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A NEW THEORETICAL APPROACH TO STEADY STATE OF TEMPERATURE MODULATED HEAT FLUX DSC

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Abstract

The steady state of temperature modulated heat flux DSC, in which the sample temperature is controlled at a fixed frequency, a fixed amplitude and a constant underlying heating rate, is theoretically investigated for complex heat capacity of the sample, taking accounts of heat capacities of heat paths, heat loss to the environment and mutual heat exchange between the sample and the reference material. Rigorous and general solutions for the temperature difference oscillation are obtained in relation to the sample temperature as a reference oscillation. The results are quite different from those obtained in functions of the heat source temperature as a reference oscillation. From these solutions, application of the technique to heat capacity measurements is discussed.

Keywords: heat capacity measurement, heat flux DSC, steady state, TMDSC

Introduction

Since its publication in 1992 [1, 2], temperature-modulated differential scanning calorimetry (TMDSC) has been investigated from various viewpoints and other varieties of TMDSC have been devised. The initial TMDSC was heat flux DSC (HF-DSC), and temperature modulation was applied to power compensation DSC (PC-DSC) later [3]. In the initial TM-HF-DSC the sample temperature is controlled at a fixed frequency, amplitude and a constant underlying heating rate, but there is another variety in which the heat source temperature is controlled at a fixed frequency, amplitude and a constant underlying heating rate [4]. Moreover, a new type of TMDSC was proposed [5], in which temperature modulation is given by oscillating light irradiation to the sample cell.

In a previous paper [6], we reported results of theoretical investigation of the steady state of TM-HF-DSC, and both the sample temperature oscillation and the reference material temperature oscillation are obtained as functions of the heat source temperature oscillation. In contrast with other previous theoretical papers

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[3, 7–9], we took accounts of the following effects, i.e., (1) heat capacities of heat paths, which may have effect of changing phase angle of oscillation, (2) mutual heat exchange between the sample and the reference material and (3) heat loss to the environment through the thermocouple wires and by the purge gas. General solutions could not be obtained, and approximate analytical solutions were obtained by neglecting the heat capacities of heat paths and mutual heat exchange, while specific solutions were obtained taking accounts of the neglected factors by applying matrix method to obtain numerical solutions for specific cases. Comparing these results, systematic errors in the approximate analytical solutions were estimated.

Afterward the effect of heat capacity in the heat paths from the heat source to the sample or the reference material was considered by Schawe and Winter [10], and the effect of mutual heat exchange between the sample and the reference material was taken into accounts by Lacy *et al.* [11].

For complex heat capacity of the sample quite similar, but more sophisticated approach has been applied to the TM-HF-DSC, and rigorous and general solutions have been obtained for the temperature difference between the sample and the reference material without neglecting the above-mentioned factors. They are obtained as functions of the sample temperature as a reference oscillation, and they are different from those in the previous paper [6]. Thermal contact between the sample cell and its holder has also been considered. These solutions for the complex heat capacity are useful to make heat capacity measurements by this technique, as well as the solutions for the thermal contact. These are described and discussed in this paper.

Standpoints of research

Before describing research results, our standpoints of research are stated below.

As was discussed in the first paper of our reports on TMDSC [12], linearity should be considered first, because in TMDSC Fourier analysis based on linearity is applied to separate output signal (the recorded oscillating temperature difference) into the in-phase component and the other. The latter consists of out of phase component and bias. This can be done with physical soundness, only when the output signal is linearly dependent on the physical quantities. In conventional DSC, both of HF-DSC and PC-DSC, linearity does not hold between the output signal (the temperature difference or the energy difference) and the sample mass (and/or the heat of transformation) [12–15] in the transformation region with heat evolution or adsorption, such as melting and reaction. But proportionality does exist between the peak area and the sample mass or the heat of transformation. Therefore, the separation by Fourier analysis has no physical meanings in the transformation region.

On the other hand, the base line in the steady state is proportional to the heat capacity of the sample, so that linearity holds in the steady state. It is clear from these facts that Fourier analysis can only be applied to the steady state. By this reason the results and discussion in this paper should be limited in the steady state and in heat capacity measurements.

For the above transformation, consideration should be made from viewpoint of linearity of mathematical operations, as shown below:

$$D(x+y) = D(x) + D(y) \tag{1}$$

and

$$D(ax) = aD(x) \tag{2}$$

where D expresses a mathematical operator, such as differentiation and integration and x and y are physical quantities, a being a constant. Fourier's fundamental equation for heat conduction is as follows:

$$\lambda\nabla^2 T = c\rho\frac{\partial T}{\partial t} + \frac{\mathrm{d}q}{\mathrm{d}t} \tag{3}$$

where λ, ∇^2, T, c, ρ, t and q are respectively thermal conductivity, a Laplacian operator, the temperature, the specific heat capacity, the density, the time and the heat evolved or absorbed. It holds at any point in a DSC apparatus and $\mathrm{d}q/\mathrm{d}t$ equals zero outside of the sample and the heat source. In the transformation region, the temperature at any point can be divided as follows:

$$T = T_{\mathrm{ss}} + T_{\mathrm{ns}} \tag{4}$$

where T_{ss} is the temperature for the case that the transformation did not occur, and T_{ns} is the additional temperature due to the transformation. Introducing this equation into Eq. (3) we have

$$\lambda\nabla^2 T_{\mathrm{ns}} = c\rho\frac{\partial T_{\mathrm{ns}}}{\partial t} + \frac{\mathrm{d}q}{\mathrm{d}t} \tag{5}$$

because we have already the solution for T_{ss} as shown later:

$$\lambda\nabla^2 T_{\mathrm{ss}} = c\rho\frac{\partial T_{\mathrm{ss}}}{\partial t} \tag{6}$$

From Eq. (5) we will be able to get solutions for analyzing TMDSC results for the transformation. For the conventional DSC we have already the solution [13].

As described above, the solutions in the functions of the sample temperature as a reference oscillation are different from those in functions of the heat source temperature. It is also made clear in the following sections, the solutions for TMDSC in the function of the sample temperature are quite different from solutions in functions of the reference material temperature as a reference oscillation. Therefore, the reference oscillation is an important key factor, while the temperature or the temperature difference to be measured is another key factor.

In this paper the temperature difference between the sample and the reference material is the output signal to be measured, and the sample temperature oscillation is the reference oscillation, though the results are briefly shown, in which the reference material temperature oscillation is the reference oscillation.

Complex heat capacity

When some thermal molecular motions have the same time scale with the temperature modulation, there occurs lag due to relaxation phenomenon, such as in glass transition. It causes phase lag in the temperature oscillation. Therefore, the heat capacity is expressed as a complex figure, as follows:

$$C^* = C' - \mathrm{i}C'' \tag{7}$$

where i, C^*, C' and C'' are the unit of imaginary numbers, the complex heat capacity, its real part and its imaginary part, respectively.

Fundamental equations

In a DSC apparatus occur a few heat flows; namely (1) the main heat flows from the heat source to the sample and the reference material, (2) the mutual heat exchange between the sample and the reference material and (3) the heat loss to the environment through the thermocouple leads and by purge gas. These are all taken into accounts. The heat paths for these heat flows have heat capacities. These heat capacities have influence on the temperature oscillations, and they are distributed along the paths, but they are approximated to be concentrated at a few points. This model for a DSC can clearly be expressed with an equivalent electric circuit shown in Fig. 1, and the fundamental equations for the steady state are as follows:

$$C_\mathrm{K}\frac{\mathrm{d}T_\mathrm{fs}}{\mathrm{d}t} = 2k_\mathrm{K}(T_\mathrm{f} - T_\mathrm{fs}) + 2k_\mathrm{K}(T_\mathrm{s} - T_\mathrm{fs}) \tag{8}$$

$$C_\mathrm{s}^*\frac{\mathrm{d}T_\mathrm{s}}{\mathrm{d}t} = 2k_\mathrm{K}(T_\mathrm{fs} - T_\mathrm{s}) + 3k_\mathrm{h}(T_\mathrm{hs} - T_\mathrm{s}) + k_\mathrm{o}(T_\mathrm{o} - T_\mathrm{s}) \tag{9}$$

$$C_\mathrm{h}\frac{\mathrm{d}T_\mathrm{hs}}{\mathrm{d}t} = 3k_\mathrm{h}(T_\mathrm{s} - T_\mathrm{hs}) + 3k_\mathrm{h}(T_\mathrm{hr} - T_\mathrm{hs}) \tag{10}$$

$$C_{\mathrm{h}}\frac{\mathrm{d}T_{\mathrm{hr}}}{\mathrm{d}t}=3k_{\mathrm{h}}(T_{\mathrm{r}}-T_{\mathrm{hr}})+3k_{\mathrm{h}}(T_{\mathrm{hs}}-T_{\mathrm{hr}}) \tag{11}$$

$$C_{\mathrm{r}}^{*}\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}t}=2k_{\mathrm{K}}(T_{\mathrm{fr}}-T_{\mathrm{r}})+3k_{\mathrm{h}}(T_{\mathrm{hr}}-T_{\mathrm{r}})+k_{\mathrm{o}}(T_{\mathrm{o}}-T_{\mathrm{r}}) \tag{12}$$

and

$$C_{\mathrm{K}}\frac{\mathrm{d}T_{\mathrm{fr}}}{\mathrm{d}t}=2k_{\mathrm{K}}(T_{\mathrm{f}}-T_{\mathrm{fr}})+2k_{\mathrm{K}}(T_{\mathrm{r}}-T_{\mathrm{fr}}) \tag{13}$$

where C, k_{K}, k_{h} and k_{o} are the heat capacity, the heat transfer coefficient between the heat source and the sample or the reference material, that between the sample and the reference material and that to the environment, respectively. The subscripts for the temperatures are as follows: f=the heat source, fs=the midpoint between the heat source and the sample, s=the sample, r=the reference material, fr=the midpoint between the heat source and the reference material, hs=a point in the heat path for mutual heat exchange, hr=another similar point near the reference material, o=the environment.

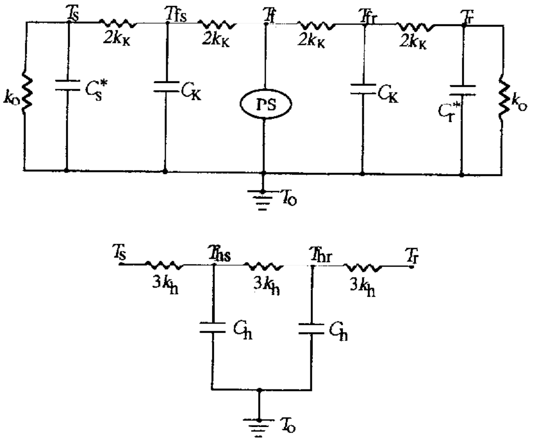

Fig. 1 Equivalent electrical circuits for main heat flows (upper) and mutual heat exchange (lower) in usual apparatus. PS is the heat source (power source)

The subscripts for the heat capacities, K, s, r and h denote (1) the heat path between the heat source and the sample or the reference material, (2) the sample, (3) the reference material, and (4) the heat path for the mutual heat exchange, respectively. These symbols are also shown in Fig. 1 of the equivalent electrical circuits. The asterisks for C_{s}^{*} and C_{r}^{*} mean that these heat capacities are assumed to be complex heat capacities consisting of the real and the imaginary parts. As the reference material, substance without the imaginary heat capacity is usually used, however the heat capacity of the reference material is assumed to be complex heat capacity to investigate various possibility of the heat capacity measurement.

In the steady state, the sample temperature changes at a fixed frequency, amplitude and a constant underlying heating rate, so that

$$T_s = T_o + A_s \exp(i\omega t) + \beta t \tag{14}$$

where A_s, ω, β are the amplitude, the angular frequency and the underlying heating rate, respectively. In this equation only the real part of $\exp(i\omega t)$ has physical meaning and the imaginary part should be neglected.

In the steady state the other temperatures change similarly with different amplitudes and phases, so that the amplitudes become complex amplitudes, A^*, and it was found that the underlying heating rates are also different from each other due to the heat loss to the environment [16]. Therefore, the other temperatures, T_i, can change as follows with definite temperature lag, B_i,

$$T_i = T_o + A^* \exp(i\omega t) + \beta t - \beta_i' t - B_i \tag{15}$$

where β' expresses the difference in the underlying heating rate due to the heat loss to the environment. In this equation and other equations below only the real parts of $A^*\exp(i\omega t)$ have physical meaning and the imaginary parts should be neglected.

Derivation and solutions

When we get difference in the fundamental equations between the symmetric points, we have

$$\Delta C^* \frac{dT_s}{dt} + C_r^* \frac{d\Delta T}{dt} = 2k_K \Delta T_f + 3k_h \Delta T_h - (2k_K + 3k_h + k_o)\Delta T \tag{16}$$

$$C_K \frac{d\Delta T_f}{dt} = 2k_K \Delta T - 4k_K \Delta T_f \tag{17}$$

and

$$C_h \frac{d\Delta T_h}{dt} = 3k_h \Delta T - 9k_h \Delta T_h \tag{18}$$

where

$$\Delta C^* = C_s^* - C_r^* \tag{19}$$

$$\Delta T = T_s - T_r \tag{20}$$

$$\Delta T_f = T_{fs} - T_{fr} \tag{21}$$

and

$$\Delta T_{\mathrm{h}} = T_{\mathrm{hs}} - T_{\mathrm{hr}} \tag{22}$$

The temperature difference, ΔT, changes similarly to Eq. (15), so that we have

$$\Delta T = \Delta A^{*}\exp(\mathrm{i}\omega t) + \beta'_{\mathrm{r}}t + B_{\mathrm{r}} \tag{23}$$

and similarly for the other temperature differences between the symmetric points, ΔT_{i},

$$\Delta T_{\mathrm{i}} = \Delta A_{\mathrm{i}}^{*}\exp(\mathrm{i}\omega t) - \Delta\beta'_{\mathrm{i}}t - \Delta B_{\mathrm{i}} \tag{24}$$

Introducing Eqs (23) and (24) into Eqs (16), (17) and (18) and comparing the coefficients, we have simultaneous equations and their solutions, similarly to the derivation in the previous paper [6].

From the terms describing the constant temperature lags, we get

$$\Delta C' = \frac{(k_{\mathrm{K}} + 2k_{\mathrm{h}} + k_{\mathrm{o}})\Delta B}{\beta} \tag{25}$$

where $\Delta C'$ is the real part of the complex heat capacity difference between the sample and the reference material, and this equation is the very base for heat capacity measurements by the conventional DSC.

From the coefficients in the oscillating terms we have

$$(S_1^2 + S_2^2)\Delta A^{*} = \omega A_{\mathrm{s}}(\Delta C'S_1 + \Delta C''S_2) + \mathrm{i}\omega A_{\mathrm{s}}(\Delta C'S_2 - \Delta C''S_1) \tag{26}$$

where $\Delta C''$ is the imaginary part of the heat capacity difference and $\Delta C'$ (in Eq. (26)) is different from $\Delta C'$ in Eq. (25) in some cases, especially in glass transition region [17]. S_1 and S_2 in the above equation are as follows:

$$\frac{S_1}{\omega} = -\frac{C_{\mathrm{K}}}{4(1 + \omega^2\tau_{\mathrm{K}}^2)} - \frac{C_{\mathrm{h}}}{9(1 + \omega^2\tau_{\mathrm{h}}^2)} - C'_{\mathrm{r}} \tag{27}$$

and

$$S_2 = \frac{k_{\mathrm{K}}}{1 + \omega^2\tau_{\mathrm{K}}^2} + \frac{k_{\mathrm{h}}}{1 + \omega^2\tau_{\mathrm{h}}^2} - (2k_{\mathrm{K}} + 3k_{\mathrm{h}} + k_{\mathrm{o}}) - \omega C''_{\mathrm{r}} \tag{28}$$

where

$$\tau_{\mathrm{K}} = \frac{C_{\mathrm{K}}}{4k_{\mathrm{K}}} \tag{29}$$

and

$$\tau_h = \frac{C_h}{9k_h} \tag{30}$$

The phase difference between the sample temperature and the temperature difference, δ is given below:

$$\tan\delta = \frac{\Delta C' S_2 - \Delta C'' S_1}{\Delta C' S_1 + \Delta C'' S_2} \tag{31}$$

$$\sin\delta = \frac{\Delta C' S_2 - \Delta C'' S_1}{\sqrt{(S_1^2 + S_2^2)(\Delta C'^2 + \Delta C''^2)}} \tag{32}$$

For heat capacity measurements we get the following equation:

$$|\Delta A| = \frac{\omega A_s \sqrt{\Delta C'^2 + \Delta C''^2}}{\sqrt{S_1^2 + S_2^2}} \tag{33}$$

where $|\Delta A|$ is the absolute amplitude of the temperature difference oscillation.

Discussion

As seen in Eqs (25) and (33), when we estimate proportionality coefficients, $(k_K+2k_h+k_o)$ and $\sqrt{S_1^2+S_2^2}$ by using standard material with known heat capacity, we can measure the real part of sample heat capacity from the base line in the conventional DSC or from the average temperature difference, $<\Delta T>$ to be obtained in TMDSC by integrating the oscillating temperature difference for n cycles,

$$<\Delta T> = \frac{\omega}{2n\pi}\int \Delta T \mathrm{d}t = \frac{\Delta C'\beta}{k_K + 2k_h + k_o} \tag{34}$$

We can measure the imaginary part of heat capacity by comparing the amplitude and the real part thus obtained (Eq. (33)). When we estimate S_1 and S_2 from heat capacity measurements of standard material with known real heat capacity and without the imaginary part, we can estimate the real part and imaginary part of sample heat capacity from the real and imaginary parts of the amplitude, as is clear in Eq. (26).

It is also made clear that the average temperature difference depends on the real part of the heat capacity difference, the underlying heating rate and the sum of the heat transfer coefficients (Eq. (25)), while the amplitude of the temperature difference oscillation around this average temperature difference depends on the square sum of the real and imaginary parts of the heat capacity difference, ($\Delta C'^2 + \Delta C''^2$), the frequency, the amplitude of the sample temperature modulation and the heat capacity of the reference material (Eq. (33)), as is shown in Fig. 2. It is worthy to note that, in order to make accurate heat capacity measurements, the heat capacity of the reference material should be made the same together with the frequency and amplitude of the sample temperature modulation (Eqs (26), (27), (28) and (33)).

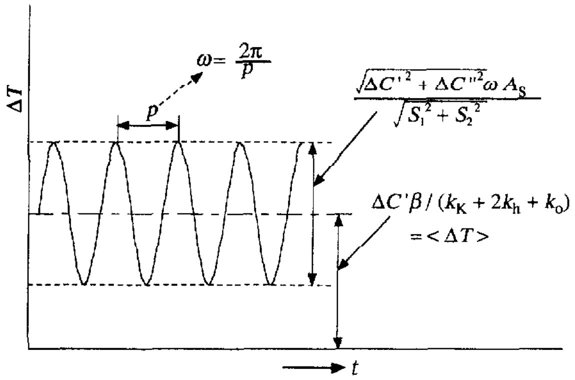

Fig. 2 Temperature difference oscillation in steady state

It should also be pointed out that when the heat capacities in the heat paths and the heat capacity of the reference material are negligibly small, the time constants τ_K and τ_h are approximately zero and we have

$$S_1 \div 0 \tag{35}$$

$$S_2 \div k_E + 2k_h + k_o \tag{36}$$

Therefore, the real part and the imaginary part of the temperature difference oscillation become respectively proportional to the imaginary part and the real part of the sample heat capacity. This relation is usually existing in dielectric and visco-elastic measurements because of availability of materials of wide characteristics for assembling the apparatuses in contrast to calorimetry of complex heat capacity.

The temperature difference oscillation can be obtained as a function of the reference material temperature oscillation. This relation can be derived by exchanging ΔC_s^*, C_s' and C_s'' by ΔC_r^*, C_r' and C_r'', respectively, in Eqs (25)–(28) and (31)–(33). The average temperature difference (or the conventional DSC method) does not change by this exchange (Eq. (25)), but the unknown sample heat capacity is involved in the proportionality coefficient in the oscillating temperature difference (Eqs (27), (28) and (33)). Therefore, it is not practical.

Thermal contact effect

Previously Hatta [9] pointed out the effect of thermal contact between the sample cell and the cell holder and proposed a method to eliminate this effect by using the phase angle on his simple model of the DSC apparatus. This effect has also been considered in this paper.

Fundamental equations

Similarly to Hatta's model [9], the reference material cell is not used, because the thermal contact is one of uncontrollable experimental factors and it is undesirable to introduce two uncontrollable factors. Thus the fundamental equations to consider the thermal contact effect are given below:

$$C_K\frac{dT_{fs}}{dt} = 2k_K(T_f - T_{fs}) + 2k_K(T_{ps} - T_{fs}) \tag{37}$$

$$C_p\frac{dT_{ps}}{dt} = 2k_K(T_{fs} - T_{ps}) + k_K'(T_s - T_{ps}) + 3k_h(T_{hs} - T_{ps}) + k_o(T_o - T_{ps}) \tag{38}$$

$$C_s^*\frac{dT_s}{dt} = k_K'(T_{ps} - T_s) \tag{39}$$

$$C_h\frac{dT_{hs}}{dt} = 3k_h(T_{ps} - T_{hs}) + 3k_h(T_{hr} - T_{hs}) \tag{40}$$

$$C_h\frac{dT_{hr}}{dt} = 3k_h(T_{pr} - T_{hr}) + 3k_h(T_{hs} - T_{hr}) \tag{41}$$

$$C_p\frac{dT_{pr}}{dt} = 2k_K(T_{fr} - T_{pr}) + 3k_h(T_{hr} - T_{pr}) + k_o(T_o - T_{pr}) \tag{42}$$

and

$$C_K\frac{dT_{fr}}{dt} = 2k_K(T_f - T_{fr}) + 2k_K(T_{pr} - T_{fr}) \tag{43}$$

where k_K' is the heat transfer coefficient due to the thermal contact, and the subscripts, p, ps and pr are the cell holder plate, that for the sample and that for the reference material, respectively. The equivalent electrical circuit is shown in Fig. 3. The temperature of the cell holder plate of the sample side is controlled instead of the sample temperature itself, so that

$$T_{ps} = T_o + \beta t + A_{ps}\exp(i\omega t) \tag{44}$$

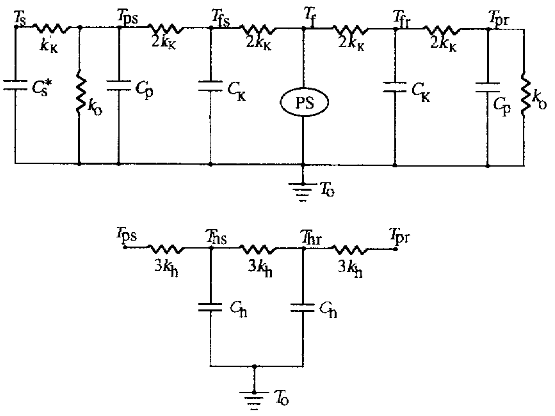

Fig. 3 Equivalent electrical circuits for main heat flows (upper) and mutual heat exchange (lower) to elucidate thermal contact effect. PS is the heat source (power source)

Derivation and solutions

In the steady state, the sample temperature follows the next equation similarly to the above:

$$T_s = T_o + \beta t + A_s^* \exp(i\omega t) - \beta_s' t - B_s \tag{45}$$

Introducing this equation into Eq. (39) we get

$$B_s = \frac{C_s'}{k_K'} \tag{46}$$

and

$$A_s^* = \frac{A_{ps}(1 + \omega\tau_s'' - i\omega\tau_s')}{(1 + \omega\tau_s'')^2 + \omega^2\tau_s'^2} \tag{47}$$

where

$$\tau_s' = \frac{C_s'}{k_K'} \tag{48}$$

and

$$\tau_s'' = \frac{C_s''}{k_K'} \tag{49}$$

Similarly to the above, by introducing Eqs (45)–(47) and the temperature differences into the differences of the fundamental equations between the symmetric points, we get final solutions quite easily and they are as follows:

$$\beta C_s' = (k_K + 2k_h + k_o)\Delta B \tag{50}$$

$$|\Delta A| = \sqrt{C_s'^2 + C_s''^2}\frac{\omega A_{ps}}{\sqrt{(S_1^2 + S_2^2)[(1 - \omega\tau_s'')^2 + \omega^2\tau_s'^2]}} \tag{51}$$

For the phase difference, δ

$$\tan\delta = \frac{P_2S_2 - P_1S_1}{P_2S_1 + P_1S_2} \tag{52}$$

and

$$\sin\delta = \frac{P_2S_2 - P_2S_1}{\sqrt{(C_s'^2 + C_s''^2)(S_1^2 + S_2^2)[(1 - \omega\tau_s'')^2 + \omega^2\tau'^2]}} \tag{53}$$

where

$$P_1 = \omega\tau_s' C_s' + (1 + \omega\tau_s'')C_s'' \tag{54}$$

and

$$P_2 = (1 + \omega\tau_s'')C_s' - \omega\tau_s' C_s'' \tag{55}$$

Discussion

Thus the solutions obtained by taking accounts of the complex heat capacity and the thermal contact are very complicated and not so useful as the above solutions neglecting the thermal contact. However, the solutions for the heat capacity without the imaginary part are simple and useful. For these cases,

$$\tau_s'' = 0 \tag{56}$$

so that we have

$$|\Delta A| = \frac{C_s' \omega A_{ps}}{\sqrt{(S_1^2 + S_2^2)(1 + \omega^2\tau_s'^2)}} \tag{57}$$

Therefore, if we can estimate the effect of thermal contact, i.e., τ_s', or the proportionality coefficient, $\sqrt{(S_1^2 + S_2^2)(1 + \omega^2\tau_s'^2)}$, we can measure the heat capacity accurately without the effect of thermal contact. For this purpose we have the next equation:

$$\sin\delta = \frac{S_2 - \omega\tau_s' S_1}{\sqrt{(S_1^2 + S_2^2)(1 + \omega^2\tau_s'^2)}} \tag{58}$$

so that we can get relation between sinδ and the proportionality coefficient by experiments for different C_s', and this experimentally obtained relations at a given temperature can be used to get the correct proportionality coefficients taking accounts of the thermal contact, as pointed out in other papers [9, 10, 18].

Concluding remarks

The steady state of TMDSC, in which the sample temperature oscillation is the reference oscillation, is dealt with in this paper, and the following points are made clear.

(1) The temperature difference oscillation can theoretically be derived in a rigorous function of the sample temperature, though it can not be obtained in a rigorous function of the heat source temperature but only in an approximate function. The difference in the reference oscillation causes large difference in the results.

(2) The real part of the sample heat capacity is proportional to the underlying temperature lag between the sample and the reference material, as used for heat capacity measurements by conventional DSC, while the amplitude of the temperature difference in TMDSC is proportional to the square root of square sum of the real part and imaginary part of the sample heat capacity. The real and imaginary parts of the temperature difference oscillation can also be used to estimate complex heat capacity. Thus, the complex heat capacity can be measurded by TMDSC.

(3) The proportionality coefficient between the amplitude and the heat capacity is dependent on the heat capacity of the reference material, so that the same reference material shall be used in heat capacity measurement by TMDSC, in contrast to conventional DSC, where the heat capacity of the reference material is not involved in the proportionality coefficient between the steady state temperature difference and the heat capacity difference.

(4) The thermal contact between the sample cell and the cell holder has influence on the proportionality coefficient between the amplitude and the heat capacity, while it does not influence on the proportionality coefficient between the underlying temperature lag and the real part of heat capacity from theoretical view point. The influence can be detected by observing the phase lag in a region where the imaginary part of heat capacity is negligible.

(5) In reality the thermal contact causes error in heat capacity measurements by conventional DSC. This fact suggests us another effect of the thermal contact and it seems due to change in heat flow distribution around the sample temperature sensor by the thermal contact.

References

1 M. Reading, D. Elliott and V. L. Hill, J. Thermal Anal., 40 (1993) 949.
2 P. S. Gill, S. R. Sauerbrunn and M. Reading J. Thermal Anal., 40 (1993) 931.
3 J. Schawe, Thermochim. Acta, 260 (1995) 1.
4 R. Riesen, G. Widmann and R. Truttmann, Thermochim. Acta, 268 (1995) 1.
5 M. Nishikawa and Y. Saruyama, Thermochim. Acta, 267 (1995) 75.
6 T. Ozawa and K. Kanari, Thermochim. Acta, 288 (1996) 39.
7 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
8 A. Boller, Y. Jin and B. Wunderlich, J. Thermal Anal., 42 (1994) 307.
9 I. Hatta and S. Muramatsu, Jpn. J. Appl. Phys., 35 (1996) L858.
10 J. E. K. Schawe and W. Winter, Thermochim. Acta, 298 (1997) 9.
11 A. A. Lacy, C. Nickopoulos and M. Reading, J. Thermal Anal., 50 (1997) 279.
12 T. Ozawa and K. Kanari, Thermochim. Acta, 253 (1995) 183.
13 T. Ozawa, Bull. Chem. Soc. Jpn., 39 (1966) 2071.
14 T. Ozawa, Netsu Sokutei, 4 (1977) 45.
15 M. J. O'Neill, Anal. Chem., 36 (1964) 1238.
16 K. Kanari and T. Ozawa, Thermochim. Acta, 304/305 (1997) 201.
17 N. O. Birge, P. K. Dixon and N. Menon, Thermochim. Acta, 304/305 (1997) 51.
18 Y. Saruyama, Thermochim. Acta, 282/283 (1996) 157.