International Journal of Thermophysics, Vol. 3, No. 1, 1982

Determination of Thermal Diffusivity of Solid Materials Near the Melting Point

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Received October 22, 1981

The paper deals with the determination of the thermal diffusivity of solid materials near the melting point by studying the unidirectional propagation of a solidification front through the melts. The method is based on Neumann's thermal analysis of the liquid/solid interface during a solidification process. Measurements are given and the thermal diffusivity is determined for ice, mercury, and aluminum. The results are in fair agreement with reference data. An attempt is also made with data from the literature to calculate thermal diffusivity in very rapidly quenched metals, namely, tin, lead, and zinc. The calculated values are substantially lower than for the solid metals under normal conditions, a result that may reflect the glassy structure of the materials attained by quenching.

KEY WORDS: Aluminum; melting point; mercury; thermal diffusivity; water (ice).

1. INTRODUCTION

Thermal diffusivity is a property of a material. Its unit is length squared divided by time, or the equivalence of a velocity times the length of a distance over which the velocity appears. This means physically that the thermal diffusivity is a measure of how fast a characteristic temperature will move by heat conduction under given conditions.

Thermal diffusivity of a solid material can be determined experimentally by several methods. The literature on the subject is comprehensive, a survey of which is given by Danielson and Sidles [1] and by Touloukian et al. [2].

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The methods fall mainly into two groups, according to the boundary conditions which they incorporate in experiment and the mathematical treatment. One group assumes a transient heat flow through the specimen and the determination of temperature response a certain distance downstream. Methods in the other group make use of a periodic heat flow superposed upon a stationary temperature field in the specimen.

Both methods imply that the specimen is kept at the testing temperature for a certain time, minutes to hours. In other words, the experiments impose a substantial heat treatment to the specimen. Heat treatment may alter the crystalline structure and thereby also the physical properties of a material. It is desirable that the available data for physical properties are relevant to actual structure and state of a material. In evaluating processes that involve solidification of a liquid/melt, it is, for example, important that thermal diffusivity of the solid phase be known at temperatures up to the melting point. This will be of special interest for very rapidly quenched materials whose glassy structure exists at high temperature only during the quenching [3]. If the quenched material had to be heated above a certain temperature for measurements, the specific structure would be lost, and the measured values for thermal diffusivity would not be relevant to the quenching process.

The methods for the determination of thermal diffusivity as reported in the literature seem therefore not to be quite adequate at temperatures near the melting point. Data for the property may also be lacking at corresponding temperatures for many materials. To make adequate measurements, it is necessary to restore the actual crystalline structure and thereby the relevant conditions for the thermal diffusion. This can be done by repeating the solidification process and by making proper measurements while the melt solidifies.

The following method describes how thermal diffusivity in the solid phase can be determined simultaneously with the formation of the solid phase. The method is based upon the pioneering analysis of solidification processes in 1862 by Neumann [4], who formulated mathematically the propagation of a solidification front through a melt.

From Neumann's analysis, an expression for thermal diffusivity can be derived which includes the measurable quantities of motion of the characteristic temperature, including the freezing point (in German: Temperaturleitzahl). If the heat of solidification is given specifically by volume, the formulation will also lead to an expression for thermal conductivity, where the heat of solidification is the relevant heat flow. The property that can be best evaluated from measurements is therefore dependent upon the available data for the heat of solidification, specific heat, and density in the solid phase at the melting point.

2. MATHEMATICAL FORMULATION

The propagation of a solidification front through a melt was first studied theoretically by Neumann. His work is widely referred to in the literature [5, 6]. Neumann formulated the transport of heat in a semiinfinite body, initially at a temperature above the melting point. At a certain time, the surface temperature was assumed to drop to a steady value below the melting point. The melt then starts to solidify, first at the surface, and then solidification unidirectionally propagates into the melt. At the interface between solid and liquid, the following condition was formulated:

$$-k_s\left(\frac{\partial T_s}{\partial x}\right)+k_l\left(\frac{\partial T_l}{\partial x}\right)+\rho h\frac{d(s(t))}{dt}=0 \tag{1}$$

where T is the temperature, x is the length coordinate perpendicular to interface, $s(t)$ is the location of the interface relative to a fixed point, ρ is the density, h is the heat of solidification referred to unit mass, t is the time, and the indices s and l indicate the solid and liquid state, respectively.

Equation (1) expresses the balance of heat conducted through the liquid phase toward the interface and heat released by solidification at the interface on one hand, and the heat conducted through the solid phase away from the interface toward the cooled surface on the other hand.

When the assumptions are made that liquid temperature is kept at the melting point and that density is not changed by the solidification, then Eq. (1) simplifies to

$$k_s\left(\frac{dT_s}{dx}\right)=\rho h\frac{dx}{dt} \tag{2}$$

or in the difference form,

$$k_s\frac{\Delta T}{\Delta x}=\rho h\frac{\Delta x}{\Delta t} \tag{3}$$

in which the differences are coupled quantities in the solid phase at the interface. These are to be measured.

Equation (3) gives the following expressions for thermal diffusivity, of alternatively, thermal conductivity:

$$a=\frac{k}{\rho c}=\frac{h}{c}\left(\frac{\Delta x}{\Delta t}\right)^2\Big/\left(\frac{\Delta T}{\Delta t}\right) \tag{4}$$

or

$$k=\rho h\left(\frac{\Delta x}{\Delta t}\right)^2\Big/\left(\frac{\Delta T}{\Delta t}\right) \tag{5}$$

where c is specific heat. Thermal diffusivity or conductivity can be evaluated from the expressions above when the heat of solidification, specific heat, and density are known and the difference quotients are measured.

Equation (3) leads to the relationship:

$$\frac{a\Delta t}{(\Delta x)^2} = Fo_s = Ph_s = \frac{h}{c\Delta T} \tag{6}$$

where the Fourier number Fo_s and the Stefan number Ph_s are defined at the interface by unidirectional solidification of the liquid at the melting point. The relation confirms that the heat released by solidification and the heat conducted into the considered volume element of the solid phase are identical.

The relation (6) can further be written as

$$\frac{a}{h/c} = \frac{k}{\rho h} = \frac{\Delta x/\Delta t}{\Delta T/\Delta x} = \frac{(\Delta x/\Delta t)^2}{\Delta T/\Delta t} \tag{7}$$

which states that the velocity of the solidification front divided by the temperature time derivative in the solid phase at the front is a constant for the given material, expressed by its physical properties. Equation (7) also gives the result that the quenching speed $\Delta T/\Delta t$ is proportional to the square of the velocity of the solidification front. This is in agreement with the findings by Ruhl [7] in his study of cooling rates by rapid quenching of metals.

Since the freezing speed at the interface is to be recognized as the free variable, we have from Eq. (7) that the dependent variable $\Delta x/\Delta t$ is proportional to the property group $(ac/h)^{1/2}$. For most metals, this group has a value of about 2–5 $\times 10^{-4}$; for water it is an order of magnitude less. This means that the actual method may be preferable for materials like metals.

The assumption that the density of the material is constant during freezing implies an error in the evaluated thermal diffusivity. Generally, the density changes on freezing, by a few percent for metals, typically, and by about 10% for water. The assumption makes the Fourier number in Eq. (6) too high [6]; correspondingly, the thermal diffusivity is evaluated at too high a value Eq. (4). The error is, however, estimated to be of the order of 1%, i.e., small enough to justify the assumption.

3. EXPERIMENTAL

The condition expressed by Eq. (2) can, in principle, be realized by a simple experiment. The melt/liquid to be studied is first brought to the melting point and then allowed to solidify/freeze in a given direction where the temperature is to be measured. In the following, experiments are described where the technique is tested on water and mecury as materials.

3.1. Apparatus

For experiments on water or mercury, an apparatus was used consisting of a cylindrical container with a plane bottom and with dimensions 65 mm in diameter and 120 mm in length. The side wall of the container was insulated on the inside by polyurethane, 7 mm thick. An open ended tube of acrylic (28 mm in diameter and 34 mm in length) was mounted concentrically in the container, touching its bottom. Through bores in the tube wall, six shielded thermocouples of 0.5 mm o.d. were mounted radially from the outside extending into the axis. The axial distance between successive elements was about 5 mm and could be measured to within ±0.1 mm. The lower element was located about 1 mm above the bottom of the container.

3.2. Technique

The experiments were started by cooling container and liquid to the freezing point of the actual liquid. Using distilled water, the liquid was placed under vacuum for air removal after cooling. It was than stored under vacuum until the experiment continued. Then it was poured into the container to 3/4 of its volume. For mercury, the liquid was first frozen in the container, subsequently heated until completely melted, and then was kept at the melting point until the experiment continued.

The solidification process was started by lowering the container into a dewar that was partly filled with a cryogenic fluid (CO_2-ice, or liquid nitrogen), until the bottom rested on the ice, or about 2–3 mm into the liquid nitrogen. At the same time, a pen recorder was started to register the output of the thermocouples.

The experiments resulted in sets of curves showing the emf, i.e., the temperature, as a function of time as the freezing front passed the respective thermocouples. A slight subcooling could be observed in water before the temperature dropped into the solid phase.

From the curves, the difference quotient of temperature versus time could be evaluated at the freezing point. Knowing the distance between two thermocouples, the thermal diffusivity could be calculated from Eq. (4), or alternatively, the thermal conductivity from Eq. (5).

3.3. Evaluation of Data

Two values for thermal diffusivity were evaluated from each run, one for the solidification front when propagating from the third to the fifth thermocouple, and the other for the front moving from the fourth to the sixth thermocouple, counted from below. The mean velocity of the front was determined as an integral mean value between the actual thermocouples.

Measured quantities entered into Eq. (5) would give values of thermal diffusivity to an estimated accuracy of about 3%. The overall accuracy depends further on the quality of data for the physical properties in the expression. The actual data are given in Table I as taken from reference sources [8], [9], [10], and [11]. With these data, Eq. (5) gives an estimated accuracy for thermal diffusivity of the order of 5% for ice and of the order of 10% for mercury.

4. RESULTS

4.1. From the Experiments

4.1.1. Ice

Thermal diffusivity as determined for ice is given in Table I. The experimental values are the mean of the two values obtained in each run. The values are in good agreement with estimated reference values. From the literature, only two measurements seem to be reported. Neumann [12] found the value 1.36×10^{-6} ($m^2 \cdot s^{-1}$) at 0°C. Laikhtman et al. [13] report values that are about 25% lower, 1.1×10^{-6} $m^2 \cdot s^{-1}$ at approximately −14°C, with an accuracy of 20%. The experimental values for thermal conductivity are on the average 1 − 2% higher than the values found by Jakob and Erk [14]. The difference may tentatively be referred to the error introduced by the assumption of constant density on freezing.

4.1.2. Mercury

Thermal diffusivity as determined for solid mercury is given in Table I. The mercury was analyzed to be of 99.9 ± 0.5% purity. No experimental values were found in the literature for the diffusivity of mercury at the actual melting temperature. Provisional values, based on estimated data for thermal conductivity, specific heat, and density, are, however, given according to orientation of crystalline structure [2]. Table I quotes values for high purity mercury at the given temperatures. The present method involves, in general, diffusion parallel to the axis of the crystalline structure. The experimental mean value lies between the estimated value for polycrystalline mercury and the estimated value for solid mercury parallel to the crystalline axis. Further investigations are desirable to confirm the findings, whether they can be referred to crystalline character or to impurities in the test material.

Table I. Thermal Diffusivity for Several Materials[a]

Mater.	Temp. (mean) (°C)	h $(\mathrm{j \cdot kg^{-1}})$	c $(\mathrm{J \cdot kg^{-1} \cdot {}^\circ C^{-1}})$	ρ $(\mathrm{kg \cdot m^{-3}})$	h/c (°C)	$\Delta T/\Delta t$ $(\mathrm{{}^\circ C \cdot s^{-1}})$	a (exp)	k (exp) $(\mathrm{W \cdot m^{-1} \cdot {}^\circ C^{-1}})$	$a_{\mathrm{rec.}}$ [2]			
									$\perp$	$\parallel$	Polycr.	Liq.
Ice	−6	333,708	2064	918	161.7	0.1	1.24	2.35			1.24	
Ice	−6	333,708	2064	918	161.7	0.1	1.22	2.31			1.24	
Ice	−6	333,708	2064	918	161.7	0.1	1.26	2.39			1.24	
Ice	−14	333,708	2008	919	166.2	0.4	1.32	2.44			1.30	
Ice	−14	333,708	2008	919		0.4	1.29	2.38			1.30	
Hg	−40	11,302	134		84.3	0.01	14.7		13.0	16.6	14.2	
Hg	−41	11,302	134		84.3	0.13	16.2		13.0	16.6	14.2	
Hg	−41	11,302	134		84.3	0.13	17.9		13.0	16.6	14.2	
Hg	−41	11,302	134		84.3	0.28	15.2		13.0	16.6	14.2	
Hg	−41	11,302	134		84.3	0.28	14.1		13.0	16.6	14.2	
Al	615	395,640	1256		315	4	68.9				70.0	
Sn	148	59,441	248		240	3.8×10^4	5.9		39.0	27.2	34.9	17.3
Pb	220	23,400	136		172	4.7×10^4	0.8				21.6	9.9
Zn	264	100,882	400		252	6.7×10^4	3.5				35.8	15.7

[a] $a \times 10^6$ $(\mathrm{m^2 \cdot s^{-1}})$.

4.2. From Data in the Literature

The method has been applied to data on aluminum, found in ref. [15], and on the quenched metals, tin, lead, and zinc, found in ref. [16].

4.2.1. Aluminum

Results from some experiments by undirectional solidification of aluminum were available. One run with aluminum of 99.996% purity permitted the evaluation of thermal diffusivity from Eq. (4). The result is given in Table I. The value is the mean of four derived from data of the temperature curves. The single values deviated ± 10%, probably due to deviations from nominal distance between successive thermocouples, 25 mm. The mean value, 68.9×10^{-6} ($\mathrm{m}^2 \cdot \mathrm{s}^{-1}$), is in good agreement with the recommended value 70.0×10^{-6} ($\mathrm{m}^2 \cdot \mathrm{s}^{-1}$) for the actual temperature, 615°C [2].

For alloys that solidify in a certain temperature interval, it can be shown that the present method for determination of thermal diffusivity can be applied [17]. It is thereby necessary to determine the solidus temperature on the curve for temperature versus time. The velocity by which the solidus temperature propagates through the solid phase, is then, together with the temperature gradient in the solid at that temperature, the basis for evaluating the thermal diffusivity at solidus.

4.2.2. Rapidly Quenched Metals, Tin, Lead and Zinc

Pond and Winter [16] made experiments by quenching liquid metals using several methods. The applied Mobley–Maringer method yields a undirectional solidification of a thin filament of the materials. From their data, the velocity of the solidification front through the filament, $\Delta x/\Delta t$, can be estimated approximately. With the referred data for quenching rate, $\Delta T/\Delta t$, the thermal diffusivity can be evaluated. The results are quoted in Table I. For comparison, diffusivity values for metals of common structure are given at the mean temperatures. It is seen from the data that estimated values for thermal diffusivity are substantially smaller for quenched metals than for metals at common conditions. This was to be expected due to the glassy structure of the metals attained by quenching. The values are even smaller than for the liquid state, which was not to be expected. The reason may be that the difference quotients are here estimated separately and without the proper consistency. A more detailed analysis of the temperature field in the filaments during quenching is therefore a necessity. It might also be worthwhile to look for methods to measure the temperature at the surface of the filament in contact with the quenching wheel. The method seems, however, to be promising even for the extreme solidification process of rapid quenching of metals.

5. CONCLUDING REMARKS

The method for determination of thermal diffusivity as presented in this paper has been shown to be usable for materials at temperatures near the melting point. It adds to the spectrum of available methods a method that involves a relatively simple experiment at temperature conditions where other methods face considerable problems.

The method will also be useful for the determination of thermal diffusivity at other exo- or endothermic transition processes. The basic need for the method is to acquire data for the heat of transition and for the specific heat at the actual temperature.

REFERENCES

1. G. C. Danielson and D. H. Sidles, Thermal diffusivity and other nonsteady-state methods, in R. P. Tye, ed., *Thermal Conductivity*, Vol. 2, (Academic Press, New York, 1969), Chap. 3, p. 149.
2. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and M. C. Nicolaou, *Thermophysical Properties of Matter*, Vol. 10 (IFI/ Plenum, New York, 1973).
3. R. E. Maringer and O. D. Hunderi, Rapid solidification, new metallurgy. SINTEF, STF 34F.81060, Trondheim (1981).
4. F. Neumann, Vorlesungen, Königsberg, (1862), in H. Weber, *Die Partiellen Differential-Gleichungen der Mathematischen Physik*, 5. ed., Vol. 2 (Friedrich Vieweg & Sohn, 1912), p. 121.
5. M. Necati Özisik, *Heat Conduction*, (John Wiley & Sons, New York, 1980), p. 410.
6. U. Grigull and H. Sandner, *Wärmeleitung* (Springer-Verlag, Berlin, 1979), p. 124.
7. R. C. Ruhl, Cooling rates in splat cooling. *Mater. Sci. Eng.* **1**:313 (1967).
8. *CRC Handbook of Chemistry and Physics*, 58th ed. (CRC Press, Cleveland, 1978).
9. Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter*, Vol. 4 (IFI/Plenum, New York, 1970).
10. K. R. Van Horn, *Aluminum*, Vol. 1 (Am. Soc. Metals, 1971).
11. H. Landolt and R. Börnstein, Zahlenwerte und Funktionen, 6. Aufl. IV Band, Technik, 2. Teil, Bandteil b, (Springer-Verlag, Berlin, 1964).
12. F. Neumann, *Experiments on the thermal conductivity of solids*. Phil. Mag. **25**:63 (1863), transl.
13. D. L. Laikhtman, N. V. Serova, and A. V. Smetannikova, Certain data on the heat conductivity and thermometric conductivity of ice and snow, and a method of determination. Am. Met. Soc. Rep. T-R-287 (1960).
14. M. Jakob and S. Erk, Die Wärmeleitfähigkeit von Eis zwischen 0 und −125°C, *Z. ges. Kälte-Industrie* **36**:229 (1929).
15. S. Johansen, Simulation of a solidification process, (norw.), SINTEF, Rep. N.340878.01 (1981).
16. R. B. Pond and J. M. Winter, Jr., Calorimetric comparison of quench rate in melt spinning and melt extraction, *Mater. Sci. Eng.* **23**:87 (1976).
17. M. Lamvik and S. Johansen, Thermal conductivity in some aluminum alloys, SINTEF/NTH, Rep. (1982), in preparation.