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Hot Filament Technique for Measuring the Thermal Conductivity of Molten Lithium Fluoride

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HOT FILAMENT TECHNIQUE FOR MEASURING THE THERMAL CONDUCTIVITY OF MOLTEN LITHIUM FLUORIDE

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ABSTRACT

Molten salts, such as lithium fluoride, are attractive candidates for thermal energy storage in solar dynamic space power systems because of their high latent heat of fusion. However, these same salts have poor thermal conductivities which inhibit the transfer of heat into the solid phase and out of the liquid phase. One concept for improving the thermal conductivity of the thermal energy storage system is to add a conductive filler material to the molten salt. High thermal conductivity pitch-based graphite fibers are being considered for this application.

Although there is some information available on the thermal conductivity of lithium fluoride solid, there is very little information on lithium fluoride liquid, and no information on molten salt graphite fiber composites. This paper describes a hot filament technique for determining the thermal conductivity of molten salts. The hot filament technique was used to find the thermal conductivity of molten lithium fluoride at 930°C, and the thermal conductivity values ranged from 1.2 to 1.6 W/mK. These values are comparable to the slightly larger value of 5.0 W/mK for lithium fluoride solid. In addition, two molten salt graphite fiber composites have been characterized with the hot filament technique and these results will also be presented.

INTRODUCTION

Molten salts are attractive candidates for thermal energy storage in solar dynamic space power systems owing to their high latent heat of fusion. Although salts such as lithium fluoride are being considered for such applications, there are several problems which must be addressed. Many of the salts exhibit a substantial change in volume during the phase change. Lithium fluoride, for example, shrinks nearly 30% on solidification. Such changes in volume inevitably lead to void formation. Alkali halide salts also possess relatively low thermal conductivity, particularly in the molten phase. One concept for enhancing the thermal conductivity of the molten phase is to prepare a salt-fiber composite utilizing high thermal conductivity pitch-based graphite fibers.

This paper describes a hot filament immersion heater added to a Perkin-Elmer differential thermal analyzer in order to first quantify the thermal conductivity of molten lithium fluoride, and second to verify the salt-fiber composite concept of thermal conductivity enhancement. A model first proposed by Van der Held et al. (ref. 1) was modified to interpret the hot filament data.

MATERIALS AND METHODS

Previous experience with measuring the thermal conductivity of molten lithium fluoride using a Dynatech Corporation thermal conductivity instrument has indicated the importance of separating the contribution of the liquid from the contribution of its container. The principle of operation for the Dynatech instrument is to establish a steady state heat flow down the length of a thermally insulated cylinder. This technique is very effective for solid samples, however, problems were encountered when trying to modify the technique for use with molten liquids. Specifically, it was difficult to isolate the heat flow in the liquid from the heat flow in the surrounding container. An alternate approach for determining the thermal conductivity of the liquid was sought. A non-steady state technique was chosen in which a submerged hot filament supplied a pulse of heat to the liquid, and the lag in filament temperature was used to measure the thermal conductivity of the liquid.

A Perkin-Elmer DTA 1700 was modified to accomplish this task. A miniature platinum immersion heater was fabricated and positioned inside the sample crucible. The filament of the immersion heater was made from a solid strand of 0.508 mm diameter pure platinum wire. The platinum wire was sufficiently long to extend each lead to the base of the furnace assembly in the DTA 1700, so there would be no junctions in the hot zone of the furnace. Hence, only a small fraction (about 1 cm) of the platinum wire was actually in contact with the molten lithium fluoride, while the balance of the platinum wire (about 49 cm) was routed through the furnace. This geometry will play an important role in the thermal conductivity calculations.

The platinum sample crucible of the DTA 1700 also had to be modified. Lithium fluoride has a low contact angle with platinum (ref. 2), causing the boule of molten material inside the crucible to be concave. To make the boule convex, assuring good contact between the platinum immersion heater and the lithium fluoride, the crucible was dipped several times in carbon paint. Lithium fluoride has a high contact angle with carbon (ref. 3), so the carbon coating on the crucible made the surface of the lithium fluoride boule convex. Using a purge gas of argon prevented the carbon paint (and carbon fibers) from oxidizing.

Highly ordered pitch-based P-75 graphite fibers having a diameter of 10 μm , were coated with 1000 \AA of tungsten using a

sputter deposition technique. Care was taken to spread the fibers in the tow and to coat individual fibers completely. Visual inspection after deposition revealed that the tungsten coverage was over 90%. The fibers were then chopped to a length of approximately 1.3 mm yielding an aspect ratio on the order of 100.

For ease of handling, the lithium fluoride powder (or a graphite-powder mixture) was pressed into pellets. Shards of the pellet were weighed and placed in the sample crucible. The furnace of the DTA 1700 was elevated to a temperature of 930°C, well above the melting point of the lithium fluoride. After equilibration, power was applied to the immersion heater for approximately 5 minutes.

In most cases, the current through the immersion heater was held constant at 1.75 amperes with a Keithley Model 228A constant current source, and the voltage across the current leads was monitored with a Keithley Model 181 nanovoltmeter. A second nanovoltmeter was used to monitor the temperature of the sample via a thermocouple situated at the base of the sample crucible, and a third nanovoltmeter was used to monitor the change in temperature of the sample. All Keithley equipment was interfaced with an IBM PC through a IEEE-488 bus to control experimental parameters and collect data. Current, voltage, and temperature data were collected at one second intervals.

The method chosen to analyze the data was developed by Van der Held (ref. 1). The Van der Held model uses both the change in temperature of the immersion heater as a function of time and the wattage dissipated by the immersion heater to calculate the thermal conductivity of the liquid, according to equation 1 where O_1 and O_2 are filament temperatures (in °C or K), t_1 and t_2 are time values (in sec.), q is the power dissipated by the immersion heater (in watts), and k is the thermal conductivity of the liquid (in W/cmK). Heat transfer from the liquid to the

$$O_2 - O_1 = [q/(4 \pi k)] \ln(t_2/t_1) \quad (1)$$

container does not interfere with heat transfer from the hot filament to the liquid. Hence, the geometry of the container plays no role in the calculation. A plot of $\ln(\text{time})$ versus filament temperature yields a straight line with a slope proportional to the thermal conductivity of the liquid. According to Van der Held, any deviation in the straight line indicates the influence of convection. The resistance of the immersion heater offers an accurate measure of the temperature of the filament, and the wattage dissipated into the liquid can be quantified easily.

Figure 1 illustrates the influence of the surrounding fluid on the response time of the filament after a constant current is established in the heater circuit. In one case, current was supplied to a filament surrounded by molten lithium fluoride and

in the other case current was supplied to a filament surrounded by argon gas. The response of the filament, as measured by the voltage across the circuit, is very fast in the case of argon but noticeably slower when the filament is in contact with the liquid. The lag in filament temperature can be attributed to the influence of the liquid. A liquid with a higher thermal conductivity would offer a sharper response curve.

To better define the relationship between filament voltage and filament temperature, the immersion heater was made part of a four-point probe. In this way, the temperature dependence of the platinum resistance and the portion of the voltage drop attributed to only the tip of the platinum heater could be found. Both of these factors play an important role in the thermal conductivity calculations. Again, platinum was chosen as the material for the voltage leads in the four point probe.

RESULTS AND DISCUSSION

Background

The concept of using graphite fibers as a filler material for enhancing the thermal conductivity of a molten lithium fluoride matrix is based on the thermophysical properties of the two materials. Specific data for pitch-based P-75 fibers and lithium fluoride liquid are scant, to say the least. However, some data are available for the thermal conductivity of pyrolytic graphite and lithium fluoride solid near the melting point of 848°C (ref. 4). As shown in figure 2, the thermal conductivity of pyrolytic graphite parallel to the graphene planes is nearly two orders of magnitude greater than the thermal conductivity of crystalline lithium fluoride at 827°C (480 W/mK and 5 W/mK, respectively). Also shown in figure 2 is the thermal conductivity of graphite perpendicular to the graphene planes, which happens to be on the same order of magnitude as the lithium fluoride (3 W/mK).

It has been shown in previous work that molten lithium fluoride is non-wetting against graphite, as indicated by a contact angle of about 93° (ref. 3). Hence, mixing pristine graphite fibers with lithium fluoride would prove fruitless for upon melting the fibers would separate from the matrix and reside on the surface. Subsequent research has identified several potential metal coatings which are both compatible with the molten lithium fluoride environment and offer a near-zero contact angle (ref. 2 and ref. 5). Tungsten was selected as the fiber coating of choice because it offers a contact angle of about 20° and exhibits long term stability in the molten lithium fluoride matrix.

Immersion Heater Calibration

In the Van der Held method of calculating the thermal

conductivity of a liquid, three parameters must be well documented; the amount of heat entering the liquid through Joule heating, the temperature of the filament as a function of time, and the length of the filament submerged in the liquid. To glean information on the former two parameters, the tip of the immersion heater was temporarily made into a four-point probe. With a constant current of 1.75 amperes applied to the circuit, the voltage across the four-point probe and the voltage across the current leads were monitored while heating the four-point probe in argon to 1000°C at a constant rate of 5°C/min. To glean information on the latter parameter, the tip of the immersion heater was restored to normal, and the heater was tested with a liquid of known thermal conductivity.

The wattage being dissipated into the liquid would be clearly overestimated in the Van der Held calculation by using the voltage across the current leads because only a fraction of the platinum wire is actually submerged. Correcting this voltage by a geometric factor (i.e., length of platinum in the liquid divided by total length of platinum) would be appropriate only at room temperature where the entire length of wire is isothermal. At elevated temperatures, the voltage across the four-point probe offers a much better estimate of the wattage dissipated by the submerged portion of platinum wire. Figure 3 presents the ratio between the voltage across the four-point probe and the voltage across the current leads as a function of temperature. This ratio is 1.48% at room temperature, and 3.10% at 930°C.

The Van der Held calculation also requires knowledge of the filament temperature as a function of time, just after activating the heating circuit. The subtle variation in filament voltage at constant current can supply this information, providing that the temperature dependence of the resistivity is known. Temperature dependence can be established from the four-point probe data because they were collected at a constant rate of 5°C/min. Dividing the rate of voltage change across the four-point probe by the rate of temperature change yields the ratio between voltage and temperature. At a constant current of 1.75 amperes, this ratio is 54.1 millivolts per degree at room temperature, and 18.7 millivolts per degree in the vicinity of 930°C.

The third parameter, length of the filament submerged in the liquid, was determined by testing the heater in a liquid of known thermal conductivity. The voltage leads from the four-point probe were removed, restoring the immersion heater to its original design. The length parameter in Van der Held calculation was obtained by testing the heater with distilled water at room temperature. Time versus filament voltage data for this liquid are summarized in figure 4. The slope of this line (multiplied by 54.1 millivolts per degree), the constant current value of 1.75 amperes, the average voltage value of 0.63 volts (multiplied by a factor of 1.48%), and a known thermal conductivity value of 0.59 W/mK were used to calculate the length of wire submerged in the liquid. Solving for the length gave a

value of 1.5 cm. This length was used in all subsequent calculations.

Pure Lithium Fluoride

Six different lithium fluoride specimens were tested with the Van der Held model, as shown in figure 5. The calculated thermal conductivity values are summarized in table 1, along with values for slope, correlation coefficient, wattage, specimen mass, and initial temperature. Note that all of the correlation coefficients are above 0.99, indicating a strong linear relationship between $\ln(\text{time})$ and filament temperature, and suggesting no convection. The average thermal conductivity value of 1.3 W/mK is slightly less than the value cited in the literature for the solid (5 W/mK). This trend should have been expected, for many elements have thermal conductivities in the liquid phase that are slightly less than in the solid phase (e.g. mercury, phosphorus, sodium, sulfur, and zinc).

Lithium Fluoride with Tungsten-coated Graphite Fibers

Only two graphite fiber molten lithium fluoride composites have been tested to-date using the Van der Held model. The results from these composites, having 1.5% and 5.0% fiber by weight, respectively, are also presented in table 1. Both composites had a thermal conductivity value of 1.3 W/mK. This value clearly indicates that there is little to no thermal conductivity enhancement imparted to the molten liquid at fiber concentrations up to 5%. The small size of the fibers combined with the low percentage of fiber may be responsible for the lack of thermal conductivity enhancement. The orientation of the fibers in the molten boule may also play an important role due to the anisotropy in their thermal conductivity. Unfortunately, the salt-fiber composite could not be viewed in the molten state due to the closed construction of the DTA 1700 furnace assembly.

For comparison, one can make a first approximation of the range of thermal conductivity values that might be expected in the lithium fluoride P-75 graphite fiber system currently under study. The thermal conductivity of P-75 graphite fibers at room temperature is actually about 1/8 the value of pyrolytic graphite. (Newer, more expensive fibers better approximate pyrolytic graphite.) Using this conversion factor, the thermal conductivity of the P-75 fibers near the melting point of lithium fluoride can be estimated to be about 60 W/mK. In the best case scenario for a composite with 5% fiber, the rule of mixtures would suggest that one part in twenty would be contributing 60 W/mK, and nineteen parts in twenty would be contributing 1.3 W/mK. Such a model would yield a thermal conductivity value of 4.2 W/mK for the salt-fiber composite. In the worst case scenario, the fibers could be aligned orthogonal to the direction of heat flow such that the fibers only serve as a diluent. In this case, the rule of mixtures would yield a thermal conductivity value of 1.2 W/mK for the composite. Given the

resolution of the hot filament technique, as demonstrated by the narrow range of values for pure lithium fluoride, one can conclude that the actual configuration of the salt-fiber composite is not represented by the best case scenario.

Another graphite fiber lithium fluoride composite was prepared, having 4.5% fiber by weight, and placed in the furnace of a Perkin-Elmer TGS-2 such that the top of the graphite crucible was visible. Upon heating through the melting point, the tungsten-coated graphite fibers could be seen residing inside the molten boule. The randomly dispersed fibers were surprising immobile, again suggesting little convection. After cooling, the crystalline sphere was cut in half to expose the void. The void was clearly located in the center of the sphere. The void in a pure lithium fluoride boule cooled in a similar fashion was located on the surface. One mechanism to account for this mode of void formation may be that the tungsten-coated graphite fibers serve to initiate crystallization on the perimeter of the sphere, forcing the void to the center upon cooling.

CONCLUSIONS

The hot filament technique has been used successfully to determine the thermal conductivity of molten lithium fluoride at 930°C. The value of 1.3 W/mK was slightly less than the thermal conductivity of the solid at 825°C, as reported in the literature (5 W/mK). Chopped tungsten-coated graphite fibers have been used to make several salt-fiber composites with fiber concentrations up to 5%. Visual inspection of one of the salt-fiber composites in the molten state indicated that the fibers were dispersed randomly inside the boule, and upon cooling, the fibers forced the void to the center of the boule. Measurements of thermal conductivity in the salt-fiber composites showed no thermal conductivity enhancement at fiber concentrations up to 5%.

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Table 1. Summary of the thermal conductivity values obtained from the Van der Held model.

	slope	corr. coef.	wattage (watts)	mass (g)	temp. (°C)	therm. cond. (W/mK)
Water						
1	127.7	0.996	0.0163	-	25	0.6
LiF*						
1	223.5	0.997	0.0608	0.0915	937	1.3
2	211.5	0.998	0.0635	0.0993	931	1.3
3**	252.0	0.997	0.0635	0.0971	932	1.6
4	208.6	0.998	0.0640	0.0979	939	1.3
5	190.8	0.999	0.0640	0.0975	931	1.2
6	210.5	0.998	0.0656	0.0946	931	1.3
LiF + P-75						
1.48%	204.8	0.996	0.0608	0.0917	938	1.2
1.48%***	75.5	0.996	0.1256	0.0932	936	1.3
4.96%	202.6	0.997	0.0656	0.0939	931	1.3

* From left to right on figure 5.

** Ar purge off

*** 2.50 amperes

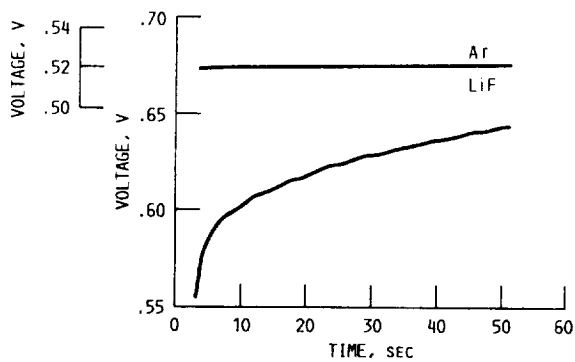


FIGURE 1. - FILAMENT VOLTAGE VERSUS TIME IN BOTH LiF AND Ar AT A CONSTANT CURRENT OF 1.75 AMP.

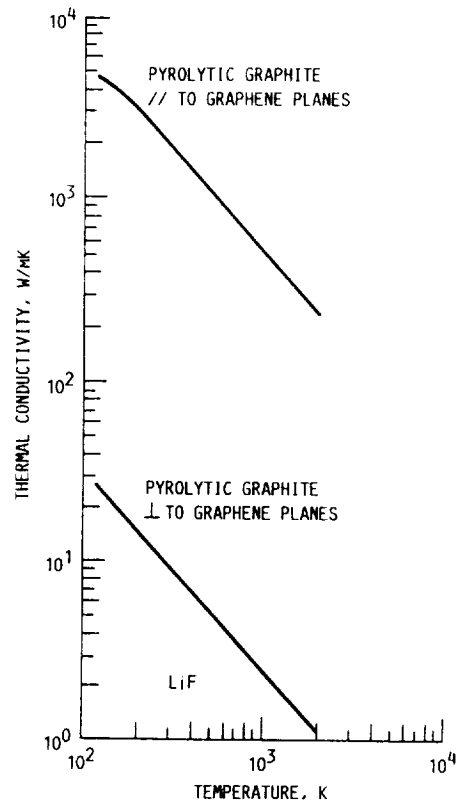


FIGURE 2. - THERMAL CONDUCTIVITY OF GRAPHITE (PERPENDICULAR AND PARALLEL TO THE GRAPHENE PLANES) AND LiF AS A FUNCTION OF TEMPERATURE.

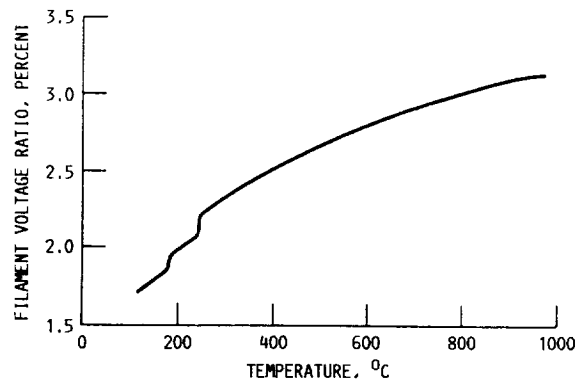


FIGURE 3. - RATIO OF FOUR-POINT PROBE VOLTAGE TO TOTAL VOLTAGE AS A FUNCTION OF TEMPERATURE.

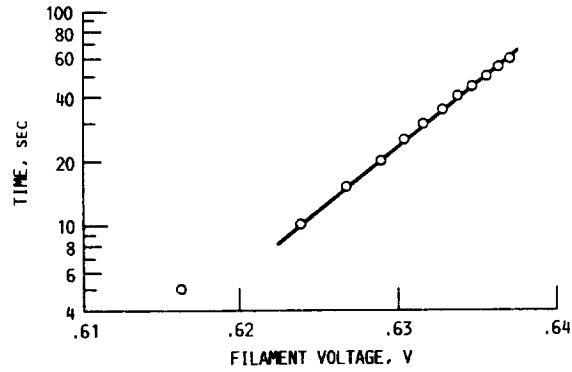


FIGURE 4. - $\ln(t)$ VERSUS FILAMENT VOLTAGE FOR DISTILLED WATER AT ROOM TEMPERATURE.

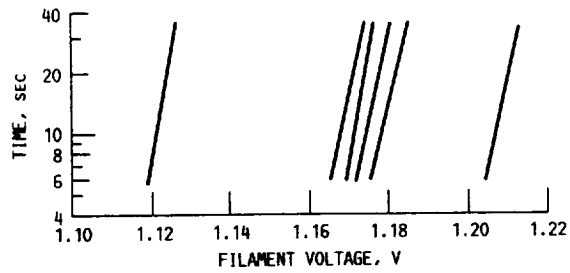


FIGURE 5. - $\ln(t)$ VERSUS FILAMENT VOLTAGE FOR SIX LiF SPECIMENS, IN THE VICINITY OF 930 °C.



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