Change in Inclusion Composition during CaO Flux Powder Blowing under Reduced Pressure

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To examine the reaction mechanism of the variation of calcium content in inclusions and the molten steel and the effect of flux composition on the reaction, the variations of molten steel content and inclusion content during CaO, 60%CaO–40%CaF2 or 50%CaO–50%CaSi powder blowing onto the molten steel under reduced pressure were investigated with 15 kg scale experiments. From the experimental results, it was found that the inclusion composition was changed from Al₂O₃ to Al₂O₃–CaO by CaO flux that did not contain CaSi alloy, and that the reaction path of the inclusion composition was changed remarkably by CaSi alloy in CaO flux. From the experimental results and the chemical thermodynamic calculation, the effects of the flux and CaSi alloy on the change in composition of inclusion and melts were examined.

KEY WORDS: calcium treatment; inclusion; kinetics; powder blowing.

1. Introduction

The major objective of calcium treatment in the secondary steel making process is to improve the product property of the steel by the inclusion shape control. Especially, the demands on sour service line pipes have become so severe that accurate inclusion shape control and high desulfurization ratio have been required. Although the reaction between calcium and sulfur in molten steel has decreased sulfur content by the addition of calcium, this reaction has caused the formation of CaO–CaS or CaO–CaS–Al₂O₃ inclusions. The more accurate control of the formation of these inclusions has been required because the increase of inclusions causes deterioration of the performance of steel.

Therefore, many studies of inclusion composition during the calcium treatment have been made, especially on the equilibrium of calcium deoxidation and calcium desulfurization.

Since calcium vaporizes from the molten steel, the change in calcium content with time is influenced by the vaporization reaction during calcium treatment as well as after calcium treatment. Thus, the inclusion composition changes with time due to the change of calcium content in molten steel. Therefore, D-Z. Lu et al. monitored the variation of composition of both sulfide and oxide inclusions during and after calcium addition to molten steel and developed the mathematical model of the kinetics based upon transport phenomena with consideration of the calcium vaporization rate.

Itoh et al. studied shape control of alumina inclusions during calcium double treatment in line pipe steel for sour service and applied the unreacted core model to experimental results. Higuchi et al. developed the mathematical model of the kinetics which considered the evaporation rate of calcium and the reaction rate between inclusions and the molten steel. There are, however, few studies on the kinetics of the inclusion composition change during calcium addition and the relationship between the flux-metal reaction rate and inclusion-metal reaction rate.

On the other hand, many studies are reported on the desulfurization using slag-metal reaction or CaO flux-metal reaction. Okano et al. studied the desulfurization ratio which was obtained with the RH-PB method and examined the relationship between the desulfurization ratio and flux consumption. They did not, however, examined the reaction rate between flux and molten steel.

The objective of the present work was to examine the reaction mechanism of the variation of calcium content in inclusions and the molten steel and the effect of flux composition on the reactions. In the present work, the variations of molten steel composition and inclusion composition during CaO, 50%CaO–50%CaF₂ or 50%CaO–50%CaSi powder blowing onto the molten steel under reduced pressure were investigated with 15 kg scale experiments.

2. Experimental Procedure

The experiments were conducted with a high frequency induction furnace in which the atmosphere was controlled. The schematic view of the experimental equipment is shown in Fig. 1 and the experimental conditions are shown in Table 1.

The furnace was set in the chamber which was connected with a vacuum pump. A lance (I.D. 5×10⁻³ m) was installed at the top of the chamber and the distance between the lance
tip and the melt surface was 1.5×10⁻² m. The structure of the nozzle was straight type and the temperature of the molten steel was controlled with a thermocouple set in the melt. 15 kg of electrolytic iron was melted in the MgO crucible (I.D. 1.45×10⁻¹ m) under argon atmosphere at 101 kPa and the temperature of the molten steel was held at 1 873 K. The average change of temperature during the experiments were about 10 K.

83 mass% Fe–17 mass% S alloy was added to the molten steel to adjust the sulfur content ranging from 0.003 mass% to 0.006 mass%. Then aluminum was added to the molten steel to adjust the aluminum content to be from 0.018 to 0.15 mass%. After the composition adjustment of the molten steel, the pressure was reduced to 665 Pa and powder was blown onto the molten steel from the lance for 1 200 s. The powder blowing condition is shown in Table 2. The melt was continuously stirred with argon from porous brick while the flux powder was blowing.

The compositions of the flux and molten steel before powder blowing are shown in Table 3. CaO powder was blown onto the molten steel, for which the aluminum content was adjusted to be 0.05%, 0.092% or 0.15% with argon gas in Heats 1, 2 and 3. In Heats 4 and 5, premelted 50%CaO–50%CaF₂ powder was blown onto the molten steel for which the aluminum content was adjusted to be 0.039% or 0.13%. In Heats 6 and 7, the powder, which was a mixed CaO powder and 30 mass%Ca–70 mass%Si alloy powder, was blown onto the molten steel for which the aluminum content was adjusted to be 0.018% or 0.045%.

The powder was supplied with the rotary feeder. The powder feeding rate and total amount of the blown powder were 0.0075 kg/min and 0.15 kg, respectively. The argon gas flow rate was 10 l/min (s.t.p) in every experiment.

The purities of the argon gas and the powder are 99.99% and 99.9%, respectively. The samples of the molten steel were taken at intervals of 10 min with steel bomb-type samplers during the experiments. The composition of the molten steel composition was determined by chemical analysis and the composition of inclusions was determined by EPMA (Electron Probe Micro Analyzer). The oxygen content of the sample was analyzed by the inert gas fusion principle with infrared absorption method using an oxygen analyzer.

3. Results

3.1. Variation of Composition of Molten Steel with Time

The variation of aluminum content in the molten steel during powder blowing is shown in Fig. 2. Aluminum content decreased steadily during powder blowing in all heats except Heat 6. The amount of the decrease of aluminum content was increased with the increase of the initial aluminum content. The variation of calcium content in the molten steel during powder blowing is shown in Fig. 3. The calcium content in the molten steel  was increased by the powder blowing in all heats. Though calcium content increased remarkably in Heats 6 and 7 where CaSi alloy containing flux was blown onto the melt, the variation of calcium content in Heats 2, 3 and 5 did not increase compared with Heats 6 and 7. In Heats 1 and 4, calcium content was maintained at 0.0002% or less. The variation of sulfur content in the molten steel is shown in Fig. 4. Sulfur content in the molten steel decreased during powder blowing in all heats, and especially, the sulfur content decreased rapidly in Heats 2 and 3. In Heat 3, sulfur content decreased from 0.0055% to 0.0007% by CaO powder blowing onto the molten steel with high aluminum concentration. The variation of oxygen content in the molten steel is shown in Fig. 5. Oxygen content in the molten steel was less than 0.001% at the start of the experiments and increased gradually during powder blowing.
3.2. Variation of Composition of Inclusion Steel with Time

The composition of inclusions changed from lumpy Al$_2$O$_3$ to Al$_2$O$_3$–CaO system including CaS during powder blowing. The variation of calcium content in Al$_2$O$_3$–CaO–CaS inclusions is shown in Fig. 6. Though calcium content in inclusions increased remarkably in Heats 6 and 7 where CaSi alloy containing flux was blown onto the melt, the variation of calcium content in inclusions in Heats 2, 3 and 5 did not increase compared with Heats 6 and 7. The variation of calcium content in inclusions had a tendency similar to the variation of calcium content in the molten steel.

CaS content in Al$_2$O$_3$–CaO–CaS inclusions was calculated from sulfur content in inclusions, and the difference between total calcium in inclusions and calcium content as CaS was assumed to be CaO content in Al$_2$O$_3$–CaO–CaS inclusions. The variation of CaO content in Al$_2$O$_3$–CaO–CaS inclusions is shown Fig. 7. CaO content in inclusions increased by powder blowing onto the molten steel and CaO content increased up to 37% in Heats 6 and 7. The variation of CaS content in Al$_2$O$_3$–CaO–CaS inclusions is shown Fig. 8. CaS content in inclusions increased by CaO–50%CaSi powder blowing in Heats 6 and 7, however, CaS content in inclusions increased slightly until 600 s and decreased after 600 s in Heats 1–5. The variation of inclusion composition is shown in Fig. 9. The dashed arrows indicate the direction of reaction with time. The composition of inclusions was changed from Al$_2$O$_3$ toward CaO maintaining low CaS concentration during CaO or CaO–CaF$_2$ powder blowing in Heats 1–5. On the other hand, the composition of inclusions...
was changed from Al₂O₃ inclusions toward CaO–CaS inclusions during CaO–50%CaSi powder blowing in Heats 6 and 7. From the above experimental results, it was clarified that the inclusion composition was changed from Al₂O₃ to Al₂O₃–CaO by CaO flux that did not contain CaSi alloy, and the reaction path of the inclusion composition was changed remarkably by CaSi alloy in CaO flux.

4. Discussion

4.1. Kinetics and Equilibrium of Desulfurization

In this work, it is considered that the desulfurization reactions are shown in the following reaction equations during powder blowing.

\[ 3(CaO) + 3S + 2Al = 3(CaS) + (Al_2O_3) \].......................... (1)

\[ Ca + S = (CaS) \].............................. (2)

(CaO) and (CaS) represent the components in CaO flux or inclusions. Since the variation of sulfur content showed first-order dependence in Fig. 4, the apparent desulfurization rate from the molten steel to flux can be written:

\[ \frac{-d[S]}{dt} = k_s A [S] \].......................... (3)

where, \([S]\) : content of sulfur in the molten steel(\%),

\[ k_s \] : apparent rate constant(m/s) and

\[ A \] : interfacial area per melt volume between melt and atmosphere(m⁻¹).

It is considered that the rate constant depends on the aluminum content in the molten steel based on Eq. (1), therefore the apparent rate constant \( k_s \) was increased due to the increase of aluminum content. The relationship between aluminum content and \( k_s \) is shown in Fig. 10. Aluminum content affected the apparent rate constant \( k_s \) and the rate was accelerated with increasing aluminum content in Heats 1–5. Therefore it is estimated that the desulfurization was affected by Eq. (1) in Heats 1–5.

In Heats 6 and 7, however, the dependency of apparent rate constant \( k_s \) showed different tendencies, and it is suggested that the desulfurization was affected by Eq. (2) in addition to Eq. (1) in Heats 6 and 7.

It is considered that experimental sulfur content in the molten steel is higher than the sulfur content for the calcium desulfurization equilibrium in the Fe–Ca–S system reported by previous studies based on Eq. (2). The relationship between calcium content and sulfur content in molten steel is shown in Fig. 11 together with the calculated results in the previous study.²⁻¹ It is found that the sulfur content was changed from the region under the calculated value to the region above the calculated value in Heats 6 and 7. Therefore, it is estimated that the desulfurization at the end of the experiments had the driving force shown by Eq. (2) because CaSi containing flux alloy was blown onto the molten steel in Heats 6 and 7. Therefore, CaS content in the inclusions increased remarkably due to the reaction expressed by Eq. (2) although aluminum content was low.

4.2. Reaction between Al in the Molten Steel and Flux

In this work, the decrease of aluminum content and the
increase of calcium content in the molten steel progressed simultaneously during powder blowing. The relationship between aluminum content and calcium content in the molten steel is shown in Fig. 12 for Heats 1–5. Calcium content in the molten steel increased gradually with the increase of aluminum content in Heats 1–5. It is suggested that the reaction between calcium and aluminum in molten steel is shown by Eq. (4) from the experimental results.

$$3(\text{CaO}) + 2\text{Al} = (\text{Al}_2\text{O}_3) + 3\text{Ca} \quad \ldots \ldots (4)$$

(CaO) and (Al$_2$O$_3$) represent the components in CaO flux. Next, the relationship between calcium content in the molten steel and calcium content in inclusion is shown in Fig. 13. Since calcium content in inclusions increased with increase of calcium content in the molten steel, it is estimated that calcium was supplied into the molten steel from CaO flux according to Eq. (4) and the supplied calcium from the flux reacted with the inclusions. Chemical thermodynamic calculation was made in order to confirm that the reaction between calcium and aluminum proceeded according to Eq. (4). Equation (4) is yielded by combination of Eqs. (5) and (6).

$$\text{CaO} = \text{Ca} + \text{O} \quad \ldots \ldots \ldots \ldots (5)$$

$$\text{Al}_2\text{O}_3 = 2\text{Al} + 3\text{O} \quad \ldots \ldots \ldots \ldots (6)$$

The relationship between aluminum activity and the equilibrium calcium activity was calculated from equilibrium constants of Eqs. (5) and (6) obtained by Itoh et al.\textsuperscript{18,19} Activity of CaO and Al$_2$O$_3$ was assumed to be 1.0 and 0.01 or 0.01 and 1.0, respectively.\textsuperscript{20} The experimental activities were calculated using experimental aluminum contents, calcium content, oxygen content and the interaction parameters. The interaction parameters used in the present work are shown in Table 4.

The relationship between the calculated values from Eq. (4) and the experimental activity are shown in Fig. 14. The dashed arrow indicates the direction of reaction. The experimental activities in Heats 4 and 5 were shown in Fig. 14 though the flux contained CaF$_2$. Calcium content was changed from the side near the Al$_2$O$_3$ saturation region to the side near the CaO saturation region by powder blowing in all heats, therefore the inclusion composition was changed from Al$_2$O$_3$ to Al$_2$O$_3$–CaO. The experimental calcium activities were lower than the calculated values in Heats 1–7, but the difference between the experimental activities and calculated values was small in Heats 6 and 7. It is considered that calcium content in inclusions increased remarkably in Heats 6 and 7 since calcium content increased up to the calcium equilibrium content by blowing CaSi alloy onto the molten steel.

From the above discussion, it is estimated that calcium content in inclusions was increased with the increase of

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<th>Table 4. The interaction parameters used in the present work.</th>
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<td>$e^{Al}<em>{Al}$ &amp; $e^{O}</em>{Al}$ &amp; $e^{Ca}<em>{Al}$ &amp; $e^{Ca}</em>{Ca}$ &amp; $e^{O}<em>{Ca}$ &amp; $e^{Al}</em>{Ca}$</td>
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<tr>
<td>0.045 &amp; -1.98 &amp; -0.047 &amp; -18 &amp; -780 &amp; -0.072</td>
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<td>Ref.(21) &amp; Ref.(18) &amp; Ref.(22) &amp; Ref.(23) &amp; Ref.(19) &amp; Ref.(22)</td>
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![Fig. 12. Relationship between aluminum content and calcium content in the molten steel.](image)

![Fig. 13. Relationship between calcium content in the molten steel and that in inclusions.](image)

![Fig. 14. Comparison of observed activities in molten steel and calculated ones.](image)

![Fig. 15. Relationship between oxygen activity and sulfur activity in the molten steel.](image)
calcium content in molten steel due to the proceeding reaction between CaO flux and aluminum in the molten steel.

Since the inclusion contained CaO and CaS in this work, it is necessary to consider relationship between oxygen and sulfur. The reaction between oxygen and sulfur is shown by Eq. (7).

\[(\text{CaO}) + S \rightarrow (\text{CaS}) + O\] .................................. (7)

Equation (7) is yielded by combination of Eqs. (5) and (2) and oxygen activity is obtained by Eq. (6). Activity of CaO was assumed to be 1.0 and 0.1\(^{24}\) and the experimental sulfur activity was calculated using \(e_{s}^{o} = -22.4\)\(^{17}\).

The relationship between the calculated values from Eq. (7) and the experimental activity are shown in Fig. 15. The dashed arrow indicates the direction of reaction. Oxygen activity and sulfur activity were changed from the side near the Al\(_2\)O\(_3\) saturation region to the side near the CaO and CaS saturation region by powder blowing in all heats.

5. Conclusions
To examine the reaction mechanism of the variation of calcium content in inclusions and the molten steel and the effect of flux composition on the reactions, variations of molten steel composition and inclusion composition during CaO, 50%CaO–50%CaF\(_2\) or 50%CaO–50%CaSi powder blowing onto the molten steel under reduced pressure were investigated with 15 kg scale experiments.

The apparent rate constant of desulfurization was dependent on the aluminum content and calcium content in the molten steel. The calcium content in the molten steel and inclusions were increased by blowing of CaO powder which did not contain CaSi alloy.

From the experimental results and the chemical thermodynamic calculation, the effects of the flux and CaSi alloy on the change in composition of inclusion and melts were examined. It was estimated that the desulfurization proceeded mainly according to Eqs. (1) and (2) in this work.

\[3(\text{CaO}) + 3S + 2\text{Al} \rightarrow 3(\text{CaS}) + (\text{Al}_2\text{O}_3)\] .......... (1)

\[\text{Ca} + S \rightarrow (\text{CaS})\] .................................. (2)

In addition, it was estimated that calcium content in inclusions was increased with the increase of calcium content in molten steel due to the proceeding reaction between CaO flux and aluminum in the molten steel.

REFERENCES