SLOVENSKI STANDARD
SIST ENV 821-3:2000

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Advanced technical ceramics - Monolithic ceramics - Thermo-physical properties - Part 3: Determination of specific heat capacity

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Hochleistungskeramik - Monolithische Keramik - Thermophysikalische Eigenschaften - Teil 3: Bestimmung der spezifischen Wärme

Céramiques techniques avancées - Céramiques monolithiques - Propriétés thermo-physiques - Partie 3: Détermination de la chaleur spécifique

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English version

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Contents list

Foreword

This European pre-standard has been prepared by CEN/TC 184 "Advanced technical ceramics", the secretariat of which is held by BSI.

ENV 821 "Advanced technical ceramics - Monolithic ceramics - Thermo-physical properties" consists of three Parts:

Part 1 : Determination of thermal expansion
Part 2 : Determination of thermal diffusivity
Part 3 : Determination of specific heat capacity

CEN/TC184 approved this European pre-standard by resolution 2/92 during its fifth meeting held in Brussels, 1992-03-31.

According to the CEN/CENELEC Internal Regulations, the following countries are bound to announce this European pre-standard:

Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

Advanced technical ceramics – Monolithic ceramics – Thermo-physical properties – Part 3: Determination of specific heat capacity

1 Scope

This Part of EN 821 describes two methods for the determination of specific heat capacity of advanced monolithic technical ceramic materials based on:

Method A: drop calorimetry

Method B: differential scanning calorimetry (DSC)

over temperature ranges from room temperature upwards, depending on the design of the equipment.

Method A may be used for measurements up to temperatures of 2000 ^{0}C, and Method B for measurements up to 1400 ^{0}C.

NOTE 1 : The methods described apply in the case of test materials free from phase transformations, annealing effects or partial melting. If any such effect occurs in a material over the temperature range of the test, spurious results will be obtained unless the data are carefully analysed. In such cases it is usually necessary to conduct repeat tests at a number of temperatures close to the discontinuity, in order to estimate correctly its contribution to the apparent heat capacity.

NOTE 2 : Care should be exercised in both methods over the selection of the cell or crucible material and in the selection of the test atmosphere, especially at high temperatures. Test-pieces may react with the crucible or the atmosphere, leading to spurious results. In general, an awareness of such problems must be maintained at all times. Especially with regard to method B, awareness must also be maintained of radiation effects at temperatures above 1000 ^{0}C, and of the reproducibility of the output signal.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 45 001 General criteria for the operation of testing laboratories

HD 446.1 S1 Thermocouples – Part 1 : Reference tables

HD 446.1 S2 Thermocouples – Part 2 : Tolerances

3 Definitions

For the purposes of this Part of EN 521, the following definitions apply:

3.1 Enthalpy, ΔH: The heat content of an object in joules released or absorbed as a result of a temperature change.

3.2 Specific heat capacity, c_p: The amount of heat (q) in joules required to raise the temperature of a 1 g mass by 1 kelvin at temperature T at constant pressure, i.e.:

$$c_p = \frac{dq}{dT} = \frac{1}{m}\frac{dQ}{dT} \qquad (1)$$

where Q is the total heat required for a test-piece of mass m.

3.3 Mean specific heat capacity, $\overline{c}_p$: The amount of heat (q) required to raise the temperature of a 1 g mass from temperature T_1 to temperature T_2, divided by the temperature interval in kelvins at constant pressure, i.e:

$$\overline{c}_p = \frac{q(T_1 \rightarrow T_2)}{T_2 - T_1} = \frac{Q(T_1 \rightarrow T_2)}{m(T_2 - T_1)} = \frac{\Delta H}{m(T_2 - T_1)} \qquad (2)$$

3.4 Calorimeter: A device for measuring the amount of heat input to or output from a test-piece.

3.5 Drop calorimeter: A calorimeter into which a test-piece at initially high temperature is dropped and allowed to cool, and the total heat content (enthalpy) of the test-piece is measured as a temperature rise or other parameter in the calorimeter.

3.6 Differential scanning calorimeter : A device in which the difference in energy input into a test-piece and into a calibrant may be measured as a function of temperature while subjected to a temperature controlled heating or cooling schedule. This difference is related to the difference in heat capacity between the test-piece and the calibrant.

4 Method A - Drop calorimetry

4.1 Principle

A test-piece, sealed in a crucible where necessary, is heated to the required temperature suspended in a vertical tube furnace positioned above a receiving calorimeter. A shutter prevents radiative heat from the furnace from reaching the calorimeter. The calorimeter may be any suitable device for recording the total amount of heat extracted from the test-piece to cool it to the ambient temperature. The test-piece, or crucible containing the test-piece, is allowed to drop through the shutter into the calorimeter. The response of the calorimeter is monitored continuously. The output curve is analysed, incorporating the calibrated response of the calorimeter and of the crucible if used, and the mean specific heat capacity is calculated.

NOTE: Using several determinations of $\bar{c}_p$ over different temperature ranges, the true c_p at temperature T can be estimated by curve-fitting routines (see 4.5).

Adherence to the procedure described below should provide results with an accuracy of better than 5% up to 1600 °C.

4.2 Apparatus

4.2.1 A vertical tube furnace of suitable design and maximum temperature capability is controlled by a Pt/Pt 13 % Rh or Pt/Pt 10 % Rh thermocouple (for temperatures to 1650 °C) or other suitable type (for higher temperatures) connected to a temperature controller capable of maintaining a given temperature to a constancy of ± 1 K. The temperature profile of the furnace shall be such as to contain a section of at least twice the length of the crucible or test-piece which is at constant temperature to within ± 0,5 K (see 4.3).

A capability for operating with an inert atmosphere is required for the testing of non-oxide materials at elevated temperatures.

4.2.2 The calorimeter may comprise any suitable device for receiving the hot test-piece and for recording the total heat transmitted to it from the test-piece. An example based on a massive copper block is shown in Figure 1. Other examples include an ice calorimeter in which the heat transmitted is recorded as the melting of ice through the volume decrease incurred, observed using a capillary level indicator.

NOTE: A simple water immersion calorimeter is not recommended for initial test-piece temperatures above 100 °C.

Whichever type is employed, it shall be capable of calibration using reference materials or a known amount of electrical power. In the example of a massive copper block, the tapered central hole is designed to mate with the crucible or test-piece to provide intimate thermal contact. The block contains a resistance heater and a platinum resistance thermometer. It is supported on three adjustable locating pins incorporating thermally insulating sections.

4.2.3 The calorimeter is placed inside a vessel in a temperature-controlled environment, such as an oil bath as shown in Figure 2. The temperature of the environment shall be constant to within ± 0,1 K over periods of 15 min.

4.2.4 The test-piece shall be either a solid test sample of size and shape appropriate to the calorimeter, or shall comprise fragments or a powder. It may be either:

a) enclosed in a platinum crucible with a tight-fitting or sealed lid, with geometry suitable for making intimate thermal contact with the calorimeter, and with the capability of being sealed and suspended by a platinum wire (all samples); or

b) in a form capable of having a platinum suspension wire attached at its upper end (solid samples only).

NOTE: The use of a crucible enables the test to be employed on powdered samples, which is especially advantageous for calibration purposes using a reference powder.

4.2.5 There shall be an arrangement whereby either the crucible or the test-piece (depending upon the design and operation of the apparatus) suspended in the furnace may be dropped through a radiation screen, such as a shutter mechanism timed to open for the passage of the test-piece and to close after its passage.

NOTE: This minimizes the heat flux directly radiated from the hot furnace to the calorimeter.

4.2.6 A balance is required to weigh the test-piece to the nearest 0,001 g.

4.3 Temperature measurement and calibration

4.3.1 The initial temperature of the test-piece in the furnace shall be measured by a Pt/Pt 13 % Rh (Type R) or Pt/Pt 10 % Rh (Type S) thermocouple manufactured in accordance with the manufacturing tolerance stated in HD 446.2 S2, allowing use of the reference tables in HD 446.1 S1, or alternatively calibrated in a manner traceable to the International Temperature Scale.

NOTE: For furnace temperatures above 1650 °C, other thermocouple types will be required.

A thermocouple is sited with its junction on the inside of the furnace tube in order to record furnace wall temperature. A similar thermocouple is placed inside a platinum capsule or a dummy test-piece. The furnace wall temperature is allowed to equilibriate for at least 15 min. The capsule or dummy test-piece is then raised or lowered through the thermal centre of the furnace in steps of not more than 10 mm in order to plot the temperature distribution. This procedure is used to establish the optimum position of the capsule or test-piece in the furnace and to calibrate the difference between capsule or test-piece and the furnace wall. This calibration is performed at a series of temperatures at intervals not exceeding 100 K up to the maximum furnace temperature, and is used as an indirect measure of initial test-piece temperature.

4.3.2 The procedure for a massive copper block calorimeter or similar device in which a temperature rise is recorded is as follows. The calorimeter temperature is measured using a platinum resistance thermometer (PRT) connected into an a.c. bridge circuit, on the opposite arm of which is a matching standard resistor kept at a known stabilized temperature ± 0,1 K, which may conveniently be the temperature of the controlled environment. In order to calibrate the calorimeter, a known electrical power is dissipated in the heating resistor for a known time period, Δt, determined either using a stopwatch or other calibrated timing device. The output of the a.c. bridge is monitored continuously and the data are recorded at intervals of not less than 30 s. The electrical input power is measured by recording the voltage, V, across the heating resistor, and across a series standard resistor to measure the current, I (Figure 3). A typical bridge output trace is shown in Figure 4. To determine the calorimeter calibration, the following procedure is used. The output curves X and Y are extrapolated as shown in Figure 4 using line-fitting routines. A time, t_{mid}, is chosen such that the areas A and B are equal. The output ΔV_e is taken as the distance between lines X and Y at time t_{mid}. The calibration factor for the calorimeter, C, is given by:

$$C = \Delta V_e / V.I.\Delta t \qquad (3)$$

in units of volts output per joule input. The value of C shall be taken as the mean of 10 determinations.

For an ice calorimeter, or other device operating at a fixed temperature, the same procedure is followed, except that the output response recorded and analysed is appropriate to the device, such as the fall in liquid level. The same basic principle shall be used.

4.3.3 To check that the apparatus is functioning correctly, and that the calibration procedure is accurate, the test may be performed with a reference material of known specific heat capacity. The usual material for performing this function is α-alumina (often in the form of sapphire single crystals), and appropriate data are given in annex A, reference 1.

4.4 Test determinations

Determine the mass of the test-piece, m_s (and of the capsule if used) to an accuracy of ± 0,001 g. Suspend the test-piece and/or capsule in the drop tube, and bring into position at the predetermined thermal centre of the furnace. Allow the test-piece temperature to equilibriate at the set furnace temperature such that there is no change in furnace wall temperature over a period of at least 15 min. Record this temperature, and read the test-piece temperature from the calibration curve.

Drop the test-piece into the calorimeter block through the radiation screen, ensuring that the screen is replaced as soon as the test-piece has passed. Record the output of the calorimeter as described in 4.3.2.

Repeat the test twice more at the same furnace temperature in order to determine a mean result. Repeat the procedure at other furnace temperatures as required.

4.5 Calculations

Calculate the total heat input to the calorimeter from the calorimeter calibration. The temperature change of the test-piece is calculated from:

$$\Delta T_s = T_{initial} - T_{final} \qquad (4)$$

where $T_{initial}$ is the test-piece temperature calculated from the furnace wall temperature by calibration, and T_{final} is the extrapolated calorimeter temperature at time t_{mid} determined from the calorimeter output, e.g. PRT temperature rise or liquid level fall.

Calculate the mean specific heat capacity, $\overline{c_p}$, over the temperature range ΔT_s from:

$$\overline{c_p} = \frac{\Delta H_s}{m_s . \Delta T_s} = \frac{\Delta V_{s+c} - \Delta V_c}{m_s . \Delta T_s . C} \qquad (5)$$

where:

ΔH_s is the heat content of the test-piece,
ΔV is the output change from the calorimeter determined by extrapolation to time t_{mid} for the capsule (subscript c) and for the test-piece + capsule (subscript s+c),
C is the calibration factor for the calorimeter.

Use this procedure for each test, and calculate the mean result for each temperature range. If required, the true specific heat capacity, c_p, may be determined as follows. The enthalpy data, ΔH_s over the temperature range, ΔT_s, from the final calorimeter temperature, T_f, is curve-fitted to the polynomial:

$$\Delta H = \overline{c_p} . \Delta T = a' T + b' T^2 + c' T^3 + d' T^{-1} \qquad (6)$$

where T is the temperature in K. Hence:

$$c_p = a' + 2b' T + 3c' T^2 - d' T^{-2} \qquad (7)$$