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Experimental determination of the nucleation rates of undercooled micron-sized liquid droplets based on fast chip calorimetry

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ABSTRACT

Accurate thermal analyzes and calorimetry measurements depend on careful calibration measurements. For conventional differential scanning calorimeters (DSC) the calibration procedure is well known. The melting point of different pure metals is measured and compared with literature data to adjust the temperature reading of the calorimeter. Likewise, the measured melting enthalpies of standard reference substances serve for enthalpy calibration. Yet for fast chip calorimetry, new procedures need to be established. For the medium-area and large-area calorimeter chips, this procedure needs to be modified, because the calibration behavior depends on the position of the sample on the measurement area. Additionally, a way to calibrate the calorimeter for measurements performed during cooling will also be shown. For this second aspect, the athermal and diffusionless martensitic phase transformation of $Ni_{49.9}$–$Ti_{50.1}$ at% was used. The well-calibrated sensor chips are ideally suited to perform nucleation rate density analyzes based on a statistical approach. Here, the nucleation rate densities of micron-sized pure Sn droplets that had been coated with a non-catalytic coating have been determined by experimental analysis of the statistical variance of the undercooling response.

1. Introduction

1.1. Calibration

Calibrating a fast scanning calorimeter involves inherent difficulties with the positioning of the samples on the measurement area of the chips. Small-area to large-area calorimeter chips are available in a range of the lateral dimension of the measurement area from 5 μm to 100 μm. As for the large-area chips, the distance from the sample to the thermopile depends strongly on the sample position, so the response from the sample to the thermopile is different for each position. This results in a calibration "drift" over the entire measurement area, which makes a position calibration necessary. In case of pure metals, the calibration can easily be performed by the comparison of the measured melting point (the onset of the melting endotherm) with known data from the literature. Accepted standards for calibration in the temperature range of interest are, e.g., gallium (Ga), indium (In), tin (Sn) or zinc (Zn). In case of alloys, the melting point depends strongly on the composition, and without exact knowledge of the composition a calibration is impossible.

Calibrating a scanning calorimeter (or a thermal analysis device) on cooling is a general problem caused by the effect of undercooling in the case of solidification (or almost generally in case of first-order phase transformations that a material undergoes during cooling). Since undercooling is a stochastic effect, a comparison of the characteristic temperature of the phase transformation obtained during cooling with the respective literature data is impossible. However, some indication on the accuracy of the obtained temperature measurements during a cooling experiment can be obtained from analyzing the thermal symmetry of the device. A check for symmetry of the heating and cooling calibration can be realized by a magnetic transition [1]. However, the calorimeter chips used here are limited to a maximum temperature of 773 K. Materials with magnetic transitions in this temperature range are, e.g., nickel and gadolinium. Yet the signal of the magnetic transition of a small sample (of the order of several 10×10^{-9} g) is too low to obtain an adequate resolution of the measurement. Instead of utilizing the magnetic transformation, a calibration on cooling can be realized by the use of a martensitic phase transformation. This transition is a diffusionless (only next nearest neighbor interaction involved) and an athermal transition (no activation energy), propagating through the sample basically with the speed of sound once the transformation temperature has been reached. The transformed volume fraction is then only dependent on the temperature,

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leading to an equilibrium condition of the volume phase enthalpy and the enthalpy arising by stress/strain mainly occurring due to the phase interfaces [2]. The experimental time scale to achieve the equilibrium state is negligible due to the high values of the speed of sound in solids (>10^3 m/s). For a 10 μm large sample at a certain temperature the transformation time can be estimated to be less than 10^{-8} s. For calibration, a sample of nickel and titanium with a composition of $Ni_{49.9}$–$Ti_{50.1}$ in at% was selected since the martensitic temperature is in the range of interest. This martensitic transformation of $Ni_{49.9}$–$Ti_{50.1}$ has a specific transformation enthalpy of 29 J/g, which results in a comparably large and more reliably measurable signal in the temperature range between 303 K and 403 K.

The calibration can be applied to nucleation rate density measurements. Utilizing a statistical approach, the nucleation rate density can be determined from a statistical data set of undercooling values [3–5]. To reduce the systematic error of the temperature measurements to a minimum, a stringent and thorough calibration is necessary.

The aim of this study is to demonstrate the dependence of the calibration on the position of the sample on the chip. Additionally, a way to calibrate alloys on the specific position and a way for calibration during cooling will be shown. At last, the calibration is applied to quantitatively determine the nucleation rate densities of crystallization of pure Sn, by utilizing a purely statistical approach that directly yields quantitative values of the nucleation rate densities. This approach is of specific significance for fast chip calorimetry, since this method can easily yield datasets with sufficient statistical significance.

1.2. Statistical analysis of nucleation rate densities

The use of statistical analyzes to determinate nucleation rate densities from experimentally collected undercooling data was first performed by Uttormark et al. [3] and later by Wilde et al. [4]. The chip-based, fast-scanning calorimetry [6] allows collecting a statistical amount of data in a short time. In combination with the experimental sampling of statistically relevant data ensembles, a new method for a rapid determination of nucleation rate densities is proposed. Yang et al. [7] utilized a similar approach by using a histogram based statistical analysis. Bokeloh et al. [5] introduce a more accurate way of data processing by the help of a so-called “survivorship” function. In the present work, the data processing based on slow-scan differential thermal analysis measurements [5] is applied for the first time onto the properly calibrated measurement results obtained by fast chip calorimetry.

The stochastic nature of the nucleation process allows measuring the nucleation rate density from the statistical scatter of the undercooling response $\Delta T = T_m - T$ during repeated measurements under identical conditions, where T_m is the melting temperature and T is the onset temperature of the phase transformation measured during cooling. Since the nucleation events are independent and occur randomly in time, they satisfy the conditions of a Poisson process [4]. Three formal mathematical requirements must be satisfied for a Poisson process: first, a parameter $\lambda > 0$ must exist such that for a time interval Δt the probability for one event to occur is $\lambda \Delta t$. Second, the probability for the occurrence of one event in the interval Δt must be negligible. As the third requirement, the number of events in an interval of width Δt must be independent of the number of events in the previous interval [5]. The parameter λ denotes the average number of events per unit time (i.e., represents the rate constant or the nucleation rate). It should be noted that the commonly used term “nucleation rate” truly represents a nucleation rate density. If λ itself depends on time, the process is called a non-homogeneous Poisson process.

As shown earlier [4,8], the nucleation rate density is proportional to the rate constant and is obtained by weighting the directly obtained rate constant by the sample mass, m, or volume, V. The nucleation rate density, J, on a per-mass basis is then given as:

$$J = \frac{\lambda(t)}{m} \tag{1}$$

which, based on the linear relation between mass and volume is similar to the approach given in [8]. t denotes the time. The number of events N expected in a time interval from t_0 to t_1 is given by:

$$N = \int_{t_0}^{t_1} \lambda(t)\mathrm{d}t \tag{2}$$

In the case of nucleation, the time elapsed while the sample was undercooled until the first nucleation event occurs is of interest. Because of the deep undercooling of the sample, it crystallizes completely after the occurrence of the first nucleation event. The cumulative distribution $c(t)$ returns the probability that one event took place after a given time. The survivorship function $F_{\mathrm{sur}}(t)$ returns the probability that no event took place after a given time [8]:

$$c(t) = 1 - \exp\left(-\int_{t_0}^{t_1} \lambda(t')\mathrm{d}t'\right) \tag{3}$$

$$F_{\mathrm{sur}}(t) = \exp\left(-\int_{t_0}^{t_1} \lambda(t')\mathrm{d}t'\right) \tag{4}$$

t' denotes the integration variable in units of time. The probability distribution function $f(t)$ returns the probability that the event takes place after the time t:

$$f(t) = \lambda(t) \times F_{\mathrm{sur}}(t) \tag{5}$$

The distribution of times elapsed between two events during continuous cooling at a given rate β with $T = T_0 + \beta t$ is given by:

$$f(T) = \lambda(t) \times \exp\left(-\int_0^T \frac{\lambda(T')}{\beta}\mathrm{d}T'\right) \tag{6}$$

T' denotes the variable of integration in units of temperature. In the present study, the statistics was probed by repeating the measurement of the crystallization onset temperature for a single sample. The experiment thus measures the time until the first nucleation event appears. Repeated measurements are used to probe the probability distribution $f(T)$ and the rate parameter $\lambda(T)$. The nucleation rate density is calculated from the survivorship function as [8]:

$$\lambda(T) = \frac{\mathrm{d}}{\mathrm{d}T}[-\ln(F_{\mathrm{sur}}(T))] \tag{7}$$

Here, the description of nucleation rate densities for phase transformations of first order according to Ehrenfest’s classification follows the classical nucleation theory. For the analysis, the following expression of the nucleation rate density was chosen:

$$J = \Omega \times \exp\left(\frac{-\Delta G^*}{k_B T}\right) \tag{8}$$

where Ω is the kinetic prefactor, ΔG^* the free enthalpy barrier of nucleation and k_B denotes Boltzman’s constant. According to Bokeloh et al. [5], the free enthalpy barrier can be described by one