Combustion Rate of Coke in Quasi-particle at Iron Ore Sintering Process

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Temperature distribution in layer of the iron ore sintering process is one of the most important factors to decide the sinter quality. To estimate the temperature distribution in sinter layer needs knowledge of coke combustion rate. The purpose of this study is to clarify that coke combustion rate in the fine layer of the quasi-particle with considerations about void ratio and liquid formation. The following results were obtained. Interface chemical reaction rate constant, k_c , was independent on the mixing ratio of coke. The higher mixing ratio of coke made the larger effective diffusion coefficient of oxygen, because the higher mixing ratio of coke made the higher void ratio in the sample after coke combustion. The coke combustion rate became small with increasing of liquid formation amount, because liquid phase in quasi-particle prevented oxygen diffusion in there.

KEY WORDS: coke combustion rate; iron ore sintering process; quasi-particle; void ratio; liquid formation.

1. Introduction

Iron sinter ore occupy almost 80% of iron burden for blast furnace in ironmaking process. In other words, quality of the iron ore sinter has a direct and great effect on operation result of blast furnace. Temperature distribution in layer of the iron ore sintering process is one of the most important factors to decide the sinter quality. Information of this temperature distribution is necessary to improve the quality of iron ore sinter.

To estimate the temperature distribution in sinter layer

needs knowledge of coke combustion rate. 3 patterns of coke existence state in the layer were reported by Hida *et al.*¹⁾ as shown in Fig. 1. The combustion rate should depend on the coke existence state. However many reports^{1–3)} used only the state of S' type for estimation about the temperature distribution in the sinter process. S' type coke combustion rate is normally too faster than the real sinter process because it ignored oxygen diffusion in fine layer of quasi-particle. The purpose of this study is to clarify that coke combustion rate in the fine layer of the quasi-particle with considerations about void ratio and liquid formation.

Fig. 1. Classification of coke distribution situation in quasi-particle.

2. Derivation of Coke Combustion Rate Equation with Considerations about Void Ratio in the Fine Layer

2.1. Experimental Sample and Procedure

The quasi-particle in iron ore sintering process mainly consists of Hematite powder and pulverized coke. In iron ore sintering process, reduction, oxidation and melting reaction of Hematite simultaneously take place during coke combustion reaction. They have complex effects on coke combustion behavior. To avoid these effects in this study, Al_2O_3 powder was used as alternative material of Hematite. Tablet samples were prepared as quasi-particle by mixture of Al_2O_3 powder and pulverized coke.

Pulverized coke, particle diameter is $\sim 125 \mu\text{m}$, and Al_2O_3 powder, particle diameter is $\sim 250 \mu\text{m}$, were well mixed as given mass ratios shown in Table 1. In order to give enough strength of the composite for handling, 5 mass% of wheat flour was added to the mixture of Al_2O_3 and coke. It was

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Table 1. Mixing ratio of experimental samples for 2.1. (mass%).

	Coke	Alumina	[Coke mixing ratio based on Hematite weight]
Type 1	12.2	87.8	[10]
Type 2	18.1	81.9	[15]
Type 3	24.9	75.1	[20]
Type 4	30.6	69.4	[25]
Type 5	36.2	63.8	[30]

Fig. 2. Schematic diagram of experimental apparatus.

thought this wheat flour could not affect the result of this experiment because it decomposed at 600 K. After the powder samples were well mixed, the mixture was pressed into tablet shape of 10 mm in the diameter by stainless dies with a little amount of water. The height of tablet was 10 mm and void ratio was 35% by adjusting of sample amount and load of compression.

Measurement of sample weight loss during coke combustion was carried out by thermobalance in this study as shown in **Fig. 2**. The sample was put into platinum basket with ceramic fiber. The ceramic fiber prevented to direct contact of the tablet with the basket. A vertical electric resistance furnace was used in order to make isothermal heating condition. The isothermal zone was heated up to 1073 K, 1223 K, 1373 K and 1523 K. Before combustion experiment, heat treatment was carried out at each given temperature under N_2 atmosphere in order to remove binder, water, and volatile matter from sample. After that, an inside of a reaction tube was changed to air atmosphere by air flow of 4 NL/min during this experiment. It was time to end of experiment when the sample weight became unchanging.

2.2. Results and Discussions

2.2.1. Measurement of Combustion Rate of Samples

Definition of reaction ratio in this study is removal ratio of fixed carbon from the sample. Carbon combustion reaction can be described as following chemical reaction, if CO gas formation would be ignored.

Fig. 3. Effect of reaction temperature on reaction curve of type 3 samples.

Fig. 4. Effect of difference of coke amount in samples on reaction curve at 1373 K.

Sample weight change was considered as decrease amount of fixed carbon in this combustion experiment. The reaction ratio, F , at elapsed time, t , could describe as Eq. (2).

$$F = \frac{w_t}{W} \quad (2)$$

Reaction curves of Type 3 sample at each temperature are shown in **Fig. 3**. From this figure, it was found that the higher temperature of reaction condition made the combustion reaction rate the larger. The other type of samples also showed same tendency.

Figure 4 shows reaction curves of each type samples at 1373 K. This figure indicated sample with the smaller coke amount made the combustion reaction rate the larger. The other reaction temperatures also showed same tendency.

These results were used for kinetic analysis of coke combustion rate.

2.2.2. Kinetic Analysis of Coke Combustion Rate

In this study, the unreacted-core model was applied to derive reaction rate constant. It was thought combustion reaction in the sample progressed through the following 5 steps.

1. O_2 transport from bulk gas to the particle surface through the gas film

$$-\dot{n}_{g-O_2} = 4\pi r_0^2 k_f (C_{O_2} - C_{O_2,s}) \quad \text{..... (3)}$$

2. O₂ diffusion from the particle surface to reaction interface through Al₂O₃ layer after coke combustion

$$-\dot{n}_{p-O_2} = (D_{O_2})_{eff} \frac{4\pi r_0 r_i}{r_0 - r_i} (C_{O_2,s} - C_{O_2,i}) \quad \text{..... (4)}$$

3. Combustion reaction at reaction interface

$$-\dot{R} = 4\pi r_i^2 k_c \left(C_{O_2,i} - \frac{C_{CO_2,i}}{K} \right) \quad \text{..... (5)}$$

4. CO₂ diffusion from the reaction interface to the particle surface through Al₂O₃ layer after coke combustion

$$\dot{n}_{p-CO_2} = (D_{CO_2})_{eff} \frac{4\pi r_0 r_i}{r_0 - r_i} (C_{CO_2,i} - C_{CO_2,s}) \quad \text{..... (6)}$$

5. CO₂ transport from the particle surface to the bulk gas through the gas film

$$\dot{n}_{g-CO_2} = 4\pi r_0^2 k_f (C_{CO_2,s} - C_{CO_2}) \quad \text{..... (7)}$$

Overall rate equation could be described by quasi-steady state analysis method as follow.

$$-\dot{n} = \frac{4\pi r_0^2 \left(\frac{K}{1+K} \right) (C_{O_2} - C_{CO_2})}{\frac{1}{k_f} + \frac{1}{D_e} \cdot \frac{r_0(r_0 - r_i)}{r_i} + \frac{1}{k_c} \cdot \frac{K}{1+K} \left(\frac{r_0}{r_i} \right)^2} \quad \text{..... (8)}$$

$$\frac{1}{D_e} = \frac{K}{1+K} \left(\frac{1}{(D_{O_2})_{eff}} + \frac{1}{K(D_{CO_2})_{eff}} \right) \quad \text{..... (9)}$$

It could be assumed that equilibrium constant, K , of coke combustion reaction would be infinity because the combustion reaction is irreversible reaction. This assumption could rewrite Eq. (8) as the following equation.

$$-\dot{R} = \frac{4\pi r_0^2 C_{O_2}}{\frac{1}{k_f} + \frac{1}{D_e} \cdot \frac{r_0(r_0 - r_i)}{r_i} + \frac{1}{k_c} \cdot \left(\frac{r_0}{r_i} \right)^2} \quad \text{..... (10)}$$

$\dot{R}$ could be describe as Eq. (11), too.

$$\begin{aligned} -\dot{R} &= -\frac{d}{dt} \left(\frac{4}{3} \pi r_i^3 \rho_{Cm} \right) \\ &= -4\pi r_i^2 \rho_{Cm} \cdot \frac{dr_i}{dt} \end{aligned} \quad \text{..... (11)}$$

The reaction ratio, F , is expressed as Eq. (12).

$$F = 1 - \left(\frac{r_i}{r_0} \right)^3 \quad \text{..... (12)}$$

Combination among above Eqs. of (10), (11), and (12), derived to Eq. (13) when boundary conditions are $r = r_0$ at $t = 0$ and $r = r_i$ at $t = t$.

$$\begin{aligned} &\left(\frac{C_{O_2}}{\rho_{Cm} r_0} t - \frac{F}{3k_f} \right) \frac{1}{[1 - (1-F)^{1/3}]} \\ &= \frac{r_0}{6D_e} \cdot \frac{[1 - 3(1-F)^{2/3} + 2(1-F)]}{[1 - (1-F)^{1/3}]} + \frac{1}{k_c} \end{aligned} \quad \text{..... (13)}$$

Gas film mass transfer coefficient, k_f , can be calculated from Ranz-Marshall's equation.

Effective diffusion coefficient, E_{eff} , and interface chemical reaction rate constant, k_c , were derived from mixed-control plot of Eq. (13) with experimental results.

2.2.3. Interface Chemical Reaction Rate Constant

Figure 5 shows relationship between mixing ratio of coke in the sample and interface chemical reaction rate constant, k_c , at each experimental temperature. k_c values are independent on the mixing ratio of coke, and the higher experimental temperature make the larger values of k_c . The temperature dependence equation of k_c was derived from average value of every type's k_c each temperature using Arrhenius plot. **Figure 6** shows Arrhenius plot of k_c in this study, and the temperature dependence equation was expressed by Eq. (14).

$$k_c = 5.36 \times 10^{-2} \exp(-10.58 \times 10^3 / RT) \quad \text{..... (14)}$$

2.2.4. Effective Diffusion Coefficient of O₂

Relationships between mixing ratio of coke in the sample and effective diffusion coefficient, D_e , at each experimental temperature are shown in **Fig. 7**. At every temperature, it was shown that the higher mixing ratio of coke make the larger D_e . It was thought that the higher mixing ratio of coke made the higher void ratio in the sample after coke combustion. Therefore, O₂ diffusivity in that sample could be improved. Effective diffusion coefficient in the sample with

Fig. 5. Effect of coke amount in sample on k_c .

Fig. 6. Temperature dependence of k_c .

consideration about void ratio and temperature dependence could be expressed as Eq. (15).

$$D_e = D_{O_2} T^n \frac{\varepsilon}{\tau} \quad (15)$$

D_{O_2} was referred from literature⁵⁾ as follows.

$$D_{O_2} = 1.78 \times 10^{-5} \left(\frac{T}{273.15} \right)^{1.75} \quad (16)$$

Equation (15) can convert to Eq. (17) using double logarithm.

$$\ln D_e = \ln \left(D_{O_2} \frac{\varepsilon}{\tau} \right) + n \ln T \quad (17)$$

Value of n can be derived from slope of relationship $\ln D_e$ and $\ln T$ as shown in Fig. 8. The n value of this study was 2.09. In general, the n value was reported around 1.75–2.0. It was thought the value had not so big deviation from reported values. It was thought that tortuosity factor, τ , would be influenced by void ratio, ε , in the sample. ε was calculated from void ratio in the sample after coke combustion. Using the Eq. (15) and the above-mentioned n values, τ values were calculated at each void ratios and temperatures. Relationship between average τ values and void ratios at each temperature are shown in Fig. 9. Equation (18) was derived from approximate expression of this relationship.

$$\tau = \frac{2.40 \times 10^3}{\exp(12.5\varepsilon)} + 1 \quad (18)$$

Fig. 7. Effect of coke amount in sample on D_e .

Fig. 8. Temperature dependence of D_e .

From these discussions, the effective diffusion coefficient of oxygen can be expressed as Eq. (19).

$$D_e = 1.78 \times 10^{-5} \left(\frac{T}{273.15} \right)^{2.09} \frac{\varepsilon}{\tau} \quad (19)$$

3. Derivation of Coke Combustion Rate Equation with Considerations about Liquid Formation

3.1. Experimental Sample and Procedure

In practical iron ore sintering process, it can be thought that formation of molten calcium ferrite during coke combustion has strong effect on oxygen diffusivity. It is thought that reduction reaction of the calcium ferrite simultaneously occurs during coke combustion. This situation is too complex to focus on coke combustion reaction. To study the effect of liquid formation on coke combustion behavior under simple condition, CaO–SiO₂–Al₂O₃ slag, without FeO, was prepared as substitution of calcium ferrite.

Pulverized coke, particle diameter is $-125 \mu\text{m}$, Al₂O₃ powder, particle diameter is $-250 \mu\text{m}$, and 23.1CaO–14.7Al₂O₃–62.2SiO₂ slag, particle diameter is $-250 \mu\text{m}$, were well mixed as given mass ratios shown in Table 2. Mixing ratios of slag were decided as 0, 10, 30, and 50 volume% against Al₂O₃ powder. These mixtures were also pressed into tablet

Fig. 9. Porosity dependence of tortuosity factor τ .

Table 2. Mixing ratio of experimental samples for 3.1. (vol%).

		Coke	Alumina	Slag
Type 1 12.1 mass% Coke	Slag 0%	21.9	78.1	0
	Slag 10%	21.9	70.3	7.8
	Slag 30%	21.9	54.7	23.4
	Slag 50%	21.9	39.05	39.05
Type 2 18.1 mass% Coke	Slag 0%	30.8	69.2	0
	Slag 10%	30.8	62.3	6.9
	Slag 30%	30.8	48.4	20.8
	Slag 50%	30.8	34.6	34.6
Type 3 24.9 mass% Coke	Slag 0%	38.6	61.4	0
	Slag 10%	38.6	55.3	6.1
	Slag 30%	38.6	43.0	23.4
	Slag 50%	38.6	30.7	30.7

shape and used for the combustion experiment in a similar way as above paragraph of 2.1. In this experiment, only 1523 K was used as the combustion temperature.

3.2. Experimental Results

Reaction curves of Type 3 are shown in Fig. 10. From this figure, it was found that the higher of slag mixing ratio made the smaller combustion reaction rate. The other Types, 1 and 2, also showed same tendency. The cross-section micro-

Fig. 10. Effect of difference of slag amount in type 3 samples on reaction curves of at 1523 K.

Fig. 11. Difference of optical micrographs between slag 0% and slag 50% samples of type 3.

graphs of Type 3 after combustion experiment, with and without slag, are shown in Fig. 11. From this observation, slag film formation in the sample with synthesis slag was confirmed. In other words, the coke combustion rate became small with increasing of slag mixing ratio because liquid slag prevented oxygen diffusion.

3.3. Derivation of Coke Combustion Rate Equation

The mixed-control plot using the unreacted-core model was applied to derive reaction rate constant. Figure 12 shows relationship between mixing ratio of slag in the sample and interface chemical reaction rate constant, k_c . It could be thought that liquid formation in the sample didn't effect on k_c values, because k_c didn't depend on the slag mixing ratio in this figure.

Relationship between the mixing ratio of slag and effective diffusion coefficient, D_e , is shown in Fig. 13. From this figure, it was found that D_e became small with increasing of the slag mixing ratio. Main reason of this result was thought prevention of oxygen diffusion due to liquid formation in the sample. Relation between slag mixing ratio and D_e at each type of samples were calculated by curve fitting method in Fig. 13 as follows.

Type 1

$$D_e = f(V_{CF}) = \frac{0.54 \times 10^{-4}}{\exp(0.044 \times V_{CF})} + 0.11 \times 10^{-5} \text{ (m}^2/\text{s)} \quad \dots\dots\dots (20)$$

Fig. 12. Effect of slag amount in sample on k_c .

Fig. 13. Effect of slag amount in sample on D_e .

Type 2

$$D_e = f(V_{CF}) = \frac{0.81 \times 10^{-4}}{\exp(0.036 \times V_{CF})} + 0.24 \times 10^{-5} \text{ (m}^2/\text{s)} \quad (21)$$

Type 3

$$D_e = f(V_{CF}) = \frac{1.0 \times 10^{-4}}{\exp(0.080 \times V_{CF})} + 1.8 \times 10^{-5} \text{ (m}^2/\text{s)} \quad (22)$$

It was assumed that change of D_e due to liquid formation was caused from change of the tortuosity factor. Therefore, $f(0)/f(V_{CF})$ was applied as compensation coefficient for correction of coke combustion rate equation. $f(0)$ is effective diffusion coefficient of oxygen without liquid formation. Relation between ratio of liquid formation and the tortuosity factor could be described as Eq. (23).

$$\tau' = \tau \cdot \frac{f(0)}{f(V_{CF})} \quad (-) \quad (23)$$

Values of physical properties to need for calculations in this study were referred from literature.⁵⁾

4. Conclusions

In order to understand the coke combustion behavior of quasi-particle in iron ore sintering process, effect of void ratio and liquid formation on coke combustion in fine layer was investigated and following results were obtained.

(1) Interface chemical reaction rate constant, k_c , was independent on the mixing ratio of coke.

(2) The higher mixing ratio of coke made the larger effective diffusion coefficient of oxygen, because the higher mixing ratio of coke made the higher void ratio in the sample after coke combustion.

(3) The coke combustion rate became small with increasing of liquid formation amount, because liquid phase in quasi-particle prevented oxygen diffusion in there.

(4) In fine layer of the quasi-particle, interfacial chemical reaction rate coefficient of coke combustion and effective diffusion coefficient of O_2 were expressed as follows.

$$k_c = 5.36 \times 10^{-2} \exp(-10.58 \times 10^3 / RT)$$

$$D_e = 1.78 \times 10^{-5} \left(\frac{T}{273.15} \right)^{2.09} \frac{\varepsilon}{\tau'}$$

$$\tau' = \tau \cdot \frac{f(0)}{f(V_{CF})}$$

$$\tau = \frac{2.40 \times 10^3}{\exp(12.5\varepsilon)} + 1$$

$$\text{Type 1: } f(V_{CF}) = \frac{0.54 \times 10^{-4}}{\exp(0.044 \times V_{CF})} + 0.11 \times 10^{-5}$$

$$\text{Type 2: } f(V_{CF}) = \frac{0.81 \times 10^{-4}}{\exp(0.036 \times V_{CF})} + 0.24 \times 10^{-5}$$

$$\text{Type 3: } f(V_{CF}) = \frac{1.0 \times 10^{-4}}{\exp(0.080 \times V_{CF})} + 1.8 \times 10^{-5}$$

Symbols

A	: Frequency factor	(m/s)
$C_{(O_2, CO_2)}$	: O_2 or CO_2 concentration in gas phase	(mol/m ³)
$C_{(O_2, CO_2)-i}$	: O_2 or CO_2 concentration at reaction interface	(mol/m ³)
$C_{(O_2, CO_2)-s}$	: O_2 or CO_2 concentration at particle surface	(mol/m ³)
D_e	: Effective diffusion coefficient in Al_2O_3 powder layer	(m ² /s)
D_{O_2}	: Molecular diffusion coefficient of O_2 in air at 0 K	(m ² /s)
$(D_{(O_2, CO_2)})_{eff}$	: Effective diffusion coefficient of O_2 or CO_2 in Al_2O_3 powder layer	(m ² /s)
E	: Activation energy	(J/mol)
F	: Reaction ratio	(-)
K	: Equilibrium constant	(-)
k_c	: Interfacial chemical reaction rate coefficient	(m/s)
k_f	: Mass transfer coefficient in gas film	(m/s)
n	: Temperature-dependent factor of diffusion coefficient	(-)
$\dot{n}$	: Overall reaction rate	(mol/s)
$\dot{n}_{g-(O_2, CO_2)}$	: Mass transfer rate of O_2 or CO_2 in gas film	(mol/s)
$\dot{n}_{p-(O_2, CO_2)}$	: Mass transfer rate of O_2 or CO_2 in Al_2O_3 powder layer	(mol/s)
R	: Gas constant	(J/mol/K)
$\dot{R}$	: Interfacial chemical reaction rate	(mol/s)
r_0	: Initial radius after sphere approximation of sample	(m)
r_i	: Radius of unreacted core after sphere approximation of sample	(m)
T	: Temperature	(K)
t	: Time	(s)
U	: Superficial velocity	(m/s)
u	: Gas flow rate	(m/s)
V_{CF}	: Volume fraction of liquid phase in fine layer	(-)
w_t	: Sample weight change from ignition to t	(g)
W	: Sample weight change from ignition to end of the experiment	(g)
τ	: Tortuosity factor	(-)
τ'	: Tortuosity factor with consideration of liquid formation	(-)
ρ_{cm}	: Carbon concentration in sample	(mol/m ³)
ε	: Void fraction in fine layer after coke combustion	(-)

REFERENCES

- 1) Y. Hida, M. Sasaki, T. Enokido, Y. Umezumi, T. Iida and S. Uno: *Tetsu-to-Hagane*, **68** (1982), 400.
- 2) E. Kasai, Y. Omori and T. Iida: *Tetsu-to-Hagane*, **72** (1986), 1537.
- 3) E. Kasai, S. Wu, T. Sugiyama, S. Inaba and Y. Omori: *Tetsu-to-Hagane*, **78** (1992), 1005.
- 4) W. E. Ranz and W. R. Marshall: *Chem. Eng. Prog.*, **48** (1952), 173.
- 5) K. Sato: Bussei Teisu Suisan Hou, Maruzen Co., Ltd., Tokyo, (1975), 129.