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SOME NON CONVENTIONAL DEVICES WITH TEMPERATURE CONTROL
Design and application

A. Amengual

Departament de Física, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain

Abstract

The development of a temperature control system based on semiconductor thermobatteries has been used in a set of devices for studying the martensitic transformation. The devices range from a simple stage for an optical microscope to a more elaborated system as a differential scanning calorimeter [1]. Here the attention is placed in this last system. The general problems of the temperature scanning calorimetry are reviewed from the signal theory point of view and the solutions applied to our system discussed. Some measurements are shown as an example of its application.

Keywords: martensitic transformation, temperature control

Introduction

The martensitic transformation, the solid-solid phase change undergone by some alloys as CuZnAl or NiTi, has been studied with methods like acoustic emission or resistance change. When those studies became more and more detailed, the need for a temperature control at the mK scale was apparent. Hence, some devices working with the same experimental set-up, with small changes to attend different measurements, and a good temperature controlled working space were built. In our devices, the temperature can be programmed and it is controlled by a computer and they are heated and cooled by using the Peltier effect of semiconductor thermobatteries. These provides a suitable means for heating the system and, more important, to extract heat from it by controlling the applied intensity. Alternatively, by the Seebeck effect a thermobattery can provide a voltage signal when there is a temperature difference between their junctions. Hence, thermobatteries can also be used to measure the evolved heat in a given sample.

Among the measurements carried out once the temperature control is attained, the data acquired from the DSC are those requiring a more elaborated analysis. The problem of the analysis can be stated as a problem of a system

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with two inputs and one single output from which one of the inputs has to be extracted. We will review the general problems involved in this process and the solutions fitting our requirements presented. The devices are developed having in mind that the main interest is the study of a physical subject: the hysteretic behaviour and related properties of Cu–based shape memory alloys, mainly CuZnAl.

The shape memory effect is the property by which an alloy deformed in the low temperature phase can recover its original shape when it is heated. This is probably the most striking property of the shape memory alloys (SMA), but, depending on the working temperature, they present other many properties very rare in metals [2, 3]. All of them, which have given to these materials many technological possibilities, are related to the martensitic transformation. In the alloys used in our work, the transformation is reversible and can be induced either by tension or by temperature change. In the transformation induced by temperature there can appear several variants: (transformed regions with the same crystallographic structure but with different orientation) but neither the direct transformation nor the reverse one takes place, in general, at a fixed temperature: the transformation can be produced along a temperature span of several degrees (the actual span depends on alloy type and composition and on thermomechanical treatments) so as the temperature change can be stopped and reversed in the middle of the transformation, this gives rise to internal hysteretic loops. In this case, we talk about a partial transformation and to it we will refer the examples of application of the devices.

The temperature control

Since the middle of this century, using of the Peltier effect of semiconductor thermobatteries has provided a very useful cooling system. Moreover, reversing the sense of the intensity the thermobatteries can also be used for heating. The Peltier effect, which is proportional to the intensity applied, appears together with the Joule effect which determines the minimum accessible temperature. For a given increase in the intensity applied to the thermobattery the increase in the temperature of the system depends on the initial value of the intensity and on the temperature. For example, from room temperature, increasing slightly the intensity from –600 mA, once the steady state have been reached, gives an increase in temperature of 0.02 K/mA whilst from 600 mA the increase is 0.10 K/mA. This means that there is not a linear relationship between intensity, the input signal, and the output or temperature increase. Nevertheless, for a small temperature span, one assumes a linear behaviour and starts working with this hypothesis.

The response of a linear system to any given input signal can be determined from the transfer function (*TF*). It is defined as the response of the system to a unitary Dirac's delta input but, experimentally, it is better determined as the derivative of the normalized response to a heaviside input signal. The product of convolution of this response with the input signal gives the output. In many instances however, it is desired to determine the input signal that produces a given output, for example, here, we wonder about the intensity required to get a given temperature evolution, and when dealing with the calorimetric problem, the situation is similar: the input, heat evolved in the sample, is not known and it has to be recovered from the curve (output signal). These are the well-known deconvolution problems for example, if the transfer function has been already determined, the input can be easily obtained in the Fourier space, despite some care is needed due to the presence of noise in the acquired signal.

The localized constant models or R–C models can describe heat transfer phenomena as those found here. In this case, the transfer function is described in terms of a set of time constants τ_i and τ_i^* (minus their inverse are the poles and zeros of the *TF*) and by a sensitivity S (the output/input ratio under stationary conditions). The number of time constants that can be determined is mainly limited by the noise level. In this description of the transfer function, the deconvolution process is known as inverse filtering and the input signal is obtained from the output, first, dividing by the sensitivity, and later, filtering the poles and zeros one by one.

The way in which the temperature is controlled has been already described elsewhere [4]. The system consist mainly of a computer which controls the intensity applied by a power supply to the thermobattery which heat or cool a copper block. Inside this block there is a platinum resistance whose resistance is read by the computer through a voltmeter. The control operates in this way with feedback: the actual evolution of the temperature is compared with the desired one and the intensity modified in consequence. If the temperature evolution is known before starting the experiments, an approximation to the intensity that will have to be supplied is calculated assuming that the system is linear and using the transfer function in Fourier space. When the temperature spans over a larger range (>5 K) the linear assumption does not hold. In such a case, a sort of learning processes is used. A first cycle is performed with the feedback algorithm modifying the intensity applied to follow the desired temperature profile; this intensity is recorded; then, once the first cycle has finished, the applied intensity is smoothed and used as the intensity to be applied in the next cycle. With this method the temperature profile is followed within 0.01 K yet in the second cycle; at least for the temperature rates used in our works where cooling/heating rates are below $\sim 0.075\ \mathrm{K \cdot s^{-1}}$ because, otherwise, the thermal distance between the sample and the detection position becomes important.

The properties of the thermobatteries used limit the maximum temperature accessible to ~360 K. The minimum one depends on the minimum accessible room temperature and working with a thermal bath to bring the calorimeter to a room temperature near 240 K, the minimum is placed to 225 K. In any case, the maximum difference between the extreme temperatures for a given cycle is approximately 60 K.

Differential scanning calorimeters

DSC is, from a signal theory point of view, the treatment of one single output signal produced by a nominally linear system due to two input signals. Then, the treatment of the curves aims to recover one of the input signals from the single output.

One of the inputs e_m is the heat evolved during the process under study. For example, heat is delivered by the sample during the forward martensitic transformation induced by cooling, and it is absobed in the reverse when the sample is heated. In general, e_m is a function of time t, despite this dependence appears mainly through the temperature programme $T(t)$.

The second input is due to the temperature evolution, $e_T(t)$. Because it is practically impossible to get a perfectly symmetrical system (despite the differential configuration aims to diminish the asymmetry as much as possible) there is always some difference which gives a non-zero signal (base-line) even in absence of thermal dissipation in the sample. These facts can be stated writing

$$e_m(t) + e_T(t) \to s(t)$$

where $s(t)$ is the acquired curve. The arrow represents the a priori unknown, dependence of the output on the input signal. If $s_T(t)$ is the base-line, hence

$$e_T(t) \to s_T(t)$$

The hypothesis made to treat the curve is that

$$s_m(t) = s(t) - s_T(t) \tag{1}$$

That is, the response of the calorimeter is assumed to be linear, (despite this should be experimentally tested). In such a case, the heat evolved in the sample e_m can be finally obtained from a proper deconvolution of the function $s_m(t)$. Now, the most important points to be dealt with in the development of the DSC system will be considered.

Symmetry sample/reference

The most important problem is to obtain two thermobatteries as similar as possible. These could be obtained by comparing a large amount of units. In our case, a severe limitation appears due to the small amount of units which can be compared.

Linearity of the system

Linear systems are characterized by the Transfer Function (*TF*). Obtained experimentally, it provides a simple way to relate the input and output signals: In Fourier space one has $O(\omega) = TF(\omega)I(\omega)$,$\omega$ being the frequency.

In the calorimeter, the output voltage of the thermobatteries depends on both, the temperature difference between their hot and cold faces, and on the mean absolute temperature. Hence, during a measurement, a same voltage acquired at two different temperatures does not correspond to the same evolved heat. In this sense, there is not a simple transfer function for the calorimeter relating the heat evolved with the acquired voltage. Despite that fact, it is possible to study the behaviour of the calorimeter at constant temperature and analyze whether it is linear or not. At constant temperature, heat can be dissipated by the Joule effect. In this way, several heavisides of different amplitude were used to test the linearity. In our system, the sensitivity was measured and it was found a very small deviation from linearity: When the power delivery changed from 9 to 0.09 mW the sensitivity change was from 308.7 to 303.8 mV/W (2%). In the martensitic transformation and at the cooling/heating rates used in our experiments, the power delivered move in that range. Hence, the system will act quite linearly and one can define a Transfer Function, or in its most simple representation, define it through the sensitivity and the first time constants. Now, one can think that there will be a continuous set of transfer functions which can be written as either $TF(T;t)$ or $S(T)$ and $\tau_i(T)$. These will be finally used to obtain the heat delivered from $s_m(T)$.

Base-line determination

In standard calorimetry, the heating/cooling rate is constant and the inversion of the temperature rate is always carried out far from the temperatures at which the phenomena under study take place. This is due to the transient behaviour induced in the calorimeter when the rate dT/dt changes its sign. Far from these zones, the base-line has a smooth behaviour and the remanent slope and curvature of the base-line can be corrected by electronic means, as in standard commercial devices, or by software adjustment of the base-line as in our case.

Nevertheless, in both cases, a final assumption for the base-line has to be done because, whilst the phenomena under study takes places, the actual evolution of the base-line is not known. The assumption made is well-known: Two regions, before and after the thermal dissipation, are estimated by the operator and a line or a parabola is adjusted between both regions. It is expected that this line should be a good approximation to the actual base-line in the middle. Note that there is not much difference between removing the base-line directly from the curve in voltage units or after its conversion to power units. This fact lies in the symmetry between a heat dissipation in the sample and the effect of the temperature evolution, another thermal dissipation from the other side of the thermobattery.

Our device, taking advantage of the temperature control give us the possibility to change smoothly the temperature rate and change it from positive to negative with a controlled base-line evolution. In this way usually the temperature have a sinusoidal profile. Then, the base-line is substracted from the whole curve by different methods depending on the temperature span of the cycling. If the cycling has a high temperature amplitude, the base line is adjusted by a sinusoidal whose phase and amplitude are fitted to the regions without thermal dissipation. Here advantage is taken of the existence of some hysteresis in the martensitic transformation, which produces some delay between the temperature inversion and the beginning of the reverse transformation. If the cycling has an amplitude small enough (below 2–3 K), the cycling is reproduced below or above the transformation region. This gives a base-line which can be used to correct the curve. In power units the corrected curve is:

$$s_m(t) = s_1(t) / S(T_1(t)) - s_2(t) / S(T_2(t)) \qquad (2)$$

$s_1(t)$ is the original curve generated with the programme $T_1(t)$ and $s_2(t)$ is the base-line obtained with the programme $T_2(t) = T_1(t) + \Delta$ (where Δ is a constant value). An important technical detail will be introduced later.

Among the sources of error on the final results obtained from the curve, the uncertainty in the base-line is by far the most important one.

Curve deconvolution

Once the base-line has been removed, the heat delivered $e_m(t)$ has to be recovered from the output $s_m(t)$. This is done by inverse filtering, which requires the knowledge of the sensitivity $S(T)$ and of the time constants. As the time constants does not affect the area (hence, the energy) under the curve, sometimes the thermal inertia in the response is not corrected, and when this is done, the dependence with temperature is usually neglected. For example in our system.

(τ_i changes linearly with temperature , moving from 6.4 s for $T = 230$ K to 8.4 s for $T = 330$ K).

The power delivered in the sample is translated from voltage to power units dividing the curve by *S(T)*. Hence, it is assumed that the static value *S(T)* can be used also when the temperature is changing at a given rate. The following measurement back up this statement: A sinusoidal temperature profile (2000 s of period, $T_{min} = 299.10$ K, $T_{max} = 319.80$ K) was used. A heaviside power delivery was produced by Joule effect (the energy being thus known). Then the curve was treated to measure the energy and the difference between the actual and the measured value was less than 1%. This is usually below the error introduced in the determination of the base-line.

The temperature control effect

The temperature is controlled by modifying the intensity applied to the thermobattery. This produces small fluctuations in the heat supplied/subtrated to/from the copper-block. These fluctuations act as small thermal dissipations which are also acquired by the calorimetric thermobatteries giving rise to an increase in the noise level of the curve. In our system, the noise is placed in this way at the level ±10μV (equivalent to a thermal dissipation of ~30μW at room temperature). However most of the noise has a well-defined source (the intensity fluctuations) and can be removed. In Fig. 1a, it is shown the calorimetric signal acquired when the intensity is increased by an amount δI during 1 second and then brought to its original value. This signal is, for our practical needs, the transfer function $F_I(t;T)$ relating the intensity fluctuation with the calorimetric signal, which obviously depends on the temperature.

To reduce the noise in the acquired curve the intensity that was applied to the thermobattery *I(t)* is smoothed. Hence, the intensity fluctuation $\delta I(t)$ are *I(t)* minus the smoothed function. The noise due to the fluctuations is then removed taking

$$s'_m(T(t)) = s(T(t)) - \delta I(t;T)*F_I(t;T)$$

The symbol * denoting the convolution product. Note that *f(t;T)* represents a set of functions of time, one for each temperature *T* and *g(T(t))*, represents that *g* can be considered either a function of time or a function of the temperature, which are related by the temperature programme. For practical reasons, this is not the expression used to remove the control noise, instead, we use:

$$s'_m(T(t)) = s(T(t)) - (\delta I(t;T) * F_I(t;T_1))\cdot \frac{S\,(T)}{S\,(T_1)}$$

where the response F_1 is evaluated at one single temperature T_1 and it is assumed that its dependence with the temperature is mainly due to the sensitivity. In Fig. 1b, it is shown how the noise level is reduced one order of magnitude by this procedure.

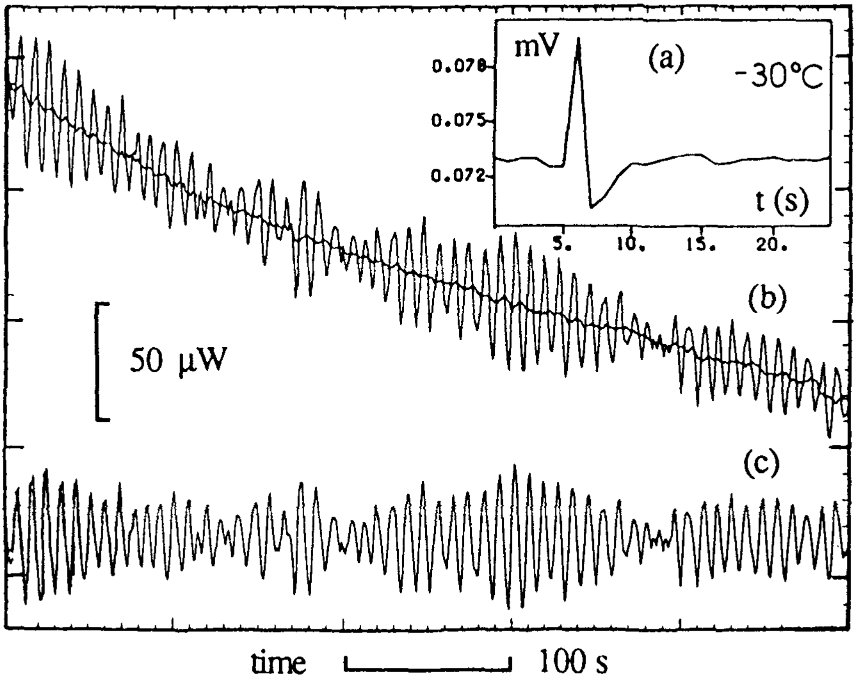

Fig. 1 (a) Perturbation produced on the base-line by a small fluctuation of intensity. (b) Original curve and curve once the control noise has been removed. (c) Effect of the control calculated from $\delta I(t)$. This curve minus curve (b) gives the line plotted through curve (b)

In the case of a programme with a small temperature span, removing the base-line by using (2) would introduce a double effect due to the control noise, first on the original curve and second on the curve at a higher temperature which is intended to be used for removing the base-line evolution. Hence, the noise level would be at least doubled. The solution we found was determining s_2 (Eq. (2)) applying the same intensity $I(t)$ used during the original curve but increased by a constant amount I_o. This I_o shifts the overall temperature of the cycle toward higher temperatures (it could be lower) outside the transformation region. This procedure is more efficient, since, despite the temperature evolution is not exactly the original shifted upwards, it enables us to remove at the same time the base-line evolution and the control noise.

The effect of the temperature control is usually neglected in standard commercial calorimetry because it is not important if the sensitivity is smaller or if the symmetry sample/reference holders is achieved at a higher level.

Some experimental results

Thermobatteries had been used long years ago to record the dynamics of the martensitic transformation and thereby determine the temperatures at which the forward and the reverse transformation starts and finishes. The heating and cooling was produced spontaneously heating the device from outside by Joule effect or cooling it, for example, inside a Dewar with liquid nitrogen. Compared with commercial DSC these non-standard systems provided a greater sensitivity with a better track of the dynamics. Afterwards, trying to use the signal acquired for determining the heat evolved during the transformation was a natural step.

With the idea of performing partial cyclings, which required a good temperature control, in our work the calorimetric thermobatteries were placed on the stage controlled in temperature giving the DSC system we have developed. Two experimental results will be shown below, the emphasis is placed on the measurements themselves, not on their consequences. Both correspond to the use of the calorimeter in conditions where commercial systems could not be used easily.

Single-variant single-interface martensitic transformation

When a CuZnAl alloy undergoes the martensitic transformation up to 24 variants can appear. The different variants appear as needles and triangular plates, accommodating and limiting among themselves, producing a characteristic relief. When the transformation is induced by tension, the appearance of one of the variants is enhanced and the transformation can be single-variant. If we have a single plate of martensite crossing through the sample and the transformation proceeds by the displacement of their interfaces, we talk about a single-interface transformation. The work carried out with this transformation brought us to the determination of the intrinsic thermoelasticity [5]: The interaction of the advancing interface with dislocation that prevents the growth of a plate at a constant temperature, even once the nucleation energy would have been overcome. Nevertheless an interface can advance at a rate of 250 $\mu m \cdot K^{-1}$ hence the temperature has to be carefully controlled to study these transformations.

We have studied the heat evolved during a single-interface single-variant transformation when the advance of the interfaces was induced (a) by increasing the applied tension at constant temperature or (b) by cooling at constant load. In both cases, the process was observed by optical microscopy [6]. Case (a) is much more simple because the temperature is constant (±0.005 K) and the output is directly related to the heat evolved in the sample: Since the temperature is constant the base-line is constant too as it can be seen in Fig. 2a where a curve is shown. In case (b), the evolution of the temperature produces an evolution of the base-line and the temperature control increases the noise level (see Fig. 2b). Here note that filtering the first time constants ($\tau_1 = 9.5$ s, $\tau_1^* = 2$ s) enables to reduce the length of the base-line, reducing in this way also the error on the measurement of the delivered energy (Fig. 2c).

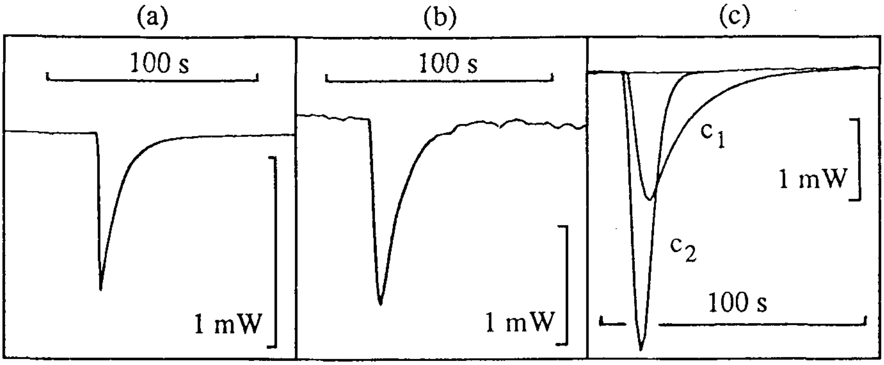

Fig. 2 (a) Curve for the reverse transformation ($m \rightarrow \beta$) induced by tension change at constant temperature. Data shown as acquired. (b) Acquired curve for the same sample than in (a) but the transformation is now induced by temperature change. (c) Curve (b) without base-line (c1) and filtered (c2)

Effect of the partial cycling

In partial cycles the control parameter, temperature or stress, is reversed in the middle of the transformation path. This kind of cycles are of interest since many shape memory devices work in those conditions; they also have theoretical interest to test theoretical and phenomenological models.

From experiments with NiTi springs, there were stated some general rules for their hysteretic behaviour. These rules were afterwards implicitly assumed to be general for other kinds of SMA. For example, when the material is partially transformed and the control parameter is modified, the foregoing transformation path depends on how that state was reached. About this it was stated that if the control parameter passes through its previous local maximum(minimum) the memory of those extremes is erased. In particular, the memory of all the internal loops would be erased when the transformation, forward or reverse, went to completion. It seems that this statement has been the root for the assumption that, having a reproducible global cycle, meaningful partial cycles could be obtained. The calorimetric measurements performed with partial cycling showed that this statement was not true.

As the resistivity of the martensite and of the parent phase is different, the transformation path can be followed recording the resistance change of the sample. This technique has been used by several authors to study partial cyclings as those studied calorimetrically with our system. However, in the resistance hysteresis cycle the effect due to previous partial cycles remained hidden. The reason is that the resistance change is accumulative, and the effects do not appear as clear as they do on the curve.

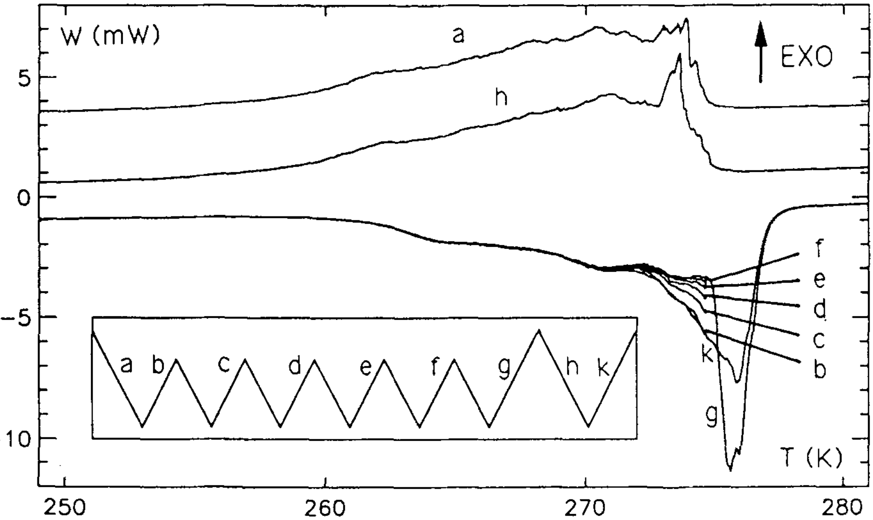

Fig. 3 Curves obtained by cycling in temperature (profile shown in the inset) of a CuZnAl sample. The letters identify each branch

In Fig. 3 it is shown the curve corresponding to the temperature profile shown in the inset. Some of the effects of the partial cycling are easily distinguished. After every partial cycling the amount of transformed material decreases (see curves b–f in the figures). Moreover, the effect produced by several partial cycles does not disappears after one global transformation: subsequent transformations are also affected (compare a and h). Other effects have been discussed elsewhere [7]. Despite a global cycling is reproducible, partial cycling really modify the transformation path and the state of the alloy.

Conclusion

With the study of the martensitic transformation on CuZnAl alloys as the primary goal, several devices have been built, being the DSC the most interesting. They have provided tools to carry out studies in other fields (e.g. studies of bacteria mobility) or information to improve some other devices (e.g. a calorimeter for studying liquid mixtures). The devices themselves are inexpensive and despite the system as a whole (the price of all of the instruments) is obviously by far higher, the instruments used are of general use in the laboratories: voltmeters, computers, ADDA converter, power supplies... giving the possibility of, first, developing several devices by using the same experimental set-up and, second, using the instruments for other purposes once the study finishes.

Our calorimeteric system, compared with a commercial one have some handicaps, for example, the range of available temperatures is, by comparison, small. The maximum available temperature in our systems is ~360 K. This simply restrict the range of alloys that can be studied to those that have the whole transformation inside the range from 350 to 235 K.

We have not still faced the problem of measuring the energy evolved during the transformation in partial cyclings in a systematic way, despite some measurements have been carried out. DSC calorimeters give a powerful tool to study the dynamics of processes exchanging energy with their surroundings, however, the measurement of that energy with an accuracy of 1 or 2% is extremely difficult, but this is the accuracy needed to compare some hypothesis formulated in the literature. The base-line determination problem when the temperature spans over a range of 40 K or more and an accurate calibration of the device makes difficult to get measurements with such an accuracy. This can be the source for the amount of works where several authors disagree about the calorimetric results obtained from calorimetry (these are discussed in [8] and [9]). The exact measurement of the energy evolved in a process activated by the temperature change, hence an energy contribution from outside, is quite difficult. At present, with our devices we can focus on some particular cases, for example, a calorimetric study of a single-interface single-variant transformation where the temperature range is small. However, the analysis of the energy evolved in larger cycles is more difficult. The martensitic transformation finishes with a long tail (Fig. 3) where the power delivered decreases very slowly, this makes unclear the exact location of the base-line, giving the most important error source and an item to be overcome.

* * *

The development of the DSC system was carried out with Prof. V. Torra who conducted my early work on calorimetry and thermal analysis in the study of the martensitic transformation.

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Zusammenfassung — Zur Untersuchung der Martensitumwandlung wurde in einer Reihe von Apparaturen ein auf Halbleiter-Thermosäulen basierendes Temperaturüberwachungssystem eingesetzt. Die Geräte reichten von einem einfachen Objekttisch eines Lichtmikroskopes bis zu komplizierteren Geräten, wie z.B. einem DSC-Kalorimeter [1]. Vorliegend befindet sich der Schwerpunkt auf letzterem. Es wird ein Überblick über die allgemeinen Fragen der Temperatur-Scanning-Kalorimetrie gegeben, angefangen vom Aspekt der Signaltheorie und der angewendeten Lösungen bis zu dem von uns behandelten System. Als Anwendungsbeispiele werden einige Messungen dargestellt.