Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 517–523

STUDY ON SEPARATION METHOD OF OVERLAPPED PEAKS IN DIFFERENTIAL THERMAL ANALYSIS WITH COMPUTER SIMULATION*

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(Received August 23, 1999; in revised form May 28, 2000)

Abstract

With the computer simulations, it has been found that in Differential Thermal Analysis (DTA) the overlapped peaks do not satisfy the linear overlapping principle, and the relationship between the overlapped peaks is rather complex that is a function of sample thermal conductivity, specific heat, quantity and latent heats, etc. If the first point where the two peaks begin to overlap is at the posterior half of the first peak curve and the two overlapped peaks can be identified by two different peaks, from the curve of overlapped peaks we can know that the temperature corresponding to the first point deviating from the sample's first phase change curve is the sample's second phase change temperature.

Keywords: DTA, overlapping principle, separation of overlapped peaks, temperature gradients within sample

Introduction

Differential Thermal Analysis (DTA) has been widely used in energy, materials, and other fields. In principle, DTA can be applied to study any physical process and chemical reaction where changes in energy or entropy of condensed phases are functions of temperature and time. In an ordinary DTA curve, there might be some overlapped peaks. How to separate these overlapped peaks correctly is a key precondition to draw correct information from this thermal curve.

There are some methods for separating overlapped peaks in current DTA theories [1, 2]. In these methods, there are implications that the overlapped peaks satisfy the linear overlapping principle. A mass of experimental facts reveals that in DTA the

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

overlapped peaks do not satisfy the linear overlapping principle. The relationship between the two overlapped peaks is rather complex, and generally it is a function of experimental conditions, such as sample thermal conductivity, specific heat, quantity and latent heats, etc., so the current separation theories for overlapped peaks need to be improved.

In this article, we will use computer dynamic simulations to deal with the separation method in DTA for overlapped peaks.

Theoretical analysis on principle of separating overlapped peaks in DTA

As mentioned above, the overlapped peaks in DTA do not satisfy the linear overlapping principle. The causes of these phenomena are due to the temperature gradients within the sample. Because the thermal conductivity of the actual sample is finite, within the sample there are temperature gradients at any time during the heating or cooling process. In an actual experiment, the amount of the sample has no possibility to be infinitesimal, thus its volume and thermal conductivity will inevitably result in temperature gradients within the whole space scale.

Now, let us analyze an actual DTA experimental process in which two-phase changes take place and two different phase transition peaks are so near that the two peaks overlap each other. For the simplicity, we assume that the phase transitions here are endothermic transitions and that the two peaks overlapped each other can be identified by two different peaks (Fig. 1). These assumptions here will not have any influence on the universality of the separation theory of the overlapped peaks.

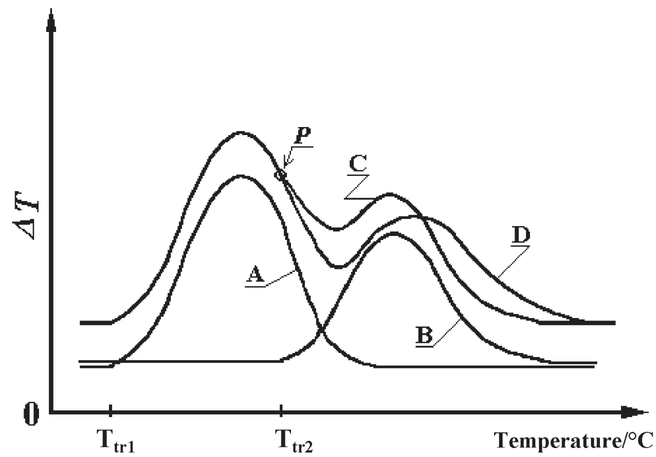

Fig. 1 Typical DTA phase change curves with overlapped peaks $\Delta T = T_r - T_s$, where T_r is the reference temperature, and T_s is the sample temperature

At first, we consider a special transition process, in which the sample's first phase transition occurs at the temperature T_{tr1}, and its second phase transition occurs at the temperature T_{tr2}. We postulate that two-phase transition temperatures T_{tr1} and T_{tr2} are so near that the two phase transition peaks in DTA overlap each other. If the two overlapped peaks obey the linear overlapping rule, the total DTA curve can be represented with curve C as shown in Fig. 1. The computer dynamic simulation shows that the real DTA curve of overlapped peaks is represented with curve D as shown in Fig. 1. Obviously, the shape of curve D is totally different from the curve C. What causes the overlapped peaks not to obey the linear overlapping rule? The main cause is the temperature gradients within the sample.

Now, let us analyze the above example. Assume that the thermal conductivity of the holder is so high that the temperature gradient can be neglected, i.e., only the temperature gradients within the sample will be considered here. The specific heat capacities of a sample are c_L, c_M and c_H respectively in the low, medium and high temperature states, and we assume that they are the same constants, which cannot affect the popularity of the separation theory of the overlapped peaks. We also assume that the sample's latent heats are L_1 and L_2 respectively.

We consider a heating phase change process. When the sample holder temperature reaches T_{tr1}, only the small section of the sample that contacts the holder wall reaches the transition temperature T_{tr1}. The temperature of other parts of the sample is still lower than the temperature T_{tr1} because of the temperature gradient. As the surrounding temperature rises, the temperature of the sample holder synchronously rises. With the rise of the temperature of the sample's outer surface, the phase transition in the parts of sample near the outer surface takes place. With the time past, the outer parts of the sample that have fulfilled the phase change continue to raise their temperatures. The two transition peaks in DTA will overlap if the amount of sample is not small enough, or the transition temperatures T_{tr1} and T_{tr2} are not apart enough, or the thermal conductivity of the sample is not high enough, etc. In other words, when the temperature of sample's outer surface reaches T_{tr2}, the whole sample has not fulfilled the first phase change, or when the whole sample has finished the first phase change but the distributions of the temperature gradients within the sample have not stabilized, i.e., the state point of the sample in DTA curve has not reach the post-transition baseline [3], the two peaks will overlap in all these situations. If the two overlapped peaks obey the linear overlapping rule, the sample will independently have their different phase changes, and the total heat energy absorbed in this complex process will equal the sum of the energy absorbed in the two independent transition processes. Because the thermal conductivity of the sample is virtually finite, the sample's total heat energy absorbed from the surrounding in a unit time is also finite. The fact is that when the sample's outer parts begin to have second phase change, most parts of the heat transferring from the surrounding will be used to provide outside sample to have second phase change, only small parts of the heat are used to enhance the sample's temperature in the inner parts, and this will obviously cause the two-phase change peaks disobey the linear overlapping rule. Sample's phase change needs a lot of heat energy, and the remnant part of the heat energy cannot satisfy the normal needs to enhance the sample's temperature in the situation as the second phase change did not happen. Because of the restriction of sample's finite thermal conductivity, only parts of the whole heat energy absorbed from the surrounding can be used to meet the needs of second phase change process, its phase change peak in DTA must be delayed. At the same time, the whole second phase transition interval must be extended.

From the above discussions, we can draw a conclusion that in DTA the two overlapped peaks disobey the linear overlapping rule. We can also know that, with finite thermal conductivity of the sample, if two peaks in DTA are overlapped, the second peak must be shifted backwards contrasting to the situation in which two peaks are apart. Because in the thermal analysis process the state of all heat energy that transfer within the sample is related to the sample's characteristics [4], the relationship between the overlapped peaks is rather complex which is a function of sample's thermal conductivity, specific heat, quantity and latent heats, etc.

Methods of computer dynamic simulation in DTA

Now, we will use a computer to dynamically simulate an imaginary DTA experiment in which there are two overlapped peaks.

We assume that the sample's thermal conductivity is κ, its quantity is M, its specific heat capacities in the low, medium and high temperature states respectively are c_L, c_M and c_H, its latent heat energies in transition 1 and 2 respectively are L_1 and L_2, and we also assume that all these physical quantities are constants, which will not affect the generality of the results.

The heat energy transfer of the sample's surface absorbed from surrounding in a unit time interval, $\mathrm{d}Q_s/\mathrm{d}t$, is:

$$\frac{\mathrm{d}Q_s}{\mathrm{d}t}=-K(T_{\text{sample's surface}}-T_{\text{surrounding}}) \tag{1}$$

where K is Newton's constant of the sample holder.

The heat energy that transfer within the sample obeys the Fourier Law:

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=-\kappa\nabla T \tag{2}$$

where κ is the thermal conductivity of the sample.

At the phase transition temperature, the latent heat absorbed by the sample satisfies:

$$\mathrm{d}Q=L\mathrm{d}M \tag{3}$$

where $\mathrm{d}M$ is the mass of the samples which take part in the phase change.

For the simplicity, in the simulation we only consider the situation that the shape of the sample is platelike. We divide this platelike sample into n pieces of equal-thick plates.

In the simulation, we assume that sample and furnace have the same initial temperatures, and make the temperature of the furnace and sample holder to enhance with the increment dT in a unit time interval. Using Eq. (1), the heat energy absorbed by the sample's outer layer can be calculated. With the Fourier Law (Eq. (2)) we can also calculate the heat energy that transfers from outer layer to its nearest layer and determine their new temperatures. Iterating this process, we can calculate the temperature of all layers. Then, we start another calculation process in the next time interval.

Results and discussions

We first simulate a DTA experimental process in which only one-phase change occurs.

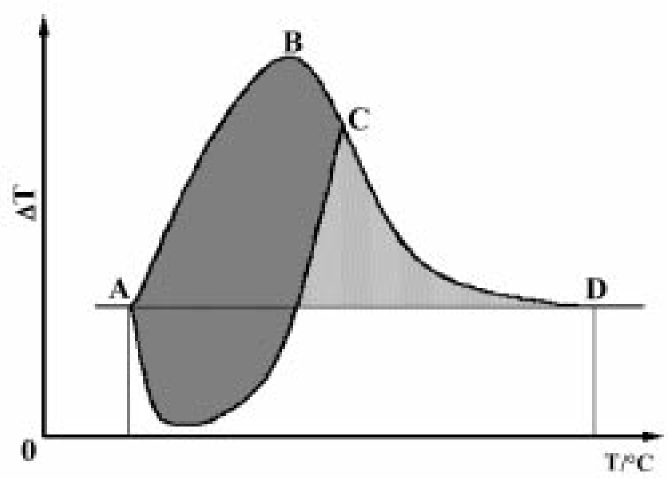

Fig. 2 A typical DTA heating (endothermic) phase change curve

The computer simulation result of the DTA process shown in Fig. 2 shows the distributions of heat energy absorbed from the surrounding with the time during the whole phase change process. Surprisingly this distribution of heat energy absorbed is unexpected, which is in conflict with our conventional picture of DTA. In Fig. 2, the part of the peak area in dark gray color is proportional to the latent heat. In this simulation, according to our assumption that the sample's specific heat capacities in high and low temperature phases are the same, the baseline in Fig. 2 is a straight level line. According to the DTA theory [5, 6], the value of latent heat in this situation is proportional to the area between the baseline and the peak, so in Fig. 2, the dark gray area below the baseline AD is equal to the light gray area, which is verified in our simulation. From Fig. 2 we can also know that the outer sample's temperature corresponding to the first point deviating the baseline (i.e. A point in Fig. 2) is its phase change temperature.

The simulation results (curve D in Fig. 1) support our above theoretical analysis results and show that the overlapped peaks do disobey the linear overlapping rule.

The distributions of heat energy absorbed from the surrounding during the phase change in which the two peaks overlap each other are shown in Fig. 3. The dark gray area represents the latent heat of the first phase that the sample absorbed from the surrounding. The median gray area represents the latent heat of the second phase, and the light gray area represents the heat absorbed by the sample which has fulfilled the first phase change to enhance its temperature before the second phase change takes place. From the Fig. 3 we can easily know that the overlapped peaks disobey the linear overlapping principle.

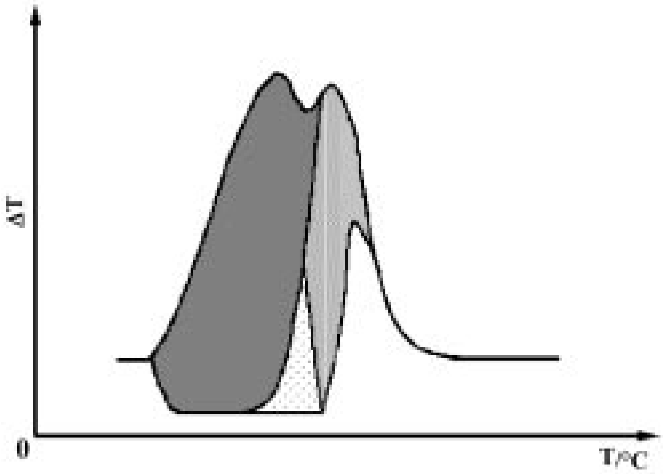

Fig. 3 A typical DTA endothermic phase change curve with two overlapped peaks

From these simulation results, we can also know that the sample temperature in point *P* as shown in Fig. 1 is the sample's second phase change temperature T_{tr2}. The *P* is the first point that deviates from the sample's first phase change curve, and corresponding to the *P* point, the outer sample temperature reaches the second phase change temperature T_{tr2} and began to have the second phase change (Fig. 3), thus we can obtain the second phase change temperature from the overlapped peaks.

In this paper, we assume the point *P* must be at the posterior half of the first peak curve, otherwise, the method here are very difficult to be used to separate the overlapped peaks properly.

If we know the shape of sample's first phase change curve, we can obtain sample's latent heat of first phase change. From the overlapped peaks, we can obtain the sample's total latent heats of phase change 1 and 2 [4], thus we can also get the sample's latent heat of second phase change. Actually, if we can experientially estimate the shape of its posterior half peak curve from sample's front half phase change curve, we can get the whole shape of the curve about the first phase change. Thus, from the overlapped peaks in DTA, we can get some important information such as sample's two different phase change temperatures and its latent heats, so the overlapped peaks can be successfully separated.

It must be pointed out that within the sensitivity of the apparatus, the best way to separate the overlapped peaks in DTA is to decrease the sample amount, decrease the heating and cooling rate and improve the heat conducting condition. Thus the overlapped peaks can be distinguished more easily.

Conclusions

From the above discussion, we can obtain a conclusion that in DTA the overlapped peaks do not satisfy the linear overlapping principle, and the relationship between the overlapped peaks is rather complex that is a function of sample's thermal conductivity, specific heat capacities, quantity and latent heats, etc. The causes of these phenomena are due to the temperature gradients within the sample. If the first point where the two peaks begin to overlap is at the posterior half of the first peak curve and the two overlapped peaks can be identified by two different peaks, from the curve of overlapped peaks we can know that the temperature corresponding to the first point deviating from the sample's first phase change curve is the sample's second phase change temperature.

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