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TRENDS IN THE METHODS OF MEASUREMENT OF THERMOPHYSICAL PROPERTIES IN THE SOLID STATE

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ABSTRACT

The differences in principle between methods of measurement of thermophysical parameters based on Tian's energy-balance equation and those based on the analysis of the temperature field within the sample are discussed. The methods are compared from the viewpoint of the productivity of measurement and the possibility of application in the thermal analysis regime. Recently, the greatest progress has been made in methods based on differential dynamic calorimetry and in pulse methods of measurement.

INTRODUCTION

The techniques employed for measurement of thermophysical parameters have recently undergone rapid development due to the progress in materials research and the introduction of new technological procedures. The methods currently available can be divided into three groups.

(1) Methods of thermal analysis, following Šesták et al. [1], based on the measurement of the thermophysical parameters of substances or reaction products as a function of temperature. The temperature of the sample is varied systematically. These methods are most frequently used to study the kinetics of processes such as transformations, reactions, structural relaxations, etc. Occasionally they are also used for determination of the basic thermophysical parameters of materials. This group includes DSC, Calvet microcalorimetry, DTA and some modifications of the pulse methods.

(2) Methods where the temperature of the sample is not systematically varied. These methods are most frequently used for solid-state research and for determination of thermophysical parameters of materials.

(3) Methods applicable under spetial conditions such as high pressures, high temperatures, special sample shape, etc.

The evaluation of any method of measurement of thermophysical parame-

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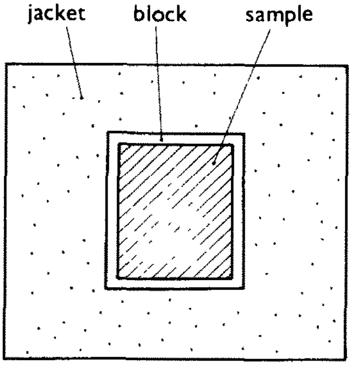

Fig. 1. A calorimeter with block, sample and jacket.

ters requires, above all, careful consideration of the following characteristics: absolute and relative accuracy of measurement; productivity of measurement; applicability to thermal analysis; working temperature interval.

The methods can be classified according to the principle of the measurement.

(a) Methods using Tian's energy-balance equation

$$q = c\frac{\partial T}{\partial t} + K(T_s - T_j) \tag{1}$$

where q is the amount of heat produced in the sample per unit volume and unit time, c is the heat capacity of the sample, K is the heat-exchange coefficient between the sample and the calorimeter jacket, T_s is the sample temperature and T_j is the temperature of the jacket (Fig. 1). This group includes the methods for heat capacity or enthalpy measurements. The analysis of the fundamental equations for different types of calorimeters based on Tian's equation was dealt with by Velíšek [2].

(b) Methods based on the analysis of the temperature field within the sample. Every physical body is characterized by internal physical parameters, i.e., by its thermal capacity and thermal diffusivity. The construction of a suitable heat source allows one to generate a temperature field within the sample. Knowledge of the temperature distribution and defined properties of the heat source then enable calculation of the thermophysical parameters of the body. This principle is used by a wide range of methods. Fundamental equations for measuring assemblies using temperature fields were published in the monograph by Krempaský [3].

The aim of this article is to characterize the principles of recent techniques for measuring thermophysical parameters. Attention will be devoted mainly to methods for measuring the specific heat, thermal diffusivity, thermal conductivity and kinetic parameters.

METHODS USING TIAN'S ENERGY-BALANCE EQUATION

The methods based on the Nernst adiabatic calorimeter are the most accurate. This calorimeter is suitable for the determination of heat capacities in the temperature interval 4–500 K. If sufficient attention is devoted to thermodynamic equilibrium of the sample, the absolute accuracy of measurement is about 0.1%. The sample temperature cannot be systematically controlled. The method is not suitable for investigations of the kinetics of transformation. A fully automatic system for measurement of heat capacity was described by Gmelin [4] and by Cheng et al. [5].

In the continuous heating calorimeter the sample is continuously heated and the sample temperature is simultaneously recorded. A uniform temperature distribution within the sample is assumed. In order to fulfil this requirement the method is applied preferentially to small samples of high thermal conductivity. The accuracy of measurements is lower in comparison with the Nernst calorimeter. The method allows systematic control of the sample temperature. In comparison with the Nernst calorimeter, the productivity of measurement of a continuous heating calorimeter is many times higher. Naito et al. [6] have described an apparatus of this type for the temperature interval 300–1000 K, and Hsieh et al. [7] analysed the influence of thermal leaks on the accuracy of measurement.

Differential dynamic calorimetry is based on the same principle as the continuous heating calorimeter. In addition to the sample, a reference is placed in the calorimeter. The measurement sensitivity can be increased several times by monitoring only the difference in dynamic equilibrium between the reference and the sample. This is permitted by differential measurement of suitable physical parameters as a function of temperature. The construction of this calorimeter allows the use of small samples, which substantially increase the dynamics of the system. Calorimeters with high dynamics are the most suitable for studying kinetic processes. A critical analysis of the applications of differential dynamic calorimeters to kinetic processes was presented in Šestak's monograph [8].

The basic experimental arrangements of commercial systems allows one to distinguish between the following types of differential dynamic calorimeters:

(1) DTA (differential thermal analysis), where the quantity measured is the temperature difference between the sample and reference,

(2) Calvet microcalorimetry, where the difference in spontaneous heat fluxes between the sample and reference is measured,

(3) DSC (differential scanning calorimetry), where the quantity measured is the difference in heat fluxes, the temperatures of the sample and the reference being systematically varied.

Recently the greatest progress has been made in the methods of differential dynamic calorimetry. Šesták [8] discussed basic heat equations for DTA, Calvet microcalorimetry and DSC with regard to the working regime. Cesari et al. [9] reviewed numerical methods for analysis of thermokinetics. Haft et al. [10] described a new multi-body method for determination of thermokinetics. House and Zimmerman [11] discussed the possibility of using an iteration method for analysis of thermokinetics. Kluge et al. [12] considered equations for kinetic processes from the point of view of non-equilibrium thermodynamics. The influence of the experimental conditions on the shape of thermoanalytical curves was discussed by Shishkin [13], Novard and Hardin [14], Gorbachev [15], Van Dooren and Müller [16] and Poore and Beezer [17], and the effect of the temperature gradient in the sample was discussed by Shishkin [18]. The accuracy of heat capacity determinations was investigated experimentally by Suzuki and Wunderlich [19] and analysed theoretically by Egunov [20].

METHOD BASED ON ANALYSIS OF THE TEMPERATURE FIELD WITHIN THE SAMPLE

This method yields information about the specific heat and such transport parameters as the thermal diffusivity and thermal conductivity. It involves two steps.

The first step, in which the partial differential equation of heat conduction is solved, is theoretical. In the case of cartesian coordinates, this equation takes the form

$$\frac{\partial T}{\partial t} = a\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \tag{2}$$

where a is the thermal diffusivity. The solution of eqn. (2) for given boundary and initial conditions describes the temperature field of the sample. In general, the temperature field is a function of the coordinates and time

$$T(x, y, z, t) = \mathrm{f}(x, y, z, t \mid c, a, \rho, Q, \alpha, \beta, \gamma, \ldots) \tag{3}$$

where c is the specific heat and a the thermal diffusivity, i.e., the thermophysical parameters of the sample, and ρ is the density. Other parameters Q, α, β, γ, etc., are incorporated in the function (3) as a consequence of the boundary and initial conditions. Most frequently they characterize the method of heat generation, heat leak from the sample surface, heat transport from the heat source to the sample, etc. The boundary and initial conditions have to be formulated in terms of the technical realization of the measurement.

The second step, which is experimental, allows one to calculate the thermophysical parameters from the measurement of the temperature distribution within the sample, by using the function (3). The absolute accuracy of methods based on the analysis of the temperature field within the sample depends substantially on the fulfilment of boundary and initial conditions which were considered in the theory.

There are a number of methods based on the analysis of the temperature field within the sample, indeed every laboratory seems to have developed its own measuring technique. However, it is possible to find certain common traits in these methods, namely the shape and the mode of generation of the temperature field.

The shape of the temperature field is characterized by isothermal surfaces. Surfaces can be planar, cylindrical or spherical. The temperature field can be generated by: a stationary heat source; a heat source with a stepped power output; a pulsed heat source or a periodic heat source.

Experimental details of methods based on the analysis of the temperature field were described by Maglic et al. [21]. Stationary methods using a stationary heat source provide information only about the thermal conductivity. Methods using a heat source with a time-dependent power output are dynamic ones. Some of them allow the simultaneous determination of the specific heat, thermal diffusivity and thermal conductivity. The advantages of dynamic methods become apparent at higher temperatures where the accuracy and productivity of measurement is higher in comparison with stationary methods.

Recently the greatest progress has been made in pulse methods. The principle of such methods lies in the generation of a heat pulse within the sample. The thermophysical parameters of the sample can then be calculated from its temperature response. Three alternatives have been developed.

(a) The flash method uses a suitable radiation heat source for generation of the heat pulse. The possibilities of application of this method were analysed by Taylor [22].

(b) A method for metallic materials based on resistive self-heating of the specimen in the shape of a thin foil or wire. These methods have been reviewed by Cezairliyan [23].

(c) A method with a planar source of heat was described in detail by Cesnak, Barta, Bielek, Illeková, Krempaský and Kubičár [24–29]. The heat pulse is derived from the Joule heat which is formed by a current pulse passing through a planar electrical resistance. The absolute accuracy of the method is limited by disturbing effects. The specific heat, thermal diffusivity and thermal conductivity can be determined with accuracies of 1–5, 4–8 and 5–13%, respectively, and the relative accuracy of measurement is $< 1\%$ for all three thermophysical quantities. Owing to full automatization of the method, a high productivity of measurement is achieved. The sample temperature can be systematically controlled. The method has been applied to bulk materials and to thin metallic foils, in the temperature range 150–1300 K.

DISCUSSION OF THE PRINCIPLES OF THE METHODS

The accuracy of the methods using Tian's energy-balance equation depends largely on the relaxation time, which characterizes the time required to establish thermodynamic equilibrium of the measuring system after the introduction of a quantity of heat. In practice this means that the data from the calorimeter are valid only after the relaxation time. When using a continuous heating calorimeter or a differential dynamic calorimeter, the relaxation time has a considerable influence on the accuracy of measurement. A detailed analysis of the relaxation time under various calorimeter working regimes was published by Bachmann et al. [30] and Flynn [31].

Tian's equation appears in the theory of temperature fields as a boundary condition of the partial differential equation of heat conduction (2). Its solution yields a time-dependent function (3), which describes the temperature distribution within the sample. A uniform temperature distribution after the introduction into the sample of a defined quantity of heat is established only after a sufficiently long period. Thus the relaxation time represents the mathematical condition for uniform distribution of temperature within the sample, and is valid for measurements of heat capacity close to thermodynamic equilibrium.

In chemical kinetics, Šesták [8] starts from the assumption that the rate of transformation of the system is a function only of the state of the system. This assumption was established on the basis of experience. The system is represented by the measured sample. For defined environment conditions, it is possible to calculate kinetic parameters for the process by analysis of the state of the system and by the use of a suitable mathematical model. DSC, Calvet microcalorimetry and DTA are most frequently used for this purpose. For slow processes (tens or hundreds of hours), the methods based on the analysis of the temperature field within the sample can also be used.

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