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Measurement of Thermophysical Properties of Molten Salts: Mixtures of Alkaline Carbonate Salts[1]

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The purpose of this study is to develop measuring methods for the thermal diffusivity, the specific heat capacity, and the density of molten salts, as well as to measure these properties of mixtures of alkaline carbonate salts. The thermal diffusivity is measured by the stepwise heating method. The sample salt is poured into a thin container, and as a result, a three-layered cell is formed. The thermal diffusivity is obtained from the ratio of temperature rises at different times measured at the rear surface of the cell when the front surface is heated by the stepwise energy from an iodine lamp. The specific heat capacity is measured using an adiabatic scanning calorimeter. The density is measured by Archimedes' principle. Thermal conductivity is determined from the above properties. Measured samples are Li_2CO_3–K_2CO_3 (42.7–57.3, 50.0–50.0, and 62.0–38.0 mol%).

KEY WORDS: alkaline carbonate salts; density; high temperatures; molten salts; specific heat capacity; stepwise heating method; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Molten salts are suitable as electrolyte materials for the fuel cell, heat carriers, thermal storage media, and so on, because of their satisfactory stability at high temperatures, their low vapor pressure, their high thermal conductivity, and their high values of specific heat capacity. Among these molten salts, mixtures of molten alkaline carbonate salts have attracted special interest as electrolyte materials of the fuel cell (the second generation) for a power-generating device with a high efficiency. However,

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the present knowledge of the thermophysical properties of these salts is insufficient to design these devices, due mainly to the lack of appropriate measuring methods for the thermophysical properties of molten salts at high temperatures. It is, therefore, necessary to develop measuring methods for the thermal diffusivity, the specific heat capacity, and the density of these molten salts, in order to obtain reliable data for these properties.

The stepwise heating method for thermal diffusivity measurements developed by Kobayasi and others [1–3] has an advantage over the laser flash method [4] in that it has a heating source with a low energy density, which allows uniformity and small temperature differences in the sample. In applications of this method to liquid samples carried out by Araki, Kobayasi, Kato, and others [4–15], it has turned out to be appropriate to pour the sample liquid into a thin layer to prevent natural convection and to obtain an accurate distance between the heat source and a measuring point of the temperature response. Two types of methods have been used; one is the method using a metallized ceramic cell with a thin metal plate heated by stepwise electric current [7–9], and the other is the method with a three-layered cell which has a sample liquid in the central layer [10–15]. In the present study, the method with the three-layered cell is used.

The specific heat capacity is measured using an adiabatic scanning calorimeter. Special treatments, such as in inert gas flow to prevent the sample vessel from contamination with the sample vapor, are adopted in this apparatus in order to use molten salts as the sample.

The density is measured by Archimedes' principle, namely, by measuring the buoyancy of a sinker in the salt. The change of weight of the sinker is detected by a balance with an elastic fulcrum and an unbonded straingauge [16].

In this paper, the results obtained by using these methods for mixtures of Li_2CO_3 and K_2CO_3 salts (42.7–57.3, 50.0–50.0, and 62.0–38.0 mol%) are presented. The thermal conductivities are obtained from the above-mentioned results, namely, the product of the thermal diffusivity, the specific heat capacity, and the density.

2. MEASURING METHODS AND APPARATUS

2.1. Measuring Method and Apparatus for Thermal Diffusivity

Three layers of an infinite parallel plane are assumed as the model of a sample and its container (Fig. 1). The first and the third layers correspond to the metalic container and the second layer corresponds to the liquid sample. When the front surface is exposed to a stepwise radiation energy,

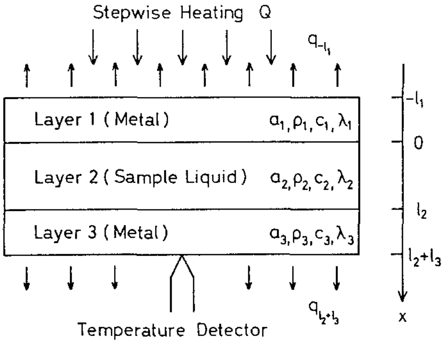

Fig. 1. Model of the sample and its container.

the resulting temperature history at the rear surface is expressed as a function of the thermal diffusivity, specific heat capacity, density, and thickness of the three-layered composite [10]. We can obtain the thermal diffusivity of the liquid sample by measuring the ratio of temperature rises at different times and comparing it with the theoretical one until they coincide with each other. Furthermore, since there exists heat loss from the surfaces of the cell wall to the circumstances, the error due to the heat loss has been corrected in this method. This correction method is based on the principle that the thermal diffusivities remain constant regardless of the measuring times [11, 15].

A schematic diagram of the measuring apparatus is shown in Fig. 2. A sample salt in a pot (9) is melted using an electric furnace (10). After

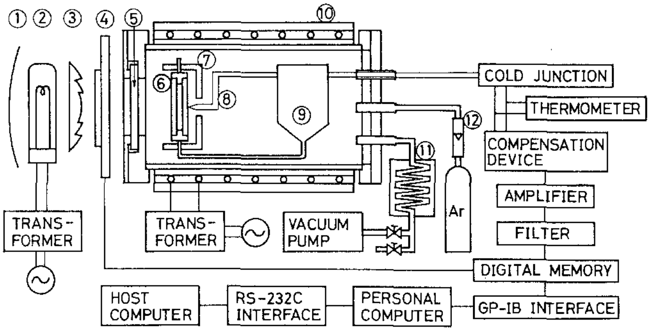

Fig. 2. Schematic diagram of the measuring apparatus of thermal diffusivity. (1) Concave mirror. (2) Halogen lamp. (3) Fresnel lens. (4) Shutter. (5) Quartz window. (6) Sample cell. (7) Shroud. (8) Thermocouple. (9) Pot. (10) Furnace. (11) Heat exchanger. (12) Flow meter.

melting, the sample salt is supplied to the cell (6) by opening a valve. In the measurement at high temperatures, an argon atmosphere is used in the furnace to protect the cell and sample salt from oxidation. The front surface of the cell is subjected to stepwise radiation from an iodine lamp (2) through a mechanical shutter (4). The resulting temperature history is recorded digitally into a memory and the data are processed by a computer.

2.2. Measuring Apparatus for Specific Heat Capacity

The specific heat capacity is measured by an adiabatic scanning calorimeter (ASC). A schematic diagram of the measuring apparatus is shown in Fig. 3. A sample salt and its vessel (1) are heated by the inner heater (2). The temperature difference between the adiabatic vessel (4) and the sample holder (3) is controlled to zero degrees so the specific heat of the sample is obtained from the power which is imparted to the inner heater. Since we use molten salt as a sample, contamination of the vessel by the sample vapor should be suppressed as much as possible. Then this apparatus has a gas flow system (10) by which inert gas flows around the sample vessel.

2.3. Measuring Apparatus for Density

The density is measured by Archimedes' principle, namely, by the measurement of the buoyancy of a sinker in a sample salt. A schematic

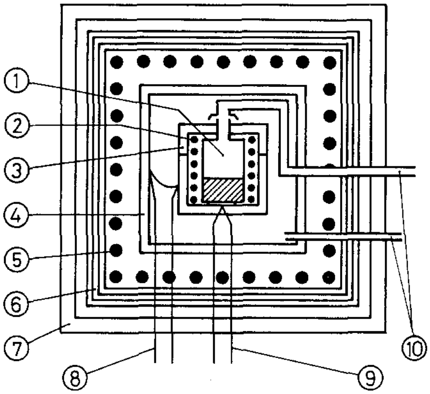

Fig. 3. Schematic diagram of the adiabatic scanning calorimeter. (1) Sample vessel. (2) Inner heater. (3) Sample holder. (4) Adiabatic vessel. (5) Outer heater. (6) Radiation shield. (7) Bell jar. (8) Thermocouple. (9) Thermocouple. (10) Gas flow pipe.

diagram of the measuring apparatus is shown in Fig. 4 [16]. The change of weight of the sinker (5) is detected by a balance (1) with an elastic fulcrum and an unbonded straingauge (2) as a sensor of weight. Nickel is chosen as the sinker material because of its advantages, such as heat resistance, corrosion resistance, machinability, and so on. The diameter of the wire (11) which suspends the sinker is 100 μm and is small enough to neglect the effect of surface tension. The temperature distribution in a sample salt is adjusted so as to avoid the generation of the natural convection in the sample container.

3. MEASURED RESULTS

Thermophysical properties of various kinds of molten salts have been measured previously by the present and other investigators [12, 13]. In this paper, mixtures of alkaline carbonate salts, such as Li_2CO_3–K_2CO_3 (42.7–57.3 mol%), Li_2CO_3–K_2CO_3 (50.0–50.0 mol%), and Li_2CO_3–

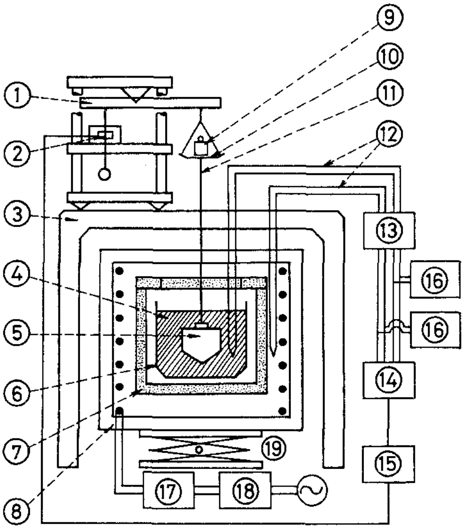

Fig. 4. Schematic diagram of the measuring apparatus of density. (1) Balance. (2) Unbonded straingauge. (3) Rack for balance. (4) Sample salt. (5) Sinker. (6) Crucible. (7) Brick. (8) Electric furnace. (9) Weight. (10) Scale pan. (11) Wire. (12) Thermocouple. (13) Cold junction. (14) Pen recorder. (15) Amplifier for straingauge. (16) Thermometer. (17) Voltmeter. (18) Transformer. (19) Laboratory jack.

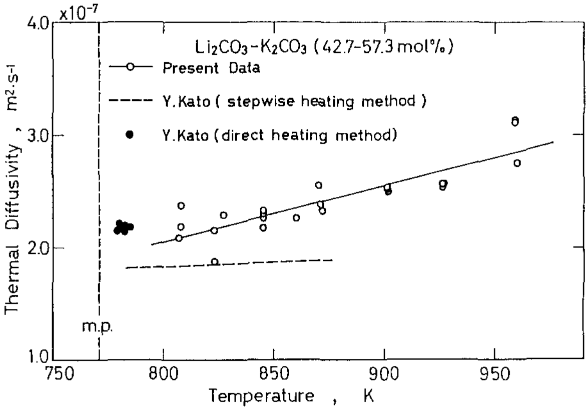

Fig. 5. Thermal diffusivity of Li_2CO_3-K_2CO_3 (42.7–57.3 mol%); $a = 1.93 \times 10^{-7} + 4.85 \times 10^{-10}\ (T - 771)\ m^2 \cdot s^{-1}$ at $807 \leqslant T \leqslant 960$ K.

K_2CO_3 (62.0–38.0 mol%), are used as sample salts. These salts have the special composition of mixtures as the eutectic and the complex and have comparatively low melting points and good stabilities in the high-temperature range. The first one and the third one are the eutectic mixtures and have melting points of 771 and 761 K, respectively. The second one is the complex of $LiKCO_3$ and has a melting point of 778 K.

Since these salts have deliquescent properties, handlings are done with care to prevent moisture adsorption. The salt samples are prepared as

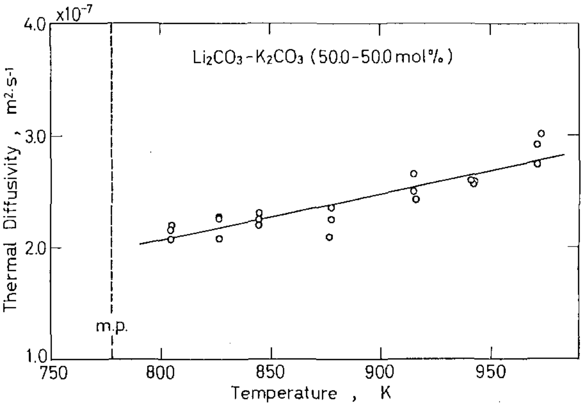

Fig. 6. Thermal diffusivity of Li_2CO_3-K_2CO_3 (50.0–50.0mol%); $a = 1.97 \times 10^{-7} + 4.17 \times 10^{-10}\ (T - 778)\ m^2 \cdot s^{-1}$ at $805 \leqslant T \leqslant 960$ K.

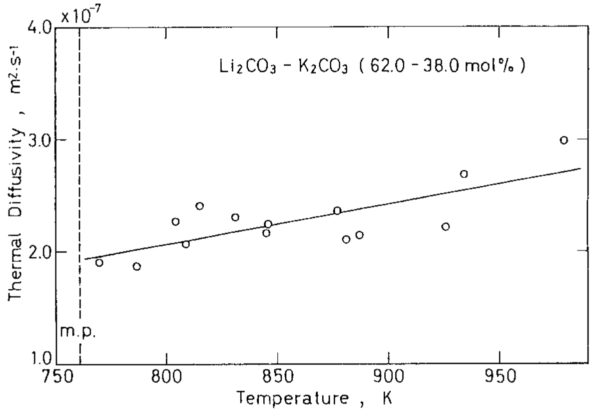

Fig. 7. Thermal diffusivity of Li_2CO_3-K_2CO_3 (62.0-38.0mol%); $a = 1.92 \times 10^{-7} + 3.56 \times 10^{-10}$ $(T - 761)$ $m^2 \cdot s^{-1}$ at $770 \leqslant T \leqslant 979$ K.

follows. The extrapure reagent dehydrated single salts (Li_2CO_3, K_2CO_3) are first dried in the vacuum drier at about 500 K for more than 6 h. After that, they are cooled in a glove box filled with argon gas and are weighed out to have the desired compositions in the sample salts. In order further to remove moisture, CO_2 gas is injected into the melting mixture for a while. This treatment is important to convert hydroxyl salts to carbonate salts. Otherwise, these hydroxyl salts are errosive and cause an increase in the impurity contents in the samples.

The data on thermal diffusivity of these mixtures are presented in Figs. 5 to 7. The uncertainty of these data is estimated to be 10% at the

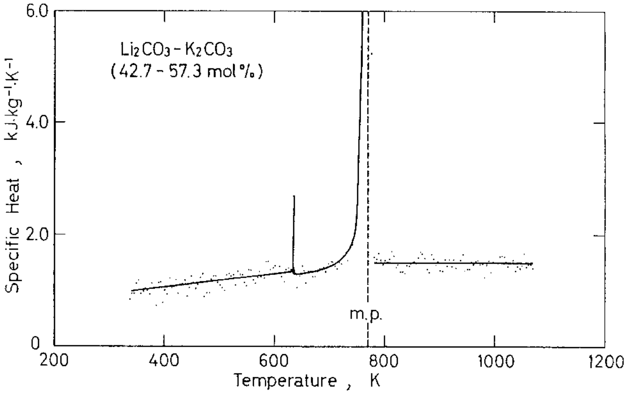

Fig. 8. Specific heat of Li_2CO_3-K_2CO_3 (42.7-57.3 mol%): $c_p = 0.592 + 1.16 \times 10^{-3}T$ kJ·kg^{-1}·K^{-1} at $341 \leqslant T \leqslant 634$ K; $c_p = 1.49$ kJ·kg^{-1}·K^{-1} at $781 \leqslant T \leqslant 1071$ K.

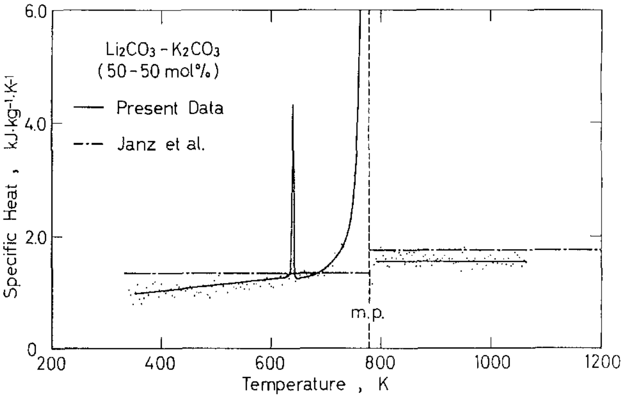

Fig. 9. Specific heat of Li_2CO_3–K_2CO_3 (50.0–50.0 mol%): $c_p = 0.618 + 1.03 \times 10^{-3} T$ kJ·kg^{-1}·K^{-1} at $352 \leqslant T \leqslant 626$ K; $c_p = 1.55$ kJ·kg^{-1}·K^{-1} at $800 \leqslant T \leqslant 1066$ K.

most. Solid lines are obtained by a least-squares method and their expressions are shown in the figure legends. In Fig. 5, data on thermal diffusivity measured by Kato and co-workers, who used the stepwise heating method with a metallized cell [8] as well as the direct heating method [17], are also shown. Since the experimental temperature range of Kato and co-workers is relatively small, a complete comparison is not possible. However, near the melting point, the results are in fair agreement.

The data on specific heat capacity of these mixtures are presented in Figs. 8 to 10. The uncertainty in these data is estimated to be 3% at the most. These figures show that big peaks exist near the transition point and

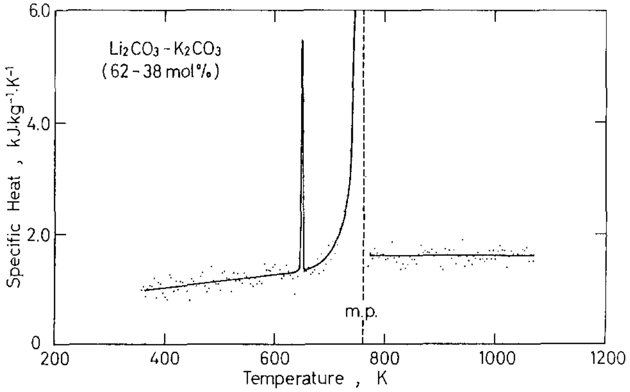

Fig. 10. Specific heat of Li_2CO_3–K_2CO_3 (62.0–38.0 mol%): $c_p = 0.562 + 1.16 \times 10^{-3} T$ kJ·kg^{-1}·K^{-1} at $365 \leqslant T \leqslant 631$ K; $c_p = 1.60$ kJ·kg^{-1}·K^{-1} at $773 \leqslant T \leqslant 1071$ K.

the melting point; the apparent specific heat capacity increases because heat is required for the transition and the melting. Experimental equations are obtained by a least-squares method in the temperature range lower than the transition point and higher than the melting point. Melting points of these mixtures turn out to be in good agreement with the pubished data. In Fig. 9, data on specific heat capacity measured by Janz et al. [18], which are slightly larger than the present data, are also shown.

The data on the density of these mixtures are presented in Fig. 11. The uncertainty in these data is estimated to be 0.9 % at the most. Solid lines are obtained by a least-squares method. These figures show that the density decreases linearly with increasing temperatures. It is also proved experimentally that the inverse of the density of these mixtures is a linear function of the mass fractions of single salts within 2 % error.

Thermal conductivities of these mixtures are obtained from the previously mentioned results, since the thermal conductivity is the product of the thermal diffusivity, the specific heat capacity, and the density. Relations for thermal conductivity, λ, are as follows:

Li_2CO_3–K_2CO_3 (42.7–57.3 mol%),

$$\lambda = 0.587 + 1.26 \times 10^{-3}(T - 771) \quad \text{at} \quad 807 \leqslant T \leqslant 960 \text{ K}$$

Li_2CO_3–K_2CO_3 (50.0–50.0 mol%),

$$\lambda = 0.617 + 1.10 \times 10^{-3}(T - 778) \quad \text{at} \quad 805 \leqslant T \leqslant 973 \text{ K}$$

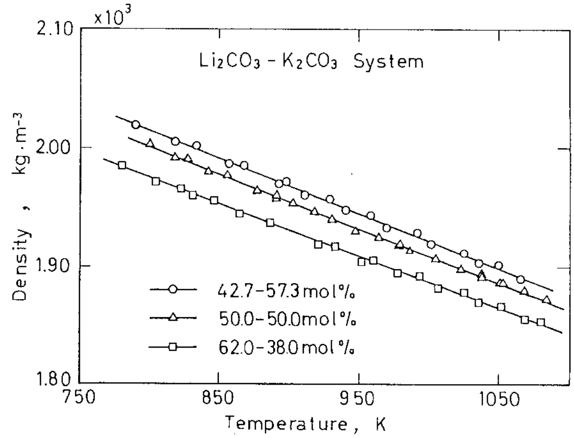

Fig. 11. Density of the Li_2CO_3–K_2CO_3 system: 42.7–57.3 mol%, $\rho = 2028 - 0.4647\ (T - 771)$ kg·m^{-3} at $819 \leqslant T \leqslant 1065$ K; 50.0–50.0 mol%, $\rho = 2011 - 0.4593\ (T - 778)$ kg·m^{-3} at $800 \leqslant T \leqslant 1083$ K; 62.0–38.0 mol%, $\rho = 1991 - 0.4341\ (T - 761)$ kg·m^{-3} at $783 \leqslant T \leqslant 1082$ K.

Li_2CO_3–K_2CO_3 (62.0–38.0 mol%),

$$\lambda = 0.618 + 9.48 \times 10^{-4}\,(T - 761) \qquad \text{at} \qquad 770 \leqslant T \leqslant 979\ \text{K}$$

where λ is in $W \cdot m^{-1} \cdot K^{-1}$. These expressions show that the thermal conductivities of these mixtures increase linearly with increasing temperatures in spite of the linear decrease in density.

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