Thermochimica Acta, 187 (1991) 309–322
Elsevier Science Publishers B.V., Amsterdam

THEORETICAL INVESTIGATIONS OF THE HEAT TRANSFER AT QUANTITATIVE DSC-MEASUREMENTS AND ITS INFLUENCE ON THE DETERMINATION OF THE THERMAL AND CALORIMETRICAL PROPERTIES

W. Poeßnecker

Fraunhofer-Einrichtung für Keramische Technologien und Sinterwerkstoffe, Dresden(1)
Helmholtzstr. 20
0 - 8027 Dresden

ABSTRACT

In this work the deviations of measured calorimetrical DSC-signals and transition temperatures from their true values are mathematically calculated by exact analytical and numerical methods.

The obtained results can be used not only for a better understanding of the procedure of measurement but also for minimizing deviations.

Especially in the case of thermal deviations two procedures for obtaining the true transition temperatures are recommended.

1.INTRODUCTION

In a previons work of the author a theory of heat transfer at DSC measurements was developed [1], but this theory was related only to specific heat. In this work the influence of heat transfer on the phase transitions and transition temperatures will be taken into account, too.

---

(1) Institut für Pulvermetallurgie und Verbundwerkstoffe, 8027 Dresden, Helmholtzstraße 20

0040-6031/91/$03.50

2.PHYSICAL MODEL

2.1. Sample holder system

In this work an usual disk-shaped arrangement of the sample and sample holder is used [2], which is shown schematically at figure 1.

The pan and the sample are substituted by disks and the heat transfer coefficients have following meaning.

α_{1R} = heat transfer coefficient between sample holder and pan

α_{3R} = heat transfer coefficient between pan and sample

α_{2R} = heat transfer coefficient between sample an the surroundings

(α_{1R} and α_{3R} are inversely proportional to contact resistances, α_{2R} is proportional to heat dissipation to surroundings).

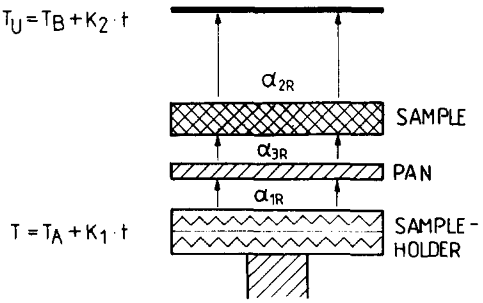


Fig. 1 Calculation model for the influence of the heat-transfer coefficients

The sample holder is heated according to

$$T = T_A + K_1 t$$

where

T_A = constant initial temperature of the sample holder
K_1 = heating rate
t = time

Thus heat flows from the sample holder through the pan and the sample to the surroundings with the temperature T_u.

This heat flux depends not only on the mentioned heat-transfer coefficients but also on heating rate, density, thickness, specific heat and heating conductivity of the pan and sample and on the specific transition heat if a phase transition is present. All these dependencies will be calculated in this work.

In the case of heat-conducting DSC the temperature T_u of surroundings is with $K_2 = K_1$ (see fig. 1)

$$T_u = T_B + K_1 \cdot t$$

and in the case of power compensated DSC the temperature T_u of the isoperibole surroundings is

$$T_u = T_B = \mathrm{const},$$

where in the case of the heat conducting DSC T_B is the constant initial temperature of surroundings and in the case of power compensated DSC the permanent constant temperature of surroundings.

This simplified one-dimensional arrangement is sufficient enough for a good thermophysical characterisation of the considered system.

2.2. REFERENCE SYSTEM

For increasing the sensitivity a reference system on the left side with the same capacity as the emty sample system on the right side is heated always in the same manner.

The sample system on the right side has the index R and the reference system on the left side has the index L. Thus the difference of heating fluxes in the right und left system is measured in the both DSC-methods.

For reducing the calculation effort in this work the power compensated DSC will be considered only.

2.3. ZERO SETTING PROCEDURE FOR DIFFERENTIAL SIGNAL OF HEAT FLUX

For emty pans in the sample system and in the left system the differential heat flux ΔW_o depends on the heat transfer coefficients α_{1L}, α_{2L}, α_{1R}, α_{2R}, α_{3R} in a complicated manner.

For simplifying the problem the following procedure is used (see fig. 2). In a first step a measurement without the sample is accomplished. By using slope correction and zero setting the differential signal $\Delta W_o \equiv 0$ is obtained.

In a second step a sample is inserted into the right system and the measurement of the first step is repeated under the same conditions. Then the obtained signal $\Delta W = W_p$ is representative for the pure thermophysical properties of sample only, that means the very complicated dependence of the differential signal on the heat transfer coefficients α_{1L}, α_{2L}, α_{1R} and α_{2R} is compensated if the values of α_{1R} and α_{2R} are exactly the same as in the first step. For the values of α_{1L}, α_{2L} and α_{1R} there is no problem because it is not necessary to alter the left and right system of empty pans before the second step.

After the second step complications may arise not only from the heat-transfer coefficient α_{3R} but also from a possible deviation of the value of α_{2R} between the first and second step.

If $(\alpha_{2R})_{(1)}$ is the heat transfer coefficient α_{2R} at the first step and $(\alpha_{2R})_{(2)}$ ist the heat transfer coefficient α_{2R} at the second step then a new effective heat transfer coefficient can be defined as

$$\alpha_{2e} = (\alpha_{2R})_{(2)} - (\alpha_{2R})_{(1)}$$

which has to be take into account after sloping correction and zero setting procedure in the first step.

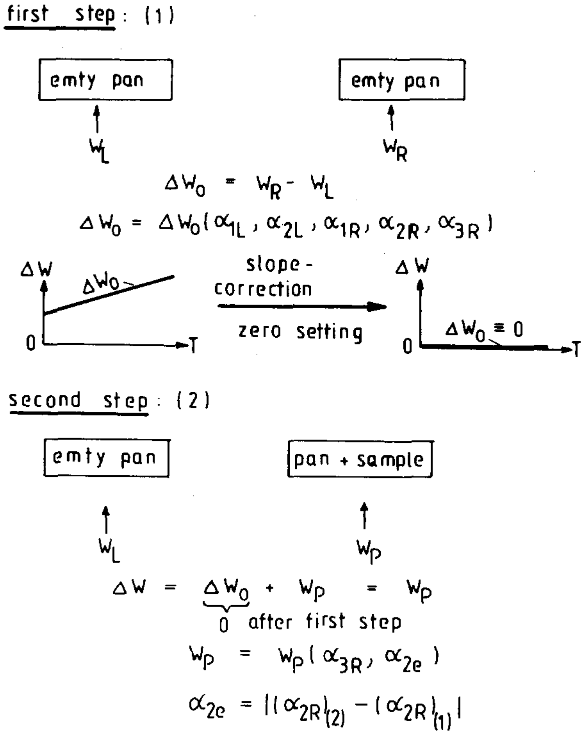


Fig. 2 Zero setting procedure

3. MATHEMATICAL SOLUTION

3.1. SPECIFIC HEAT

The parabolical initial-boundary condition problem of the third kind (see fig. 1) was solved by analytical and numerical methods.

The solution W(T) is the heating flux for heating the sample system with the heating rate K_1 from the constant initial temperature T_A to the constant final temperature T_E. $W(T_A)$ and $W(T_E)$ are the time independant heat fluxes for maintaining the constant temperatures T_A and T_E.

The deviations between analytical and numerial solutions are smaller than 10^{-4}% in temperature ranges where phase transitions are absent.

With the definitions

D_2 = thickness of sample D_1 = effective thickness of pan
λ_2 = heat conductivity of sample λ_1 = heat conductivity of pan
ρ_2 = density of sample ρ_1 = density of pan
c_2 = specific heat of sample c_1 = specific heat of pan

and the abbreviations

$a_1 = \lambda_1/(\rho_1 c_1)$ $a_2 = \lambda_2/(\rho_2 c_2)$
$h_1 = \alpha_{1R}/\lambda_1$ $h_2 = \alpha_{2R}/\lambda_2$
$h_{13} = \alpha_{3R}/\lambda_1$ $h_{23} = \alpha_{3R}/\lambda_2$

$a = h_2 h_{23} D_2 + h_2 + h_{23}$

$b = D_2 + h_2 h_{23} D_2^3/6 + (h_2 + h_{23})\ D_2^2/2$

$c = 1 + h_2 D_2$

$d = h_2 h_{23} D_2 + h_2 + h_{23}$

$e = D_2^2/2 + h_2 D_2^3/6$

$g = h_1 h_{13} D_1 + h_1 + h_{13}$

$r = D_1 + h_1 h_{13} D_1^3/6 + (h_1 + h_{13})\ D_1^2/2$

$s = a_2/a_1$

$A = g\ .\ a - h_{13} h_{23} c\ (1 + h_1 D_1)$

$E = (1/a_2)\ [gb - h_{13} h_{23}\ (1 + h_1 D_1)\ e] +$

$(1/a_1\ [dr - h_{13} h_{23}\ c\ (D_1^2/2 + h_1 D_1^3/6)]$

$z = (T - T_A)/K_1 - E/A$

the solutions are

$$W(T_A) = \frac{\lambda_2 \, T_A}{(1/h_{23}) \quad (1 + h_{13}/h_1 + D_1 h_{13}) + 1/h_2 + D_2} \tag{1}$$

$$W(T_E) = \frac{\lambda_2 \, T_E}{(1/h_{23}) \; (1 + h_{13}(h_1 + D_1 h_{13}) + 1/h_2 + D_2} \tag{2}$$

$$\begin{aligned} W(T) \; = & - (\lambda_1 h_1 K_1/A) \; [(h_{13} \; h_{23} \; c \; - \; h_{13} \; a) \; z \; + \\ & (1/a_2) \; (h_{13} h_{23} \; (e \; + \; s \; c \; D_1^2/2) \; - \; h_{13} \; b \; - \\ & s \; d \; (D_1 \; + \; h_{13} \; D_1^2/2))] \; - \; (1/\lambda_1) \; W(T_A) \end{aligned} \tag{3}$$

The expression W(T) is the equation of a straight line with the slope m_B and with the ordinate section W_o, therefore

$$W_B \; (T) = W_o + m_B \; T \tag{4}$$

W_o and m_B are functions of the thermophysical and geometrical parameters and of the heating rate and the heat-transfer coefficients according (3).

For $D_1 = 0$ and $\alpha_{1R} \text{ ---> } \infty$ the pure heat flux W_p into the sample without pan is obtained, which is necessary for the application of the procedure of zero setting (see 2.3.).

In the following this procedure will be used consequently.

Figure 3 shows a typical calculated heat flux curve.

For ideal heat contacts ($\alpha_{3R} \text{ ---> } \infty$) and adiabatic behaviour ($\alpha_{2e} \text{ ---> } 0$) no temperature dependence is visible and the signal has the ideal value (Fig. 3 (i))

$$W = W_s = D_2 \, \varrho_2 \, c_2 \, K_1$$

An example of ideal phase transition with the transition temperature T_s is shown, too.

For real heat contacts ($\alpha_{3R} < 0$) and heat dissipation to the isoperibole surroundings ($\alpha_{2e} > 0$) the quasistationary heat flux W(T) is temperature dependant (see Fig. 3 (ii)) and the signal $\Delta W = W_*$ is smaller than the ideal signal W_s.

The isothermal heat fluxes $W(T_A)$ and $W(T_E)$ do not disappear under real conditions, where

$$W(T_E) > W(T_A)$$

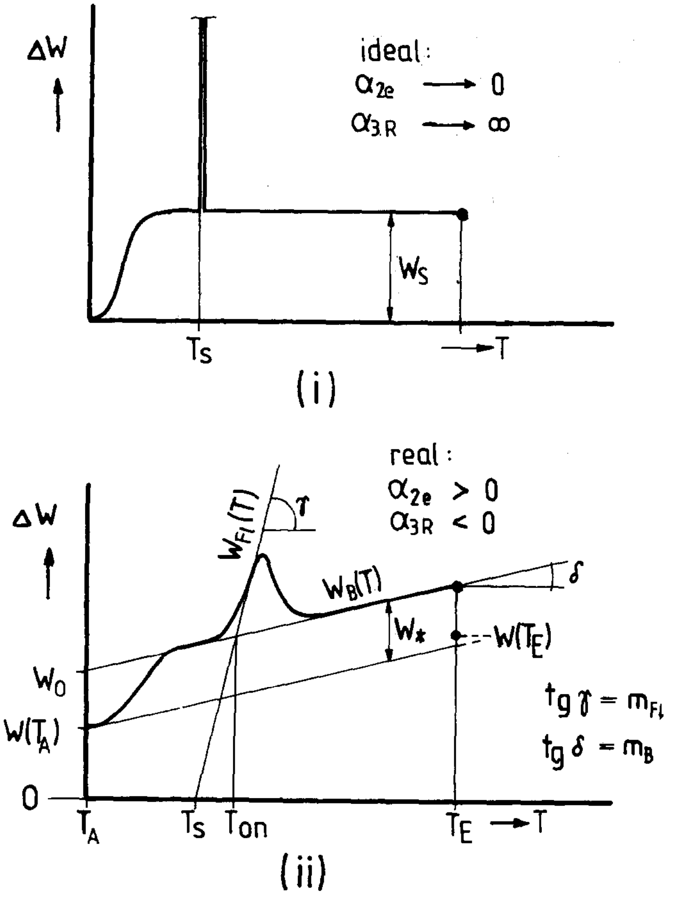


Fig. 3 Graphical representation of mathematical solution

The deviation of the real signal W_* from the ideal signal W_s is defined as

$$F = \frac{|W_* - W_s|}{W_s}$$

and the difference between $W(T_A)$ and $W(T_E)$ related to W_s is defined as isothermal distance

$$V = \frac{W(T_E) - W(T_A)}{W_s}$$

In figure 4 the deviation F is shown as a function of isothermal distance V at different values of α_{2e} and α_{3R}.

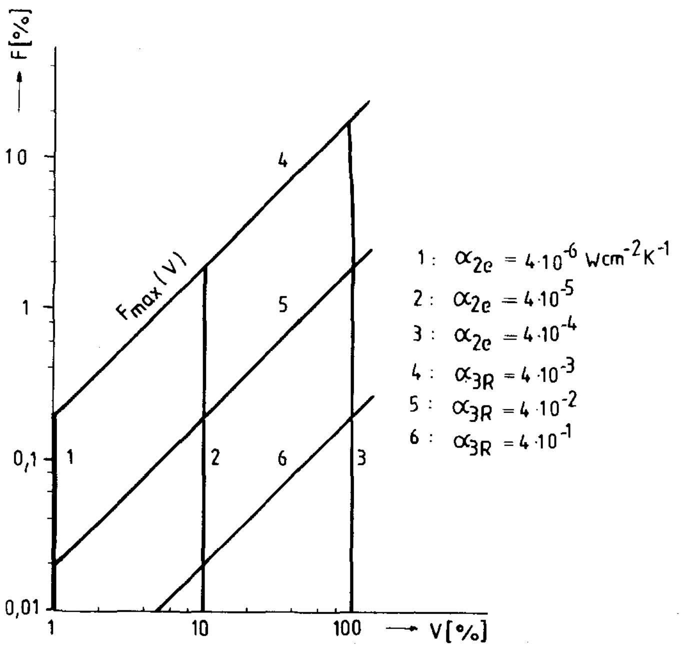


Fig. 4 Deviation F between true and real calorimetrical signal as a function of isothermal distance

It is seen that the deviation F can be hold small (for example $F \leq 0,2\ \%$) for two conditions:

1. strong dissipation of heat (curve 3) with very good heat contacts (curve 6)

2. small dissipation of heat (curve 1) with any heat contact (for example curve 4 which represents very poor heat contact)

On the other side the deviation F can be very great if there are very poor heat contacts (curve 4) and great heat dissipation (curve 3), therefore F = 17 % for the crossing point of the curves 3 and 4 will be reached. It can be also seen that only the maximal values $F_{max}(V)$ caused by maximal heat resistances ($\alpha_{3R} = 4 \cdot 10^{-3}\ Wcm^{-2}K^{-1}$) have a unambigous relation to the isothermal distance V(here represented by curve 4). For smaller heat resistances there is no such unambigous relation between F and V.

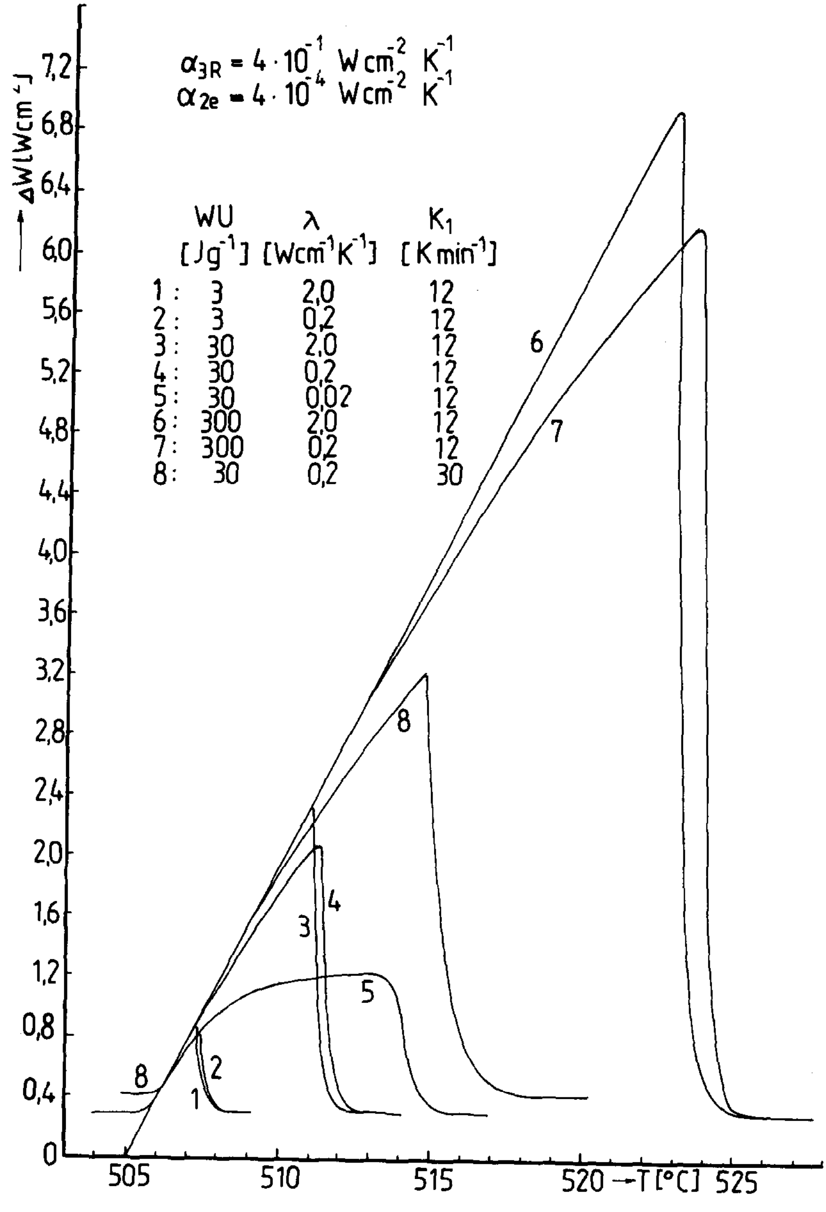
An influence of the heat conductivity and of the heating rate on the value of F was not found.

3.2. TRANSITION HEATS AND TRANSITION TEMPERATURES

The true value of specific transition energy is generally not influenced by the thermophysical and geometrical properties of sample neither by the heating rate and the heat-transfer coefficients. Only the shape of the DSC-signal is modified. Figure 3 (ii) shows schematically and figure 5 precisely the deformation of the originally very sharp transition mainly caused by small values of α_{3R}. Under the supposition of using the zero setting procedure (see 2.3.) the slope at the point of inflexion of the ascending parts of the transition curves is in every case equal to α_{3R} independently from heat capacity, specific transition energy, heat conductivity and heating rate (see fig. 5) for small heat capacities especially.

The tangent at the point of inflexion cuts the zero line exactly in the true transition temperature T_s, which is here 505°C.

It is remarkable that for smaller values of heat conductivity the slope decreases more or less near the maximum of the ΔW-signal (see curves 2, 4, 7, 8 and especially curve 5).



	WU [J g^{-1}]	λ [W cm^{-1} K^{-1}]	K_1 [K min^{-1}]
1 :	3	2,0	12
2 :	3	0,2	12
3 :	30	2,0	12
4 :	30	0,2	12
5 :	30	0,02	12
6 :	300	2,0	12
7 :	300	0,2	12
8 :	30	0,2	30

Fig. 5 Numerically calculated transition shapes under different conditions

In figure 6 the relations between the true transition temperature T_s, the extrapolated onset temperatures T_{on} and different values of spezific heat, density, heating rate and heat-transfer coefficients are presented, because the height of every baseline A, B, or C is proportional to spezific heat, density, heating rate and the heat-transfer coefficient α_{2e}.

The higher the baseline the greater the difference between T_s and T_{on}.

The smaller the value of α_{3R} the smaller the slope and therefore the greater the shifting of T_{on} to higher temperatures. (See the slopes labelled by I and II).

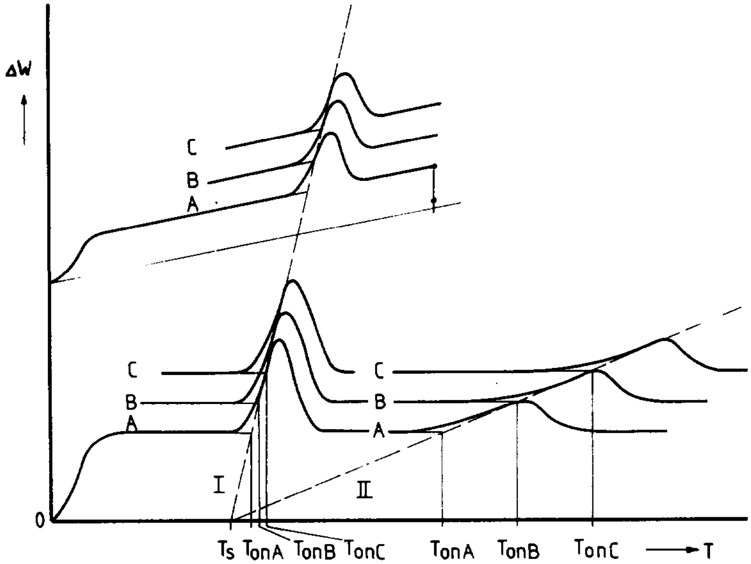


Fig. 6 Relations between true transition temperature, onset temperatures, thermophysical properties, heating rates and heat-transfer coefficients (schematically)

3.3. THEORETICAL DETERMINATION OF THE TRUE TRANSITION TEMPERATURE T_s

3.3.1. ZERO-CUT-METHOD

The equation for the tangent at the point of inflexion has in every case the form (see fig. 3)

$$W_{FL}(T) = \quad 3R\,(T - T_s) \tag{5}$$

For $W_{FL}(T) \equiv 0$ follows

$$T = T_s$$

Thus the crossing point of (5) with the axis $W \equiv 0$ represents the true transition temperatur T_s for all cases.

3.3.2. CROSSING-POINT-METHOD

The crossing point of the baseline (4) with the tangent (5) at the inflexion point is the onset temperatur T_{on}.

From (4) and (5) follows

$$T_{on} = \frac{m_{FL} \cdot T_s + W_o}{m_{FL} - m_B} \quad \text{or} \tag{6}$$

$$T_s = \frac{T_{on}\,(m_{FL} - m_B) - W_o}{m_{FL}} \tag{7}$$

Every DSC-measurement with a phase transition produces T_{on}, m_{FL}, m_B and W_o. Thus it is possible to determinate T_s also in this manner.

4. CONCLUSION

As shown in this work, the DSC-measurement produces neither true calorimetrical signals for determination of specific heat nor the true transition temperatures.

Whereas it is impossible to reconstruct the true calorimetrical signal from the measured signal, the determination of the true transition temperatur from the measured values can be accomplished at the same measurement independently from mass, heat capacity, heating rate and heat-transfer coefficients. This has the consequence of a remarkable simplification of the determination of transition temperatures and of a essential improvement of precision at the same time. Up to now it has been usual to measure the onset temperature at very many masses and heating rates for determination the true transition temperature by extrapolating the mass and the heating rate towards zero.

With the theoretically derived methods of the zero-cut-method and the crossing-point-method it is easy to develop a suitable software for precise und quick calculation of the true transition temperatures instead of using the time consuming onset methods.

5. REFERENCES

[1] W. Poeßnecker, Journal of Thermal Analysis, Vol. 36 (1990), 1123 - 1139

[2] Hemminger/Höhne, Grundlagen der Kalorimetrie, Verlag Chemie, Weinheim, New York, 1979