Measurements of Thermal Conductivity and Thermal Diffusivity of Molten Carbonates

Wicaksono, Hendro
Department of Energy and Environmental Engineering Interdisciplinary Graduate School of Engineering Sciences Kyushu University

Zhang, Xing
Institute of Advanced Material Study Kyushu University

Fujiwara, Seiji
Institute of Advanced Material Study Kyushu University

Fujii, Motoo
Institute of Advanced Material Study Kyushu University

https://doi.org/10.15017/7945

出版情報：九州大学機能物質科学研究所報告. 15 (2), pp.165-168, 2001-12-14. 九州大学機能物質科学研究所
バージョン：

Measurements of Thermal Conductivity and Thermal Diffusivity of Molten Carbonates

Hendro WICAKSONO*, Xing ZHANG, Seiji FUJIWARA, Motoo FUJII

The thermal conductivity and thermal diffusivity of molten carbonates (Li_2CO_3/K_2CO_3 and Li_2CO_3/Na_2CO_3) were measured using the transient short-hot-wire method in the temperature range from 530 to 670 ℃. Two types of probes were examined. One was a platinum short-hot-wire probe coated with alumina (Al_2O_3) thin film to prevent current leakage and corrosion. The other was a bare gold short-hot-wire probe. For the platinum probe, the quality of coating reduces gradually during the measurements of molten carbonates due to their high corrosiveness. The quality reduction has caused relatively large errors of measured thermal conductivity and thermal diffusivity around ± 10 and ± 40 %, respectively. For the bare gold probe, the corrosion due to electro-chemical reaction can be neglected and the effect of current leakage into the molten carbonates can be estimated. Then the temperature dependency of the electrical resistivity was calibrated accurately and compared with existing data. By using this gold probe without coating on the hot wire surface, the thermal conductivity and thermal diffusivity of molten carbonates can be measured within errors of ± 3 and ± 9 %, respectively. It is further confirmed that the gold probe can be used repeatedly without the reduction of quality.

Introduction

Molten carbonates are considered to be the electrolyte candidates for new type of fuel cells, that is, MCFC. The thermophysical properties of molten carbonates are strongly required to develop a new MCFC for practical case. However, it is very difficult to measure those thermophysical properties. These difficulties are mainly attributed to the high corrosiveness and electrical conductivity of molten carbonates.

The present authors [1] proposed an effective method so called 'Transient Short-Hot-Wire Method' that can be used to measure the thermal conductivity and thermal diffusivity of liquids simultaneously. The probe used in this method was a very short platinum wire compared with that used in the conventional hot wire method. With this short hot wire, we had measured the thermal conductivity and thermal diffusivity of many kinds of liquids, such as alternative refrigerants [2] and polymer melts [3]. Also, the method had been applied to the measurements of molten carbonates [4]. In the last case, however, the platinum probe had to be coated with alumina (Al_2O_3) film to prevent the corrosion and current leakage, because the molten carbonates are generally highly corrosive and electrically conductive. During the measurements at the high temperature ranged from 550 to 650 °C, however, the quality of coating film reduces gradually with time. Due to this reduction of the probe quality, the reproducibility and accuracy of thermal conductivity and thermal diffusivity became inevitably poor. The measured values of thermal conductivity and thermal diffusivity scattered around ± 10 and ± 40 %, respectively.

In the present study, two types of short-hot-wire probes were used, a platinum probe coated with alumina film and a bare gold probe. From the comparison of the results obtained from these two types of probes, the gold probe is found to be much better than the platinum one, because the former is free from corrosion and is able to estimate the effect of current leakage. Uncertainty analysis shows the gold probe can be used to measure the thermal conductivity and thermal diffusivity of molten carbonates within errors of ± 3 and ± 9 %, respectively.

Principle of Measurement

The present method is based on the numerical solutions of two-dimensional unsteady heat conduction from a short wire. The dimensionless temperature history θ_v $(=(T-T_i)/(q_v r^2/\lambda))$ is expressed by a linear equation with respect to the logarithm of Fourier number Fo (=(α

Received November 15, 2001
*Department of Energy and Environmental Engineering, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University.

$t)/r^2$) with the coefficients A and B. While the measured temperature rise T_v of the wire is also expressed by the similar linear equation with coefficients a and b. Comparing the two expressions, the thermal conductivity and thermal diffusivity of a liquid are evaluated by

$$\lambda = \frac{VI}{\pi l}\frac{A}{a} \quad (1)$$

$$\alpha = r^2 exp\left(\frac{b}{a} - \frac{B}{A}\right) \quad (2)$$

Where r and l are the radius and length of the hot wire, V and I are the voltage and current supplied to the wire, respectively. Equations (1) and (2) are similar to those obtained for the conventional transient hot-wire method [5], except that the A and B are changed with the wire aspect ratio and thermal conductivity ratio of wire and sample liquid, etc.

From Eqs. (1) and (2) the relative uncertainties of the thermal conductivity and thermal diffusivity are estimated as

$$\frac{\delta\lambda}{\lambda} = \left\{\left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta I}{I}\right)^2 + \left(\frac{\delta l}{l}\right)^2 + \left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta a}{a}\right)^2\right\}^{\frac{1}{2}} \quad (3)$$

$$\frac{\delta\alpha}{\alpha} = \left\{\left(\frac{2\delta r}{r}\right)^2 + \left[\delta\left(\frac{B}{A}\right)\right]^2 + \left[\delta\left(\frac{b}{a}\right)\right]^2\right\}^{\frac{1}{2}} \quad (4)$$

In the present measurements, the magnitudes of the main factors in Eqs. (3) and (4) were estimated as follows. The length and radius of the hot wire were measured with a microcathetometer and microscope, and both $\delta l/l$ and $\delta r/r$ are accurate to 1%. The possible uncertainty in the slope of the temperature against ln$t$ includes the uncertainties induced by electrical noise and the timing of the voltage measurements. The maximum deviation of the measured temperature rise is less than 0.4%. The values of $\delta a/a$ and $\delta(b/a)$ are around 0.01 and 0.05, respectively. From numerical solutions, $\delta A/A$ is found to be 0.002 and $\delta(B/A)$ is 0.003. The voltage and current through the wire were measured with digital multimeters and the values of $\delta V/V$ and $\delta I/I$ in the measurement are less than 10^{-4}. Therefore, the total uncertainties of this method including additional systematic uncertainties were estimated to be 3 and 9 % for the thermal conductivity and thermal diffusivity, respectively.

Experiments

A pure gold crucible of 50 mm in inner diameter and 100 cm^3 in volume was used as the sample vessel and its temperature was regulated with a temperature controller. Both the platinum and gold wires were annealed at 800 °C for a few hours, and the temperature dependency of the electrical resistance was determined through calibration for the range from 0 to 860 °C. As for the platinum probe, an alumina film was coated using a plasma sputtering apparatus. It was a very complicated process to get high quality film on the platinum probe, because the film quality depends on several factors such as the cleanness and the roughness of wire surface, and the conditions of sputtering.

Figure 1 shows the electrical resistance versus temperature ranged from 0 to 860 °C for the pure gold wire. The present results of electrical resistivity ρ are further compared with those recommended by Ref.6 shown the dashed line and Laubitz [7] shown the solid line. The present results denoted by open circles are very closed to the solid line (0.6% difference at most) that was expressed by Laubitz as

$$\rho = -0.1982 + 8.3123\times10^{-3}T - 0.7091\times10^{-6}T^2 + 1.4795\times10^{-9}T^3 \quad (5)$$

In the following, therefore, Eq. (5) was used to evaluate the temperature of gold hot wire.

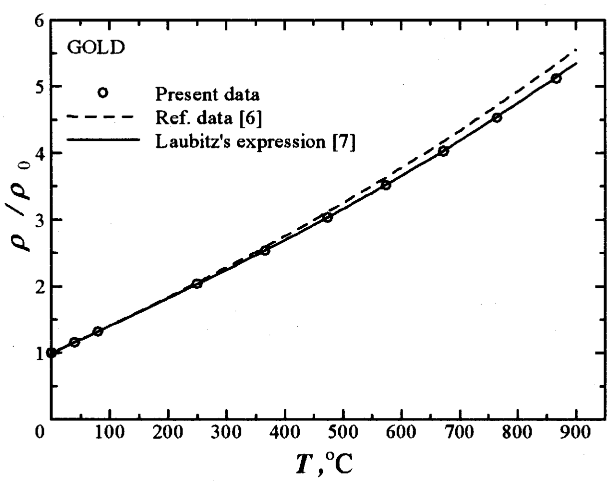

Fig. 1 Electrical resistivity of gold wire

Figure 2 shows a typical example of the current leaked into the molten carbonates at the different constant voltages for an actual gold probe where the bare hot wire was cutoff at the middle and two gold terminals were coated with ceramics to reduce the effect of current leakage. The value of leak current is also changed from different carbonates and even the same carbonates at the different components. Therefore, the leak current must be measured individually for any test samples. In the actual measurements, the temperature rise of hot wire is usually set around 5 ℃ at 1 s after heating. In this case, the current and voltage supplied to the bare gold probe were the order of 1.1 A and 0.2 V, respectively. As shown in Fig. 2, the leak current at V=200 mV is about 0.05 mA. Although such a small leak current does not affect the measurement accuracy of the thermal conductivity, it must be considered for estimating the thermal diffusivity because the value of the thermal diffusivity is very sensitive to the absolute temperature rise.

Figure 3 further shows a typical example of the leak current changed with time for step heating case. The value of leak current decreases rapidly at the beginning, and becomes almost independent of time after 0.5 s. This leak current is excellently repeatable. Therefore, the temperature rise for the step heating can be estimated accurately after the value of electrical resistance is compensated with the leak current in real time.

The specifications of the present probes were determined by using pure water and toluene as standard liquids with known thermal conductivity and thermal diffusivity. The platinum wire has a typical length of 10.5 mm and diameter of 100.4 μ m with coating layer of 5 μ m. These values were slightly different from the respective probe used in each measurement. The gold wire is 18.7 mm in length and 100.4 μ m in diameter.

In fact, the gold probe can be used repeatedly because there is no quality reduction after the measurements of the molten carbonates. This differs much from the platinum probe, which has to be newly made whenever a new measurement is done for different molten carbonates.

Results and Discussion

Figure 4 shows the reproducibility of measured temperature changes with time. The symbols represent the measured temperature rises. The dashed and solid lines were obtained by the linear least-squares approximation. The absolute values of temperature rise for three measurements are repeatable and accurate to 0.02K. This is particularly important for estimating the thermal diffusivity with high accuracy.

Figure 5 and 6 show the thermal conductivity and thermal diffusivity of Li_2CO_3/Na_2CO_3 (53/47 mol%) measured with the platinum probe, respectively, and compare with the existing data.

The present results for the thermal conductivity in this temperature range are almost independent of temperature and agree well with the data obtained by Zhang and Fujii [4] as shown in Fig. 5. However, they are lower about 30% than those obtained by Araki *et al* [8] that shows large temperature dependency. As shown in Fig. 6, the measured thermal diffusivity scatters largely, however, the mean values show only a little bit of difference in temperature tendency obtained by Araki *et al*. The values obtained by Zhang and Fujii are quite low. Because the thermal diffusivity is very sensitive to the absolute temperature rise of the hot wire as indicated by Eq. (2),

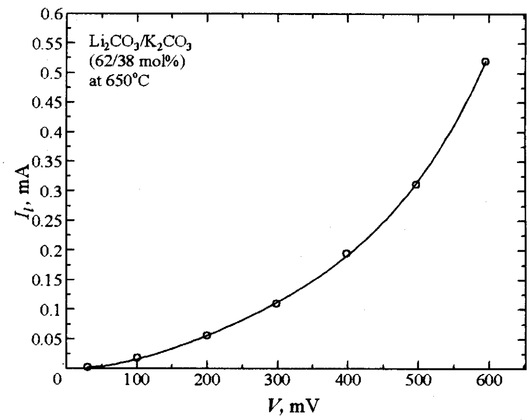

Fig. 2 Leak current at steady state

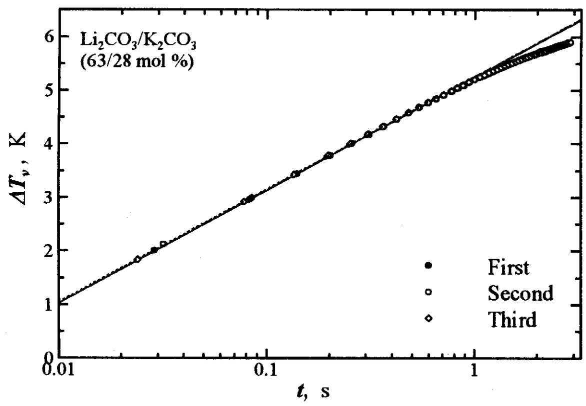

Fig. 4 Temperature rise variation with time

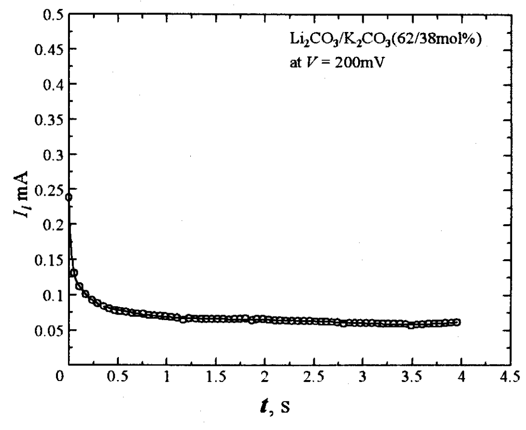

Fig. 3 Leak current changed with time

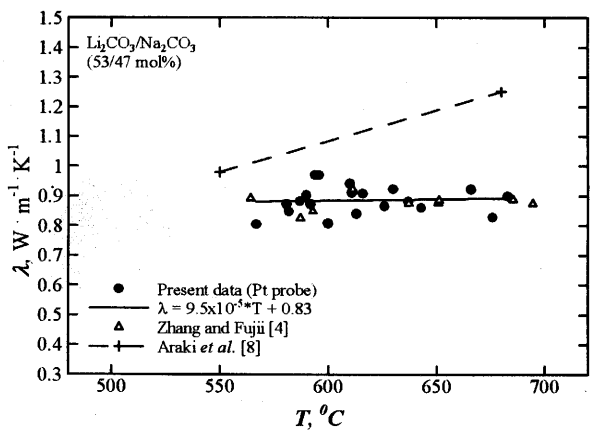

Fig. 5 Thermal conductivity of Li_2CO_3/Na_2CO_3

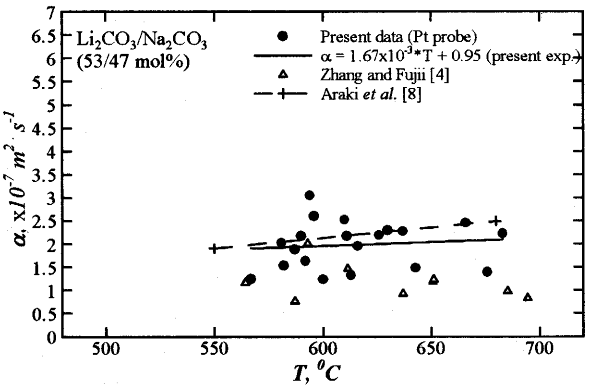

Figure 6 Thermal diffusivity of Li_2CO_3/Na_2CO_3.

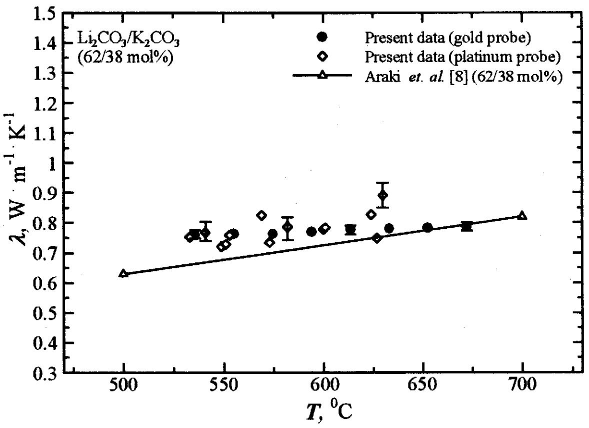

Figure 7 Thermal conductivity of Li_2CO_3/K_2CO_3.

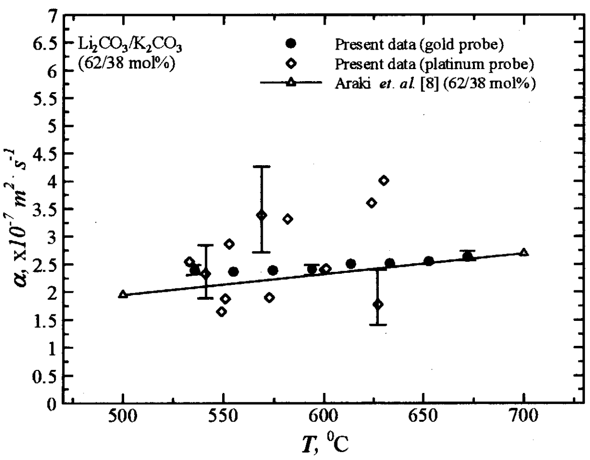

Figure 8 Thermal diffusivity of Li_2CO_3/K_2CO_3.

such a large scatter is attributed to the quality reduction of platinum probe due to the corrosion.

As for the molten carbonate Li_2CO_3/K_2CO_3 (62/38 mol%), both the platinum and gold probes are used to measure the thermal conductivity and thermal diffusivity. The results are shown and compared each other in Figs. 7 and 8. In these figures, the error bars indicating the reproducibility of measurements are attached for the typical data. It is clear that the reproducibility of the data obtained by the gold probe is much better than those by the platinum probe.

The thermal conductivities measured with Au and Pt probes agree well with each other. Both of them show little changes with temperature comparing with the solid line recommended by Araki *et al* [8] as shown in Fig. 7. In Fig. 8, large scattered data of the thermal diffusivity measured with Pt probe are observed, however, the data obtained with Au probe are closed to the solid line recommended by Araki *et al* in magnitude, but a little bit of difference in temperature dependency.

As a whole, the present results for the thermal diffusivity agree well with those of Araki *et al.* On the other hand, for the thermal conductivity the difference between them is large. Because the thermal conductivity given by Araki *et al* is evaluated from the measured thermal diffusivity, the difference may be attributed to the uncertainty of the density and specific heat of these molten carbonates.

Conclusions

The thermal conductivity and thermal diffusivity of molten carbonates have been measured with two types of probes, the bare gold and coated platinum probes. The main conclusions are as follows:

(1) The coating quality of the platinum probe reduces gradually during the measurements.
(2) Because the bare gold probe is free from corrosion and the effects of leak current can be calibrated, the reproducibility of measurements with it is excellent and the probe can be used repeatedly.
(3) The uncertainty of the data obtained with the gold probe is estimated to be within ± 3 and ± 9 % for the thermal conductivity and thermal diffusivity, respectively.

References

1. Zhang, X., Tomimura, T., and Fujii, M., *Proc. 14th Japan Symposium on Thermophys. Properties* (1993), 23-26.
2. Tomimura, T., Maki, S., Zhang, X., and Fujii, M., *Japan J. Thermophys. Properties*, 15:1(2001), 9-14.
3. Wicaksono, H., Zhang, X., Tomimura, T., and Fujii, M., *37th National Heat Transfer Symposium of Japan* (2000), 911-912.
4. Zhang, X., and Fujii, M., *Int. J. Thermophysics*, 21:1(2000), 71-84.
5. Nagasaka, N., and Nagashima, A., *Rev. Sci. Instrum.* 52:2(1981), 229-232.
6. Metals Data Book, Edited by the Japan Institute of Metals, Maruzen Ltd., (1993), 29.
7. Laubitz, M. J., *Can. J. Phys.* 47:23(1969), 2633-2644.
8. Araki, N., Matsuura, M., and Hirata, T., *8th Japan Symposium on Thermophys. Properties* (1987), 1-4.