THE TEMPERATURE DEPENDENCE OF THE THERMAL CONDUCTIVITY OF MOLTEN SALTS

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ABSTRACT

By using newly developed transient methods, namely transient hot-wire method with ceramic-coated probe and forced Rayleigh scattering method, the thermal conductivities of two molten nitrates (NaN03 and KNO3 up to about 440 °C) and five molten alkali metal chlorides (LiCl, NaCl, KCl, RbCl and CsCl up to about 1200 °C) have been determined. The present thermal conductivity results show a weak negative temperature dependence and one of the smallest values among other previous data obtained by steady-state methods; the difference is a factor of four at most.

INTRODUCTION

Reliable data for the thermal conductivity of molten salts are required for the thermal design of latent-heat thermal storage system, molten salt fuel cell and so on. However, there have been a very limited number of experimental studies, with discrepancies often far beyond their claimed accuracy. It seems quite difficult to judge which data are reliable from the experimental results scattering by a factor of two to four. We even do not know the temperature dependence of the thermal conductivity of molten salts. This is mainly due to the fact that the thermal conductivity measurement of molten salts is very intricate, owing to their corrosiveness and high melting temperatures. Moreover, by using conventional methods such as the steady-state concentric-cylinder and the parallel plate, it is extremely difficult to avoid the effects of natural convection and radiation which considerably increase the apparent measured thermal conductivity under high temperature conditions.

In order to overcome above-mentioned problems on the measuring techniques for the thermal conductivity of molten salts, we recently have developed two new methods: the transient hot-wire method with ceramic-coated probes and the forced Rayleigh scattering method. Employing these methods, we have obtained the results for two molten nitrates (NaN03 and KNO3) and five molten alkali metal chlorides (LiCl, NaCl, KCl, RbCl and CsCl). All these thermal conductivity results do not exhibit a positive temperature dependence as previously believed but a weak negative dependence like other common liquids.
EXPERIMENTAL

Transient hot-wire method with ceramic-coated probe:
The most valuable feature of the transient hot-wire method when applied to fluids is its capability to experimentally eliminate the convective error; this is a great advantage, especially for high-temperature conditions. In order to apply this method to molten salts, however, a bare metallic wire has to be insulated. We have developed ceramic-coated probes which can be appropriate up to about 440 °C (1,2). It has to be noted that the most essential element of the present apparatus is an insulated probe which possesses enough electrical resistivity in corrosive atmosphere at high temperature. It is therefore very important what kind of insulation materials are used and also which insulation techniques are applied both on thin metallic wire and thick struts which are electrical leads at the same time.

Figure 1 illustrates the present ceramic-coated probe and the cross-sectional view of the insulated strut which has been developed through many trials and errors. The construction of the probe is as follows. Titanium rods (ϕ 3 mm) (6) coated with plasma sprayed Al₂O₃ of thickness 0.2 to 0.4 mm (7) and with protective layer (8) are fastened to the ceramic disc (3) by means of titanium screw (1). The reason for using titanium as a strut material is that the thermal expansion coefficient of titanium is very close to that of platinum (which is a material for wire) thus we can avoid slacking or tightening of the wire during the course of temperature cycles. The electrical resistivity of the insulated struts is high enough by employing high purity (99.9 %) small particles (16 μm) of Al₂O₃ for plasma spray. The thickness of the plasma-sprayed layer is chosen so as not to make any cracks at high temperatures. Furthermore, in order to fill small pores in the sprayed layer, Si-Ti-C-O ceramic paint (Ube : Tyranno coat) is used as extra protective layer (thickness is 0.2 to 0.3 mm). These insulating materials and insulating techniques were chosen by examining their heat-resisting properties and insulating resistance in molten salts at high temperatures. The thin platinum hot-wire (ϕ 30 μm) (5) is insulated also by Al₂O₃ produced with the aid of ion plating. The covering ability of ion plating is excellent with fine structure and the layer thus produced sticks tightly enough on the wire. After assembling the probe with insulated struts, a bare platinum wire is spot welded to the struts whose insulation layer at the ends are removed with diamond-cutter. Then the entire probe is brought into the ion plating chamber. It took six hours to produce ion plating coating layer of about 4 μm thickness.

The experimental apparatus is shown in Fig. 2. The main part of this apparatus was previously developed (3). All data acquisition and instrument control can be performed using a computer (HP-9000 model 310) communicating via the IEEE-488 interface. In order to apply this apparatus to molten salts, the sampling period of a digital voltmeter (Advantest : TR-6861) was improved to be much shorter (25 ms). The temperature of the electric furnace is controlled by three separate heaters. Upper and lower heaters are used to keep a temperature gradient preventing initial natural convection in the sample. Also a sheathed heater (1) is attached above
the probe to reduce the heat loss through the leads. A sample container (4) is made of high purity alumina (SSA-S) in order to avoid unexpected electrical combinations with the molten salts. The temperature of the sample is measured with the aid of a sheathed thermocouple (3) (Φ 1.6 Type K) inserted into a alumina tube. The thermocouple was calibrated with a standard resistance thermometer on IPTS-68 from about 100 °C - 200 °C and with three fixed points, namely, tin (231.968°C), zinc (419.58°C) and aluminum (660.40°C).

**Forced Rayleigh scattering method:**
The forced Rayleigh scattering method is a contact-free optical technique for the thermal diffusivity measurement. The distinguishing features of this method are summarized as follows. (1) The method has an advantage in the case when it is difficult to insert sensors in a sample such as high-temperature corrosive melts because of its basic feature of contact-free measurement. (2) The influence of natural convection is negligible, since the measuring time is very short (typically within 1 ms). (3) The temperature rise during measurement is very small (less than 0.1 K), thus the error due to radiation may not be significant even at high temperatures. (4) A sample volume of only a few cubic millimeters is required, which is also advantageous at high temperatures. The detailed theory and apparatus have been described elsewhere (4-8).

Figure 3 displays the present experimental apparatus. The heating laser is a single-mode argon-ion laser (wavelength: 514.5 nm, 1.8 W) and its continuous light is chopped by a rotating mechanical chopper into a short pulse. The heating pulse duration can be changed from 40 to 1200 μs. The heating lasers, divided into two beams of equal intensity by means of a beam splitter, intersect in the sample to produce interference pattern. A He-Ne laser (wavelength: 632.8 nm, 5 mW) is employed for probing the relaxation of the temperature distribution. The first order diffracted beam is detected by a photomultiplier through a pinhole of 500 μm diameter and an interference filter. The output from photomultiplier is recorded by a digital memory (12 bits, sampling time: 5 μs) and is transferred to a computer.

A sample cell is made of two quartz glasses (15 mm x 18 mm thickness 1 mm) with spacers. The thickness of the sample layer is fixed about 1 mm by employing quartz glass spacers which are welded onto cell walls with the aid of a micro-torch. The amount of sample needed for this cell is only 0.2 - 0.3 grams. An infrared furnace is utilized for the measurement at high temperatures because it readily heats up small amount sample and also ensures the optical path of the laser beams. It is to be noted that the surface of cell wall is painted by a high emissivity coating excluding the laser spot area in order to secure enough absorption of infrared light from the furnace. The temperature is measured by a thermo-couple (Type K) enclosed in a cell holder, since it is difficult to insert the thermo-couple directly into the sample. Thus the accuracy of the temperature is estimated to be ±15°C, which is not so inferior taking into account the weak temperature dependence of the thermal diffusivity of molten salts.
Finally, the grating period is determined by means of a CCD image sensor which has been written in Ref. 6.

RESULTS

Molten nitrates:
The results for molten NaN0₃ and KNO₃ are compared with earlier works in Figs. 4 and 5, respectively. The measurements have been performed with the aid of the transient hot-wire method with ceramic-coated probes (1,2). The results have an estimated accuracy of ±3%. In these figures, the references of earlier works are omitted for the sake of space. In the case of NaN0₃, the present results agree with the data of Omotani et al. obtained by the liquid-metal-probe transient hot-wire method near melting point. The results of Bloom et al., White and Davis, and McDonald and Davis, measured by the steady-state concentric cylinder method, are about 5% to 10% higher at the melting point and show a positive temperature dependence of the thermal conductivity. However, the results of Tufeu et al., obtained by the same method with a thin fluid layer (0.2 mm) to minimize the error due to the heat transfer by convection and radiation, have a weak negative temperature dependence, and their results agree well with the present results within the estimated accuracy. From a comparison of the present results with other data, it may be concluded that the past experimental data for molten NaN0₃ and KNO₃, mainly measured by steady-state methods, contain systematic errors owing to radiation and convection.

Molten alkali metal chlorides:
Figure 6 shows the present thermal conductivity for molten NaCl derived from the measured thermal diffusivity by the forced Rayleigh scattering method and the density with the heat capacity (8). The accuracy of the thermal conductivity is estimated to be ±8%. It should be particularly noted that the previous thermal conductivity values of molten NaCl scatter from about 0.4 to 1.5 W/(m·K) and their temperature coefficients are considerably large positive values. In contrast, the present results are the one of the smallest of all and agree with the data of Golyshev et al. obtained by the concentric-cylinder method with careful radiation correction. Moreover, the temperature dependence of the thermal conductivity exhibits a weak negative. We may conclude these significant differences attribute to the systematic error caused by radiation and convection which become more serious as the temperature goes higher.

Figure 7 displays the thermal conductivity of molten alkali metal chlorides measured by the forced Rayleigh scattering method. Again, all of them exhibit weak negative temperature dependence and their absolute values are smaller than the ones obtained by the steady-state method.
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REFERENCES

1. S. Kitade, Y. Kobayashi, Y. Nagasaka and A. Nagashima, *High Temperatures-High Pressures*, 21, 219 (1989).

2. S. Kitade, Y. Kobayashi, Y. Nagasaka and A. Nagashima, *Trans. JSME*, 55, 2411, (1989) (in Japanese).

3. N. Kawaguchi, Y. Nagasaka and A. Nagashima, *Rev. Sci. Instrum.*, 56, 1788 (1985).

4. T. Hatakeyama, Y. Nagasaka and A. Nagashima, *Proc. ASME/JSME Thermal Engineering Joint Conf.*, Vol.2, 311 (1987).

5. T. Hatakeyama, Y. Miyahashi, M. Okuda, Y. Nagasaka and A. Nagashima, *Trans. JSME*, 54, 1131 (1988) (in Japanese).

6. Y. Nagasaka, T. Hatakeyama, M. Okuda and A. Nagashima, *Rev. Sci. Instrum.*, 59, 1156 (1988).

7. Y. Nagasaka and A. Nagashima, *Int. J. Thermophys.*, 9, 923 (1988).

8. N. Nakazawa, M. Akabori, Y. Nagasaka and A. Nagashima, *Trans. JSME*, (1990) (in press).
Figure 1. Ceramic-coated probe for the transient hot-wire method: 1, titanium screw; 2, drilled hole for thermocouple; 3, ceramic disc; 4, insulated strut; 5, insulated platinum wire ($\phi$ 30 $\mu$m); 6, titanium rod ($\phi$ 3); 7, plasma-sprayed Al$_2$O$_3$; 8, protective layer of painted Si-Ti-C-O ceramic.

Figure 2. Experimental apparatus for the transient hot-wire method: 1, sheathed heater; 2, probe; 3, thermocouple; 4, alumina sample container; 5, thermocouple for temperature control; 6, radiation shields.
Figure 4. Thermal conductivity of molten NaNO₃: — White and Davis (1967), —— McDonald and Davis (1970), — Santini et al. (1984), ○ McLaughlin (1964), ◦ Bloom et al. (1965), △ Gustafsson et al. (1967), □ Omotani et al. (1982), ▽ Tufeu et al. (1985), Present work; • probe 1, △ probe 2, ■ probe 3.

Figure 3. Experimental apparatus for the forced Rayleigh scattering method.
Figure 5. Thermal conductivity of molten KNO₃; White and Davis (1967), McDonald and Davis (1970), Santini et al. (1984), Bloom et al. (1965), Gustafsson et al. (1967), Tufeu et al. (1985), Karasawa et al. (1986), Present work; probe 4, ▲ probe 5.

Figure 6. Thermal conductivity of molten NaCl; Bystrai et al. (1976), Smirnov et al. (1987), Fedorov et al. (1970), Golyshov et al. (1983), Present work.
Figure 7. Temperature dependence of the thermal conductivity of five molten alkali metal chlorides.