A NEW TYPE OF QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

In this paper we report a new type of quantitative differential thermal analysis in which the temperature gradient within the thermal barrier surrounding the sample cell is measured with a thermopile. The heats of transformation obtained with this apparatus are in good agreement with the reported ones. The sample weight is decreased, and the sensitivity, the thermal response time and the accuracy are improved considerably.

INTRODUCTION

In the forties, several theories on heat measurement with differential thermal analysis (DTA) were set forth[1-4]. In the most of them, the possibility of the heat measurement with DTA is postulated without considering temperature distribution within a sample. However, in the fifties some critical views against the possibility were advocated[5-7]. The views are confirmed by the mathematical analysis of heat flow within the sample. The problem to be considered is what the temperature difference recorded in DTA is. According to their theories, the temperature difference is the difference between the temperature gradient within the sample and that within the reference material. Although the peak area becomes proportional to the heat of transformation, the proportionality coefficient depends upon the apparent thermal conductivity and the geometry of the sample. Then, the proportionality coefficient is not the coefficient characteristic of the apparatus, but the coefficient varying run by run. In the early theories postulated the possibility of the heat measurement, the coefficient is misunderstood *a priori* to be the constant independent on the thermo-physical properties of the sample and on the temperature, but it is hypothetically regarded as a constant only for the mathematical treatment of a particular run of a given sample.

In the sixties new devices were made on the apparatus and a few experimental evidences on the possibility are published with the new apparatus by David[8] and by Barrall II *et al.*[9]. In a previous paper[10], one of the present authors reported a new theory and method of measuring the heat with DTA considering the heat flow within and around the sample, and it is elucidated that the heat measurements with DTA

become possible by recording the difference between the temperature gradient within a thermal barrier put around the sample and that within the similar thermal barrier put around the reference material. The thermal barrier, thus, plays a role of a heat-flow-meter, developing within itself the proportional magnitude of the temperature gradient to be measured. In the apparatus of David[8] and Barrall II et al.[9], air plays a role of the thermal barrier and the thermocouple is put outside of the sample cell. If the proportionality coefficient is calibrated by using electric energy, DTA becomes an absolute method of calorimetry[11].

However, the above method of quantitative differential thermal analysis has a few defects. The sensitivity of the apparatus increases proportionally to the square of the dimension of the sample cell, and the sensitivity of the apparatus for the small amount of the sample becomes very low[10]. As the theory is based on the cylindrical symmetry of the temperature gradient, the sample must be filled full of the cell[10].

Recently, some attempts to overcome these defects have been made and satisfactory results have been obtained in our laboratory. The sensitivity is increased without increase of the amount of the sample, the temperature gradient becomes more close to the cylindrical symmetry and the accuracy becomes high. In this paper, these results are reported.

THEORY

As was apparent in the previous paper[10], the additional temperature due to the heat of transformation T' is given by the next equation;

$$\lambda \nabla T' = c\rho \partial T'/\partial t + \Delta H \rho \partial m/\partial t \tag{1}$$

where ∇, λ, c, ρ, ΔH, t and $\partial m/\partial t$ are a Laplacian, the thermal conductivity, the specific heat, the density, the heat of transformation, the time and the rate of conversion, respectively. The initial and final conditions are as follows;

$$T' = 0 \qquad\qquad\qquad \text{at } t = t_i \tag{2}$$

and

$$T' = 0 \qquad\qquad\qquad \text{at } t = t_e \tag{3}$$

where t_i and t_e are the beginning of the peak and its end, respectively. The integration of Eqn. (1) from t_i to t_e gives the next equation;

$$\lambda \int_{t_i}^{t_e} \nabla T' \, dt = \rho \Delta H \tag{4}$$

and integration of T' from t_i to t_e is the desired peak area, A, since T' is the temperature added to the steady state, the temperature difference recorded becomes constant at the steady state and peak at the transformation. Then, the integration of Eqn. (4) over the volume leads to the following equation.

$$\lambda \int_V dV \nabla A = \int_V \rho \nabla H \, dV \tag{5}$$

Then, as with Boersma[7],

$$S\lambda \frac{\partial A}{\partial r} = \rho V \Delta H \tag{6}$$

where r is the radius and S is the surface. When the integration of Eqn. (6) is made within the thermal barrier, V is equal to the volume of the sample and constant, since the heat is produced or consumed in the sample only. Thus, if the temperature is measured at two points within the thermal barrier and if the difference between them is recorded,

$$A = \frac{M\Delta H \ln (r_1/r_2)}{2\pi l \lambda_b} \tag{7}$$

where r_1, r_2, M, l and λ_b are the radii of the two points $(r_1 > r_2)$, the mass of the sample, the length of the cylindrical sample cell and the thermal conductivity of the thermal barrier, respectively. If the difference of n pairs of the similar temperatures are added by using the thermocouple of $2n$ junctions, the peak area and the sensitivity become n-fold.

EXPERIMENTAL

Apparatus

The thermal barrier is shown in Fig. 1. It is made of mulite. The platinel thermocouple of 20 junctions are wound along the groove (a) of a part A of the thermal barrier. The 10 junctions are located at half-depth of the outside and the others are at half-depth of the inside. Another platinel thermocouple for measuring the temperature of the sample is inserted through the side groove (b). Then, a part C is inserted in the bottom of the part A and a nickel cylinder of 1.5 mm thickness is also inserted from the top, and it is used to diminish the temperature gradient of the side of the cell. They are fixed with alumina paste; a part B is a lid. The cylindrical sample cell is made of nickel; the inner diameter is 5 mm and the length is 20 mm. The outside of it slightly tappers and it is fitted to the nickel cylinder inserted into the thermal barrier to make close thermal contact.

The two thermal barriers are inserted into the two holes drilled in the cylindrical nickel block. The dimension and the shape of the apparatus is shown in Fig. 2. The temperature is controlled with a PI-type programme controller and a SCR regulator (Ohkura Electric Co., Ltd.) The temperature is measured with a d.c. voltage current standard (type 2853, Yokogawa Electric Works, Ltd.) and the two-pen recorder (Rika Denki Kogyo Co., Ltd.), and the temperature difference is amplified with a d.c. amplifier (Ohkura Electric Co., Ltd.) and recorded on the same chart with the temperature.

The electric heater for the calibration of the thermal barrier is made of nichrome wire of about 10 Ω covered with alumina tubes, and the length is the same as that of the cell. The electric power is supplied from a d.c. regulated source (Showa Electronic

A   B   C

50mm

Heater
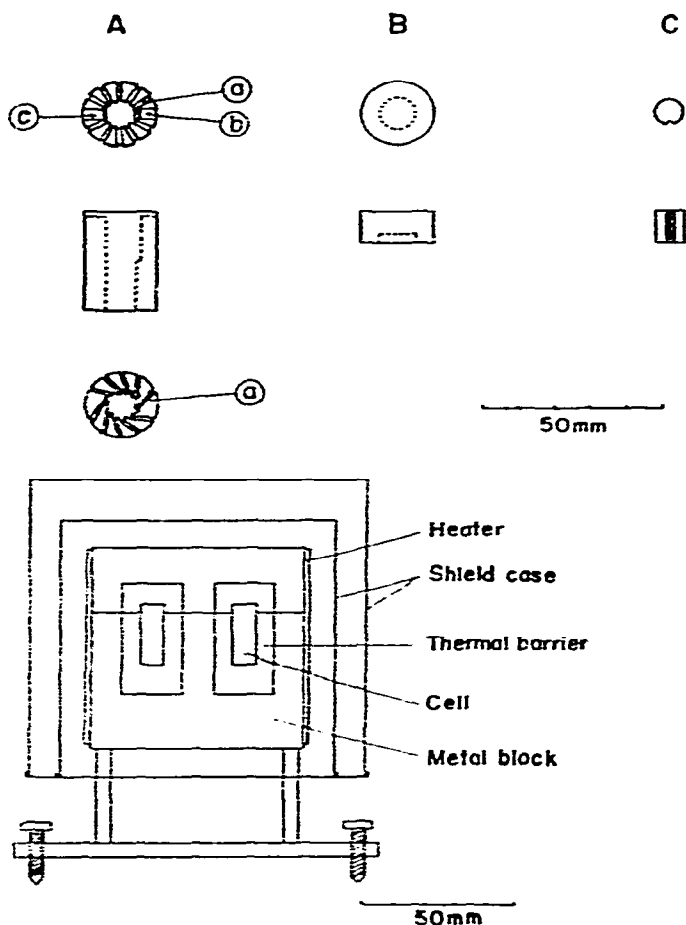
Shield case

Thermal barrier

Cell

Metal block

50mm

Fig. 1. The thermal barrier.

Fig. 2. The apparatus.

Co., Ltd., 155M). The voltage and the current are measured with a voltmeter and a milliammeter (both, Yokogawa Electric Works, Ltd.) respectively, both to a precision of $\pm 0.5\%$. The period of supplying the power is measured by a stopwatch to a precision of 1/10 sec.

Materials

The substances used for the measurement of the heat of transformation are listed in Table I, as are the manufacturers and the method of purification. The reference material is a 200–300 mesh powder of α-alumina (Nishio Kogyo Co., Ltd.).

RESULTS AND DISCUSSION

The calibration of the thermal barriers are made isothermally or heating at 30 or 60°C/h, as previously reported[11]. Some peaks obtained in the calibration and

TABLE I

THE HEATS OF TRANSFORMATION OBTAINED BY THE PRESENT METHOD OF DIFFERENTIAL THERMAL ANALYSIS

Sample	Present work		Lit.		Ref.
	Temp. (°C)	ΔH (cal/g)	Temp. (°C)	ΔH (cal/g)	
Benzoic acid[a]	122	38.0	——	35.2	14
			——	34.8	15
KNO₃[b]	129	13.2	128	13.8	16
			127.5	11.78	17
			——	12.83	18
			127.9	12.05	19
			127	13.0	11
KNO₃[b]	336	25.3	338	27.7	16
			334.3	22.75	19
			——	27.20	20
			331	28.1	11
AgNO₃[c]	161	3.42	160	3.9	16
			160	3.44	21
			158.9–160.6	3.49	17
			164	3.03	11
AgNO₃[c]	206	17.7	211	16.2	16
			210	17.57	21
			207	17.0	11
Al[d]	658	102.5	659	95.2	16
			660	96.3	22

[a]Purified sample by recrystallization from aqueous solution. [b]The G. R. grade reagent manufactured by Kanto Chemical Co., Inc. [c]The G. R. grade reagent manufactured by Showa Chemical Co., Ltd. [d]The sample of 99.999% purity purchased from Tanaka Noble Metal Co., Ltd.

the typical results of the calibration are shown in Figs. 3 and 4, respectively. The variation of the data is small and the temperature dependency of the proportional coefficient is approximated with a cubic function as is shown as a line in Fig. 4. The variation of the data around the line is less than 2% of the coefficient. The temperature dependency is higher at low-temperature region and the lower dependency at higher temperature is desirable.

The thermal response time[10] of the system is measured by using the back part of the peak of the melting of benzoic acid. The effect of the metal plate which is inserted in the sample cell to diminish the temperature gradient in the sample to the thermal response time is observed. As is seen in Fig. 5, the response time with the metal plate is 36 sec and that without the metal plate is 39 sec. The effect is scarcely found. Then, the metal plate is not used afterwards.

The typical thermogram of the crystalline transition of KNO₃ at 128 °C at the heating rate of 120 °C/h is shown in Fig. 6. The best estimate of the temperatures of transformation is obtained with the apparatus at the point where the temperature difference begins to deviate from the base line. The effect of the sample weight is observed with the crystalline transition of KNO₃ at 128 °C. The heat of transition is
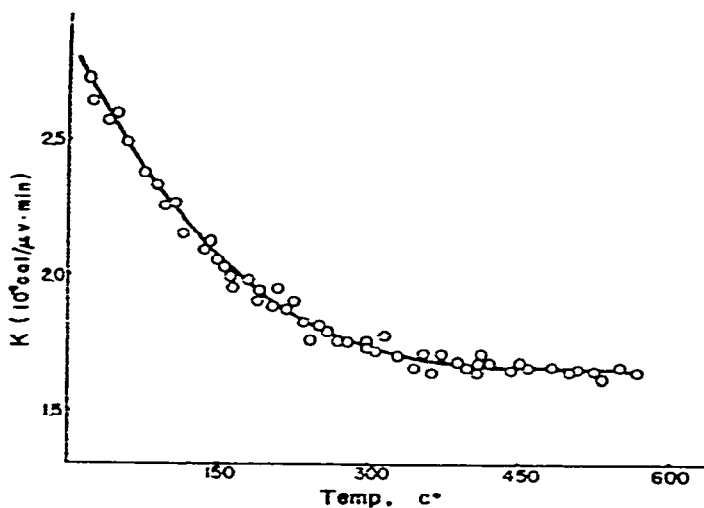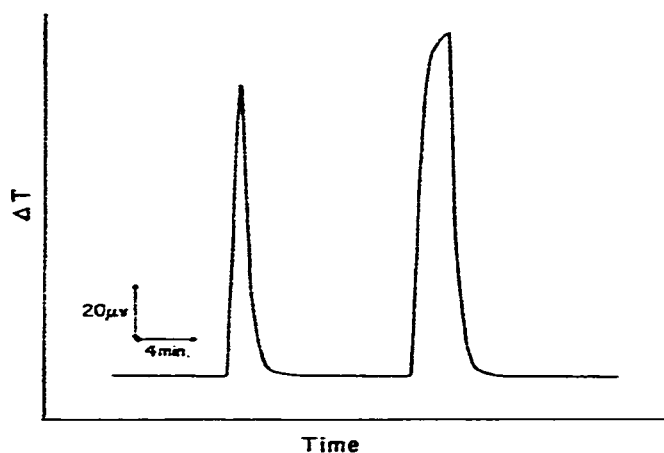
Fig. 3. The typical peaks of calibration.

Fig. 4. The typical temperature dependency of the proportionality coefficient of the thermal barrier.

measured varying the depth of packing the sample; the sample amount is one fourth, half, three fourths, and full of the cell, respectively, and the heat observed is 13.5, 13.6, 13.6, and 13.5 cal/g, respectively. The fact that no effect is observed presents striking contrast to the previous results[10]. The nickel cylinder inserted in the thermal barrier seems to have a remarkable effect on the longitudinal temperature gradient.

The heats of transformation of a few substances at the heating rate of 30 or 60 or 120°C/h are measured and the results are tabulated in Table I. The standard deviation is less than 2%. The agreement between the present results with DTA and the reported values is satisactory. The small discrepancy found for benzoic acid seems to be due to the sharp temperature dependency of the proportionality coefficient in the temperature region.

In the new type of quantitative DTA, the reference material is not indispensable, but it is used, since the base line is less fractuated with the reference material than
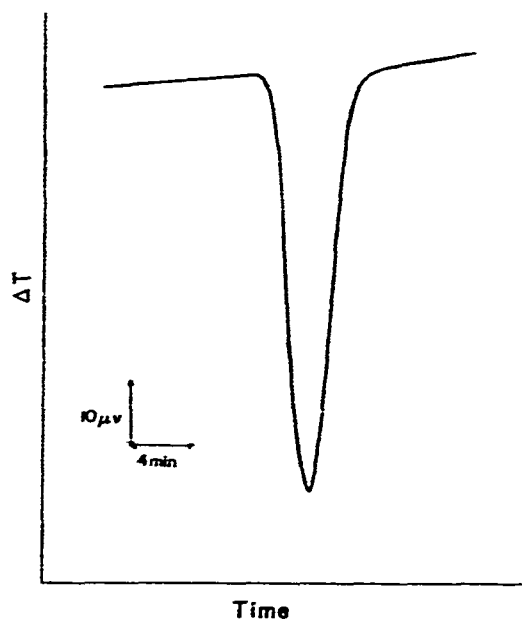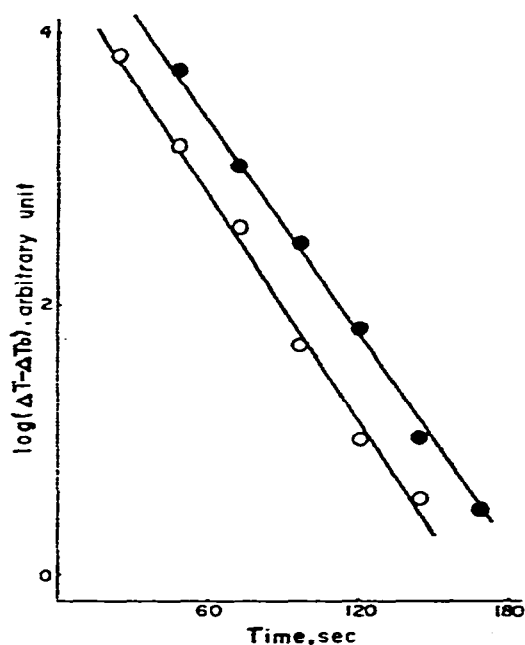
Fig. 5. The change of the temperature difference after the completion of the melting of benzoic acid without the metal plate (●) and with it (O).

Fig. 6. The thermogram of the crystalline transition of KNO_3 at 128 °C.

without it. The sensitivity of the present apparatus is about 5 times higher than the previous one, and the sample weight is about one third of the previous one; apparently, the sensitivity is considerably improved. If the thermopile is made in the more sophisticated way, the sensitivity becomes remarkably higher.

By this new arrangement of the thermocouples, the accuracy is also improved. In the previous method, the temperature within the metal block is assumed to be uniform, but the uniformity tends to be disturbed during the transformation; in the apparatus of the thermal conductivity measurement based on the same principle as that of the quantitative DTA[12], the temperature of the metal block is measured at the point on the thermal barrier and it was found that the temperature distribution is disturbed and that it also disturbs the measurement of the thermal conductivity. Thus, the present apparatus does not suffer from the disturbance. Moreover, the temperature difference is measured at one point in the previous apparatus, while the differences are measured at many points located circularly around the sample cell in the present one. Then, the deviation of the temperature distribution from that of concentric circles causes little inaccuracy.

The response time is also decreased in the present apparatus, while that of the previous one is about 90 sec. The results are in accordance with the theoretically estimated value[13]. It improves the resolution of the apparatus[10].

DTA is an independent method of calorimetry. Although the principle of DTA is complicated, it is easy to realize the condition assumed in the theory, as it is based on the heat conduction within the solid, while it is difficult, especially at higher temperatures and/or at high pressure, to realize the condition in such calorimeter as the adiabatic calorimeter and the differential scanning calorimeter (DSC), the principle of which is based on the equality of the temperature between the sample cell and the shield case or the reference cell. Furthermore, DSC should be calibrated with some material standards at the temperature range to be measured. Then, the precision of DSC depends on the reported value of the heat of transformation. On the other hand, DTA described above is an independent method and does not suffer from inaccuracy of the other calorimetric method.

The theory of DTA is based on the cylindrical symmetry of the temperature distribution, but strictly speaking, the symmetry does not exist actually. The research of the general theory which is not based on the symmetry and in which the theoretical consideration is given for the general shape of the apparatus is now in progress in our laboratory, and it will be reported in the near future.

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