Zn IMC formation behavior in this study can be explained as follows. In the case of 1.0Si/Mn, both SiO$_2$ and Mn$_2$SiO$_4$ formed on the surface. The initial Fe–Zn IMC did not form on the surface with SiO$_2$, and these areas correspond to the bare area in Fig. 9. As the Si/Mn ratio decreased, the amount of SiO$_2$ decreased, while the amount of Mn$_2$SiO$_4$ increased, which means the reactivity of the surface became higher. In the case of 0.6Si/Mn, SiO$_2$ formation was almost completely suppressed, and as a result, Fe–Zn IMC nucleation occurred over almost the entire surface.

The growth behavior of the Fe–Zn IMC is shown in Fig. 11. The difference between the diffused Fe in the coating was small with the shorter galvannealing reaction time and increased with increasing time. Although almost the same tendency was observed at both galvannealing temperatures, the difference was larger at 520°C. In this experiment, the Fe–Zn IMC which formed during the galvannealing reaction was identified as δ$_1$-phase at both temperatures. Therefore, the difference of the galvannealing behavior with the temperature of 520°C and 540°C seems to be due to the reaction temperature. These results mean that the growth rate of the Fe–Zn IMC is attributable to the reaction at the interface between the Zn and the steel. Figure 12 shows that the steel surface was totally covered by Fe–Zn crystals at an early time in the galvannealing reaction, and the Si-containing oxide on the steel surface no longer existed. Therefore, the Si-containing oxide on the steel surface should not affect the growth behavior of the Fe–Zn IMC. This result indicates that another factor, i.e., the solute Si in the steel, affects the growth rate in the Fe–Zn reaction. As discussed above, the density of the Si-containing oxide was larger in the 0.6Si/Mn sample. This indicates that the actual Si content decreases near the surface area where Fe is used in the galvannealing reaction, and this results in suppression of the delay in the galvannealing reaction. Since the galvannealing reaction proceeds more slowly at lower galvannealing temperatures, the effect of solute Si appears more strongly in the result for the samples galvannealed at 520°C.
This result shows that solute Si affects the growth rate of the Fe–Zn IMC. The effects of Si/Mn on the Si oxidation behavior and galvannealing behavior of Si-added steel discussed above are summarized schematically in Fig. 13.

5. Conclusions

The influence of the Si/Mn ratio on the galvannealing behavior of 1.5 wt% Si-added steel in the Fe oxidation-reduction process was investigated. The Si/Mn ratio affected the oxidation behavior of Si, which has a large effect on the galvannealing behavior of Si-added steel. In the case of selective surface oxidation, the amount of SiO$_2$ increased with increasing Si/Mn ratio while the amount of Mn$_2$SiO$_4$ decreased. The species of Si-containing oxide affected the initial Fe–Zn reaction during hot-dipping in molten Zn. A smaller amount of the initial Fe–Zn IMC formed on the higher Si/Mn ratio sample, which had a larger SiO$_2$ as the Si-containing oxide, because SiO$_2$ has a strong barrier effect against the Fe–Zn reaction. In the case of internal oxidation, as Si/Mn ratio decreased, more Si-containing oxide formed near the surface in the lower Si/Mn ratio sample. As a result, the amount of solute Si in the subsurface area decreased, and this accelerated the growth of the Fe–Zn IMC on the lower Si/Mn ratio sample. Therefore, this study revealed that the galvannealing behavior of Si-added steel can be controlled by the Si/Mn ratio of the steel.

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