Effect of Changes in Sulfur and Oxygen Concentration on Change in Nitrogen Concentration in Liquid Steel during CaO–CaSi Powder Blowing under Reduced Pressure

Mitsuhiro NUMATA* and Yoshihiko HIGUCHI


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In this paper, 1,500 kg scale experiments of CaSi mixed CaO powder top blowing onto the Al killed steel were carried out under reduced pressure. And the effects of CaSi alloy ratio in the mixture on reactions of desulfurization and nitrogen removal were examined. Aluminum decreasing rate decreased and rate constant of desulfurization and nitrogen removal increased with increasing CaSi mixing ratio to flux. It is supposed from the above that deoxidation and desulfurization reaction can simultaneously occur by blowing the mixture of CaSi and CaO powder and the effect of calcium mixing powder on desulfurization can be explained by promotion of CaO desulfurization and CaS formation. It is suggested that lower oxygen and sulfur activity due to reaction between molten steel and powder with CaSi increased rate constant of nitrogen removal.

KEY WORDS: secondary steelmaking; ladle metallurgy; powder blowing; nitrogen desorption; desulfurization.

1. Introduction

Nitrogen in steel can easily diffuse even at room temperature, induces strain aging and affects mechanical properties by forming nitride and carbide, so it is necessary to decrease nitrogen content in steel.

So far, many researches have been carried out on reaction of nitrogen removal from molten steel and important findings have been obtained. For instance, mass transfer resistance in gas and liquid phases has been discussed in the light of rate-controlling step and chemical reaction rate constant is also being clarified.1–7)

Moreover, effects of surface active elements such as sulfur and oxygen on chemical reaction rate constant have been recently studied by many researchers.8–10) Many studies have also been reported on measurement method of nitrogen removal.11–18)

The present authors previously performed CaO powder top blowing experiments to remove sulfur and nitrogen from molten steel, examined increase of nitrogen removal rate constant due to activity changes in sulfur and oxygen resulting from reaction between CaO powder and melt, and confirmed that the same phenomenon occurred at the comparatively large scale (1,500 kg) experiments as well as the small scale experiments mentioned above.19) And it was found out that powder compositions affected nitrogen removal rate through the change in oxygen activity due to the change in alumina activity in the powder.

Eventually, it was suggested that lower oxygen activity caused by reaction between aluminum in steel and alumina in powder led to lower sulfur activity and higher removal rate of nitrogen. In short, it could be assumed that activity of oxygen and sulfur is controlled with reaction between molten steel and powder. It also suggests that the higher removal rate of nitrogen could be obtained by lowering the activities in other ways.

As a way to lower the activities without flux power, addition of metal capable of oxidation and desulfurization can be included. Ca, Mg, alkali earth metal and lanthanoids (for example, Ce) are known as the suitable kinds of metal for that purpose. In the present study based on CaO flux, Ca was selected and CaSi alloy was adopted as stable addition agent.

In this paper, 1,500 kg scale experiments of CaSi mixed CaO powder top blowing onto the Al killed steel were carried out under reduced pressure. And the effects of CaSi alloy ratio in the mixture on reactions of desulfurization and nitrogen removal are examined to confirm that nitrogen removal rate could increase with lowering activities of oxygen and sulfur.

2. Experimental Procedure

The schematic diagram of experimental apparatus is shown in Fig. 1. The induction vacuum furnace of 600 kW and 1 kHz was used in the experiments. Ultra low carbon steel of 1,500 kg was inserted as raw material in the furnace with magnesia lining(φ7.5 × 10⁻¹ m). Raw material was heated in the chamber in which the pressure was maintained...
at 13 kPa by introducing argon gas. After the temperature of molten steel was held at 1873 K, molten steel was stirred with bottom blowing of 10 l(STP)/min argon from two porous bricks located in the bottom of the furnace. After confirming the stable gas stirring, metal silicon, manganese, manganese nitride alloy, aluminum and FeS(26 mass%S-74%Fe) alloy were added to the molten steel and the compositions were adjusted as shown in Table 1. The additive amount of aluminum and FeS were 1.5 kg, 0.15 kg, respectively.

Thereafter, the chamber pressure of 100 Pa was maintained under argon atmosphere with steam ejector. The argon gas of 500 l(STP)/min was blown to the metal surface through the lance tip with the height of 0.4 m. The straight-shape nozzle with inner diameter of $1.0 \times 10^{-2}$ m was used. After confirming the stable top blowing gas flow rate and atmospheric pressure, flux power was blown with feeding rate of 0.5 kg/min and feeding time of 1500–2100 s.

Metal samples were obtained with bomb-shape steel samplers before and during powder blowing at arbitrary time intervals. Concentrations of collected samples were quantitatively analyzed. Main experimental conditions are shown in Tables 2 and 3.

Next, flux powder compositions used in the experiments are shown in Table 4. In heats 1 and 2, the powders of premelted CaO–CaF$_2$ or CaO–CaF$_2$–Al$_2$O$_3$ fluxes were used as reference without CaSi alloy. In heats 3 to 6, the mixture of CaO and granular CaSi alloy(40 mass%Ca-60 mass%Si, average particle diameter: $2.3 \times 10^{-4}$ m) was chosen. The weight ratio of CaO powder to CaSi alloy was varied at 97 to 3, 95 to 5, 90 to 10 and 85 to 15. Well-mixed CaO powder and Ca–Si alloy grain with the ratio mentioned above were charged in the power feeding device. The total feeding rate of the mixture was set at 500 g/min irrespective of the mixing ratio.

3. Experimental Results

In the present experiments, the base point in time was set at the start of powder blowing. Changes in aluminum content in molten steel during powder blowing are shown in Fig. 2. Aluminum content decreased during blowing in all heats. Aluminum contents decreased from 0.06% to 0.035% in the heat of CaO-40%CaF$_2$ powder and from 0.045% to 0.035% in the heat of CaO-15%CaSi. It is found that aluminum decreasing behavior varies with the kind of used flux power.

Changes in sulfur content in molten steel during powder blowing are shown in Fig. 3. The sulfur content decreased during blowing in all heats. Sulfur contents at 1500 s were under 0.0016% in the heats of CaO-40%CaF$_2$, CaO-15%Al$_2$O$_3$-50CaF$_2$ and CaO-3%CaSi.

Sulfur decreasing rate lowered especially after 1000 s in the heat of CaO-3%CaSi while sulfur contents at 1500 s were under 0.0012% in the heats of CaO-5%CaSi, CaO-10%CaSi and CaO-15%CaSi. Sulfur content was easily lowered with the mixture over 5%CaSi as just shown above.

Changes in nitrogen content in molten steel during powder blowing are shown in Fig. 4. The nitrogen content monotonously decreased to 0.003 mass% or lower at the end.
of blowing in all heats. Changes in nitrogen contents were nearly identical in the heats of CaO-15%Al₂O₃-50%CaF₂, CaO-40%CaF₂ and CaO-3%CaSi powders. Reduced amount of nitrogen contents increased with increasing CaSi mixing ratio from 5% to 15%.

Changes in calcium content in molten steel during powder blowing are shown in Fig. 5. Calcium contents shown in the figure are not soluble but total contents. Calcium content increased sharply to around 500 s and thereafter, showed steady value or modest increase. Calcium contents increased to 0.0007 mass% at 500 s and stayed constant in the heats of CaO-40%CaF₂ and CaO-3%CaSi. Calcium contents increased to 0.0022 mass% at 600 s and showed constant values in the heats of CaO-15%Al₂O₃-50%CaF₂. Calcium contents increased sharply until 480 s and continued to increase to 0.0034 mass% at a modest rate in the heats of CaSi mixing ratio of 5% or more.

Changes in total oxygen content in molten steel during powder blowing are shown in Fig. 6. The oxygen contents were measured as the values between 0.0008 and 0.002 mass% immediately prior to the start of powder blowing. Oxygen contents equally increased at a slow rate in all heats except for CaO-15%CaSi. In the heat of CaO-15%CaSi, oxygen content increased just after blowing start and decreased finally to the same value as the other experiments.

4. Discussions

4.1. Relationship between Aluminum Decreasing Rate and Calcium Contents

In the present experiments, it is important to examine either calcium or aluminum is dominant in deoxidation reaction. So, first of all, effects of Ca content on aluminum decreasing rate were examined.

It is assumed that aluminum decreasing rate can be expressed by the following first order equation shown in Eq. (1):

\[
\frac{d[Al]}{dt} = -k_{\text{Al}} [Al] \quad \left[ A \cdot t \right] 
\]

\[
[AI] = [AI]_0 \exp \left( -k_{\text{Al}} \cdot A \cdot t \right) \quad \text{......... (1)}
\]
where t: elapsed time(s), [Al]: aluminum content in molten steel at arbitrary time(mass%), [Al]₀: initial aluminum content in molten steel(mass%), A: area of free surface(m²), V: volume of molten steel(m³) and k_{Al}: apparent rate constant of aluminum decrease(m/s).

Relationship between calcium content at the end of blowing and calculated k_{Al} based on the experimental results and Eq. (1) is shown in Fig. 7. While the heat with CaO-50%CaF₂-15%Al₂O₃ powder showed higher k_{Al} due to its high liquid phase ratio at 1 873 K, the other heats displayed a characteristic tendency that k_{Al} decreased with increasing calcium content in molten steel. It is indicated that aluminum contributed to deoxidation reaction because k_{Al} did not show zero even in the region of higher calcium content.

It is suggested from the above that CaSi addition in the mixture changed the dominant deoxidant from Al to Al–Ca complex and that oxygen activity should be decreased as a result.

### 4.2. Relationship between Desulfurization Rate and Contents of Deoxidizing Elements in Molten Steel

It is presumed that desulfurizing rate increased due to the change from Al to Al–Ca complex deoxidation. Desulfurization rate constants were calculated on the assumption of the first-order rate equation as shown in Eq. (2).

\[
[S] = [S]_0 \exp \left( -k_s \frac{A}{V} t \right) \tag{2}
\]

where t: elapsed time(s), [S]₀: initial sulfur content in molten steel(mass%), A: area of free surface(m²), V: volume of molten steel(m³) and k_{s}: apparent desulfurization rate constant (m/s).

Changes in the logarithm of $[S]_0/[S]$ as time are shown in Fig. 8 where each slope provides the value of k_{s}/V. k_{s} can be thereby obtained from the slope based on Eq. (2). However, each slope does not necessarily indicate the complete linearity. The slopes gradually decreased after 900 s in the heats of CaO-50%CaF₂-15%Al₂O₃ and CaO-40%CaF₂ and increased after 900 s in the heat of CaO-3%CaSi. Nevertheless, k_{s} was assumed to be the averaged slope values throughout the whole blowing time to examine the effects of aluminum and calcium contents on desulfurization.

Relationship between k_{s} and aluminum content at the end of blowing is shown in Fig. 9. It is found that k_{s} increased with increasing aluminum content in molten steel in the heats of CaO-50%CaF₂-15%Al₂O₃, CaO-40%CaF₂ and CaO-3%CaSi.

The above tendencies can be explained by the inference that increase of aluminum content leads to lower oxygen activity and equilibrium content of sulfur is lowered in accordance with desulfurization reaction shown in Eq. (3).

\[
(CaO)_{in \ flux} + S = (CaS)_{in \ flux} + O \tag{3}
\]

On the other hand, ks values have no relation to aluminum content in the heats of CaSi mixing ratio of 5% or more Fig. 9. To take the effect of calcium into account, relationship between k_{s} and calcium content at the end of blowing is shown in Fig. 10. While k_{s} stayed constant regardless of calcium content in the heats without CaSi, ks
increased with increasing calcium content in 4 heats with CaSi. It suggests that sulfur decreasing rate is facilitated by CaSi mixed in the powder.

4.3. Mechanism of Desulfurization Reaction

On the assumption mentioned above, desulfurization reaction can be expressed by Eq. (4) as well as Eq. (3). Desulfurization reaction in CaO powder is promoted by lowering oxygen activity with calcium in Eq. (3). On the other hand, the rate is accelerated by floatation of CaS that is formed in direct reaction between calcium and sulfur in Eq. (4) taking place in the molten steel.

\[ \text{Ca} + \text{S} = \text{CaS} \]  

It is necessary to determine whether desulfurization reaction proceeded based on Eqs. (3) or (4) or on both to fully understand the desulfurization behavior. First, the trial of determination was made on the basis of Eq. (3) of which equilibrium relation was clarified by Inoue et al. and Taguchi et al. Taguchi et al. obtained the relation between oxygen and sulfur in molten steel using equilibrium constant of calcium deoxidation reaction reported by Itoh et al. In this paper, activities of oxygen and sulfur are calculated in accordance with the procedure proposed by Taguchi et al based on Henrian standard with mass% in unit. Oxygen activity is obtained from Ca–O equilibrium relation assuming that lime activity is unity. Sulfur activity is calculated from the measured sulfur content, calcium content and

\[ e^{\Delta G} = -22.4 \]  

The obtained results are shown in Fig. 11. The arrows indicate the direction of proceeding with time. The measured activities of sulfur show higher than the calculated equilibrium line in all heats, which indicates that the desulfurization reaction had the driving force in this work. The experimental results approach equilibrium values as time progresses. It is suggested that low apparent rate constant of ks in the heat of CaO-3%CaSi is due to the low driving force of reaction.

Next, the same treatment was made on the basis of Eq. (4) of which equilibrium relation has reported by Nadif et al., Han et al., Inoue et al., and Taguchi et al. The comparison between experimental data and the literature is shown in Fig. 12. The arrows also indicate the direction of proceeding with time.

It is difficult to determine whether reaction of Eq. (4) can occur or not because the measured sulfur contents are lower than the equilibrium values on the basis of Nadif et al. and higher than the values by others researchers. If one refers to the line based on Taguchi, occurrence of Eq. (4) is probable. The figure also shows that the driving force in the heat of CaO-3%CaSi is the lowest of all heats.

It is hard to confirm that Eqs. (3) and (4) may proceed simultaneously because the Ca–S relations are widely dispersed.

4.4. Rate Constant of Nitrogen Removal Reaction

It is known that removal reaction of nitrogen from molten steel can be expressed by the first-order equation of Eq. (5) or by the second-order equation of Eq. (6).

\[ \frac{d[N]}{dt} = \frac{A}{V} k([N] - [N]_e) \]  

\[ \frac{d[N]}{dt} = \frac{A}{V} k\left([N]^2 - [N]_e^2\right) \]  

where A: area of free surface(m²), V: volume of molten steel (m³), [N]: nitrogen content in molten steel (mass%), [N]e: equilibrium nitrogen content in molten steel (mass%) and k: rate constant of nitrogen removal (m/s or m/(s·%) for Eqs. (5) or (6), respectively).

Area of free surface A was assumed to be constant since it was observed that the powder particle moved to the fur-
nace wall immediately. Whether the measured values coincide with Eqs. (5), (6) or mixed-controlled equation depends on experimental conditions. The present author conducted the similar experiments in the same apparatus earlier and clarified that the reaction is controlled only by Eq. (6).\(^{19}\)

Similarly, the present experimental results are arranged as \(1/[N]_0-1/[N]\) according to Eq. (6) and shown in Fig. 13. \([N]_0\) is the initial nitrogen content in the molten steel and \([N]_e\) was approximated to be 0.

It shows comparatively good linearity and the rate constant of nitrogen removal is calculated from the slopes. The rate constant increases with increasing CaSi mixing ratio.

The obtained rate constants are plotted against \(K_{\text{a}}a_\text{a}+ K_{\text{s}}a_\text{s}\) to confirm the influence of calcium content on the tendency mentioned above. \(K_i\) is adsorption coefficient of \(i\) species. Ban-ya \textit{et al.}\(^{6}\) measured rate constants by sampling method for a wide range of nitrogen content and reported that the values of \(K_0, K_s\) is 300 and 130, respectively by applying the statistical analysis.

Figures 14 and 15 can be drawn using the oxygen activity calculated from Eqs. (7), (8) and Eqs. (9), (10), respectively. The activities were calculated by using contents in molten steel after powder blowing.

\[
\begin{align*}
\text{Al}_2\text{O}_3(s) &= 2\text{Al} + 3\text{O} \\
\log K_{\text{Al}} &= 64 000 / T - 20.57 \\
\text{CaO}(s) &= \text{Ca} + \text{O} \\
\log K_{\text{Ca}} &= -9.08
\end{align*}
\]

The rate constants previously measured by the present authors with CaO–CaF\(_2–\)Al\(_2\)O\(_3\) powder blowing onto aluminum killed steel are shown in both figures.\(^{19}\) The measured \(k\) values increase with decreasing oxygen or sulfur activity and is in good agreement with the results of earlier researchers and the present authors.

In comparison of Figs. 14 and 15, it can be concluded that the increase of \(k\) is due to CaSi mixed to powder because the \(k\) values show smaller variations including the authors’ results in Fig. 15 based on calcium deoxidation. Focusing on the range of 300\(a_\text{a}\) + 130\(a_\text{s}\) \(\approx\) 0.1–0.3, \(k\) shows almost the same value in the heats of CaO–CaSi and CaO–Al\(_2\)O\(_3–\)CaF\(_2\).

It is suggested that lower oxygen activity and sulfur activity due to the reaction between aluminum in molten steel and the powder increased the rate constant of nitrogen removal.

Recently Al–O equilibrium constants of Eq. (8) were reassessed by Itoh \textit{et al.},\(^{29}\) Fujiwara \textit{et al.}\(^{30}\) and Kang \textit{et al.}\(^{31}\). Ca–O equilibrium constants of Eq. (10) were experimental determined by Cho \textit{et al.}\(^{22}\) and Itoh \textit{et al.}\(^{23}\). Therefore thermodynamic data have been altered to see if Fig. 15 is affected with the values reported by the recent data. Figure 16 shows the results of recalculation using the equilibrium constants of Eqs. (8) and (10) by Itoh \textit{et al.}. The \(k\) values in Fig. 16 show smaller variations than those in Fig. 15. This comparison indicates that equilibrium constants of deoxidation reaction also plays important role in analyzing the rate of nitrogen removal.
5. Conclusions

1500 kg scale experiments of CaSi mixed CaO powder top blowing onto the Al killed steel were carried out under reduced pressure to confirm that effects of CaSi alloy in the mixture on reactions of desulfurization and nitrogen removal. The obtained results are as follows:

1. Aluminum decreasing rate decreased with increasing CaSi mixing ratio to flux.

2. The rate constant of desulfurization increased with increasing CaSi mixing ratio to flux.

3. The rate constant of nitrogen removal increased with increasing CaSi mixing ratio to flux.

4. It is supposed from the above that deoxidation and desulfurization reaction can simultaneously occur by blowing the mixture of CaSi and CaO powder.

5. It is supposed that facilitative effect of calcium mixing powder on desulfurization can be explained by promotion of CaO desulfurization and CaS formation.

6. It is suggested that lower oxygen and sulfur activities due to the reaction between molten steel and powder with CaSi increased rate constant of nitrogen removal.

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