Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment

by S. Zhao*, F-L. Zhang†, L. Ma*, T. Yan*, J-C. Lv*, and S-P. He‡

Synopsis

To eliminate nozzle clogging during continuous casting of ship plate steel and reduce the calcium addition required, the composition of CaO-MgO-Al_2O_3 inclusions in the liquid phase region must be controlled. Thermodynamic calculations using FactSage show that when the balanced Al content is 0.03 mass %, a_{Ca} in the liquid steel is 1–10 ppm, and a_{Mg} is 0.01–0.3 ppm; and when the balanced Al content is 0.06 mass %, a_{Ca} in the liquid steel is 1–30 ppm, and a_{Mg} is 0.05–0.9 ppm. The CaO-Al_2O_3-CaS inclusions can be controlled in the liquid region below 1600°C at a_{Ca} values of 5 ppm, 15 ppm, and 30 ppm, and the balanced Al content should be controlled in the range of 0.001–0.050, 0.005–0.250, and 0.010–0.50 mass %, respectively. Based on theoretical analysis, the refining slag composition should be controlled to 45–53 mass % CaO, 30–37 mass % Al_2O_3, 6–12 mass % SiO_2, and 6–8 mass % MgO. Optimization of the slag system and steel composition can reduce, or even eliminate, the requirement for calcium treatment. The total oxygen content in the slab can be controlled to 15–21 ppm, with typical micro-inclusions ≤10 μm in size, with compositions in the CaO-Al_2O_3-MgO and CaO-Al_2O_3-CaS systems.

Keywords

calcium treatment, refining slag, inclusions, ship plate steel, melting point.

Introduction

With the rapid growth in steel output in China and the changes in the macroeconomic environment, competition in the steel industry has become more intense. The technology for economical cleaning of high-grade steel is important for improving product quality and reducing production costs. However, the functions of refining equipment have not been fully taken into consideration, and the combination of refining methods has not been optimized completely. These problems have become a bottleneck, restricting modern steel enterprises from developing an economic clean steel production process. Ship plate steel produced by the converter long process has been selected as the example in this study. The composition of the steel is shown in Table I. This steel is a high-strength low-alloy steel for rolling media and heavy plates, mainly used for ocean-going vessels and other steel structures. The carbon content in the steel is far from the peritectic point, and the crack sensitivity of the slab surface is weak, so impurities and gas content are strictly limited.

Therefore, the process route BOF (basic oxygen furnace) – LF (ladle furnace) – CC (continuous casting) needs to be studied.

The Al_2O_3 deoxidation products in ship plate steel are extremely hard, with angular geometries, and resist deformation due to having a melting point above processing temperatures. As such, it is inevitable that scabs and cracks are formed during the casting process, and significant complications arise as a result of adherence to the submerged entry nozzle (SEN) inner wall during casting, which can cause blocking of the SEN. Such inclusions also could damage the steel surface during cold rolling (Zhang, Aoki, and Thomas, 2006' Joo, 2007; Xu, 2009). Thus, the process cannot meet the hot charging requirements and the compact layout demand for continuous casting and rolling. At present, the most commonly used method to reduce the impact of these complications is to change the Al_2O_3 inclusions in the molten steel into calcium aluminate by feeding Ca within the ladle (Kaushik, Lehmann, and Nadi, 2012; Pretorius, Oltmann, and Cash, 2009; Wang, Li, and Wang, 2009; Zhao et al., 2013). In addition, manipulation of the molten steel is sometimes performed to change the distribution of inclusions in order to avoid the inclusions adhering to the SEN inner wall; a side effect of which is to homogenize the microstructure of the billet, resulting in improved steel quality. However, the calcium efficiency is very low and the content is difficult to control accurately during the feeding process. This increases the production cost and the possibility of secondary oxidation (Geldenhuis and Pistorius, 2000; Coletti et al.,

---

* *College of Materials Science and Engineering, Hebei University of Engineering, China.*
† *Hebei Research Institute of Iron and Steel Technology, China.*
‡ *College of Materials Science and Engineering, Chongqing University, China.*

Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment

2003; Fuhr, Cicutti, and Walter, 2003; Holappa, Liukkonen, and Lind, 2003). For operations producing thousands of tons of steel per annum, the reduction or elimination of calcium treatment can greatly reduce the operating costs.

In response to the above problems, this investigation was carried out to optimize the Ca feeding process in the manufacturing of ship plate steel, as well as the equilibrium reaction of different refining slag systems, to obtain a reasonable calcium content in the molten steel and refining slag composition. We have developed the most advantageous method of controlling the inclusion morphology, reducing the total oxygen and impurity content in the steel, and laying the foundation for the economic processing of ship plate steel via the steps converter tapping, ladle furnace, reduced or no calcium treatment, and slab casting.

Thermodynamic analysis of the reaction between inclusions and liquid steel

Typical inclusion compositions can be controlled in the low melting-point area by manipulating the Ca, Al, Mg, and O contents of the molten steel. Because the high-strength ship plate steel belongs to the class of high-Al and low-Ti steels [Al] = 0.015-0.070 mass %, [Ti] = 0.010-0.020 mass %, the deoxidation products are mainly Al_2O_3 inclusions in the stable region. Only if the Ti content is higher than 0.1% will a $Al_2O_3 \cdot TiO_2$ phase be formed. As a result, this paper mainly focuses on the modification and removal of the Al_2O_3 inclusions in steel.

Equilibrium calculation of Al_2O_3-MgO inclusions and liquid steel

$MgO \cdot Al_2O_3$ spinel inclusions are often found in steel that has been treated by aluminum deoxidation. The thermodynamic conditions for $MgO \cdot Al_2O_3$ spinel inclusions and their formation were calculated using FactSage software.

The MgO-Al_2O_3 phase diagram calculated using the FactSage software is shown in Figure 1. The MgO content is less than 30 mass % in the $MgO \cdot Al_2O_3$ spinel zone. $MgO \cdot Al_2O_3$ is very hard and has a melting point of 2135°C. It undergoes no deformation in the hot rolling process, which reduces the anti-fatigue properties of the steel and, greatly decreases the steel quality.

When Mg is present in the molten steel, there are two possible reactions by which $MgO \cdot Al_2O_3$ inclusions can form. The Mg and dissolved O can react, forming MgO directly in the steel, then MgO and Al_2O_3 combine to form spinel inclusions; alternatively, the dissolved Mg may react directly with the Al_2O_3 inclusions present in the steel (Seo *et al.*, 2003; Yang, Yamasaki, and Kuwabara, 2007; Yang *et al.*, 2011). To calculate the phase boundary between MgO and $MgO \cdot Al_2O_3$, Equation [1] is used (Todoroki and Mizuno, 2004).

$$2Al + 4MgO_{(s)} = MgO \cdot Al_2O_{3(s)} + 3Mg$$

$$\log K_{\text{Al-Mg}} = -33.09 + \frac{50880}{T} \quad [1]$$

Similarly, to calculate the phase boundary between $MgO \cdot Al_2O_3$ and Al_2O_3, Equation [2] is used (Todoroki and Mizuno, 2004).

$$2Al + 3MgO \cdot Al_2O_{3(s)} = 4Al_2O_{3(s)} + 3Mg$$

$$\log K_{\text{MgO} \cdot Al_2O_3} = -34.37 + \frac{46950}{T} \quad [2]$$

In the calculation, MgO and magnesia spinel grains were considered to exist in the pure solid standard state at 1600°C, and the activities were taken as $a_{\text{MgO}} = 1$ and $a_{\text{MgO} \cdot Al_2O_3} = 1$ separately. Then, the Mg-Al balance relationship can be found when $f_{[Al]} = 1.03$ is brought into Equations [1] and [2] (the activity coefficient of Mg is greatly influenced by the O content, and many interaction coefficients are unknown between the Mg in molten steel and other dissolved elements, so the Mg activity coefficient calculation is not entirely accurate; due to the lack of thermodynamic data, and this is only a brief discussion). Using FactSage, the Mg-Al-O system stability diagram is drawn (Figure 2).

According to Figure 2, the stability regions for MgO, Al_2O_3, and $MgO \cdot Al_2O_3$ can be found corresponding to different Al and Mg contents in the liquid steel, and the O content is in calculated equilibrium with the Al and Mg contents (see curves in Figure 2). At 1600°C, as long as the Mg and Al contents are very low, there is a high possibility of generating $MgO \cdot Al_2O_3$. When [Al] = 0.02-0.06 mass % and [Mg] = 0.5-10 ppm, $MgO \cdot Al_2O_3$ can be generated, thereby avoiding the formation of Al_2O_3. When [Mg] > 10 ppm, it can form MgO. It can be concluded that if there is only a small amount of Mg in the liquid steel, the formation of Al_2O_3 and the spinel precipitate or MgO will be avoided. Therefore, by
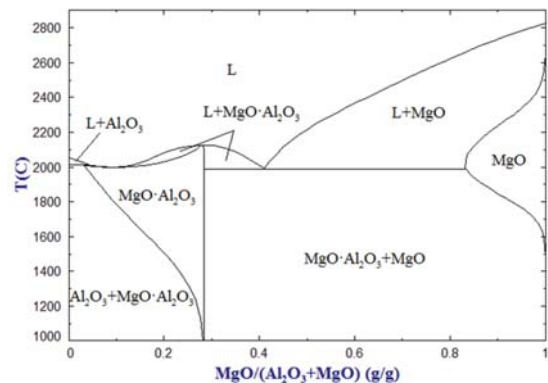

Figure 1—MgO-Al₂O₃ phase diagram

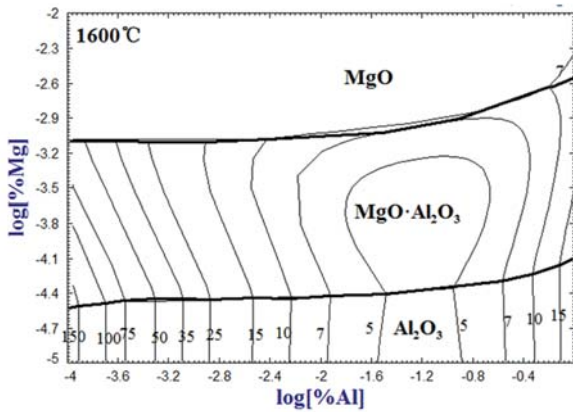# Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment

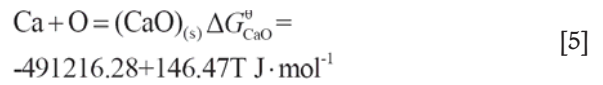**Figure 2—Relationship between Mg, Al, and inclusions in the steel at 1600°C**
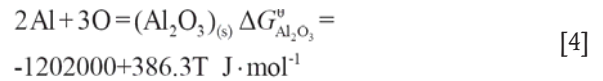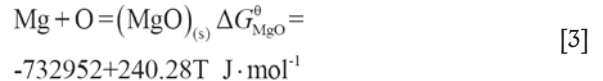
changing the slagging or deoxidation mode, and controlling the contents of dissolved Mg, Al, and Ca in the steel, $MgO \cdot Al_2O_3$ will possibly be converted to another low-melting product.

Equilibrium calculation of CaO-Al₂O₃-MgO inclusions and liquid steel
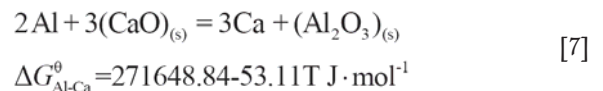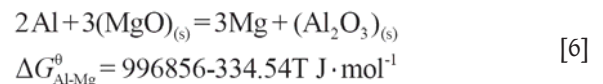
Spinel inclusions are high melting-point inclusions with a dispersed distribution in the steel. They will cause nozzle clogging and affect the steel quality. The effects of Al_2O_3 inclusions, however, are less serious. There have been very few studies on precipitation thermodynamics in the Fe-Mg-Ca-Al-O-S system. Therefore, the phase diagrams of the CaO-Al_2O_3-MgO and CaO-Al_2O_3-CaS systems were calculated. By controlling the Al, Ca, Mg, O, and S contents in molten steel, the inclusions can be restricted to the low melting-point area. Then, the conditions that generate CaO-Al_2O_3-MgO inclusions in the low-alloy steel were calculated when the Al content was taken as between 0.03 mass % and 0.06 mass %.

In order to calculate the equilibrium relationship between liquid steel and inclusions, first, the activity of each substance in the CaO-Al_2O_3-MgO system was calculated at 1600°C, using FactSage. To control the CaO-Al_2O_3-MgO system inclusions in the 1600°C liquid zone, the activities of Al_2O_3, CaO, and MgO need to be controlled separately in the ranges of 0.01–0.25, 0.1–0.9, and 0.01–0.9 respectively.

In addition to Equations [1] and [2], there are also the following equilibrium reactions between the liquid steel and inclusions in the CaO-Al_2O_3-MgO system (Chen, 1984).

$$Mg + O = (MgO)_{(s)} \quad \Delta G^{\theta}_{MgO} =$$
$$-732952 + 240.28T \ J \cdot mol^{-1} \tag{3}$$

$$2Al + 3O = (Al_2O_3)_{(s)} \quad \Delta G^{\theta}_{Al_2O_3} =$$
$$-1202000 + 386.3T \ J \cdot mol^{-1} \tag{4}$$

$$Ca + O = (CaO)_{(s)} \quad \Delta G^{\theta}_{CaO} =$$
$$-491216.28 + 146.47T \ J \cdot mol^{-1} \tag{5}$$

The following can be obtained from Equations [3], [4], and [5]:

$$2Al + 3(MgO)_{(s)} = 3Mg + (Al_2O_3)_{(s)}$$
$$\Delta G^{\theta}_{Al-Mg} = 996856 - 334.54T \ J \cdot mol^{-1} \tag{6}$$

$$2Al + 3(CaO)_{(s)} = 3Ca + (Al_2O_3)_{(s)}$$
$$\Delta G^{\theta}_{Al-Ca} = 271648.84 - 53.11T \ J \cdot mol^{-1} \tag{7}$$

For high-strength ship plate steel, the inclusions should be controlled in the 1600°C liquid region when Al = 0.03 mass % and 0.06 mass % in molten steel. The demand of the Ca and Mg contents is shown in Figure 3. A number of Ca and Mg iso-activity curves were drawn in FactSage, as shown in Figure 3a and 3b, respectively.

It can be seen from Figure 3 that to control the inclusion component range in the 1600°C liquid region, when Al = 0.03%, $a_{[Ca]}$ should be controlled to 1–10 ppm , and $a_{[Mg]}$ to 0.01–0.3 ppm. The lower equilibrium Ca requirement in steel can effectively reduce the amount of Si-Ca cored wire fed during secondary refining.

It can be surmised from Figure 4 that when Al = 0.06 mass %, to control the inclusions in the 1600°C low melting-point region, a_{Ca} should be controlled to 1–30 ppm, and a_{Mg} should be controlled to 0.05–0.9 ppm. Through comparative analysis, it is also known that in order to ensure inclusions in the low melting-point region, a_{Mg} and a_{Ca} must gradually increase when the Al content in liquid steel increases from 0.03 mass % to 0.06 mass %, and the corresponding range of activity is also expanded.
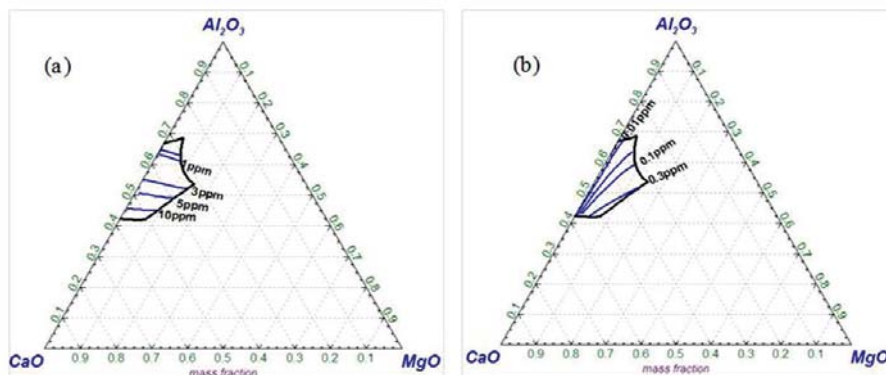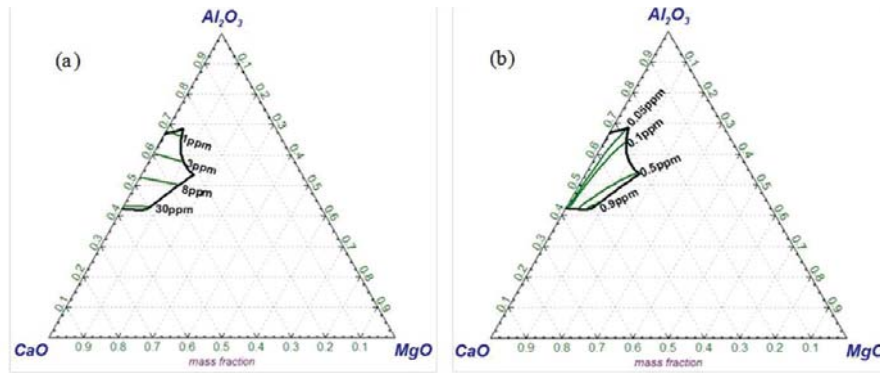

Figure 3—Iso-activity curves of the CaO-Al₂O₃-MgO ternary system at Al = 0.03 mass %, 1600°C. (a) Iso-$a_{[Ca]}$ curves, (b) iso-$a_{[Mg]}$ curves
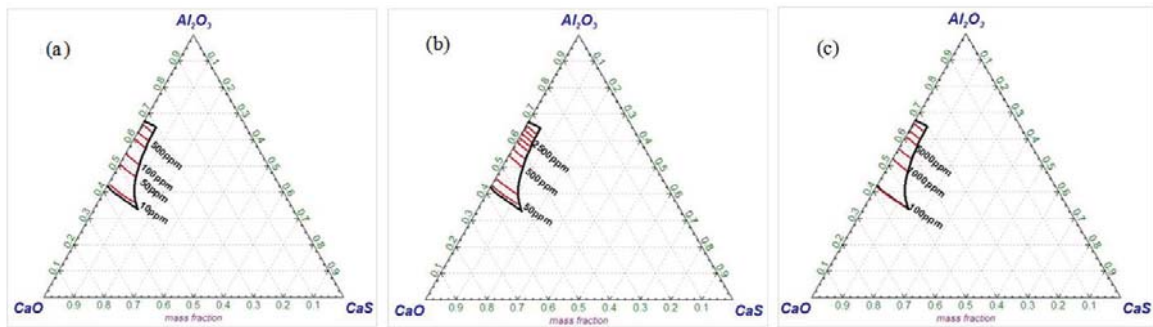
Figure 4—Iso-activity curves of the CaO-Al$_2$O$_3$-MgO ternary system at Al = 0.06 mass %, 1600°C (a) Iso-$a_{[Ca]}$ curves, (b) so-$a_{[Mg]}$ curves

Figure 5—Iso-Al curves of the CaO-Al$_2$O$_3$-CaS ternary system at different Ca activities, 1600°C (a) $a_{[Ca]}$ = 5 ppm, (b) $a_{[Ca]}$ = 15 ppm, (c) $a_{[Ca]}$ = 30 ppm

Additionally, according to the Al-Mg-O equilibrium thermodynamic calculation, at 1600°C, the Al content increases from 0.02 mass % to 0.06 mass % when the Mg content is in the range of 0.5 10 ppm, and MgO·Al$_2$O$_3$ spinel inclusions will be able to form; and the a_{Mg} needed to control the CaO-MgO-Al$_2$O$_3$ system inclusions in the liquid region is much lower, only 0.01–0.9 ppm. That is, only the lower Mg content is required in the presence of the liquid steel for generating the CaO-MgO-Al$_2$O$_3$ system composite inclusions, but a certain amount of calcium is required. It can be assumed that as the Mg content of the liquid steel increases, MgO·Al$_2$O$_3$ spinel inclusions are generated first, and then CaO-MgO-Al$_2$O$_3$ inclusions.

Equilibrium calculation of CaO-Al$_2$O$_3$-CaS inclusions and liquid steel

The iso-activity diagrams of Al$_2$O$_3$, CaO and MgO in the CaO-Al$_2$O$_3$-CaS ternary inclusions at 1600°C were calculated by FactSage. It can be seen from Figure 5 that in order to control the CaO-Al$_2$O$_3$-CaS inclusions in the liquid region at 1600°C, the activities of Al$_2$O$_3$, CaO, and CaS should be controlled to 0.01 in 0.25, 0.1 in 0.9, and 0.1 in 0.9. In addition to Equation [7], there is also the following reaction (Equation [8]) between the molten steel and inclusions in the CaO-Al$_2$O$_3$-CaS system.

$$Ca + S = (CaS) \quad lgK_{CaS} =$$
$$lg\left(\frac{a_{(CaS)}}{a_{[Ca]} \cdot a_{[S]}}\right) = \frac{19980}{T} - 5.9 \qquad [8]$$

At 1600°C, several iso-Al curves should be drawn by FactSage when a_{Ca} = 5 ppm, 15 ppm, and 30 ppm in steel,

corresponding to the inclusions located in the low melting-point region, as shown in Figure 5.

It can be seen from Figures 5a c that to control the compositional range of the inclusions in the low melting-point area, when a_{Ca} is 5 ppm, 15 ppm, and 30 ppm the Al content should be controlled in the range of 0.0010 to 0.050, 0.0050 to 0.250, and 0.010 to 0.50 mass %, respectively. Clearly, the a_{Ca} activity in the target steel can be controlled at 5 15 ppm. As a_{Ca} is increased, the Al content in liquid steel should be increased gradually for controlling the liquid inclusions.

Characterization of precipitated inclusions

The theoretical liquidus temperature of the target steel is about 1515°C. The temperature at the nozzle is generally 20°C higher than the liquidus temperature. In the casting process, in order to avoid a large number of precipitated inclusions adhering to the inner wall of the nozzle as the temperature decreases, it is necessary to consider the types and amounts of inclusions precipitated and their influence on the castability when the temperature of the molten steel is reduced from 1600°C to the liquid line.

Because refining slag floats and is separated from molten steel at the end of soft-blowing, remaining on the top of the ladle to form top slag, the mass transfer and equilibrium reaction between the molten steel and the top slag can be ignored from a thermodynamic point of view, leaving the main balance between the inclusions in the steel and the steel components to be considered. With decreasing temperature of the molten steel, the dissolved O, S, and alloy elements will reach supersaturation again, thereby generating the inclusions.

Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment

Under the internally controlled components of molten steel after refining and interaction coefficients of the metal elements in the molten steel at 1600°C, the activities of various elements were calculated by FactSage. The Ca and O activities in molten steel cannot be measured accurately *in situ*. They should be calculated according to the balance relationship in Equations [9] and [10]. The results are shown in Table II.

$$2Al + 3O = (Al_2O_3) \quad \Delta G_{Al_2O_3}^{\theta} = \\ -1205090 + 387.73T \ \mathrm{J \cdot mol^{-1}} \tag{9}$$

$$Ca + O = (CaO) \quad \Delta G_{CaO}^{\theta} = \\ -641300 + 149.26T \ \mathrm{J \cdot mol^{-1}} \tag{10}$$

The ΔG of each reaction at 1600°C was first calculated from the relevant thermodynamic data (Table III). According to the Gibbs free energy minimum principle, the first inclusions generated are CaS. After reaching the reaction balance between Ca and S, the Ca content in the molten steel is very low, and therefore no calcium precipitates will be formed during casting and cooling. Because large quantities of MnS are formed during the final solidification process, they will not be considered here. Therefore, the elements in the steel are mainly C, Si, Mn, Al, and O.

As the temperature continues to decrease, the equilibrium of the various reactions is broken and the inclusions continue to generate. The possible types of oxide inclusions generated in the molten steel and the associated reaction Gibbs free energies (ΔG^{θ}) are shown in Table IV. Calculated from the related data, Al_2O_3 inclusions begin to be generated when the molten steel temperature decreases from 1600°C to 1527°C. When the temperature falls to the liquidus temperature (1515°C), Al_2O_3 precipitates. Because the Al_2O_3 Gibbs free energy is the minimum negative value, only the reaction $2/3Al + O \rightarrow 1/3Al_2O_3$ is considered.

According to the activity value of each element at 1535°C and 1515°C in Table V, the ΔG of Al_2O_3 formation has always been smaller than the ΔG values for other inclusions, which indicates that when the $2/3Al + O \rightarrow 1/3Al_2O_3$ reaction reaches equilibrium, the reactions forming the other inclusions are already balanced, and Al_2O_3 inclusions are the primary precipitate in the molten steel during the cooling process. Without taking into consideration the secondary oxygenation of the molten steel, no Al_2O_3 inclusions

---

Table II

Activities and activity coefficients of various elements in steel

Element (i)	Si	Mn	S	Al	Ti	Ca	O
f_i	1.165	0.976	0.998	1.038	1.058		
a_i	0.349	1.317	0.018	0.0311	0.016	2.9×10^{-7}	1.27×10^{-4}

Table III

Gibbs free energies for the formation of inclusions ($\Delta G < 0$), 1600°C

Type of inclusion	Reaction	Gibbs free energy ΔG, J·mol⁻¹
CaS	$Ca + S \rightarrow CaS$	−1866.94
$3CaO \cdot 2TiO_2$	$2Ti + 7O + 3Ca \rightarrow 3CaO \cdot 2TiO_2$	−749.60

Table IV

Gibbs free energy (ΔG) of deoxidation reactions at different temperatures

Type of inclusion	Reaction	$\Delta G/n_{[o]}$, J·mol⁻¹			
		1600°C	1535°C	1527°C	1515°C
Al_2O_3	$2Al + 3O \rightarrow Al_2O_3$	16112.9	1613.4	−171.2	−2848.0
MnO	$Mn + O \rightarrow MnO$	83550.5	70438.2	68824.4	66403.7
SiO_2	$Si + 2O \rightarrow SiO_2$	64627.7	52311.3	50795.4	48521.6
$MnO \cdot Al_2O_3$	$Mn + 2Al + 4O \rightarrow MnO \cdot Al_2O_3$	24365.5	10094.2	8337.7	5703.0
$2MnO \cdot SiO_2$	$2Mn + Si + 4O \rightarrow 2MnO \cdot SiO_2$	72268.9	59152.7	57538.4	55117.0
$MnO \cdot SiO_2$	$Mn + 3O + Si \rightarrow MnO \cdot SiO_2$	63325.1	50683.6	49127.7	46793.9
$3Al_2O_3 \cdot 2SiO_2$	$6Al + 2Si + 13O \rightarrow 3Al_2O_3 \cdot 2SiO_2$	27870.6	14129.9	12438.7	9901.9
$3MnO \cdot Al_2O_3 \cdot 3SiO_2$	$3Mn + 2Al + 3Si + 12O \rightarrow 3MnO \cdot Al_2O_3 \cdot 3SiO_2$	48235.9	35175.2	33567.7	31156.5

Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment

Activities of elements in steel

| Temp.	$a_{[Si]}$	$a_{[Mn]}$	$a_{[Al]}$	$a_{[O]}$
1535°C	0.349	1.317	0.031	0.00005
1515°C	0.349	1.317	0.031	0.000037

precipitate during cooling from 1600°C to the nozzle temperature (1535°C). The amounts of Al_2O_3 precipitated are 19.1 mg per 10 kg of molten steel, when the temperature is reduced from 1600°C to the liquidus temperature (1515°C).

The above analysis indicates that thermodynamic equilibrium is achieved at a constant temperature. However, in the actual cooling-solidification process, the temperature of the molten steel decreases rapidly, and the reaction cannot achieve a full balance. Therefore, it is possible to find only the approximate precipitate types and sequence of inclusions for reducing calcium treatment.

Composition of refining slag

To improve the castability of molten steel, an effective method is to change the deoxidation products into low-melting-point inclusions during the tapping process. It is also necessary to control the reaction between the refining slag and molten steel, particularly to inhibit the formation of the high-melting phase in low-alloy steel. Therefore, in order to maintain a low level of high melting-point inclusions and to obtain better fluidity of the molten steel, the final composition of the refining slag needs to be controlled, and excessive slag-steel reaction must be avoided. The appropriate refining slag should be determined using the following principles. It should have an appropriate melting point and viscosity, to better maintain fluidity. The slag is weakly oxidizable, so it does not react easily with the Al in steel. Thus, the formation of Al_2O_3 inclusions is prevented. The slag should have good desulphurization ability. Inclusions in the steel can be assimilated in the low melting-point area and can then be easily absorbed by the slag. It should help prevent lining erosion, and use little fluorite in order to protect the environment.

Because the aluminium activity of the ship plate steel is higher, according to Equation [11] it is relatively easy for the reduction reaction with SiO_2 in the slag to occur during the refining process (Huang, 2007; Maeda *et al.*,1989), thus Al_2O_3 system inclusions with a high melting point would be generated.

$$Al + 0.75(SiO_2)_{slag} = 0.75\ Si\ + 0.5(Al_2O_3)_{inc} \qquad [11]$$
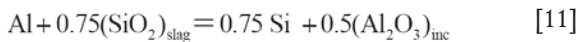
According to the Gibbs free energy isothermal equation, $\Delta G = \Delta G^\theta + RT\ln J$, where ΔG^θ is the Gibbs free energy in the standard state, and J is the activity ratio of the substances under the actual reaction conditions. To suppress the high-melting-point Al_2O_3 products when [Al] = 0.030%, the necessary condition is $a_{(Al_2O_3)}^{0.5}\ /\ a_{(SiO_2)}^{0.75}$ therefore improving the Al_2O_3 activity or reducing the SiO_2 activity in the slag can inhibit the steel-slag reaction. According to the isoactivity phase diagram for $a_{(Al_2O_3)}$ and $a_{(SiO_2)}$, the slag compositions that inhibit reaction [11] were identified and are plotted on the phase diagram, as shown in Figure 6.

As can be seen, the refining slag compositions are controlled in the highlighted region when the Al_2O_3 content is more than 30 mass % and the SiO_2 content is less than 12 mass %, which demonstrates the benefits of the inhibiting reaction [11] from a thermodynamic point of view. However, in the actual smelting process, the SiO_2 content of the tapped slag is high and the raw slag materials may carry some SiO_2 into the ladle. It was therefore decided that the $CaO-Al_2O_3-SiO_2$ system refining slag would be used.

The sulphur content in steel should be stringently controlled to less than 0.012 mass %, and the refining slag must also have a strong desulphurization capability. The desulphurization reaction in which Al in steel and CaO act simultaneously (Ghosh, 1989), can be expressed as Equation [12]. To control the sulphur content to less than 0.012 mass %, the activities must be controlled to is $a_{(Al_2O_3)}\ /\ a_{(CaO)}^3$ < 2.1, so improving the CaO activity in the slag can promote the desulphurization reaction. Under controlled conditions, according to the iso-activity phase diagram for $a_{(Al_2O_3)}$ and $a_{(CaO)}$, the slag components that promote reaction [12] were identified and are plotted on the phase diagram, as can be seen from Figure 7. The refining slag compositions should be controlled within the range for promoting the reaction: 45–60 mass % CaO, 20–50 mass % Al_2O_3, and <25 mass % SiO_2.

$$2Al + 3S + 3(CaO)_{slag} = 3(CaS)_{slag} + (Al_2O_3)_{slag} \qquad [12]$$
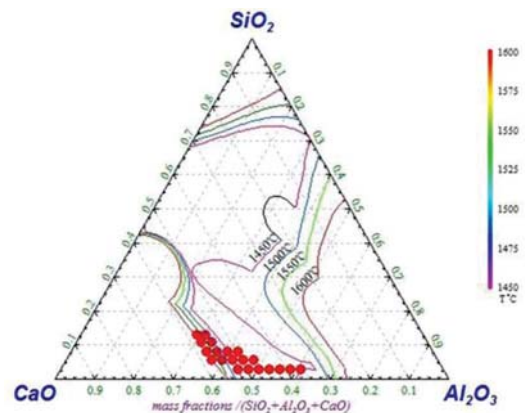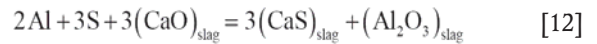

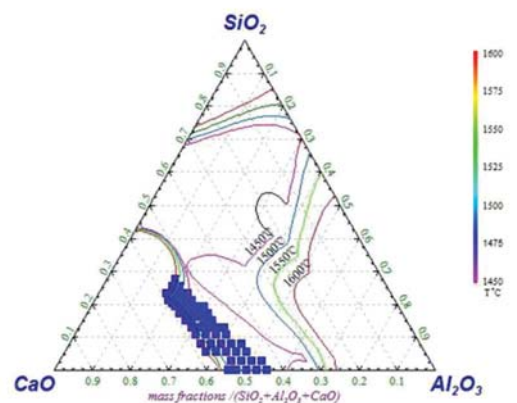**Figure 6—Range of refining slag for inhibiting reaction [11] (red circles)**

Figure 7—Range of refining slag for promoting reaction [12] (blue circles)

Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment

In order to ensure that the inclusions are strongly assimilated and absorbed, the refining slag must also have a lower melting point and viscosity. Furthermore, the liquid region can be expanded by adding about 8 mass % MgO to the refining slag (Dong *et al.*, 2014), which plays a role in protecting the lining of the ladle. In order to control the melting point of the refining slag in the liquid phase region below 1500°C, the CaO/Al$_2$O$_3$ mass ratio should not be more than 1.8. With a view of inhibiting the steel-slag reaction, in conjunction with its desulphurization ability, the refining slag composition is ultimately controlled in the liquid region to 45–53 mass % CaO, 30–37 mass % Al$_2$O$_3$ 6–12 mass % SiO$_2$, and 6–8 mass % MgO. This conclusion is related to the formulation of Yoon *et al.* (2002). When the CaO content of refining slag was a fixed value, increasing the Al$_2$O$_3$ content in the slag was conducive to deoxidization.

Industrial application

Control of T[O] content

The changes in the T[O] content in steel at different stations are shown in Figure 8. By optimizing the slag composition and reducing the calcium treatment, the steel cleanliness improved significantly after slag washing. Compared to the previous optimization, the average T[O] content in CAS (composition adjustment by sealed argon bubbling) was 80 ppm, a decrease of 32%, T[O] removal rate was 58.5% during LF refining, and the average T[O] content was below 18 ppm in the slab. Although LF treatment time was shorter than in the original process, the quick slagging could extend the slag-steel contact time. This can not only complete the interface reaction, but also reduces the risk of entrapment; and secondary oxidation was successfully prevented in the tundish, so that the oxygen content can be maintained at a lower level.

Control of inclusions in steel

The morphology and type of major inclusions are listed in Figure 9. Under the original conditions, although a large amount of calcium wire was fed into the molten steel, the yield was particularly low, the micro-inclusions contained a lot of high-melting Al$_2$O$_3$, CaO·Al$_2$O$_3$, or CaO·2Al$_2$O$_3$, the actual amount of calcium wire significantly reduced after optimizing the refining process, spherical inclusions were located near 12CaO·Al$_2$O$_3$ in the slab, the outer calcium aluminates were enclosed with MnS or CaS, because of the interaction with the furnace lining, top slag, and molten steel, and this led to a certain amount of MgO in the inclusions.

Before LF treatment, many Al$_2$O$_3$ inclusions were observed in the steel, and there was also a small amount of MnO-SiO$_2$-Al$_2$O$_3$. After LF treatment, the typical inclusions changed into spherical CaO-Al$_2$O$_3$-MgO-(MnS) or CaO-Al$_2$O$_3$-(CaS) (≤ 10 μm) in the tundish and slab, most of the CaO-Al$_2$O$_3$-MgO inclusions were located in the area of 3CaO·Al$_2$O$_3$ and CaO·Al$_2$O$_3$ in the ternary phase diagram, in which the melting points were lower than 1600°C (see Figure 10), and there was only a small amount of CaO-MgO or MgO-Al$_2$O$_3$ inclusions.
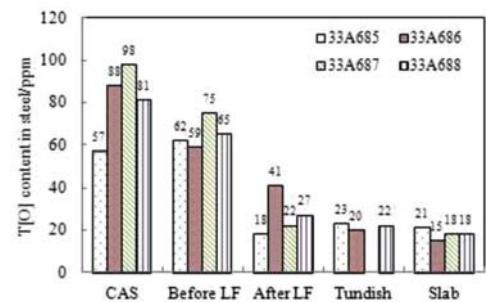

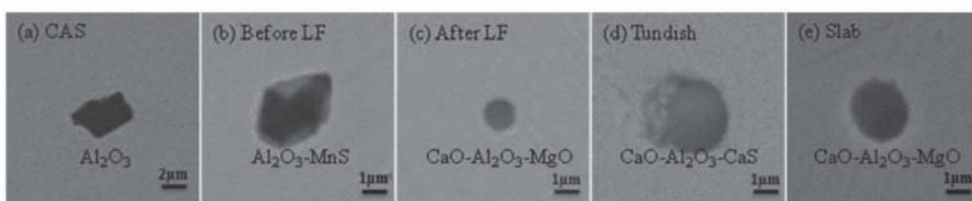Figure 8—Change of T[O] content in different stations

Figure 9—Morphologies of typical inclusions in steel in different stations (a) CAS, (b) before LF, (c) after LF, (d) tundish, (e) slab
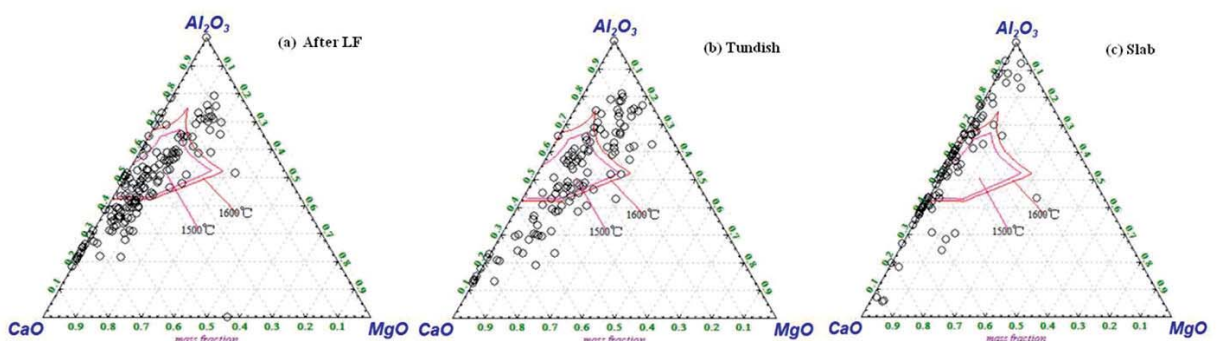

Figure 10—Melting points of CaO-MgO-Al$_2$O$_3$ inclusions in each station after optimization (a) after LF, (b) tundish, (c) slab

Control of complex inclusions in high-strength ship plate steel by reducing calcium treatment
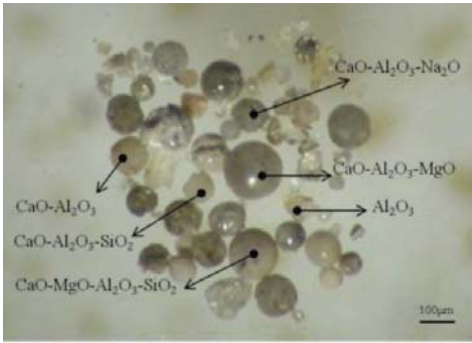

Figure 11—Morphology of macro-inclusions in slab

The amount of electrolysed macro-inclusions was less than 13.9 mg per 10 kg in the slab. After process optimization, spherical CaO-Al_2O_3 and CaO-Al_2O_3-MgO-(SiO_2) system inclusions were mainly present in the steel, at sizes less than 200 μm (Figure 11). Only individual inclusions contained a small amount of Na_2O, which indicated that entrapment does not occur in the mould.

Conclusions

1. When the contents of Ca and Mg in the liquid steel are very low, the inclusions can be controlled in the 1600°C liquid region of the CaO-Al_2O_3-MgO system. For high-strength ship plate steel, to control the compositions of the CaO-MgO-Al_2O_3 inclusions in the liquid phase region of MgO <10 mass %, Al_2O_3 45–60 mass %, CaO 40–55 mass %, when the balanced Al content is 0.03 mass %, the $a_{[Ca]}$ in the liquid steel is 1–10 ppm and $a_{[Mg]}$ is 0.01-0.3 ppm; when the balanced Al content is 0.06 mass %, the $a_{[Ca]}$ in the liquid steel is 1–30 ppm and $a_{[Mg]}$ is 0.05–0.9 ppm.
2. The CaO-Al_2O_3-CaS inclusions can be controlled in the liquid region below 1600°C, when $a_{[Ca]}$ in the liquid steel is 5 ppm,15 ppm, and 30 ppm separately, and the balanced Al content should be controlled in the range of 0.001–0.050 mass %, 0.005–0.250 mass %, and 0.01–0.50 mass %. Obviously, with increasing $a_{[Ca]}$, the Al content in liquid steel is gradually increased.
3. With a view to controlling the melting point of the refining slag in the liquid phase region below 1500°C and inhibiting the steel-slag reaction, in conjunction with its deoxidization and desulphurization ability, the composition range of the refining slag is ultimately controlled in the liquid region, with 45–53 mass % CaO, 30–37 mass % Al_2O_3, 6–12 mass % SiO_2, and 6–8 mass % MgO.
4. The reducing Ca treatment improved the cleanliness of the ship plate steel. Micro-inclusions, with sizes below 10 μm, are mainly in the CaO-Al_2O_3-MgO or the CaO-Al_2O_3 system, with only a small amount of MgO-Al_2O_3, and the T[O] content was controlled to 18 ppm or less in the slab.

References

CHEN, J.-X. 1984. Steelmaking Chart and Data Manual, 1th edn. Metallurgical Industry Press, Beijing.

COLETTI, B., VANTILT, S., BLANPAIN, B., and SRIDHAR, S. 2003. Observation of calcium aluminate inclusions at interfaces between Ca-treated, Al-killed steels and slags. *Metallurgical and Materials Transactions B*, vol. 34B, no. 5. pp. 533–538.

DONG, Y-W., JIANG, Z.-H., CAO, Y.-L, ZHANG, H.-K., and SHEN, H.-J. 2014. Effect of MgO and SiO2 on surface tension of fluoride containing slag. *Journal of Central South University*, vol. 21, no. 11. pp. 4104–4108.

FUHR, F., CICUTTI, G., and WALTER, G. 2003. Relationship between nozzle deposits and inclusion composition in the continuous casting of steels. *Iron and Steelmaker*, vol. 32, no. 12. p. 53.

GELDENHUIS, J.M.A. and PISTORIUS, P.C. 2000. Minimization of calcium additions to low carbon steel grades. *Ironmaking and Steelmaking*, vol. 27, no. 6. pp. 442–449.

GHOSH, A. 1989. Secondary Steelmaking: Principles and Applications. CRC Press, Boca Raton, Florida.

HOLAPPA, L., LIUKKONEN, H.M., and LIND, M. 2003. Thermodynamic examination of inclusion modification and precipitation from calcium treatment to solidified steel. *Ironmaking and Steelmaking*, vol. 30, no. 2. pp. 111–115.

HUANG, X-H. 2007. Iron and Steel Metallurgy Principle. 3rd edn. Metallurgical Industry Press, Beijing.

JOO. H.P. 2007. Formation mechanism of spinel-type inclusions in high-alloyed stainless steel melts. *Metallurgical and Materials Transactions B*, vol. 38, no. 4. pp. 657–663.

KAUSHIK, P., LEHMANN, J., and NADI,F.M. 2012. State of the art in control of inclusions, their characterization, and future requirements. *Metallurgical and Materials Transactions B*, vol. 43, no. 4. pp. 710–725.

MAEDA, S., SOEJIMA, T., SAITO, T., MATSUMOTO, H., FUJIMOTO, H., and MIMURA, T. 1989. Shape control of inclusions in wire robs for high tensile tire by refining with synthetic slag. *Proceedings of the 72nd Steelmaking Conference*. Chicago. ISS-AIME, Warrendale, PA. pp. 379–385.

PRETORIUS, E.B., OLTMANN, H.G., and CASH, T. 2009. The effective modification of spinel inclusions by Ca Treatment in LCAK steel. *AIST2009 Proceedings*. Association for Iron and Steel Technology, St Louis. pp.1035–1049.

PRETORIUS, E.B., OLTMANN, H.G., and CASH, T. 2009. The effective modification

SEO, W.G., HAN, W.H., KIM, J.S., and PAK, J.J. 2003. Deoxidation equilibria among Mg, Al and O in liquid iron in the presence of MgO·Al2O3 spinel. *ISIJ International*, vol. 43, no. 2. pp. 201–208.

TODOROKI, H. and MIZUNO, K. 2004. Effect of silica in slag on inclusion compositions in 304 stainless steel deoxidized with aluminum. *ISIJ International*, vol. 44, no. 8. pp. 1350–1357.

WANG, X-H., LI, H-B., and WANG Y. 2009. Composition change of the non-metallic inclusions during the secondary refining of low oxygen alloyed structural steels. *AIST2009 Proceedings*. Association for Iron and Steel Technology, St Louis. pp.965–972.

XU, K-D. 2009. Certain basic subjects on clean steel. *Acta Metallurgica Sinica*, vol. 45, no. 3. pp. 257–269.

YANG, J., YAMASAKI, T., and KUWABARA, M. 2007. Behavior of inclusions in deoxidation process of molten steel with *in situ* produced Mg vapor. *ISIJ International*, vol. 47, no. 5. pp. 699–708.

YANG, S-F., LI, J.-S., WANG, Z.-F., LI, J., and LIN, L. 2011. Modification of MgO·Al2O3 spinel inclusions in Al-killed steel by Ca-treatment. *International Journal of Minerals, Metallurgy and Materials*, vol. 18, no. 1. pp. 18–23.

YOON, B.H., HEO, K.H., KIM, J.S., and SOHN, H.S. 2002. Improvement of steel cleanliness by controlling slag composition. *Ironmaking and Steelmaking*, vol. 29, no. 3. pp. 214–217.

ZHANG, L-F., AOKI, J., and THOMAS, B.G. 2006. Inclusion removal by bubble flotation in a continuous casting mold. *Metallurgical and Materials Transactions B*, vol. 37B, no.5. pp. 361–379.

ZHAO, S., WANG, Q., XU, J.-F, PENG, M-M., and HE, S-P. 2013. Control on melting temperature of CaO-Al2O3-SiO2-MgO inclusions in low carbon low alloy steel. *Journal of Central South University* (*Science and Technology*), vol. 44, no. 8. pp. 3121–3128. ◆