

Power Compensated Differential Scanning Calorimeter for Studying of Solidification of Metals and Polymers on Millisecond Time Scale

Evgeny Zhuravlev Zhuravlev and Christoph Schick

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Fast scanning calorimetry becomes more and more important because an increasing number of materials are created or used far from thermodynamic equilibrium. Fast scanning, especially on cooling, allows for the in-situ investigation of structure formation, which is of particular interest in a wide range of materials like polymers, metals, pharmaceuticals to name a few. Freestanding silicon nitride membranes are commonly used as low addenda heat capacity fast scanning calorimetric sensors. A differential setup based on commercially available sensors is described. To enhance performance of the device a new power compensation scheme was developed. The fast analog amplifiers allow calorimetric measurements up to 100,000 K s⁻¹. The lower limit is defined by the sensitivity of the device and is 1 K s⁻¹ for sharp melting or crystallization events in metals and ca. 100 K s⁻¹ for broad transitions in polymers. A few examples to demonstrate the performance of the device are given.

Keywords: Fast scanning nano calorimetry, differential power compensation, crystallization, polymers, metals.

1. Introduction — Fast scanning calorimetric techniques

In polymers, pharmaceuticals, and metal alloys metastability is the rule rather than the exception, and the study of the kinetics of such systems has become an important issue.^{1,2)} For a thorough understanding of the kinetics of all kinds of temperature- and time-dependent processes related to metastability there is an urgent need for new (calorimetric) techniques enabling the use of high cooling and heating rates.³⁾

Conventional DSC is one of the few techniques that have already a relatively large dynamic range of scanning rates. They allow (quasi) isothermal measurements and scanning rates up to 10 K s^{-1} for power compensated DSC's.^{1,4}) Several approaches are known how to overcome these limitations. Most of them are based on thin film techniques. Quasi-adiabatic scanning calorimetry at high heating rates, ca. 500 K s⁻¹, was developed by Hager⁵⁾ and even for rates up to 10^7 K s^{-1} , by Allen and co-workers.^{6,7)} But as mentioned above further investigation of metastable phase formation can be obtained only if the same high controlled cooling rates are available too. The maximum cooling rate is generally limited by the ratio between maximum heat flow rate away from the measuring cell and the heat capacity of measuring cell and sample.⁸⁻¹¹⁾ Fast scanning non-adiabatic nano-calorimeters based on thin film sensors (**Fig.1**)¹²⁾ with extremely small addenda heat capacity and sample masses therefore extend scanning rate range at cooling dramatically. This is a technique capable of applying both controlled heating and controlled cooling at rates up to $10^6 \text{ K s}^{-1,8-11}$

The single sensor ultra-fast scanning device was successfully applied for the investigation of polymer melting and crystallization. The reorganization kinetics in poly(ethylene terephthalate) (PET) and isotactic polystyrene (iPS) was studied at scanning rates covering



Fig.1 Thin film chip sensor based on a thin free standing SiN_x film on a silicon frame and measuring area of 60 \times 80 μ m² in the centre of the film. (a)- Different photographs of the sensor. (b) - Schematic cross section of the sensor with sample (not to scale). (c) - Microphotograph of a sample loaded sensor XI 296.

8 orders of magnitude.¹³⁻¹⁵⁾ Isothermal and non-isothermal crystallization and the formation of different crystal polymorphs were studied in isotactic polypropylene (iPP) and other polymers.^{16,17}) The complex behaviour in the temperature range between glass transition and melting temperature was investigated in poly(butylene terephthalate) (PBT).¹⁸⁾ The crystallization and cold crystallization suppression in polyamide 6 (PA6) confined to droplets and in the bulk was studied using such a fast scanning calorimeter.¹⁹⁾ The dynamic range of scanning rates of the device allowed the investigation of superheating in polymers.8,20) The isothermal and nonisothermal crystallization in a wide range of temperatures and scanning rates and subsequent melting of iPP were investigated by means of DSC and the fast scanning setup.21-23)

The examples given below show that the effective range of controlled heating and cooling rates using different sensors is $100...10^6 \text{ K s}^{-1}$.¹²⁾ For some experiments with the smallest sensor and sub-nanogram samples even a cooling rate of 2 MK s⁻¹ was achieved.²⁴⁾ Unfortunately, at low rates signal to noise ratio and therefore sensitivity is dramatically reduced. Usually the device is limited to rates above 100 K s^{-1} . Nevertheless, the scanning rate range between conventional DSC and this technique in the range $10...10 \text{ K s}^{-1}$ is of high interest because several material processing steps are applying cooling rates just in this range.³⁾

The very successfully applied single sensor device as described in ^{9-11,25,26}) was therefore first analyzed and the weak points were identified.

- The first problem is the non-interactive temperature control, which is based on a predefined voltagetime profile yielding an essentially linear temperature increase of the sensor. But the needed voltage is only known for the empty sensor but not for the sample loaded one. Therefore the voltage profile should be corrected for each experiment by making at least one test scan with the sample under investigation.¹¹ This limits the application to "first scans", which are often needed if the influence of the sample history is of particular interest.
- Another problem is the sample temperature discontinuity at phase transitions. Even if a preliminary scan was performed to adjust the voltage profile for linear heating and cooling, the scanning rate during sharp transitions may significantly deviate from the programmed value. This results in smearing and inaccuracy of heat capacity and enthalpy determination. Similar problems exist for the adiabatic fast scanning

devices.27)

• The main problem for heat capacity determination for the non-adiabatic single sensor device is the subtraction of the heat loss function. It is realized as a subtraction of a 3^{rd} to 5^{th} order polynomial function¹¹ providing C_p values symmetric around zero. But as soon as we have several sharp events in the sample, the error in determination of the loss polynomial increases dramatically. Details of the problem are discussed elsewhere.²⁸

To overcome these difficulties a differential scheme of two such sensors and power compensation was constructed. It is based on the same thin film sensors as previously used.^{9,11,29)} The presence of an empty reference sensor reduces the influence of heat losses and addenda heat capacity on the obtained data dramatically. For a better sample temperature control, particularly in the transition regions, a power compensation was introduced, this way following the work by Rodriguez-Viejo et al.³⁰⁾ To improve signal to noise ratio and resolution of the device even under fast scanning conditions an analog power compensation technique was implemented. A differential power compensation scheme provides, under conditions of ideal symmetry of both sensors, directly the heat flow rate into the sample, which simplifies heat capacity calculation. Furthermore, a user-friendly experiment management software and a software package for data evaluation was developed. The device including control and data treatment algorithms and measurements on polymeric and metal samples on solidification are presented next to demonstrate the benefits of the instrument.

2. The Device

The developed instrument is intended to measure heat flow rate into the sample as the power difference between empty and sample loaded sensor during fast temperature scans on heating and cooling at controlled rate. Finally, the obtained heat flow rate can be recalculated into heat capacity.

A very successful version of a power compensation differential scanning calorimeter was realized by PerkinElmer.³¹⁻³⁴⁾ It is based on the measurement of the energy difference required to keep both sides, sample and reference, at the same temperature throughout the analysis. When an endothermic transition occurs, the energy absorbed by the sample is compensated by an increased energy input to the sample to maintain the temperature balance. Because this energy input, under the assumption of a perfectly symmetric measuring system, is precisely equivalent in magnitude to the energy absorbed in the transition, a recording of this balancing energy yields a direct calorimetric measurement of the energy of the transition. The block diagram of the PE power compensation DSC is shown on **Fig.2**. It consists of two separate control loops: one for the control of the average temperature of both cups, the second for the control of the temperature difference between the cups.

The average controller compares the arithmetic average of sample and reference temperature with the program temperature. In case of a deviation the average controller corrects the electrical power to both cups accordingly. Due to the feed back the difference between measured average temperature and program temperature is minimized. If the temperature called for by the programmer is greater than the average temperature of sample and reference holders, more power will be fed to both heaters, which, like the thermometers, are embedded in the cups to realize a short response time of the whole system.

The second controller measures the temperature difference between both cups. Signals representing the sample and reference temperatures, measured by the platinum thermometers, are fed to the differential temperature amplifier. The differential temperature amplifier output will then adjust the power difference increment fed to the reference and sample heaters in the direction and magnitude necessary to correct any temperature difference between them. In case of a lower temperature of the sample cup, e.g. due to an endothermic transition, an additional power is added to the sample cup. In order to minimize the difference most effectively and to keep a strict symmetry of the measuring system the same power is subtracted on the reference side. Consequently, the heat of transition is provided by the average controller keeping the average temperature following the program temperature. The remaining temperature difference between both cups, which is proportional to the power difference,^{31,33)} is recorded and together with the average temperature profile it provides the complete information about the heat flow rate to the sample. This scheme proves itself in PerkinElmer



Fig.2 Perkin Elmer power compensation scheme. The average temperature controller makes both sensors to follow programmed temperature. The differential controller compensates the heat flow changes due to events in the sample. Symmetric compensation to both reference and sample side simplifies computation of heat flow to the sample which was critical for that time when computers were not yet available.³¹⁻³⁴⁾

DSC calorimeters working up to 10 K s⁻¹ scanning rate with milligram samples. Summarizing, in the PE differential power compensation DSC the additional heat needed (or released) during an endothermic (exothermic) event in the sample is finally provided by the average controller because the differential controller does not add or remove heat from the system due to his symmetric operation. This scheme allows for a relatively simple determination of the heat flow difference from the remaining temperature difference between sample and reference cups,^{31,33)} not requiring measuring multiple signals or computing capabilities. But in this case both controllers must be fast to avoid deviations from the programmed temperature. Therefore it is common practice to use proportional control for both controller, average as well as differential.

But as soon as we want to go to higher rates and sensitivity we met the problem of controller performance limitations. This is because the differential signal can contain fast events from the nanogram samples, requiring fast response of the controllers. Time resolution for the control of the average temperature could be much slower if the fast sample events would not be included. Output power range (dynamics) of the average controller is orders of magnitude larger than needed for the compensation of the sample related effects. Therefore it may be beneficial to separate average and difference control



Fig.3 Modification of power compensation scheme for operation at high scanning rates. Separation of differential (small voltages, fast events) and average temperature control (large voltages, slow changes).

totally avoiding any cross talk between both control loops.

Following this idea we developed a new power compensation scheme to realize such separate control loops as shown on **Fig.3**.³⁵⁾ First, we measure and control reference sensors' temperature alone. No average temperature is used. There is no influence of any, even very strong, events on the sample sensor on the reference temperature controller. This allows us to use a relatively slow but precise PID controller for the reference temperature control. The integral part of the controller assures that the difference between program temperature and reference temperature is practically zero. Applying the output voltage of the PID also to the sample sensor heater yields nearly the same temperature profile in the sample sensor as in the reference sensor if a high symmetry between reference and sample sensor is realized. Next, the differential controller detects any difference between reference and sample sensor temperatures and adds or subtracts its output voltage to the PID output to the sample sensor alone. This way a total separation between both controllers is realized. It allows us to use a precisely but relatively slow working PID controller for the control of the reference temperature and a high sensitive and fast proportional controller for the difference controller.

Compared to the PerkinElmer power compensation scheme this allows a more precise control of the temperature of both sensors. But the proportionality between the remaining temperature difference in the differential control loop and the differential heat flow rate is lost. Therefore the new scheme requires the measurement of more than only one signal to allow recalculation of the power difference as it is described elsewhere.²⁸⁾

The resistive film-heaters of the sensors, ca. 1 k Ω provide the power, which is supplied to the membrane/sample interface and propagates through the sample, membrane and the ambient gas. For a perfectly power compensated system power is distributed in a way that both sensors are always at the same temperature, T, and scanned at the programmed rate, dT/dt, independend of any heat effect in the sample. Assuming an ideally symmetric differential system, which means equal addenda heat capacities C_0 on both sides and equal heat losses $P_{loss}(T)$ to the sourrounding on both sides. Then the heat balance equations for both sensors are as follows:

reference:
$$C_0(T) \frac{\mathrm{d}T}{\mathrm{d}t} = P_0(T) - P_{loss}(T)$$
 (1.1)

sample:
$$[C_0(T) + C(T)] \frac{\mathrm{d}T}{\mathrm{d}t} = P_0(T) + P_{diff}(T) - P_{loss}(T)$$
 (1.2)

where *C* is sample heat capacity. In this particular case the difference between equation (1.1) and (1.2) yields $C(T)\frac{dT}{dt} = P_{diff}(T)$ (1.3)

where P_{diff} is the difference between the power supplied to the sample and the reference sensors. Consequently, the aim was to set up a system with near to perfect power compensation, which allows determination of P_{diff} and finally to correct for unavoidable asymmetries between both sides in real measurements at high scanning rates.

3. Hardware and Software Realization

The setup consists of thermostat, control electronics, ADC/DAC converter, computer and software package as schematically shown on **Fig.4**.

The scheme of the cryostat was originally developed for an AC-calorimeter¹⁰⁾ and used for the single sensor fast scanning chip calorimeter.³⁶⁾ It was further developed for differential AC-chip-calorimeters³⁷⁾ and adapted for the fast scanning chip calorimeter described here. Both calorimeters, AC and fast scanning, are planned to be integrated and used complementary on the same sample in future.

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Fig.4 The Fast Scanning Calorimeter setup. Sensors are placed in the oven at the bottom of a tube in a (reduced pressure) gas environment. Heaters and thermopiles are connected to analog electronic devices. The electronics is driven from a computer by a fast ADC/DAC board (temperature setpoint determination and data collection). The electronic devices are controlled by software which is also used for data collection/evaluation.

Systems (SRS) Small Instrumentation Modules (SIM).³⁸⁾ The simple handling, block architecture, flexible adjustment of unit parameters and high performance were the reason to choose the SRS Small Instrumentation Modules to develop the new calorimeter.

The reference temperature amplifier feeds the analog PID controller, which compares it with a setpoint received from the computer. A bandwidth of 100 kHz, very low noise (8 nV Hz^{-0.5} above 10 kHz) and digital control of all parameters makes it a very flexible temperature control unit. Even larger bandwidth of 1 MHz and smaller noise level has the amplifier for the proportional power compensation circuit. Same amplifiers were used for thermopile voltage and voltage difference preamplification.

Hardware manipulation, experiment control and obtained data evaluation were realized in a software package programmed in LabView. The data evaluation software also includes the heat capacity recalculation which is described elsewhere.²⁸⁾

4. Solidification of Metals and Polymers Studied by Fast Scanning Calorimeter

For testing the device melting and crystallization of small spherical metal particles (μ m diameter) was studied. For such first order phase transitions the expected heat capacity and the resulting heat flow curves are



Fig.5 Heating - cooling of a tin sample of 250 ng at 500 K s⁻¹. (a) - Remaining temperature difference and temperature profile, (b)- recalculated heat capacity and (c) - scaled peaks for comparison (be aware of the different scales for heat capacity as well as for time).

known. Even the particles were small the heat of fusion was large compared to the addenda heat capacity of the sensors. Therefore strong deviations of the programmed temperature profile were detected at low differential gain settings as shown below. Nevertheless, at proper gain settings the instrument is capable to handle such transitions in a very good manner.

In order to observe melting and crystallization the Sn particle was heated from room temperature up to 650 K and cooled back at 500 K s⁻¹. The temperature profile and the obtained remaining temperature difference are shown on **Fig.5(a)**. Recalculated heat capacity on heating and cooling are represented on **Fig.5(b)**.

On heating the peak shape is determined by the heat transfer from the sensor to the relatively heavy



Fig.6 Influence of gain setting of the differential controller on the resulting curves for a tin sample of about 250 ng at 1,000 K s⁻¹ heating rate. A
Remaining temperature difference during the melting transition. B - recalculated power difference and heat of fusion (inset), which saturates with higher gain settings indicating that power compensation works properly.



Fig.7 Heating scans of a 24 ng tin sample at different rates on sensor XI 296. Data from the single sensor device (dashed lines) and the differential setup with power compensation (solid lines) are shown for comparison. The same sample on the same sensor was measured in both devices.

sample. The well known linear leading edge of the peak is therefore seen on Fig.5(c). Crystallization on cooling is much faster because of about 100 K supercooling. Therefore heat flow rate during crystallization can be considered as a delta function. The observed response of the instrument then corresponds to the apparatus function and the width of the measured peak gives a good estimate of the time resolution. As shown on Fig.5(c) the width of the crystallization peak is only 3 ms. The sharp crystallization peak nicely demonstrates the power of the device in handling fast processes. Here we show the reaction time of the device for the sensor XI-320. If one wants to study faster reactions one should use sensors with one thermopile and smaller heated area (*e.g.* XI-292), which is also



Fig.8 (a) (upper panel)- Temperature time profile for investigation of isothermal crystallization of a ca. 20 ng iPP. A (bottom panel) - Temperature increase due to the release of crystallization enthalpy. The inset shows the approach to isothermal conditions, which takes about 3 ms. (b) - Evaluation of the data considering a superposition of an exponential decay of the heat flow rate and the Avrami function (1.4).

suited for faster heating/cooling rates.

The effect of differential gain is shown on **Fig.6(a)** for a relatively large tin sample of about 250 ng. For low gain settings the melting peak is much broader than for higher gain settings. Not enough heat is given to the sample sensor, and consequently to the sample, allowing the sample to melt as fast as limited by the heat transfer (thermal resistivity) between sensor and sample. Only at high gain settings this limit is reached and a limiting shape of the peak is seen. At low gain settings prerequisites for the power determination like equal temperature for reference and sample sensor are

not fulfilled during melting. Therefore the area, see inset, is smaller and reaches the true value only for gain settings above 10. The tin particle diameter of ca 20 μ m corresponds to sample mass of ng, which heat of fusion is 0.017 mJ. The measured heat of fusion (**Fig.6(b**)) was 0.016 mJ. This rough estimation (diameter determination as a main source of error) shows that quantitative determination of heat of fusion is possible. This functionality is also realized in FSC Viewer software.

Fig.7 shows a comparison of data obtained by the single sensor fast scanning calorimeter without power compensation and the differential fast scanning calorimeter with power compensation. The power compensation yields much sharper peaks, which show the expected shape for a thermal resistivity limited heat flow rate to the melting sample. The estimated enthalpy of fusion from the size (ca. 10 μ m) is 2.5 μ J. The measured value was 2.9 μ J which corresponds to 11 μ m particle.

The possibility to quench samples at controlled high rates allows us to study isothermal crystallization after such quenches. Isothermal crystallization of iPP was investigated at very low temperatures where crystallization occurs in several milliseconds, what is outside the resolution of conventional DSC's.^{22,2326,39)}

The temperature profile and the temperature difference during the isothermal experiment are shown on **Fig.8(a)**. The sample temperature shows a 3 ms undershoot of 0.1 K before the programmed temperature is reached. After that the crystallization peak is observed at essentially constant temperature. It can be fitted using a superposition of an exponential decay and the Avrami model.^{22,40)}

5. Summary

A differential power compensated fast scanning calorimeter on the basis of thin film chip sensors was constructed. The power compensation scheme was slightly modified compared to the well known scheme used in the PerkinElmer DSCs. Instead of controlling the average temperature of both sensors the new scheme controls only the temperature of the reference sensor forcing it to follow the programmed temperature profile. A PID controller is used here and the output is fed not only to the reference sensor, which temperature is measured, but to the sample sensor too. Any occurring temperature difference between reference and sample sensor is recognized by a second controller. The output of this differential controller is subtracted from the PID output on the sample side alone. Contrary to the PerkinElmer scheme the differential controller does not act on the reference sensor at all. This way the two control loops are fully separated and can be designed according the particular task they have to solve. We use a PID controller for the reference temperature and a very fast proportional controller for the differential loop.

The device was applied to the study of melting and crystallization of metals and polymers. Response time is typically in the order of 5 ms and allows investigation of very fast processes on heating and cooling as shown in the given examples.

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Evgeny Zhuravlev

University of Rostock, Institute of Physics, Wismarsche Str. 43-45, 18051 Rostock, Germany



Christoph Schick

University of Rostock, Institute of Physics, Wismarsche Str. 43-45, 18051 Rostock, Germany e-mail: christoph.schick@uni-rostock.de