Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 779–784

TEMPERATURE CALIBRATION OF TMAs USING MODULATED TEMPERATURE AND CURIE TEMPERATURE REFERENCE STANDARDS

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Abstract

This article presents the concept of calibrating temperature in thermomechanical analyzers (TMA) using reference standard magnetic materials whose Curie temperatures are well-known. This concept has not been tested experimentally to the best of the author's knowledge. Electrical current applied to a unifilarly wound furnace results in the furnace acting as an electrical inductor. A magnetic material sample located within such a furnace practically constitutes a solenoid core. A modulated temperature program directly results in a corresponding varying force exerted by the sample against the TMA probe, if the probe's axis and the central induced magnetic field line of force are coaxial, and, furthermore, if the direction of the central magnetic field line of force and the expansion direction of the probe are identical. If a sample undergoes a Curie transition, then the force which the sample exerts against the probe will diminish to zero as the transition goes to completion. Using a modulated temperature program throughout this phase transition allows determination of transition completion, by observation of the point at which the force required to maintain the sample's physical position reaches a steady state from it's previously non-steady state.

Keywords: chirp modulation, Curie transition, modulated temperature, temperature calibration, TMA

Introduction

Bifilarly wound furnaces are necessary in thermogravimetric analyzers when samples with magnetic properties are analyzed, because such samples can be undesirably thrown from their pans by the sudden application of a large electrical current to a unifilarly wound furnace. A unifilarly wound furnace acts as an electrical inductor in such cases, and such sudden electrical currents often occur at the start of a TG experiment as the furnace temperature controller works to bring the furnace temperature into compliance with the desired time-temperature program. This electrical inductor phenomenon can hypothetically be used to the analyst's advantage in the case of calibrating temperature in thermomechanical analyzers.

It is well-known that temperature calibration in TMAs is plagued by imprecision. Direct contact of the thermocouple with the sample is preferable to proximity of the

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1418–2874/2000/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

thermocouple to the sample, and calibrations done with penetration probes and melting point reference standards may not always be accurate for all types of probes and samples. Clearly the physical size of the hot zones in the furnaces involved, sample size and reactivity, probe type, and contact or non-contact of the thermocouple with the sample all significantly impact the accuracy and precision of the results obtained.

Ideally, of course, the only difference between calibration experiments and sample analysis experiments is the presence of a sample in the sample analysis experiment. If a probe type other than penetration is required by the sample, however, and a melting point standard must be used for temperature calibration, this is not always possible. Hypothetically, it should be possible to eliminate this discrepancy and increase the precision of results by calibrating temperature in thermomechanical analyzers using reference standards with well-known Curie temperatures, also known as magnetic transitions. A list of such standards is found in [1]. Calibrating a TMA in this matter is similar to calibrating a thermogravimetric analyzer (TGA) using magnetic standards, [2].

Results and discussion

The solenoid principle is the basis of this suggested method for calibrating temperature in TMA using reference standards with well-known Curie temperatures. Electrical current applied to a unifilarly wound furnace results in the furnace acting as an electrical inductor, or solenoid. A sample with ferromagnetic properties located within such a furnace practically constitutes a solenoid core. The force required to maintain the sample's position is provided by the TMA probe (Fig. 1). When electrical current passes through the furnace – considered here to be a finite, straight, thin-shell movable core solenoid (Figs 2 and 3) – the magnetic field strength B along the axis of the solenoid may be calculated by Eq. (1).

$$B=\frac{\mu_0 iN}{2l}\left[\frac{x_2}{\sqrt{x_2^2+r^2}}-\frac{x_1}{\sqrt{x_1^2+r^2}}\right] \qquad (1)$$

where μ_0 is the permeability constant $4\pi\times10^{-7}$ Tm/A
i_0 is the electrical current in amps passing through the solenoid windings,
N is the total number of turns in the solenoid,
l is the length of the solenoid in meters,
r is the radius of the solenoid in meters, and
x_1 and x_2 are the distances, on axis from the ends of the solenoid to the magnetic field measurement point, in meters.

In the special case where the magnetic field strength is measured at the center of the solenoid, that is, where the sample lies in the geometric center of the solenoid such that x_1=($-x_2$), Eq. (1) reduces to Eq. (2).

$$B=\frac{\mu_0 iN}{\sqrt{l^2+4r^2}} \qquad (2)$$

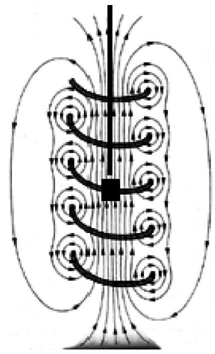

Fig. 1 Cut-away view of unifilarly wound TMA furnace showing probe (vertical solid line), sample (centrally located square) and magnetic lines of force induced by the passage of DC current through the windings. Sample cradle, furnace tube and thermocouple are not shown for clarity. Note that the probe and the central magnetic line of force are coaxial and that the direction of the magnetic field is the same as that of the probe's upward (expansion) movement. (Modified from [3])

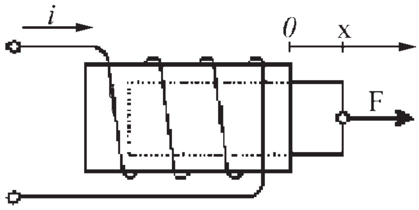

Fig. 2 Movable core solenoid, [4]

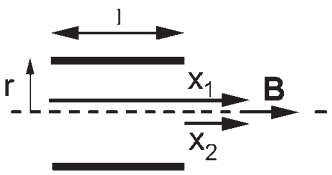

Fig. 3 Cross-sectional view of a theoretical finite, straight, thin-shell solenoid [5]

Equations (1) and (2) show that the magnetic field of a solenoid is controlled by a finite number of easily quantitated variables. The corresponding displacing force, however, exerted by a sample with ferromagnetic properties, in response to the magnetic field of strength B, depends on many variables. These variables may be combined into a comprehensive term called the inductor flux linkage, λ. The dimensions of the solenoid core, the thickness of the solenoid walls, and the dimensions of the sample are easily quantitated flux linkage variables, but the magnitude of the ferromagnetic properties of the sample are not as easily quantitated. The flux linkage variable includes many other factors, also, and so the complex relationship between the variables in the equation for the force is usually represented as Eq. (3), the specifics of which will vary according to the sample and the furnace.

$$F=F(\lambda, x) \quad (3)$$

where x is the position of the solenoid core (sample) along the central axis of the solenoid relative to the geometric center of the solenoid [5].

A modulated temperature program generated by the electrical current passing through a unifilarly wound furnace directly results in a corresponding varying force exerted by the sample against the TMA probe, if the probe's axis and the central induced magnetic field line of force are coaxial, and, furthermore, if the direction of the central magnetic field line of force and the expansion direction of the probe are identical (Fig. 1). In short, the sample exerts a force against the probe proportional to the magnitude of the induced magnetic field, and, quite importantly, that force over time qualitatively follows the profile of the current *vs.* time, unless the sample undergoes a Curie transition. Theoretically and quite advantageously, the force exerted by the sample against the probe should follow the temperature *vs*. time profile without phase lag, but feedback and response time constants of the TMA apparatus would certainly cause some phase lag. The advantage here lies in the fact that, if calibration reference standards and samples have similar dimensions and mass, then heat transfer issues are minimized.

If a sample undergoes a Curie transition under experimental conditions as described above, then the force which the sample exerts against the probe will diminish to zero as the transition goes to completion and all of the ferromagnetic character of the sample disappears. Using a modulated electrical current throughout this phase transition hypothetically allows determination of transition completion by observation of the time at which the force required to maintain the sample's physical position reaches a steady state from its previously non-steady state, which tracked the applied current *vs*. time profile. Consider the case of a sawtooth temperature modulation program, as shown in Fig. 4. Essentially, as the sample experiences a varying displacive force, it exerts a corresponding force against the TMA probe. In a TMA with static masses, the sample may physically move, but a TMA with an electromechanically

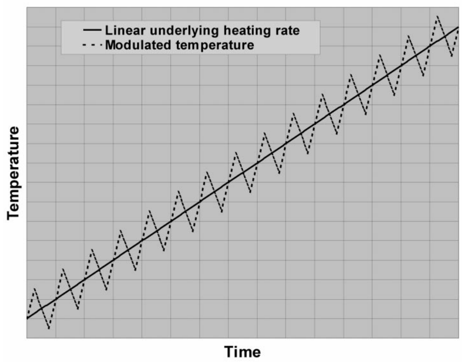

Fig. 4 Linear and sawtooth modulated temperature *vs*. time programs

controlled probe would likely keep the sample in place. The force required to keep the sample stationary in the latter case could easily be used as the analytical signal. In either case, though, the result would be the same: as the sample undergoes a Curie transition, an analytical signal of measureable magnitude would change significantly to allow non-arbitrary determination of the process end point, that is, the assigned Curie temperature, and thus allow accurate and precise TMA temperature calibration.

Figure 5 shows the sample response of a sample with ferromagnetic properties, subjected to a sawtooth temperature modulation with linear underlying heating rate, before, during and after a Curie transition. For the sake of simplicity, the Curie transition is presumed to occur linearly over a finite temperature range and over the duration of five modulation cycles. Also shown in Fig. 5 is the first derivative of the sample response to the modulated temperature program. The point at which all magnetic properties of the sample disappear – the definition of the material's Curie temperature – is easily discerned from these graphs. This ease of analysis presents a great advantage to the analyst.

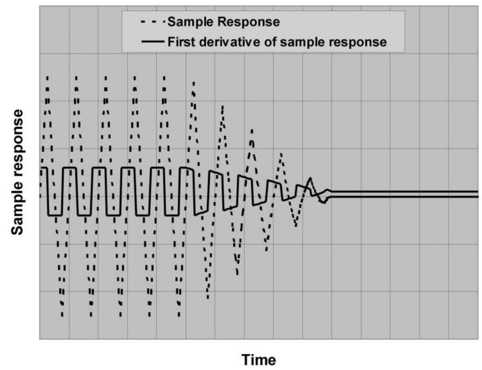

Fig. 5 Response of a sample with ferromagnetic properties to a sawtooth modulated temperature program, before, during and after a Curie transition. The dashed line is the derivative *vs*. time of sample response

The modulated electrical current used in these calibrations could be of any type – sawtooth, square wave, sine wave or other – so long as the displacive force experienced by the sample was significantly different between local minima and maxima on the modulation current *vs*. time profile. In other words, the analytical signal must be of magnitude sufficient to detect, and with differences great enough to exceed the signal-to-noise threshold. This is most easily accomplished using a proposed type of modulation dubbed here as chirp-type.

Chirp-type electrical modulation would have the benefits of minimized system temperature modulation and maximized displacive force experienced by the sample. Chirp-type modulation would consist of large periodic increases in the power applied to the furnace. Chirps would be sufficiently large to cause significant increases in the instantaneous magnetic field strength, but sufficiently brief to cause virtually no disruption to the temperature of the system. For example, suppose that a 100 W furnace heater requires 50 W to heat a sample at 10°C min^{-1}. 50 W over 60 s translates to

3000 J transferred to the system. If a 50 W chirp lasting 10 ms was applied sixty times during that minute, then only thirty additional joules would be added to the system during that time. Thirty additional joules represents a 1% increase in the energy applied to the system and a corresponding temperature increase of 0.1°C over 1 min.

Another benefit of chirp-type modulation would be avoiding the difficulty of assigning a single temperature to a system undergoing significant temperature modulation. Millisecond duration full-power chirps to the electrical current required to generate an otherwise linear time-temperature profile should result in minimal temperature disturbances to the sample and furnace hot zone, while simultaneously inducing the maximum strength magnetic field within the furnace hot zone. As long as the sample is not thrown from the sample cavity by this, the response of the instrument to this disturbance would resemble the disturbances observed when short, relatively strong vibrations occur proximate to a running TMA, e.g., a lab drawer slamming shut under the instrument. These disturbances would diminish as the sample undergoes a Curie transition, and the end point would be empirically simple to determine because it would be the time at which the sample baseline becomes smooth. As shown in Fig. 5, analyzing the first derivative would further enhance the accuracy of this end-point assignment.

Conclusions

Hypothetically, any standard reference material which undergoes a Curie transition may be used to accurately and precisely calibrate temperature in thermomechanical analyzers with unifilarly wound furnaces, if the TMA probe's axis and the central induced magnetic field line of force are coaxial, and, furthermore, if the direction of the central magnetic field line of force and the expansion direction of the probe are identical. The displacive force which such a sample exerts against the TMA probe will diminish to zero as the Curie transition goes to completion. Using a modulated electrical current throughout this phase transition allows determination of transition completion, by observation of the time at which the force required to maintain the sample's physical position reaches a steady state from its previously non-steady state.

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