Measurement of Effective Thermal Conductivity of Coke

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Effective thermal conductivity of metallurgical coke was measured in the temperature range from 100 to 1400°C by using the laser flash method. Effective thermal conductivity k of coke increased with a rise of temperature, and decreased with an increase of porosity of coke. The effect of radiation in the pore of coke on the value of effective thermal conductivity of coke was very small. The following empirical equation was obtained for the determination of effective thermal conductivity k (W/m K) as a function of temperature T (K) and porosity ε (–) of coke.

$$k = \{0.973 + 6.34 \times 10^{-3}(T - 273)\}(1 - \varepsilon^{2/3})$$

KEY WORDS: ironmaking; coke; effective thermal conductivity; thermal diffusivity; laser flash method; porosity.

1. Introduction

The effective thermal conductivity or the thermal diffusivity of metallurgical coke has not been reported so much,^{1–3)} although those are important basic physical properties in the analysis of the temperature distribution in the blast furnace. The values of the thermal diffusivity reported previously are shown in Fig. 1. Y. Tadokoro and N. Oda¹⁾ measured the effective thermal conductivity up to 645°C and extrapolated the measured values up to 850°C. The values of effective thermal conductivity reported by Y. Tadokoro and N. Oda slightly increased with temperature as shown in Fig. 1. Sato *et al.*²⁾ and Suzuki *et al.*³⁾ measured the thermal diffusivity with the high-temperature thermal shock testing apparatus. However, the values of effective thermal conductivity were uncertain due to the insufficiency of the information on properties of the coke used in their experiments. Sato *et al.*²⁾ measured the thermal diffusivity up to 1500°C. Their experimental values

decreased with a rise of temperature from about $9 \times 10^{-6} \text{ m}^2/\text{s}$ at room temperature to a minimum (about $2 \times 10^{-6} \text{ m}^2/\text{s}$) at 400°C and then increased up to 1000°C. The values fluctuated near $5 \times 10^{-6} \text{ m}^2/\text{s}$ over 1000°C. Suzuki *et al.*³⁾ also measured the thermal diffusivity up to 1800°C. Their values decreased with a rise of temperature from about $14 \times 10^{-6} \text{ m}^2/\text{s}$ at room temperature to a minimum (about $6 \times 10^{-6} \text{ m}^2/\text{s}$) at 1400°C and increased over 1400°C. The values of thermal diffusivity converted from the values of thermal conductivity reported by Y. Tadokoro and N. Oda¹⁾ were in the range of 1×10^{-6} – $2 \times 10^{-6} \text{ m}^2/\text{s}$. Their values were smaller than the ones reported by the former two groups and had different temperature dependency from the former. The effective thermal conductivity of coal measured by Miura *et al.*^{4,5)} should be referred to. The values obtained by Miura *et al.* were one order of magnitude smaller than the values by Y. Tadokoro and N. Oda,¹⁾ because Miura *et al.* used coal powder packed bed. However, the values reported by Miura *et al.* were almost the same values as the values by Y. Tadokoro and N. Oda¹⁾ at about 700°C, because coal became coke.

As mentioned above, the experimental values and the temperature dependency varied largely among the investigators.

The amount of graphite crystal in coke varies depending on the career temperature.⁶⁾ As temperature rises, the graphitization advances more easily and the amount of graphite crystal in coke increases. The value of the effective thermal conductivity of graphite is large (130–170 W/m K) at room temperature and decreases with a rise of temperature.⁷⁾ With an increase of the amount of graphite crystal in coke, the influence on the value and the temperature dependency of effective thermal conductivity of coke is supposed to become

Fig. 1. Thermal diffusivities of coke and coal.

significant.

Moreover, the value of the effective thermal conductivity is thought to vary with the pore structure of coke, because coke is porous.

The effects of the porosity of coke and the graphitization on the effective thermal conductivity of coke were investigated in this research by using the laser flash method.^{8,9)}

2. Sample and Experimental Method

2.1. Principle of Measurement^{10,11)}

The principle of the measurement of the thermal diffusivity by the laser flash method is as follows. The sample disc of thickness L was kept thermally insulated. After the surface was instantaneously heated up by the laser beam pulse, the temperature response of the back side of the sample was measured with the thermocouple. **Figure 2** shows a schematic temperature change of the sample. Dimensionless temperature $T(t)'$ on the back of the sample at time t after the laser irradiation is given by Eq. (1),

$$T(t)' = \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 \alpha t}{L^2}\right) \right\} \times (T'_{\max} - T'_0) + T'_0 \quad \dots\dots\dots(1)$$

where α is the thermal diffusivity, T'_0 is the dimensionless temperature of the sample at time $t=0$, and $T'_{\max}$ is the maximum dimensionless temperature on the back of the sample. The values of t , $T(t)'$, and $T'_{\max}$ were read on the observed temperature variation curve and the thermal diffusivity α and T'_0 were obtained by the curve fitting method with use of Eq. (1). The Marquardt method¹²⁾ was used for the curve fitting. The value of thermal diffusivity was adopted only when the standard deviation of the error of the fitting was within 10%. The value of T'_0 was included in the fitting, because the noise by the laser irradiation caused a shift of the base line on the recording chart.

A simple method,¹³⁾ by which thermal diffusivity was obtained by measuring the time when the back of sample attained at half of the maximum temperature, was used sometimes in the measurement with the laser flash method. However, in the method, it was not able to judge whether the experiment had been properly carried out or not. Therefore, this method was not adopted in this work.

Fig. 2. Schematic temperature change of the sample.

The effective thermal conductivity k was obtained by Eq. (2), i.e., by multiplying the thermal diffusivity α obtained by the curve fitting by the specific heat C_p and the apparent density ρ .

$$k = \alpha \rho C_p \quad \dots\dots\dots(2)$$

2.2. Sample

Thirteen kinds of coke shown in **Table 1** were used for the thermal diffusivity measurement. Nos. 1 and 2 in the table were the charge coke of "A" company. No. 1 was the dry-quenched coke and No. 2 was the water-quenched coke. Nos. 3–12 were the cokes which were sampled by inserting a sampler from the raceway into a blast furnace and are abbreviated hereafter core coke. Nos. 3–8 were core cokes of "A" company and Nos. 9–12 were core cokes of "B" company. No. 13 was the charge coke of "B" company and was dry-quenched coke.

They were prepared to the sample disks of about 10 mm in diameter and about 2 mm in thickness for the thermal diffusivity measurement. Table 1 shows thickness, apparent density, and porosity of each sample. The porosity of the sample was obtained from measured true and apparent densities. The porosity of each sample was in the range of 37–60%.

2.3. Experimental Apparatus

The thermal constants analyzer^{13,14)} by the laser flash method was used for the measurement of the thermal diffusivity.

2.4. Experimental Method

The experiment was carried out as follows. At first, the sample was set up in the furnace and was heated up to the desired temperature under the vacuum of 1×10^{-3} Pa or less. After the furnace was maintained at a fixed temperature, the laser was irradiated from the upper side on the surface of the sample. The temperature on the back of the sample, which rose by the heat of irradiation of laser, was measured with the Pt–Pt13%Rh thermocouple of 0.1 mm in diameter.

Next, the measurement method of the thermal diffusivity of the porous sample by the laser flash method is explained. **Figure 3** shows a schematic diagram for measuring effective thermal conductivity of porous

Table 1. Physical properties of samples.

Sample No.	Thickness (10^{-3} m)	Bulk density (10^3 kg/m ³)	Porosity (—)
1	1.94	0.982	0.496
2	2.00	0.895	0.539
3	2.08	1.11	0.526
4	1.80	1.07	0.543
5	1.41	1.08	0.500
6	2.08	1.02	0.528
7	1.98	1.09	0.528
8	1.98	1.03	0.556
9	1.99	1.05	0.507
10	1.83	1.19	0.422
11	1.78	0.928	0.597
12	1.91	0.952	0.544
13	1.74	1.17	0.378

solid. In a measurement by the conventional laser flash method, the abnormality was found occasionally in the shape of the temperature response curve. It was thought that the laser light might penetrate into the sample because the sample was porous. Therefore, the following method was adopted in the experiment. After the thermocouple was welded on the platinum plate, the platinum plate was bonded on the lower side of the sample with the platinum paste. Moreover, another platinum plate was bonded on the upper side of the sample. The laser light was prevented from entering the sample by bonding the platinum plates on the sample by the method mentioned above. The energy could be instantaneously given on the sample surface. The thickness of the platinum plate, which was 0.05 mm, was thin in comparison with the thickness of the sample. Thermal conductivity of platinum is 70–100 W/mK at 200–1400 K. It is a number of one to two figures larger than one of coke. The thermal resistance of the platinum part is extremely small. Therefore, the total thickness of coke and platinum was assumed to be the thickness of the sample. The Pt–Pt13%Rh thermocouple was used to measure the temperature response. Therefore, it was imagined that the measured value might be affected by the thermal conduction through the thermocouple. Moreover, there was the possibility in which the measured value might be affected by the thermal leak because of radiation heat transfer in the high temperature region over 1000°C. However, both influences were supposed to be small, because the diameter of the thermocouple was as small as 0.1 mm. Moreover, the temperature drop on the back of the sample was not observed after attainment of maximum temperature in the temperature response curve (at least twice during the term which it took for the temperature of back side of sample to reach the maximum temperature). This means that both influences were small. Therefore, the correction,¹³⁾ by which those influences were considered, was not carried out.

The measurements were carried out at intervals of 100°C from 100 to 1400°C. The specific heat of coke was estimated by interpolation of the reference values.¹⁵⁾

Fig. 3. Schematic diagram for measuring effective thermal conductivity of porous solid.

3. Experimental Results and Discussion

Figure 4 shows an example of the observed data and the fitting results of the temperature response curve. The calculated results agreed well with observed data as shown in Fig. 4.

Next, an example of the temperature dependency of the effective thermal conductivity of the charge coke (No. 1) is shown in Fig. 5. Figure 6 shows an example of the temperature dependency of the effective thermal conductivity of the core coke (No. 7). The values reported

Fig. 4. Comparison between observed data and calculated curve.

Fig. 5. Temperature dependence of thermal conductivity of No. 1 charge coke.

Fig. 6. Temperature dependence of thermal conductivity of No. 7 core coke.

by Y. Tadokoro and N. Oda¹⁾ are also shown in Figs. 5 and 6. As shown in these figures, the present data were on a similar level with the values by Y. Tadokoro and N. Oda¹⁾ up to 850°C. The present data over 850°C were on the extrapolated line of the values by Y. Tadokoro and N. Oda. Moreover, the observed effective thermal conductivity increased with a rise of temperature and showed the same tendency as the values by Y. Tadokoro and N. Oda.¹⁾

The Kunii's equation¹⁶⁾ has been usually used for the estimation of effective thermal conductivity of porous media. The Kunii's equation has some problems that the pore was assumed to have the cylindrical form and that the tortuosity of pore was not considered. However, the following examination was carried out by assuming that the Kunii's equation was able to be applied to the present data.

At first, the influence of the radiation on the effective thermal conductivity was examined by using the Kunii's equation,¹⁶⁾ which is given by Eq. (3),

$$\frac{k}{k_s} = (1 - \varepsilon^{2/3}) + \frac{\varepsilon^{2/3}}{1 - \varepsilon^{1/3} + \frac{k_F}{k_s} + \left(\frac{2}{3}\right)\left(\frac{h_r d_p}{k_s}\right)} \quad \dots(3)$$

where k_s is thermal conductivity of solid, k_F is thermal conductivity of fluid, h_r is the radiation heat transfer coefficient, d_p is pore diameter and ε is porosity. The radiation heat transfer coefficient h_r in Eq. (3) is given by Eq. (4) as a function of emissivity E on solid surface and temperature T .

$$h_r = 0.2269 \left(\frac{E}{2 - E} \right) \left(\frac{T}{100} \right)^3 \quad \dots(4)$$

The right hand side of Eq. (3) is divided into two terms. Then, the first term shows conductive heat transfer in the solid part and the second term shows the rest. Then, k' is defined by Eq. (5).

$$k' = k_s(1 - \varepsilon^{2/3}) \quad \dots(5)$$

The parameter, which shows the degree of conductive heat transfer in the solid part in Eq. (3), is assumed to be k_1 . Then, k_1 is the ratio of k' to effective thermal conductivity k and is given by Eq. (6).

$$k_1 = k'/k \quad \dots(6)$$

If k_1 is nearly equal to one, the influence of conductive heat transfer in the solid part is large and the one of the radiation is negligible. The measured values of No. 5, which were shown in Fig. 7, were substituted into effective thermal conductivity k , pore diameter d_p , and the porosity ε in the Kunii's equation, and the influence of the radiation on the effective thermal conductivity was examined. Sample No. 5 was selected because the average pore diameter was the largest among Nos. 1–8. Here, the emissivity E was assumed to be 0.9.⁷⁾ Further, the value of thermal conductivity k_F of fluid was assumed to be 0 because the thermal diffusivity was measured in a high vacuum. The influence of the radiation was calculated as follows. At first, the value of k_s was obtained

Fig. 7. Temperature dependence of k_1 for No. 5 sample.

Fig. 8. X-ray diffraction pattern of sample No. 2 using CuK α .

by solving Eq. (3) which is a quadratic equation of k_s . Next, the value of k_1 was obtained from Eqs. (5) and (6) by using the value of k_s .

Figure 7 shows the results. As shown in Fig. 7, the value of k_1 was about 0.98 and approximately 1 even at 1400°C. Therefore, it was thought that conductive heat transfer in the solid part was mostly predominant in the heat transfer in coke. The influence of the radiation on the effective thermal conductivity of coke was concluded to be negligibly small.

Here, k_s in Eq. (3) is the thermal conductivity of solid coke without porosity. This value is supposed to increase with an increase of the amount of graphite crystal in coke. The amount of graphite crystal increases with an increase of lattice constant L_c defined by Eq. (7). Therefore, the L_c dependency of the effective thermal conductivity was considered as follows. Figure 8 shows an example of powder X-ray diffraction pattern of coke. The peak of the (002) reflection of the graphite shows the size in the direction of C axis, *i.e.* the piled thickness L_c of carbon reticulation plane. The value of L_c can be estimated by Scherrer's equation⁶⁾ that is given by Eq. (7).

$$L_c = A\lambda / (B \cos \theta) \quad \dots(7)$$

Here, A is a constant decided by the diffraction plane and is 0.9 in this case. λ is wave length of X-ray and B is the peak width at half peak height and θ is angle at peak position.

Then, the powder X-ray diffraction analysis was carried out and the value of L_c was obtained by using

 Fig. 9. L_c dependence of thermal conductivity.

Fig. 10. Porosity dependence of thermal conductivity.

Eq. (7). Figure 9 shows the L_c dependency of the effective thermal conductivity at 1000°C.

Only the values of thermal conductivity of coke, whose porosity was about 50 %, were shown in Fig. 9. As L_c increased in turn of charge coke, (Nos. 1 to 2) core coke (Nos. 9 to 12), and core coke (Nos. 3 to 8), the effective thermal conductivity increased slightly. However, the scattering of data was very large. It was estimated that the scattering was caused by the difference of the porosity and pore structure of each kinds of coke.

Then, the porosity dependency of the effective thermal conductivity was examined at 1000°C as shown in Fig. 10. Although the data scattered slightly, the effective thermal conductivity decreased with an increase of porosity. Moreover, the effective thermal conductivity of core coke (Nos. 9 to 12) or core coke (Nos. 3 to 8) was slightly larger than the thermal conductivity of the charge coke (Nos. 1 to 2) if those were compared with each other at the same porosity, because L_c of core coke was approximately three to four times larger than L_c of the charge coke and the graphitization of those former cokes proceeded. However, the effect of L_c on the thermal conductivity of coke was small, because the change in L_c was small in this work. The effect of the porosity was large as shown in Fig. 10.

As the effects of the radiation and L_c on the effective thermal conductivity of coke were small in this case, the thermal conductivity of the solid was estimated by using Eq. (5). The thermal conductivity k_s of the coke with zero porosity was estimated as follows. The measured values of effective thermal conductivity and porosity

 Fig. 11. Temperature dependence of k_s .

were substituted into k' and ε in Eq. (5) and then the values of k_s were obtained. The average values at each temperature were adopted for k_s . Figure 11 shows the results. The thermal conductivity of the solid increased linearly with a rise of the temperature as shown in Fig. 11. The temperature dependence of the thermal conductivity was represented by Eq. (8).

$$k_s = 0.973 + 6.34 \times 10^{-3}(T - 273) \quad (373 \text{ K} \leq T \leq 1673 \text{ K}) \quad \dots\dots\dots(8)$$

Further by using Eq. (8), Eq. (9) was obtained for the effective thermal conductivity k of all kinds of coke.

$$k = \{0.973 + 6.34 \times 10^{-3}(T - 273)\}(1 - \varepsilon^{2/3}) \quad \dots\dots(9)$$

4. Conclusion

The effective thermal conductivity of metallurgical coke was measured by using the laser flash method in temperature range from 100 to 1400°C. The results were summarized as follows.

- (1) Effective thermal conductivity k of coke increased with a rise of the temperature and decreased with an increase of porosity of coke.
- (2) The effect of radiation on the effective thermal conductivity of coke was very small.
- (3) The following empirical equation for the effective thermal conductivity k (W/m·K) of coke was obtained as a function of temperature T (K), and porosity ε (—).

$$k = \{0.973 + 6.34 \times 10^{-3}(T - 273)\}(1 - \varepsilon^{2/3})$$

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Nomenclature

- A : constant (—)
 B : peak width at half peak height (rad)
 C_p : specific heat (J/kg K)
 d_p : pore diameter (m)
 E : emissivity (—)
 h_r : radiation heat transfer coefficient (W/m² K)
 k : effective thermal conductivity (W/m K)
 k_F : thermal conductivity of fluid (W/m K)
 k_S : thermal conductivity of solid with zero porosity (W/m K)
 k_1 : parameter defined by Eq. (6) (—)
 k' : effective thermal conductivity defined by Eq. (5) (W/m K)
 L : thickness of sample (m)
 L_c : lattice constant defined by Eq. (7) (m)
 T : temperature (°C)
 $T'_{\max}$: maximum dimensionless temperature (—)
 $T(t)'$: dimensionless temperature at $t=t$ (—)
 T'_0 : dimensionless temperature at $t=0$ (—)
 t : time (s)
- Greek
 α : thermal diffusivity (m²/s)
 ε : porosity (—)
 θ : angle at peak position (degree)
 λ : wave length of X-ray (m)
 ρ : apparent density (kg/m³)

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