Other TM techniques

DEVELOPMENT OF A NEW TYPE OF LIGHT MODULATED DSC

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Abstract

A new type of the light modulated DSC was constructed. Optical fibers are used to separate the light source from the furnace. The sample can be handled accurately because the lamp and the intensity modulator are not above the furnace. Quality of the measured signal is much improved by extracting the analog signal from the electronic circuit board in the commercial DSC. Light intensities of the sample and reference sides are controlled independently from each other. A method to compensate for the asymmetry of the thermal system utilizing the independent control of the light intensity is proposed.

Keywords: compensation for asymmetry, light modulated DSC, optical fiber

Introduction

Commercial instrumentation is used for most temperature modulated DSC (TMDSC) studies where the modulated temperature to the sample is generated by the same heater used in conventional DSC. We have developed another type of temperature modulated DSC called light modulated DSC (LMDSC) in which the light energy was used to generate the modulated heat flow [1, 2]. The apparatus reported in references [1] and [2] will be referred to as the original apparatus hereafter. It was found that LMDSC can be operated at much higher modulation frequencies than commercial instruments. The highest frequency reached by the original apparatus was 0.5 Hz. Commercial instrumentation can reach about 0.1 Hz, but at frequencies higher than 0.05 Hz the time dependence of the modulated heat flow notably deviates from the programmed one. The benefits of the high modulation frequency were shown in the study of the complex heat capacity in the melting temperature range of polyethylene crystals [3]. In the results from

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conventional DSC information of the heat capacity of the crystal during melting was obscured by the contribution from the latent heat. We have shown that the contribution from the latent heat can be excluded at a modulation frequency equal to or higher than 0.1 Hz. High modulation frequencies are useful, as well, for measuring the frequency dependent heat capacity near the glass transition temperature. It should be noted that at high modulation frequencies a high underlying heating rate does not contradict the temperature resolution because the integral period of Fourier transformation becomes shorter as the modulation frequency becomes higher.

The original apparatus worked successfully to give useful results at high modulation frequencies, however, there are three problems with the original apparatus. The first problem is that handling of the sample is inconvenient because the light heating system is rigidly fixed above the furnace. The second problem is that the quality of the measured signal is not good enough for the TMDSC experiment. In the original apparatus the signal to the pen-recorder is monitored by a personal computer, however, a signal at a point closer to the signal source should be monitored. The third problem is that the commercial heat flux type DSC used is an old model and lacks sufficient sensitivity. In order to solve these problems a second apparatus was constructed. In this paper the structure and the characteristic features of the second LMDSC apparatus are reported.

Structure of the second apparatus

The second apparatus is constructed by combining the light heating system with a commercial DSC. A diagram of the whole system is shown in Fig. 1. The heat flux type DSC indicated by 'e' in Fig. 1 is a Thermo Plus 8230 from Rigaku Co. The sensitivity of this DSC is ten times greater than that of the original apparatus. The third problem was solved by using a new commercial DSC.

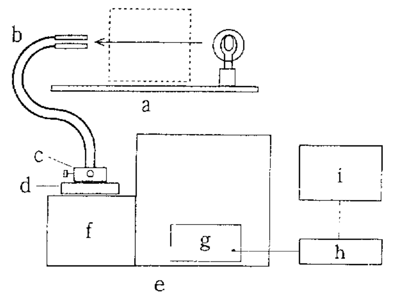

Fig. 1 A diagram of the second apparatus of the light modulated DSC; a) light modulating system, b) optical fibers, c) an adjustable xy table, d) a furnace lid, e) a commercial DSC, f) shell of the furnace, g) an electric circuit board, h) a digital multimeter and i) a personal computer

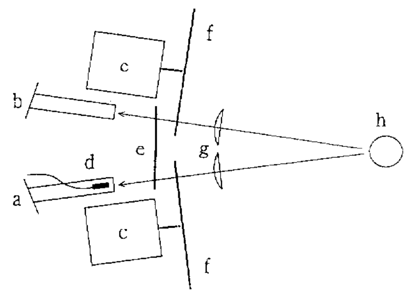

Fig. 2 Structure of the light intensity modulator; a) an optical fiber for the sample side, b) an optical fiber for the reference side, c) stepping motors, d) photo transistor, e) a fixed polarizer, f) rotated polarizers, g) condenser lenses and h) a lamp

The light modulating system is not fixed above the furnace but on a frame 'a' apart from the furnace. The structure inside the box of dashed lines will be explained later (Fig. 2). The light modulating system is connected to the furnace by optical fibers 'b'. The furnace lid can be removed completely from that top of the furnace and handling of the sample is as easy as with conventional DSC. Therefore the first problem was solved. The light emitting ends of the optical fibers are inserted into the holes in the furnace lid 'd' and held by the two dimensionally adjustable table 'c' which makes optimizing the optical fiber positions easily. A furnace lid larger than the standard one used in commercial instrument is necessary to support the adjustable table. The shell 'f' of the furnace is specially designed to fit the larger lid. Two pins are set on the furnace shell to determine the direction of the lid. Inner lids have glass windows to pass the light. It should be noted that this type of light modulating system can be used with any type of commercial instrument by only making an appropriate furnace lid.

The second problem was solved as explained below. In order to monitor the signal at a point close to its source the electronic circuit board 'g' in the commercial DSC is modified. The analog input signal to the AD converter is extracted and measured by the digital multimeter 'h', type 2000 from Keithley Instruments Inc., operated at a sampling rate of 25 Hz with 22 bits resolution. Typical sampling rate for a commercial instrument is 10 Hz which is not high enough for a modulation faster than 0.1 Hz. The data are sent to a personal computer 'i'.

Light intensity modulator

Figure 2 shows the light intensity modulator in the box of dashed lines in Fig. 1. The essential idea of the light intensity modulator is similar to that of the original apparatus. The light from the lamp 'h' in Fig. 2 goes into the optical fibers 'a' and 'b' after passing through the lens 'g' and the polarizers 'f' and 'e'. The optical fibers 'a' and 'b' are for the sample and reference sides, respectively. The polarizers 'f' are rotated by the stepping motors 'c' and the polarizer 'e' is fixed. The light intensity $I(t)$ after the two polarizers is given by

$$I(t) = I_0(1 + \sin\omega t)$$

where I_0, ω and t are the amplitude of the modulated light intensity, the angular frequency of the modulation and time, respectively. The light intensity is monitored by the photo transistor 'd' which is set just above the optical fiber 'a'. The monitored signal is used as a standard for the phase of the cyclic component of the DSC signal. Therefore the phase difference between the temperature modulation and the modulated heat flow can be obtained. This is an advantage of LMDSC because the phase of the modulated heat flow can not be directly measured by the commercial TMDSC.

In the original apparatus only one rotated polarizer was used. The light intensities incident to the sample and reference sides changed simultaneously. In the second apparatus the light intensities of the sample and reference sides are controlled independently from each other. The independent control has an advantage of compensating for the deviation from the symmetry of the furnace and the sample cells as explained later.

Measured signals

The output signals were investigated at a fixed temperature of 313 K and during heating process from 313 to 433 K at the heating rate of 5 K min^{-1}. A thin aluminum plate (an aluminum lid) was used as a test material, which was put in an aluminum pan and placed on the sample side. An empty pan was placed on the reference side. Carbon powder was sprayed over the materials for light absorption. The modulation frequency was 0.1 Hz and the modulated light was incident to both the sample and reference sides. Data sampling of 500 points were accumulated in the digital multimeter during 20 s. After the data were sent to the personal computer data accumulation was restarted and this cycle was repeated every 30 s.

The standard deviations of the amplitude and the phase of the cyclic component were calculated from the data of the fixed temperature measurement. The results are 0.1% for the amplitude and 0.06 deg for the phase. The standard deviations are less than a quarter of those of the original apparatus. The result of the heating measurement is shown in Fig. 3 with the open and solid circles being the amplitude and phase of the cyclic component, respectively. The quality of the data does not change during the heating process which indicates a sufficient stability of the apparatus with changing temperature. Temperature dependence of the amplitude and phase are due to the temperature dependence of the complex calibration constants [2] . In the case of ac calorimetry the value of the phase is –90 deg. The observed values larger than –90 deg mean that the cyclic component of the heat flow from the sample and reference materials to the base plate is not negligible.

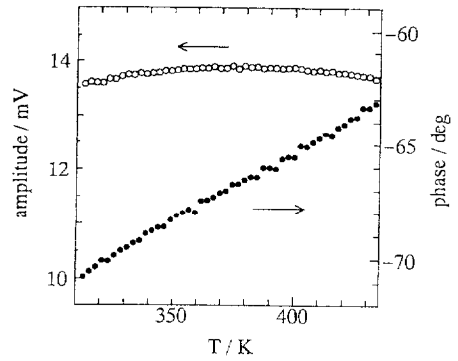

Fig. 3 Temperature dependence of the amplitude and the phase of the cyclic component. Modulation frequency and underlying heating rate are 0.1 Hz and 5 K min^{-1}, respectively

Compensation for asymmetry

The thermal system composed of the furnace and the sample cells is not completely symmetric. Asymmetry of these components gives rise to errors of the experimental results. The independent control of the light intensities provides a method to compensate for the asymmetry. There are various origins of the asymmetry. We express the asymmetry by parameters s_i and r_i where s and r mean the sample and reference sides, respectively, and for example i=1 means the mass of the sample cell, i=2 means the thermal resistance between the sample cell and the base plate, and so on. The values of r_i are different from s_i byΔ_i, that is, $r_i=s_i+\Delta_i$. The complex amplitude of the modulated light incident to the sample and reference sides are written as s_L and r_L, respectively, and the difference between s_L and r_L is written as Δ_L ($r_L=s_L+\Delta_L$). The complex amplitude of the cyclic component of the temperature difference between the sample and reference sides is written as $\Delta T(s_1, ..., r_1, ..., s_L, r_L)$. It is assumed that ΔT is well approximated by a linear expansion.

$$\Delta T(s_1, ..., r_1, ..., s_L, r_L) =$$

$$= \Delta T(s_1, ..., s_1, ..., s_L, s_L) + \sum_i \frac{\partial \Delta T}{\partial r_i}\Delta_i + \frac{\partial \Delta T}{\partial r_L}\Delta_L \qquad (1)$$

The value of Δ_L can be adjusted to make the asymmetric part of Eq. (1) is equal to zero, that is,

$$\sum_{i}\frac{\partial \Delta T}{\partial r_i}\Delta_i + \frac{\partial \Delta T}{\partial r_L}\Delta_L = 0 \qquad (2)$$

Therefore the asymmetric thermal system becomes virtually symmetric.

We investigated a practical possibility of the above theoretical consideration following the procedures below.

(1) The amplitude of the cyclic component of the output signal from the empty furnace was minimized by adjusting the amplitude and the phase of the incident light to the reference side.

(2) An aluminum pan containing one aluminum lid was placed on each of the sample and reference sides. The mass of the materials and the thermal resistance between the pan and the base plate were not completely symmetric. The modulated light was incident only on the sample side.

(3) The modulated light was incident only on the reference side.

(4) Modulating both the sample and reference sides the amplitude was minimized again.

(5) Another lid was added to the sample side. Both of the sample and reference sides were modulated.

The amplitude was measured after each procedure. After the procedure (4) the amplitude was measured seven times resetting the pan on the sample side each time before measurement to investigate reproducibility. A mark was drawn on the side wall of the pan and the pan was reset to keep the mark in the same direction. The results are (1) 0.22, (2) 58.92, (3) 50.62, (4) 0.84±0.28 and (5) 13.62 mV. The difference between the results of (2) and (3) is due to the asymmetry of the mass of the materials and the thermal contact between the pan and the base plate. This difference, 8.30 mV, is decreased down to about one tenth of it by optimizing Δ_L. The minimized amplitude and its standard deviation are, respectively, 6.2% and 2.1% of the result of (5) which corresponds to the difference of heat capacity of one lid. The amplitude was much reduced by optimizing Δ_L but the minimized value is not small enough to neglect the asymmetric part of Eq. (1). At present the phase angle can be changed stepwise by 1.44 deg, which is determined by single stepping of the motor. The minimum amplitude will be decreased by controlling the phase angle continuously. After the procedure (4) the furnace was heated to 453 K at 5 K min^{-1}. The amplitude changed by 0.3 mV during the heating process because of temperature dependence of the values of s_i and r_i. The amount of change is comparable with the standard deviation of (4). The lower limit of the asymmetric part is determined by the standard deviation accompanying the sample setting and the temperature change of the calibration constants. This method of compensation for the asymmetry will be useful for semi-quantitative measurement.

Summary

1) A second light modulated DSC instrument was constructed using optical fibers to separate the light source from the furnace.

2) The quality of the measured signal was found to be much improved.

3) Light intensities of the sample and reference sides were controlled independently from each other.

4) A method to compensate for the asymmetry of the thermal system was proposed.

References

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