

## Modification of MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions in Al-killed steel by Ca-treatment

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**Abstract:** The modification of MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions in Al-killed steel by Ca-treatment has been studied by industrial trials and thermodynamic calculations. In the industrial trials, samples were taken systematically during the refining process in which the molten steel was treated by calcium, and the characters of the inclusions were analyzed using scanning electron microscopy (SEM) and energy dispersive spectra (EDS). The effects of Ca-treatment were evaluated by tracking the compositions of the inclusions. The results show that the modification of MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions by Ca-treatment is effective and the transformation sequence of the inclusions during the refining is Al<sub>2</sub>O<sub>3</sub>→MgO·Al<sub>2</sub>O<sub>3</sub>→liquid complex inclusions. The modification of spinel inclusions by Ca-treatment was calculated by FactSage6.0 utilizing its free-energy minimization routines. The results of thermodynamic calculations indicate that spinel inclusions are easier to be modified than Al<sub>2</sub>O<sub>3</sub> inclusions and the spinel inclusions in 30CrMo steel would transform to liquid complex inclusions when the content of dissolved Ca in the molten steel exceeds  $1 \times 10^{-6}$ . Also, the results show that adding more calcium into the molten steel would lower the contents of Al<sub>2</sub>O<sub>3</sub> and MgO and increase the CaO content of the inclusions, while the change in SiO<sub>2</sub> content is little.

**Keywords:** steel metallurgy; inclusions; magnesia; alumina; chemical modification; thermodynamics

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### 1. Introduction

MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions have been considered to be very harmful to both the quality and the castability of products for a long time due to their high melting point and great hardness. It has been reported that MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions would deteriorate corrosion resistance and cause surface defects and cracks during deep drawing or spinning manufacturing [1]. In addition, spinel inclusions tend to accumulate on the inner wall of a submerged entry nozzle of a continuous casting machine [2-4]. So far, a number of investigations have been reported on the formation mechanism of spinel inclusions in liquid iron and steels. The stability diagrams of oxide inclusions have been created corresponding to both Mg and Al contents using the thermodynamic data obtained experimentally [5-7]. It has been proven that very small amount of Mg and Al enables the formation

of spinel. Both the effects of slag-basicity and composition on the formation of spinel inclusions in Fe-16wt%Cr stainless steel deoxidized by Al were investigated by Okuyama *et al.* [8] and Todoroki [9].

There are different opinions on the fact that whether spinel inclusions can be modified to liquid inclusions by calcium treatment. Some papers suggest that the modification of spinels by calcium is less effective than that of pure alumina [10-11]. However, more recent work indicates that under reduction conditions (steel and slag) the modification of some spinels by calcium treatment is possible, and it also suggests that the modification of spinel inclusions by calcium treatment is easier than that of alumina inclusions [12-15]. Young *et al.* [16] studied the formation mechanism of liquid calcium alumina inclusions from the MgO·Al<sub>2</sub>O<sub>3</sub> spinel, and found that the spinel reacted with the dissolved Ca, forming a liquid calcium aluminate phase.

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In the current study, the modification of MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions by Ca-treatment was investigated by industrial trials and thermodynamic calculations. The theoretical and practical aspects of the modification of spinels were discussed, and the requirements for effective modification were elucidated.

## 2. Experiment

In the present work, the experimental steel is 30CrMo with a composition (wt%) of C 0.30, Si 0.22, Mn 0.52, P 0.015, S 0.007, Mo 0.10, Al<sub>s</sub> 0.025, V 0.12, Cu 0.07, and Cr 0.94. The process to produce 30CrMo is: scrap+direct reduction iron+hot metal→100 t EAF→100 t LF-VD→CaSi treatment→CC. The time of LF refining is about 60 min, and the time of VD treatment is 40 min. During tapping, aluminum (300 kg), SiMn (800 kg), and FeMn (400 kg) were added in order to deoxidize and alloy. After 30 min of LF refining, 60 kg of aluminum wires, 56 kg of ferromanganese, 113 kg of ferromolybdenum, and 180 kg alloy of standard ferrochromium were added to adjust the composition of the molten steel. The size of the billet is 210 mm. Steel samples under four heats were taken during refining (before and during LF treatment, and before and after VD treatment). During sampling, the samplers were immersed in the molten steel to 300 mm below the bath surface. The inclusions were observed and analyzed using scanning electron microscopy (SEM) and energy dispersive spectra (EDS). In order to observe the three-dimensional morphology of inclusions, the samples were treated by partial acid extraction [17].

## 3. Results and discussion

### 3.1. Changes in the morphology and composition of inclusions during refining

For each steel sample, the composition and size of 15-20 inclusions were analyzed, and a total of 320 inclusions were detected and analyzed using SEM in the current study. Figs. 1-4 show the composition distribution of inclusions in the isothermal section of the CaO-Al<sub>2</sub>O<sub>3</sub>-MgO system generated by the FactSage software (Version 6.0). Fig. 1 shows that nearly all the inclusions locate in the solid phase area before LF refining and most of them are Al<sub>2</sub>O<sub>3</sub> inclusions. The Al<sub>2</sub>O<sub>3</sub> inclusions observed are either cluster or wedge angular, and the size is 0-20 μm, as shown in Fig. 5. These Al<sub>2</sub>O<sub>3</sub> inclusions are the deoxidized products of the liquid steel with Al during EAF tapping. The Al<sub>2</sub>O<sub>3</sub> content of most inclusions is more than 90wt%. Fig. 2 shows that the inclusions are mainly MgO·Al<sub>2</sub>O<sub>3</sub> after 30 min in LF. The mor-

phology of MgO·Al<sub>2</sub>O<sub>3</sub> spinel is square or rhombus, and the size is 0-6 μm, as shown in Fig. 6. After 30-min refining, aluminum wires were added into the molten steel and the top slag had formed, so the change from Al<sub>2</sub>O<sub>3</sub> inclusions to MgO·Al<sub>2</sub>O<sub>3</sub> systematical inclusions in the early period of LF refining is due to the reaction between [Al] and MgO either in the slag or in the ladle lining as expressed by Eq. (1). Since strong deoxidizers and high basicity slag were adopted in the refining process, MgO in the slag or in the ladle lining could be reduced by [Al] and generated [Mg] in liquid steel, then it further reacted with Al<sub>2</sub>O<sub>3</sub> inclusions forming MgO·Al<sub>2</sub>O<sub>3</sub> based inclusions (Eq. (2)) [16]:

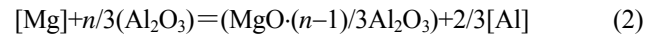
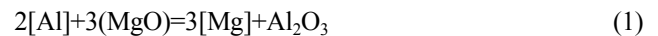


Fig. 3 shows that before Ca-treatment, the inclusions contain a little CaO, while most of which still plot in the solid area. This is mainly due to the reaction between [Ca] and MgO·Al<sub>2</sub>O<sub>3</sub>, as expressed by Eq. (3), and the high-basicity top slag may be the source of [Ca]. It can be seen in Fig. 4 that after Ca-treatment, the change from CaO-MgO-Al<sub>2</sub>O<sub>3</sub> solid inclusions to CaO-MgO-Al<sub>2</sub>O<sub>3</sub> liquid inclusions takes place and most of the inclusions transfer into the liquid phase area with the increase in the CaO

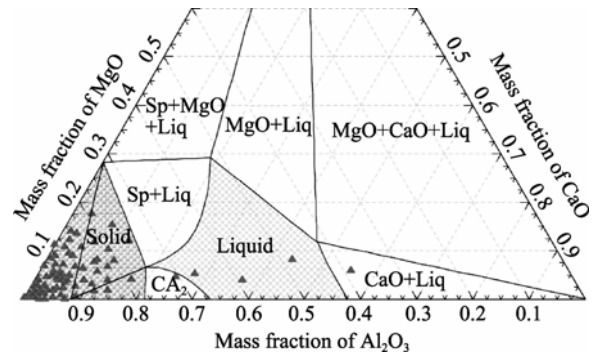


Fig. 1. Composition of inclusions before LF refining (Sp: MgO·Al<sub>2</sub>O<sub>3</sub> spinel).

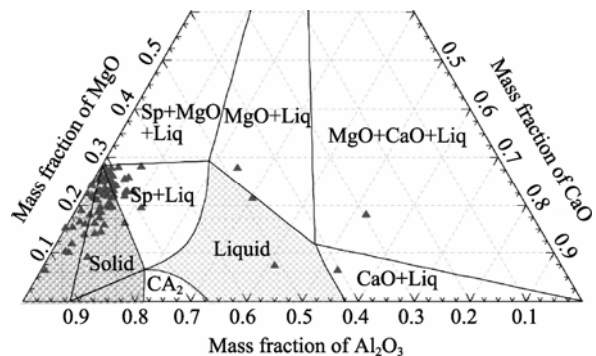


Fig. 2. Composition of inclusions during LF refining.

content of inclusions. This is mainly due to the reaction of [Ca] added into the molten steel and CaO-MgO-Al<sub>2</sub>O<sub>3</sub> solid inclusions. Fig. 7 shows the morphology and the energy

spectrum of MgO-Al<sub>2</sub>O<sub>3</sub>-CaO liquid inclusions.

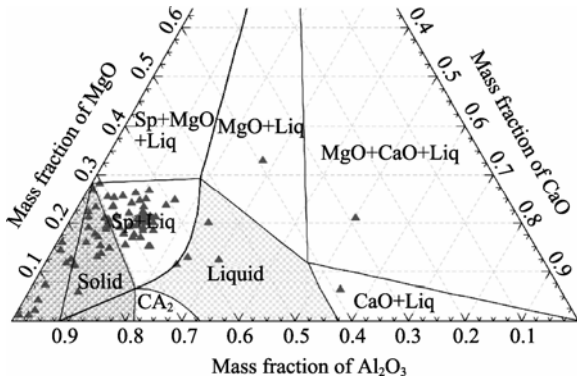
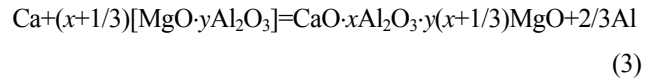


Fig. 3. Composition of inclusions before Ca-treatment.

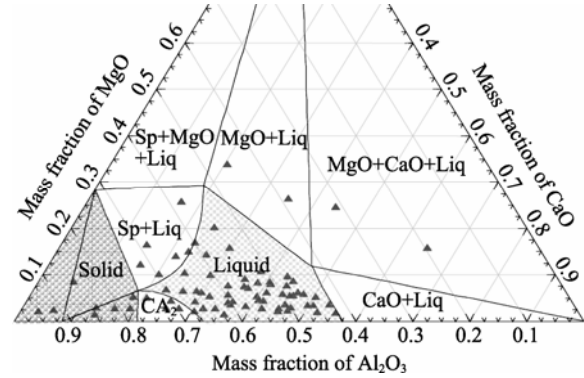


Fig. 4. Composition of inclusions after Ca-treatment.

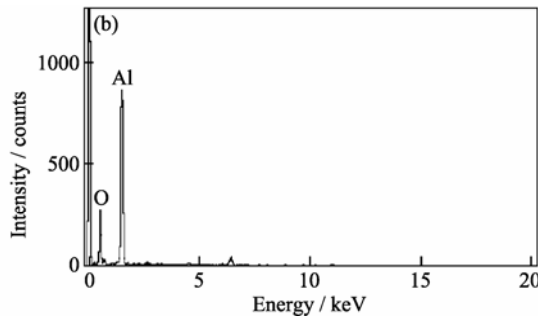
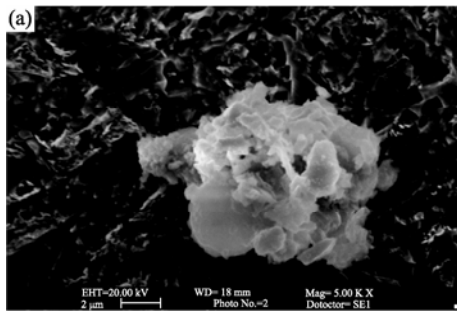


Fig. 5. Morphology (a) and energy spectrum (b) of Al<sub>2</sub>O<sub>3</sub> spinel.

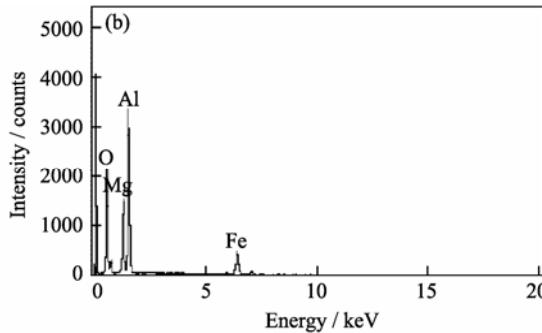
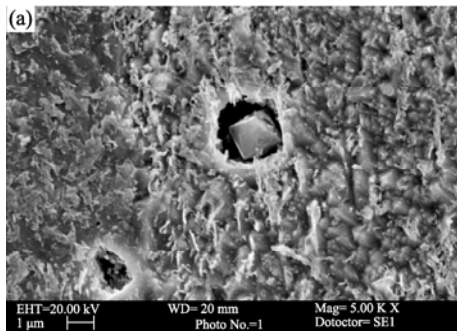


Fig. 6. Morphology (a) and energy spectrum (b) of MgO-Al<sub>2</sub>O<sub>3</sub> spinel.

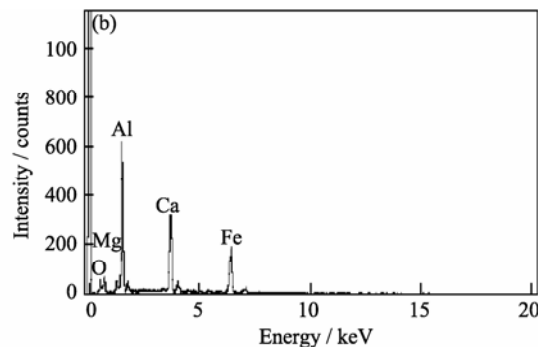
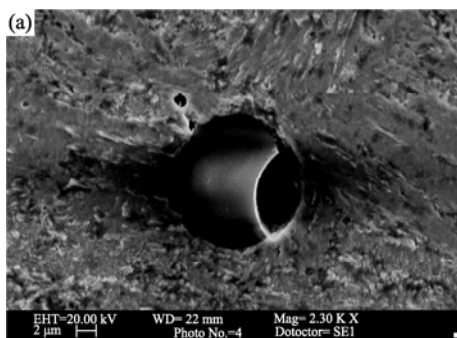


Fig. 7. Morphology (a) and energy spectrum (b) of MgO-Al<sub>2</sub>O<sub>3</sub>-CaO inclusions.

### 3.2. Phase relations in the CaO-Al<sub>2</sub>O<sub>3</sub>-MgO system

Fig. 8 shows the isothermal section at 1600°C of the CaO-Al<sub>2</sub>O<sub>3</sub>-MgO system generated by the FactSage software (Version 6.0). Line *ab* in Fig. 8 shows the modification path of pure Al<sub>2</sub>O<sub>3</sub> inclusions into the all-liquid area. Line *cd* shows a potential modification path of pure MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions by Ca. The diagram shows that 21wt% of CaO is required before an Al<sub>2</sub>O<sub>3</sub> inclusion is modified into a liquid Ca-aluminate or the first liquid phase will appear; in contrast, when CaO is added into the spinel (*cd*), a liquid phase forms immediately. This is graphically shown in Fig. 9. These diagrams indicate that from a strictly fundamental phase relation perspective, pure spinel (MgO·Al<sub>2</sub>O<sub>3</sub>) can be modified to form liquid inclusions but not liquid inclusions completely. Furthermore, the reaction of CaO with spinel to form a liquid phase at low CaO levels suggests that spinel inclusions may be easier to be modified than Al<sub>2</sub>O<sub>3</sub> inclusions because of the faster transformation through a liquid boundary layer.

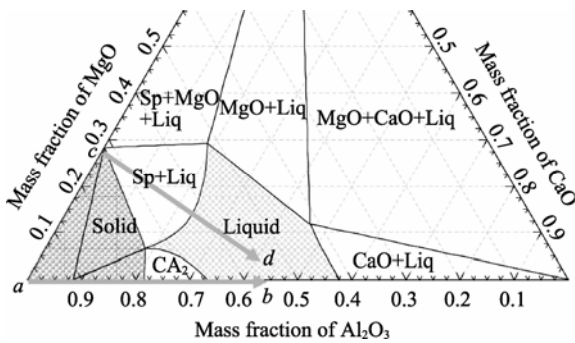


Fig. 8. Isothermal section through the CaO-Al<sub>2</sub>O<sub>3</sub>-MgO system at 1600°C.

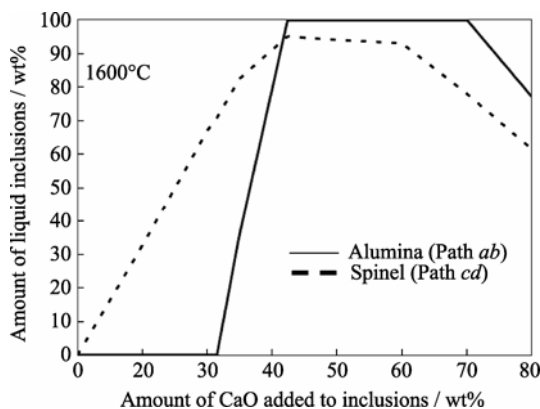


Fig. 9. Amount of liquid that will form when CaO is added to alumina and spinel inclusions at 1600°C.

### 3.3. Thermodynamics of the transformation of MgO·Al<sub>2</sub>O<sub>3</sub> inclusions

Fig. 10 is the equilibrium diagram of Fe-O-Mg-Al-Ca,

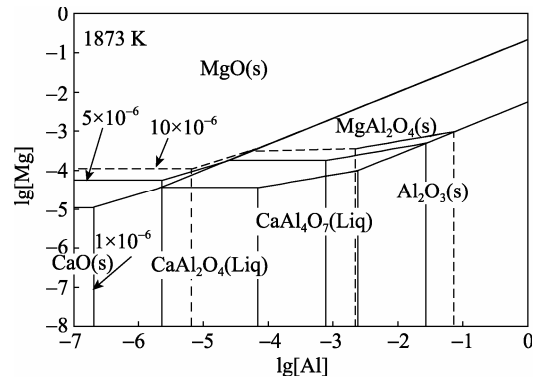


Fig. 10. Equilibrium diagram of Fe-O-Mg-Al-Ca.

and the calcium aluminate inclusions are CaAl<sub>2</sub>O<sub>4</sub> and CaAl<sub>4</sub>O<sub>7</sub> in calculation. In Fig. 10, when the dissolved Al content in the molten steel is less than 10<sup>-2.6</sup>, the content of dissolved Mg is less than 10×10<sup>-6</sup>, and the content of dissolved Ca in the molten steel is about 1×10<sup>-6</sup>; the complex inclusions containing calcium aluminate is stable in the molten steel. Taking 30CrMo alloy steel for example, the content of Al in the molten steel is 0.034wt%, and the Mg content is about 0.0005wt%; when the dissolved Ca content in the molten steel is about 1×10<sup>-6</sup>, the MgO·Al<sub>2</sub>O<sub>3</sub> spinel can be transformed into a liquid complex inclusion. In Fig. 10, when the dissolved Ca content in the molten steel is increased, the liquid complex inclusion region expands rapidly; the lower content of dissolved Mg is in the liquid steel, the lower dissolved Ca content is required to transform into liquid inclusions from MgO·Al<sub>2</sub>O<sub>3</sub> spinels.

### 3.4. Effect of Ca-treatment on the transformation of MgO·Al<sub>2</sub>O<sub>3</sub> inclusions

Fig. 11 shows the effect of Ca-treatment on the compositions of liquid inclusions. According to Fig. 11, when adding 1×10<sup>-6</sup> Ca into the molten steel, MgO·Al<sub>2</sub>O<sub>3</sub> inclusions are transformed into liquid complex inclusions and both the Al<sub>2</sub>O<sub>3</sub> and MgO contents in liquid complex inclusions decrease rapidly, while the CaO content increases sharply. The contents of Al<sub>2</sub>O<sub>3</sub> and MgO in liquid complex inclusions continue to decrease with the increasing amount of Ca added into the molten steel. The content of CaO in liquid complex inclusions goes on increasing with the increasing amount of Ca added into the molten steel, while the content of SiO<sub>2</sub> in liquid complex inclusions changes little. When the amount of Ca added into the molten steel reaches 10×10<sup>-6</sup>, the content of MgO in liquid complex inclusions gets to 7.0wt%, the contents of Al<sub>2</sub>O<sub>3</sub>, CaO, and SiO<sub>2</sub> are 47.5wt%, 44wt%, and 1.5wt%, respectively. The reason for the increase of both CaO and MgO contents in liquid complex inclusions is that MgO in the inclusions is reduced by

Ca, producing CaO into inclusions.

Fig. 12 shows the effect of Ca-treatment on the amount of MgO·Al<sub>2</sub>O<sub>3</sub> in the molten steel. It shows that, when  $2 \times 10^{-6}$  Ca is added into the molten steel, MgO·Al<sub>2</sub>O<sub>3</sub> inclusions can transform liquid complex inclusions completely. Figs. 13 and 14 show the effect of the amount of Ca added on the composition of the molten steel. Fig. 13 shows that the content of dissolved O decreases with the increasing amount of Ca added into the molten steel. The reason is that Mg is a very active element, and it can react with O easily. The content of dissolved Mg increases with the increasing amount of Ca added into the molten steel. The Ca added will react with MgO·Al<sub>2</sub>O<sub>3</sub> inclusions; Mg in MgO·Al<sub>2</sub>O<sub>3</sub> inclusions can be replaced and goes into the molten steel. This is why the content of dissolved Mg increases. Fig. 14 indicates that the content of dissolved Ca increases a little with the

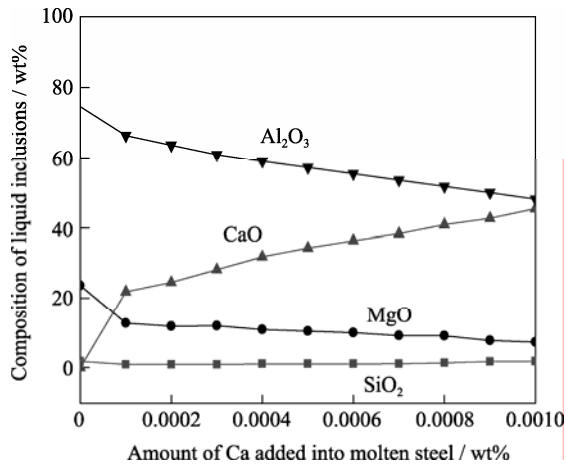


Fig. 11. Relation between the amount of Ca added and the compositions of liquid inclusions.

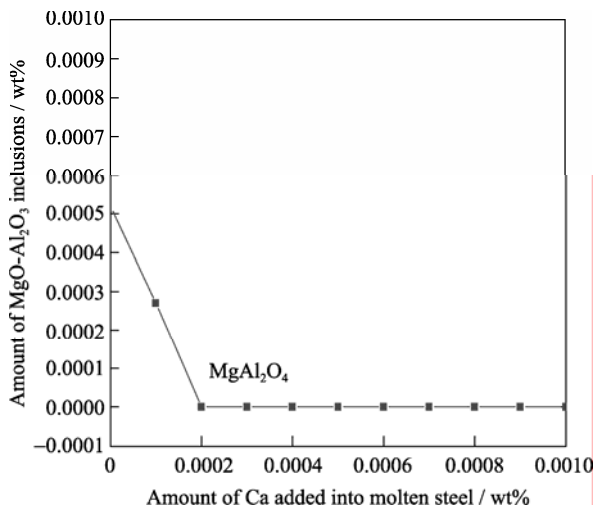


Fig. 12. Relation between the amount of Ca added and the amount of MgO·Al<sub>2</sub>O<sub>3</sub>.

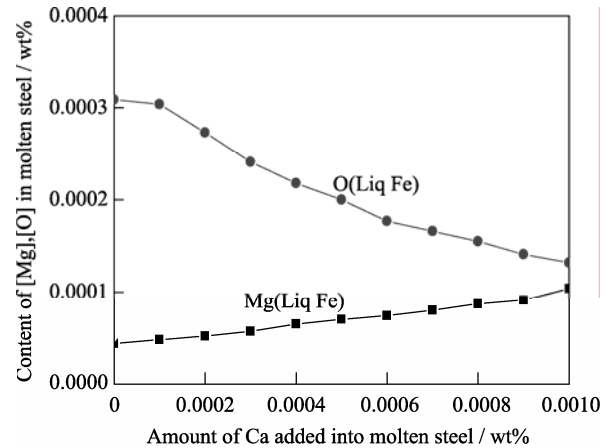


Fig. 13. Relation between the amount of Ca added and the composition of the molten steel.

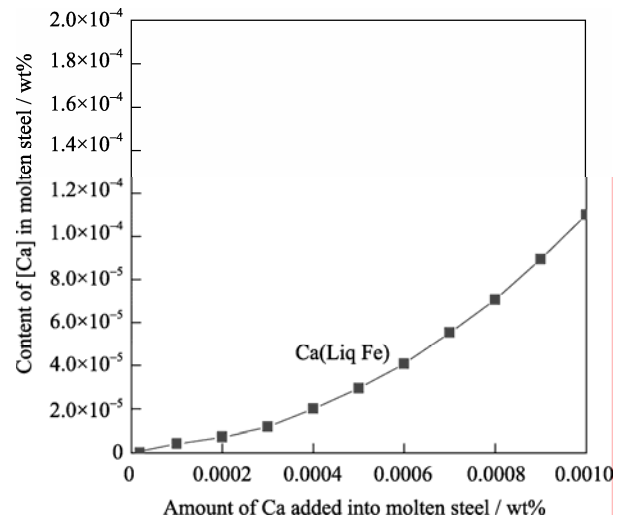


Fig. 14. Relation between the amount of Ca added and the dissolved Ca.

increasing amount of Ca added into the molten steel. When the amount of Ca added reaches  $10 \times 10^{-6}$ , the content of dissolved Ca is less than  $1.2 \times 10^{-6}$ . It should be noticed that the Ca yield is assumed to be 100% in the thermodynamic calculations.

#### 4. Conclusions

(1) The transformation sequence of inclusions during refining is  $\text{Al}_2\text{O}_3 \rightarrow \text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow$  liquid complex inclusions, and the modification of MgO·Al<sub>2</sub>O<sub>3</sub> spinel inclusions by Ca-treatment is effective.

(2) Spinel inclusions are easier to be modified than Al<sub>2</sub>O<sub>3</sub> inclusions, and for 30CrMo steel when the content of Ca in the molten steel reaches  $1 \times 10^{-6}$ , MgO·Al<sub>2</sub>O<sub>3</sub> inclusions will transform into liquid complex inclusions.

(3) The content of dissolved Mg increases with the increasing amount of Ca added into the molten steel; more Ca added into the molten steel lowers the content of Al<sub>2</sub>O<sub>3</sub> and MgO, increases the CaO content in the inclusions, and changes the SiO<sub>2</sub> content a little.

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