Optimization of Steel Chemistry for MnS Precipitation on Oxide Inclusions in Si/Mn Deoxidized Steel

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A technique for optimization of steel chemistry for MnS precipitation on oxide inclusions has been developed through employing the computational thermodynamic method. The optimum composition of Si/Mn deoxidized steel was estimated to be Fe-0.1mass%C-0.1mass%Si-1.5mass%Mn-0.01mass%O-0.007mass%S. The prediction was validated by experiments using a semi-levitation melting technique. The inclusions mainly consisted of MnO-SiO₂ oxides with MnS precipitates. The observed morphology revealed a possibility of both oxide and sulfide having been precipitated as liquid phase, although the existing thermodynamic data do not support this to occur.

KEY WORDS: steel; deoxidation; inclusion; oxides; MnS precipitation; steel chemistry; optimization.

1. Introduction

Since the early 1990s, effective utilization of fine oxides as nucleation site for austenite-to-ferrite transformation of steel has attracted much attention¹⁻⁸⁾, and sulfides precipitated on oxide inclusions are considered to play an important role in providing nucleation site for intragranular acicular ferrite. In particular, oxides or inclusions that are formed during solidification in a few micrometers or smaller in size have been reported to be effective for the formation of intragranular acicular ferrite⁶⁾. Such formation of the intragranular ferrite(IGF) phase is considered to greatly contribute to ferrite grain refinement^{6,9-12)}.

Several mechanisms have been proposed to account for the way in which non-metallic inclusions enhance the nucleation of acicular ferrite¹³⁻¹⁷⁾. Manganese sulfide(MnS) precipitated on an oxide inclusion has been suggested to provide a potent nucleation site for formation of IGF^{3,13,18-19)}. Creation of Mn-depleted zone in the vicinity of MnS in the steel matrix are considered to facilitate the formation of IGF^{16,20-22)} since Mn is an austenite stabilizer.

Behavior of MnS precipitation on oxide inclusions is affected to a great extent by the chemistry of both the inclusions and the matrix steel. However, the chemistry of the inclusions that are formed during solidification is governed primarily by the steel chemistry. Therefore, it is vitally important to elucidate in a quantitative manner the interrelationship among the steel chemistry, the inclusions chemistry and the precipitation behavior of MnS on the inclusions.

In the present study, it has been attempted to develop a technique using thermodynamic computational technique to optimize the steel chemistry to result in precipitation of secondary inclusions during solidification on which MnS islands readily precipitate out during a prolonged heating process afterwards such as reheating for hot rolling. Si/Mn deoxidized structural steel has been employed for sample

computation for the optimization and the theoretically derived results were tested and proved to be valid through experiments.

2. Optimization of steel chemistry

In the present study, the optimum steel chemistry is defined as the steel chemistry that results in formation of inclusions on which MnS can readily precipitate out. Si/Mn deoxidized structural steel has been chosen for the optimization, and hence the carbon and manganese contents were predetermined to be 0.1 and 1.5 mass%, respectively. Since the number density of inclusions is important for ferrite grain refinement^{10,23-24)}, somewhat higher total oxygen content of 100ppm was chosen. Then optimum silicon and sulfur contents were estimated using thermodynamic equilibrium computation. An extensive computer software called ChemSage²⁵⁾, which has been developed for use with PC, together with solution databases provided by GTT-Technologies²⁶⁾ was employed for thermodynamic prediction. In summary, the steel chemistry to start with for optimization is Fe - 0.1 mass% C - X mass% Si - 1.5 mass% Mn - 0.01 mass% O - Y mass% S. The task on hand is now to find X and Y.

2.1 Optimization of silicon content

Inclusions or precipitates that form in Si/Mn deoxidized steel are mainly manganese silicates. Therefore, variation of the sulfur solubility of the Mn-Si-O-S system was first evaluated using thermodynamic computational technique and the results are given in **Figure 1**. These results are favorably compared with the experimental data reported by Hasegawa et al²⁷⁾. It is seen that, for all the temperatures examined, the sulfur solubility sharply increases with increasing the relative content of MnO in the system. However, there is a MnO fraction for a given temperature above which increase in the sulfur solubility with MnO

fraction becomes insignificant. It is also seen that there is a range of MnO fraction in which the sulfur solubility drastically decreases with decreasing temperature. In other words, there is a range of MnO fraction in which MnS can readily precipitate out on cooling.

Fig.1 Solubility of sulfur in Si-Mn-O-S system

Since the relative content of MnO and level of sulfur in inclusions formed in Si/Mn deoxidized steel are determined by silicon and sulfur content of the steel, respectively, it should be possible to find a steel chemistry which results in formation of inclusions whose compositions are the optimum for MnS precipitation on them. Figure 2 is the computed results of compositions of inclusions that form in a number of different steel chemistry and different temperatures. In the computation the sulfur content was fixed at 70ppm, the reason for this choice will be given shortly. It is seen that the MnO fraction in the manganese silicate inclusions is dependent to a large extent on the silicon content in the steel; the higher the Si content in the steel, the lower the MnO fraction in the inclusions. At 1,600°C the sulfur content in the inclusions is low regardless of silicon content in the steel. As the temperature decreases below 1,500°C, however, the sulfur content sharply increases until MnS precipitates out. This increase is due to solidification of steel and preferential distribution of sulfur in the liquid phase. Further decrease in temperature results in a gradual change of inclusions composition, and the sulfur content varies, but stays at the saturation limit for the given composition of the inclusions.

Fig.2 Prediction of change in sulfur solubility in MnO-SiO₂ inclusion

An important fact to be seen in Fig.2 is that the extent of the decrease in sulfur content after the initial precipitation of MnS, i.e., from point 4 to point 5, is different for different Si content in the steel. The larger the extent of decrease, the greater susceptibility of MnS precipitation. With this in mind, it can easily be seen from the figure that the results with 0.1mass% Si show the optimum condition for MnS precipitation on the inclusions.

2.2 Optimization for sulfur content

Obviously, Sulfur is required for MnS precipitation, but existence of excessive amount of sulfur should be avoided because of its harmful effect on the physical properties of steel.

The effect of sulfur content on the initiation temperature of MnS precipitation is thermodynamically evaluated and the results are given in Figure 3. In the calculation, Mn was kept at 1.5 mass%. With increasing the sulfur content, the initiation temperature of MnS precipitation increases until the sulfur content reaches about 70ppm. At this level of sulfur content, the first precipitation of MnS occurs at the solidus of the steel, 1,480°C. Since the majority of the secondary inclusions form near or below the solidus, MnS precipitation will most likely occur on the secondary inclusions of manganese silicates. at a temperature above the solidus, however, some MnS precipitations would occur independent of the secondary inclusions, because the secondary inclusions would hardly form at the temperature. Therefore, the optimum sulfur content should be around 70ppm for 1.5mass% Mn.

2.3 Thermodynamic behavior of the optimized steel on

Fig.3 Effect of sulfur content on the initiation temperature of MnS precipitation

cooling

Table 1 shows the optimized composition of steel that can best result in MnS precipitation on manganese silicate secondary inclusions. The thermodynamic behavior of this steel on cooling from 1,600°C to 1,100°C was computed and the results are given in Figure 4. It is clearly seen that the sulfur content in the inclusions increases sharply as the temperature approaches the solidus and eventually reaches the saturation limit. Further cooling results in decrease in the sulfur content in the inclusions, meaning MnS precipitating out from the inclusions. Mass balance analysis

enables it possible to predict the amount of MnS precipitated not on the inclusions, but independently in the steel matrix. Fig. 4 shows that the amount of the independent MnS should not be appreciable, in comparison with MnS precipitated on the inclusions.

Table 1 The optimum steel chemistry for MnS precipitation on MnO-SiO₂(estimated).

C	Si	Mn	S	O
0.1	0.1	1.5	0.07	0.001

Fig.4 Precipitation behavior of MnS during cooling for the optimized steel chemistry(estimated).

From Fig. 4 it may be possible to draw the following summary:

- 1) There exist some primary inclusions formed at temperatures above the liquidus, but the majority of the inclusions are secondary ones since they form during solidification.
- 2) The sulfur content in the inclusions is far from saturation until the temperature has been lowered close to the solidus, at which the inclusions become saturated with sulfur.
- 3) Further decrease in temperature results in MnS precipitation mostly on the existing inclusions. The amount of independent MnS is not appreciable.

In general, primary inclusions are large in size, and harmful to the physico-chemical properties of steels in most cases. The secondary inclusions which form during solidification are small in size (a few micrometers or smaller in diameter), and are beneficial, for instance, for grain refinement.

3. Experimental

In order to confirm the validity of the optimization technique above-mentioned, experimental work was undertaken by employing the semi-levitation technique which enables the removal of primary inclusions to be possible with ease.

3.1 Master Alloy Preparation

About 300g of electrolytic iron with 0.33g of Fe₂O₃

powder and 0.05g of FeS powder was melted by induction heating in a magnesia crucible of 40mm in diameter and of 100mm in depth under Ar gas atmosphere. After stabilizing the melt at 1600°C, ferro-carbon of 6wt.%C was added aiming at 0.1%C in the steel melt. Then pure metal of Mn and Si were added subsequently.

The melt was held for 30s after deoxidation and then about 100g of melt was sucked into fused silica tubes(5mm ID) to make samples in a rod shape. The composition of the rod specimen is given in Table 2.

3.2 Semi-levitation Experiment

Samples for semi-levitation experiment were prepared by cutting the rod specimen. The weight of each sample was adjusted to 0.75g. The schematic diagram of experimental apparatus employed in the semi-levitation experiment is shown in Figure 5. The samples were melted on an alumina substrate using induction heating (200kHz) in an atmosphere of He and CO gas mixture. CO gas was used to prevent oxidation reaction between oxygen and carbon in the melt from taking place. By controlling the partial pressure of CO in the atmosphere in an adequate range, the oxygen content in the samples could be maintained to the desirable value during semi-levitation experiment.

Table 2 The composition of master alloy of rod specimen

C	Si	Mn	S	O
0.11	0.11	1.56	0.0072	0.0099

Fig.5 Schematic diagram of experimental arrangement for semi-levitation melting.

After melting, the melt was held at 1,600°C in the period of 1 min., and then cooled to 850°C at a predetermined cooling rate using a PID controller. Three different cooling rates, i.e., 50°C/min., 200°C/min. and 500°C/min. were employed. The samples were then cut, polished and

quantitatively analyzed on the transverse cross section using SEM. The morphology and the size of inclusions in each sample were evaluated. And the compositions of inclusions were also measured by EDS analysis.

3.3 Experimental Results

The typical morphology of the inclusion found in the steel is shown in **Figure 6**. It is readily seen that the inclusion is MnO-SiO_2 oxide containing small amount of sulfur, and MnS has precipitated out on it. The bright area of the inclusion corresponds to MnS phase while the dark area is the MnO-SiO_2 oxide. This is in good agreement with the prediction from the thermodynamic computation given in Fig.4. From the morphological image, it can be easily deduced that MnS was formed by precipitation and growth on the oxide inclusion which had acted as the heterogeneous nucleation site for MnS precipitation.

Fig.6 Typical example of MnS precipitation on a MnO-SiO_2 oxide inclusion.

MnS precipitates were formed mainly on the oxide inclusions and the number of MnS particles which exist independently in the matrix was extremely scarce even in the case of high cooling rate of $500^\circ\text{C}/\text{min}$. The above experimental results are good accord with the theoretical prediction through thermodynamic computation given earlier.

4. Discussion

4.1 Probability of MnS precipitation on inclusions

It is true that solidification process does not follow the equilibrium path, and hence there must be discrepancy to some extent between the experimental results of solidification and the thermodynamic equilibrium prediction. Although the thermodynamic analysis predicts formation of MnS on the secondary inclusions, there might be some inclusions which do not have MnS precipitates on them. In the present experimental study, it was found that there indeed exist some inclusions without MnS islands on them. However, its fraction is not large, and more than 90% of the secondary inclusions are with MnS precipitation. Wakoh et al.^(28,29) have reported the influence of various kinds of oxide nuclei on the MnS precipitation. It was

reported in their study that Mn-Ti oxide provided a most effective substrate for MnS precipitation and thus facilitated fine dispersion of MnS in the steel matrix. **Figure 7** compares the present results with the ones of Wakoh et al.⁽²⁸⁾ It is clearly seen that the precipitation ratio of MnS in present study is comparable to or even higher than that of Mn-Ti oxide, which had been reported to have the highest precipitation ratio.

Fig.7 Change in the precipitation ratio of MnS with sulfur content in steel for different kinds of deoxidation elements.

4.2 Some considerations on the mechanism of MnS precipitation on MnO-SiO_2 inclusions

From the thermodynamic estimation as shown in Fig.4, MnS was expected to precipitate after sulfur saturation in MnO-SiO_2 inclusions. Further decrease in temperature will cause MnS to grow owing to the solubility of Mn and S in MnO-SiO_2 inclusion decreasing. From the morphological features of both oxide and sulfide shown in Fig. 6, however, it is strongly suspected that MnS as well as MnO-SiO_2 were liquid phases when they formed. MnS islands in fact contain Si and O as well, although the amounts are small. Oikawa et al.⁽³⁰⁾ suggested in their study on the formation of MnS that nucleation and growth of MnS as liquid phase may occur via monotectic transformation. However, thermodynamic data available do not support existence of such miscibility gap in the MnO-SiO_2 -MnS system at $1,200^\circ\text{C}$. This warrants further thermodynamic and kinetic study on clarification of mechanism of MnS precipitation on manganese silicate inclusions.

5. Conclusion

A technique for optimization of steel composition for precipitating MnS on MnO-SiO_2 has been developed using computational thermodynamic method. The technique was applied to the Si/Mn deoxidized structural steel, and the optimum chemistry was found to be Fe – 0.1 mass% C – 0.1 mass% Si – 1.5 mass% Mn – 0.01 mass% O – 0.007 mass% S. The prediction was validated by experimental results. It was observed that more than 90% of secondary inclusions were with MnS precipitates. This ratio was comparable or even higher than that with Mn-Ti deoxidized steels reported in the literature.

The morphology of inclusions observed in the present study revealed a possibility of both oxide and sulfide inclusions having been precipitated as liquid phase. Since the existing thermodynamic data do not support this to occur, further study on the mechanism of MnS precipitation on the MnO-SiO₂ inclusion is warranted.

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