Thermal Diffusivity of Molten Carbonates at Elevated Temperatures

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ABSTRACT

Thermal diffusivities of molten carbonates, Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3 and Cs_2CO_3 have been determined as a function of temperature using the differential three-layered laser flash method. The thermal diffusivity values of five carbonates in the molten state were found to be in the range of 3~4 x 10^{-7} m^2/s with slightly positive temperature dependence. In addition, the thermal diffusivity values of molten carbonates are independent of the type of cation. These features agree well with the results reported by Otsubo *et al.* in 1997 using the forced Rayleigh scattering method.

Keywords: laser flash technique, molten carbonates, thermal diffusivity, high temperature

1. INTRODUCTION

Thermal properties of molten carbonates are of importance for designing a fuel cell. However, the experimental results of thermal properties, especially thermal diffusivity, of molten carbonates are rather limited due to the experimental difficulties at elevated temperatures. These difficulties arise mainly from onset convection in molten sample, heat leakage to the container and ambiguity of thickness of molten sample at high temperature. To overcome these difficulties, the differential three-layered laser flash method has been developed /1-4/. This method was successfully utilized for measurement of thermal diffusivity of molten oxides under air atmosphere at temperatures range from 1000 K to 1600 K /3,4/. This differential three-layered laser flash method has been extended to molten carbonates under CO_2 atmosphere with 0.1 M Pa. This condition prevents us from measuring with decomposition of carbonates at elevated temperatures.

The purpose of this paper is to describe the results of five molten carbonates, Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3 and Cs_2CO_3, in the temperature range between 1000 and 1280 K.

2. EXPERIMENTAL

Fundamentals of the differential three-layered laser flash method have been described in detail /1-3/, so that only essential points are given below.

A sample is melted in a platinum crucible and then a cell consists of the liquid sample sandwiched by two

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platinum crucibles as shown in Fig.1. The front surface of the upper platinum crucible was spontaneously irradiated by a YAG laser, then two different temperature response curves of the bottom surface of the lower platinum crucible were measured by an infrared detector. One temperature response curve was measured under a condition with the sample thickness of l. Next, the sample thickness was varied to $l+\Delta l$ by lifting the upper platinum crucible upward with a linear moving stage and then the temperature response curve was again measured. It may be suggested that the value of Δl was obtained by a micrometer. The initial time region of the two temperature response curves was analyzed to obtain the thermal diffusivity value /3,4/. This analysis method enables us to reduce the effects of two-dimensional heat flow of the platinum crucibles on the measured temperature response curves and heat leakage from the sample to the container during measurements.

3. RESULTS and DISCUSSION

The thermal diffusivity values obtained in this work are summarized in Fig. 2 as a function of temperature as open marks. Available literature values are also given in

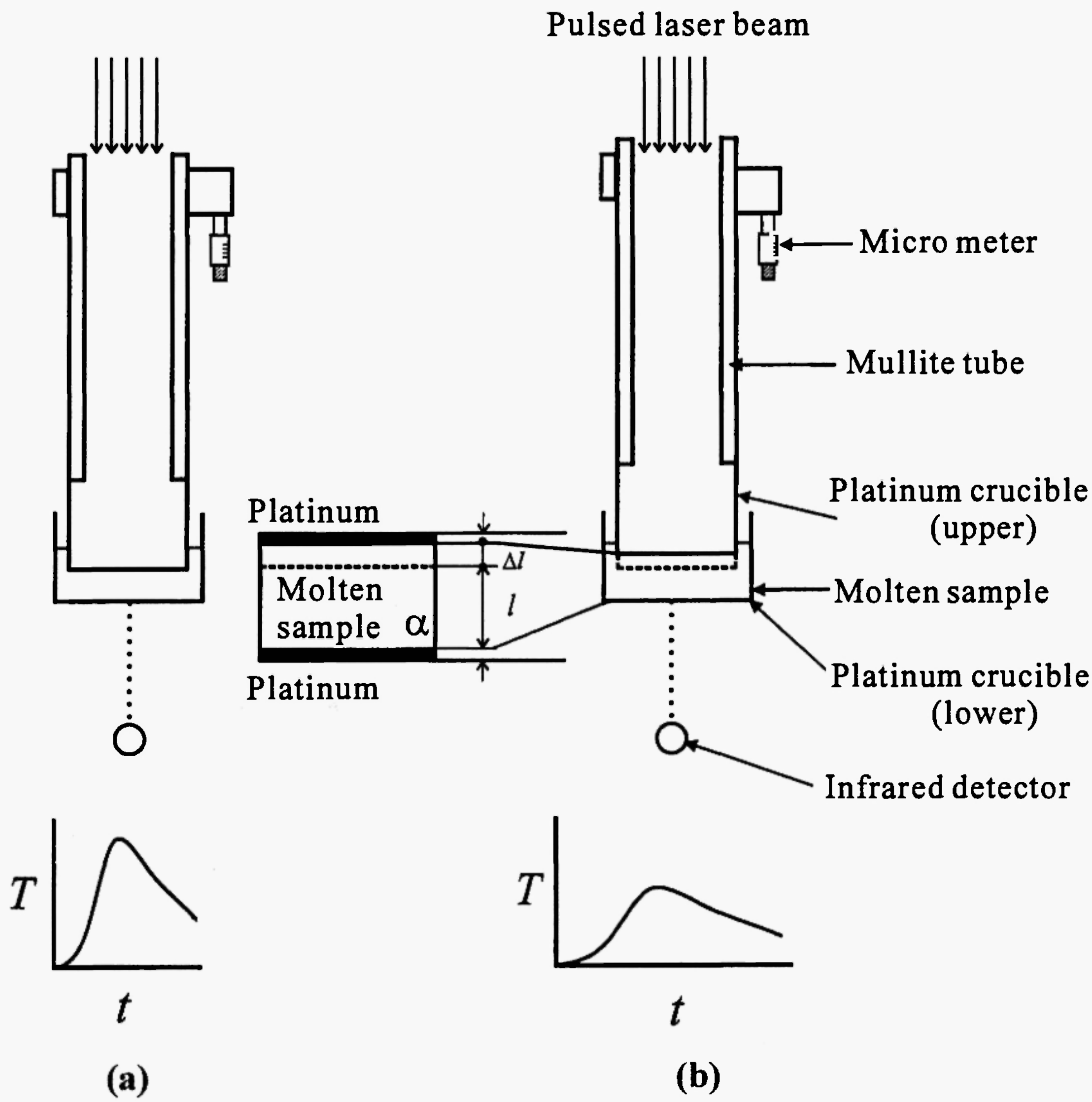

Fig. 1: Schematic diagram of the three-layered laser flash method.

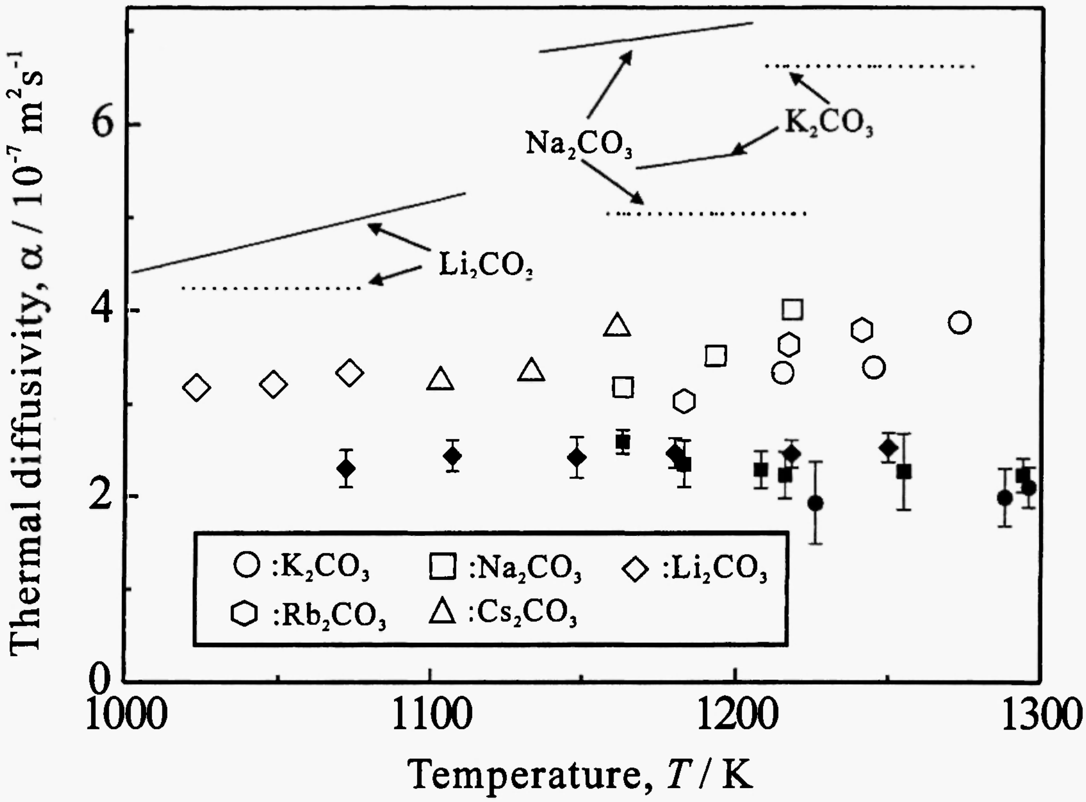

Fig. 2: Thermal diffusivity of molten carbonates; solid lines /7/, dotted line /8/ and filled marks /5/.

this figure as lines and filled marks. The thermal diffusivity values of five carbonates were found to be in the range of 3~ 4×10^{-7} m^2/s. No significant difference is detected in the thermal diffusivity when changing the type of cation in these molten carbonates. The temperature variation of the thermal diffusivity values is small, but slightly positive temperature dependence is notified in the temperature range between 1000 K and 1280 K, presently investigated.

Egorov and Revyakina /7/ measured the thermal conductivity of molten Li_2CO_3, Na_2CO_3 and K_2CO_3 by the steady-state concentric cylinder method. These thermal conductivity values can be converted to the thermal diffusivity in the following equation when the values of density and specific heat capacity are available /6,7/;

$$\alpha = \frac{\lambda}{\rho Cp} \qquad (1)$$

where λ is thermal conductivity, ρ is density and Cp is specific heat capacity of the sample.

On the other hand, Otsubo *et al.* /8/ reported the thermal diffusivity values of molten carbonates, Li_2CO_3, Na_2CO_3 and K_2CO_3 obtained from the forced Rayleigh scattering measurements and the results are shown in Fig. 2 with filled marks. Otsubo *et al.* /8/ suggest no temperature dependence of the thermal diffusivity values in the wide temperature range and they also stress that their results are not affected by any convection in molten sample.

The results obtained in this work may include a radiative heat transfer effect at elevated temperature because such radiative heat transfer is likely to take place between two platinum crucibles. In order to eliminate the radiative heat transfer effect in the three-layered laser flash method, a devised method coupled with the absorption coefficient of molten sample has already been developed by Ohta *et al.* /3,4/. Since the absorption coefficients of molten carbonates are not available, only the following comment may be given. When molten carbonates are considered transparent, the radiative heat transfer effect on the thermal diffusivity values appears to increase with increasing temperature and it becomes the order of 20 % at 1300 K /3,4/. This implies that slightly positive temperature dependence of the thermal diffusivity detected in molten carbonates is attributed to the radiative heat transfer effect. Then, it is not too much to say that the radiative heat transfer effect in the values obtained in this work is smaller than 20 % and it is rather reduced with decreasing temperature. For this reason, the present authors maintain the view that there is no essential difference between the thermal diffusivity values obtained by the three-layered laser flash method and those of Otsubo *et al.* /5/ using the forced Rayleigh scattering method.

The thermal diffusivity values of five molten carbonates are considered not to be influenced by convection as described in the following three reasons.

1) The sample thickness of molten carbonates is less than 0.5 mm and it is not so large as to exceed the uniform temperature region of the furnace. This condition provides that the sample temperature is kept uniform.
2) Since the upper side of the molten sample is spontaneously heated by a pulsed laser, the resultant temperature gradient dose not induce any convection.
3) The time required for obtaining the thermal diffusivity value is very short – less than 0.5 s when using the laser flash method. This is also very convenient in reducing the contribution from convection.

4. CONCLUSION

The thermal diffusivity values of five molten carbonates, Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3 and Cs_2CO_3, have been successfully measured by means of the differential three-layered laser flash method at elevated temperatures. The present results are found to be relatively insensitive to the variation of temperature and the type of the cations in carbonates. The usefulness of the differential three-layered laser flash method was again confirmed. Thus, it would be interesting to extend this laser flash method to other molten samples at elevated temperature in order to obtain the thermal diffusivity values.

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