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A THEORETICAL APPROACH TO TEMPERATURE MODULATED POWER COMPENSATION DSC

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Abstract

The steady state of temperature modulated power compensation DSC has been theoretically investigated for measurements of complex heat capacity, taking accounts of heat capacities of heat paths, heat loss to the environment, and mutual heat exchange between the sample and the reference material. Thermal contact between the sample cell and the cell holder is also taken into accounts. Rigorous and general solutions are obtained. From these solutions application of the technique to heat capacity measurements is discussed.

Keywords: heat capacity measurement, power compensation DSC, steady state, temperature modulated DSC, temperature modulated power compensation DSC

Introduction

Modulation technique was first applied to differential scanning calorimetry (DSC) by Reading and his co-workers in 1992 [1, 2]. Since then various approaches have been made to explore possibilities in this new technique. The initial temperature modulated DSC (tm-DSC) was heat flux DSC (hf-DSC), and the temperature modulation was applied to power compensation DSC (pc-DSC) later [3]. Moreover, a new type of tm-DSC was proposed [4], in which temperature modulation is given by oscillating light irradiation to the sample cell (photo-modulated DSC; pm-DSC). However, rigorous theoretical studies have not yet been made thoroughly for these varieties of modulated DSC, and studies should be made especially on their applicability and methods for analyzing obtained data [5, 6].

In previous papers, we reported results of theoretical investigation of the heat source temperature controlled tm-hf-DSC [6] and the sample temperature controlled tm-hf-DSC [7]. We took accounts of four factors, which may have effect of changing phase angle and amplitude of oscillation; they are (1) heat capacities of heat paths, (2) heat loss to the environment by the purge gas and through the thermocouple leads, (3) mutual heat exchange between the sample and the reference material and (4) thermal contact between the sample cell and the sample cell holder, while these

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factors were taken into accounts only partly in other theoretical papers [3, 8–10]. Though these factors complicate the model used in the approaches, general solutions could be obtained for the latter type of tm-hf-DSC by our approach [7]. However, for the former type of tm-hf-DSC only approximate analytical solutions were obtained by neglecting the heat capacities of heat paths and mutual heat exchange, and specific solutions were obtained taking accounts of the neglected factors by applying matrix method to obtain numerical solutions for specific cases [6].

A quite similar approach has been applied to the tm-pc-DSC, in which both the sample temperature and the reference material temperature are controlled to be equal at a fixed frequency, amplitude and a constant underlying heating rate. Without neglecting the above-mentioned factors, rigorous and general solutions have been obtained for complex heat capacity of the sample, and they are quite different from those in the previous papers [6, 7]. These solutions for the complex heat capacity are useful to make heat capacity measurements by these techniques. These are described and discussed in this paper.

Models

Besides the main heat flow from the micro-heaters to the sample and the reference material, a few additional heat flows occur in a pc-DSC apparatus, as pointed out above. In some pc-DSC an outside furnace was used to maintain uniform temperature distribution beside the micro-heaters for the sample and the reference material, so that there are the other heat flows, i.e., the heat flows from the furnace to the sample and the reference material. 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, so that they are taken into accounts and approximated to be concentrated at a few points. Moreover, oscillating energy input is given by the micro-heaters to the sample and the ref-

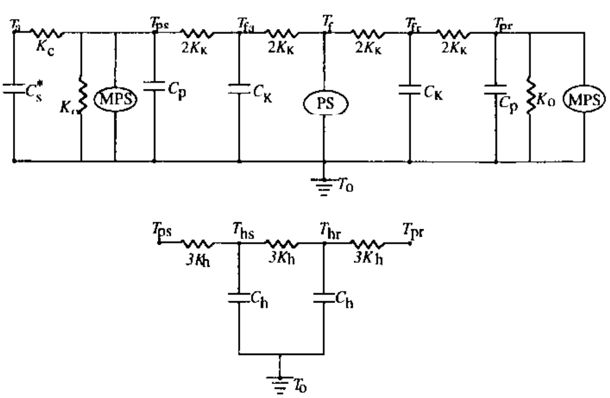

Fig. 1 Equivalent electrical circuits for main heat flows (upper) and mutual heat exchange (lower). PS is the heat source (power source), and MPS's are the micro-heaters

erence material with constant bias in tm-pc-DSC dealt with in this paper. This model can be clearly expressed by an equivalent electric circuit, as shown in Fig. 1. The micro-heaters and the outside furnace are shown as micro-power sources (MPS) and a power source (PS) in the figure, and these micro-power sources supply both alternating and direct current power. The reference material and its cell are not used, because they cause uncontrollable experimental factors, as pointed out by Hatta and his co-worker before [10].

In this model, temperature difference among the sample and the cell is neglected, and that among the micro-heater, the temperature sensor and the sample cell holder is assumed also to be negligibly small.

Fundamental equations

The fundamental equations for theoretical approach are given below and they are corresponding to the equivalent circuit in Fig. 1.;

$$C_K dT_{fs}/dt = 2K_K(T_f - T_{fs}) + 2K_K(T_{ps} - T_{fs}) \quad (1)$$

$$C_p dT_{ps}/dt = 2K_K(T_{fs} - T_{ps}) + K_c(T_s - T_{ps}) + 3K_h(T_{hs} - T_{ps}) + K_o(T_o - T_{ps}) + P^*_{ps}\exp(i\omega t) + P_{ps0} \quad (2)$$

$$C^*_s dT_s / dt = K_c(T_{ps} - T_s) \quad (3)$$

$$C_h dT_{hs}/dt = 3K_h(T_{ps} - T_{hs}) + 3K_h(T_{hr} - T_{hs}) \quad (4)$$

$$C_h dT_{hr}/dt = 3K_h(T_{pr} - T_{hr}) + 3K_h(T_{hs} - T_{hr}) \quad (5)$$

$$C_p dT_{pr}/dt = 2K_K(T_{fr} - T_{pr}) + 3K_h(T_{hr} - T_{pr}) + K_o(T_o - T_{pr}) + P^*_{pr}\exp(i\omega t) + P_{pr0} \quad (6)$$

and

$$C_K dT_{fr}/dt = 2K_K(T_f - T_{fr}) + 2K_K(T_{pr} - T_{fr}) \quad (7)$$

where C, T, t, K, P^*, P_0 and ω are the heat capacity, the temperature, the time, the heat transfer coefficient, the complex amplitude of oscillating energy input, the constant energy input and the angular frequency, respectively. The subscripts for the temperatures and energy inputs, f, fs, ps, s, pr, fr, hs, hr and o denote respectively (1) the outside furnace, (2) the midpoint between the furnace and the sample, (3) the sample cell holder, (4) the sample, (5) the reference material cell holder, (6) the midpoint between the furnace and the reference material, (7) a point in the heat path for mutual heat exchange, (8) another similar point near the reference material, and (9) the environment respectively, while the subscripts for the heat capacities and the heat transfer coefficients, K, p, s, h, c and o denote respectively (1) the heat paths between the outside furnace and the sample or the reference material cell holder, (2) the cell holders, (3) the sample, (4) the heat path for the mutual heat exchange, (5) the thermal contact and (6) the heat paths to the environment. These symbols are also shown in Fig. 1 of the equivalent electrical circuits. For the apparatus without the outside furnace, K_K equals to zero.

The asterisks mean that these quantities are complex numbers consisting of the real and the imaginary parts. The complex numbers are introduced to express both the amplitude and the phase angle of the modulation, while i is the unit of imaginary numbers and exp(ix) is equal to cosx+isinx. The micro-heaters do not cool the sample or the reference material, so that the absolute value of P^* is not larger than P_0. Because the sample heat capacity may shift the phase angle, it is also expressed as a complex figure, as follows;

$$C^* = C' - iC'' \tag{8}$$

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

The temperature of the cell holder plate of the sample side controlled instead of the sample temperature itself [11, 12], so that

$$T_{ps} = T_b + \beta t + A_{ps}\exp(i\omega t) \tag{9}$$

where T_b, and β are the initial temperature and the underlying heating rate, respectively. Temperature is a real quantity, so that only the real parts have physical meanings in Eq. (9) and in the other similar equations below. The temperature of the outside furnace is also controlled at the same constant heating rate;

$$T_f = T_b + \beta t \tag{10}$$

Derivation and solutions

In the steady state the other temperatures can be assumed to 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 [13]. Therefore, the other temperatures, T_i, can change as follows with definite temperature lag, B_i,

$$T_i = T_b + A_i^*\exp(i\omega t) + \beta t - \beta_i' t - B_i t \tag{11}$$

where β' expresses the difference in the underlying heating rate due to the heat loss to the environment [13].

Because the sample temperature changes as described in Eq. (11) in the steady state, the equation for the sample temperature is introduced into Eq. (3) together with Eq. (9). Thus we obtain the following relations;

$$\beta_s' = 0 \tag{12}$$

$$\beta C_s' = K_c(B_s - B_{ps}) \tag{13}$$

and

$$A_s^* = A_{ps}(1 + \omega\tau_s'' - i\omega\tau_s') / [(1 + \omega\tau_s'')^2 + \omega^2\tau_s'^2] \tag{14}$$

where

$$\tau_s' = C_s' / K_c \tag{15}$$

$$\tau_s'' = C_s'' / K_c \tag{16}$$

Thus the thermal contact causes phase shift and amplitude decrement.

Introducing Eq. (11) for the other temperatures into the fundamental Eqs (1), (2) and (4–7) together with Eqs (9), (10), (12–14), and comparing the coefficients in these equations, as was done before [6, 7], we can get the following relations;

$$\beta C_s' = (K_K + 2K_h + K_o)\Delta B_p + \Delta P_0 \tag{17}$$

and

$$\Delta A_p^{fwd5*}[(2K_K + 3K_H + K_o) + i\omega C_p - K_K / (1 + i\omega\tau_K) - K_h / (1 + i\omega\tau_h)] =$$
$$-i\omega C_s^* A_{ps}(1 + \omega\tau_s'' - i\omega\tau_s') / [(1 + \omega\tau_s'')^2 + \omega^2\tau_s'^2] + \Delta P^* \tag{18}$$

where

$$\Delta B_p = B_{ps} - B_{pr} \tag{19}$$

$$\Delta P_0 = P_{ps0} - P_{pr0} \tag{20}$$

$$\Delta A_p^* = A_{ps} - A_{pr}^* \tag{21}$$

$$\Delta P^* = P_{ps}^* - P_{pr}^* \tag{22}$$

$$\tau_K = C_K / 4K_K \tag{23}$$

and

$$\tau_h = C_h / 9K_h \tag{24}$$

The temperature difference between the sample side and the reference material side is controlled to be zero in pc-DSC, so that

$$\Delta B_p = 0 \tag{25}$$

and

$$\Delta A_p^* = 0 \tag{26}$$

Therefore,

$$\beta C_s' - \Delta P_0 \tag{27}$$

which is the base for heat capacity measurements by conventional pc-DSC, and

$$i\omega C_s^* A_{ps}(1+\omega\tau_s''-i\omega\tau_s')/[(1+\omega\tau_s'')^2+\omega^2\tau_s'^2] = \Delta P^* \tag{28}$$

When the thermal contact is good enough and its effect can be neglected, τ_s' and τ_s'' are approximated to be zero. By separating the real parts and the imaginary parts, we get

$$\omega C_s'' A_{ps} = \Delta P' \tag{29}$$

and

$$\omega C_s' A_{ps} = -\Delta P'' \tag{30}$$

where

$$\Delta P^* = \Delta P' - i\Delta P'' \tag{31}$$

When the reference material is used and both the thermal contacts of the sample cell and the reference cell are good enough, Eqs (29) and (30) can be applied by replacing C_s' and C_s'' by the real part and the imaginary part of the heat capacity difference between the sample and the reference material.

Discussion

It is quite clear that the relation of the real and imaginary parts of the output signal, ΔP^*, with those of the complex heat capacity is very simple. This is caused by the power compensation, and it is a large advantage of tm-pc-DSC over tm-hf-DSC. However, in tm-hf-DSC we can get another signal, i.e., the phase difference between the controlled temperature, such as the sample temperature, and the output signal of the temperature difference. We have possibility that the effect of the thermal contact can be eliminated by using this phase difference, as pointed out first by Hatta and his co-worker [10] and confirmed later by the present authors for a more realistic model [7]. Thus, the power compensation gives us the above advantage but brings us a disadvantage.

It should be pointed out that the temperature distribution among the sample, the cell holder, the temperature sensor and the micro-heater is neglected in the model in this paper. The temperature distribution seems very small, but it may cause phase difference among those temperatures and amplitude decrement similarly to the effect of the thermal contact, because thermal resistances among them [11, 12] and heat capacities also cause phase lag and amplitude decrement. This may be a cause of errors in tm-pc-DSC.

It should be noted that the conventional heat capacity measurement by pc-DSC is not influenced by the thermal contact, as is clearly seen in Eq. (27).

Concluding remarks

The steady state of tm-pc-DSC is dealt with in this paper, and the following points are made clear.

(1) The phase of the output signal (the compensation power difference) is directly related with the real and imaginary parts of the complex sample heat capacity, so that the imaginary part of the sample heat capacity can clearly be detected by tm-pc-DSC, when the thermal contact between the sample cell and its cell holder is good enough.

(2) While the thermal contact has no effect on the conventional heat capacity measurement, it causes the phase shift and amplitude decrement of the output signal, and thus it may cause error of the measurement in tm-pc-DSC. In contrast with tm-hf-DSC, we do not have any mean to estimate this effect, because there is no phase difference between the output signal and the controlled sample temperature modulation.

(3) The heat capacities and the thermal resistances accompanied with the sample cell, the cell holder, the temperature sensor and the micro-heater may cause the phase shift and amplitude decrement of the output signal, and hence they may cause error.

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