MEASUREMENT OF EFFECTIVE THERMAL DIFFUSIVITY OF MOLTEN SLAG USING DOUBLE HOT THERMOCOUPLE TECHNIQUE

Yoshiaki Kashiwaya*, Kuniyoshi Ishii*, Carl F. Orrling** and Alan W.Cramb**

* Dep. of Materials Science and Eng., Grad. school of Eng., Hokkaido Univ., Sapporo, 060-8628, JAPAN. FAX & TEL +81-11-706-6340
** CISR, Carnegie Mellon University , Pittsburgh, PA USA

Key words: thermal diffusivity, thermal conductivity, slag, silicate, laser flash, hot thermocouple,

Abstract

The mold slags that are used in a continuous caster play a decisive role in lubrication and heat transfer between the water cooled copper mold and the strand. The authors initially developed the double hot thermocouple technique (DHTT) for in situ observation of mold slag crystallization. These studies indicate that the overall heat transfer rate in the actual process must be very complicated due to the interaction of crystallization of the slag with the primary mechanisms of heat transfer: radiation, conduction and convection. In this study, the DHTT was further developed to allow measurement of the overall thermal diffusivity of molten slag using the principle of the laser flash method. In this report, the development of the technique will be discussed and initial results presented.

1. INTRODUCTION

The physicochemical and the thermal properties of mold slag have large influences on the quality of products in continuous caster. The former ones such as the viscosity and melting-solidifying behavior have been widely investigated. Also the thermal conductivity(or diffusivity) was measured by many researchers, however, the overall heat transfer rate will be more important variable in actual processes than the single phonon conduction, in which the bubbles formation and the crystallization might affect the heat transfer and the intensive radiation must dominant. In such processes, the direct observation during measurement of thermal diffusivity can be a key technique to understand the obtained results adequately. The authors initially developed the double hot thermocouple technique (DHTT) for *in situ* observation of mold slag crystallization. These studies indicate that the overall heat transfer rate in the actual process must be very complicated due to the interaction of crystallization of the slag with the primary mechanisms of heat transfer: radiation, conduction and convection.

In this study, to clarify the effective thermal diffusivity during the bubble formation and crystallization, the DHTT was further developed and measurements were carried out using the principle of laser flash method. The obtained data was analyzed and discussed the adaptability of the equation in the application of the laser flash method which assumed the one dimensional heat transfer under insulated condition.

2. EXPERIMENTAL

In laser flash method, a thermal diffusivity can be obtained using the one dimensional heat transfer under insulating condition. The fundamental equation was given by Carslaw and Jaeger. [1)]

$$T(x,t) = \frac{1}{L}\int_0^L T(x,0)dx + \frac{2}{L}\sum_{n=1}^{\infty}\exp\left(\frac{-n^2p^2at}{L^2}\right)\times\cos\frac{npx}{L}\int_0^L T(x,0)\cos\frac{npx}{L}dx \qquad (1)$$

where $T(x,t)$ is temperature distribution at any later time t, α is the thermal diffusivity. L is the thickness of sample. The temperature history at rear surface, x=L, can be expressed by

$$T(L,t) = \frac{Q}{\rho C_p L}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \times \exp\left(\frac{-n^2\pi^2}{L^2}\alpha\ t\right)\right] \qquad (2)$$

where ρ is the density of sample, Q is radiant energy of pulse. Then dimensionless temperature history V is obtained using maximum temperature $T_M = Q/\rho C_p L$ at the rear suface.

$$V = \frac{T(L,t)}{T_M} = 1 + 2\sum_{n=1}^{\infty}(-1)^n \times \exp\left(\frac{-n^2\pi^2}{L^2}\alpha\ t\right) \qquad (3)$$

From Eq.(3), the time $t_{0.5}$ can be defined by that of V = 0.5, the half value of maximum temperature. Then, the thermal diffusivity α is calculated by Eq.(4).

$$\alpha = 0.1388\frac{L^2}{t_{0.5}} \qquad (4)$$

Figure 1 shows the comparison of the alignment of heat source and detector between DHTT and laser flash method. The laser flash method is excellent method and can predict a good value of thermal diffusivity using Eq.(4). However, it will need a special alignment for the measurement of liquid and transparent material such as silicate slag($2SiO_2Na_2O$) and is quite difficult to obtain a correct value. Furthermore, direct observation during measurement is almost impossible. On the other hand, the DHTT can observe the melted sample directly and hold a molten slag. As shown in previous study,[2,3] solidification of mold slag is complicated phenomena including bubble formation and crystallization. It would be very important to know the sample image during measurement. The thermal diffusivity obtained from DHTT, however, is not yet established and it is not reported what kinds of factors affected on the measurement.

For the preliminary approach to the application of DHTT on the measurement of thermal diffusivity, we assumed that the Eq.(4) can be applied. In this case, the temperature of one side thermocouple (CH-1, in Fig.1) increased in a pulse shape and the other side of thermocouple (CH-2) was used as a detector. The typical temperature profiles both of CH-1 and CH-2 are shown in Fig.2. The time $t_{0.5}$ at the half maximum temperature (1/2 ΔT_{max}) was defined as shown in Fig.2. Using Eq.(4), overall thermal diffusivity was obtained.

The sample was the sodium silicate having the composition of $Na_2O.2SiO_2$, whose chemical and physical properties were well known.

3. RESULTS AND DISCUSSION

Figure 3 shows the effect of bubble on the thermal diffusivity obtained. The thermal diffusivity of the sample having bubbles has relatively large scattering. It was found that the bubbles were not stable and being coalescent and/or disappearing always during observation. It is considered that the relatively large scattering was caused by the unstable heat transfer resulted from the movement of bubbles. Figure 4 shows the image of sample with/without bubbles. The clear sample without bubbles was prepared by heating up to 1550°C. It was important to remove the bubbles in short time, because the sodium oxide would vaporize at high temperature. Once the bubbles were disappear, the measured values were stable and the scattering decreased. The clear sample was used for subsequent experiment in which the condition such as the distance between the thermocouple (or thickness of sample) was changed.

In the long experimental duration (> 8 hours in this experiment) with same sample, the crystallization phenomenon was observed and affected the thermal diffusivity measurement. Figure 5 shows the obtained thermal diffusivity during crystallization. The time sequence was started from high temperature (1550°C) to low temperature (400°C). Crystallization was observed from 1250°C to 950°C. The quite fine crystal in cloud type appeared.[4] In order to latent heat of crystallization, the measured value increased drastically. However, it does not mean that the existence of crystal increases the overall thermal diffusivity but the evolution of heat during measurement affects the measurement of thermal diffusivity strongly. It was considered that the crystallization did not complete in the temperature range from 1250°C to 950°C, because relatively high value of thermal diffusivity was observed in the lower temperature in which the effect of radiation on the heat transfer would be negligible. From these results, the points observed from 1250°C to 950°C (encircled points) were removed for later analysis.

Figure 6 shows the effect of distance between thermocouple (sample thickness, L) on the thermal diffusivity measurement. The obtained thermal diffusivities were increased with increasing temperature and the amount of increasing was also increased with the thickness of sample. If the measured value consisted of pure phonon conduction, the thermal diffusivity could not change with the thickness of sample. It was considered that the effect of radiation might be high in the high temperature on the measurement by DHTT.

The thermal conductivity k can be calculated using Eq.(5) with the density of sample ρ and heat capacity *Cp*.

$$k = a \cdot Cp \cdot r \qquad (5)$$

The calculated thermal conductivities were shown in Fig.7. The whole profile of the thermal conductivity was almost the same as the thermal diffusivity (Fig.6). However, since the Cp from literature [9] has a discontinuity between 874°C and 687°C, the obtained thermal conductivity had also discontinued region in the same temperature range. The reference data measured by Nagata et al [5,6] was plotted in Fig.7. They had used the hot-wire method to measure the thermal conductivity of molten slags, in which the radiation effect would be very small. Their value decreased with increasing temperature from about 700°C. However, the present data shows remarkable increase from 700°C. It would be explained by the effect of radiation from both of the thickness of sample and the temperature.

$$k_{eff} = k_L + k_R \qquad (6)$$

Generally, effective thermal conductivity k_{eff} is expressed by the summation of phonon conductivity (k_L) and radiation conductivity (k_R) as shown in Eq.(6). The radiation conductivity (k_R) is expressed by Eq.(7). [7]

$$k_R = \frac{16 \cdot n^2 \cdot s \cdot T^3}{3} g \qquad (7)$$

where n is the reflective index of sample, σ is the Stefan-Boltzman constant and γ is the function of optical thickness and temperature. In the case of transparent sample, radiation at each volume element will propagate to every direction. Then, the sum of radiation energy will increase in the longer sample, so that the γ will increase with increasing thickness of sample.

In the present data, the values at low temperature around 400°C, which the effect of radiation will be negligible, are almost the same. However, the values at this temperature range were quite lower than that of Nagata et al. In this study, the effective thermal diffusivity was calculated using Eq.(4) which was derived using the assumptions of one dimensional heat flow under a insulated circumstance and instantaneous heat pulse by laser. R.C. Heckman [8] showed the effect of finite pulse-time and heat loss on the measurement of thermal diffusivity by laser flash method. He showed the temperature profile under the delayed pulse and heat loss. When the pulse of heat source was delayed, the heating curve of the rear surface of sample was also delayed, then, the factor '0.1388' in the Eq.(4) increased to 0.34 in case of triangle pulse. This result shows that the shape of pulse in heat source is quite important and the factor for the thermal diffusivity should be corrected depending on the shape of heat pulse. As shown in Fig.2, the temperature profile of CH-1 was not square and the shape was changed in the temperature of experiment, the amount of sample and distance between thermocouple. So the factor for the thermal diffusivity must be changed with the shape of heat pulse in the case of DHTT measurement. It is consider that the factor of '0.1388' would increase from 3 times to 5 times in all pulse at present experiment, and it could be explained the difference of thermal diffusivity in the low temperature range.

4. Summary

The measurement method of overall thermal diffusivity using double hot thermocouple method (DHTT) was developed. Direct observation during measurement gave the important information about the obtained data. The crystallization of slag and the behavior of bubbles affected the thermal diffusivity measurement. Also, the factor for calculating thermal diffusivity should be changed (increased) depending on the shape of heat pulse.

References

1) H.S. Carslaw and J. C. Jaeger, Conduction of Heat Transfer in Solids (Oxford University Press, New york, New York, 1959), 2nd ed., p.101.
2) Y. Kashiwaya, C.E. Cicutti, A.W. Cramb and K. Ishii: ISIJ International 38(1998), p.348.
3) Y. Kashiwaya, C.E. Cicutti and A.W. Cramb: ISIJ International 38(1998), p.357.
4) C. Orrling, A.W. Cramb, A.Tilliander and Y. Kashiwaya: Transactions ISS, 27(2000), p.53
5) K.Nagata and K.S Goto: Proc. of 2nd Intl. Symp. on Metallurgical Slag and Fluxes, Lake Tahoe (1984), p.875,
6) K.Nagata, M. Susa and K.S. Goto: Tetsuto-Hagane, 69(1983),p.1417
7) H. Charnock: J. Amer. Ceram. Soc., 44(1961), p.313.
8) R.C. Heckman: J. Appl. Phys. 44(1973), p.1455
9) S. Banya and M. Hino: Chemical Properties of Molten Slags, ISIJ (1991)

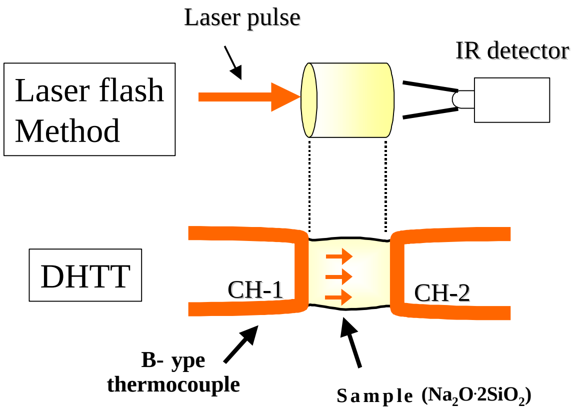

Fig.1 Comparison between DHTT and laser flash method.

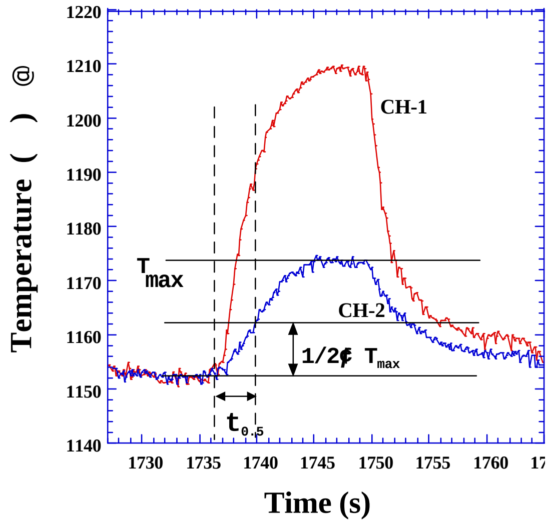

Fig.2 Typical temperature profiles during measurement in DHTT.

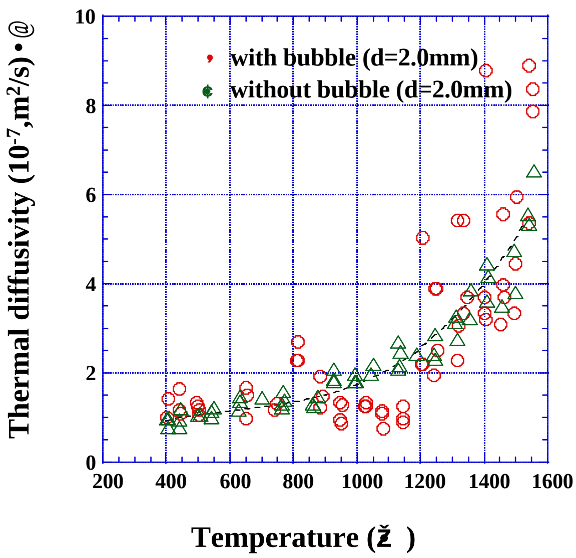

Fig.3 Effect of bubble on the thermal diffusivity obtained.
(Na_2O $2SiO_2$)

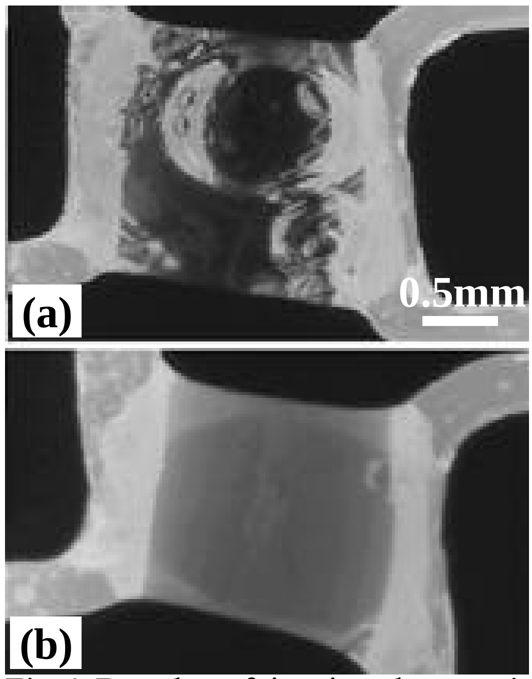

Fig.4 Results of *in situ* observatio
during measurement.
(a) sample with bubbles,
(b) without bubbles.
(Na_2O $2SiO_2$)

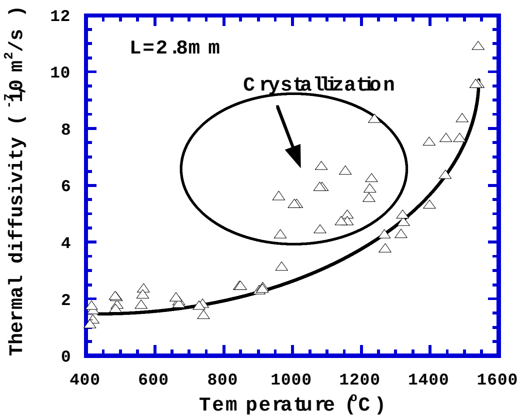

Fig.5 Effect of crystallization on the measurement of thermal diffusivity. ($Na_2O\ 2SiO_2$)

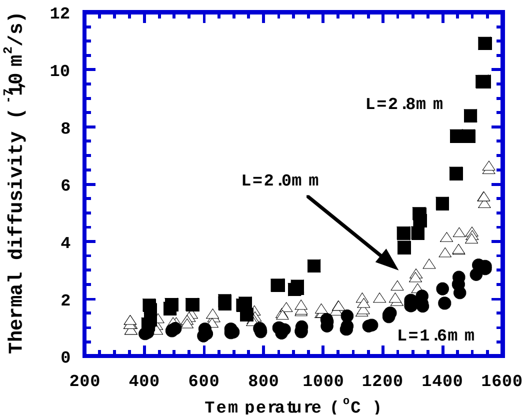

Fig.6 Effects of distance between thermocouples (thickness of sample) on the thermal diffusivity measurement. ($Na_2O\ 2SiO_2$)

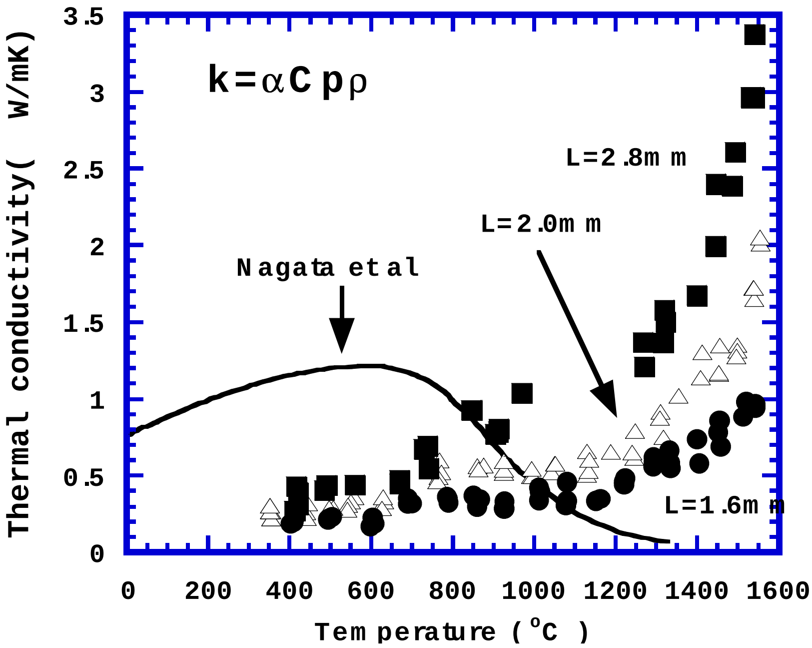

Fig.7 Comparison of thermal conductivity between present result and literature. ($Na_2O\ 2SiO_2$)