Control of Low Melting Point Mno-SiO$_2$-Al$_2$O$_3$ Inclusions in Low Carbon Thin-Strip Continuous Casting Steel

Jing Chen, Qing Zhu, Di Huang, Shaobo Zheng, Jieyu Zhang, Huigai Li

State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China.
E-mail: chen.jing.1217@hotmail.com

Abstract. There is a significant difference in the demand for molten steel quality between thin-strip continuous casting and traditional continuous casting. In order to make sure the better surface quality of the thin strips, to generate an oxidation film on the surface of cooling roller is required. This will require that the higher oxygen potential in molten steel and inclusions with low melting point. In this article, the possibility of producing low-melting inclusions which is mainly consisted of SiO$_2$ and MnO is studied by controlling the initial oxygen potential and addition order of deoxidizing alloys. The interaction activity between each component in the ternary system of Al$_2$O$_3$-SiO$_2$-MnO is obtained by Action Concentration model. The equal [Mn], [Si], [O], [Al] curve under the temperature of 1823K and equilibrium condition in ternary system of Al$_2$O$_3$-SiO$_2$-MnO is obtained by relative thermodynamic calculation as well. The control method for getting the low-melting point inclusion is as below. While the weight percentage of Si is 0.35% and the one of Mn is 0.90%, in order to maintain the melting point of inclusion around 1200°C, the free oxygen potential in melted steel $F[O]$ should be maintained between 0.002% ~ 0.004%. On the contrary, the requirement for acid dissolved [Al] content in melted steel is as low as 0.0001% ~ 0.0005%.

1. Introduction

Thin-strip continuous casting is a new technology which connects the continuous casting and continuous rolling by using a twin roll caster to produce the strip products directly from molten metal[1]. It makes the steel making process more compact, more successive, more efficient and more environment-friendly. The molten steel could be casted into a thin-strip steel with thickness less than 5mm, which achieves the integration of casting and rolling. In a twin roll caster, molten metal is introduced between a pair of counter-rotated horizontal casting rolls, which are cooled so that metal sheels solidify on the moving roll surfaces and brought together at the nip between the rolls to produce a solidified thin-strip product delivered downwardly from the nip[2].

When casting thin-strip in a twin roll caster, the molten metal in the casting pool will be generally at a very high temperature of 1500°C and above, and the high cooling rates are required during solidification, which is as high as 1000K/s. It is significant to achieve a high heat flux and extensive nucleation at the initial solidification process on the strip surfaces to form the metal shells. As Lazar S[3] described that the heat flux on the initial solidification can be increased by adjusting the steel melt chemistry. So that a substantial proportion of the oxides formed as deoxidation products are liquid state at the initial solidification temperature so as to form a substantially liquid layer at the interface between the molten metal and the casting surface for the role of covering slags in casting. Obviously, it is not advantageous to cast with clean steel in thin-strip continous casting in which the
number of inclusions in steel is required. This will require that the higher oxygen potential in molten steel and inclusions with low melting point. The molten steel contains a distribution of oxide inclusions (typically MnO, SiO$_2$, CaO and Al$_2$O$_3$) sufficient to provide an adequate density of nucleation sites on the roll surfaces for initial and continued solidification and the resulting strip product exhibits a characteristic distribution of solidified inclusions and surface characteristics. According to Suito and Inoue [4], inclusion composition can be estimated from thermodynamic as a function of steel composition and the reaction temperature, provided that the equilibrium between steel and inclusion is established. Okuyama [5] proved that the reactions between inclusions and steel is fast enough to establish the local equilibrium between inclusions and molten steel.

2. Experimental

2.1. Preparation of Metal Samples

A Medium-frequency induction furnace was used for experiments in the present work. The experimental procedures were as follows:

1. Melt 32Kg steel in furnace at 1873K (1600°C).
2. Add 385g MnFe alloys into the molten steel for deoxidation.
3. After 2 minutes, add SiFe alloys into the molten steel for continuous deoxidation to generate MnO-SiO$_2$ inclusions.
4. After 2, 5, 10, 15, 25, 30 minutes, take steel samples No.1 to No.5 using copper-formed samplers.

2.2. Chemical Analysis and SEM Investigation of Inclusions

The chemical compositions of in the steel samples were analyzed by Inductively Coupled Plasma-atomic Emission Spectroscopy (C, Si, Mn), Nitrogen-oxygen determinator (T[O], N), Chemistry Analysis (S), respectively. And the inclusions were analyzed by scanning Electron Microscopy (SEM)-Energy Dispersive X-ray Spectroscopy (EDX). The compositions of the steel before and after the experiments were shown in Table 1.

The inclusion particles were extracted from metal sample by a potentiostatic electrolysis using nonaqueous organic electrolytic. The dissolved sample weight during electrolysis was in the range of 0.2 to 0.3 g. The inclusion particles extracted were separated using a polycarbonate film filter with an open pore size of 0.8 μm, and were estimated three-dimensionally (3-D) by using SEM-EDX at magnifications of 5000 and 10000. The size of each inclusion was evaluated as the equivalent spherical diameter, dV, which was measured on the SEM photographs using a semi-automatic image analyzer.

| samples | T[O]  | [N]  | Fe    | C     | Si     | Mn    | S    |
|---------|-------|------|-------|-------|--------|-------|------|
| 1       | 0.0167| 0.0043| 98.4  | 0.101 | 0.354  | 0.898 | 0.0209|
| 2       | 0.0206| 0.0056| 98.5  | 0.0988| 0.335  | 0.87  | 0.0229|
| 3       | 0.0262| 0.0039| 98.5  | 0.102 | 0.323  | 0.855 | 0.0234|
| 4       | 0.0114| 0.0087| 98.6  | 0.0927| 0.295  | 0.817 | 0.0207|
| 5       | 0.0066| 0.0043| 98.6  | 0.0908| 0.255  | 0.782 | 0.0201|

3. Thermodynamic Fundamentals

In this work, reactions between liquid steel and inclusions are listed in Table 2. Where, $\Delta G^0_i$ is the standard Gibbs free energy, K is the equilibrium constant, $a_i$ is the activity of element i. Here, the activity of element i ($a_i$) in the steel melts can be estimated from Eq.(1) and Eq.(2).
\[ \log f_i = \sum_{j=1}^{n} e_{ij} \times \%_j \]

\[ a_i = f_i \times \%_i \]  

(1) \hspace{1cm} (2)

Table 2. Chemical reactions occurring between molten steel and inclusions and their standard Gibbs free energy\[6,7\]

| No. | Chemical Reaction | \( \Delta G^\theta \) [J·mol\(^{-1}\)] | \( K \) |
|-----|-------------------|---------------------------------------|-------|
| 1   | \( 2(MnO) + [Si] = (SiO_2) + 2[Mn] \) | \(-5700 - 34.8T\) | \( K_1 = \frac{a_{SiO_2} \cdot a_{[Mn]}^2}{a_{MnO} \cdot a_{[Si]}^2} \) |
| 2   | \( [Si] + 2[O] = (SiO_2) \) | \(-580550 + 221.03T\) | \( K_2 = \frac{a_{SiO_2}^3 \cdot a_{[Al]}^2}{a_{Al}_{2}O_3 \cdot a_{[Si]}^3} \) |
| 3   | \( 2(Al_2O_3) + 3[Si] = 3(SiO_2) + 4[Al] \) | \(658200 - 107.1T\) | \( K_3 = \frac{a_{SiO_2}^3 \cdot a_{[Si]}^2}{a_{[Al]}^4 \cdot a_{[O]}^3} \) |

Where, \( e_{ij} \) is the first-order interaction coefficient of element \( j \) to \( i \) relative to dilute solution whose value can be obtained by Eq.(3) and Table 3, \( \%_j \) is the mass percentage content in the liquid steel of element \( i \), \( f_i \) is the activity coefficient.

\[ e_i(T) = \left( \frac{2557}{T} - 0.365 \right) e_i(1873K) \]  

(3)

Table 3. First-order activity interaction coefficients \( e_i \) of solutes at 1873K\[9\]

| \( i \) | \( j \) | Al | C | O | Mn | Si |
|-------|-------|----|---|---|----|----|
| Al    |       | 63/T+0.011 | 0.091 | 34.740/T+11.95 | - | 0.056 |
| C     |       | 0.043 | 158/T+0.0581 | -0.34 | -0.12 | 162/T-0.008 |
| O     |       | -20600/T+7.15 | -0.043 | -1750/T+0.734 | -0.021 | -0.131 |
| Mn    |       | -0.07 | -0.083 | 0 | 0 |
| Si    |       | 0.058 | 380/T-0.023 | -0.23 | 0.002 | 34.5/T+0.089 |

\[ \text{Iso-}a_{SiO_2}, T=1823K \]

\[ \text{Iso-}a_{SiO_2}, T=1823K \]
Several thermodynamic models for liquid slag systems have been developed over several decades by many researchers and some of these have shown good reproducibility to experimental data and are convenient to use with a computer. In this work, the Action Concentration[8] model is used to calculate the activity coefficient of the oxidation in the melts. Figure 1 shows the calculated iso-activity curves of Al$_2$O$_3$/SiO$_2$/MnO in Al$_2$O$_3$-SiO$_2$-MnO melts at 1823K.

4. Results and discussion

4.1. Characteristics and Variation of Inclusions in Mn/Si Deoxidized Steel

It’s desired to keep inclusions in a liquid state in molten steel during the casting stage and to make the inclusions soft enough during the rolling and plastic deformation stage. Low melting point and soft inclusions are in general easily elongated during plastic deformation of the steel. The formation of inclusions is dependent on both steel chemistry and prevailing temperature. Even though FeSi alloys and FeMn alloys are mainly added to deoxidize molten steel, the alloys containing small amounts of Al (0.02–3.5wt%) enables on the formation behavior of inclusions was investigated. Mn/Si deoxidized liquid steel with a small amount of Al and O may produce inclusions of MnO-SiO$_2$-Al$_2$O$_3$ type. Figure 2 is a diagram of the liquidus surface of the MnO-SiO$_2$-Al$_2$O$_3$ system optimized by FactSage. The low melting point region of the MnO-SiO$_2$-Al$_2$O$_3$ ternary oxide system is good target for the inclusions composition.
Figure 2. Calculated liquidus surface of the MnO-SiO$_2$-Al$_2$O$_3$ system

4.2. SEM Investigation of Inclusions Deoxidating by Mn/Si

It was found by the observation using SEM-EDS that MnO-SiO$_2$-Al$_2$O$_3$ inclusions widely dispersed in steel samples, globular, the typical inclusion detected was shown in figure 3. The change of inclusions compositions observed by the reaction time are showed in figure 4 and the 3-D morphology and the corresponding compositions of MnO-SiO$_2$-Al$_2$O$_3$ type inclusions are showed in figure 5. In particularly, they were small (about 2~5 μm), spherical, and their composition is as below Al$_2$O$_3$: 30%~35%, SiO$_2$: 30%~35%, MnO: 30%~35%. The melting point is within the range between 1300°C~1500°C, which is lower than the liquidus temperature of 1522°C.

![Figure 3. Typical inclusion detected in steel sample No.1.](image)

| Element | O   | Al  | Si  | Mn  |
|---------|-----|-----|-----|-----|
| Atom (%)| 64.37 | 13.70 | 12.80 | 9.13 |

Figure 4. Changement pattern of inclusion in thin-strip along with reaction time
4.3. Equilibrium between the Observed MnO-SiO$_2$-Al$_2$O$_3$ inclusions and molten steel

Theoretically, the [Mn] content in liquid Fe with C=0.10 and Si=0.35 mass%, which is in equilibrium with the inclusions of MnO-SiO$_2$-Al$_2$O$_3$ system, can be deduced from Reaction (1) that the inclusion composition is expressed as a function of the activities of Mn, Si, activity of MnO and SiO$_2$ and temperature.

The iso-Mn(mass%) lines at C=0.10 and Si=0.35 mass% were obtained at 1823K by the iterative method, using the $\Delta G^0$ value, the activities of MnO(s) and SiO$_2$(s) and the respective interaction coefficients for the activity coefficients of $f_{\text{Si}}$ and $f_{\text{Mn}}$. The results are shown in figure 6(a). The iso-Si(mass%) lines were also calculated from Reaction (1) at C=0.10 and Mn=0.90 mass% in a similar manner and the results are shown in figure 6(b). The hatched areas in figure 6 correspond to the inclusions compositions in equilibrium with the steels containing [Mn]=0.3~2.0 mass% and [Si]=0.1~2.0 mass%.

The iso-[Al] (mass ppm) lines were calculated from Reaction (2) at C=0.10 and Si=0.35 mass%, by using the $\Delta G^0$ value, the activities of Al$_2$O$_3$(s) and SiO$_2$(s) and the respective interaction coefficients.
for the activity coefficients of $f_{Si}$ and $f_{Al}$. The results are shown in figure 7(a).

The iso-[O] (mass ppm) lines can be calculated from Reaction (3) at C=0.10 and Si=0.35 mass% in a similar manner and the results are shown in figure 7(b).

The solid lines indicated in figure 7(a) and 7(b) have the same meaning as those in figure 6(a) and 6(b). And the dash-dotted line indicated correspond to the iso-[Mn]=0.9 (mass%) in figure 6(a). It can be seen in figure 7(a) and 7(b) that the [Al] and [O] contents in the hatched areas are 1-5 ppm and 20-40 ppm, respectively.

The control method for getting the low-melting point inclusion is as below. With the increasing of Mn, Si and Al contents in melted steel, the corresponding contents of MnO, SiO$_2$ or Al$_2$O$_3$ in complex composite inclusion is increasing relevantly. While the mass percentage of Si is 0.35% and Mn is 0.90%, in order to maintain the melting point of inclusion around 1200°C, the free oxygen potential in melted steel F[O] should be maintained between 0.002% ~ 0.004%. On the contrary, the requirement for acid dissolved Al content in melted steel is as low as 0.0001% ~ 0.0005%.

5. Conclusions

Inclusions chemistry of Mn/Si deoxidized steel was studied through both thermodynamic calculation and laboratory experimental confirmation. It has proved that the computational thermodynamics provides a powerful tool for engineering inclusions and precipitates in steel. The following conclusions were obtained:

1. For metal samples with total content of Al<0.002%, Si:0.25~0.35% and Mn:0.77~0.90%, MnO-SiO$_2$-Al$_2$O$_3$ type inclusions were generated in liquid steel. The particles were small (about 2~5μm), spherical, and their composition is as below Al$_2$O$_3$: 30%~35%, SiO$_2$: 30%~35%, MnO: 30%~35%. The melting point is within the range between 1300°C~1500°C, which is lower than the liquidus temperature of 1522°C.

2. It is possible to predict the inclusions composition from steel chemistry. For instance, while the mass percentage of Si is 0.35% and the Mn is 0.90%, in order to maintain the melting point of inclusion around 1200°C, the free oxygen potential in melted steel F[O] should be maintained between 0.002% ~ 0.004%. On the contrary, the requirement for acid dissolved Al content in melted steel is as low as 0.0001% ~ 0.0005%.
6. References

[1] Clay Cross, Rama Ballav Mahapatra, Walter W. Blejde, Steve Leonard Wigman. LADLE REFINING OF STEEL[P]. US:6547849B2, Apr.15, 2003.

[2] Kiroyuki Otsuka, Koshiro Yamane, Satoshi Terasaki, Mark Schlichting, Rama Ballav Mahapatra. THIN CAST STEEL STRIP WITH REDUCED MICROCRACKING[P]. US:7975754B2, Jul.12, 2011.

[3] Lazar Strezov. CASTING OF METAL[P]. US:5720336, Feb. 24, 1998.

[4] Suito H, Inoue R. Thermodynamics on control of inclusions composition in ultraclean steels[J]. ISIJ international 1996; 36: 528-36.

[5] Ohta H, Suito H. Activities in CaO-MgO-Al2O3 Slags and Deoxidation Equilibria of Al, Mg, and Ca[J]. ISIJ international 1996; 36: 983-90.

[6] Gaye H, Gatellier C, Nadif M, et al. Slag metal reactions and control of the residual inclusions composition in secondary steel making[J]. Rev Metall Cah Inf Tech. 1987, 84(11):759.

[7] Ohta H, Sutto H. Activities in MnO-SiO2-Al2O3 Slags and Deoxidation Equilibria of Mn and Si[J]. Metall Mater Trans B. 1996, 27(B):263.

[8] Xiaochun Ma, Guoguang Cheng. Calculating Model of Action Concentration For MnO-SiO2-Al2O3 Slag System[J]. SHANGHAI METALS, 2011, 33(2):40-44.

[9] Fujisawa T, Sakao H. Equilibrium Relations Between The Liquid Iron Components and The Deoxidation Products Resulting From Mn-Si-Al alloys[J]. Tetsu-to-Hagane. 1977, 63(9):1494.