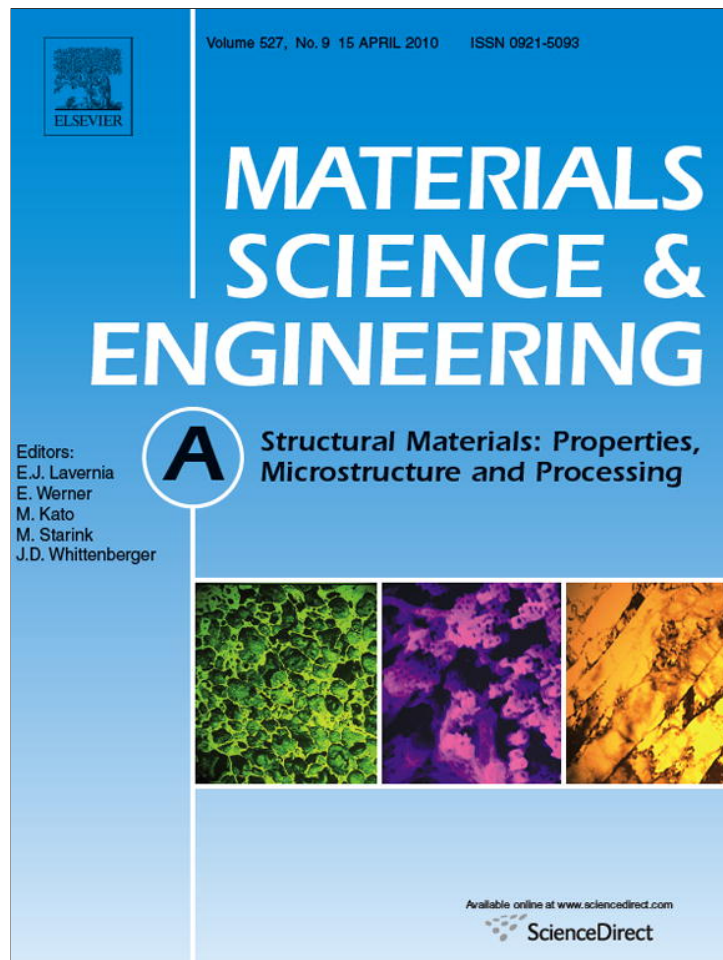


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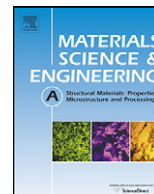
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## Commentary

## Comment on “Effects of heat-flux features on the differential scanning calorimetry curve of a thermoelastic martensitic transformation” by Benke et al. [Mater. Sci. Eng. A 481–482 (2008) 522]

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## ABSTRACT

The martensitic transformation of a Cu–Zn–Al single crystal was measured in a differential scanning calorimeter at different heating rates. The curves were analyzed in order to detect the initial and final temperatures of the transition. The results were analyzed using both, the method suggested by Benke et al. and the conventional method of extrapolating the temperatures to zero rate. They were also compared with those determined in the same calorimetric sample using the electrical resistance measurement. It is concluded that the transition happens in a range higher than that detected by calorimetry and that the inflexion point is not a useful point for a proper temperature determination.

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## 1. Introduction

In a recent paper on differential scanning calorimetric (DSC) measurements of thermoelastic martensitic transformations, Benke et al. [1] proposed a new method for the determination of the characteristic transition temperatures. As they state: “to evaluate the DSC curve with less error, one must determine the finish temperature as the inflexion point of the curve, while no heat is absorbed/disengaged after the inflexion point”. Its application to DSC measurements as a function of the temperature variation rate was then presented. The corrected values seemingly have a lower scatter than the uncorrected ones, but neither of the two sets showed a reasonable scanning rate dependency. This rather arbitrary criterion for the evaluation of the transition temperatures was neither justified nor contrasted with additional experimental techniques.

In the thermoelastic martensitic transformation of Cu-based single crystals, four temperatures are of interest. On cooling, the martensite starts to form at  $M_S$  and finishes at  $M_F$ , while on heating the austenite starts to form at  $A_S$  and finishes at  $A_F$ . When the martensite has the 18R structure, the inequalities  $M_F < A_S < M_S < A_F$  hold [2]. A good determination of the thermodynamic equilibrium temperature,  $T_0 = (M_S + A_F)/2$ , requires precise measurements of the characteristic temperatures on heating as also on cooling.

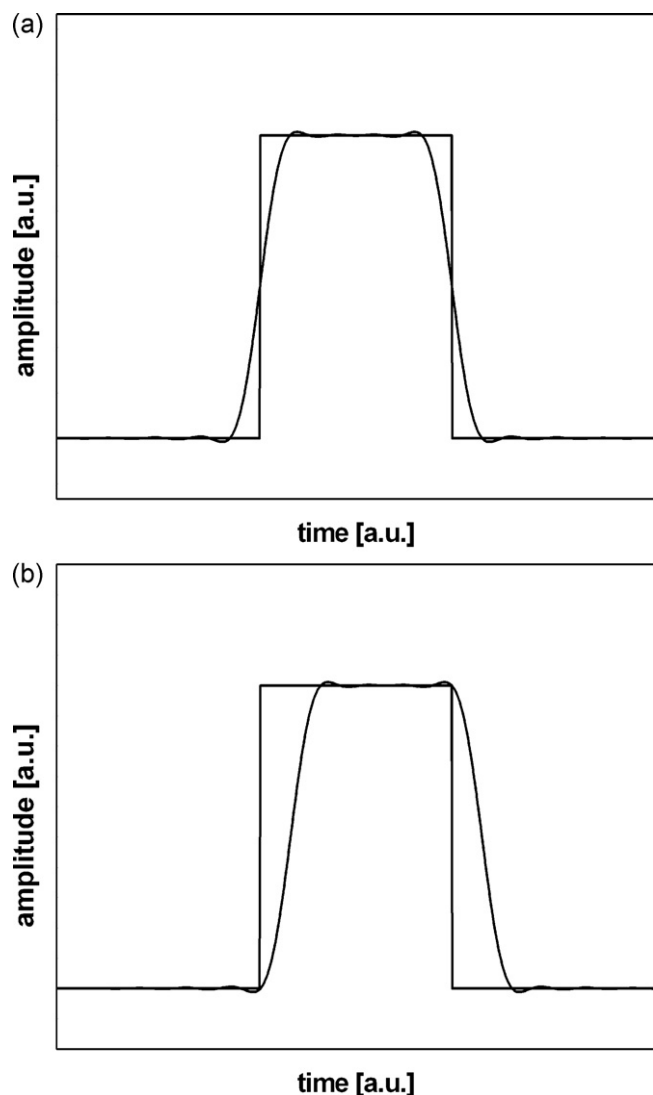
The concept that the inflexion point is related with the end of a process belongs to the control theory and signal processing areas. In Fig. 1a, a unit pulse can be seen, which constitutes the input to a system. The response is obtained by applying a low pass filter and making an adjacent averaging according to its cut off frequency. In this special case, the inflexion points fall exactly at the position where the source presents a variation. It can be also seen in Fig. 1a that the response is symmetric at both sides of the unit pulse.

In the real case of a calorimetric signal, the response cannot happen before the variation of the source occurs. This means that the response must present a delay, as shown in Fig. 1b. The amount of this delay, as is also the slope of the response variation, is a complex function of the several steps involved in the heat flow inside the calorimeter. They also depend on the temperature variation rate. Therefore, it is necessary to analyze in detail how the transformation temperatures can be recovered from the DSC curves.

It is known that accurate temperature determinations are necessary for a proper calibration of the calorimeter. The established procedure recommends to measure at least two calibration samples at at least five different heating rates, including the smallest possible one [3]. After comparison and elimination of possible differences from the samples and their location in the calorimeter, the desired characteristic temperature is represented as a function of the heating rate and extrapolated to zero. This systematic procedure can be applied to the determination of characteristic transition temperatures also. As symmetry of the heat transfer phenomena has been generally taken for granted [3], at least in heat-flux DSCs, this measurement method can be applied both for cooling and heating experiments.

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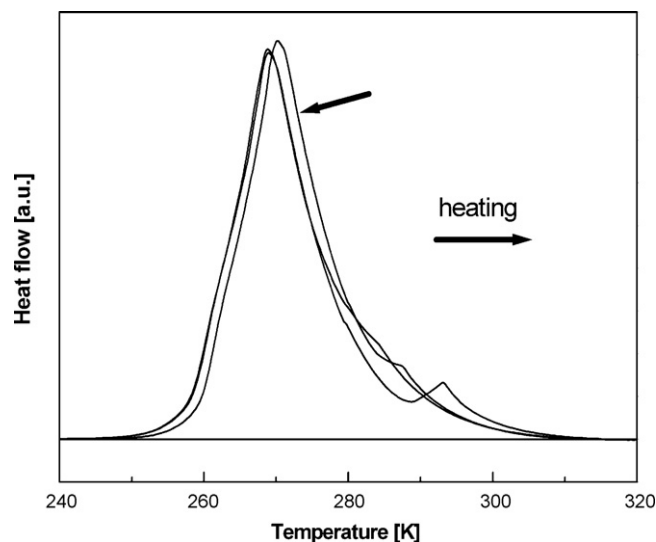
**Fig. 1.** Response to a unit pulse. (a) Ideal case in which only the perturbation of the signal is considered. (b) Real case in which the measuring instrument imposes a time delay.

The aim of the present paper is to experimentally show that it is wrong to use the inflexion points of the calorimetric curves as representative points of the transition and to propose an alternative method.

## 2. Experimental

A Cu–16.49 at.%Zn–15.75 at.%Al alloy was prepared from pure elements in a sealed Vycor capsule with an Ar atmosphere. From it, a cylindrical shaped single crystal of around 7.4 mm diameter was grown by the Bridgman method. The mold was also a sealed Vycor capsule with an Ar atmosphere. The crystal was homogenized at 1123 K during 14,400 s. A disc of about 2.5 mm thickness was cut with a low speed diamond saw. The two bases were then mechanically polished, resulting in a sample with a mass of 864 mg. It was then again heat treated at 1123 K for 1200 s and let to cool slowly down to room temperature. The sample rested at room temperature at least 3 days before the measurements were performed.

A calibrated TA 2910 DSC was used for the measurements, working at different scanning rates and with an Ar flow of 40 ml/min. The sample and the reference, a Cu disc of similar dimensions, were put directly onto the holder, avoiding the use of Al pans. In this way,



**Fig. 2.** Heat evolution in three consecutive retransformation runs at 5 K/min. The upper arrow indicates the position of the inflexion point.

additional thermal resistances for the heat conduction to and from the calorimeter were avoided.

Afterwards, the resistance of the same calorimetric sample as a function of the temperature was measured by the four terminal method, at typical scanning rates of around 3 K/min. The temperature was determined with a chromel–alumel thermocouple, which was point welded at the center of the disk.

## 3. Results and discussion

The reproducibility of the DSC curves was examined first for a temperature scanning rate of 5 K/min. Three consecutive curves recorded on heating are shown in Fig. 2. It can be clearly seen that the heat evolution at the transition does not follow the same endothermic path. Small fluctuations of the peak maximum position can be observed, as also bigger fluctuations (including the appearance of an additional peak) when the last regions of martensite are retransformed. On different runs this smaller peak appears at 287 and 293 K. On the other hand, the inflexion point of the main peak is located at nearly a constant temperature, whose mean value is  $(271.6 \pm 0.5)$  K. Therefore, the inflexion point occurs at a temperature several degrees lower than those where additional retransformation activity can clearly be established. This behavior brings forward a proof against the model of defining the finish of the retransformation at the inflexion point.

In trying to understand the transformation behavior, a better insight can be obtained by analyzing the effect of varying the heating rate, as is shown in Fig. 3 for five different values. In Fig. 3a the heat flow as a function of the temperature is shown. It can be seen that the main retransformation peak moves to higher temperatures and increases its height as the scanning rate is increased. On the other hand, the rise of the calorimetric signal at the beginning of the transition is similar in all the cases. This characteristic is related to the way in which the martensite retransforms, but the important fact is that the calorimeter has a high enough response to follow the heat evolution at any of the used speeds.

This can be better understood by observing Fig. 3b, where the heat evolution as a function of the time is presented. The calorimetric signal rises with a time constant that decreases with increasing heating rate. This means that an increase of the amount of martensite that retransforms at a given time interval can be followed by the faster calorimeter response. In Fig. 4 the adjusted time constants for an exponential growth at the beginning ( $\tau_s$ ) and similarly for the

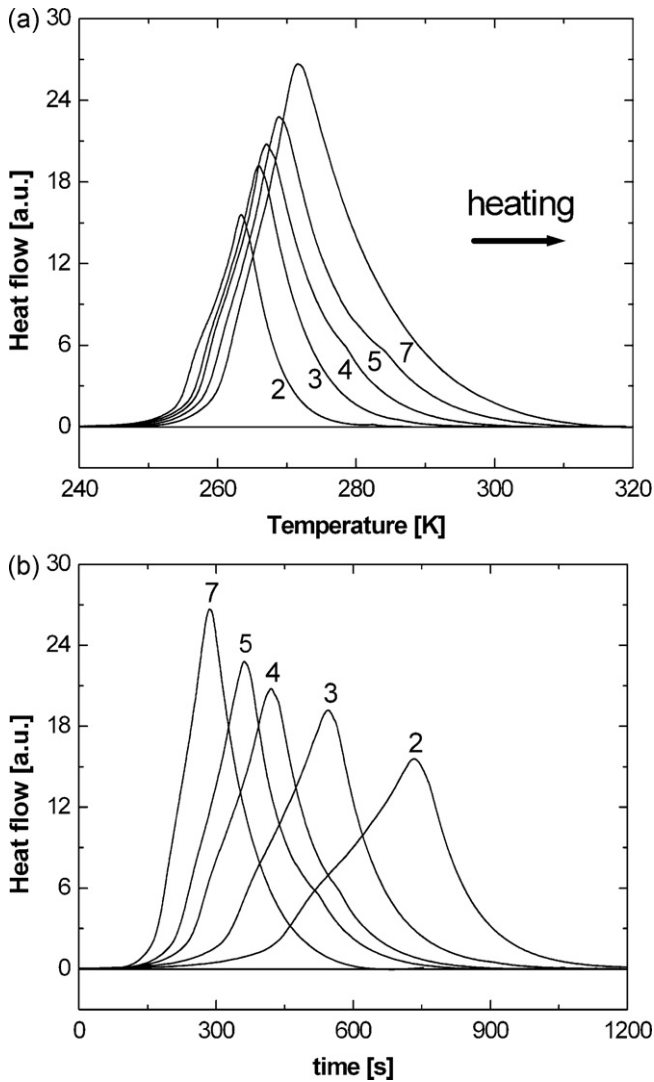


Fig. 3. DSC endothermic peaks at five different heating rates indicated in K/min, as a function of: (a) the temperature and (b) the time. The origin of time was arbitrarily set when the sample reached the temperature of 240 K.

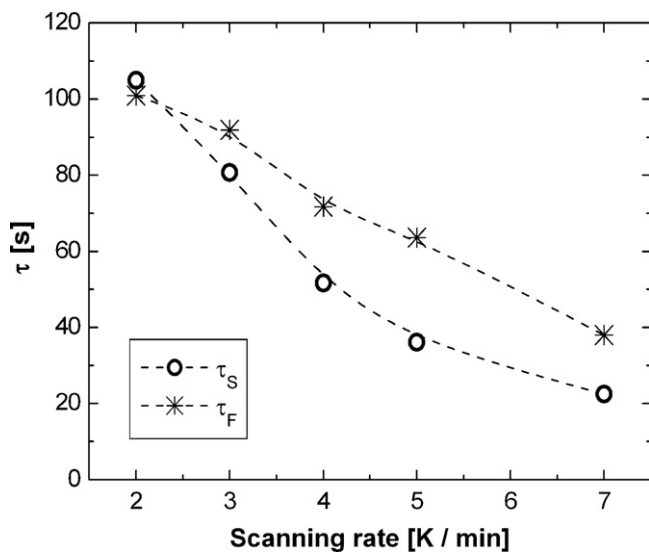


Fig. 4. Time constants for the exponential behavior at the beginning ( $\tau_S$ ) and at the end ( $\tau_F$ ) of the retransformation peak, as a function of the scanning rate. The lines are a guide for the eyes.

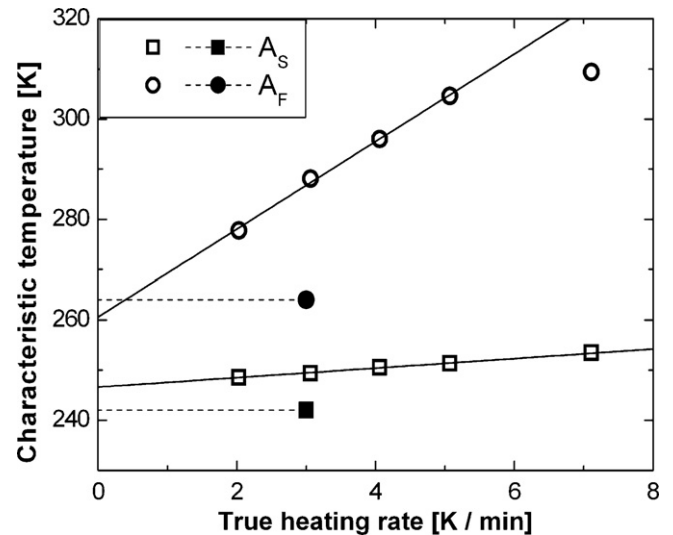


Fig. 5. Characteristic retransformation temperatures at the beginning ( $A_S$ ) and at the end ( $A_F$ ) of the peak, as a function of the true scanning rate. The filled symbols were extracted from electrical resistivity measurements.

decay at the end ( $\tau_F$ ) of the peaks are shown as a function of the scanning rate. They differ for the higher heating speeds, being faster the response at the beginning of the peak. This behavior is an indication that what the calorimeter detects at the end of the peak is still retransforming martensite and not simply the heat transfer to a cool sample. It can also be observed that the difference reduces at the lowest scanning rate. This is an indication that at low scanning rates the conditions of an ideal calorimetric system are progressively reached. The peak itself is not symmetric because the low scanning rate allows detecting the inhomogeneities of the actual material.

From the curves in Fig. 3a, the characteristic retransformation temperatures can be extracted. This was implemented by taking the temperature values corresponding to arbitrary small heat-flux values (0.6, 0.9 and 1.2 in arbitrary units), at the beginning of the peak for  $A_S$  and at the end for  $A_F$ . They were then extrapolated to zero heat flux. The resulting values are shown in Fig. 5 as a function of the experimentally determined heating rates, which differ a little bit from the set point of the DSC. The characteristic temperatures present a linear dependence with the scanning rate, at least for the four lowest ones. The extrapolation to zero rate gives  $A_S = 247$  K and  $A_F = 261$  K.

For comparison, the characteristic temperatures of the sample determined by means of the measurement of the electrical resistance as a function of the temperature were  $A_S = 242$  K and  $A_F = 264$  K, as denoted with filled symbols in Fig. 5. As this measurement does not depend on the heat transfer to the sensing device, it can be thought as an instantaneous detection of the variations. The temperature interval determined by calorimetry fall inside that detected with the resistance measurement, and is nearly centered within experimental scatter. This can be rationalized in the following way: both, the very initial and the very final part of the retransformation are related with a small volume that undergoes the transition. This transforming volume cannot provide sufficient heat per unit time in order to be detected by the calorimeter. On the other hand, the appearance or disappearance of this small volume is accompanied by a change in the density of defects (surfaces) inside the sample, that can be easily detected by means of the electrical resistance measurements. That is, electrical resistance (with four significant figures) has a higher sensitivity to the changes related to the martensitic transformation than calorimetry.

#### 4. Conclusion

The martensitic transformation of a Cu–Zn–Al single crystalline sample was analyzed using differential scanning calorimetry measurements at different scanning rates and electrical resistance measurements. The main conclusions are:

- The transformation occurs in a temperature interval that is wider than that observed in the DSC curve at low scanning rates. Therefore the inflexion points of the calorimetric peak are of no interest in the analysis.
- It is necessary to extrapolate the transition temperatures to zero scanning rate in order to obtain confident results.
- Electrical resistance has a higher sensitivity than calorimetry to detect the martensitic transition.

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