INTERPRETATION OF THE THERMAL CURVE IN
DIFFERENTIAL THERMAL ANALYSIS

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On the basis of an analysis of the heat transfer between samples and the surrounding medium, principles are formulated for the correct interpretation of the thermal curves in DTA. The influence of the type of phase transformation and the test conditions on the form of the thermal curve is shown.

Thermal analysis is one of the most traditional and, to date, the most effective methods of physicochemical analysis. Improvement in the instrumentation by which the method is carried out has been continuous. In this connection, it is of interest to investigate the possibility of improving the accuracy of thermal analysis by refinements in certain long-standing practical principles which are used in interpreting thermal curves.

In thermophysical terms, thermal analysis is a means of obtaining information on the changes of a material by observations of the thermal effects accompanying these changes. In what is called quantitative analysis, the thermal effect and temperature range of the transformation are recorded, and in qualitative analysis only the temperature at the beginning and end of the transformation.

According to the traditional scheme of differential thermal analysis, the test sample and a comparison sample (the standard) are placed in an identical position with respect to the heat source. The heat-source temperature varies monotonically (and in the optimal case at a constant rate). The temperature difference between the samples is recorded as a function of time or the temperature of one of the samples. The nonmonotonic behavior of this curve is used to identify the temperatures at the beginning and end of the thermal effect in the sample.

In the region of the transformation, the thermal curve has the shape of a bell or peak, the base of which is the "base line" corresponding to the background level of the thermal curve. The beginning, end, and maximum of the bell (peak) are usually taken as the characteristic points. The following interpretations of the physical meaning of these points, while not entirely correct (as will be shown below), are fairly widespread.

The point corresponding to a maximum distance of the thermal curve from the base line is the most controversial. It is often called the main characteristic temperature of the transformation (most of the thermal curves in [1] were interpreted in this way, for example). It has also been suggested that it corresponds either to the end of the transformation or to the temperature at which the rate of transformation is a maximum (a review of several works adopting one viewpoint or the other is given in [2]). The point at the end of the bell-shaped curve is often interpreted as the temperature of the end of the transformation [3]. The point at which the bell-shaped curve begins has been subject to the least disagreement; many authors have correctly identified it with the temperature at which the transformation begins [3].

The temperature of the heat source (t_i), the test sample (t_s), and the comparison sample (t_c) are important for the analytic description of heat-transfer processes in thermal analysis. Heat transfer between the heat source and the samples is determined by the temperature difference and the thermal resistance R.

The thermal scheme in which the resistance R is realized in the layer external to the sample is the most unambiguous for analytical description and also potentially the most accurate; this resistance is much larger than the internal resistance of the sample. This scheme is most often realized in explicit form in testing metallic materials. In [4], e.g., metallic test samples and comparison samples were placed inside a metallic case, and were insulated from it by asbestos padding. Essentially the same scheme is realized in many industrial setups for different thermal analysis (DTA), in which the samples are placed, independently, in a fur-

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Fig. 1. Effect of intensity distribution of thermal effect in the temperature range of the transformation on the form of the thermal curve ($Q = 400°K$, $\Delta = 10°K$); φ is a dimensionless quantity; δ, $°K$; $t_s - T_i$, $°K$; I-VI) thermal-curve variants (see Table 1).

nace in crucibles.* In this case the evacuated or gas-filled space between the furnace and the crucibles makes the main contribution to R.

However, in apparatus in which the test and comparison material directly fills a depression in a highly heat-conducting heated block [5], the layer of the sample itself should be taken as R. In this case the analytical description of the heat-transfer process is complicated, and the number of parameters affecting the process is increased.

If the thermal scheme is optimal, the heat-balance equations for the test and comparison samples take the form

$$A\,(c_s + q)\,\frac{dt_s}{d\tau} = \frac{1}{R}\,(t_i - t_s), \tag{1}$$

$$Ac_c\,\frac{dt_c}{d\tau} = \frac{1}{R}\,(t_i - t_c), \tag{2}$$

where $q = dQ/dt_s$.

Introducing the notation $\delta = t_s - t_c$, $\varphi = (c_s + q)/c_c$, and $\Delta = t_i - t_c$, Eqs. (1) and (2) yield the result

$$\varphi\left(1 + \frac{d\delta}{d\tau_c}\right) = 1 - \frac{\delta}{\Delta}. \tag{3}$$

In Eq. (3), one may set $t_c \sim b\tau$, $\Delta = \text{const}$.

The accuracy with which these conditions are satisfied increases as the thermal conditions in the system approach regular conditions of the second kind. Then, for the initial condition $\delta = \delta_0$ when $\tau = 0$, the solution of Eq. (3) in the temperature range in which $\varphi = \text{const}$ takes the form

$$\delta = [\delta_0 + \Delta\,(\varphi - 1)]\exp\,(-\tau b/\varphi\Delta) - \Delta\,(\varphi - 1). \tag{4}$$

If the intensity of the thermal effect is constant in the temperature range of the transformation, then for $\delta_0 = 0$ the thermal curve in this range is described by the dependence

$$\delta = -\Delta\,(\varphi - 1)[1 - \exp\,(-\tau b/\varphi\Delta)]. \tag{5}$$

For the purpose of the subsequent discussion, the section of the thermal curve which follows the temperature range of the transformation will be called the aftereffect section. Note that the beginning of this section and, correspondingly, the moment when q becomes zero, correspond to a nonzero value of δ. Denoting this moment of time by τ_f, the following expression is obtained for the description of the aftereffect section (for

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*See, e.g., the descriptions of analyzers in the catalogues of the companies Setaram, Netzsch-Gerätebau, Mettler, Linseis, etc.

TABLE 1

Variant No.	Dependence of φ on sample temp. (form of the function)	values of coefficients	Tem. corresponding to max. q	Q', °K	Tem. range of transformation, °K	Δ, °K	$T_i'-T_i$, °K	$T_f'-T_f$, °K	T_m-T_i, °K
I	$\varphi-1=M=\text{const}$ $T_i \leqslant t_s \leqslant T_f$	$M=10$	$T_i - T_f$	400	40	5 10 50	0 0 0	62 112 388	40 40 40
		$M=20$		800	40	5 10 50	0 0 0	76 147 466	40 40 40
		$M=20$		400	20	5 10 50	0 0 0	84 131 410	20 20 20
II	$\varphi-1=Nt$ $T_i \leqslant t \leqslant T_f$	$N=0,5$	T_f	400	40	5 10 50	0 0 0	71 104 409	40 40 40
		$N=1$		800	40	5 10 50	0 0 0	81 155 491	40 40 40
		$N=2$		400	20	5 10 50	0 0 0	77 129 436	20 20 20
III	$\varphi-1=M-Nt$ $T_i \leqslant t \leqslant T_f$	$M=20$ $N=0,5$	T_i	400	40	5 10 50	0 0 0	58 108 396	23 27 34
		$M=40$ $N=1$		800	40	5 10 50	0 0 0	87 137 474	27 29 36
		$M=40$ $N=2$		400	20	5 10 50	0 0 0	79 123 409	14 16 19
IV	$\varphi-1=Nt$ $T_i \leqslant t \leqslant \dfrac{T_f-T_i}{2}$ $\varphi-1=M-Nt$ $\dfrac{T_f-T_i}{2} \leqslant t \leqslant T_f$	$M=40$ $N=1$	$\dfrac{T_f-T_i}{2}$	400	40	5 10 50	0 0 0	62 108 394	32 33 37
		$M=80$ $N=2$		800	40	5 10 50	0 0 0	87 145 462	32 33 35
		$M=80$ $N=4$		400	20	5 10 50	0 0 0	74 121 403	17 18 19
V	$\varphi-1=M-N\left(t-\dfrac{T_f-T_i}{2}\right)^2$ $T_i \leqslant t \leqslant T_f$	$M=15$ $N=3/80$	$\dfrac{T_f-T_i}{2}$	400	40	5 10 50	0 0 0	62 111 400	33 36 38
		$M=30$ $N=3/40$		800	40	5 10 50	0 0 0	86 143 480	34 37 39
		$M=200/9$ $N=1/15$		400	20	5 10 50	0 0 0	74 122 411	19 20 23
VI	$\varphi-1=\exp(Nt-M_1)$ $T_i \leqslant t \leqslant \dfrac{T_f-T_i}{2}$ $\varphi-1=\exp(-Nt+M_2)$ $\dfrac{T_f-T_i}{2} \leqslant t \leqslant T_f$	$M_1=9,9$ $M_2=20,5$ $N=0,76$	$\dfrac{T_f-T_i}{2}$	400	40	5 10 50	10,5 11,0 11,5	74 134 550	25 26 28
		$M_1=9,9$ $M_2=21,9$ $N=0,795$		800	40	5 10 50	11,0 11,5 12,0	111 178 546	26 27 29
		$M_1=9,9$ $M_2=21,9$ $N=1,59$		400	20	5 10 50	6,0 6,5 7,0	121 199 606	12 14 17

*The dependence of φ on the sample temperature is shown graphically in Fig. 1.

$\varphi = 1$ and $\delta(\tau_f) = \delta_f$

$$\delta = \delta_f \exp\left[-\frac{(\tau-\tau_f)b}{\Delta}\right].\tag{6}$$

In the case of an arbitrary intensity distribution of the thermal effect, in the temperature range of the conversion the thermal curve may be calculated by dividing this range into sections with constant values of φ.

Calculations are made on a Mir-2 computer to illustrate the effect of the intensity distribution of the thermal effect on the form of the thermal curves. In Fig. 1 thermal curves with different heat-absorption
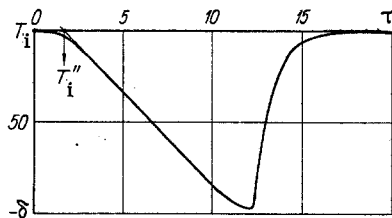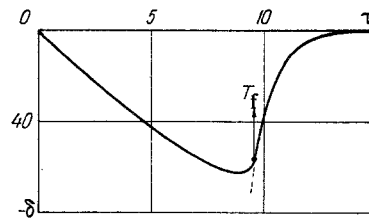
Fig. 2. Temperature at the beginning of transformation as determined using linear extrapolation (variant VI, $Q = 400°K$, $\Delta = 10°K$, $b = 10°K/sec$): $T_i'' - T_i = 13°K$, $T_i' - T_i = 10$, 5 and $8°K$ with the deviation from the zero line fixed at 0.5 and 0.1% of the maximum value δ, respectively, δ, °K; τ, sec.

Fig. 3. Temperature at the end of the transformation as determined using extrapolation of the aftereffect section (variant III, $Q = 400°K$, $\Delta = 10°K$, $b = 10°K/sec$). The dashed curve indicates exponential extrapolation.

laws are shown for constant Q and temperature range of the transformation. The value of Q is fixed by specifying the parameter $Q' = \int_{T_i}^{T_f} \varphi dT$.

The value of Q', equal to 400°K, and the temperature range of transformation (40°K) approximately correspond to the characteristic values of these quantities in the melting of a series of nickel—chromium alloys. To show the effect of the rate of heating b and the value of R on the form of the curves and their characteristic points, calculations are made for $\Delta = 5, 10, 50°K$. Results for the case $\Delta = 10°K$ are shown in Fig. 1.

Increase in Δ is equivalent to increase in the rate of heating at fixed R and increase in R at fixed rate of heating. The thermal effect and the temperature range of transformation are also varied.

The results of an analysis of the thermal curves obtained are shown in Table 1, in which the temperatures at the beginning (T_i) and end (T_f) of the transformation are compared with the temperatures at the beginning (T_i') and end (T_f') of the deviation of the thermal curve from the base line. In the asymptotic approach to this line, the characteristic point was found at a deviation from the line amounting to 0.5% of the largest (in modulus) value. The temperature corresponding to the maximum intensity of the thermal effect and also the temperature T_m corresponding to the maximum (in modulus) value of δ are shown. The temperature point T_i is taken as the origin.

Analysis of the heat transfer between the samples and the surrounding medium in DTA leads to the following conclusions regarding the treatment of the thermal curve.

1. The temperature at the beginning of the transformation corresponds to the point at which the thermal curve deviates from the base line extrapolated from the temperature range preceding the transformation.

The levels of the base line before and after transformation often differ [6]. The ineradicable cause of this is the difference in the specific-heat ratio of the samples before and after transformation. In interpreting the beginning of the transformation, accordingly, only the section of the curve preceding transformation should be taken into account.

It should be emphasized that there is no physical basis for the widely used method of finding the temperature at the beginning of transformation as the point of intersection of the base line with the rectilinear extrapolation of the section of the thermal curve which deviates from it. The thermal curve corresponding to variant VI in Table 1 is shown in Fig. 2, where the point T_i'' corresponding to this method is indicated. Note that the improvement in accuracy obtained by using the method of determining the temperature at the beginning of the transformation proposed in the present work rather than the traditional method increases with increase in the sensitivity with which the thermal curve is recorded.

2. The characteristic element of the thermal curve is the section following the temperature range of transformation, for which the term aftereffect section has been proposed. On this section the temperature difference between the samples varies exponentially with time.

The temperature at the end of transformation may be determined by noting that it coincides with the beginning of the aftereffect section. This temperature may be found as the point at which extrapolation of the aftereffect section toward the temperature range of transformation leads to deviation from the thermal curve (point T_f in Fig. 3). It is expedient to align the dependence in semilogarithmic coordinates [7].

3. The temperature corresponding to the maximum deviation of the thermal curve from the base line, the temperature of the maximum, is not a characteristic temperature of the transformation in the general case. It lies in the range $T_i \leq T_m \leq T_f$; its value depends both on the type of transformation and on the test conditions (see Fig. 1 and Table 1). In particular cases, T_m may coincide with the temperature at the end of the transformation, for example, for the intensity distribution of the thermal effect in variants I and II of the calculation, or with the unique characteristic temperature of the transformation (for invariant transformations).

With increase in heating rate and the size of the thermal effect, T_m may shift toward higher temperatures (increase in T_m with increase in Δ and Q' in variants III–V of Table 1).

No unique correspondence is observed between the temperature T_m and the temperature (temperature range) of maximum heat–liberation intensity.

4. The temperature at the "end" of the thermal curve T_f' is a fundamentally undetermined point on the exponential section of the curve. It is not a characteristic temperature of the transformation, and falls outside the limits of the transformation range: in the case of heating, $T_f' > T_f$. With increase in heating rate, the point T_f' is shifted toward higher temperatures (increase in T_f' with increase in Δ; see Table 1). This had more than once been established experimentally, e.g., in [8]; however, this is usually associated with change in the character of the processes occurring in the test material.

Because of the relation noted between Δ and R, it has been established that the increase in T_f' may also be the result of deterioration in heat transfer between the samples and the heat source. The point T_f' is shifted in the same direction with increase in the thermal effect; the shift is larger for T_f than for the temperature range of transformation (see Table 1).

In conclusion, note that in real experiments the form and interpretation of the thermal curves may be complicated by a series of factors whose effects were assumed to be small in considering the optimal thermal scheme. Among these are the presence of a temperature distribution over the cross section of the test sample and heat absorption in the layer at which the thermal resistance R is realized.

NOTATION

t_i, t_s, t_c, temperature of the heat source, the test sample, and the comparison sample, respectively; δ, temperature difference between the test sample and the comparison sample; Δ, temperature difference of the heat source and the comparison sample; τ, time; b, heating rate; T_i', t_i, initial and final temperatures of the deviation of the thermal curve from the base line; T_m, temperature of maximum deviation of the thermal curve from the base line; T_i'', temperature at the beginning of the transformation determined by the traditional method; A, coefficient taking account of the geometric factor; R, thermal resistance; c_s, c_c, specific heat of the tests sample and the comparison sample; Q, volumetric thermal effect of transformation; q, intensity of thermal effect referred to unit volume; T_i, T_f, temperature at the beginning and end of transformation.

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