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Evolution of Interfacial Features of MnO-SiO₂ Type Inclusions/Steel Matrix during Isothermal Heating at Low Temperatures

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Abstract: To clarify the evolution of interfacial features between MnO-SiO₂ type inclusions and Si-Mn killed steel during isothermal heating at low temperatures, two diffusion couple samples were investigated under heat treatment at 1173 K and 1273 K, respectively. The experimental results show that the diffusion of oxygen from the oxide to the alloy is the restrictive link of the solid-state reaction between MnO-SiO₂-FeO oxide and steel matrix at low heating temperatures. With increasing heating time or temperature, more FeO in the oxide decomposed, and the resulting oxygen diffused into the alloy and reacted with Mn and Si elements. The critical heating temperature at which the interfacial reaction can occur was determined to be 1173 K. And a dynamic model that predicts the change in the width of the particles precipitation zone at low temperatures was also established based on Wagner equation.

Keywords: interfacial reaction, isothermal heating, low temperatures, oxide inclusions

Introduction

Effective control of non-metallic inclusions in steel is important for improving performance of steel products. Many researches on the removal and modification of

inclusions in molten steel have been reported [1–8]. However, some inclusions in final products may be different from that in molten steel after thermo-mechanical treatment [9–14].

Recently, much more attention has been paid to the behavior of non-metallic inclusions during heat treatment. Li et al. [15] investigated the behavior of Al-Ti-O inclusion in Fe-Al-Ti alloy during heat treatment. Due to the diffusion of Al and O elements in the inclusions during heating at 1573 K, heterogeneous irregular Al-Ti-O inclusions with Al-rich and Ti-rich parts, forming from the homogeneous spherical ones, were observed. Ren et al. [16] studied the evolution of oxide inclusions in 304 stainless steel during isothermal heating at temperatures of 1273 K to 1473 K. It's found that the MnO-SiO₂ type inclusions changed to MnO-Cr₂O₃ type inclusions after heat treatment. With increasing heat-treatment temperature or reducing inclusion size, the transformation rate of inclusions increased.

Reaction between inclusions and steel matrix during heat treatment is critical for the change in composition, morphology and size of inclusions in solid steel. Kim et al. [17, 18] revealed the interfacial reaction between Fe-Mn-Si alloy and MnO-SiO₂-FeO oxide at 1673 K and 1473 K by diffusion couple method. The FeO in the oxide reacted with the alloy elements in the steel during heat treatment, causing the precipitation of fine oxide particles in the alloy near the interface. With increasing treating time, the reaction was strengthened. Liu et al. [19, 20] employed confocal scanning laser microscopy (CSLM) to prepare diffusion couples at 1673 K, making the interfacial reaction between Fe-Mn-Si alloy and MnO-SiO₂-FeO oxide at 1473 K be better understood. However, the evolution of the interfacial reaction at low heat-treatment temperatures and the critical temperature at which the reaction can occur are still unclear.

In the present work, the solid-state reaction between MnO-SiO₂-FeO oxide and Si-Mn killed steel was investigated at 1173 K and 1273 K for different time, respectively. Based on the experimental results obtained in this study, the evolution of interfacial features between MnO-SiO₂ type inclusions and steel matrix at low heat-treatment temperature was clarified. And the critical heat-treatment temperature was also determined.

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Experimental

The experimental materials used in this study are Fe-Mn-Si alloy and MnO-SiO₂-FeO oxide, and the composition of that are shown in Table 1.

Table 1: Initial compositions of the alloy and oxide used for diffusion couple experiments.

Alloy (mass%)			Oxide (mass%)		
Fe	Mn	Si	MnO	SiO ₂	FeO
Bal.	3.1	0.1	66	31	3

Electrolytic iron, ferromanganese and silicon were used to prepare the Fe-Mn-Si alloy in a vacuum induction furnace. The mixture of reagent-grade MnO, SiO₂ and FeO powder were melted to produce the target oxide under Ar atmosphere by an electrical resistance furnace. The composition of the alloy was analyzed by an electron probe microanalyzer (EPMA). Then, the alloy was machined into a regular shape (5 mm × 5 mm × 3 mm, about 0.40 g). Meanwhile, a hole with 1.5 mm in diameter was also drilled in the alloy block to place the oxide.

Ensuring good contact between the oxide and alloy during isothermal heating is very necessary. So, in this study, a confocal scanning laser microscope (CSLM) was first employed to melt the oxide before heat-treatment experiments to prepare diffusion couple samples. The specific operation is as follows: firstly, about 0.005 g oxide (~100 mesh) was placed in the hole manufactured in the alloy block. Then the alloy containing oxide was moved to the CSLM chamber. High-purity Ar gas (> 99.999%, flow rate: 50 mm³/min) was introduced into the CSLM chamber after its vacuum pressure was lower than 5×10^{-3} Pa. Following that, the sample was heated to 1673 K at 100 K/min to melt the oxide. When the oxide was melted, the sample was immediately cooled at 1000 K/min.

To prevent the oxidation of sample during heat treatment, the diffusion couple sample, an alloy block with the same composition and a Ti foil were sealed into a quartz tube (O.D. 9 mm, L. 10 mm), into which Ar was introduced at 20 KPa pressure. The quartz tube was placed in a Si-Mo resistance furnace when actual temperature of the furnace was increased to 1173 K and 1273 K, respectively. Four diffusion couple specimens were then heat treated for different time. The specific heat-treatment conditions are listed in Table 2. After the heat treatment, the quartz tube was quenched by ice water, and the cross section of each sample was analyzed by EPMA.

Table 2: Experimental heat-treatment conditions.

Diffusion couple	Heat treatment temperature	Heat treatment time	
T1	1173 K	10 h	50 h
T2	1273 K		

Results

Interfacial features of the alloy and oxide before heat treatment

Figure 1 shows the morphology of the interface between the oxide and alloy before heat treatment at 1173 K and 1273 K (diffusion couple T-0). It's found that the oxide was contacted well with the alloy. Most of the oxide was homogenous phase, but some loose striped patterns were also observed in the oxide. It's considered that the chemical composition of partial oxide changed owing to the phase separation during cooling in the CSLM. For the alloy, the interior of the alloy was very clean. Some fine particles were precipitated near the interface, the chemical composition of which was identified as MnO-SiO₂. The Width of particle precipitated zone (PPZ) was 8 μm.

Figure 1: Morphology of the interface between the oxide and alloy before heat treatment.

Figure 2: Concentration profiles of MnO, SiO₂ and FeO in the oxide near the interface before heat treatment.

Figure 2 shows the concentration profiles of MnO, SiO₂ and FeO in the oxide near the interface before heat treatment. The chemical composition of the oxide was uniform, and which was close to 2MnO·SiO₂ phase. The mass fraction of FeO in the oxide was about 3.5%.

The variation of Mn and Si contents in the alloy away from the interface before heat treatment is shown in Figure 3. The Mn content near the interface decreased from 3.1 mass% to about 2.5 mass%. The width of the Mn-depleted zone (MDZ) was approximately 9 μm. The Si content also slightly decreased from 0.1 mass% to 0.07 mass% within 10 μm of the interface.

Figure 3: Variation of Mn and Si contents in the alloy away from the interface before heat treatment.

Evolution of interfacial features at low heating temperatures

Figure 4 shows the morphology of the interface between the oxide and alloy after heat treatment at 1173 K for (a) 10 h (T1-10) and (b) 50 h (T1-50). The morphology of the interface between the oxide and alloy was similar to that before heat treatment. The composition of the oxide was still mainly homogenous 2MnO·SiO₂. The composition of the loose dark phase in the oxide was identified as MnO·SiO₂. With increasing heating time from 10 h to 50 h, some fine metallic iron particles formed in the oxide, which mainly distributed on the MnO·SiO₂ phase (loose striped patterns). For the alloy, the number and size of the oxide particles precipitated in the alloy near the interface didn't change obviously.

The concentration profiles of FeO content in the oxide near the interface after heat treatment at 1173 K is shown in Figure 5. The FeO content in the oxide didn't change significantly, and which was only reduced from 3.5 mass% to 3.0 mass% within 25 μm of the interface after heat treatment for 50 h.

Figure 6 shows the variation of Mn and Si contents in the alloy near the interface after heat treatment at 1173 K. It can be seen that the Mn and Si contents in the alloy only decreased within approximately 10 μm of the interface after heat treatment at 1173 K. And the change in the Mn and Si contents was nearly same as that before heat treatment.

Figure 7 shows the morphology of the interface between the oxide and alloy after heat treatment at 1273 K for (a) 10 h (T2-10) and (b) 50 h (T2-50). It can be found that the oxide consisted of 2MnO·SiO₂ and MnO·SiO₂ phase. Some metallic iron particles were also observed in the oxide. For the alloy, the range of oxide particles precipitated didn't change after heat treatment for 10 h. With increasing heat-treatment time from 10 h to 50 h, more iron particles and oxide particles were found near the interface of the alloy and oxide.

The concentration profiles of FeO content in the oxide away from the interface after heat treatment at 1273 K is shown in Figure 8. After isothermal heating at 1273 K for 10 h, the FeO content in the oxide near the interface decreased from 3.5 mass% to approximately 1.8 mass%. With increasing heating time to 50 h, more FeO in the oxide was reduced.

Figure 9 shows the change in Mn and Si contents of the alloy away from the interface after heating at 1273 K. The Mn content near from the interface slightly decreased from 2.5 mass% to 2.3 mass% after heating for 10 h,

Figure 4: Morphology of the interface between the oxide and alloy after heat treatment at 1173 K for (a) 10 h and (b) 50 h.

Figure 5: Concentration profiles of FeO content in the oxide near the interface after heat treatment at 1173 K.

which was similar to the experimental results before heat treatment. With increasing heat-treatment time to 50 h, the Mn content significantly decreased to 0.5 mass%, but it increased to 2.5 mass% within 20 μm of the interface. The change in Si content was similar to that in Mn content.

Figure 10 shows the change in the width of the PPZ and MDZ with heating time. As can be seen, both the width of the PPZ and MDZ in T1 diffusion couple didn't change during heating at 1173 K. For T2 diffusion couple, the width of the MDZ increased from 9 μm to 26 μm after isothermal heating at 1273 K for 10 h, while there was little change in the width of the PPZ. With increasing heating time to 50 h, the width of the PPZ and MDZ increased to 20 μm and 100 μm, respectively.

Figure 6: Variation of Mn and Si contents in the alloy away from the interface after heat treatment at 1173 K.

Figure 7: Morphology of the interface between the oxide and alloy after heat treatment at 1273 K for (a) 10 h and (b) 50 h.

Figure 8: Concentration profiles of FeO content in the oxide near the interface after heat treatment at 1273 K.

The shape of the oxide particles precipitated in the alloy was assumed to be spherical. The total volume of oxide particles in $1000 \mu\text{m}^2$ of the PPZ is calculated and shown in Figure 11. After heating at 1173 K, the total volume of particles only increased from $2.9 \mu\text{m}^3$ to $4 \mu\text{m}^3$. However, the total volume of particles significantly increased to $10.5 \mu\text{m}^3$ after heat treatment at 1273 K for 50 h.

Discussion

The $\text{MnO-SiO}_2\text{-FeO}$ oxide equilibrated with the Fe-Mn-Si alloy at 1873 K became unstable at a lower temperature [17]. During heat treatment at low temperatures, the FeO

in the oxide decomposed, and white iron particles formed in the oxide. The resulting oxygen diffused into the alloy

Figure 9: Variation of Mn and Si contents in the alloy near from the interface after heat treatment at 1273 K.

Figure 10: Change in the width of the PPZ and MDZ with heat treatment time.

Figure 11: Total volume of oxide particles in 1000 μm² of the PPZ after heat treatment.

Figure 12: Comparison of the measured width of the PPZ with the theoretical calculations.

and reacted with manganese and silicon elements of the alloy, causing the decrease in Mn and Si contents of the alloy and the formation of fine oxide particles.

During isothermal heating, the evolution of interfacial features between the oxide inclusions and solid steel is closely related with the diffusion of oxygen from the oxide to the alloy. As shown in Figure 8, there was an obvious decrease in the FeO content in the oxide after heating at 1273 K for 10 h. While the Mn and Si contents in the alloy near the interface did not change significantly. With increasing heating time to 50 h, more oxygen diffused from the oxide into the alloy and the Mn and Si contents were reduced obviously.

Liu et al. [19] accurately estimated the width of the PPZ at 1473 K using Wagner's equation shown in eq. (1) [21]. In this study, the equation was also adopted to predict the change in the width of the PPZ at lower heating temperatures (1173 K and 1273 K).

$$\xi = \left[\frac{2N_O^{(S)}D_O}{vN_B^{(O)}} t \right]^{1/2} \quad (1)$$

where ξ is the width of the internal oxidation zone; $N_O^{(S)}$ represents the mole fraction of oxygen at the interface; D_O is the diffusivity of oxygen in the alloy; v means the number of oxygen atoms per A atom in an AO_v oxide; $N_B^{(O)}$ indicates the mole fraction of the solute elements in the alloy; t is the heating time.

As described in the Ref. [19], the same method was used to determine the parameters ($N_O^{(S)}$, D_O , $N_B^{(O)}$ and v) in eq. (1) at 1173 K and 1273 K. The calculation results of the width of the PPZ are shown in Figure 12. It can be seen that the experimental values of the width of the PPZ at 1273 K are accordance with the theoretical calculations. With increasing heating time, the width of the PPZ significantly increases. After heating at 1173 K, the experimental values of the width of the PPZ are higher than the theoretical results. This may be caused by the intense reaction between the liquid oxide and the solid alloy during pretreatment at 1673 K. Although the contacting time of the oxide and alloy at 1673 K has been reduced as much as possible through rapidly cooling, the reaction between them during pretreatment is inevitable. As shown in Figure 12, there is no obvious change in the measured width of the PPZ at 1173 K. And with increasing heating time, the increase of the theoretical width of the PPZ at 1173 K is also very slow. Therefore, it may be concluded that the critical heating temperature at which the interfacial reaction between MnO-SiO₂ type inclusions and Si-Mn killed steel could happen is 1173 K.

Conclusions

In the present study, heat-treatment experiments were performed at 1173 K and 1273 K, respectively, to investigate the evolution of interfacial features between MnO-SiO₂ type inclusions and solid steel during isothermal heating at low temperatures. Based on the experimental results, the following conclusions were obtained:

1. The critical heating temperature at which the interfacial reaction between MnO-SiO₂ type inclusions and solid steel can occur is 1173 K.
2. The diffusion of oxygen from the oxide to the alloy is the restrictive link of the solid-state reaction between oxide inclusions and steel matrix during isothermal heating at low temperatures. With increasing heating time or temperature, the reaction was strengthen.
3. A dynamic model that predicts the variation of the width of the PPZ during isothermal heating at low temperatures was established based on Wagner equation, and it proved to be valid.

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