Desulphurization of Molten Iron Stirred by Rocking Motion*

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Synopsis

By the use of laboratory scale rocking furnace, carbon saturated liquid iron ($[\%S]=0.5\sim 0.7$) was desulphurized by calcium carbide powder in the temperature range from 1 250° to 1 450°C with the rocking speed of 0 to 36 c/min, and the mechanism of this reaction was discussed based on the results obtained.

The mass transfer coefficient K obtained from the experimental results may be expressed by the following equation.

$$K = (1.6 \times 10^{10} \cdot R_c + 1.1 \times 10^{10})^{1/2} \exp(-40\,000/RT)$$

where R_c is the rocking speed, R and T are the gas constant and temperature (°K), respectively.

From the value of apparent activation energy obtained, however, it could not be definitely determined whether the desulphurization process is controlled by the chemical reaction or the diffusion.

I. Introduction

As far as the extent of desulphurization during the steelmaking process of iron is limited, it is desirable to remove sulphur as much as possible in advance of this process.

Recently, many effective methods of desulphurization have been practically used, in which solid desulphurizers were used and the mixing condition of the iron bath and the desulphurizer was improved.

For instance, the methods of Domnarfvét,¹⁾ shaking ladle²⁾⁻⁴⁾ and others affect favorably the desulphurization in a short time.

The present authors have been studying the kinetics of the desulphurization of iron with lime and calcium carbide powder by using a small scale rocking furnace. Since magnesia was used for the lining of the wall of the furnace at the early stage of this work, the same experimental conditions were hardly maintained for all the experiments. This problem was solved by replacing magnesia lining by a graphite cylinder and the reproducible results were obtained for every experiment on the desulphurization with calcium carbide powder. Thus, the mechanism of desulphurization under the conditions mentioned above was discussed

from the results obtained.

II. Experimental Procedure

The graphite cylinder shown in Fig. 2 was set inside of the rocking furnace, as shown in Fig. 1. Four kilograms of carbon saturated iron containing 0.5 to 0.7% of sulphur which was previously prepared was melted and held at temperatures of 1 250°, 1 350°, and 1 450°C. After taking out the sample metal of 7 to 8 g from the melt by drawing with a quartz tube of 9 mm ID, the quartz tube was sealed at the end and bored a hole of 5 mm ID above the sealed end. Then, 240 g of CaC_2 powder (150 g of the powder is 14 to 30 mesh, and the rest is 30 to 48 mesh) were spread over the metal surface in a short time and the rocking motion was started. Samples were taken out of the melt at various times by using the method above mentioned and were subjected to the conventional chemical analysis of sulphur. Temperatures were measured by two thermocouples of Pt-Pt-Rh 13%, one of which was set at the exterior of the graphite cylinder and the other was immersed in the bath intermittently.

III. Experimental Results and Discussion

The motion of the furnace during the rocking and the condition of contact between the lining and CaC_2 powder are schematically shown in Fig. 3. The graphite wall had a tilt of 60 degrees on both sides, but

Fig. 2. Schematic representation of graphite cylinder (unit: mm)

- ① Electrode terminal
- ② Spring (for pressing electrode)
- ③ Electrode (water cooled)
- ④ Graphite resistance heating element
- ⑤ Handle (for inclining the body)
- ⑥ Gas outlet
- ⑦ Gas inlet
- ⑧ Driving gears for rocking motion
- ⑨ Motor (for rocking motion)

Fig. 1.
10 kg rocking furnace using graphite resistance heating element

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Fig. 3. Model of the motion of liquid iron inside the rocking furnace

the movement of the melt was observed to be much smaller than 60 degrees at any rocking cycle. Most of CaC_2 powder stuck on the wall within a short time and the remainder floated on the bath in the globular shape of various sizes owing to the binding with liquid iron. The powder stuck more easily on the wall as the rocking speed decreased and the temperature increased. The contact area between the wall and the melt, and the surface area of the bath at static state were about 270 cm^2 and 300 cm^2 , respectively.

Figure 4 shows the relationships between [%S] and time for unrocked melts at 1250°C , 1350°C and 1450°C . On the other hand, Fig. 5 shows the results obtained at a rocking cycle of 13 cycles per minute for various temperatures. The results for various rocking cycles at 1350°C are shown in Fig. 6. From these figures, it is obvious that the rate of desulphurization increases as the temperature and the rocking cycle increase.

By the addition of rocking motion, more than 90% of sulphur was removed within 15 minutes except the case at 1250°C and 13 cycles per minute.

The mechanism of desulphurization for the period of initial 15 min after the beginning of experiments will be discussed below. If the reaction of desulphurization can be expressed by Eq. (1),

the rate determining step of this reaction is considered to be one of the following three :

- (1) Diffusion of sulphur in the boundary layer of the metal.
- (2) Chemical reaction at the interface between CaC_2 and the melt.
- (3) Diffusion of sulphur in CaS to interface between CaC_2 and CaS .

Unfortunately, there is no available diffusivity data for item (3), except the diffusivity of sulphur in NiS ($3.1 \times 10^{-7} \text{ cm}^2/\text{sec}^5$) at 1250°C , $1.7 \times 10^{-6} \text{ cm}^2/\text{sec}^5$) at 1350°C , $8.7 \times 10^{-6} \text{ cm}^2/\text{sec}^5$) at 1450°C). The diffusivity of sulphur in liquid iron saturated with carbon were measured to be $2.3 \times 10^{-5} \text{ cm}^2/\text{sec}^6 \sim 7.1 \times 10^{-6} \text{ cm}^2/\text{sec}^7$) at 1250°C , $2.7 \times 10^{-5} \text{ cm}^2/\text{sec}^6 \sim 1.1 \times 10^{-5} \text{ cm}^2/\text{sec}^7$) at 1350°C , $3.2 \times 10^{-5} \text{ cm}^2/\text{sec}^6 \sim 1.6 \times 10^{-5} \text{ cm}^2/\text{sec}^7$) at 1450°C . Thus, it is considered that the diffusion of sulphur in CaS may be slower than in liquid iron.

It is therefore reasonable to assume that CaC_2 does

Fig. 4. Relation between [%S] and time at 1250°C , 1350°C , and 1450°C (0 c/min)

Fig. 5. Relation between [%S] and time at 1250°C , 1350°C , and 1450°C (13 c/min)

Fig. 6. Relation between [%S] and time at 1350°C (13, 25, and 36 c/min)

not act as the desulphurizer any more once CaC_2 is covered with the reaction product having the form of CaS . The rate determining step may be (1) or (2) as far as a fresh surface of CaC_2 is present.

When the reaction is controlled by the step (1), the flux of sulphur, which diffuses from the bath to the interface, is shown by Eq. (2).

$$\begin{aligned} \dot{n} &= -(D_s A / \delta)(C_s - C_s^0) \\ &= -(D_s A / \delta)([\%S] - [\%S]^0) \cdot \rho / 100 \cdot M_s \dots(2) \end{aligned}$$

where,

- $\dot{n}$: the quantity of sulphur removed ($\text{mol}/\text{sec} \cdot \text{cm}^2$)
- D_s : the diffusivity of sulphur in the metal (cm^2/sec)
- A : the interfacial area (cm^2)
- δ : the boundary layer thickness in the metal (cm)
- C_s , [%S]: the concentration of sulphur in liquid iron (mol/cm^3 , w/o)
- C_s^0 , [%S] ^{0} : the concentration of sulphur at the interface (mol/cm^3 , w/o)
- ρ : the density of liquid iron (g/cm^3)
- M_s : the molecular weight of sulphur.

The quantity of sulphur converted to CaS by the chemical reaction at the interface is given by the following equation.

$$\dot{n} = -kA(C_s^o - C_s^*) = -kA([\%S]^o - [\%S]^*) \cdot \rho / 100 \cdot M_s \quad \dots\dots\dots(3)$$

where,

k : the coefficient of reaction rate
 C_s^* , $[\%S]^*$: the equilibrium concentration of sulphur in the metal (mol/cm³, w/o)

The value of $[\%S]^*$ is very small, that is, the values thermodynamically calculated are 1.63×10^{-8} at 1200°C, 6.65×10^{-7} at 1415°C. Assuming that $[\%S]^*$ is zero, Eq. (4) is obtained by the combination of Eqs. (2) and (3).

$$\dot{n} = -(D_s k A / \delta k + D_s) \cdot [\%S] \rho / 100 \cdot M_s \quad \dots\dots\dots(4)$$

Since $\delta k \gg D_s$ in the case that the diffusion of sulphur is the rate determining step, Eq. (4) becomes,

$$\dot{n} = -(D_s A / \delta) \cdot [\%S] \rho / 100 \cdot M_s \quad \dots\dots\dots(5)$$

On the other hand, if the chemical reaction at the interface is the rate determining step, Eq. (6) is given because of $\delta k \ll D_s$

$$\dot{n} = -kA \cdot [\%S] \rho / 100 \cdot M_s \quad \dots\dots\dots(6)$$

Equations (5) and (6) can be rewritten as follows by the use of weight percent.

$$d[\%S]/dt = -(D_s A / \delta) V \cdot [\%S] \quad \dots\dots\dots(7)$$

$$d[\%S]/dt = -(kA/V) \cdot [\%S] \quad \dots\dots\dots(8)$$

where, V : the volume of liquid iron (cm³).

Integrating Eqs. (7) and (8), one obtains,

$$\log [\%S] = -(D_s A / 2.3 \delta V) \cdot t + \log [\%S]^i \quad \dots\dots\dots(9)$$

$$\log [\%S] = -(kA / 2.3 V) \cdot t + \log [\%S]^i \quad \dots\dots\dots(10)$$

where, $[\%S]^i$: the initial concentration of sulphur in the metal (w/o).

In both cases, the relationship between $\log [\%S]$ and time should be linear. As shown in Figs. 7, 8, and 9, linear relations holds between $\log [\%S]$ and time for the experimental results obtained under conditions mentioned above.

It is confirmed from this fact that either diffusion of sulphur or the chemical reaction is the rate determining step. In order to clarify the rate determining step, the following consideration has been made for the activation energies of diffusion and of chemical reaction.

The relationship between δ and Reynolds number of Re can be given by Eq. (11)⁸⁾ under the present conditions.

$$\delta = \gamma / \sqrt{Re}, \quad Re = r u \rho / \eta \quad \dots\dots\dots(11)$$

where, γ : the constant
 r : the characteristic length
 u : the velocity of fluid
 ρ : the density of fluid
 η : the viscosity coefficient of fluid.

At a constant temperature, Eq. (11) can be simplified as follows.

$$\delta = K_1 / \sqrt{u} \quad (K_1 = \gamma / \sqrt{r \rho / \eta}) \quad \dots\dots\dots(12)$$

Fig. 7. Relation between $\log [\%S]$ and time at 1250° and 1350°C (0 c/min)

Fig. 8. Relation between $\log [\%S]$ and time at 1250°, 1350°, and 1450°C (13 c/min)

Fig. 9. Relation between $\log [\%S]$ and time at 1350°C (13, 25, and 36 c/min)

If u is linear with cycles R_c , that is, $u = aR_c + b$, it becomes,

$$\delta = K_1 / \sqrt{aR_c + b} \quad \dots\dots\dots(13)$$

According to the experimental results, the temperature and rocking cycles do not affect the area of chemical reaction. Combining Eqs. (9) and (13), one obtains,

$$(D_s A / \delta)^2 = (D_s A / K_1)^2 (aR_c + b) \quad \dots\dots\dots(14)$$

Therefore, if the diffusion is the rate determining step, the relationship between square of $(D_s A / \delta)$ and R_c should be linear. Figure 10 shows that this relationship is realized for all the case including $R_c = 0$.

The relationship between δ and temperature will be given for the constant R_c . As the effect of temperature on the density of liquid iron is small, the relationship between density and viscosity coefficient of liquid iron may be given by Eq. (15).

Fig. 10. Relation between $(D_s A/\delta)^2$ and R_c

$$\delta = K_2(\eta)^{1/2} \quad (K_2 = \gamma/(r\rho)^{1/2}) \dots\dots\dots(15)$$

From Eqs. (13) and (15), Eq. (16) is obtained.

$$\delta = K_3\{\eta/(aR_c+b)\}^{1/2} \quad (K_3 = \gamma/(r\rho)^{1/2}) \dots\dots\dots(16)$$

Based on Eq. (16), the relationship between δ and T can be expressed as follows.

$$\delta = K_3\eta_0^{1/2} \exp(E_\eta/2RT)/(aR_c+b)^{1/2} \\ (\eta = \eta_0 \exp(E_\eta/RT)) \dots\dots\dots(17)$$

where, E_η : the activation energy of viscosity
 R : gas constant.

Thus, it becomes,

$$D_s A/\delta = A D_0 \exp(-E_D/RT) \\ (aR_c+b)^{1/2}/K_4 \exp(E'_\eta/RT) \\ (K_4 = K_3\eta_0^{1/2}, E'_\eta = E_\eta/2) \\ D_s = D_0 \exp(-E_D/RT) \dots\dots\dots(18)$$

where, E_D : the activation energy of diffusion.

Squaring the both side of Eq. (18), it gives

$$(D_s A/\delta)^2 = (\alpha R_c + \beta) \exp\{-2(E_D+E'_\eta)/RT\} \\ \alpha = a(D_0 A/K_4)^2, \beta = b(D_0 A/K_4)^2 \dots\dots\dots(19)$$

Differentiating Eq. (19) by R_c and taking the logarithm, one obtains,

$$\log(\partial(D_s A/\delta)^2/\partial R_c) = \log \alpha - 2(E_D+E'_\eta)/2.3RT \dots\dots\dots(20)$$

The values of α and $E_D+E'_\eta$ can be determined by the intercept and the slope of the straight line obtained by plotting $\log(\partial(D_s A/\delta)^2/\partial R_c)$ against $1/T$. The values of α and $E_D+E'_\eta$ obtained from Fig. 11 are 1.6×10^{10} and 40 kcal/mol respectively. On the other hand, the value of β can be determined from the intercept of the lines, which represent the relationship between $(D_s A/\delta)^2$ and R_c in Eq. (21) derived from Eq. (19), as shown in Fig. 10.

$$(D_s A/\delta)^2 = \alpha R_c \exp\{-2(E_D+E'_\eta)/RT\} \\ + \beta \exp\{-2(E_D+E'_\eta)/RT\} \dots\dots\dots(21)$$

Table 1 summarizes the values of α and β , where the values of α except the last column are obtained from the slope of the straight line showing the relationship between $(D_s A/\delta)^2$ and R_c in Eq. (21)

The values of α and β at three different temperatures agree well excluding the case at 1450°C, so that this reaction model is confirmed to be valid. The value

Fig. 11. Relation between $\log \partial(D_s A/\delta)^2/\partial R_c$ and $1/T$ at 1250°, 1350°, and 1450°C

Table 1. Numerical values of α and β at 1250°, 1350°, and 1450°C

	1250°C	1350°C	1450°C	From Fig. 11
α	1.4×10^{10}	1.9×10^{10}	1.3×10^{10}	1.6×10^{10}
β	1.2×10^{10}	1.5×10^{10}	6.7×10^9	

of α in the last column, 1.6×10^{10} is considered to be a mean value of those in the temperature range 1250° to 1450°C. The mean value of β shown in Table 1 is 1.1×10^{10} . Using the activation energy of viscosity for Fe-C alloy, which is calculated from other reference,⁹⁾ E'_η is obtained to be 4.8 kcal/mol.

If it is the chemical reaction controlled, the activation energy calculated, 40 kcal/mol, would be that of the chemical reaction shown in Eq. (10). Using the values of 7.5 kcal/mol⁶⁾ for E_D and 4.8 kcal/mol for E'_η , the difference between the obtained activation energy of 40 kcal/mol and $E_D+E'_\eta$ is 27.7 kcal/mol. When the other value, 21 kcal/mol,⁷⁾ is used for E_D , the difference becomes 14.2 kcal/mol.

If these values, 27.7 and 14.2 kcal/mol, are within the limit of error for $E_D+E'_\eta$, the rate determining step can be considered to be the diffusion of sulphur. However, the value of 35.2 kcal/mol seems to be too large for the value of the activation energy of diffusion.

On the other hand, the value of the activation energy of chemical reaction may be considered to be 35 kcal/mol which is calculated by dividing the standard enthalpy of CaC_2 , 212 kcal/mol at 1600°K by the number of bonds between Ca^{2+} and C_2^{2-} which is six. However, it is unable to conclude from this estimation of the activation energy that the process may be the chemical reaction controlled.

Y. Oguti *et al.*^{10),11)} investigated the desulphurization of carbon saturated liquid iron by the rotating CaC_2 cylinder and determined the mass transfer coefficient. According to their results, the activation energy of the mass transfer coefficient is 13.4 kcal/mol. They concluded that the rate determining step was the diffusion of sulphur in the boundary layer of the metal, from the fact that the two above-mentioned were in agreement, when the dimensionless equation proposed by other investigators was used. For the case that CaC_2 powder was used as the desulphurizer, the activation energy was reported to be 38 kcal/mol, which agrees with that obtained by present authors. However, the

observation on the behavior of sintering of CaC_2 is opposite to their's, as mentioned above, so that their concept on the relationship between temperature and the interfacial area is not applicable to the results of this study.

The experimental results are expressed by Eq. (22) in terms of mass transport, although the mechanism was not clarified sufficiently.

$$K = (1.6 \times 10^{10} R_c + 1.1 \times 10^{10})^{1/2} \exp(-40\,000/RT) \quad \text{.....(22)}$$

IV. Conclusion

Although it was not determined whether the rate determining step of desulphurization by the use of a small scale rocking furnace is diffusion or chemical reaction, the mixing of solid CaC_2 powder and molten iron was found to be very important for rapid and effective desulphurization.

The effects of temperature and rocking cycle on the desulphurization of carbon saturated iron with CaC_2 powder were studied and the experimental results obtained are expressed by the following equation

$$K = (1.6 \times 10^{10} R_c + 1.1 \times 10^{10})^{1/2} \exp(-40\,000/RT)$$

where, K : the mass transfer coefficient

R_c : the rocking speed

R : the gas constant

T : temperature ($^{\circ}\text{K}$).

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