Application of Square-wave Pulse Heat Method to Thermal Properties Measurement of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ System Fluxes

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The square-wave pulse heat method was improved to measure thermal properties of vitreous samples by considering radiation heat transfer between the front and back faces of the samples, and the measurement accuracy of the method was examined.

Thermal properties of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ samples were measured by the method. Thermal diffusivities of the crystalline $40\text{CaO-40SiO}_2\text{-20Al}_2\text{O}_3$ (mol%) sample are about 1.5–2.5 times larger than those of the vitreous sample. Specific heat of the crystalline and vitreous samples shows almost the same temperature dependency, except the highest measurement temperature due to crystallization of glass.

Finally, we investigated the reason that the thermal conductivity values measured by the improved square-wave pulse heat method differ from those by the line source method. As a result, crystallization of glass during the measurements would cause the difference of the temperature dependencies of the values measured by the two methods.

KEY WORDS: square-wave pulse heat method; thermal diffusivity; specific heat; thermal conductivity; slags.

1. Introduction

Thermal properties of molten slags and fluxes are very important factors affecting the efficiency in metallurgical operations and the values are also essential to mathematical modeling for various phenomena involved in iron and steel-making processes. For examples, mould powders used in the continuous casting of steels exist as both liquid and solid states between the steel and the mould, and control the heat transfer. The heat transfer between the steel and the mould largely affects the surface quality of the steel.

Major components of the mould powders are CaO , SiO_2 , and Al_2O_3 . **Figure 1** summarizes a part of previous studies on thermal properties (thermal diffusivity, thermal conductivity and heat capacity) measurements^{1–8)} of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system slags. For example, thermal properties of fused and crystalline SiO_2 were measured by Wray *et al.*¹⁾ and others.^{2,3)} Regarding the CaO-SiO_2 binary system, only the thermal conductivity of 57CaO-43SiO_2 (mol%) slags were measured by several researchers.^{2,4)} Not enough numbers of measurements were conducted on Al_2O_3 containing slags.

The square-wave pulse heat method^{9–11)} can measure thermal diffusivity, specific heat and thermal conductivity of crystalline samples which have very small values of thermal diffusivity such as oxides and heterogeneously structured composite materials simultaneously with a high degree of accuracy because a halogen lamp having several hundred watts output power is usually used as energy

source instead of laser pulse in the laser pulse method. However, radiation heat transfer between the front and back faces of the samples during the measurements should be considered when the thermal properties of vitreous samples are measured by the square-wave pulse heat method.

Therefore, in this work, we improved the square-wave pulse heat method to be able to measure the thermal properties of vitreous samples. Then we measured thermal diffusivity, heat capacity and thermal conductivity of CaO-SiO_2 and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system slags. Finally, we investigated the difference of the thermal conductivity values, 45CaO-

Fig. 1. Compositions of samples whose thermal properties were measured.

Fig. 2. Boundary conditions for the square-wave pulse heat method.

42SiO₂-13Al₂O₃ (mol%) as an example, measured by the improved square-wave pulse heat method and line source method.⁸⁾

2. Experimental Method

2.1. Principle of the Square-wave Pulse Heat Method

Consider an infinite plate of l (m) in thickness, which is in thermal equilibrium with its surrounding atmosphere. A square wave pulse (H (W/m²) in heat flux and δ (s) in time width) is directed onto the front face of the plate (**Fig. 2**). When the temperature rise from the initial temperature is u (K), governing equation and boundary conditions are given by the following equations.^{9,11)}

$$\frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial x^2} \quad (0 < x < l) \quad \dots\dots\dots(1)$$

$$k \left[\frac{\partial u}{\partial x} \right]_{x=0} = q_{x0}(t) \quad \dots\dots\dots(2)$$

$$k \left[\frac{\partial u}{\partial x} \right]_{x=l} = H - q_{xl}(t) \quad \dots\dots\dots(3)$$

$$H = \begin{cases} 0 & (t < 0, t > \delta) \\ H & (0 \leq t \leq \delta) \end{cases} \quad \dots\dots\dots(4)$$

where it is assumed that thermal properties of samples such as thermal conductivity k (W/m·K), specific heat C_p (kJ/kg·K), thermal diffusivity α (m²/s) are independent of temperature and position. $q_{x0}(t)$ and $q_{xl}(t)$ in Eqs. (2) and (3) are heat losses by radiation at the front and back faces (W/m²), respectively. When the initial temperature $T_0 \gg$ the temperature rise u , the heat loss at the front face $q_{xl}(t)$ can be linearized as $q_{xl}(t) = 4\epsilon_x \sigma T_0^3 u$. When $F_0 = \alpha t / l^2$ and $F_\delta = \alpha \delta / l^2$, u at the back face can be calculated from Eqs. (5) and (6).

$$u = \frac{1}{a + b} - 2 \sum_{n=0}^{\infty} \frac{1}{P_n \sin P_n \left(1 + a - 2 \frac{b}{a} + \frac{P_n^2}{a} + \frac{b}{P_n^2} + \frac{b^2}{a P_n^2} \right)} \times \exp(-F_0 P_n^2); \quad (0 \leq t < \delta) \quad \dots\dots\dots(5)$$

Fig. 3. Relationship between temperature response curve and radiation parameter.

$$u = 2 \sum_{n=0}^{\infty} \frac{\{ \exp(P_n^2 F_\delta) - 1 \} \exp(-P_n^2 F_0)}{P_n \sin P_n \left(1 + a - 2 \frac{b}{a} + \frac{P_n^2}{a} + \frac{b}{P_n^2} + \frac{b^2}{a P_n^2} \right)}; \quad (\delta \leq t) \quad \dots\dots\dots(6)$$

where P_n is the n th solution satisfying $\cot P = P/a - b/(aP)$, a and b are heat radiation parameters. When the emissivities of the front and back faces are the same

$$a = \frac{8\epsilon_0 \sigma u_0^3 l}{k}, \quad b = \left(\frac{4\epsilon_0 \sigma u_0^3 l}{k} \right)^2, \quad b = \frac{a^2}{4} \quad \dots\dots\dots(7)$$

Therefore, u is a function of F_0 , F_δ and a . **Figure 3** shows temperature response-curves calculated from Eqs. (5) and (6), when $F_\delta = 0.5$, $a = 0.0-1.0$. In Fig. 3, $a = 0.0$ means no heat loss from the faces by radiation.

The Marquardt method¹²⁾ has been used to calculate thermal diffusivities of samples by fitting Eqs. (5) and (6) to the monitored temperature response-curves at the back face during measurements. Fitting parameters for the Marquardt method used in this work are thermal diffusivity α and heat radiation parameter a .

Specific heats of samples are calculated from Eq. (8).

$$C_p = \frac{H\delta}{\rho l u_{\text{cnst}}} \quad \dots\dots\dots(8)$$

where ρ (kg/m³) is the density and u_{cnst} (K) is the maximum temperature rise without heat loss by radiation. It is impossible to measure u_{cnst} directly because of heat loss from the front and back faces by radiation, especially, at high temperatures. Therefore, in this work, at first α , and a were obtained by fitting Eqs. (5) and (6) to the monitored temperature response-curve at the back face. Secondly, a temperature response-curve at the back face without heat loss from the faces was calculated by substituting α obtained from the parameter fitting and $a = 0.0$ into Eqs. (5) and (6). At last, the maximum temperature rise without heat loss by radiation (u_{cnst}) was calculated from the temperature rise at $F_0 \geq 1.0$. Since thermal diffusivities and specific heats of samples were calculated by the procedure mentioned above, thermal conductivities of the samples were calculated from Eq. (9).

Fig. 4. Example of monitored and numerically calculated temperature response-curves in the square-wave pulse heat method.

Fig. 6. Example of monitored and numerically calculated temperature response-curves in the improved square-wave pulse heat method.

Fig. 5. Boundary conditions for the improved square-wave pulse heat method.

$$k = \alpha \rho C_p \dots \dots \dots (9)$$

An example of monitored temperature response-curves of a vitreous sample and numerically calculated temperature response-curves by the square-wave pulse heat method is shown in **Fig. 4**. The numerically calculated temperature response-curve does not agree with the monitored one because radiation heat transfer between the front and back faces of the vitreous sample is not considered in the square-wave pulse heat method. Therefore, radiation heat transfer between the front and back faces of samples should be considered correctly to measure thermal properties of transparent materials by the square-wave pulse heat method.

2.2. Improved Square-wave Pulse Heat Method

Consider a transparent infinite plate of l (m) in thickness, which is in thermal equilibrium with its surrounding. A square wave pulse is directed onto the front face of the plate (**Fig. 5**). When the temperature of the sample is T (K) and the initial temperature is T_0 (K), governing equation and boundary conditions are given by the following equations.

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (0 < x < l) \dots \dots \dots (10)$$

$$k \left[\frac{\partial T}{\partial x} \right]_{x=0} + \phi_2 (T_{xl}^4 - T_{x0}^4) = \phi_1 (T_{x0}^4 - T_0^4) \dots \dots \dots (11)$$

$$k \left[\frac{\partial T}{\partial x} \right]_{x=l} - \phi_2 (T_{xl}^4 - T_{x0}^4) = H - \phi_1 (T_{xl}^4 - T_0^4) \dots \dots (12)$$

$$H = \begin{cases} 0 & (t < 0, t > \delta) \\ H & (0 \leq t \leq \delta) \end{cases} \dots \dots \dots (13)$$

where ϕ_1 (–) is the geometrical factor of the both faces to the surrounding, ϕ_2 is the geometrical factor between the front and back faces, T_{xl} (K) is the temperature of the front face, T_{x0} is the temperature of the back face.

Difference equations were derived from the equations based on the finite difference method. The difference equations were solved by the Crank–Nicholson method on equally spaced grids of the one-dimensional coordinate system. The number of the grids was 40. Time increment was 1.0×10^{-3} s. The Marquardt method has been also used to calculate thermal diffusivity and specific heat of samples. Fitting parameters are thermal diffusivity α and specific heat C_p and geometrical factors ϕ_1 and ϕ_2 . α and C_p were accepted when the geometrical factors satisfied geometrical conditions. An example of monitored temperature response-curves of the vitreous sample and numerically calculated ones by the improved square-wave pulse heat method is shown in **Fig. 6**. The numerically calculated temperature response-curve reproduces properly the complicated monitored one. Thermal conductivity of the sample k was calculated by multiplying thermal diffusivity α , density ρ and specific heat C_p as described in Eq. (9).

2.3. Experimental Equipment

A schematic diagram of the experimental equipment to measure thermal properties of samples is shown in **Fig. 7**. The front and back faces of the sample were coated with a black body paste to fix surface emissivity. Fine ceramic fiber was filled between the side face of the sample and the sample holder to prevent radiation heat transfer between the sample and the holder. Pt–Pt–13%Rh thermo-couples of 0.1 mm in diameter were attached at the back face of the sample to monitor back face temperatures during measurements. There is a shutter equipped with a photo-sensor between a halogen lamp and a silica glass window to measure irradiation time of a square-wave pulse. The temperature was recorded with a personal computer through a digital volt meter every 0.1 s.

2.4. Experimental Procedure

At first, the sample holder was placed on a designated position in the chamber. The pressure of the chamber was

reduced with the rotary and diffusion pumps less than 1.0×10^{-3} Pa to prevent convection heat transfer. Temperature of the sample was maintained at a certain measurement temperature. A square-wave pulse of 2–10 s was irradiated onto the front face of the sample after the sample had attained thermal equilibrium. The back face temperature of the sample was recorded during the experiment. Measurements were conducted in the temperature range 293–1 150 K at intervals of 100 K. Heat fluxes onto the samples, which are required to calculate specific heat of samples, were measured in advance as a function of measurement temperature with as received MgO samples whose specific heat and density were known. Thermal diffusivity, specific heat and thermal conductivity of crystalline samples were measured by the square-wave pulse heat method, and those of vitreous samples were measured by the improved square-wave pulse heat method to eliminate the effect of radiation heat transfer between the front and back faces of the samples.

3. Sample Preparation

Fused SiO_2 (10.0 mm in diameter, 10.0 mm in height,

Fig. 7. Schematic diagram of experimental equipment.

99.9 mass% in purity) was employed for the validation of the improved square-wave pulse heat method.

Samples of $x\text{CaO}-(100-x)\text{SiO}_2$ (mol%) were prepared from reagent grade CaCO_3 and SiO_2 powders. Weighed mixtures of CaCO_3 and SiO_2 were melted in platinum crucibles in air for 1 800 s at 1 923 K and poured into a water-cooled copper mold. The bulk samples were crushed into powder. The powder was pressed at 250 MPa by a hydraulic press, crystallized and sintered in air for 24 h at 1 673 K. Properties of the samples are shown in **Table 1**.

Samples of $x\text{CaO}-x\text{SiO}_2-y\text{Al}_2\text{O}_3$ (mol%), where $y=0-20$ and $2x+y=100$, and $45\text{CaO}-42\text{SiO}_2-13\text{Al}_2\text{O}_3$ (mol%) were prepared from reagent grade CaCO_3 , SiO_2 , Al_2O_3 powders. Weighed mixtures of CaCO_3 , SiO_2 , and Al_2O_3 were placed in platinum crucibles and melted in air for 1 800 s at 1 923 K. Bulk glasses were prepared by pouring the melts into the water-cooled copper mold. Then the bulk samples were annealed in air for 10 800 s at 973 K to remove residual stress. The bulk samples were cut and machined into a disc of 10.0 mm in diameter and 4.5 mm in height to make vitreous samples. Properties of the samples are shown in **Table 2**. The bulk glass samples mentioned above were crushed into powder, pressed at 125 MPa by the hydraulic press, crystallized and sintered in air for 24 h at 1 173 K. Properties of the samples are shown in **Table 3**. The phases in the vitreous and crystalline samples were determined by X-ray diffraction analysis. No crystalline was detected in the vitreous samples. Differential thermal analysis (DTA) of the vitreous samples was performed at cooling and heating rates of 0.167 K/s.

Table 1. Properties of $\text{CaO}-\text{SiO}_2$ samples.

No.	$\text{CaO}:\text{SiO}_2$ (mol%)	Mass(g)	Diam.(mm)	Height(mm)	Porosity(%)
1	35:65	1.509	9.75	10.6	30
2	40:60	1.509	9.50	10.7	24
3	45:55	1.339	9.45	7.75	19
4	50:50	1.489	9.70	8.80	20
5	55:45	1.497	9.10	8.15	4

Table 2. Properties of $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ vitreous samples.

No.	CaO (mol%)	SiO_2 (mol%)	Al_2O_3 (mol%)	Mass(g)	Diam.(mm)	Height(mm)	Apparent density (10^3kg/m^3)
6	50	50	0	0.91	9.80	4.40	2.74
7	47.5	47.5	5	0.96	9.70	4.40	2.81
8	44.5	44.5	11	0.96	10.0	4.50	2.71
9	40	40	20	0.93	9.85	4.55	2.68
10	45	42	13	0.94	9.85	4.55	2.71

Table 3. Properties of $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ crystalline samples.

No.	CaO (mol%)	SiO_2 (mol%)	Al_2O_3 (mol%)	Mass(g)	Diam.(mm)	Height(mm)	Apparent density (10^3kg/m^3)
11	50	50	0	1.01	9.70	5.90	2.32
12	47.5	47.5	5	0.99	8.75	5.90	2.81
13	44.5	44.5	11	1.00	8.85	6.70	2.43
14	40	40	20	1.02	8.85	6.00	2.76
15	45	42	13	1.03	8.90	6.00	2.76

Fig. 8. Comparison of thermal properties measured in this work with those by other methods.

Fig. 9. Thermal properties of crystalline CaO-SiO₂ samples as functions of temperature.

4. Results and Discussion

4.1. Validation of the Improved Square-wave Pulse Heat Method

Figure 8 shows thermal diffusivity, specific heat, and thermal conductivity of fused SiO₂ measured by the improved square-wave pulse heat method. The thermal diffusivities in this work decrease with increasing measurement temperature from room temperature to 700 K, and increase progressively above 700 K. Values reported by Li *et al.*¹³⁾ and Corning¹⁴⁾ show similar temperature dependencies. The specific heats increase from 723 J/kg·K at 294 K to 862 J/kg·K at 1142 K. Kelley's values¹⁵⁾ agree well with the values obtained in this work. Regarding the thermal conductivities, Wray and Connolly's values¹⁾ are slightly higher (by 8 to 23%) than the values in this work. This is probably due to the thermal boundary layer of the cooling water around SiO₂ rod in their experimental apparatus.

Considering the facts that the numerically calculated back face temperature reproduces the monitored one with minute accuracy, that the variations of values measured by Li *et al.*¹³⁾ shown in Fig. 8 are relatively large, and that specific heats and thermal conductivities obtained in this work almost agree with ones measured by the other methods, we concluded that the thermal properties of vitreous samples can be measured by the improved square-wave pulse heat method.

4.2. CaO-SiO₂ System

Figure 9 shows thermal diffusivity, specific heat and thermal conductivity of crystalline CaO-SiO₂ samples measured by the square-wave pulse heat method. The effect of pores was removed by using Kunii's equation.¹⁶⁾ Regarding the thermal diffusivity and thermal conductivity, an increase in SiO₂ content causes increases in the thermal diffu-

sivity and conductivity values, except 55CaO-45SiO₂. Thermal diffusivity and thermal conductivity of 55CaO-45SiO₂ are larger than those of 50CaO-50SiO₂. This is probably due to the effect of Ca₃Si₂O₇(3CaO·2SiO₂) formation. There is no obvious relation between the specific heats and compositions.

4.3. CaO-SiO₂-Al₂O₃ System

4.3.1. Vitreous Samples

Figure 10 shows thermal diffusivity, specific heat and thermal conductivity of vitreous CaO-SiO₂-Al₂O₃ samples measured by the improved square-wave pulse heat method. The temperature dependencies of the thermal diffusivity and specific heat are insensitive to Al₂O₃ concentration at temperatures below 1000 K. The thermal diffusivity of samples, however, are scattered and suddenly decreased around 1000–1200 K. For example, the glass transition temperature (T_g) for 40CaO-40SiO₂-20Al₂O₃ (mol%) sample obtained by DTA was 1153 K. When the measurement temperature slightly exceeded T_g , glass structure partially changed due to the temperature rise caused by irradiation of the square-wave pulse to the sample. Therefore, measured thermal diffusivities decrease apparently because glass transition is an endothermic reaction. The specific heats of samples increase gradually as increasing the measurement temperatures up to 500 K, and settle down around 500 K. The specific heats of samples are scattered above 1000 K due to transition of glass as in the case of the thermal diffusivities. The thermal conductivities of samples were obtained by multiplying densities, thermal diffusivities and specific heats of samples as described above; thus, the thermal conductivities of the samples were insensitive to Al₂O₃ concentration, and the values are scattered above 1000 K as in the cases of the thermal diffusivities and specific heats.

Fig. 10. Thermal properties of vitreous $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ samples as functions of temperature.

Fig. 11. Effect of crystallization on thermal properties of $40\text{CaO-40SiO}_2\text{-20Al}_2\text{O}_3$.

4.3.2. Effect of Crystallization

Figure 11 shows the effect of crystallization on thermal diffusivity, specific heat and thermal conductivity of $40\text{CaO-40SiO}_2\text{-20Al}_2\text{O}_3$ samples. The thermal diffusivities of the crystalline sample are about 1.5–2.5 times larger than those of the vitreous sample. The thermal diffusivities of the crystalline sample decrease as increasing measurement temperature. In contrast, the thermal diffusivities of the vitreous sample are nearly constant. The specific heats of the crystalline and vitreous samples show almost the same temperature dependencies, except the highest measurement temperature due to crystallization of glass. The thermal conductivities of the crystalline sample are about 1.5–2.5 times larger than those of the vitreous sample as in the case of the thermal diffusivities because the specific heats of the crystalline and vitreous samples are almost the same values. Regarding the thermal conductivities, values of crystalline samples decrease as increasing measurement temperature due to a decrease of mean free path of phonon.

4.3.3. Comparison with Line Source Method

Figure 12 shows thermal conductivities of $45\text{CaO-42SiO}_2\text{-13Al}_2\text{O}_3$ (mol%) samples measured with the line source method by Susa *et al.*⁸⁾ and in this work. The thermal conductivities of the vitreous sample measured in this work are about 20–45% lower than those measured by the line source method. The thermal conductivities of the crystalline sample measured in this work are almost equal to or slightly larger than those measured by the line source method below 750 K. Considering the facts that glass transition temperature of the sample is 1 153 K and that thermal conductivities of the vitreous and crystalline samples in this work show almost the same values at 1 000 K, glass probably crystallized progressively as increasing measurement temperature in their work as shown by the broken line in

Fig. 12. Comparison between thermal conductivities for $45\text{CaO-42SiO}_2\text{-13Al}_2\text{O}_3$ measured by the line source method and the improved square-wave pulse heat method.

Fig. 12. The reason that thermal conductivities measured by the improved square-wave pulse heat method are about 15–30% lower than those by the line source method is still under examination.

5. Conclusions

The square-wave pulse heat method was improved to measure thermal properties of vitreous samples. Thermal properties of crystalline CaO-SiO_2 and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ samples were measured by the square-wave pulse heat method; those of vitreous $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ samples were measured by the improved square-wave pulse heat method. The following results were obtained.

(1) The improved square-wave pulse heat method is applicable to the measurement of vitreous samples. The thermal diffusivities, thermal conductivities and specific heats of fused- SiO_2 measured by the improved square-wave pulse

heat method were in good agreement with those measured by other methods.

(2) There is no obvious effect of Al_2O_3 concentration on the thermal properties of vitreous $x\text{CaO}-x\text{SiO}_2-y\text{Al}_2\text{O}_3$ samples ($y=0-20$ mol%).

(3) The thermal diffusivities of the crystalline $40\text{CaO}-40\text{SiO}_2-20\text{Al}_2\text{O}_3$ (mol%) sample are about 1.5–2.5 times larger than those of the vitreous sample. The specific heats of crystalline and vitreous samples show almost the same temperature dependencies, except the highest measurement temperature due to crystallization of glass.

(4) The thermal conductivities of the $45\text{CaO}-42\text{SiO}_2-13\text{Al}_2\text{O}_3$ (mol%) sample measured by the improved square-wave pulse heat method are about 15–30% lower than those by the line source method. The reason is still under examination.

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