Reaction between MnO–SiO₂–FeO Oxide and Fe–Mn–Si Solid Alloy during Heat Treatment

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(Received on April 10, 2014; accepted on June 4, 2014)

The diffusion behavior of each element at the interface has to be clarified to comprehensively understand the reaction between oxide inclusions and solid steel at heat treatment temperatures. To this end, we performed diffusion couple experiments to investigate the interaction between Fe–Mn–Si alloy and MnO–SiO₂–FeO oxide. As the first step, we investigated the composition of the oxide equilibrated with the molten steel deoxidized by Mn–Si. Results indicate that the equilibrium oxide was not a binary compound of MnO and SiO₂ but a ternary compound of MnO, SiO₂, and FeO. In diffusion couple experiments, fine oxide particles and fine metal particles were observed near the interface in the alloy and in the bulk oxide, respectively, after heat treatment at 1673 K and 1473 K. This phenomenon indicated that the alloy and bulk oxide in the diffusion couple were not equilibrated at these temperatures, despite the equilibration of both phases at 1823 K. The precipitation behavior of the particles can be related to the diffusion of oxygen from the oxide to the alloy. The oxide particles were precipitated near the interface, and the Mn content in the alloy decreased in this region owing to the consumption of Mn for particle formation. The formation of metal particles and the decrease of FeO content in oxide indicate the reduction of unstable FeO in oxide at these temperatures.

KEY WORDS: inclusion; manganese silicate; heat treatment; diffusion; oxygen.

1. Introduction

Non-metallic inclusions play an important role in determining the quality of steel products, and hence have attracted significant research interest. Thus far, several studies have clarified the behavior of non-metallic inclusions in molten steel and during the solidification process. However, the quality of steel products is typically affected by the final state of the non-metallic inclusions after thermal and mechanical treatments. It has been reported that the composition of oxide inclusion changed after heat treatment from that observed in molten steel.^{1–6)} This has been particularly observed in austenitic stainless steel.

Takahashi *et al.*^{1,2)} investigated the change in the composition of inclusion by heat treatment at 1373 K and 1573 K for 18 mass%Cr–8 mass%Ni stainless steel containing about 1 mass%Mn and 0.5 mass%Si. According to their study, the composition of the inclusion changed from MnO–SiO₂ to MnO–Cr₂O₃ after heating at 1373 K, while the composition did not change by heat treatment at 1573 K. Furthermore, Takano *et al.*³⁾ investigated the effect of oxide inclusions on the grain size of steel after heat treatment. In that study, 18 mass%Cr–mass8%Ni stainless steel containing 0.7

mass%Mn and 0.4 mass%Si was heated at 1523 K for 10 h after melting at 1873 K. The steel was re-heated at 1373 K for the maximum time duration of 40 min after 65% cold working. As a result of the heat treatment process, the MnO–SiO₂ oxide inclusion changed to fine MnO–Cr₂O₃ of diameter about 0.2 μm. They concluded that MnO–Cr₂O₃ was precipitated by the decomposition of MnO–SiO₂ at 1473 K, and grain growth was suppressed by the pinning effect of these fine precipitates. Meanwhile, Shibata *et al.*^{4,5)} in our group reported that the oxide composition in Fe–10 mass%Cr alloy with low Si content changed from MnO–SiO₂ to MnO–Cr₂O₃ by heat treatment at 1473 K. In addition, the formation of MnO–Cr₂O₃ at the interface between Fe–Cr alloy and MnO–SiO₂ oxide after annealing at 1473 K was observed as a result of the diffusion couple of the solid steel and oxide. Based on these results, they made an attempt to predict the thermodynamically stable oxide, which is equilibrated with solid steel at 1473 K, and demonstrate the feasibility of changing the stable oxide from MnO–SiO₂ to MnO–Cr₂O₃ at the decreased temperature. In addition to stainless steel, researchers have just recently focused on these phenomena in plain carbon steel. For instance, Choi *et al.*⁶⁾ investigated the behavior of inclusions in Al–Ti deoxidized steel by heat treatment at 1473 K. According to their study, heat treatment induced a change in the composition of inclusions from pure Al₂O₃ to Al–Ti–Fe–

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DOI: <http://dx.doi.org/10.2355/isijinternational.54.2144>

O, from Al–Ti–O to Al–Fe–O, and from TiO_x to Fe–Ti–O, depending on the content of Al and Ti. Nevertheless, this phenomenon is relatively unexplored in plain carbon steel in comparison with stainless steel. The diffusion behavior of each element at the interface between the oxide and solid steel has to be clarified to gain deeper insights into the fundamental mechanism underlying this phenomenon. However, it is rather difficult to study the diffusion behavior of elements at the interface, as the inclusions are often too small to measure their concentration change in steel around them.

Some studies have attempted to probe into this phenomenon using diffusion couple consisting of bulk oxide and solid steel by the authors.^{7,8)} In a typical study, the diffusion couple of Fe–Mn–Si alloy and a MnO–SiO₂–FeO oxide system, which has an equilibrium relation at 1 823 K, was prepared, and heat treatments were conducted at 1 673 K and 1 473 K. After heat treatment, several fine oxide particles were observed in the alloy near the interface and concentration of Mn decreased in this region. This result suggests the diffusion of oxygen from bulk oxide. Nevertheless, the precise condition and mechanism underlying this phenomenon are still unclear. Therefore, in this study, we investigated the solid-state reaction between MnO–SiO₂–FeO oxide and Fe–Mn–Si alloy under various conditions.

For this research, the equilibrium composition of the deoxidation product in molten steel has to be known. In general, the deoxidation product of the Fe–Mn–Si alloy is considered as a binary compound of MnO and SiO₂. However, considering the oxygen activity determined by the deoxidation reaction of Si and Mn, the formation of FeO in the deoxidation product has to be considered. Given this consideration, the deoxidation product becomes a ternary compound of MnO, SiO₂, and FeO. Kojima *et al.*⁹⁾ measured the activity coefficient of elements in iron and oxide using the equilibrium between FeO–MnO–SiO₂ slag saturated by SiO₂ and molten iron at 1 823, 1 873, and 1 923 K. Fujita *et al.*¹⁰⁾ reported the equilibrium relation between FeO–MnO, FeO–MnO–SiO₂ slags and molten iron, at 1 833 K by a rotating crucible furnace. The iron and slag were melted for 40–60 min in a SiO₂ crucible or a MgO crucible. Based on the results obtained, they determined the activity of FeO, MnO, and SiO₂ in the slag and evaluated the interaction parameter of the regular solution model. In addition, they showed that the equilibrium composition of the oxide inclusion in steel deoxidized by Si and Mn, as calculated using the evaluated regular solution model, is consistent with the experimentally observed composition of the inclusion. According to their study, the inclusion contained 4–5 mass% of FeO. Similarly, Ban-ya *et al.*¹¹⁾ determined the activity of iron oxide equilibrated in a FeO–SiO₂–MnO system under H₂O–H₂ gas in an Fe crucible at 1 723 K. They demonstrated that the results could be expressed by a regular solution model, which and showed the iso-activity curve of the MnO–SiO₂ oxide. However, most of the previous experiments were conducted under a highly oxidation atmosphere. Therefore, the precise equilibrium composition of the inclusion in steel deoxidized by Mn and Si is still unclear.

Therefore, in this study, we first investigated the composition of the oxide equilibrated with the molten steel deoxidized by Mn–Si. Based on the results obtained, we determined the initial compositions of bulk oxide and solid steel for the dif-

fusion couple experiment.

2. Estimation of the Equilibrium Composition of Deoxidation Product at 1 823 K

2.1. Experimental Methods

Figure 1 shows the experimental setup used for determining the equilibrium composition of the deoxidation product at 1 823 K. The furnace was equipped with a Kanthal Super heating element and an alumina reaction tube with an inner diameter of 42 mm and a height of 1 000 mm. The temperature of the sample was measured using a Pt–6%Rh/Pt–30%Rh thermocouple, maintained at an accuracy of within ± 5 K. In the typical process, approximately 3 g of slag was charged on approximately 15 g of the alloy in the fused SiO₂ crucible with an inner diameter of 22 mm and a height of 50 mm. The alloy and slag were melted at 1 823 K under a suitable CO/CO₂ atmosphere. Following that, the crucible with the sample was removed from the furnace and quenched in water. The holding time of the sample in the furnace was varied at 30, 60, and 90 min. The content of Mn, Si, and Fe in the slag was analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). The slag composition was calculated on the basis of the assumption that FeO, MnO, and SiO₂ are oxides with stoichiometric components. The composition of the alloy was analyzed using an electron probe micro analyzer (EPMA).

First of all, chemical composition of the alloy was chosen. To determine the initial slag composition, the equilibrium relation between the binary oxide MnO–SiO₂ and Fe–Mn–Si alloy at 1 827 K was calculated using Eqs. (1) and (2), as the activities of MnO and SiO₂ have been measured beforehand.¹⁰⁾ In this calculation, the activity coefficients of Mn, Si, and FeO were assumed to be unity. Accordingly, the oxygen activity was determined, and the FeO content in the oxide was calculated using Eq. (3).

Fig. 1. Experimental apparatus used for estimating the equilibrium composition of deoxidation product at 1 823 K.

Table 1. Initial and final compositions of the alloy and oxide, as compared with the calculated equilibrium relation at 1 823 K.

	Alloy (mass%)		Slag (mass%)			P_{O_2}
	Mn	Si	MnO	SiO ₂	FeO	
Equilibrium	0.90	0.30	45.0	52.0	3.0	2.3×10^{-12}
Initial	1.0	0.3	52.6	44.4	3.0	2.3×10^{-12}
Final	0.73	0.36	46.1	50.2	3.7	

$$\Delta G^\circ = -404634 + 124.67T \text{ J/mol}^{12)}$$

$$\Delta G^\circ = -811034 + 212.614T \text{ J/mol}^{12)}$$

$$\Delta G^\circ = -23450 + 45.2T \text{ J/mol}^{13,14)}$$

As the sample was melted in a SiO₂ crucible, the oxide was saturated by SiO₂. The calculated equilibrium composition of the Fe–Mn–Si alloy and MnO–SiO₂–FeO oxide saturated with SiO₂ at 1 823 K is shown in **Table 1** with the equilibrium partial pressure of oxygen. Based on this calculation, the initial composition and partial pressure of oxygen determined by the CO/CO₂ ratio using Eq. (4) were set as shown in Table 1. The initial composition of oxide was not saturated with SiO₂. However, it was close to the equilibrium composition of the alloy, so as to reach the equilibrium composition in short time. During the experiment, the flow rate of CO and CO₂ were $165 \times 10^{-6} \text{ m}^3/\text{min}$ and $1 \times 10^{-6} \text{ m}^3/\text{min}$, respectively.

$$\Delta G^\circ = -565160 + 172.03T \text{ J/mol}$$

2.2. Results and Discussion

Figure 2 shows the change in the composition of slag and alloy with time. As is seen, equilibrium was achieved after 30 min. The composition of both phases after 90 min of treatment is listed in Table 1. It was found that the equilibrium oxide is not a binary oxide of MnO–SiO₂ but a ternary oxide containing 3.7 mass% FeO. The content of Mn and Si in the alloy and that of the MnO, SiO₂, and FeO in the oxide approximately corresponds to the equilibrium relation. **Figure 3** shows the change in the equilibrium composition of the oxide as a function of the Mn content in the alloy for 0.3 mass%Si (a) and 0.1 mass%Si (b). The corresponding re-plotted values of the equilibrium composition of alloy and slag after the experiment are shown in Fig. 3(a). As is seen, the experimental results are consistent with the calculation results. Accordingly, the equilibrium relation can be estimated using this figure for the alloy with different composition. In the diffusion couple experiment, which will be described in the forthcoming section, we selected the composition of the oxide with high sulfide capacity and low melting point, as indicated by black circles in Fig. 3(b). Besides, the equilibrium composition of the alloy was determined from this figure.

Fig. 2. Change in the composition of the alloy and slag with time.

(a) 0.3 mass %Si

(b) 0.1 mass %Si

Fig. 3. Comparison of the experimental result with the calculated equilibrium oxide composition for the alloy containing 0.3 mass%Si (a) and the determination of the oxide composition for the diffusion couple A0 based on the equilibrium oxide composition for the alloy containing 0.1 mass%Si (b).

3. Reaction between Oxide and Solid Alloy by Heat Treatment

3.1. Methodology of the Diffusion Couple Experiment

In this study, two sets of diffusion couples were prepared, as listed in **Table 2**, to observe the solid-state reaction between the oxide and alloy. In both the cases, the basic compositions of the oxide and alloy were determined by the equilibrium relation shown in Fig. 3(b). In the case of diffusion couple O, the composition of the oxide was determined without considering FeO, while in the case of diffusion couple A0, the oxide composition was determined considering both FeO and MnO–SiO₂. In either case, the composition of MnO–SiO₂ with low liquidus temperature was selected for the experiment.

In the typical process, the Fe–Mn–Si alloys were pre-melted using electrolytic iron, ferromanganese, and silicon in an arc furnace. The obtained alloy was machined into cube-shaped blocks with about 10 mm on each side. Subsequently, the MnO, SiO₂, and FeO powders were pre-melted under Ar atmosphere in an electrical resistance furnace at 1 673 K. The obtained oxide was placed in the hole that was incorporated in the alloy. Following that, the specimen and a Ti foil were sealed in a quartz tube (O.D. 12 mm, I.D. 10 mm), into which high-purity Ar gas was introduced at a pressure of 20 kPa. The Ti foil functioned as a getter to reduce the oxygen partial pressure in the tube. **Figure 4(a)** shows the photograph of the alloy block containing the oxide powder that is covered using a thin foil of the same

Table 2. Initial composition of the alloy and oxide used in the diffusion couple experiments.

Diffusion couple	Alloy (mass%)			Oxide (mass%)		
	Mn	Si	S	MnO	SiO ₂	FeO
O	1.0	0.1	0.005	57	43	0
A0	3.1	0.1	0.009	66	31	3

Fig. 4. Photograph of the diffusion couple (a) and the specimen sealed in a quartz tube (b).

alloy. The specimen sealed in the quartz tube is shown in Fig. 4(b). The specimen was heated at 1 623 (O) or 1 673 K (A0) for 10 min to melt the oxide. To ensure effective interaction between the alloy and oxide, the heating temperature was maintained at approximately 50 K higher than the liquidus temperature of each oxide. In some cases, the heating time was prolonged for 30 min. After the melting of oxide, the quartz tube containing the sample was quenched in water. Subsequently, the sample was heat treated at 1 473 K for 10 or 50 h. The temperature of the furnace used in this study was controlled using a proportional integral differential controller. After the second heat treatment, the sample was once again quenched in water. The cross section of the interface between the alloy and oxide was analyzed using EPMA. In this study, the oxide which consists of the diffusion couple is called bulk oxide.

3.2. Results

Figure 5 shows the EPMA image of the cross section at the interface between the alloy and bulk oxide after heat treatment at 1 623 K for 10 min ((a); O-0) and that of the specimen heat-treated at 1 473 K for 10 h after 1 623 K for 10 min ((b); O-10). As can be seen, the sample heat treated at 1 623 K for 10 min (Fig. 5(a)) shows a uniform glassy oxide phase, which is considered to be the liquid phase formed during the heating process. Besides, it can be observed that the bulk oxide is in good contact with the solid alloy. The FeO content in the oxide phases was about 1.5 mass%, which further increased to 4.1 mass% near the interface, despite the absence of FeO in the initial bulk oxide, as shown in **Table 3(a)**. Furthermore, the EPMA image of the bulk oxide heated at 1 473 K for 10 h (Fig. 5(b)) shows dark

Fig. 5. EPMA image of the interface between the alloy and oxide of the diffusion couple O after heat treatment at 1 623 K for 10 min (a), 1 473 K for 10 h after 1 623 K for 10 min (b).

and gray phases. The chemical composition of the gray phase (point 1) was close to $2\text{MnO}\cdot\text{SiO}_2$, while that of the dark phase (point 2) was close to $\text{MnO}\cdot\text{SiO}_2$, as listed in Table 3(b). The FeO content in both phases was 0.4–0.8 mass%, which further increased to 4.0 mass% near the interface. **Figure 6** shows the concentration profiles of Mn and Si in the alloy away from the interface after heat treatment at 1 623 K for 10 min and those of the specimen heat-treated at 1 473 K for 10 h after 1 623 K for 10 min. As is seen, the Mn content increased from 1 mass% to about 1.5 mass% toward the interface, and the Si content also slightly increased from 0.1 mass%. Similarly, in case of the alloy specimen heat-treated at 1 473 K for 10 h after 1 623 K for 10 min, the Mn and Si content increased. More quantitatively, the Mn content increased to 3.5 mass% toward the interface, while the Si content increased to about 0.5 mass%. These results indicate the diffusion of Fe from the alloy to oxide, thereby increasing the FeO content in the oxide after heat treatment. That apart, Mn and Si also diffused from the oxide to the alloy, contributing to an increase in the content

Table 3. Composition of the bulk oxide in the diffusion couple O after heat treatment at 1 623 K for 10 min (a), 1 473 K for 10 h after 1 623 K for 10 min (b) (Analyzed points are shown in Fig. 5).

(a) (mass%)			
Analyzed point	MnO	SiO ₂	FeO
1	55	43	1.5
2	54	44	1.4
3	53	43	4.1

(b) (mass%)			
Analyzed point	MnO	SiO ₂	FeO
1	68	31	0.8
2	52	47	0.4
3	55	41	4.0

of these elements in the alloy near the interface. As indicated earlier in the section 2, the equilibrium molten oxide at 1 823 K contained about 3 mass% of FeO. This result substantiates the fact that the solid oxide, which is in equilibrium with solid steel, is not a binary oxide of $\text{MnO}\text{--}\text{SiO}_2$ but is a ternary oxide of $\text{MnO}\text{--}\text{SiO}_2\text{--}\text{FeO}$.

Figure 7 shows the EPMA images of the cross section at

Fig. 6. Change in Mn and Si contents in the alloy with distance from the interface of the diffusion couple O after heat treatment at 1 623 K for 10 min (a), 1 473 K for 10 h after 1 623 K for 10 min (b).

Fig. 7. EPMA image of the interface between the alloy and oxide of the diffusion couple A0 after heat treatment at 1 673 K for 10 min (a), 1 673 K for 30 min (b), 1 473 K for 10 h after 1 673 K for 10 min (c), and 1 473 K for 50 h after 1 673 K for 10 min (d).

the interface between the alloy and bulk oxide of the diffusion couple A0 after heat treatment at 1 673 K for 10 min; A0-0 (a), 1 673 K for 30 min; A0-0 (30) (b), 1 473 K for 10 h after 1 673 K for 10 min; A0-10 (c) and 1 473 K for 50 h after 1 673 K for 10 min; A0-50 (d). The melting point of the bulk oxide is about 1 613 K; hence, the bulk oxide heat-treated at 1 673 K should be observed as a uniform glassy oxide phase. However, dark striped patterns were observed in the bulk oxide heat-treated at 1 673 K for 10 and 30 min, as shown in Figs. 7(a) and 7(b), respectively. The phase separation is expected to occur during quenching. In case of the bulk oxides heat-treated at 1 473 K for 10 h and 50 h, the EPMA images shown in Figs. 7(c) and 7(d) indicated the presence of dark and gray phases. Besides, the bulk oxide phase contained small bright particles, which were identified to be metallic iron containing 3–5 mass% of Mn and 0.1–0.4 mass% of Si. The chemical composition of each phase formed in the bulk oxides after heat treatment is listed in **Table 4**. The results summarized in Table 4(a) are the average values of the analysis results of three or more different points. Compared with the initial composition of bulk oxide shown in Table 2, there was no significant change in the FeO content of the bulk oxide after heating at 1 673 K for 10 min. After heat treatment at 1 473 K, the chemical composition of the dark phase was close to MnO·SiO₂, while that of gray phase was close to 2MnO·SiO₂. In both cases, the FeO content was relatively lesser than the initial content in bulk oxide. Table 4(b) shows the composition of the bulk oxide near the interface, indicated by the arrow in Fig. 7. The FeO content in the bulk oxide near the interface did not vary significantly from the average composition of bulk oxide after heat treatment at 1 673 K for 10 and 30 min. In case of the specimen heat-treated at 1 473 K for 10 or 50 h after 1 673 K for 10 min, the FeO content near the interface was 0.3–0.8 mass% higher than the average content. However, the difference in FeO content between the bulk oxide near the interface and bulk was not significantly large when compared with the diffusion couple O shown in Table 3.

Table 4. Average composition (a) and composition near the interface (b) of the bulk oxide in diffusion couples A0 after various heat treatments (Analyzed points of (b) are shown in Fig. 7).

(a) Average composition		(mass%)	
	MnO	SiO ₂	FeO
A0-0	68	29	3.4
A0-0 (30)	67	31	2.1
A0-10 (dark)	57	42	1.2
A0-10 (gray)	69	30	1.7
A0-50 (dark)	55	44	0.7
A0-50 (gray)	70	29	0.9
(b) Composition of oxide near interface		(mass%)	
	MnO	SiO ₂	FeO
A0-0	68	29	3.6
A0-0 (30)	68	30	2.2
A0-10 (dark)	55	45	2.0
A0-50 (gray)	69	29	1.2

The EPMA images indicated the presence of several small particles in the alloy near the interface. From that, we selected the so-called particle precipitation zone (PPZ), wherein more than two particles are counted in a rectangle area of 50 μm parallel to the interface and 5 μm perpendicular to the interface. Hasegawa *et al.* determined the phase diagram of a MnO–MnS–SiO₂ system at 1 523 K and 1 623 K.¹⁵⁾ The chemical composition of these particles are plotted in the phase diagram of the MnO–MnS–SiO₂ system at 1 523 K,¹⁵⁾ as shown in **Fig. 8**. The content of MnS was calculated from the analyzed content of S, assuming a stoichiometric composition of MnS. Furthermore, by subtracting the Mn content as MnS from the analyzed Mn content, the MnO content was calculated assuming stoichiometric MnO composition. In the samples heat-treated at 1 673 K for 10 min and 30 min, the main chemical composition of the particle was close to the 2MnO·SiO₂ phase, with an increase in the MnS content to about 20% after heat treatment at 1 473 K for 10 h. Upon heating at 1 473 K for 50 h, the MnS content in the particle became almost negligible. Besides, most of the particles did not exist in the liquid area of the phase diagram, although the temperature of the phase diagram was 50 K higher than that of the experimental condition.

The plot presenting the size and number of particles observed in the PPZ is shown in **Fig. 9**. The width of the counted area was equal to that of the PPZ, and the length of the counted area was 44 μm in the direction parallel to the interface. As the area measured in each case was different depending on the width of PPZ, the number of particles in 1 000 μm^2 was calculated and shown in Fig. 9. The size of the particles was mainly less than 1 μm in diameter after heat treatment at 1 673 K for 10 min or 30. Compared with A0-0, the number of the particle that are larger than 1.0 μm slightly increased after heat treatment at 1 473 K for 10 h or 50 h. **Figure 10** shows the total volume of particles in 1 000 μm^2 of the PPZ. For the calculation of volume, the particles were assumed to be spherical in shape. The radius of each sphere was considered to be one half of the measured diameter of the particle. Results indicate that the total volume of the particles increased after heat treatment time at 1 473 K.

Fig. 8. Chemical composition of the particles precipitated in the PPZ after various heat treatments on the phase diagram of MnO–SiO₂–MnS system at 1 523 K.

Fig. 9. Size distribution of the particles in the PPZ after heat treatment.

Fig. 10. Total volume of the particles in the PPZ after heat treatment.

Fig. 11. Change in Mn and Si content in the alloy with distance from the interface of the diffusion couple A0 after various heat treatments.

Figure 11 shows the Mn and Si concentration profiles in the alloy near the interface. For the point analysis of the region using EPMA, we carefully selected a location that is devoid of particles. The Mn content decreased from 3 mass% to 1.3 mass% toward the interface, while it slightly increased in the region closer to the interface by about 20 μm or less. The region in which the Mn content is lower than that in the bulk is named as the Mn-depleted zone (MDZ). In this study, the MDZ was found to increase with the heat treatment time. Upon heating at 1673 K, the Si content decreased to about 0% (almost nil) from the initial content near the interface. On the other hand, after heat treatment at 1473 K, the Si content near the interface increased gradually.

Figure 12 shows the change in the width of the MDZ and PPZ with heat treatment time at 1473 K after heating at 1673 K for 10 min. In addition, the results corresponding to heat treatment at 1673 K for 30 min have been plotted for comparison. The width of the MDZ and PPZ increased with heating time. However, after heat treatment at 1473 K for 50 h, the MDZ became larger than the PPZ. Similarly, with increase in heating time from 30 min to 10 min at 1673 K, the MDZ and PPZ increased, with the MDZ being larger than the PPZ.

Fig. 12. Change in the width of the MDZ and PPZ with heat treatment time at 1473 K.

3.3. Discussion

3.3.1. Mechanism Underlying the Formation of MDZ and PPZ

In this study, the PPZ and MDZ were formed near the interface in the alloy upon heating at 1673 K and 1473 K. This phenomenon indicates that the alloy and bulk oxide in

the diffusion couples are not in equilibrium at these conditions, despite equilibrating both phases at 1823 K. The mechanism underlying this phenomenon can be explained by considering the thermodynamics between the alloy and bulk oxide at each temperature. For the experimental condition adopted in this study, the equilibrium activity of oxygen ($a_{O^{eq}}$) in the alloy is 0.0056 at 1823 K, as calculated using Eqs. (1) and (2). In this calculation, the activities of MnO and SiO₂ were determined as 0.55 and 0.27, respectively.¹⁰⁾ Meanwhile, the equilibrium activity of FeO ($a_{FeO^{eq}}$) in the bulk oxide is calculated to be 0.031 using Eq. (3). If the thermodynamic data can be extrapolated to the lower temperature, the equilibrium activity of oxygen and FeO can be calculated at 1673 K and 1473 K. The corresponding results shown in **Table 5** suggest that the equilibrium activity of oxygen ($a_{O^{eq}}$) at 1673 and 1473 K are 0.0008 and 0.0001, respectively. The excess oxygen forms oxide in the alloy not only near the interface but also in the other positions. On the other hand, the activity of FeO at 1673 K and 1473 K is 0.009 and 0.002, respectively. In this case, FeO in the bulk oxide becomes unstable. Consequently, the excess FeO is decomposed to metallic iron, and the resulting oxygen diffuses to alloy. The formation of metallic iron particles and the corresponding decrease of FeO content in the bulk oxide, as shown in Fig. 7 and Table 4, suggest the possible reduction of unstable FeO in the bulk oxide. Therefore, the precipitation of the particles can be associated with the diffusion of oxygen from the bulk oxide to the alloy. As a result of oxygen diffusion, the particles are precipitated near the interface, facilitating the formation of the PPZ. Meanwhile, the Mn content in the alloy near the interface decreased, favoring the formation of the MDZ associated with Mn consumption.

The phenomenon pertaining to the precipitation of oxide particles via the diffusion of oxygen from the interface is similar to internal oxidation.¹⁶⁾ It is known that the internal oxidation of solute elements facilitated by the diffusion of

oxygen from surface scale results in sub-scale formation. The mechanism underlying the internal oxidation process has already been elaborated in the literature. For instance, Wagner¹⁷⁾ proposed the following equation to predict the thickness of the internal oxidation zone.

$$\xi = \left[\frac{2N_O^{(s)}D_O}{\nu N_B^{(o)}} t \right]^{1/2} \dots\dots\dots (6)$$

In the abovementioned equation, ξ indicates the depth of the internal oxidation zone; $N_O^{(s)}$ is the mole fraction of oxygen at the interface, which is determined by the solubility of oxygen in the alloy; D_O is the diffusivity of oxygen in the alloy; ν is the number of oxygen atoms per A atom in AO _{ν} oxide; $N_B^{(o)}$ is the mole fraction of the solute element in the alloy; and t is time. The values of the various parameters involved in this equation are shown in **Table 6**. In this table, the literature data^{18,19)} of the diffusion coefficient of oxygen in austenite at each temperature is listed. The solubility of oxygen was reported by Swisher *et al.*¹⁸⁾ In addition, ν was calculated by assuming the formation of pure 2MnO·SiO₂, and $N_B^{(o)}$ was calculated from the composition of the alloy used in this experiment. **Figure 13** shows the results corresponding to heat treatment at 1673 K and 1473 K, with the values of the PPZ and MDZ in this experiment. The calculation results greatly depend on the diffusion coefficient.

Table 5. Change in the activity of oxygen and FeO with temperature in equilibrium with Fe-3 mass%Mn-0.1 mass%Si alloy.

Temp.(K)	$a_{O^{eq}}$	$a_{FeO^{eq}}$
1823	0.0056	0.031
1673	0.0008	0.009
1473	0.0001	0.002

Table 6. Parameters used for calculating sub-scale layer thickness.

Oxide	ν	$N_B^{(o)}$
SiO ₂	2	0.0020
MnO	1	0.0304
MnSiO ₃	1.5	0.0324
Mn ₂ SiO ₄	1.33	0.0324

Temp.	$N_O^{(s)}$	D_O (cm ² /s) ¹⁸⁾	D_O (cm ² /s) ¹⁹⁾
1473 K	1.3×10^{-5}	5.92×10^{-6}	1.69×10^{-6}
1673 K	2.8×10^{-5}	3.08×10^{-5}	8.53×10^{-6}

Fig. 13. Comparison of the observed width of the PPZ and MDZ with the calculated sub-scale thickness at 1673 K (a) and 1473 K (b).

Nevertheless, the experimental values are still within the range of the calculated curves. In this experiment, prior to heating at 1 473 K, the diffusion couple was heated at 1 673 K to melt the bulk oxide. Therefore, in the case of the specimen heat-treated at 1 473 K, the concentration of FeO in the bulk oxide decreased, and the corresponding oxygen potential was lowered before heating. On the other hand, in Eq. (6), oxygen is considered to be supplied from the scale layer with high oxygen potential. Therefore, the observed difference between the calculated results and experimental values could be the synergistic effect of the variation of the reported diffusion coefficient of oxygen in the alloy and the difference of oxygen potential at the interface. Some amount of manganese and silicon in bulk oxide also diffused to the alloy during heat treatment as observed in Fig. 11. However, the effect of the diffusion of manganese and silicon on formation of the PPZ and MDZ do not predominate comparing with the effect of oxygen as discussed in this section.

3.3.2. Difference in the Width of MDZ and PPZ

As shown in Fig. 12, the width of the PPZ and MDZ was almost the same, after heating at 1 673 K for 10 min and at 1 473 K for 10 h. However, upon heating at 1 673 K for 30 min and at 1 473 K for 50 h, the width of the MDZ becomes greater than that of the PPZ.

As mentioned earlier in Fig. 10, the total volume of particles increased upon heating at 1 473 K for 10 h. The equilibrium activities of FeO are 0.031, 0.009, and 0.002 at 1 823 K, 1 673 K and 1 473 K, respectively. The diffusion flux of oxygen can be determined from the difference in FeO activity. Therefore, although most of the FeO is decomposed during heat treatment at 1 673 K, the diffusion of oxygen still occurs during the subsequent heat treatment at 1 473 K. This causes the increment of the total volume of particle. In terms of the size distribution, larger-sized particles were observed after heating at 1 473 K. These results suggest the possibility of the coarsening of the particles during heat treatment. Therefore, one of the reasons underlying the observed difference is the coarsening of the particles with prolonged heating time. As shown in Fig. 10, the total volume of the precipitated particles increased with the heating time at 1 473 K.

The consumption of Mn during the precipitation of oxide is considered to be the mechanism underlying the formation of the MDZ. On the other hand, the PPZ corresponds to the region wherein visible-sized particles precipitate near the interface. Considering the other mechanism associated with the difference, it is speculated that several fine particles, the size of which are too small to be observed, precipitated during heat treatment at 1 473 K. As most of the excess FeO is reduced during heat treatment at 1 673 K for 10 min, the diffusion flux of oxygen during the subsequent heat treatment is much smaller than that during the initial heating at 1 673 K for 10 min. Therefore, it can be considered that the particles precipitated at 1 473 K for 50 h or those precipitated at 1 673 K for 30 min are much finer than those precipitated at 1 673 K for 10 min. The hypothesis of the formation of small particles was further substantiated by the following calculation.

Assuming that the decrease of the average Mn content in the MDZ is $x\%$ and the mass of the MDZ is " W (kg)," the

mass of decreased Mn is calculated as " $Wx/100$ (kg)." On the other hand, assuming that the radius of spherical $2\text{MnO}\cdot\text{SiO}_2$ oxide is r (m) and the number of precipitated oxide is " n ," the total mass of Mn (" P , kg") that is consumed to form oxide can be calculated by Eq. (7),

$$P = n \cdot \left(\frac{4}{3} \right) \cdot \pi \cdot r^3 \cdot \rho \cdot (2 \times 55 / (2 \times 71 + 60))$$

$$= 9\,534 \cdot n \cdot r^3 = W \cdot x / 100, \quad \dots\dots (7)$$

where ρ is density of the oxide ($4\,182 \text{ kg/m}^3$). Using this equation, the density of the oxide particles in the MDZ (n/W , $1/\text{kg-Fe}$) can be estimated. The number of particle per $1\,000 \mu\text{m}^2$ can be estimated by converting the number of particles per unit volume to the number of particles per unit area. The calculated result is shown in Fig. 14 as a function of oxide radius for various average values of Mn decrease in the MDZ. For example, if the average decrease in Mn is 0.5%, then several hundreds of oxides particles of diameter $0.5 \mu\text{m}$ should be precipitated within the area of $1\,000 \mu\text{m}^2$. On the other hand, the observed number of particles with diameter $0.5 \mu\text{m}$ is smaller than 100 in the area of $1\,000 \mu\text{m}^2$, as shown in Fig. 9. Therefore, if the MDZ is formed by the precipitation of oxide particles, then several fine particles of smaller size have to be considered. The precise investigation of these smaller-sized particles could be performed by TEM, which will be a future focus of this study.

3.3.3. Composition of Precipitated Particles

Figure 8 shows the composition of the precipitated particles. In case of the specimen heat-treated at 1 673 K, most of the content of MnS in the precipitated particles was 10 mass% or less. With subsequent heat treatment at 1 473 K for 10 h, the MnS content increased to about 20 mass%. This phenomenon can be related to the change in the solubility of MnS in the alloy. The solubility product can be described using Eq. (8).²⁰ For the Fe–3 mass%Mn alloy, the critical content of sulfur required to form MnS at 1 673 K is 0.0085 mass%, while that at 1 473 K is 0.0010 mass%. This indicates that the precipitation of MnS was not precipitated during heating at 1 673 K, due to the decrease in Mn content by the formation of the MDZ.

Fig. 14. Density of oxide particles in the MDZ that was calculated using the mass balance of Mn.

$$\log[\%Mn][\%S]^{\gamma} = -\frac{11\,200}{T} + 5.10 \dots\dots\dots (8)^{20)}$$

Upon subsequent heat treatment at 1 473 K for 50 h, the MnS content in the particles became low. In this experiment, the content of S in the alloy was 0.009 mass% and that in the oxide was zero. Therefore, it can be realized that the S content in the alloy decreased as a result of the diffusion from the alloy to the oxide during the prolonged heat treatment.

4. Conclusions

In summary, we investigated the composition of the oxide that was equilibrated with the molten alloy deoxidized by Mn–Si at 1 823 K. Results indicate that the equilibrium oxide is not a binary oxide of MnO–SiO₂ but a ternary oxide of MnO–SiO₂–FeO.

The diffusion couple method was used to understand the solid-state reaction between the Fe–Mn–Si alloy and MnO–SiO₂–FeO oxide. When the binary oxide of MnO–SiO₂ was made to interact with the Mn–Si deoxidized steel under heating conditions, the Mn and Si content in the steel and the FeO content in the oxide increased near the interface. This result also indicates that the equilibrium composition of the inclusion formed by the deoxidation of steel by Mn and Si is not a binary compound of MnO and SiO₂ but a ternary compound of MnO, SiO₂ and FeO. When the ternary oxide of MnO–SiO₂–FeO interacted with the Mn–Si deoxidized steel under heat treatment at 1 673 K and 1 473 K, fine oxide particles and fine metal particles were formed near the interface in the alloy and in the bulk oxide, respectively. This phenomenon indicates that the alloy and bulk oxide in the diffusion couple are not equilibrated at these temperatures, despite the equilibration of both phases at 1 823 K. The precipitation behavior of the particles can be related to the diffusion of oxygen from the oxide to the alloy. The oxide particles were precipitated near the interface, with decrease in the Mn content in the alloy in this region owing

to the consumption of Mn for particle formation. The formation of metal particles and the decrease of FeO content in the oxide indicate the reduction of unstable FeO in the oxide at these temperatures.

Acknowledgments

The authors appreciate the financial support of the ISIJ Research Activity Grant of Iron and Steel Institute of Japan.

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