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CALIBRATION COEFFICIENT OF A HEAT-FLOW DSC
Part 1. Relation to the sensitivity of a thermocouple

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Abstract

Relation between the calibration coefficient of a DSC sensor $k(T)$ and the sensitivity of a thermocouple $\varepsilon(T)$ which the sensor is made from was derived from the analysis of a heat transfer inside a DSC cell. Ratio $\varepsilon(T)/k(T)$ is equal to $A+BT^3$. The first component depends on heat conduction and the second one on radiation.

The relationship was tested for DSC-204 Netzsch using (*i*) data on calibration *vs*. enthalpies of phase transitions (reference samples) and (*ii*) measurements of heat capacity of corundum. Both tests show very good agreement between experimental data and predicted theoretical function.

Keywords: heat conductivity, heat-flow calibration, radiation, sensor, thermocouple

Introduction

Heat-flow sensor in a DSC is made from a thermocouple. The sensitivity of a thermocouple (ε) depends on temperature and, hence, the calibration coefficient (k) of the sensor depends on temperature as well. But the functions $\varepsilon(T)$ and $k(T)$ differ from one another. Functions $k(T)$ for three calorimeters (DSC-30 Mettler, DSC-111 Setaram and DSC-204 Netzsch) are shown in Fig. 1. These were provided with manufacturers: Setaram and Netzsch use polynomials, Mettler showed a picture in the User's Manual. Function $\varepsilon(T)$ for thermocouple '*E*' is also shown in Fig. 1, for this thermocouple works as a sensor in DSC-204. The type of thermocouple in DSC-30 and DSC-111 was not indicated by the manufacturers. The difference between $\varepsilon(T)$ and $k(T)$ is evident. The former increases with temperature over the whole temperature range, but the latter increases at low temperatures reaching the maximum and decreases after.

There is no theory predicting correct value of the electromotive force (e.m.f.) for a thermocouple at a given temperature. It is conventional that function $\varepsilon(T)$ is measured and then used in a tabular or polynomial form. Similarly, the sensitivity of a

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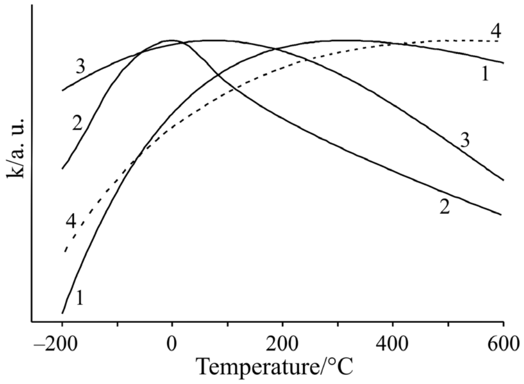

Fig. 1 Calibration coefficient as a function of temperature: 1 – DSC-111 Setaram; 2 – DSC-30 Mettler (metal sensor); 3 – DSC-204 Netzsch. For comparison, sensitivity of thermocouple '*E*' is shown (4)

sensor made from the thermocouple is measured and used in a polynomial form. No analytical functional relation between $\varepsilon(T)$ and $k(T)$ is there in the literature. In the recommendation of the working group 'Calibration of Scanning Calorimeters' of the GEFTA, no analytical expression for $k(T)$ is recommended, the graphics are discussed only [1].

The objective of this work was to develop adequate model explaining the difference between sensitivity of thermocouple and heat-flow sensor and to test it. The equation derived from the model is intended to be useful in the arrangement of a sensitivity calibration for heat-flow DSCs.

The model

A scheme of a DSC cell operating is shown in Fig. 2. Two crucibles, one with a sample (*S*) and one empty, i.e., reference (*R*), are at their positions. Thermocouple is positioned as close as possible to a bottom of a crucible to measure its temperature as correct as possible. At steady heating, the built-in furnace increases temperature of the

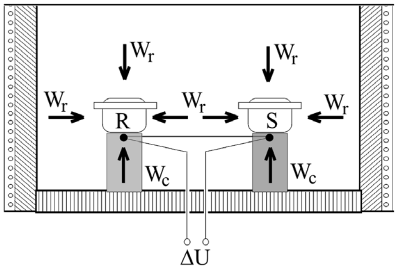

Fig. 2 Heat transfer to the crucibles, reference (*R*) and sample (*S*), inside a DSC cell at heating: W_r – radiation; W_c – heat conductivity. Voltage readings of a thermocouple: ΔU

DSC cell with a constant heating rate $\beta=\mathrm{d}T_F/\mathrm{d}t$. Temperatures of two crucibles, sample (T_S) and reference (T_R), increase nearly with the same heating rate but differ from one another at every moment: $T_F>T_R>T_S$. It is the heat transfer from overheated inner walls of the DSC cells toward underheated crucibles that increases their temperatures. Two kinds of energy act inside the cell and change the temperature of crucibles: 1) vibration of atoms constituting solids and 2) radiation. These provide also two kinds of heat transfer. Vibrational energy propagates by means of a direct contact between a source and recipient. Heat transfer is described by equation

$$\frac{1}{S}W_c=\frac{1}{S}\frac{\mathrm{d}Q}{\mathrm{d}t}=q=-\lambda\,\mathrm{grad}T, \tag{1}$$

where q is the rate at which heat Q crosses an area S, and λ is the coefficient of heat conductivity. For a crucible inside the DSC cell,

$$\frac{\mathrm{d}Q_1}{\mathrm{d}t}=\lambda S_1\frac{T-T_F}{l}, \tag{2}$$

where S_1 is the area of a contact between crucible and sensor, i.e. the area of a bottom of the crucible, l is the distance between a heat source and a sample holder.

Surface of a crucible simultaneously absorbs and emits radiation according to the Stefan–Boltzman equation

$$\frac{1}{S}W_r=\frac{1}{S}\frac{\mathrm{d}Q}{\mathrm{d}t}=\varepsilon\sigma T^4, \tag{3}$$

where ε is the emissivity of the substance which the crucible is made of ($\varepsilon=1$ for an ideal 'blackbody', $\varepsilon\cong0.85$ for oxidized metals and $\varepsilon\cong0.3$ for unoxidized metals, especially when they are polished), σ is the Stefan's constant ($5.6697\cdot10^{-8}$ W m^{-2} K^{-4}). The sum of energy change due to the radiation is

$$\frac{\mathrm{d}Q_2}{\mathrm{d}t}=\varepsilon\sigma S_2(T^4-T_F^4), \tag{4}$$

where S_2 is the area of a crucible exposed to the radiation.

Heat flow to the reference crucible is the sum of the two contributions:

$$W_R=\frac{\mathrm{d}(Q_{1R}-Q_{2R})}{\mathrm{d}t}=\varepsilon\sigma S_{2R}(T_R^4-T_F^4)+S_{1R}\frac{\lambda_R}{l_R}(T_R-T_F). \tag{5}$$

In a DSC, all the parameters for crucibles and sample holders are identical:

$$S_{1R}=S_{1S}=S_1,\ S_{2R}=S_{2S}=S_2,\ \lambda_R=\lambda_S=\lambda,\ l_R=l_S=l. \tag{6}$$

The difference in heat flow between sample and reference crucibles is

$$\Delta W=W_S-W_R=\varepsilon\sigma S_2(T_S^4-T_R^4)+S_1\frac{\lambda}{l}(T_S-T_R). \tag{7}$$

The formula can be transformed into linear expression of the temperature difference:

$$T_S^4 - T_R^4 = (T_S^3 + T_S^2 T_R + T_S T_R^2 + T_R^3)(T_S - T_R) \approx 4T^3 (T_S - T_R), \tag{8}$$

because

$$T_S - T_R = \Delta T << T_F \approx T_S \approx T_R. \tag{9}$$

The equation for the difference in heat flow is

$$\Delta W = \left(4\varepsilon\sigma S_2 T^3 + S_1 \frac{\lambda}{l} \right) \Delta T. \tag{10}$$

The temperature difference between two crucibles is measured with a thermocouple

$$\Delta T = \frac{\Delta U}{\varepsilon(T)} \tag{11}$$

where ΔU is the e.m.f. Now the relationship between heat flow and readings of a sensor is

$$\Delta W = \frac{4\varepsilon\sigma S_2 T^3 + S_1 \lambda / l}{\varepsilon(T)} \Delta U = \frac{1}{k(T)} \Delta U, \tag{12}$$

where $k(T)$ is the sensitivity of the sensor or the calibration coefficient of a heat-flow calorimeter. The values of S_1, S_2, ε, σ and l do not depend on temperature. Thermal conductivity depends on temperature but the functions $\lambda(T)$ differ for particular substances. It increases significantly at very low temperatures but changes slightly at elevated temperatures. In a temperature range of 200–900 K, λ increases for several metals and most alloys, decreases for most metals and several alloys, or is nearly constant for several metals and alloys. Most changes are within the limits of ±50%. The data for aluminium, constantan and inconel are listed in Table 1. Aluminium is a most suitable material for DSC crucibles, the alloys are used for the construction of sample holders [2]. As thermal conductivity changes with temperature much less than sensitivity of a thermocouple and radiation heat transfer, it is reasonable to consider λ constant. Now the calibration coefficient is

$$k(T) = \frac{\varepsilon(T)}{S_1 \lambda / l + 4\varepsilon\sigma S_2 T^3} = \varepsilon(T) \frac{1}{A + BT^3}. \tag{13}$$

Table 1 Thermal conductivity (in W m^{-1} K^{-1}) of selected materials as a function of temperature [4]

Material	Temperature/K							
	200	300	400	500	600	700	800	900
Aluminium	237	237	240	236	236	225	218	210
Inconel		11	12	14	15	17	19	20
Constantan		21	23	26	31	37		

Thus, the calibration coefficient of a heat-flow DSC is equal to the sensitivity of a thermocouple, which the sensor is made from, divided by sum $A+BT^3$. Shown in Fig. 1, the decrease of the calibration coefficient at elevated temperatures is the result of increasing radiation heat transfer.

Testing the relationship

Sensitivity of a thermocouple changes significantly with temperature but, fortunately, the function ε(*T*) is well known for conventional types of thermocouples. In DSC-204, function ε(*T*) for thermocouple '*E*' is used for the correction of measured values. This operation is built in the measuring procedure that is governed by controller TASC 414/4 and is used for all instruments operating with the latter [3]. Instead of true experimental data Δ*U*(*T*) at controller's input, a user receives corrected data

$$\frac{\Delta U(T)}{\varepsilon(T)}=\Delta T(T) \tag{14}$$

at controller's output. The calibration coefficient for the corrected DSC signal can be derived immediately from Eq. (10):

$$\Delta W=\left(S_1\frac{\lambda}{l}+4\varepsilon\sigma S_2 T^3\right)\Delta T=\frac{1}{k^*(T)}\Delta T=(A+BT^3)\Delta T \tag{15}$$

We can test the validity of the relationship between thermocouple sensitivity and calibration coefficient just checking how experimental data on the inverse of calibration coefficient for DSC-204 fit polynomial $A+BT^3$. The results of the testing are shown in Fig. 3. Here, two types of data are presented. Squares indicate the results of the calibration *vs*. phase transitions. The measurements were proceeded by the manu-

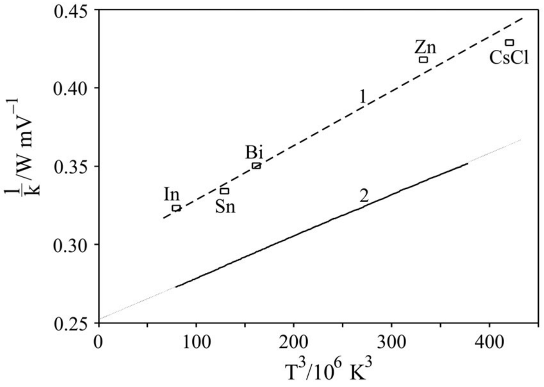

Fig. 3 Testing the calibration coefficient corrected for sensitivity of the thermocouple: the calibration *vs*. the enthalpies of phase transitions of reference materials (1) and that *vs*. heat capacity of corundum measured at scanning heating (2). Dashed line is a guide for eyes. Dotted line is a linear polynomial fitting the experimental data better than 1%

facturer in November, 2001. Dotted line indicates the fitting polynomial $A+BT^3$. We know nothing about the accuracy of the calibration measurements carried out by the manufacturer (number of runs, the standard deviation, quality of the standards, the order in which they were measured, etc.). Hence, we cannot conclude to what extent the difference between experimental data and fitting line is produced by experimental error or by inadequacy of the formula. Anyway, the difference is nearly equal to the random experimental error. This proves that the model explains relation between $\varepsilon(T)$ and $k(T)$ correctly.

The second type of data is a heat-capacity measurement of corundum. The experiment was carried out with a single crystal of Al_2O_3 (Reference Sample COTC-1a, distributed by the Physico-Technical and Radio-Technical Measurements Institute, Ural Branch). Seven runs with the crystal (sample mass 60.68 mg) and seven runs with empty crucible were performed at a heating rate of 15 K min^{-1} over the temperature range 350–720 K. At scanning heating, heat capacity is calculated according to formula

$$C_P(T)=\frac{1}{m}\frac{W}{\beta}=\frac{1}{m\beta}\frac{V_S(T)-V_B(T)}{k(T)}=\frac{1}{m\beta}\frac{\Delta T_S(T)-\Delta T_B(T)}{k^*(T)} \tag{16}$$

where m is the sample mass, W is the heat flow, β is the heating rate, V and ΔT are the readings (uncorrected and corrected, respectively) of a thermocouple-sensor. Subscribes S and B refer to the experiments with and without sample, respectively. Heat capacity of corundum is well known, and we can calculate the calibration coefficient according to

$$k^*(T)=\frac{1}{m\beta}\frac{\Delta T_S(T)-\Delta T_B(T)}{C_P(T)} \tag{17}$$

The results are shown in Fig. 3 as the solid line. The line fits to polynomial $A+BT^3$ with very high accuracy. The difference does not exceed 1%.

Two lines, the calibration *vs*. melting points and that *vs*. heat capacity, differ systematically from one another. This is the result of a drift in the sensitivity of the sensor of DSC-204. Users' Manual for DSC-204 recommends to make new calibration after two months. The heat capacity measurements were performed one year after the manufacturers' calibration. Intermediate calibrations produced the results falling in between these two lines.

The temperature range where the relationship between the calibration coefficient of a DSC and sensitivity of the thermocouple was tested is that most suitable for calorimetric investigations of molecular crystals and pharmaceuticals [5, 6].

Terms and units

Correcting the voltage readings of a sensor to the sensitivity of a thermocouple makes an unusual problem for users. Strictly speaking, $k^*(T)$ and $k(T)$ are measured in different units, K W^{-1} and V W^{-1}, respectively, because $\varepsilon(T)$ is measured in V K^{-1}. All handbooks on thermal analysis explain the operation of a sensor of a heat-flow DSC in terms of voltage as $\Delta V(T)$. Function $\Delta T(T)$ was never discussed. Probably, for the sake of convenience, Users' Manual and computer Help documents for Netzsch-204 operate only with convenient μV (measured and corrected signal) and μV mW^{-1} (calibration coefficient). This can be justified if we agree that fictitious function $\varepsilon^*(T)$ identical in value with $\varepsilon(T)$, but dimensionless, is used instead of the latter. Such a complicated consideration makes simultaneous correction of a DSC signal for thermocouple sensitivity and measuring the signal in volts accurate. Alternatively, we have to measure and discuss the corrected DSC signal in K (mK, μK, etc.) and the calibration coefficient in μK/mW.

Conclusions

Temperature functions for a thermocouple sensitivity $\varepsilon(T)$ and a calibration coefficient of a heat-flow DSC sensor $k(T)$ are related with one another. Ratio $\varepsilon(T)/k(T)$ equals to a function $A+BT^3$, where the first term deals with the heat transfer due to the heat conduction and the second one to the radiation. The coefficients A and B depend on the construction of a sensor and crucibles.

Experimental testing of the ratio $\varepsilon(T)/k(T)$ for DSC-204 was carried out using two ways of calibration: (*i*) enthalpies of the phase transitions in reference materials and heat capacity of corundum. The results prove that the relationship is valid.

This report is the first one of the series. Next reports will consider optimizing temperature calibration (an experiment and evaluation), calibration of $k(T)$ as a function of heating rate, and a relation between thermal event in a crucible and detected DSC signal.

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References

1 S. M. Sarge, E. Gmelin, G. W. H. Hohne, H. K. Cammenga, W. Hemminger and W. Eysel, Thermochim. Acta, 247 (1994) 129.
2 B. J. Holland, J. R. Atkinson and J. N. Hay, J. Therm. Anal. Cal., 69 (2002) 371.
3 J. Blumm and E. Kaisersberger, J. Therm. Anal. Cal., 64 (2001) 385.
4 Handbook 'Theoretical backgrownd of heating engineering. Experiment' Part 2, 2nd Ed., Energoatomizdat, Moscow 1988, p. 168 (in Russian).
5 E. V. Boldyreva, V. A. Drebushchak, T. N. Drebushchak, I. E. Paukov, Y. A. Kovalevskaya and E. S. Shutova, J. Therm. Anal. Cal., 73 (2003) 419.
6 P. Mura, F. Maestrelli, M. Cirri, S. Furlanetto and S. Pinzauti, J. Therm. Anal. Cal., 73 (2003) 635.