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Thermochimica Acta 432 (2005) 177–185

thermochimica acta

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Non-adiabatic thin-film (chip) nanocalorimetry

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Received 7 November 2004; received in revised form 25 January 2005; accepted 31 January 2005
Available online 23 March 2005

Abstract

To study the kinetics of processes on a millisecond time scale a thin-film nanocalorimeter based on a commercially available microchip (thermal conductivity vacuum gauge, TCG 3880, from Xensor Integration, NL) was constructed. The gauge consists of a submicron silicon nitride membrane with a film-thermopile and a film-heater, which are located at the 100 μm × 100 μm central part of the membrane. Controlled fast cooling is possible in addition to fast heating at essentially non-adiabatic conditions. To allow fast cooling the measurements are performed in an ambient gas atmosphere. It is proved that the maximum rate of the controlled cooling can be achieved with a gas cooling agent, rather than in a system with a solid heat-sink. The advantage of the gauge TCG 3880 is that its central heated region is small enough to be considered as a point source of the heat-flow into the gas, which essentially simplifies the calorimeter calibration. The maximum cooling rate is inversely proportional to the radius of the heated region. The gauge is placed in a thermostat with controlled gas pressure and temperature to be utilized as a device for fast scanning calorimetry of sub microgram samples with sensitivity 1 nJ/K and time resolution ca. 5 ms.

Keywords: Ultra fast scanning calorimetry; Thin-film calorimetry; Nanocalorimetry; Melting and crystallization

1. Introduction

Ultra fast scanning nanocalorimetry is required to study kinetics of fast processes. It provides important information on thermodynamic properties and structure changes in materials at fast thermal treatments. This is of interest because a lot of modern materials are used in non-equilibrium states. The actual thermodynamic state of semicrystalline polymers, as an example, can be investigated only at sufficiently high heating rates ca. 10^3 K/s and even more [1–4]. Such rates are needed to prevent reorganization during the temperature scan. Only in this case it is possible to study exclusively the melting of the crystals originally present in the sample [5,6]. These non-equilibrium states are often generated by rapid cooling during material processing. Therefore, calorimetric experiments at high cooling rates comparable to processing conditions are required too. Thus, cooling rates up to 10^3 K/s are necessary for studies of phase transitions under the same conditions as during injection moulding of polymers [2–4]. The possibility of heat capacity measurements at high cooling rates is necessary for the investigation of crystallization and amorphization processes at quenching too.

Though heating rate can be enlarged by increasing heating power and decreasing sample mass [7–10], the only way to increase the cooling rate up to 10^3 K/s and larger is diminishing of the cell-sample dimensions, since the cooling possibility of any system is restricted by a finite heat transfer from the system. That is why a thin-film nanocalorimeter is very promising for fast cooling measurements. Obviously fast cooling measurements must be performed under essentially *non-adiabatic* conditions.

Thin-film calorimetry has been developed rapidly in recent years [7–16]. The major impulse is the general drive towards nanoscale objects in condensed matter physics. The capabilities of calorimetric techniques have been greatly enhanced with introduction of the silicon nitride membrane technology [16]. Constructing of a thin-film microchip module on

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0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.073

a submicron silicon nitride membrane [17] therefore opens extensive capabilities. Sensitivity of such thin-film calorimeters can be very high primarily due to the very small addenda produced by the cell itself.

Recently Allen et al. developed a thin-film nanocalorimetry based on silicon nitride membranes for ultra fast heating, which was successfully applied for the study of numerous effects in a wide variety of nanosized samples [7–10,13–15]. The cell of the calorimeter consists of a thin-film heater deposited on a silicon nitride membrane. The heater simultaneously serves as a resistive thermometer. Thus, the heat capacity of ultra thin films [8,9] and separated polymer crystals [10], as well as nanoparticles and nanostructures [8,10] at ultra fast heating up to 10^5 K/s were investigated. Near-adiabatic conditions were achieved, when the cell was placed in vacuum ca. 10^{-5}–10^{-6} Pa. In the pioneering works custom designed sensors were constructed. At present, a number of commercially available microchip modules can be used as a sensor for thin-film nanocalorimetry [11,17–23].

In our study a commercially available thermal conductivity vacuum gauge TCG 3880 from Xensor Integration [17], which was applied for AC nanoscale calorimetry in [23], was used for non-adiabatic fast scanning calorimetry [5,6,22]. The measurements were performed in an ambient gas atmosphere rather than under adiabatic conditions to allow fast controlled cooling. Compared to specially designed calorimeter structures, the gauge TCG 3880 has significantly smaller active area (the heater size is about 50 μm × 100 μm), which presents a considerable advantage for non-adiabatic calorimetry [5,6,22]. Thus, the measurements at controlled heating and cooling rates up to 10^4 K/s were realized [5,6,22]. The kinetics of recrystallization and melt memory in semicrystalline poly(ethylene-terephthalate) (PET) on the time scales ranging from 5 ms to hours was investigated in previous papers [5,6]. As it was found for PET crystallized at 130 °C reorganization needs less than 40 ms between 150 and 200 °C. Additionally it was shown in [6] that isothermal reorganization of semicrystalline PET at 223 °C is about two orders of magnitude faster than isothermal crystallization from the isotropic melt at the same temperature.

The pressure gauge TCG 3880 is actually not optimized for fast scanning calorimetry. In the present work we therefore focused on basic aspects of non-adiabatic fast scanning calorimetry to allow the development of an even better sensor for fast scanning calorimetry. Finally, we present an improved experimental set-up of the thin-film (chip) nanocalorimeter.

To realize calorimetry at high scanning rates the addenda and the sample should have sufficiently small heat capacity. The cooling agent must be thermally “inertia less” too, i.e. it must have a small heat capacity as shown below. There are two possibilities to realize a fast cooling device: (i) using a solid heat sink (cold finger) made from high thermal conducting materials like metals but adding a large heat capacity to the system or (ii) using a low thermal conducting gas with very low heat capacity as the cooling medium. In order to make a decision which cooling medium is best suited for fast cooling we estimate the maximum cooling rate for both cases.

We assume at this point that the cooling system has no moving parts, i.e. no movement of the cooling agent occurs. In this case, as it is proved below, the highest cooling rate can be attained at the lowest heat capacity of the cooling agent, while the thermal conductivity is not a governing factor.

2. Upper limit of the scanning rate in fast cooling calorimetry

First, we determine the upper limit of the scanning rate for a system with a “cold finger” shown in Fig. 1.

A cell with a sample is placed at the flat face of a uniform rod with a specific heat capacity c, density ρ, thermal conductivity λ, and length L. The other face of the rod is coupled with a massive cooler, which is kept at a low temperature T_0. The temperature of the sample/rod interface is controlled by a thin flat heater with a negligible heat capacity and thermal resistance. Ideal thermal contacts between the sample and the heater, as well as between the heater and the rod, are assumed. To determine the upper limit of the scanning rate first suppose the heat capacities of the cell and the sample are small enough to be neglected. A uniform heat flux $q(t)$ is supplied to the face of the rod at $z = 0$ and transmitted along the rod axis. The heat leakage from the lateral surface of the rod is negligible. The temperature distribution in the rod $T(z, t)$ is described by Fourier’s heat-transfer equation:

$$\rho c \cdot \partial T(z,t)/\partial t = \lambda \cdot \partial^2 T(z,t)/\partial z^2. \quad (1)$$

Usually, the sample temperature is scanned linearly with time. Consider a saw-tooth shaped heating–cooling process with a period τ_0 and amplitude ΔT. The sample temperature is driven by a periodic heat flux $q(t)$ with an amplitude q_0 (the flux is changed in the range from 0 to $2q_0$). This periodic process can be presented as a sum of harmonic functions with pe-

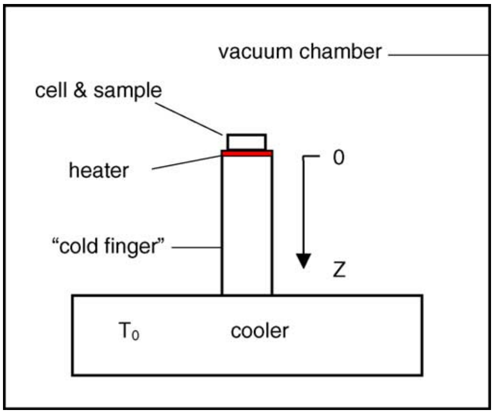

Fig. 1. Scheme of the system with a “cold finger”. The cell with the sample is placed at the flat face of a “cold finger” coupled with a cooler, which is kept at a low temperature T_0. The temperature of the sample is controlled by a thin heater located at the face of the finger.