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Thermochimica Acta 304/305 (1997) 201–207

thermochimica
acta

Simulation of temperature modulated DSC of temperature dependent heat capacity[1]

Katsuhiko Kanari[a,*], Takeo Ozawa[2,b]

[a] *Electrotechnical Laboratory, Tsukuba 305, Japan*
[b] *Daicel Chemical Industries, Ltd., Kasumigaseki, Tokyo 100, Japan*

Received 25 June 1996; accepted 4 April 1997

Abstract

Mathematical analysis can be applied to elucidate dynamic steady state in temperature modulated DSC, because it is a linear process, and its results were reported previously, but it was done on assumption of constant heat capacity. In real measurement the heat capacity is not constant instead it is dependent on the temperature. To elucidate thermal response during heat capacity change, computer simulation has been applied. Two cases have been simulated: heat capacity with linear temperature dependence and ramp change of heat capacity like a glass transition. The results are reported in this paper in relation to additional errors due to this temperature dependence. © 1997 Elsevier Science B.V.

Keywords: Computer simulation; Glass transition; Heat capacity measurement; Temperature modulated DSC (dynamic DSC)

1. Introduction

In temperature modulated differential scanning calorimetry (tm-DSC), oscillating thermal responses of the sample and the reference material, under linearly increasing temperature change with superposed sinusoidal temperature modulation, are recorded and analyzed. Since this new technique has been proposed by Reading et al. [1,2], it has drawn much attention because of its new characteristics.

One of the remarkable applications of this new technique was postulated to be heat capacity measurements of high accuracy and precision [3]. However, the theory described in this paper is based on a simple model in which some factors are not taken into account.

In a previous paper [4], we analyzed heat capacity measurements by an analytical mathematical method for more realistic models, and analytical general solutions were obtained, while approximate analytical solutions were numerically calculated for furthermore realistic models on some specific cases. Thus, we pointed out some factors influencing accuracy and precision of this technique. However, in this investigation it was assumed that the heat capacity is constant and independent on the temperature. In real measurements, the heat capacity usually depends on the temperature, hence the application of tm-DSC to heat capacity measurements have not been fully understood.

To elucidate the effect of the temperature dependence, the thermal response of tm-DSC in heat capacity measurements has been simulated by computer,

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*Corresponding author. Fax +81-3-3507-3159.

[1] A paper submitted to TCA Special Issue on dynamic DSC.

[2] Present address: Chiba Institute of Technology, Tsudanuma 275, Japan

PII S0040-6031(97)00173-1

because the analytical mathematical method and approximate analytical calculation cannot be applied exactly to this response. The obtained thermal response has been compared with the approximate analytical solutions calculated on assumption of the constant heat capacity. The simulated results and their comparison are described and discussed in this report in relation to additional errors in heat capacity measurements.

2. Simulation method

In our previous report [4], two models for tm-DSC apparatus were derived considering real commercial heat flux DSC and used to obtain the solutions for dynamic steady state or base lines. The same models are used in this computer simulation; in Model A mutual heat exchange exists between the sample and the reference material, while Model B is made for an apparatus without the mutual heat exchange. For these models fundamental heat transfer equations were derived in the previous paper [4] (Eqs. (A1–A7)). Basic concept and its validity for these fundamental equations were discussed in the previous report [4]; the temperature distribution within the sample and the reference material is assumed to be negligible, and the heat capacities of the heat paths among the heat source, the sample and the reference material are concentrated at points, though they are distributed along the paths in the real apparatus. It is also assumed that the heat transfers only by conduction, and convection and radiation are assumed to be negligibly small in the numerical calculations for the specific cases. However, the effect of the latter two can be taken into account in the above fundamental equations and in the analytical solutions, because the heat transfers due to these are roughly proportional to the temperature difference for small difference, as is the case for conduction.

The temperature in the heat source is uniform and controlled according to the next equation.

$$T_f = T_b + bt + A_f \exp(i\omega t) \tag{1}$$

where T, t, b, A_f and ω are the temperature, the time, the rate of heating or cooling, the amplitude and the

Table 1
Parameters of apparatus and operating conditions for simulation

	Model A	Model B
(1) Apparatus		
K/mWK^{-1}	73.6	73.6
k/mWK^{-1}	0.348	0.348
h/mWK^{-1}	36.8	0
C_{fs}/mJK^{-1}	6.61	6.61
C_{fr}/mJK^{-1}	6.61	6.61
C_{h1} [a]/mJK^{-1}	6.61	0
C_{h2} [a]/mJK^{-1}	5.81	0
C_{h3} [a]/mJK^{-1}	6.61	0
(2) Operation		
Case	0	1
Amplitude/K	4	1
Period/s	60	60
Angular Frequency/s^{-1}	0.105	0.105
Frequency/Hz	0.0167	0.0167
Heating Rate/K min^{-1}	2	2
C_r(empty pan [b])/mJK^{-1}	24.21	24.21
Initial Temperature (T_b)/K	290	290
Environmental Temperature (T_0)/K	290	290

[a] The subscripts, h1, h2 and h3 are the points between the sample and the reference material [2].
[b] An empty pan is used as the reference material.

Table 2
Thermophysical properties of simulated samples

Case 0: Constant heat capacity		
Heat capacity (C_s [a]) (mJ/K)	63.6	
Case 1: Linearly temperature dependent heat capacity		
	Ex. 1	Ex. 2
Initial heat capacity (C_s [a]) (mJ/K)	63.6	6.36
Increasing rate (%/K)	0.168	0.504
Case 2: Glass transition		
Initial heat capacity (C_s [a]) (mJ/K)	44.2	
Increasing rate (%/K)	3.15	
Transition temperature range (K)	353–363	

[a] The heat capacities contain those of the sample and the pan.

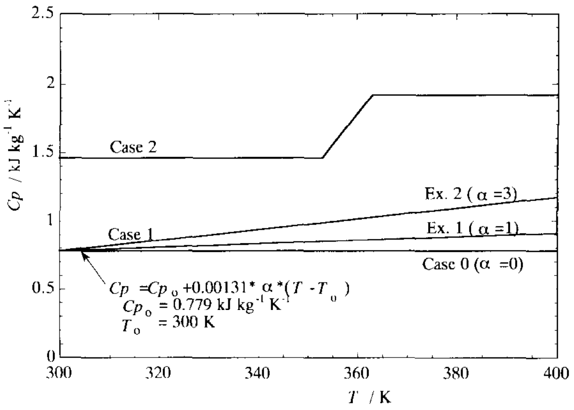

Fig. 1. Thermophysical properties of simulated sample. (a) Constant heat capacity (Case 0), (b) Temperature dependent heat capacity (Case 1), and (c) Stepwise heat capacity change (Case 2).

angular frequency of modulation, respectively. The subscripts f and b are the heat source and the initial time, respectively, and i is the unit of imaginary numbers; $\exp(iy) = \cos y + i \sin y$ (Euler equation).

For the simulation, finite difference method (FDM) was applied to the fundamental equations. The time interval for the calculation was 0.1 ms. The parameters in the fundamental equations were estimated for two real commercial apparatus taking into account the designs and the materials, and the effect of the radiation and the convection are neglected in this simulation. They are shown in Table 1 together with the operating conditions.

Two cases of simulated phenomena are also tabulated in Table 2 and shown in Fig. 1 together with a case of constant heat capacity for examining the simulation method (Case 0). The Case 1 is for the heat capacity of linear temperature dependence. Two

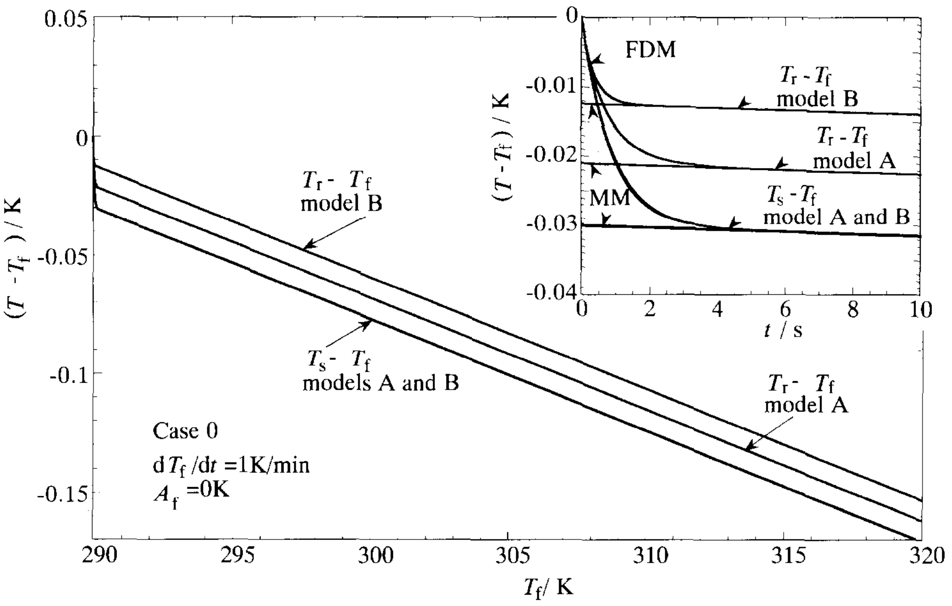

Fig. 2. Temperature lags of the sample and the reference material from heat source temperature for both models. Initial temperature lags are shown in an inserted figure.

examples were simulated; the initial specific heat capacity of the first example (0.779 kJ/kgK) increases at 0.168 %/K, which is similar to the heat capacity change of alpha alumina (synthetic sapphire, the standard material for heat capacity), and the temperature dependence of the second example is taken to be three times higher than the first example. For Case 2, a model of a ramp change of heat capacity is adopted for a glass transition; the specific heat capacity increases from 1.46 kJ/kgK to 1.92 kJ/kgK in the temperature range from 353 to 363 K (see Fig. 2), as for polystyrene.

3. Examination of simulation (Case 0)

To examine the accuracy of simulation, simulation was made for the constant heat capacity (Case 0, the heat of transformation=0 and the sample heat capacity C_s = constant, see Table 2).

It was elucidated by the simulation that, even in dynamic steady states, the temperature difference between the heat source and the sample or the reference material increases gradually with increase in the heat source temperature due to the heat loss from the sample and the reference material to the environment through the temperature sensors. The increase in the temperature difference is linear, so that for the approximate analytical solutions the following equations are applied as the assumed solutions to the temperatures of the sample, the reference material and the other points of the models. Namely, the additional term $b't$ was added to the solutions provided in the previous paper [4].

$$T = T_b + bt + A^* \exp(i\omega t) + B - b't \qquad (2)$$

where B is the steady-state non-oscillating constant temperature lag from the heat source temperature and A^* is the complex amplitude, its imaginary part expressing phase shift, which corresponds to the temperature lag in the oscillating response. Eq. (2) expresses the temperature responses in the models, and A^*, B and b' are specific to each point, though the subscripts are not added to each parameter for expressing the points. Introducing Eq. (1) and Eq. (2) into the above-mentioned fundamental heat transfer equations, we get a series of simultaneous equations for a series of A^*, B and b', and the simultaneous equations were solved by the matrix method (MM) to get numerically the approximate analytical solutions for specific cases as in the previous paper [4].

One of the typical results of the simulation for Case 0 is reproduced in Fig. 2, where the non-oscillating temperature lags behind the heat source temperature are shown for both the models. As seen in Fig. 2, the non-oscillating lags are linearly increasing with increase of the heat source temperature, and this is the reason for introducing the new term, $b't$ in Eq. (2).

As seen in Fig. 2, the temperature difference $(T_f - T_s)$ in the Model A is almost the same as that in the Model B, but the temperature differences $(T_f - T_r)$ are different from each other. This is due to the mutual heat exchange. Namely, the heat flow from the heat source to the sample in the Model A is approximately equal to that in the Model B. In both models, the heat supplied to the sample side is used only to heat up the sample, so that the differences $(T_f - T_s)$ are roughly the same. On the other hand, the heat supplied to the reference material side in the Model A is used to heat up the reference material and the heat path for the mutual heat exchange, while that in the Model B is used only to heat up the reference material itself. Therefore, the temperature differences $(T_f - T_r)$ are different from each other. This is also seen in Eq. (4) below.

Comparisons between the simulation results and the approximate analytical solutions are shown in Fig. 3. As clearly seen, agreements between them are satisfactorily good, except the short initial transient period

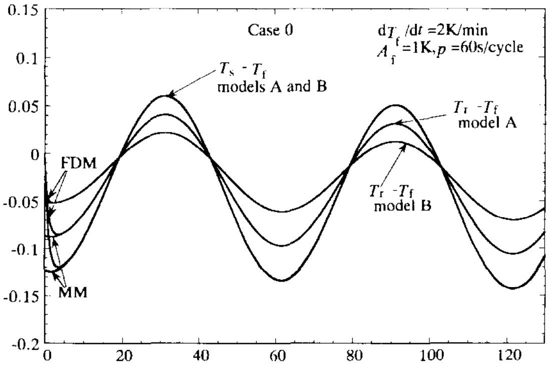

Fig. 3. Comparison of results of oscillating response between simulation (FDM) and numerical solution (MM) for Case 0.

where the approximate analytical solutions are invalid, because they were obtained assuming the steady state (see Eq. (2)).

To examine it in more detail, comparison was made in the amplitude of the sample temperature oscillation between the simulation results and the approximate analytical solutions, and the difference obtained was less than 0.05%, whereas the phase difference between the simulation results and the approximate analytical solutions is also not detectable. This difference seems attributable to computational error. Thus the excellent accuracy of the simulation method is clearly confirmed.

It should also be noted that the initial transient non-oscillating temperature change (see Figs. 2 and 3) can be exactly expressed by a single exponential function with high accuracy. The logarithms of these temperature changes are in linear relations with the time. This is due to the models adopted in this research, and linearities in these plots are another evidence for reliability of the simulation. Although the thermal response times are dependent on the heat capacities of the sample and the reference material, those of the two models estimated by these exponential functions are approximately equal to each other and they are less than 1 s. These short thermal response times should be noted in interpretation of simulation results below.

It is also worthy to note that the following solution is obtained for the steady-state temperature difference of the non-oscillating responses, namely,

$$b'_{\mathrm{s}} = 2b'_{\mathrm{fs}} = b'_{\mathrm{r}} = 2b'_{\mathrm{fr}} \tag{3}$$

where the subscripts, s and r represent the sample and the reference material, respectively, and the double subscripts, fs and fr express the midpoints between the heat source and the sample or the reference material, respectively, and

$$(B_{\mathrm{s}} - B_{\mathrm{r}}) = (b - b'_{\mathrm{s}})(C_{\mathrm{s}} - C_{\mathrm{r}})/(K/2 + k + 2h) \tag{4}$$

where $K/2$, k and h are the heat-transfer coefficients between the heat source and the sample or the reference material, that from the sample or the reference material to the environment, and that for the mutual exchange between the sample and the reference material, respectively. Therefore the conventional method of heat capacity measurement can surely be applied, even when the heat loss to the environment exists, and the real heating rate $(b - b'_{\mathrm{s}})$ should be used instead of the nominal rate, b. Because the dynamic steady state is a linear process, the thermal responses of the sample and the reference material are composed of non-oscillating responses, such as Eq. (4), and superposed oscillating responses, so that the introduction of $b't$ does not change the oscillating terms, that is, the amplitudes and the phase shifts, as shown in the previous report [4].

4. Heat capacity of linear temperature dependence (Case 1)

In real heat capacity measurement, the measured heat capacity is not constant as in the above case and the previous paper [4], but changes with the temperature, as seen in Table 2 and Fig. 1. This situation is simulated.

Because applicability of the heat capacity determination methods [4] assuming the constant heat capacity is the problem to be discussed, simulated DSC curves are compared with the approximate analytical solutions for the constant heat capacity, which can be obtained by solving the simultaneous equations by the matrix method as was described in the previous paper [4].

Thermal response for the Examples 1 and 2 in the Model A are shown in Fig. 4 together with the approximate analytical solutions, and in the figure no detectable discrepancy is seen between them. The same results were also obtained for the Model B. Thus quasi-steady state occurs, and the heat capacity

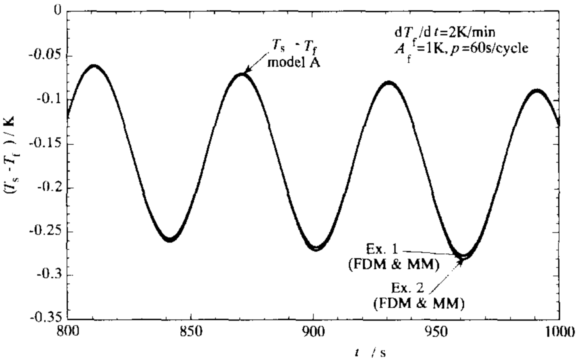

Fig. 4. Simulated DSC curves for Example 1 and 2 of Case 1. Approximate analytical solutions (MM) are also shown with simulation (FDM) for Model A.

measurement methods described in the previous paper [4] can be applied to these examples with high accuracy, and the error due to the linear increase in heat capacity seems little. To make it sure, comparison was made in the amplitude of the sample temperature oscillation between the simulation results and the approximate analytical solutions, and the differences for the Examples 1 and 2 are not larger than the simulation error of 0.05%, as mentioned above. Thus, in both the examples of Case 1 the quasi-steady state was confirmed, and in the quasi-steady state the sample temperature is always approaching with the short response time to the dynamic steady-state oscillation (the approximate analytical solutions), which is also changing due to the change in the heat capacity, because the approximate analytical solutions are the thermal response in the true dynamic steady state.

5. Glass transition (Case 2)

Much larger temperature dependence is encountered in glass transition, and it is simulated in Case 2, where relaxation phenomena inevitably associated with the real glass transition is neglected [3,5] (see Table 2 and Fig. 1).

The sample thermal response for the Model B is produced in Fig. 5. The glass transition like ranges are shown with arrows. Because the sample temperature is oscillating, it crosses the transition range borders a few times at the beginning and the end of transition. Due to the increase of heat capacity in the glass transition like region, the amplitude is gradually increasing.

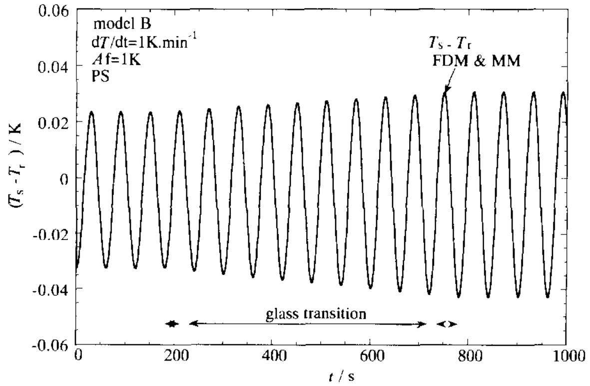

Fig. 5. Simulated DSC curves for Case 2. Approximate analytical solutions (MM) are also shown with simulation (FDM) for Model B.

Comparison between the simulation results and the approximate analytical solutions was made similarly to the Case 1, and the difference is little even in the glass transition like region. To examine the errors in more detail, the amplitudes were compared between the simulation and the approximate analytical solutions, and the difference was not larger than the simulation error of 0.05%. Thus, the difference is not detectable and the difference in the phase is also not detectable, therefore the quasi-steady state occurs even in the glass transition-like region. Fairly similar results were also observed for the Model A. This is presumably due to the short response times of both the Models, A and B, as mentioned above. This situation would be existing in a real apparatus.

Thus the thermal responses of both the models of tm-DSC in the glass transition like change of heat capacity are elucidated to be linear. On the other hand, Wunderlich [6] detected non-linear response in glass transition, so that it was elucidated that this non-linearity is caused by the kinetic effect of hole concentration change.

6. Conclusions

In measurements of heat capacity of usual temperature dependence, the sample thermal response is approaching with the short response time to the dynamic steady state, which is also changing due to the temperature dependence as is expressed by the equations for heat capacity determination [4]. The error due to this temperature dependence is negligible when compared with the error in the above equations by neglecting the effects of the heat capacity of the heat paths and the mutual heat exchange between the sample and the reference material [4]. Thus, the equations for heat capacity determination by tm-DSC can be applied to measurements of heat capacity of usual temperature dependence. For the glass transition like change in heat capacity the situation is quite the same as the above.

This is due to the short thermal response time of the simulated models of tm-DSC, and the dynamic quasi-steady state can exist in temperature dependent heat capacity and even in glass transition like region.

Finally, it should be noted that the above investigation was made for heat source temperature controlled tm-DSC. In many cases the sample temperature is controlled as in Eq. (1), instead of the heat source temperature, but the conclusion described above can also be applied to the sample temperature controlled tm-DSC, because dynamic quasi-steady state is dealt with in this paper and the relations among the heat source temperature, the sample temperature and the reference material temperature are the same with each other for both the types of temperature control.

We are now applying this simulation method to hypothetical first-order transitions of simple and typical nature to reveal the sample thermal response during the transitions. The results will be published in the near future [7].

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