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Measurement of thermal conductivity by differential scanning calorimetry

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Abstract

A technique of measurement of thermal conductivity of solid materials by differential scanning calorimetry is presented. It concerns small samples having a diameter less than 8.0 mm, a height less than 2.0 mm and a low thermal conductivity. This method requires many samples with different heights which are heated in such a way that a calibration substance put on their top undergoes a first-order phase transition. The analysis of heat transfer of a such experiment predicts that the slope of the differential power during the transition is proportional to the factor 2 and inversely proportional to the sum of the thermal resistances. A measurement of the thermal conductivity of samples made of polytetrafluoroethylene powder, compressed at the density of $2.10 \pm 0.03\,\mathrm{g\,cm^{-3}}$, has been performed; the value obtained is $0.33 \pm 0.02\,\mathrm{W\,m^{-1}\,K^{-1}}$. Measurements of thermal conductivity of small metal hydride pellets are also presented. The precision of the measurements are on average 10%.

Keywords: DSC; Metal hydride; Polytetrafluoroethylene; Slope; Thermal conductivity

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1. Introduction

Several studies of methods for measurement of thermal conductivity of solid materials by differential scanning calorimetry have been carried out [1–8]. Some methods require addition of a thermal reservoir with temperature sensors [4–6], others use a technique in which a pure metallic substance on the top of the sample melts [1–3,7]. The advantage of the latter is its simplicity and the rapidity with which measurements can be obtained. Hakvoort et al. [1] and Khanna et al. [2] use this technique, but do not take into account the thermal contact resistance between the sample and furnace, which may not be negligible compared with the thermal resistance of the sample. Flynn and Levin's method [3] includes the effects of thermal contact resistances, however, results obtained by their method are too large [7]. We therefore present a more general theory which gives better results.

2. Theory

Basic knowledge of differential scanning calorimetry and heat transfer necessary for understanding this paper have been presented elsewhere [9,10].

The solid sample for which we want to determine the thermal conductivity is placed into the sample furnace of the calorimeter, and a calibration substance such as indium is placed on top of the sample. The reference furnace is kept empty. During melting of the calibration substance, the temperature of the calibration substance must be constant. A scan is performed to measure the differential power produced during the melting of the calibration substance. The curve obtained is increasing and approximately linear during the melting and decreases exponentially after melting is complete (see Fig. 1). Measurement of the slope of the increasing part of the curve allows determination of the thermal conductivity of the sample.

Solving the heat differential equation, we get that the slope is ruled by the following equation [7]:

$$\text{Slope} = \frac{\mathrm{d}\Delta P}{\mathrm{d}T_{\mathrm{P}}} = \frac{2}{R} \tag{1}$$

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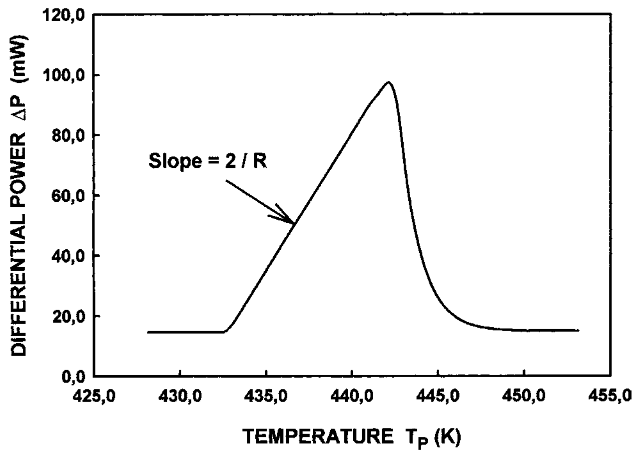

Fig. 1. Curve obtained for a scan with a fused quartz sample having on its top an indium disk (quartz height: 1.51 ± 0.01 mm, quartz diameter: 5.08±0.01 mm, quartz mass: 62.9±0.1 mg, indium mass: 112.4±0.1 mg, scan rate: 10.0 ± 0.3 K min^{-1}).

where ΔP is the differential power of the calorimeter obtained after the subtraction of the zero line, T_P the programming temperature of the calorimeter and R the total thermal resistance:

$$R = R_1 + R_2 + R_\mathrm{S} \tag{2}$$

where R_1 is the thermal contact resistance between the sample and the sample furnace, R_2 the thermal contact resistance between the sample and the calibration substance and R_S the thermal resistance of the sample:

$$R_\mathrm{S} = \frac{L_\mathrm{S}}{\lambda_\mathrm{S}\, A_\mathrm{S}} \tag{3}$$

where L_S, λ_S, A_S are, respectively, the height of the sample, its thermal conductivity and the area of an horizontal cross-section of it. Eq. (1) says that samples with relatively small thermal conductivity will have in general a lower slope than more conductive materials.

To measure the thermal conductivity of a material, it is necessary to repeat the experiment with samples having known, different heights and constant cross-sectional areas. Assuming the samples have the same thermal contact resistance $R_1 + R_2$, according to Eqs. (2) and (3), the total thermal resistance is a linear function of the $L_\mathrm{S}/A_\mathrm{S}$ ratio. Therefore, a plot of the total thermal resistance versus the $L_\mathrm{S}/A_\mathrm{S}$ ratio is in principle a straight line. The inverse of the slope is equal to the λ_S thermal conductivity of the material and the ordinate intercept is equal to the sum of $R_1 + R_2$.

3. Experimental

Measurements were made on a Perkin-Elmer DSC 7 power compensated differential scanning calorimeter with a nitrogen flow of 20.0 ± 0.1 ml min^{-1} and without ice in the thermal reservoir. The power scale of the calorimeter was calibrated by measuring the enthalpy of fusion of indium. The temperature scale was calibrated by measuring the melting temperatures of indium and tin.

Ten cylindrical pellets of compressed polytetrafluoroethylene powder (Aldrich #43,093-5) with different heights and equal diameters (5.48 ± 0.01 mm) were made by placing the powder in a cylindrical die compressed with a hydraulic press at 800 ± 100 MPa for 15 ± 1 min. The mean density of the pellets was 2.10±0.03 g cm^{-3}. An indium disk was made from indium wire (1.0 mm diameter, Alfa Aesar #00470, 99.999% purity) wound in a tight spiral. The indium disk had a 5.4 ± 0.2 mm diameter and weighed 74.4 ± 0.1 mg. The disk was fused several times inside the calorimeter to make one surface flat. The pellets and the furnaces of the calorimeter were cleaned with pure alcohol and dried.

A first scan with two empty furnaces was done to obtain the zero line. For each experiment, a pellet is put in the center of the sample furnace and the indium disk is put on top of the pellet. The reference furnace is kept empty. The indium disk must cover the top surface of the sample so temperature will be uniform during melting of the indium. A slow scan (2.0 K min^{-1}) is done to melt the indium to reduce the thermal contact resistance between it and the pellet. A more rapid scan (10.0 K min^{-1}) is then performed beginning at a sufficiently low temperature to avoid perturbing the signal during the melting. The zero line is then subtracted from the signal obtained for this scan. Finally, a slope of the linear part of the curve is determined to obtain the total thermal resistance, see Eq. (1).

4. Results

Table 1 presents the results of measurements of heights with an electronic caliper, slopes and total thermal resistances obtained for each pellet. The total thermal resistance increases linearly with height of the pellets (Fig. 2). Linear regression gives a thermal conductivity of 0.33 ± 0.02 W m^{-1} K^{-1} and the sum of the thermal contact resistances as 150 ± 10 K W^{-1}. The relative error on the thermal

Table 1
Results of measurements on compressed polytetrafluoroethylene powder samples

Height, L_S (± 0.01 mm)	Slope, $2/R$ (± 1% m W K^{-1})	Total thermal resistance, R (± 1% K W^{-1})
0.41	9.26	216
0.53	9.71	206
0.80	7.81	256
0.95	7.19	278
1.14	6.49	308
1.19	6.58	304
1.31	5.71	350
1.45	5.81	344
1.65	5.52	362
1.93	5.05	396

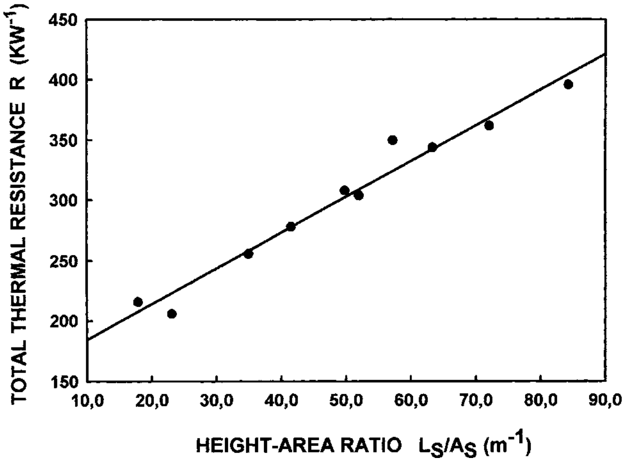

Fig. 2. Total thermal resistance vs. height–area ratio for compressed polytetrafluoroethylene pellets (density: 2.10 ± 0.03 g cm^{-3}, diameter: 5.48 ± 0.01 mm).

conductivity is 6%. Twenty-four literature values of the thermal conductivity of polytetrafluoroethylene have a mean of 0.26±0.06 W m^{-1} K^{-1} [7]. The difference between the thermal conductivity measured in this part of the study and the mean literature value is 27%.

In other work, we measured the thermal conductivity by fitting the decreasing part of the thermograms obtained during the scan of samples with an indium disk on the top [7]. This method requires only one sample and uses a constraint equation determined by the slope of the increasing part of the curve. The variation between the experimental results and the literature values obtained previously from this method had a magnitude of 100% [7].

Table 2 presents the results of the measurements of thermal conductivity achieved from this method for one sample of polytetrafluoroethylene, one disk of fused quartz and four metal hydride pellets, but re-calculated using Eq. (1) as a constraint equation instead of Flynn and Levin's slope equation [3]. The precision of these measures is in mean 11%. The difference between the thermal conductivity measured for fused quartz and polytetrafluoroethylene in this part of the study and the literature values are less than 4%.

Table 2
Results of measurements on quartz, polytetrafluoroethylene and compressed metal hydride powders

Material	Density (g cm^{-3})	Thermal conductivity, λ_S (W m^{-1} K^{-1})
Polytetrafluoroethylene	2.12 ± 0.02	0.27 ± 0.03 (0.26 ± 0.06 [7])
Fused quartz	2.06 ± 0.02	1.5 ± 0.2 (1.57 ± 0.02 [11])
Nanocrystalline MgH_2	1.36 ± 0.01	0.40 ± 0.02
Nanocrystalline MgH_2+ 33.7% Al matrix	1.57 ± 0.02	0.75 ± 0.07
Nanocrystalline FeTi	3.92 ± 0.04	0.53 ± 0.04
Polycrystalline $LaNi_5$	6.15 ± 0.06	3.1 ± 0.7

5. Discussion

The differences of values observed in the results is attributable to sources of errors which are: the one-dimensional model does not take into account the effects due to the other dimensions; the sum of the thermal contact resistances vary from one sample to another; some heat is lost from the samples by convection and radiation; the thermal conductivity varies with temperature; there is dilation of the samples; the width of the discontinuity of the temperature field at the contact surfaces is not nil; the temperature of the surface on which the sample is put is not necessarily the same at each point [12]; the samples do not have exactly the same diameter; the bottom and upper surfaces of the samples are not perfectly flat; the thermal conditions seen by the polytetrafluoroethylene before the measurement could influence its thermal conductivity [13]; the weight of the samples could influence the thermal contact resistances; in reality the indium mass does not entirely cover the upper surface of the samples; the bottom surfaces of the indium disks are not perfectly smooth; finally, the temperature gradients inside the calibration substance may not be negligible compared to the thermal gradients inside the sample if the sample.

Our theoretical and experimental results show that the slope of the curve during melting of the calibration substance is equal to 2 divided by the sum of the thermal contact resistances plus the thermal resistance of the sample. With samples having different heights it is possible to measure the thermal conductivity with a precision less than 10% if the thermal conductivity is not too high. With an only one sample, a measure of thermal conductivity with an experimental error of less than 5% can be obtained by fitting the decreasing part of the thermogram.

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