High Efficiency Hot Metal Desulfurization by Enhancing Flux Dispersion in Mechanical Stirring Process†

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Abstract:
The effect of flux addition method on hot metal desulfurization in a mechanical stirring process was investigated in a 1/12-scale water model and a 70 kg-scale hot model experiments. Powder blasting, in which the desulfurization flux is blasted with a carrier gas onto the molten hot metal surface, was the most effective method for improving desulfurization efficiency. The effect of the powder blasting method was quantitatively estimated by a flux aggregation model based on granulation theory. Flux dispersion was also enhanced by generating an inclined vortex by using a hot metal transfer ladle with bottom inclination. As desulfurization slag consists of aggregated flux particles, the reaction efficiency of the desulfurization flux was further improved by adopting hot slag recycling through a process of thermal destruction, resulting in the creation of new interfaces including unreacted CaO in the slag. In comparison with the conventional process, application of these techniques improved desulfurization flux efficiency by 2.1 times and reduced desulfurization slag generation by approximately 30%.

1. Introduction
Requirements for low sulfur content in steel materials have increased in recent years in response to stricter quality requirements for steel products, represented by steel plates and linepipe materials. The amount of hot metal desulfurization in the steelmaking process is increasing, as this is the most rational stage for performing desulfurization. Improvement of the reaction efficiency of the desulfurization flux is necessary and indispensable for satisfying both increased hot metal desulfurization amount and reduced desulfurization slag generation. However, CaO-based flux has poor wettability with hot metal, and when it is entrained in hot metal, it aggregates while also picking up hot metal. As a result, increased generation of desulfurization slag reduces the iron yield of hot metal. Against this backdrop, development of a technology which makes it possible to reduce both consumption of desulfurization flux and generation of hot metal desulfurization slag by fundamentally improving the reaction efficiency of the desulfurization flux had been strongly desired.

In the hot metal desulfurization process, JFE Steel had adopted a process utilizing mechanical stirring, which is characterized by large stirring force and enables treatment to the lower sulfur content region in a short period of time. Because the flux aggregates during entrainment in hot metal, the fact that unreacted desulfurization flux remains inside the aggregated slag was an issue in this mechanical stirring desulfurization process†1. In this work, a rational hot metal desulfurization process which greatly improves desulfurization efficiency and enables effective utilization of the sensible heat and iron component in the desulfurization slag was established by development of a desulfurization flux powder blasting method, bottom inclination ladle technique, and hot slag recycling method. This desulfurization process has been applied in practical operation.


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2. Technique for Enhancing Dispersion of Desulfurization Flux

2.1 Reduction of Reaction Efficiency by Aggregation of Desulfurization Flux

Hot metal desulfurization with mechanical stirring is a process which accelerates the reaction between hot metal and desulfurization flux by immersing or inserting an impeller made of refractory material in hot metal and stirring the bath by rotating the impeller, causing entrainment of the added desulfurization flux in hot metal. In the conventional powder addition method, the flux was added to the bath surface by natural dropping while the bath was stirred. At that time, the powdery flux with a diameter of 1 mm or less aggregated as a result of the process of stirring and addition, and finally achieved a size of several mm to several 10 mm. Fig. 1 shows the results of observation of aggregated desulfurization flux. Because sulfur is distributed on the surrounding edge of the aggregated desulfurization flux, it can be understood that the flux in the interior of the aggregate has not contributed to the reaction. This aggregation phenomenon is a factor in low reaction efficiency of desulfurization flux.

2.2 Desulfurization Flux Powder Blasting Technique

Focusing on the desulfurization flux addition method as a method for suppressing flux aggregation during desulfurization flux addition and thereby improving desulfurization efficiency, JFE Steel conducted a study of three addition methods in a water model experiment and 70 kg-scale hot metal desulfurization experiment to investigate the effect of the desulfurization flux addition method on desulfurization behavior. The three methods examined in that study were batch addition (conventional method), continuous addition and powder blasting using a carrier gas.

Photo 1 shows the results of the particle dispersion behavior in the water model experiment after addition of a simulated flux (plastic particles). With batch addition, the diameter of the aggregated particles was large, and a phenomenon in which large aggregated particles rotated in the water was observed. On the other hand, with powder blasting, the diameter of the dispersed particles was small, and the bath had a cloudy white appearance. From these observational results, flux aggregation was thought to occur as the flux was entrained from the water surface into water bath, and because the particles were penetrated directly in the water under the blasting conditions in this water model, aggregation during entrainment of the blasted particles was small in comparison with the batch addition method, and as a result, the diameter of the particles dispersed in the bath was small.

Next, a study of the same three methods was carried out by a hot desulfurization experiment using a 70 kg-scale high frequency induction furnace in order to investigate the effect of the desulfurization flux addition method on desulfurization behavior. Figure 2 shows the desulfurization behavior obtained in the 70 kg-scale hot metal desulfurization test. In the case of powder blasting, the desulfurization rate increased during flux addition. The desulfurization rates measured in 10 min shown by Eq. (1) were C: 0.130...
(1/min) by powder blasting, B: 0.074 by continuous addition, and A: 0.057 by batch addition. That is, the desulfurization rate obtained with the powder blasting method was approximately 1.8 times larger than with continuous addition and approximately 2.3 times larger with batch addition.

\[-\frac{d[S]}{dt} = K_S \cdot [S] \]  \hspace{1cm} (1)

where, \(K_S\): apparent desulfurization rate constant (1/min), \([S]\): sulfur content in hot metal (mass%) and \(t\): time (min).

The calculated results shown in Fig. 2 were calculated from a model in which solid particles aggregates in a bath, and the desulfurization reaction proceeds at the surface of the aggregated particles, as explained in the following.

The particle diameter of the desulfurization flux that contributes to the reaction interfacial area in the desulfurization reaction is determined by the dispersion and aggregation behavior of the added flux in hot metal. The dispersion and aggregation phenomena of a powder in a liquid are expressed by the function of the potential energy and distance between powder particles, and the changes in monodispersed particles due to aggregation are assumed to be expressed by a bimolecular reaction equation. That is, if the number of particles in a unit volume after time \(t\) is \(\gamma\), and the aggregation rate constant is \(k_a\), the change in the monodispersed particles due to aggregation is expressed by a bimolecular equation, as shown in Eq. (2).

\[\frac{d\gamma}{dt} = k_a \cdot (\gamma - \gamma_e)^2 \]  \hspace{1cm} (2)

where, \(\gamma\): number of particles in unit volume of liquid (−), \(\gamma_e\): number of particles in equilibrium state (−), \(k_a\): aggregation rate constant (m³/s) and \(t\): time (s).

From the granulation rate of spherical particles in a wet condition, the number of particles can be expressed by Eq. (3).

\[\gamma = \sum \frac{n}{(\pi/6) \cdot D^3 \cdot \rho_f (1 - \varepsilon)^3} \times W_f \times \frac{1}{V_m} \]  \hspace{1cm} (3)

where, \(n\): number of particles whose diameter is \(D\) (−), \(W_f\): total weight of granulates (flux) (kg), \(V_m\): volume of particle dispersed in liquid (hot metal) (m³), \(\varepsilon\): void ratio in aggregated particles (−) and \(\rho_f\): particle (flux) density (kg/m³).

In the case of continuous addition of the desulfurization flux, it can be thought that the previously-added desulfurization flux and the newly-added desulfurization flux contribute to the reaction. Furthermore, as the aggregated particle diameter in the equilibrium state \(D_e\) is determined by the balance of cohesive forces (granulation strength of granulate) and destructive forces (centrifugal force of stirring), Eq. (4) is materialized. Finally, the diameter \(D_{(t)}\) of the aggregate at time \(t\) is expressed by Eq. (5).

\[K \left(1 - \frac{\varepsilon}{\varepsilon_e}\right) \frac{\tau}{D_1^2} D_e^2 = \frac{4}{3} \rho_f (1 - \varepsilon) \pi \left(\frac{D_e}{2}\right)^3 \cdot r o a \]  \hspace{1cm} (4)

\[D_{(t)} = \left[\frac{W_f(t)}{(\pi/6) \cdot \rho_f (1 - \varepsilon)^3} \times \frac{1}{V_m} \cdot \frac{1}{k_a \cdot t + \frac{1}{(\gamma(t) - \gamma_{(t)})}} \cdot 2 \cdot \tau \cdot \rho_o \right]^{1/3} \]  \hspace{1cm} (5)

where, \(D_e\): initial added-particle diameter (flux diameter) (m), \(D_{(t)}\): aggregated particle diameter in equilibrium state (m), \(K\): constant depending on condition of granulation (−), \(W_f(t)\): weight of desulfurization granulates (flux) added up to time \(t\) (kg), \(\tau\): interfacial tension between particle and hot metal (N/m), \(r\): radius of impeller (m), \(o\): angular velocity of impeller rotation (rad/s), \(\gamma_{(t)}\): number of granulate (flux) particles newly added at time \(t\) (−), \(\gamma_{(t)}\): initial number of granulate (flux) particles at time \(t\) (−) and \(\gamma_e\): number of particles in equilibrium state (−).

Figure 3 shows the results of a calculation of the change over time in the average particle diameter during the experiment by these equations, together with the actual measured results of the average particle diameter.
of the slag. The average particle diameter of the desulfurization slag after the experiment was 0.76 mm with batch addition, but in contrast, the average diameter decreased to 0.39 mm with continuous addition and 0.38 mm with powder blasting. In the case of batch addition, the particle diameter increases with time, whereas with continuous addition and powder blasting, the degree of increase in the particle diameter during and after addition of the desulfurization flux is different, and inflection points occur. Based on this, with the continuous addition and blasting processes, it is thought that the diameter increase during desulfurization flux addition is small, the particle diameter increases as a result of aggregation which proceeds after addition. Moreover, when the desulfurization flux addition time was shortened, the treatment time after desulfurization flux addition was long, and from this, it can be estimated that the aggregate diameter increased after treatment.

Under the assumption that mass transfer in hot metal is rate-controlling for the desulfurization reaction, an evaluation was performed by the desulfurization reaction rate equation shown in Eq. (6). The reaction interfacial area \( A \) is expressed by Eq. (7), and the behavior of the S content in hot metal can be estimated by substituting the particle diameter \( D \) (Eq. (5)) calculated by the aggregation model into this equation\(^5\).

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\frac{d[S]}{dt} = K_S \cdot [S] = \frac{A \cdot k_m \cdot \rho_m}{W_m} \cdot [S] \quad \text{·····························································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································································
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Figure 5 shows the calculated results obtained by a numerical analysis of the vertical downward flow velocity at the hot metal-air interface with the inclined bottom in the 70 kg-scale induction furnace experiment. It can be understood that the rotating vortex which forms around the impeller is eccentric and inclined as a result of the inclined bottom, and a region with a strong downward flow velocity exists in the vicinity of this inclined vortex. Since the calculated downward flow velocity is sufficiently high in comparison with the desulfurization flux entrainment velocity, it was estimated that the increase in desulfurization efficiency due to bottom inclination is the result of the contribution of the bottom inclination to an increase in the desulfurization flux entrainment capacity in hot metal.

Based on these study results, an experiment was conducted using the inclined bottom vessel in actual operation (350 ton-scale transfer ladle at West Japan Works (Fukuyama)). The transfer ladle used in desulfurization treatment has a bath inner diameter of 3.5 m and a bath depth of 5.15 m. The maximum height difference of the inclined part of the ladle bottom is 0.16 m.

The relationship between the S concentration in hot metal before treatment and CaO-based flux utilization efficiency is shown in Fig. 6. CaO efficiency was defined by the equation shown in the figure. CaO efficiency was increased by 1.25 times by using the bottom inclination vessel, confirming that bottom inclination also increases desulfurization efficiency in actual hot metal desulfurization equipment.

3. Desulfurization Hot Slag Recycling

Although desulfurization efficiency is improved by accelerating desulfurization flux dispersion, unreacted CaO exists within the desulfurization slag, which forms aggregates with a size of several mm to several 10 mm. A study of various recycling conditions (i.e., cooling and crushing, etc.) was carried out in advance, and it was found that the desulfurization slag, which consists of the aggregated desulfurization flux, destructs into small sizes at high temperature, and this creates the new unreacted interfaces.

The effect of the SiO₂ in the recycled desulfurization slag which is carried over from the preceding process such as blast furnace slag was investigated in the 70 kg-scale hot metal experiments. Figure 7 shows the relationship between the (SiO₂) content in the desulfurization slag after treatment and the desulfurization rate constant K. The desulfurization rate decreases as the (SiO₂) content increases. This is consistent with the quantity calculated under the assumption that the effective CaO fraction for desulfurization decreases due to the fact that CaO forms the compounds shown in the
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Based on the experimental results, the effect of SiO$_2$ was quantified and reflected in the operational standard for the actual equipment, enabling recycling use of hot desulfurization slag multiple times$^{(10)}$. This has made it possible to reduce desulfurization flux consumption and slag generation, and at the same time, has also contributed to recovery of the iron content and sensible heat of the desulfurization slag.

4. Conclusion

This report has introduced the desulfurization flux powder blasting technique, bottom inclination technique and hot slag recycling technique in hot metal desulfurization treatment by the mechanical stirring process, and has shown the effectiveness of these techniques in improving the reaction efficiency of the desulfurization flux by application to actual equipment.

Figure 8 shows the desulfurization flux reaction efficiency and the amount of slag generation. In comparison with the conventional technique of top addition of the desulfurization flux on the bath surface, application of these techniques increased the reaction efficiency of the desulfurization flux by 2.1 times and reduced slag generation by approximately 30%.

As a result, low-S has been achieved in hot metal pretreatment in industrial operation, making it possible to supply high quality products. As application of these techniques also reduces heat loss and slag generation in the steelmaking process, a global environment-friendly hot metal desulfurization process was established. In the future, we will continue our efforts to develop even higher efficiency hot metal desulfurization methods, and to contribute to the establishment of a steel manufacturing process with the world’s most advanced energy efficiency, resource recycling and environmental protection technologies.

References