Mixing and Mass Transfer in Ladle Refining Process

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The mixing time and slag–metal mass transfer coefficient in gas bubbling and induction stirring were measured by water model and plant scale experiments. The mixing time could be related to parameter $\tau V^{-1/3}$. In the range of low $\tau V^{-1/3}$, the mixing time for induction stirring was shorter than that for gas bubbling. In the range of large $\tau V^{-1/3}$, there was little difference between the two methods of stirring. These phenomena can be explained by a circulating time of bulk flow in gas bubbling and induction stirring. Metal-phase mass transfer coefficient in water model and plant scale experiments could be related to parameter $\tau V^{-1.3}$. The metal-phase mass transfer coefficient for gas bubbling was larger than that for induction stirring. These phenomena can be explained by the turbulence fluctuation velocity near the slag–metal interface in gas bubbling and induction stirring.

KEY WORDS: ladle refining; mixing; slag–metal reaction; stirring; water model experiment; ASEA-SKF; Ar bubbling

1. Introduction

The ladle refining process has functions of deoxidation, desulfurization, shape control of inclusion and homogeneity of temperature. The production of clean steel depends on the combination of these functions. The stirring of molten steel is indispensable to these functions.

On the homogeneity of temperature or chemical composition, Mori and Sano11 and Nakanishi et al.12 studied the relation between the mixing time and the stirring intensity. Kawai et al.13 studied the relation between the metal-phase mass transfer coefficient and the stirring intensity. In their studies, however, stirring power density was adopted as the correlating variable.

In this report, a water model experiment was carried out, and the mixing time and the metal-phase mass transfer coefficient in gas bubbling and induction stirring processes were measured. The result was related to the distribution of velocity and turbulence fluctuation velocity and the influence of the stirring method on mixing and slag–metal mass transfer rate was clarified.

2. Experimental Apparatus and Method

2.1. Measurement of Mixing Time

Fig. 1 shows the experimental apparatus for measurement of mixing time in the water model experiment. Two types of acryl vessels with the inner dimensions of $30 \times 25$ cm and $47 \times 45$ cm were used. The gas bubbling nozzle had a $4 \text{ mm}$ inner diameter and air was injected horizontally. A small pump was used as a simulation for induction stirring and the direction of pump outlet was upward or downward. As a tracer, a constant volume of aqueous solution saturated with KCl was added to the surface and the change in concentration of KCl with time was measured with an electrical conductivity meter. The mixing time was defined as the time until the change in the conductivity was less than 1% of the steady state value.

2.2. Measurement of the Metal-phase Mass Transfer Coefficient

Fig. 2 shows the experimental apparatus for the measurement of metal-phase mass transfer coefficient in the water model experiment. The vessel used in this experiment was the same as 2.1. A constant volume of foaming polystyrol particles coated with KCl or foaming alumina particles coated with benzoic acid was added to the surface and the change in concentration of KCl or benzoic acid in water was continuously measured with an electrical conductivity meter. The metal-phase mass transfer coefficient defined by Eq. (1) was calculated from Eq. (2). The stirring method was the same as 2.1. The interfacial area between slag and metal, $A$, in Eq. (2) was mea-
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do:
hot or and mixing is mixing large bubbling relation bubbling result the O in gas the mixing 200 conductivity gas this mixing is the Good (t).

\[ \frac{dC}{dt} = K_w \frac{A}{V} (C_i - C) \] \hspace{1cm} (1)

\[ \ln (1 - C/C_i) = -K_w \frac{A}{V} t \] \hspace{1cm} (2)

2.3. Measurement of Velocity Distribution

The distribution of velocity and turbulence fluctuation velocity in gas bubbling or induction stirring process was measured with a hot film anemometer. The vessel used in this experiment had dimensions of 30 cm x 25 cm x 45 cm. The stirring method was the same as 2.1.

3. Result and Discussion

3.1. Estimation of Stirring Power Density

The stirring power density of gas bubbling was calculated from Sundberg's equation\(^4\) given by Eq. (3).

\[ t = 0.0062Q TL \left( \ln (1 + 0.000968 \rho _L H) \right) \]

\[ + (1 - T_d/T_L) \] \hspace{1cm} (3)

where, \( t \): (W/t), \( Q \): (l/min), \( T_L \): (K), \( \rho_L \): (g/cm\(^3\)), \( H \): (cm), \( M_L \): (t).

The stirring power density of induction stirring in the water model experiment was calculated from the kinetic energy of water at the pump outlet given by Eq. (4).

\[ t = 0.3927 \times 10^{-7} d_0^2 \rho L V^3/M_L \] \hspace{1cm} (4)

where, \( d_0 \): (cm), \( V \): (cm/s).

The stirring power density in ASEA-SKF (induction stirring of 85 t molten steel) was calculated from the swelling height of molten steel in induction stirring. Namely, the height of molten steel \( h_L \) in Fig. 3 is given by Eq. (5-1). It is assumed that the profile of swell of molten steel is fitted to a quadratic equation. The average swelling height is equal to \( h_L/2 \). The stirring power density in ASEA-SKF is obtained from the kinetic energy required to lift the molten steel up to \( h_L/2 \), as shown in Eq. (5-2).

\[ h_L = 316 \sqrt{\frac{P}{\rho \cdot F}} \] \hspace{1cm} (5-1)

\[ t = 0.0012D^2 \rho _L h_L^2/M_L \] \hspace{1cm} (5-2)

where, \( \rho \): (\( \rho \)), \( \rho \): (\( \Omega \)-cm), \( F \): (Hz), \( P \): (kW), \( S \): (cm\(^2\)), \( D \): (cm), \( h_L \): (cm).

3.2. Relationship between the Mixing Time and the Stirring Power Density

Fig. 4 shows the relationship between the mixing time measured from the water model experiment and the parameter \( tV^{2/3} \). The mixing time in 85 t molten steel was measured with the use of Cu as a tracer. The relationship between the mixing time measured in plant scale experiment and parameter \( tV^{2/3} \) is also shown in Fig. 4. Good agreement between the results of the water model and plant scale experiments was obtained by using parameter \( tV^{2/3} \).

Moreover, it was cleared that the mixing time was influenced by the stirring method (Ar bubbling, ASEA-SKF). Namely, the difference in mixing time between gas bubbling and induction stirring was small in the range of high \( tV^{2/3} \), but it was large in the range of low \( tV^{2/3} \). The slope of relation between the mixing time and parameter \( tV^{2/3} \) differs with the stirring method. This can be explained by the difference of a circulating time of bulk flow\(^5\) \((t_c \text{ in Fig. 5})\). Two conductivity cells were set in the vessel as shown in Fig. 6, and the time transferred between two cells in gas bubbling or induction stirring was measured with the use of KCl aqueous as a tracer. The result is shown in Fig. 6. \( t_c \) was not influenced by the stirring method, while \( t_i \) was influenced by
the stirring method. The time in gas bubbling was longer than that in induction stirring and a circulating time of bulk flow in gas bubbling was longer than that in induction stirring. Therefore, the mixing time in gas bubbling was longer than that in induction stirring.

Fig. 7 shows the velocity distribution in gas bubbling and induction stirring measured with a hot film anemometer. The velocity distribution in gas bubbling is different from that in induction stirring. The velocity in gas bubbling was the highest near bubble swarm and free surface region and was the lowest at the corner of the vessel. The velocity distribution in induction stirring was more homogeneous. From these results, it is considered that the dead space is induced at the corner of the vessel in gas bubbling and a circulating time of bulk flow in gas bubbling is longer than that in induction stirring.

3.3. Metal-phase Mass Transfer Coefficient

3.3.1. Estimation of Metal-phase Mass Transfer Coefficient

In the case which slag-metal reaction is determined by metal phase mass transfer rate, the mass transfer coefficient is given by Eq. (6) derived from penetration theory.

\[ k_m = 2\sqrt{\frac{D_m}{\pi T_s}} \]  

(6)

Here, \( T_s \) is assumed to be proportional to a circulating time of bulk flow \( (T_s) \). \( T_s \) is proportional to the mixing time.\(^{11)}\) As the mixing time can be related to parameter \( \xi V^{-2/3} \), the metal-phase mass transfer coefficient \( (k_m) \) is given by Eq. (7). In this report, the influence of the stirring method on the metal-phase mass transfer coefficient was expressed using Eq. (7).

\[ k_m = \frac{k_a}{\sqrt{4D_t}} \propto (\xi V^{-2/3})^m \]  

(7)

3.3.2. Measurement of Metal-phase Mass Transfer Coefficient in the Water Model Experiment

Fig. 8 shows a typical example of change in concentration with time obtained by the water model experiment. In this figure, \( \ln(1-C/C_i) \) linearly decreases with time in the initial period but the data in the final period is out of the line. This phenomenon can be explained by the fact that the concentration of KCl or benzoic acid near the particles-water interface is below saturation. Therefore, in this report, the region of straight line was adopted for the calculation of the metal-phase mass transfer coefficient.

Table 1 shows the diffusion coefficients of KCl and benzoic acid in water. The ratio of the metal-phase mass transfer coefficient \( (k_{KCl}/k_{benzoic acid}) \) from the result of Fig. 9 is proportional to about 1/2 power of the ratio of diffusion constant \( (\sqrt{D_{KCl}/D_{benzoic acid}}) \). The result coincides with Eq. (7). Fig. 10 shows the relation between the metal-phase mass transfer coefficient and the parameter \( \xi V^{-2/3} \). The metal-phase mass transfer coefficient in gas bubbling was larger than that in induction stirring at the same value of parameter \( \xi V^{-2/3} \).
Mean velocity and turbulence fluctuation velocity near the interface were measured with a hot film anemometer. Fig. 11 shows the metal-phase mass transfer coefficient plotted against the mean velocity and the interfacial turbulence fluctuation velocity near the interface. It was clear that the metal-phase mass transfer coefficient is determined with the turbulence fluctuation velocity rather than mean velocity. Therefore, a process having high turbulence near the slag-metal interface, for example gas bubbling, is superior.

3.3.3. Desulfurization Rate in Plant Scale

The desulfurization reaction with basic flux is controlled by metal-phase mass transfer. The change in sulfur content with time in Ar bubbling ladle and ASEA-SKF was measured. Table 2 shows the operating conditions of Ar bubbling ladle and ASEA-SKF (85 t molten steel). Fig. 12 shows the change in sulfur content in molten steel with time. Using these data, the metal-phase mass transfer coefficient was calculated from Eq. (8).

\[ \ln C/C_0 = -k_m A \sqrt{V}t \]  

Here, \( A \): the slag-metal interfacial area.

Fig. 13 shows a schematic diagram for the estimation of the interfacial area in desulfurization reaction. In this figure,

Gravity force acting on slag:

\[ (F) \propto \rho_S g (h-h')A \]  

Shear force exerted by molten steel on slag:

\[ (F') \propto \rho_S \mu g A \]  

Here,

\[ U_s \propto (\sqrt{D})^{a_3} \]  

Table 2. Operational condition.

|                | Ar bubbling | ASEA-SKF |
|----------------|-------------|----------|
| Weight of molten steel | 85 t       | 85 t     |
| Ar flow rate    | 35 Nm³/h    |          |
| Lance           | 16 mmØ×2 holes |        |
| Immersion depth of lance | 2.7 m  |        |
| Flux            | CaO-Al₂O₃-CaF₂ | CaO-Al₂O₃-CaF₂ |
| Weight of flux  | 500 kg      | 800 kg   |

Table 1. Diffusion constant.

|                    | KCl           |
|--------------------|---------------|
| \( D_i \)          |               |
| \( 0.8 \times 10^{-4} \) | \( 1.9 \times 10^{-5} \) |

\( \text{At } 25^\circ \text{C (m}^2/\text{s}) \)
It was assumed that $A/A'$ was proportional to Eq. (9)/Eq. (10) and friction factor ($f$) was constant. From Eqs. (9) to (11) and mass balance of slag,

$$A' \propto A (p_{sh}/p_{L})^{0.26} \text{ [watt/ton] D}$$

The interfacial area was measured in the water model experiment using kerosine as slag, and the interfacial area of ASEA-SKF was also measured with a photograph. Using these result of the water model and plant scale experiments, multiple regression analysis was carried out for the determination of parameter $a$, $b$ and $c$ in Eq. (12). The equation for the determination of the slag-metal interfacial area can be given by Eqs. (13) to (14).

Fig. 13. Schematic diagram for estimation of interfacial area.

Fig. 14. Relation between $k_{m}/\sqrt{D}$ and $\dot{\epsilon} V^{-2/3}$.

$$A' \propto A \cdot 10^{-10} (p_{sh}/p_{L})^{0.382-0.19} \text{ [gas bubbling]}$$

$$A' \propto A \cdot 10^{-0.01} (p_{sh}/p_{L})^{0.382-0.08} \text{ [ASEA-SKF]}$$

The desulfurization rate constant was calculated from Eq. (8) together with Eqs. (13) and (14). Fig. 14 shows the relation between the stirring power density and desulfurization rate constant. The data in the plant scale experiment agreed satisfactory with the data in the water model experiment. It is shown that the slag–metal mass transfer coefficient in plant scale could be estimated from the result of the water model experiment by using Eq. (7).
4. Conclusion

The characteristics of mixing and slag-metal reaction in the ladle refining process were studied by the water model and plant scale experiments. The results are summarized as follows:

1) The mixing time can be related to parameter \( \theta V^{-2/3} \), and plant scale data can be estimated from the water model experimental data.
2) The mixing time in gas bubbling is longer than that in induction stirring at the same value of \( \theta V^{-2/3} \).
3) The metal-phase mass transfer coefficient can be related to the parameter \( \theta V^{-2/3} \). The result of the water model experiment is in good agreement with the desulfurization rate constant of molten steel with basic flux.
4) The mass transfer coefficient in gas bubbling is larger than that in induction stirring. This can be explained by the turbulence fluctuation velocity near the interface.

Nomenclature

\( A \): slag-metal interfacial area
\( A' \): cross-sectional area of vessel
\( C \): concentration
\( C_s \): saturated concentration
\( C_0 \): initial concentration
\( D \): vessel diameter
\( D_i \): diffusion constant
\( d_0 \): pump diameter
\( F \): frequency
\( f \): friction factor
\( H \): depth of immersion lance
\( h \): thickness of slag
\( h' \): thickness of slag before stirring
\( k_L \): swelling height of liquid
\( k_a \): metal-phase mass transfer coefficient
\( M_L \): liquid weight
\( P \): supplied electric power
\( Q \): gas flow rate
\( \delta \): \( \pi D \times \) liquid height
\( T_L \): liquid temperature
\( T_0 \): gas temperature
\( T_c \): contact time of liquid element
\( t \): time
\( U_s \): surface velocity near slag-metal interface
\( \partial U_s \): turbulence fluctuation velocity near slag-metal interface
\( V \): liquid volume
\( v \): liquid velocity at pump outlet
\( \dot{z} \): stirring power density
\( \mu \): permeability
\( \rho_L \): liquid density
\( \rho_s \): slag density
\( \rho \): resistivity
\( \tau \): mixing time

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