Note

A SYSTEMATIC ERROR IN THE TEMPERATURE DETERMINATION OF A DTA EFFECT BY USING THE ONSET POINT

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The Committee on Standardization of the ICTA proposed a method for determination of the temperature of a DTA effect. This procedure is easy to perform, but leads to a systematic deviation from the true value. It is demonstrated that this deviation depends on the heating or cooling rate and the thermal conductivity of the sample.

In the report "Requirements and Realization on Thermal Analysis Standards" [1] the Committee on Standardization of the International Confederation for Thermal Analysis proposes a procedure for determination of the temperature of a DTA effect. It is recommended [1, 2] to use the point of intersection of the tangent drawn at the point of greatest slope of the leading edge of the DTA peak with the extrapolated base line. This procedure is easy to perform, but the temperature determined in this way (the onset temperature, T_{on}) differs from the true value.

The deviation

It will be shown that the temperature should be determined by the point where the DTA curve departs from the base line for the first time (this point will be defined as the departure point and the deduced temperature as the departure temperature, T_{Ab}). Experiments have shown that $T_{on} > T_{Ab}$ ($T_{on} < T_{Ab}$) for any heating (cooling) programme, that T_{Ab} is independent of the temperature programme, and that T_{on} depends on the thermal conductivity of the sample.

To study these observations systematically, differential thermal analysis of the metals Ag, Al, Zn, Sn and Pb was performed up to temperatures above their melting points. The melting of metals was chosen since all material constants involved [3] are well-known, the influence of particle size and porosity of a powder sample can be excluded, and the interpretation of the curves is easy because of the large thermal effects associated with melting.

The experiments were performed in the Thermoanalyzer TA1 [4] (Mettler Instrumente A. G.). The low-temperature furnace (25 – 1000 °), the crucible holder DTA 22 (for one experiment DTA 20), an Al_2O_3 crucible, and platinum as reference material were used. All runs were made in an argon atmosphere. The following results were obtained:

1. T_{Ab} is independent of the heating rate.*

2. The difference $T_{on} - T_{Ab}$ is proportional to the heating rate. This was deduced from the melting curves of lead (see Fig. 1). The runs were performed varying only the heating rate of each run.

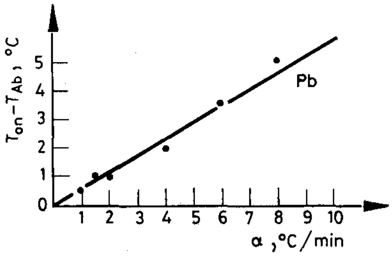

Fig. 1. The difference $T_{on}-T_{Ab}$ as a function of the heating rate α for the melting of lead (crucible holder DTA 20)

3. Table 1 shows the influence of the thermal conductivity λ of the sample (λ is the conductivity of the sample before melting). To exclude the influence of the heating rate, the slope m of the curve $T_{on} - T_{Ab}$ versus heating rate α is used. Table 1 shows that m is small (great) for materials with high (low) conductivity.

Explanation for the difference $T_{on} - T_{Ab}$

To explain these results, the progress of melting in time will be analyzed using the following assumptions: the temperature of the sample surface is equal to the programme temperature; the thermocouple is located in the center of the sample; the transition is endothermic; only a heating programme will be considered.

If the temperature distribution of the steady state and therefore the base line are established (see equations 20 and 21 in [6]), the temperature inside the sample is always lower than the surface temperature. If the surface temperature is equal to the transition temperature, the phase change starts at the surface. While the surface is heated according to the programme, the phase boundary moves towards the center of the sample. During this process the area of the new phase is separated from the starting phase by the moving phase boundary and the thermocouple is enclosed by the phase boundary. The heat flows from the surface to the center, but most of the energy is needed for the transition. Therefore, less heat flows from the phase boundary to the center and in the area enclosed by the boundary the sample thermocouple shows a slower increase in temperature than the reference temperature, and thus a DTA effect will be detected.

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* Numerical simulation of DTA effects [5] showed that the departure point is independent of the geometry, the heat of transition, the material constants involved, and their change after melting.

When the surface temperature of the sample is equal to the transition temperature and the phase transition starts, the heat flow to the center is delayed, and the DTA curve departs from the base line. Thus, the departure point shows the beginning of the transition and it is obvious that the departure temperature must be independent of sample mass, heating rate, geometry, and material constants.

A DTA curve normally consists of five characteristic parts:

a. the base line before the effect starts;
b. the initial part of the DTA curve, in the form of a curvature beginning at the departure point and going asymptotically to
c. a straight line;
d. an exponential part [7, 8] when the transition is finished and the DTA curve returns to
e. a (new) base line.

The curvature (b) and the straight line (c) can be explained easily: During the transition the heat flow towards the center of the sample is delayed so that in the area enclosed by the phase boundary the temperature distribution tends to equalize (b and c). Soon the temperature changes in this area become so small that the termocouple cannot detect them any more. A constant signal is measured (c) while the reference temperature rises with $T_R(\vec{r}', t) = \alpha t + f(\vec{r}')$ [6] (T = temperature, R = reference, $\vec{r}'$ = position of the reference thermocouple, t = time, α = heating rate, f = a function dependent only on the position $\vec{r}'$). The DTA signal δ is

$$\delta = T_S - T_R \approx T_P - \alpha t - f(\vec{r}') = \text{const.} - \alpha t$$

(S = sample, T_P = transition temperature), until the phase transition is finished.

A similar analysis can be made without the assumptions made before. The qualitative results will be the same.

Conclusions

The curved part of a DTA curve between the departure point and the beginning of the straight line depends on the conductivity of the new phase, the heating or cooling rate, the sensitivity of the thermocouple, and probably the heat of transition.

If a transition temperature is determined by constructing the onset point [1, 2], the initial curved part of the DTA curve is neglected, i.e. the starting period of the transition is neglected, and the onset temperature must have a deviation from the true value of the transition temperature. In principle the departure temperature is the correct one for the determination of the transition temperature, but in most cases its determination is difficult. For practical reasons, therefore, it is

Table 1

The slope m of the curve $T_{on}-T_{Ab}$ versus heating rate as a function of the thermal conductivity λ of the sample [3]

Sample	λ watt/cmK	m, min
Ag	3.55	0.1
Al	2.11	0.5
Zn	1.00	0.5
Sn	0.66	1
Pb	0.31	2
SiO_2*	0.04	2.5

* SiO_2 powder, α-β transition

better to use the onset temperature. In order to make the error of this procedure small, the following points should be considered:

I. The heating or cooling rate must be as small as possible.

II. If samples with low thermal conductivities are examined the systematic deviation is large. For calibration one should choose a material with a similar conductivity.

III. The standard deviation characterizes only the reproducibility of the experiments. Additionally, the systematic deviation should be taken into consideration.

If the experimenter pays attention to these points the procedure based on the onset point [1, 2] is a simple, fast, and good way to determine the temperature of a DTA effect.

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