

Inclusion Modification by Calcium Treatment

Yoshihiko HIGUCHI, Mitsuhiro NUMATA, Shin FUKAGAWA and Kaoru SHINME

Corporate Research and Development Laboratories, Sumitomo Metal Industries, Ltd., Sunayama, Hasaki-cho, Kashima-gun, Ibaraki-ken, 314-02 Japan.

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A major objective of calcium treatment in steelmaking is to improve product performance through inclusion modification. To establish inclusion modification, shape and composition of inclusions were monitored using SEM during and after addition of calcium wire into 2 kg heats of steel under various conditions of Ca consumption and Ca addition pattern. A mathematical model of the kinetics considering the evaporation of calcium and the reaction between inclusions and melt was developed to thoroughly examine these phenomena in calcium treatment. The calculated results were compared with the observed ones which were obtained in experiments.

(1) Shape and composition of inclusions changed from a spherical $\text{SiO}_2\text{-MnO}$ system to almost lumpy Al_2O_3 with the addition of aluminum, and to spherical $\text{CaO-Al}_2\text{O}_3$ including CaS after addition of CaSi.

(2) The process and consumption of calcium were found to affect the change of CaO and CaS contents of inclusions.

(3) A mathematical model was developed assuming that vaporization rate of calcium from the melt and rate of reaction between melt and inclusions can be described by equations of the first order reaction, and that the size and number of inclusions remain constant during treatment.

(4) The calculated [Ca] and CaO, CaS contents of inclusions showed good agreement with observed ones regardless of the conditions of CaSi addition.

KEY WORDS: kinetics; calcium; deoxidation; inclusions; calcium aluminate; calcium sulfide.

1. Introduction

A major objective of calcium treatment in steelmaking is to improve product performance through inclusion modification. To establish inclusion modification, the shape and composition of inclusions should be controlled within a desired range. While many investigations have been made on the thermodynamics of calcium oxidation and desulfurization based on equilibrium experiments,¹⁻¹⁴⁾ differing results have been obtained. These differences are thought to have been obtained because the aspect of possible kinetics has been ignored.

Ito *et al.*¹⁵⁾ recently investigated the time variation of compositions of inclusions assuming the unreacted core model in which the process could be diffusion-controlled in the reaction layer in the inclusions. But the time variation of composition of inclusions could not be predicted without analysis of the calcium content because they neglected the vaporization phenomenon.

D-Z. Lu *et al.*¹⁶⁾ monitored the modification of both sulphide and oxide inclusions during and after injection into steel by frequent sampling and developed a mathematical model of the kinetics based upon fundamental transport phenomena with consideration of the evaporation rate. They did not, however, pay any attention to the reaction between inclusions and melt because they assumed that the diffusion within the inclusions was rapid enough.

The objective of the present work was to develop a mathematical model of the kinetics which considered the evaporation rate of calcium and the reaction rate between inclusions and melt.

2. Experimental Procedure

A general view of the induction furnace unit is schematically shown in Fig. 1. The furnace is enclosed in a chamber which is equipped with an argon inlet, a viewing window and a port for adding additives and

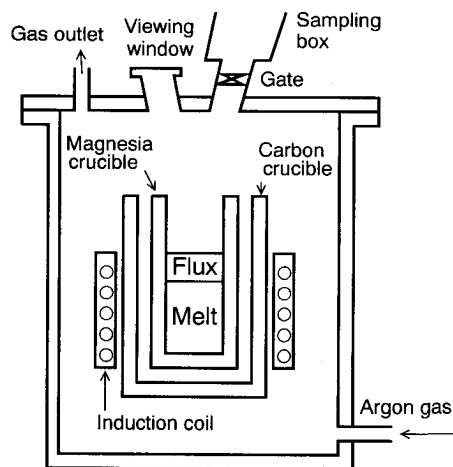


Fig. 1. Schematic diagram of experimental equipment.

sampling specimens of the melt. Two kg of electrolytic iron was melted in a MgO crucible by high frequency induction furnace in a stream of purified argon gas and the temperature of melt was held at 1873 K.

The experimental procedures were: Firstly, reagents of Fe_2O_3 were added to control the oxygen activity of the melt at 0.03 which is Henry's standard based on the output of zirconia oxygen sensor. Secondly, alloy containing 14%Si-86%Mn and aluminum were consecutively added to the melt as deoxidizers. The composition of the melt was thus kept at 0.05% C, 0.2% Si, 1.2% Mn, 0.001% S and 0.03% Al. Thirdly, the flux of 48%CaO-40% Al_2O_3 -4% SiO_2 -6%MgO-2% CaF_2 was added to the melt surface as cover slag. Five minutes after flux addition, the 30%Ca-70%Si steel-clad calcium silicon wire wrapped with steel was used as reagent for inclusion modification.

Samples of the melt were taken frequently with steel bomb-type samplers during and after calcium addition and the composition was determined by chemical analysis. Shape of inclusions was monitored using SEM and their compositions were determined by EPMA within the scatter of 5%.

3. Results

Shape and composition of inclusions changed from spherical SiO_2 -MnO system to almost lumpy Al_2O_3 with the addition of aluminum, and to spherical CaO- Al_2O_3 including CaS after adding CaSi. Changes in [Ca] and CaO and CaS content of inclusions are shown in Figs. 2 and 3 as examples of calcium addition with the consumption of CaSi 2g and 6g at a time, respectively. [Ca] and CaO content in these heats showed maximum values just after calcium addition and then decreased gradually. CaS content of inclusions was analyzed to be 22% only 3 min after adding calcium to the heat with the consumption of CaSi 6g, though calcium sulphide was not observed in the heat of CaSi 2g. Changes in [Ca] and CaO content of inclusions are shown in Fig. 4 in the heat with 4 calcium additions. [Ca] and CaO content in this heat increased gradually each time CaSi was added. Calcium sulphide was not observed in this heat. Process and consumption of calcium were found to affect the change of inclusion composition as stated

earlier.

The size of inclusions was found to be constant at nearly 1 micro-meter within a small scatter in all experiments. The total sulphur in the samples was also constant with analyzed values of nearly 10 ppm in each heat.

4. Discussion

4.1. Rate Controlling Factors

These phenomena are shown schematically in Fig. 5. Calcium dissolved in the melt just after adding calcium silicon reacts rapidly with alumina inclusions to form calcium aluminate or calcium sulphide. The contents of CaO and CaS in the inclusions decrease gradually as the dissolved calcium vaporizes and decreases with the lapse of time. The change of [Ca] and inclusion compositions was very fast in the present experiments, and is assumed to result from the high evaporation rate of calcium due to the high specific surface area of molten steel. The instantaneous reactions between calcium and sulphur and oxygen in the melt are inevitable and complicate the phenomena. The present authors¹⁸⁾ earlier investigated the relationship between [Ca] and CaO, CaS contents of inclusions and showed that the critical condition for the presence of CaS phase in inclusions had good agreement with thermodynamic prediction based on reaction $\text{CaO} + \text{S} = \text{CaS} + \text{O}$. But the factors were not

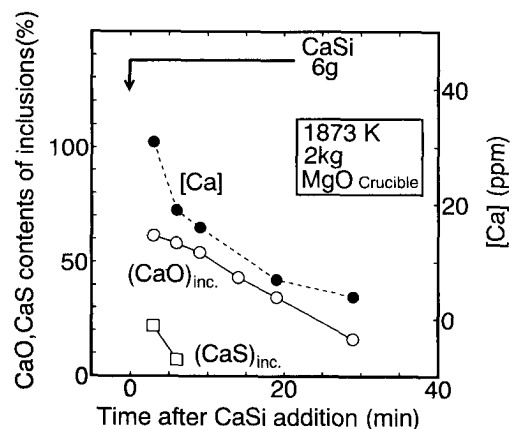


Fig. 3. Change of CaO contents of inclusions and [Ca] after CaSi addition.

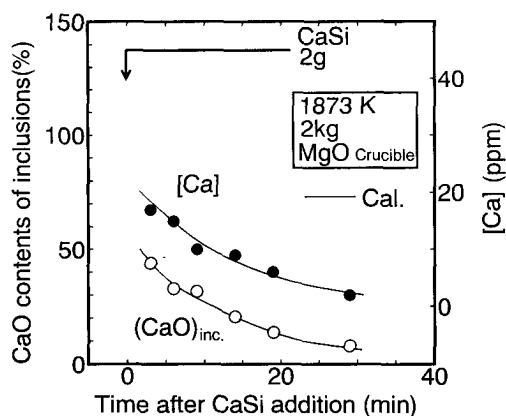


Fig. 2. Change of CaO contents of inclusions and [Ca] after CaSi addition.

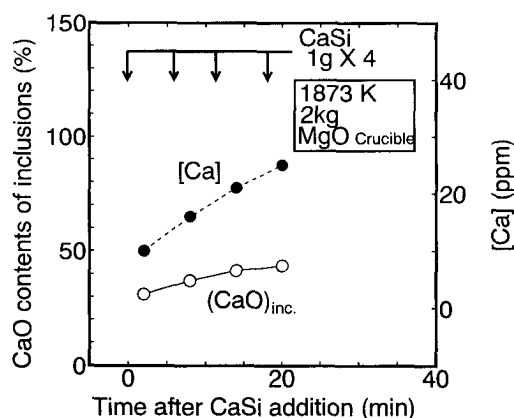


Fig. 4. Change of CaO contents of inclusions and [Ca] after CaSi addition.

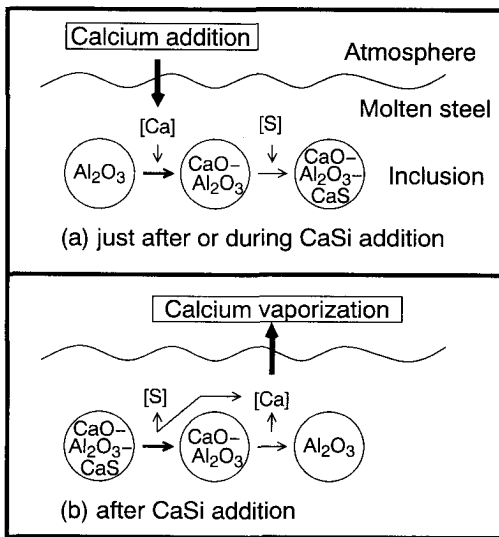


Fig. 5. Mechanism of change of inclusion composition.

clarified that control the time variation of $[\text{Ca}]$ and inclusion compositions. Ito *et al.*¹⁵⁾ studied the time variation of inclusion compositions under the assumption of the unreacted core model in which the process could be controlled by diffusion in the reaction layer in the inclusions. They found, however, that the inclusion compositions could be predicted only when calcium content was chemically analyzed, because they neglected the vaporization of calcium from the melt. D-Z. Lu *et al.*¹⁶⁾ on the other hand, developed a mathematical model of the kinetics based upon fundamental transport phenomena with consideration of the evaporation rate; but they did not give attention to the reaction between inclusions and melt because they assumed that diffusion within them was fast enough.

4.2. Mathematical Model of Kinetics

A mathematical model of the kinetics was thus developed here which takes into account both the evaporation rate of calcium and the reaction rate between inclusions and melt. These phenomena were formulated as follows:

The evaporation rate of calcium from the melt to the atmosphere can be written:

$$-dCa/dt = ksAsCa$$

where, Ca : concentration of calcium in the melt (%),
 ks : mass transfer coefficient (m/s), and
 As : interfacial area per melt volume between melt and atmosphere (m^{-1}).

The mass transfer coefficient was determined to be 0.0075 m/s based on previous work.¹⁶⁾ Theoretically, the diffusion term of calcium from the bulk to the surface within the melt should be taken into consideration, but they were neglected in this model.

The rate of reaction between calcium in the melt and inclusions can be written:

$$-dCa_i/dt = Ki(Ca_i - Ca_e)$$

where, Ca_i : concentration of calcium in inclusions (%),

Ca_e : equilibrium concentration of calcium in inclusions, and

Ki : apparent rate constant (s^{-1}).

The activity of CaO in inclusions can be expressed as follows:

$$a_{\text{CaO}} = f_{\text{Ca}}[\text{Ca}]a_{\text{O}}/K_{\text{CaO}}$$

where, K_{CaO} : equilibrium constant of $\text{Ca} + \text{O} = \text{CaO}$,

a_{CaO} : activity of CaO in inclusions,

a_{O} : activity of oxygen, and

f_{Ca} : activity coefficient of Ca.

Ca_e could be obtained using calculated a_{CaO} and the relationship between the activities of CaO and CaO contents in the calcium aluminate system evaluated previously.⁴⁾

The rate of reaction between sulphur in melt and inclusions can be written:

$$-dS_i/dt = Ks(S_i - S_e)$$

where, S_i : concentration of sulphur in inclusions (%),

S_e : equilibrium concentration of sulphur in inclusions (%), and

Ks : apparent rate constant (s^{-1}).

The activity of CaS in inclusions can be expressed as follows:

$$a_{\text{CaS}} = K_{\text{CaS}}a_{\text{CaO}}f_{\text{S}}[\text{S}]/a_{\text{O}}$$

where, K_{CaS} : equilibrium constant of $\text{CaO} + \text{S} = \text{CaS} + \text{O}$, and

f_{S} : activity coefficient of sulphur.

S_e could also be obtained using calculated a_{CaS} and the relationship between the activities of CaS and CaS contents reported previously.⁴⁾ The parameters of Ki and Ks were determined to be 0.006 and 0.01 s^{-1} by parameter fitting, respectively.

4.3. Comparison of Calculated with Experimental Results

These three differential equations were calculated by a numerical method simultaneously under the condition that the size and number of inclusions was kept constant during and after calcium addition. The calculated $[\text{Ca}]$ and CaO contents of inclusions are shown by the solid line in Fig. 2 for the heat in the consumption of CaSi 2 g. The calculated values showed good agreement with observed ones in both the $[\text{Ca}]$ and CaO contents of inclusions. The calculated CaO contents of inclusions also are in good agreement with the observed ones in both the heat with CaSi 6 g and the heat with 4 calcium additions as shown in Figs. 6 and 7, respectively. In the latter heat, CaO contents of inclusions were presumed to increase and decrease repeatedly during the treatment from the calculation though they appeared to increase monotonously.

5. Conclusions

To establish a technology for inclusion modification, the shape and composition of inclusions were monitored by SEM during and after addition of calcium wire into 2 kg heats of steel under various conditions of Ca consumption and addition pattern. A mathematical

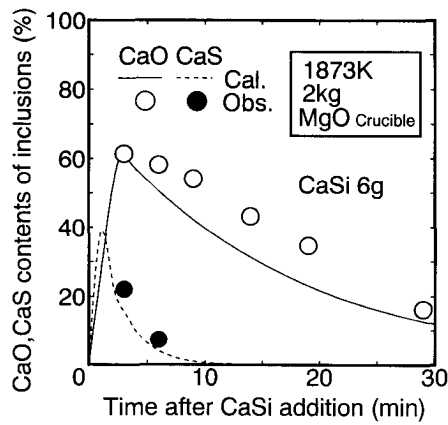


Fig. 6. Comparison of observed CaO, CaS contents of inclusions and calculated ones.

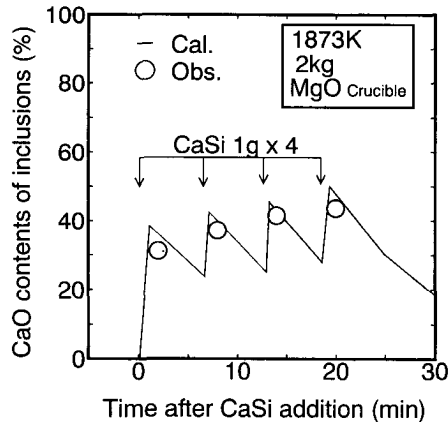


Fig. 7. Comparison of observed CaO, CaS contents of inclusions and calculated ones.

model of the kinetics was developed taking into consideration the evaporation of calcium and the reaction between inclusions and melt to thoroughly examine the phenomena in the calcium treatment. The calculated and observed results were compared.

(1) Shape and composition of inclusions changed from a spherical $\text{SiO}_2\text{-MnO}$ system to almost lumpy Al_2O_3 with the addition of aluminum, and to spherical $\text{CaO-Al}_2\text{O}_3$ including CaS after adding CaSi.

(2) Process and consumption of calcium were found

to affect changes in CaO and CaS contents of inclusions.

(3) A mathematical model was developed by assuming that vaporization rate of calcium from the melt and rate of reaction between melt and inclusions can be described with equations of the first order reaction and that the size and number of inclusions remain constant during treatment.

(4) The calculated [Ca] and CaO, CaS contents of inclusions showed good agreement with those observed regardless of the conditions of CaSi addition.

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