Influence of Si Addition on Reduction Behavior of Fe Oxide on Mn-Added Steel Sheet

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The influence of the Si content of Mn-added steel sheets on the reduction behavior of Fe oxide during oxidation followed by annealing in a 10% H₂ atmosphere simulating the Fe oxidation-reduction process was investigated using 5.2 mass% Mn steel with 0, 0.2 and 0.5 mass% added Si. Reduction of the Fe oxide was more rapid in the 0.2% and 0.5% mass% Si steels than in the 0 mass% Si steel. Because Si addition increased the proportion of hematite (Fe₂O₃) and decreased that of wustite (FeO) in the Fe oxide, the difference in reduction speed due to Si addition is thought to depend on the composition of the Fe oxide. It was suggested that reduction from hematite to magnetite (Fe₃O₄) induces larger lattice defects in the Fe oxide, resulting in a higher diffusion rate of O.

KEY WORDS: Fe oxidation-reduction process; Fe oxide composition; hematite; magnetite; lattice defect.

1. Introduction

Reduction of auto body weight has become an important issue in recent years due to environmental concerns, and use of high strength steel is seen as an effective approach to weight saving.^{1,2)} At the same time, use of galvanized high strength steel has also increased in response to more stringent corrosion protection requirements. Si and Mn are frequently added to galvanized high strength steels to acquire the requisite balance of high strength and good elongation, which is necessary for press forming. But those elements form surface oxides during recrystallization annealing, which have adverse effect on the Zn coating property.^{3,4)}

To prevent surface oxidation during recrystallization annealing, the Fe oxidation-reduction process is used in the continuous galvanizing line (CGL).⁵⁾ In this process, the steel sheet is heated in an oxidizing atmosphere for Fe before recrystallization annealing to oxidize the steel surface. The resulting Fe oxide on the sheet surface is then reduced during recrystallization annealing, and the surface is covered with reduced Fe, which limits diffusion of easily-oxidizing elements. Easily-oxidizing elements near the steel surface can also be oxidized by oxygen and water vapor supplied by reduction of the Fe oxide; this phenomenon is termed internal oxidation. These effects prevent surface oxidation and improve surface quality.

Fe oxidation of Si- and Mn-added steels has been studied extensively. It is well known that Si suppresses Fe oxidation by segregating and forming an oxide between the Fe oxide layer and the steel surface, while Mn has little effect

on Fe oxidation because Mn dissolves in the Fe oxide^{6,7)} However, few reports have examined the influence of Si and Mn on reduction of the Fe oxide, and most of that research is related to the smelting process,^{8,9)} which is characterized by high temperatures exceeding 800°C and a long reduction time of more than 1 h. Since those conditions are far from those of the Fe oxidation-reduction process in continuous annealing, in this paper, we investigated the effect of Si addition on the behavior of Fe oxidation and Fe oxide reduction under the typical time and temperature conditions of the Fe oxidation-reduction process. The specimen materials were 5 mass% Mn steel with 0, 0.2 and 0.5 mass% added Si, which has been reported as a next-generation high elongation steel.^{10–12)}

2. Experimental Procedure

Samples of 5.2 mass% Mn-added steel containing 0, 0.2 or 0.5 mass% Si were prepared in the laboratory. In the following, these steels are denoted 0% Si steel, 0.2% Si steel and 0.5% Si steel, respectively. The steels were cold-rolled to a thickness of 1.0 mm and cut to dimensions of 70 mm × 180 mm, degreased with ethanol, electrolytically degreased with 3 mass% NaOH aq and then pickled with 5 mass% HCl to clean the sample surface.

Oxidation treatment and the subsequent reduction annealing were conducted in an infrared furnace with a controlled atmosphere. First, Fe oxidation was performed using the heat cycle shown in Fig. 1(a). The samples were heated at a rate of 10°C·s⁻¹, held at 0 or 20 s at each temperature (oxidation temperature), and then cooled to room temperature with N₂ gas. Basically, the atmosphere used in oxidation treatment was 0.2 vol% O₂-N₂ with a 20°C D.P., but in one

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particular experiment, the O_2 concentration was changed from 0.1 vol% to 1.0 vol% to control the composition of the Fe oxide. In the following, the samples prepared by oxidation treatment are called Fe oxidation steels.

Next, the heat cycle used in reduction annealing is shown in Fig. 1(b). The samples were heated to 600°C at $13^\circ\text{C}\cdot\text{s}^{-1}$, followed by heating to the specified temperature (reduction temperature) in 100 s. The samples were then cooled to room temperature with N_2 gas. The atmosphere used in reduction annealing was 15 vol% H_2 - N_2 with a -35°C D.P. Short-time reduction annealing was also conducted using the heat cycle shown in Fig. 2 to investigate the initial reduction behavior. The samples which were subjected to reduction annealing are called annealing steels. The following analyses were carried out with the Fe oxidation steels and annealing steels.

Conventionally, Fe oxidation and Fe oxide reduction were quantified by measuring mass change.⁸⁾ However, measurement of mass change was not possible in this experiment, as the thickness of the Fe oxide was less than $1\ \mu\text{m}$, which was considered too small to measure. Therefore, as an alternative method, we investigated the change in the oxygen content in the steel. The oxygen content was measured by infrared absorption,¹³⁾ and the amounts of Fe oxidation and Fe oxide reduction were quantified by the increase and decrease of oxygen. The increase of oxygen per $1\ \text{m}^2$ during Fe oxidation treatment was defined as the

oxidation amount, and decrease during reduction annealing was defined as the reduction amount.

The composition of the Fe oxide was identified by X-ray diffraction (XRD). Characteristic X-rays of Cu K (alpha) were used, and the angle of X-ray incidence was 2.0° . The amount of Fe oxide was evaluated by the integrated intensity of $\alpha\text{-Fe}_2\text{O}_3(104)$, $\text{Fe}_3\text{O}_4(220)$ and $\text{FeO}(200)$.

The surface and cross section of the Fe oxide were observed with a scanning electron microscope (SEM) at an accelerating voltage of 1–5 kV. Back scattered electron (BSE) images were used to distinguish metal from oxides. The cross section of the Fe oxide was also observed with a transmission electron microscope (TEM), and energy dispersive X-ray spectrometry (EDX) was used to measure its composition.

3. Results

3.1. Effect of Si Addition on Fe Oxidation Behavior

The effect of Si addition on Fe oxidation behavior was observed as a preliminary investigation, before examining the reduction of the Fe oxide. Figure 3 shows the influence of the oxidation temperature and Si addition on the oxidation amount. The oxidation amount decreased with increasing Si addition. Figure 4 shows the XRD results for each Si-added steel when oxidized at 600°C . Here, the

Fig. 1. Heat pattern of (a) Fe oxidation and (b) annealing. (Online version in color.)

Fig. 2. Heat pattern of annealing for investigating Initial reduction behavior.

Fig. 3. Influence of Fe oxidation temperature and Si addition on the amount of Fe oxide.

Fig. 4. Relationship between Si addition and diffraction intensity of Fe oxide (Fe oxidation temperature: 600°C).

FeO intensity decreased and the Fe₂O₃ intensity increased with increasing Si addition. This tendency was substantially the same at the other oxidation temperatures. **Figure 5** shows cross-sectional TEM images of the surface of each Si-added steel when oxidized at 500°C and 550°C. A thin 30 nm layer was observed between the Fe substrate and the Fe oxide in the 0.2% and 0.5% Si steels. **Figure 6** shows the results of an EDX line analysis across the boundary of the Fe substrate and Fe oxide in the 0% and 0.5% Si steels.

The Si and O intensities were high near the thin layer in the 0.5% Si steel.

3.2. Effect of Si Addition on Reduction Behavior of Fe Oxide

To investigate the reduction behavior of the Fe oxide, reduction annealing was conducted with each Si steel. The oxidation amount of all samples was adjusted to be about 0.4 g·m⁻² as O. **Figure 7** shows the cross-sectional BSE images of the surface of each Si-added steel annealed at 650°C and 750°C with approximately 0.4 g·m⁻² as O.

Fig. 5. TEM images of the cross section of each Si-added steel oxidized at 500°C and 550°C.

Fig. 6. EDX line analysis of A-B(0%Si) and C-D(0.5%Si) in Fig. 5.

Fig. 7. BSE images of the surface of each Si-added steel annealed at 650°C and 750°C with approximately 0.4 g·m⁻² as O Fe oxide.

images of the annealing steels. At the annealing temperature of 650°C, numerous pores with a size of about 0.2 μm were observed in the 0.2% and 0.5% Si steels. **Figure 8** shows the cross-sectional BSE images and EDX results of the annealing steels. In the 0% Si steel, a thin outermost layer of reduced Fe with a thickness of 0.05–0.1 μm and a thicker underlying layer of Fe oxide were observed after annealing at 650°C, and internal oxides comprising mainly Mn were observed after annealing at 750°C. In contrast, the Fe oxide layer was not observed in the 0.2% and 0.5% Si steels, and internal oxides, mainly of Mn and Si, were observed at a deeper level than in the 0% Si steel. **Figure 9** shows the reduction amount of each Si steel. The reduction amounts of the 0.2% and 0.5% Si steels were 2.5 times larger than that of the 0% Si steel, providing a clear indication that Si addition accelerates reduction of the Fe oxide.

Since Si addition caused a pronounced change in the reduction behavior after reduction annealing, the initial reduction behavior was investigated with the heat pattern shown in Fig. 2. The 0% Si steel oxidized at 550°C and the 0.5% Si steel oxidized in 600°C were used in this experiment. **Figure 10** shows surface BSE images after heating at each temperature (cooling temperature) and quenching with N_2 . At the 500°C cooling temperature, the surface was covered with Fe oxide. However, as the temperature was increased, the Fe oxide was partially reduced 600°C, and the surface was covered with reduced Fe at 750°C. Although the surface oxide reduction speed differed slightly in the 0% and 0.5% Si steels, porosity was observed only in the 0.5% Si steel in the initial stage of reduction, and the number of pores increased as Fe oxide reduction proceeded. **Figure 11** shows the cross-sectional BSE images and EDX results around a pore in a 0.5% Si steel sample prepared with the 600°C cooling temperature.

In this figure, considerable reduction of the Fe oxide has occurred around the pore.

To investigate the effect of the Fe oxide composition on reduction behavior, reduction annealing was conducted using oxidation steels having different Fe oxide compositions. The Fe oxide composition was controlled by changing the O_2 concentration in the atmosphere. **Figure 12** shows the effect of the O_2 concentration on the Fe oxide composition of the 0.5% Si steel for the oxidation temperature of 600°C and holding time of 20 s. With increasing O_2 , Fe_3O_4 decreased and Fe_2O_3 increased. **Figure 13** shows the reduction amounts of these samples. In particular, it should be noted that the reduction amount was larger in the steel with the large composition of Fe_2O_3 , even though the oxidation amount was substantially the same in both materials.

Fig. 9. Effect of Si addition on decrease in amount of oxygen through annealing.

Fig. 8. BSE images and EDX analysis of cross section of each Si-added steel annealed at 650°C and 750°C with approximately 0.4 $\text{g}\cdot\text{m}^{-2}$ as O Fe oxide.

Fig. 10. BSE images of the surface of 0%Si and 0.5%Si steels at each stage of Fe oxide reduction.

Fig. 11. The SEM image and EDX analysis of initial reduction of Fe oxide near the pore (0.5%Si steel, cooling temperature: 600°C).

Fig. 12. Influence of O₂ concentration of Fe oxidation on diffraction intensity of Fe oxide of 0.5%Si steel oxidized at 600°C.

Fig. 13. Influence of O₂ concentration of Fe oxidation on decreasing the amount of Fe oxide of 0.5% Si steel at annealing of 650°C. (Online version in color.)

4. Discussion

4.1. Reduction of Fe Oxide by Internal Oxidation

Si addition accelerated the reduction of the Fe oxide, which will be discussed based on the change in behavior accompanying Si addition. Figure 8 showed that the amount and composition of internal oxidation with Si addition. Table 1 summarizes the internal oxidation behavior of each Si steel. In the following, reduction of the Fe oxide by internal oxidation will be discussed based on equilibrium thermodynamics.

Although the chemical compositions of the internal oxides were not identified in this experiment, based on past studies^{14–16)} investigating the internal oxides of Si- and Mn-added steels, we assumed that the four internal oxides

shown below were produced by the following equations.

The equilibrium O_2 partial pressure of each reaction was calculated from the free energy change $\Delta G^{\circ(17,18)}$ of the respective reactions. The activity of Mn and Si was assumed to be equal to the atomic concentration. **Figure 14**⁽¹⁷⁾ shows the temperature dependency of the equilibrium O_2 partial pressure of each oxide. According to Fig. 14, the O_2 partial pressure of Fe oxide is higher than those of SiO_2 , Mn_2SiO_4 , MnSiO_3 and MnO at 650–750°C. Therefore, reduction of the Fe oxide by formation of internal oxides containing Si and Mn is possible. In addition, the O_2 partial pressures of MnSiO_3 and Mn_2SiO_4 are also lower than that of MnO . This means that MnSiO_3 and Mn_2SiO_4 can form under a lower O_2 partial pressure than MnO , resulting in a thicker internal oxide layer in Si-added steel, as shown in Fig. 8. This formation of internal oxides may accelerate the reduction of the Fe oxide in Si-added steels.

The maximum reduction amount of the Fe oxide by internal oxidation is equal to the O_2 consumption by the internal oxidation reaction. Here, internal oxidation of solute Si is a concern because Si addition increases internal oxidation.

From Eqs. (2), (3) and (4), the O_2 consumption when 1 mol of solute Si is oxidized to SiO_2 , MnSiO_3 and Mn_2SiO_4 can be calculated as 1 mol, 1.5 mol and 2 mol, respectively. This means that the largest amount of Fe oxide reduction occurs in the case of Mn_2SiO_4 formation. Therefore, in this discussion, the reduction amount was calculated assuming Mn_2SiO_4 formation in the 0.2% Si steel in order to estimate the maximum reduction amount by internal oxidation. The reduction amount per unit area ($X \text{ g} \cdot \text{m}^{-2}$ as O) by oxidation of solute Si into Mn_2SiO_4 in a unit volume (1 m^3) is calculated by the following equation.

$$X = N \times \rho_{\text{Fe}} \times C_{\text{Si}} \times \frac{\text{O}_2}{\text{Si}} \quad \text{..... (5)}$$

N : Molar fraction of Si and O_2 in internal oxidation reaction (2 -)

ρ_{Fe} : Density of Fe ($7.8 \times 10^6 \text{ g} \cdot \text{m}^{-3}$)

C_{Si} : Si mass concentration in steel (0.2 mass%)

Si : Atomic weight of Si ($28 \text{ g} \cdot \text{mol}^{-1}$)

O_2 : Molecular weight of O_2 ($32 \text{ g} \cdot \text{mol}^{-1}$)

From Fig. 8, the depth of internal oxidation of the 0.2% Si steel was approximately $1.0 \mu\text{m}$ from the steel surface. Accordingly, the reduction amount of Fe oxide by solute Si in a volume of $1 \text{ m}^2 \times 1 \mu\text{m}$ is calculated as $3.6 \times 10^{-2} \text{ g} \cdot \text{m}^{-2}$ as O. This value is much smaller than the oxidation amount of $3.5 \times 10^{-1} \text{ g} \cdot \text{m}^{-2}$ as O. Therefore, reduction of the Fe oxide by internal oxidation is one cause of acceleration of the reduction of the Fe oxide, but its contribution is small.

4.2. Effect of Fe Oxide Composition on H_2 Reduction

As shown in Fig. 9, the reduction amounts in the 0.2% and 0.5% Si steel are 2 to 2.5 times larger than that in the 0% Si steel. Since this value represents the decrease of O in the steel during reduction annealing, a larger amount of Fe oxide was reduced by H_2 in the Si-added steel than in the Si-less steel. As shown in Figs. 7, 10 and 11, Si addition changed the morphology of the reduced Fe. Specifically, the reduced Fe in the Si-less steel has a solid morphology, whereas the reduced Fe in the Si-added steel is porous. In the reduction process, contact between H_2 and the Fe oxide is limited when the Fe oxide surface is covered with a layer of solid reduced Fe, as in the 0% Si steel, and this delays the Fe oxide reduction by H_2 . In contrast, the porous morphology of the reduced Fe in the Si-added steel does not display this barrier effect. Therefore, it can be inferred that this difference in morphology is responsible for the change in the reduction rate of the Fe oxide. It can also be conjectured that the reduced Fe layer is porous in the Si-added steel, but not in the Si-free steel, due to some change in the Fe oxide composition associated with Si addition. Figure 4 showed that Si addition increased the content of Fe_2O_3 while decreasing the content of FeO. A similar change due to Si addition has also been reported elsewhere,^{6,19,20)} and is thought to be due to the following mechanism: Because Si can be oxidized under a low O_2 potential, Si is oxidized preferentially and forms Si oxides between the Fe substrate and the Fe oxide in the oxidation process. This Si oxide layer suppresses outward diffusion of Fe, resulting in a relative increases in the O_2 concentration at the steel surface, which increases the oxidation number of the Fe oxide. In this experiment, segregation

Table 1. Characteristics of internal oxide of each Si steel.

		Annealing temperature (°C)			
		650	750		
	type	Depth (μm)	type	depth (μm)	
0%Si	No oxide		Mn	0.3	
0.2%Si	Si, Mn	0.3	Si, Mn	0.8	
0.5%Si	Si, Mn	0.3	Si, Mn	0.5

Fig. 14. Equilibrium oxygen partial pressure of Fe, Si, Mn and Si–Mn complex oxides. (Online version in color.)

of Si and O was detected between the Fe substrate and Fe oxide, as shown in Fig. 5. Regarding the effect of the Fe oxide composition on the reduction of the Fe oxide, Fig. 13 shows that an increase of Fe_2O_3 in the Fe oxide increases the reduction rate. This is consistent with the experimental results that Si addition increased Fe_2O_3 and reduction of Fe oxide was accelerated in the Si-added steel.

Although very few reports concerning reduction of the Fe oxide on the steel surface have been published,^{21,22)} many reports have examined hydrogen reduction of Fe oxides used to simulate iron ore. For example, in FeO reduction, when a dense layer of solid reduced Fe covered the FeO surface, Tokuda *et al.*²³⁾ reported that the reaction was limited by O diffusion in the dense reduced Fe, and as a result, reduction was delayed.

One cause of the change in the morphology of the reduced Fe by Si addition is presumably the difference in volume contraction caused by the difference in the compositions of the various Fe oxides. Therefore, the proportion of volume contraction was calculated from the density and crystal structure of Fe and Fe oxides. Fe, Fe_2O_3 and Fe_3O_4 are assumed to be perfect crystals, and FeO is assumed to be $\text{Fe}_{0.95}\text{O}$ because FeO generally has lattice vacancy.^{24,25)} Table 2 shows the calculation results, together with the crystal structure²⁶⁾ and density²⁷⁾ of each Fe oxide. The volume contraction from Fe oxide to metallic Fe is largest in the case of Fe_2O_3 , followed by Fe_3O_4 and FeO in that order. Thus, in comparison with FeO, Fe_2O_3 forms a porous substance more readily when reduced, which is consistent with the results of this research shown in Fig. 4 and Figs. 7 to 9. That is, because the proportion of FeO in the Si-less steel is large, the volume contraction in the reduction process is small, and as a result, the reduced Fe has a solid morphology. On the other hand, owing to the large proportions of

Fe_2O_3 and Fe_3O_4 in the Si-added steels, volume contraction is also large, and the reduced Fe is porous. D. H. St. John *et al.*²⁸⁾ investigated the effect of lattice vacancy concentration on the reduction behavior of FeO and reported that reduced Fe had a larger number of pores in $\text{Fe}_{0.9}\text{O}$ than in $\text{Fe}_{0.95}\text{O}$. This experimental result also showed that an increase in volume contraction changes the morphology of reduced Fe, resulting in a more porous morphology, and is consistent with the tendency observed in the present study.

Figures 12 and 13 showed that Fe_2O_3 is reduced more rapidly than Fe_3O_4 , but since the volume contraction during reduction of Fe_2O_3 and Fe_3O_4 is 52% and 53%, respectively, the difference between the two is minimal. This implies that some other cause must be responsible for acceleration of the reduction of Fe_2O_3 . Generally, the following reactions proceed sequentially in Fe oxide reduction at temperatures exceeding 570°C.

Compared to reduction of Fe_2O_3 , reduction of Fe_3O_4 seems to proceed more quickly because Fe_3O_4 can be reduced to Fe in a smaller number of reactions. However, Fig. 13 showed that Fe_2O_3 was reduced more rapidly than Fe_3O_4 . This may be attributable to a change in the lattice structure during reduction. Specifically, the lattice structure of Fe_2O_3 is a hexagonal close-packed structure, while the lattice structures of Fe_3O_4 and FeO are cubic close-packed structures, as shown in Table 2. Therefore, when Fe_2O_3 is reduced, the lattice structure must be changed through reaction (6), which may cause lattice defects in the reduced Fe_3O_4 . Assuming

Table 2. Density, structure and volume reduction rate through reduction to Fe of each Fe oxide.

	Density	Crystal structure	Oxygen coordination	Fe mass per unit volume	Volume reduction rate through reduction to Fe
unit	$\text{g}\cdot\text{cm}^{-3}$			$\text{g}\cdot\text{cm}^{-3}$	%
α -Fe	7.84	Body-centered cubic	—	7.84	—
$\text{Fe}_{0.95}\text{O}$	5.74	Sodium chloride type	Cubic	4.41	44
Fe_3O_4	5.20	Inverse spinel	Cubic	3.76	52
Fe_2O_3	5.26	Corundum	Hexagonal	3.68	53

Fig. 15. Schematic images of Fe-oxide reduction in 0%Si and Si-added steels. (Online version in color.)

this kind of defect can accelerate O diffusion and increase the porosity of the reduced Fe, reduction would be accelerated. On the other hand, since both Fe_3O_4 and FeO have cubic close-packed structures, the crystal structure does not change in reaction (7), hence lattice defects cannot be introduced. In this connection, J. O. Edstrom *et al.*²⁹⁾ also reported that the reduction rate of Fe_2O_3 is faster than that of Fe_3O_4 .

From this discussion, we concluded that the effect of Si addition on Fe oxide reduction is as shown in Fig. 15. Si addition changes the composition of the Fe oxide, increasing the proportion of Fe_2O_3 , while decreasing the proportions of Fe_3O_4 and FeO . These changes increase the number of pores in the reduced Fe and lattice defects in the Fe oxide, and this has the effect of accelerating Fe oxide reduction by H_2 .

5. Conclusion

The effect of Si addition on the reduction behavior of Fe oxide in annealing of 5.2 mass% Mn steel in a H_2 atmosphere was investigated. As a result, the following points were clarified.

(1) In Si-less steel, a layer of Fe oxide remained on the steel surface after annealing at 750°C , but in Si-added steel, virtually all Fe oxide was reduced. The morphology of the reduced Fe was solid in the Si-less steel and porous in the Si-added steel.

(2) Si addition changed the composition of the internal oxide from a Mn oxide to an Si–Mn complex oxide, and as a result, the amount of internal oxidation increased. Although this change accelerated the reduction of the Fe oxide, the amount of Fe oxide reduction by internal oxidation was negligibly small.

(3) Si addition also changed the composition of the Fe oxide, resulting in an increase in Fe_2O_3 and decreases in Fe_3O_4 and FeO . These changes increase the porosity of the reduced Fe and the number of lattice defects in the Fe oxide, and this has the effect of accelerating Fe oxide reduction by H_2 .

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