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An Experimental Technique for Liquid/Solid Thermal Conductivity Measurements at the Melting Point[1]

Y. Yang[2,3] and J. Zhou[2]

Based upon the theory that the thermal conductivity can be determined by measuring the speed of the propagation of the solid/liquid phase interface during a phase transition, a system was developed to investigate the thermal conductivity of metals and alloys at the liquid/solid phase transformation point. Furthermore, a mathematical method was applied to represent the melting and solidifying process in the phase transformation chamber, by which the error could be analyzed. In order to test the feasibility of the method and the measuring system, a series of verification experiments on lead have been performed to estimate the precision and the applicability of the measuring system. From comparisons with recommended data from the literature, the uncertainty of the experimental results is estimated to be about 5% which means the measuring method is suitable to determine the thermal conductivity of eutectic alloys and metals at the liquid/solid phase transformation point. This work provides a relatively precise method for thermal conductivity measurements on new materials such as lead-free solders.

KEY WORDS: liquid/solid phase transformation; thermal conductivity; transient method.

1. INTRODUCTION

As the predominant joining materials of electronics packaging, lead solders have been widely used in joining chips, assembling substrates, mounting components, *etc.* over the past several decades. Nevertheless, with

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[2] School of Energy Science and Engineering, Central South University, Changsha, Hunan, P. R. China.

[3] To whom correspondence should be addressed. E-mail: yangying_csu@126.com

the increasing focus on environmental protection, proposals to restrict or forbid the use of lead solders have been enacted, and it is an international trend to develop, investigate, and use lead-free solders as conductive adhesives to replace lead solders [1, 2]. In order to better develop and use lead-free solders, much fundamental work must be done such as the determination of the thermal properties, mechanical properties, *etc.*, especially in special states such as a melt, solidification, *etc.*

Since latent heat is released or absorbed during the solidification/melt process, the phase-interface position and the inner temperature of materials vary dynamically. So most traditional methods of thermal conductivity determination are inapplicable. Neumann initially put forward the transformation interface propagation theory. Based on Neumann's theory, Lamvik [3] proposed that the thermophysical parameters at the solid/liquid transformation point could be determined by measuring the velocity of the phase interface propagation and successfully measured some low melting-point materials such as benzene and gallium with Zhou [4, 5]. Also, according to the Wiedemann–Franz law, Monaghan [6] determined the thermal conductivity of metals and alloys by measuring their resistivity. Nevertheless, a barrier to the use of the methods above is that the boundary condition of temperature saltation is difficult to be realized at relatively high temperatures. Li and Zhou [7] broke through the technical problems, effectively expanded the material range, and carried out thermophysical property measurements on materials at relatively high temperatures.

In this research, based on the work of Li and Zhou [7], a system, including a transient experimental method, numerical approximant fitting, numerical simulations, bias error estimation, and resulting experimental modifications, was developed to determine the thermal conductivity of medium/low melting-point metals and alloys such as lead/tin eutectic alloys, *etc.*

2. METHOD

2.1. Experimental Principle

The method is based upon the result [3–5] that the thermal conductivity can be determined by measuring the speed of propagation of the solid/liquid phase interface during a phase transition. For a cylindrical specimen, when the radial heat flux can be ignored relative to the axial heat flux, the phase transition process can be considered as a one-dimensional heat conduction process.

In order to describe the freezing process, several assumptions are made:

(a) the point of origin is set at the center of the bottom surface;

(b) the x axis is the symmetric axis of the specimen with orientation from bottom to top;

(c) the specimen of a homogenous liquid is at the melting point initially.

At a certain time, the bottom surface temperature was assumed to drop to a steady value T_0 below the freezing point T_m. The melt starts to solidify at the bottom surface and then a solidification front propagates unidirectionally into the melt along the x axis. Then, the heat transfer process could be formulated mathematically as

$$\frac{\partial^2 T_s(x,t)}{\partial x^2} = \frac{1}{a_\mathrm{s}} \frac{\partial T_s(x,t)}{\partial t}, \quad 0 < x < s(t), \quad t > 0 \tag{1}$$

With the following initial and boundary conditions:

$$\begin{aligned} t<0,\ 0<x<L:&\quad T_s(x,t)=T_m \\ t\geqslant 0, x=0:&\quad T_s(x,t)=T_0<T_m \\ x=s(t),\ t\geqslant 0:&\quad T_s(x,t)=T_m \\ x=s(t),\ t\geqslant 0:&\quad -k_s\tfrac{\partial T_s(x,t)}{\partial x}=\rho_s h\tfrac{d(s(t))}{dt} \end{aligned}$$

where a is the thermal diffusivity, k is the thermal conductivity, L is the length of the specimen, T is the instantaneous temperature, T_0 is the desired value, T_m is the freezing point temperature, $s(t)$ is the location of the interface relative to the original point, ρ is the density of the phase undergoing a transition, h is the latent heat of solidification per unit mass, t is the time, and the subscript s denotes the solid state.

The analytical solution [8] of Eq. (1) is

$$\lambda \exp(\lambda^2)\mathrm{erf}(\lambda) = C_p(T_m - T_0)/\left(h\sqrt{\pi}\right) \tag{2}$$

where λ is the specific solution satisfying the equations above and C_p is the specific heat.

A two-stage approximation of the transcendental Eq. (2) by expanding the left term is

$$\lambda^2\left(1+2\lambda^2/3\right) = C_p(T_\mathrm{m} - T_0)/2h \tag{3}$$

and

$$a_\mathrm{s} = s(t)^2/\left(4\lambda^2 t\right) \tag{4}$$

$$a_{\mathrm{S}} = k_s/\rho_{\mathrm{S}} C_p \tag{5}$$

When the relationship between $s\,(t)$ and t could be determined by measurements, according to Eqs. (3)–(5), λ and a_s could be evaluated, and then k_s could be determined. The parameter of $s\,(t)$ could also be determined by a probe, which also could be determined from the temperature curves.

In addition, the melting process can be mathematically described analogously. The controlling equation, initial and boundary conditions, and two-stage approximate solutions are as follows:

$$\frac{\partial^2 T_l(x,t)}{\partial x^2} = \frac{1}{a_l}\frac{\partial T_l(x,t)}{\partial t}, \quad s(t) < x < L, \ \ t > 0$$

$$\begin{aligned} t<0, \ \ 0<x<L: &\quad T_l(x,t) = T_{\mathrm{m}} \\ t \geqslant 0, \ \ x = L: &\quad T_l(x,t) = T_0 > T_{\mathrm{m}} \\ x = s(t), \ \ t \geqslant 0: &\quad T_l(x,t) = T_{\mathrm{m}}, \ -k_l \tfrac{\partial T_l(x,t)}{\partial x} = \rho_l h \tfrac{d(s(t))}{dt} \end{aligned}$$

$$\lambda^2\left(1 + 2\lambda^2/3\right) = C_p(T_0 - T_{\mathrm{m}})/2h$$

and

$$\begin{aligned} a_l &= s(t)^2/(4\lambda^2 t) \\ a_l &= k_l/\rho_l C_p \end{aligned}$$

where the subscript l indicates the liquid state.

2.2. Instrument

The equipment used in this investigation is illustrated in Fig. 1. Its main component is the phase transition chamber made of corundum with an internal diameter of 21 mm and a height of 180 mm surrounded with refractory and insulation materials. The top and bottom temperatures are controlled by independent temperature control systems. Meanwhile, an additional temperature control system is provided to reduce the radial heat dissipation from the side wall.

2.3. Measuring Process

For the melting process, the chamber and the specimen in the solid state was initially kept at a temperature, typically 0.1 K below the melting point, T_m; then, the top surface was quickly exposed to a copper plate

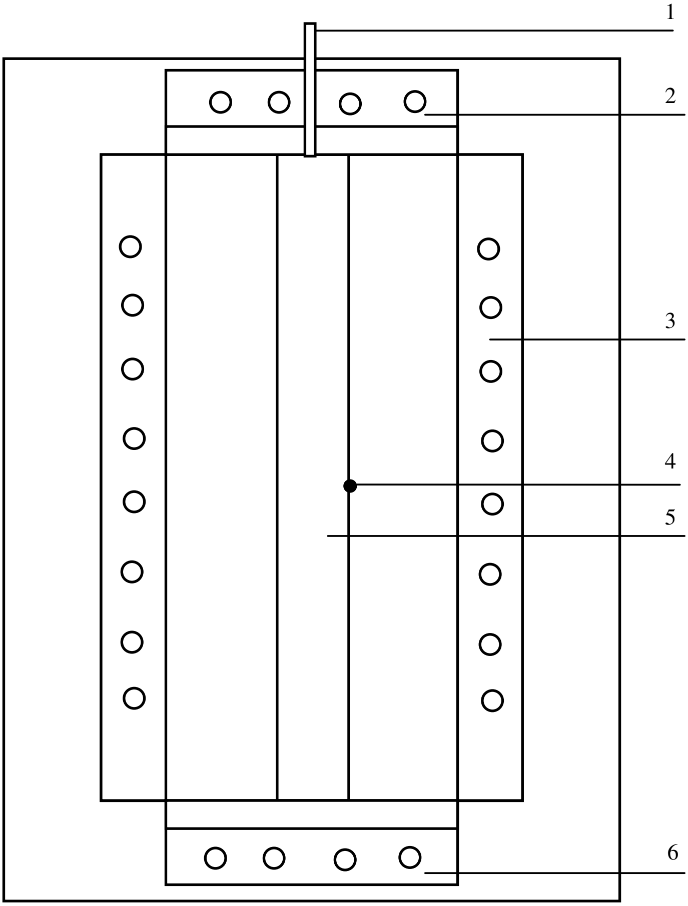

Fig. 1. Schematic diagram of measuring system: 1—probe; 2—top temperature control system; 3—tubular furnace; 4—thermocouple; 5—phase transition chamber; 6—bottom temperature control system.

with a temperature of T_0, which is typically about 15 K above the melting point, while the bottom surface remains at T_m. The transient temperature was recorded automatically by a multi-channel data data collection system that could output the time-temperature curves or lists of various measurement points, and the location of the phase transition interface was read directly from the scale.

Similar measurements were made for the freezing process. First, the melted specimen was kept at a temperature no more than 0.1 K above

Table I. Thermophysical Properties of Lead

T_m(K)	H (J·kg^{-1})	T(K)	K(W·m^{-1}·x K^{-1})	C_p(J·kg^{-1}·K^{-1})	ρ(kg·m^{-3})
600.65	26442	293	34	127	11340
		573	31.5	139	10680
		600	–	148	
		623	15.9	147	10658

the melting point until the temperature was uniform and the specimen is homogenous; then the freezing process was started by quickly reducing the temperature of the bottom surface to a temperature of T_0, typically about 15 K below the melting point. The transient temperature and $s(t)$ was recorded analogously.

3. RESULTS AND DISCUSSION

3.1. Temperature Curves at Different Positions

In this research, pure lead material was chosen as the test subject because lead is a typical solder component and its properties are well known; thus, it would be a suitable reference material to test the applicability of the method and the measuring system. In Table I the properties of the metal [9] are listed.

Figure 2 illustrates the freezing process of lead. The initial temperature of the system was 600.75 K (327.6°C), 0.1 K above the melting point. At $t = 0$ s, the temperature of the bottom surface was reduced to 580.65 K (307.5°C) and freezing started from the bottom surface. Assuming that the original point is the center of the bottom surface and the x-axis is the symmetrical axis, curves 1–12 represent the temperature change at times corresponding to 0.005, 0.01, 0.015, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.085, and 0.09 m along the x-coordinate. From the curves, the propagation of the phase transition interface was determined which is shown in Fig. 3. In addition, the displacement was directly detected by the probe method [7] in related research which is consistent with the indirect method; the indirect method provides multi-point measurements automatically and simultaneously using an advanced multi-channel data acquisition instrument.

3.2. Error Analysis

The average values of thermal conductivity are 14.7 W·m^{-1}·K^{-1} in the liquid state and 34.0 W ·m^{-1}·K^{-1} in the solid state, and the relative

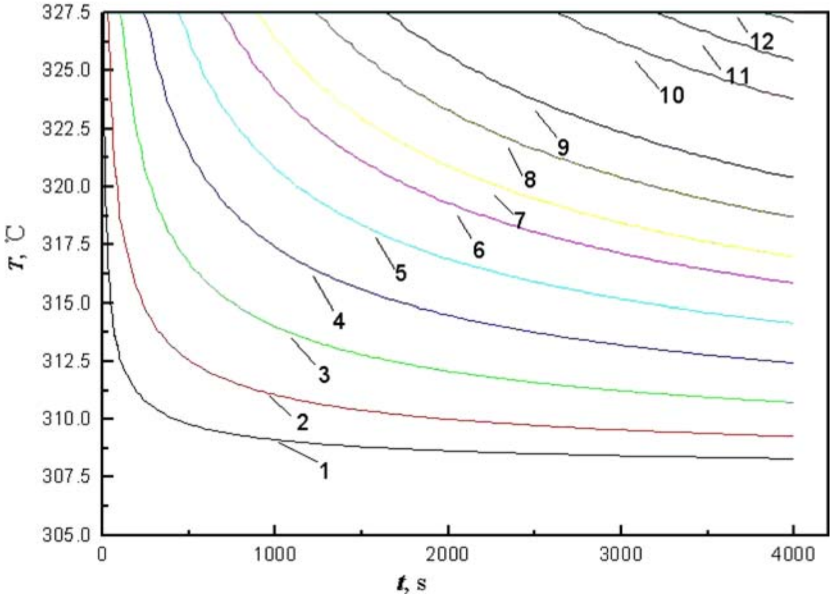

Fig. 2. Temperature curves at different positions along the symmetric axis.

errors are −7.6% and 7.9%, respectively, compared with the reference values [9].

The thermal conductivity is a derived parameter, and the factors that influence the experimental results are complicated. We will consider the main factors.

In the actual process, the phenomena of "excess solidification" and "deficient solidification" existed, which resulted from the fluctuations of the heat flux and fluctuations of the actual front edge. Sometimes, lattice defects formed during solidification and the heterogeneous phase existing in the initial state are the reasons for such phenomena. "Excess solidification" and "deficient solidification" would lead to deviations of the actual propagation of the phase transient interface from ideal conditions.

3.3. Analysis of the Experimental Results

In order to reduce the influence of the phenomena mentioned above, a method combining mathematical analysis and least-squares approximation was applied to best fit the experimental results [7]. First, the secondary fitted curves of Fig. 2 were acquired directly using software-MATLAB, and then approximate values of the thermal conductivity were determined, whose

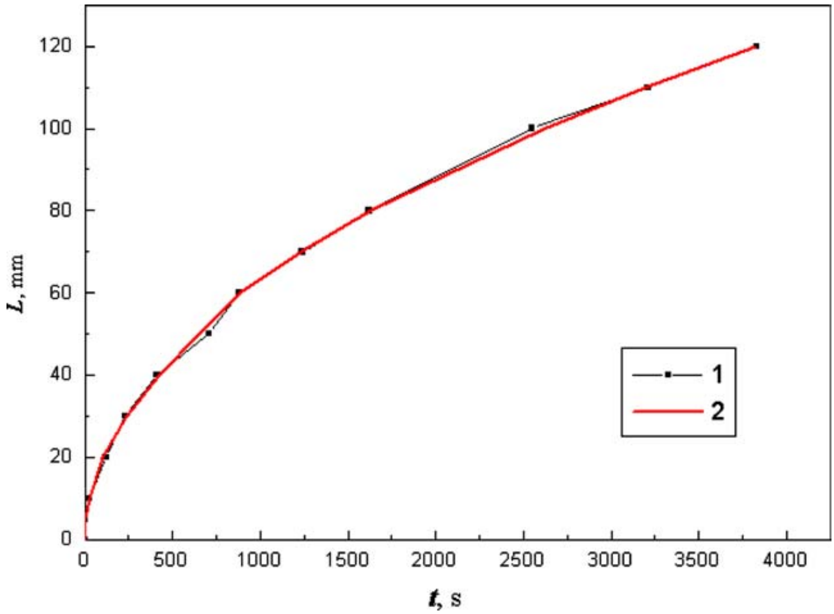

Fig. 3. Propagation of the phase transition interface: 1—experimental curve; 2—fitted curve.

mean value was designated k_0. k_0 was used as the tentative value near the melting point for the first step, from which the transient temperature distribution and the propagation of the interface were evaluated. According to the residual error between the simulation and the experimental curves, the variable increment Δk is determined and $k_{i+1} = k_i + \Delta k$ is applied to the next iteration. If the residual error is within the allowable range after the nth iteration, the calculation is terminated and the corresponding k is regarded as the correct value. In this process, the experimental data were corrected by this approximation method rather than by simple fitting such as polynomial and multiple fitting, and could more objectively describe the actual propagation of the phase boundary.

In order to determine the thermal conductivity near the melting point, the melting and freezing processes at different conditions were investigated and fitted results are shown in Fig. 4. curves 1 and 2 represent the melting process with the temperature of the top surface controlled at 10 and 20 K above the melting point, respectively, and curves 3 and 4 represent the freezing process with the temperature of the bottom surface controlled at 10 and 20 K below the melting point, respectively.

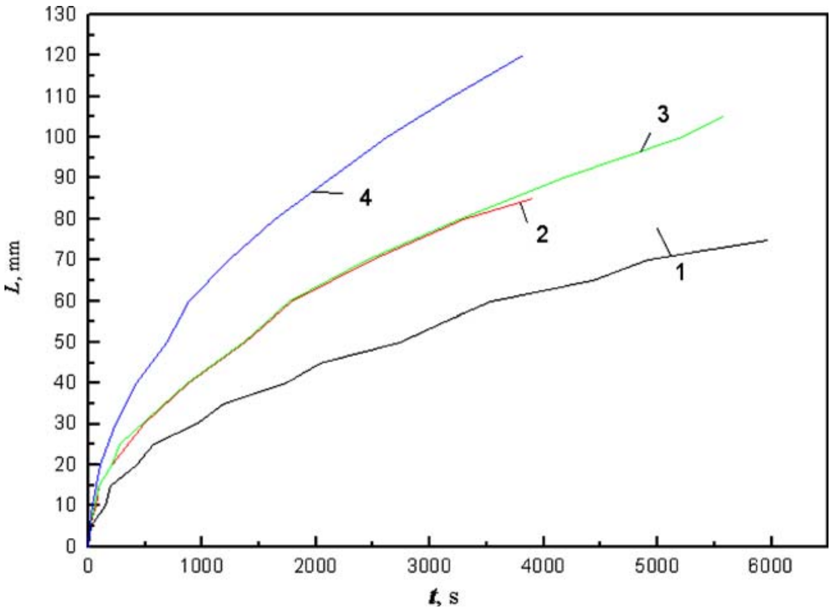

Fig. 4. Propagation curve of the transition phase interface: 1—melting process 1; 2— melting process 2; 3—freezing process 1; 4—freezing process 2.

It is obvious that the preset boundary temperature is a major factor that influences the speed of the processes, so a feasible approach is to speed up the processes by appropriately increasing the difference between the preset value and the melting point or even by applying a double-sided temperature control method. It should be noted that the temperature gradients in a double-sided experiment would produce natural convection during the transformation process and cause the crystal grain size to grow at the solidification boundary; the resultant errors would increase with the temperature difference (see Table II) and would be difficult to correct. The relationship between the experimental precision and rate should be considered carefully. Generally, the maximum temperature difference should be no more than 20 K and the top should be at a temperature greater than the bottom to minimize convection.

3.4. Thermal Conductivity

After data analysis, the values of the thermal conductivity of lead were calculated and are presented in Table II; the results without adjustments are

Table II. Calculated Results for the Thermal Conductivity ($W \cdot m^{-1} \cdot K^{-1}$) of Lead

Melting process			Freezing process		
+5[a]	+10	+20	−5[b]	−10	−20
15.2	15.1	14.8	33.4	33.9	34.8
Recommended data [9]	15.9		Recommended data [6]	31.5	
Adjusted results after analysis	Average value	15.0	Adjusted results after analysis	Average value	32.4
	Difference (%)	−5.1		Difference (%)	2.9
Without Adjustment	Average value	14.7	Without adjustment	Average value	34.0
	Difference (%)	−7.6		Difference (%)	7.9

[a] ‘+5’ represents the preset temperature in one side is 5 K above the melting point.
[b] ‘−5’ represents the preset temperature in one side is 5 K below the melting point.

also presented for comparison. It is found from Table II that the estimated uncertainty of the adjusted thermal conductivity value is about 5%.

4. CONCLUSIONS

The method presented in this paper is applicable to the determination of the thermal diffusivity and thermal conductivity of metals and alloys.

(a) The instability of temperature curves due to “excess melting” and “deficient melting” phenomena can be reduced by curve fits;

(b) Compared with recommended data [9], the overall uncertainty of the thermal conductivity value is about 5%;

(c) Mathematical analysis can demonstrate the temperature distribution, the propagation of the interface, and lead to optimum performance of the apparatus.

Thus, this method for determining the thermal conductivity of metals and eutectic alloys is suitable for research on lead-free solders.

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