

Direct Calorimetric Measurements in Stress Induced Transformations

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Introduction

It is known that the mechanism of martensitic transformations in shape memory alloys, involves irreversible processes as for example frictional forces in the moving parent-martensite interfaces. At the same time defects are created during the transformation as has been shown (1 - 2).

In thermally induced transformations without external stress, it might be supposed that there is no entropy production, that is, irreversible processes taking place can be described as frictional work done by the transforming material, without dissipation of heat. Within this hypothesis it is possible to evaluate the elastic and frictional contributions in thermally induced thermoelastic transformations (3). This is supported by calorimetric measurements in Cu-Zn-Al alloys for which the thermal released energy $Q(\beta \rightarrow \beta')$ during the direct transformation, coincides within the experimental error with that $Q(\beta' \rightarrow \beta)$ absorbed during the retransformation. This indicates that the value of the total frictional work W_{fr} is low, in agreement with the calculations of W_{fr} as the area enclosed in the entropy change (ΔS) vs. temperature (T) cycle (4).

A thermodynamic analysis applied to stress induced transformations at constant temperature shows that the difference $Q(\beta \rightarrow \beta') - Q(\beta' \rightarrow \beta)$ accounts for the dissipated irreversible heat in a pseudoelastic cycle, and that the area enclosed in the stress-strain cycle must be equal to the sum of the irreversible heat dissipated and the irreversible work done by the transforming system.

Until now, experimental results concerning thermal effects in stress-induced transformations are based on the detection of the temperature increase ΔT in the sample, measured with thermocouples (5 - 6). This method implies the approach to adiabatic conditions during the transformation, thus requiring measurements at high (and extrapolation to infinite) cross-head speeds.

Indirect measurements through the application of the Clausius-Clapeyron equation has also been a current method to obtain thermodynamic data (7).

An attempt has now been made to clarify the existence of irreversible energy contributions in stress-induced transformations, by direct measurements of exchanged heats. Preliminary results will be presented here.

Experimental procedure

Beta phase single crystals (composition: Cu - 15.74 Zn - 16.13 Al at.%, $M_s = -20$ °C) were grown by the Bridgman method. The Schmid factor related to the normal habit plane and the shear direction was 0.3. Flat samples (10x4x2 mm³) were obtained. All experiments were performed in tension. Prior to the tensile tests the samples were thermally treated (2 hours at 800 °C and air cooled) and polished mechanically till 600 grade paper and electrologically.

In order to perform thermal energy measurements, a heat flow differential calorimeter was directly attached to a flat face of the specimen.

The detection of thermal effects was achieved by means of semiconductor piles (heat fluxmeters) of the same type employed in other calorimetric studies of thermally induced transformations (8). The detection area of each semiconductor pile was $8 \times 8 \text{ mm}^2$ and the total size of the calorimeter was $8 \times 8 \times 9 \text{ mm}^3$, including a copper piece between the piles which acted as calorimetric block, and a copper reference sample attached to one of the piles.

A calibration of the system in conditions as close as possible to the experimental ones was needed in order to obtain reliable energy values. A heating resistance (constantan wire, $\phi = 0.05 \text{ mm}$) was wrapped round the transforming area of one of the used samples. The sample was fixed at both ends to the grips which were used in the testing machine. Constant power in the range $10 - 100 \text{ mW}$ was dissipated in the resistance during $\sim 100 \text{ s}$. This produced maximum outputs of the calorimeter between 0.5 and 10 mV which were similar to those obtained in the tensile experiments.

The obtained calorimeter sensitivity was $45 \pm 2 \text{ mV/W}$ at room temperature. The same type of calorimeter when applied to thermally induced transformations, i. e. without significant energy losses, show a sensitivity of $250\text{--}300 \text{ mV/W}$ at room temperature. The difference indicates the importance of thermal conduction to the grips.

The curves stress - strain ($\sigma - \epsilon$), $y - \epsilon$ and $y - t$ (where y = detected calorimetric signal in mV , t = time) were simultaneously registered. The area under the $y - t$ curve is proportional to the exchanged heat through the calibration factor.

Results and discussion

Figure 1 shows the stress - strain curve and the calorimetric output due to the true elastic deformation (in the region $\sigma < \sigma(\beta + \beta')$, critical value to induce the direct transformation). This is an illustration of the sensitivity of the method. It should be noted that an estimation of the temperature change due to elastic loading under adiabatic conditions gives a value of 0.3 K (9).

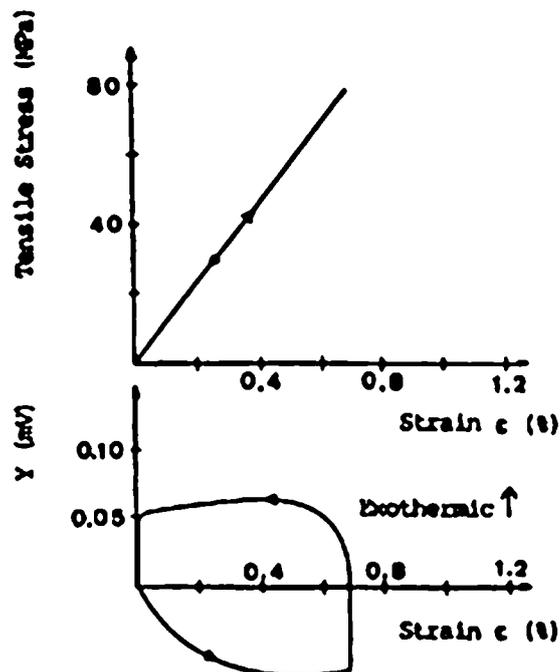


Fig. 1: Tensile cycle and calorimetric signal in the range of true elasticity: $\sigma < \sigma(\beta + \beta')$.

In Figure 2 are shown the pseudoelastic cycles and calorimetric signals for different strain rates. As it can be seen, calorimetric curves give evidence of discontinuous formation of martensite, especially in experiments conducted at small strain rates. For higher strain rates, the calorimeter time constant (~ 10 s) is not small enough to follow discontinuities in thermal effect and a smoothed output is detected.

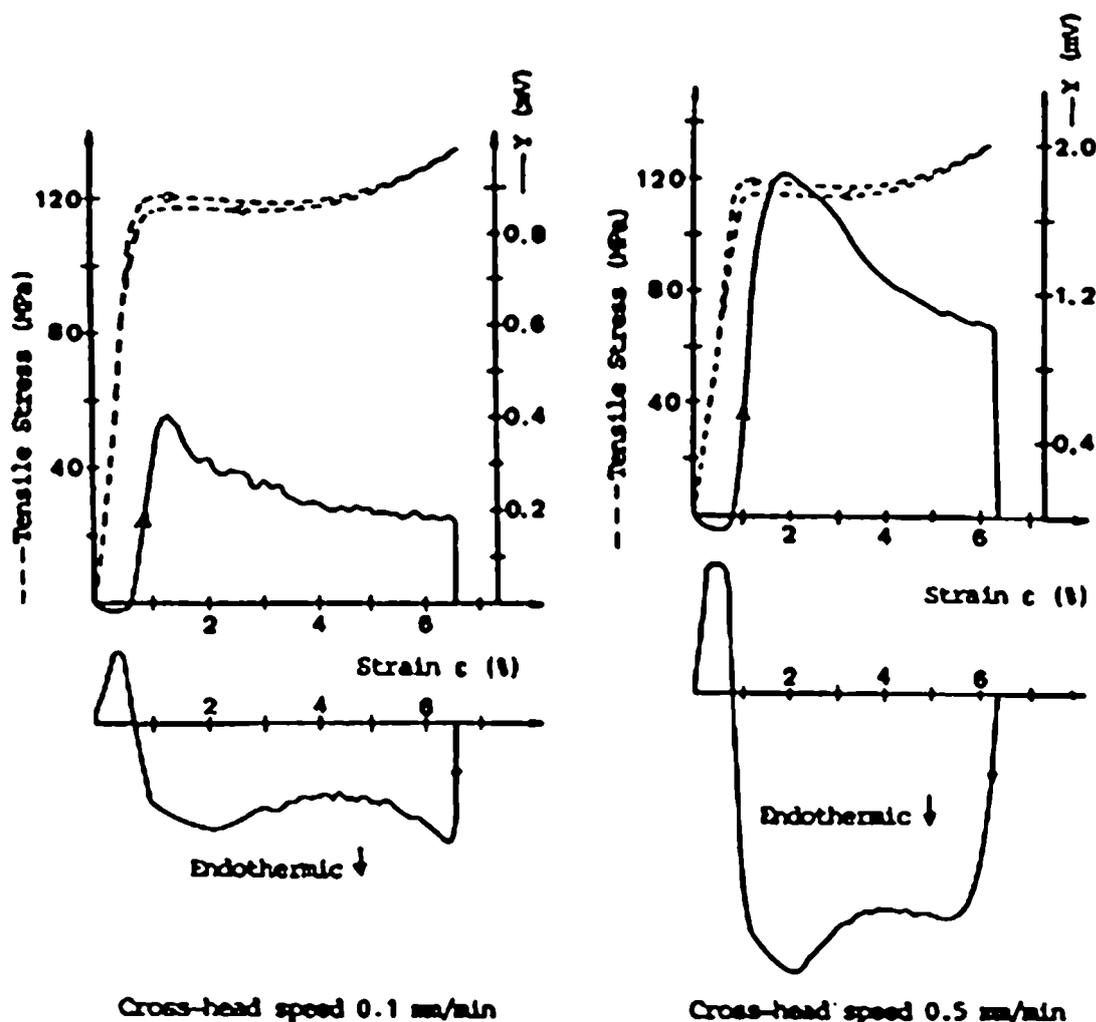


Fig. 2: Pseudoelastic cycles and calorimetric signals for two strain rates.

(assuming as a first approximation that irreversible heat dissipation is the same in the direct and in the reverse transformations).

In Table 1 are presented some examples of the heats $Q(\beta \rightarrow \beta')$ and $Q(\beta' \rightarrow \beta)$ (absolute values) measured. A higher value is found for the direct transformation. Under the same experimental conditions the results were reproducible. The difference between the exchanged heats during the direct and reverse transformation would indicate irreversible processes producing heat dissipation during a complete stress - induced transformation cycle.

For higher strain rates, higher values of the exchanged heats were obtained. This could be caused by the interaction with sample heads and grips which gives a poorer determination of the transformed mass. It should be mentioned that calorimeter calibrations gave reasonably coincident values for different thermal power in the heating resistance (equivalent to different strain rates). Different energy conduction to the grips could also influence the detected variation.

Sample	T (K)	Cross-head speed (mm/min)	$Q(\beta \rightarrow \beta')$ (J/mol)	$Q(\beta' \rightarrow \beta)$ (J/mol)
EM6	293	0.5	402	375
EM6	293	0.5	392	365
EM6	310	0.5	384	347
EM6	295	10	478	413
EM9	263	5	358	337

Table 1: Heats exchanged (absolute values) during the direct, $Q(\beta \rightarrow \beta')$, and reverse, $Q(\beta' \rightarrow \beta)$, transformation in experiments conducted at different temperatures and strain rates.

The values of measured $Q(\beta \rightarrow \beta')$ and $Q(\beta' \rightarrow \beta)$ are higher than the detected exchanged heats during a thermal induced transformation. The difference is mainly due to the mechanical work performed on (or done by) the sample. For example, for sample EM6 at room temperature (293 K) a value of 70 J/mol is obtained as an average of the area under stress - strain curve during the direct and the reverse transformation. If this quantity is added to the measured heat in a thermal induced transformation of the same alloy ($Q = 320$ J/mol, average value of direct and reverse transformations) (or to $\Delta H_{ch} = 325$ J/mol, the difference $\Delta H_{ch} - Q$ accounts for the elastic energy) a rather good agreement is found with the average values of heats measured during stress - induced transformations.

A direct determination of the average value of heats exchanged in a pseudoelastic cycle performed at temperature T should also give a first approximation to ΔS as Q / T . Using the values of Table 1 (except for the measurement at 10 mm / min) values within the range 1.18 - 1.33 J / mol K are obtained. The ΔS value in a thermal induced transformation of the same alloy is 1.28 J / mol K, and values reported in the literature (7) are close to 1.29 J / mol K .

Irreversible processes include different mechanisms like acoustic emission or production of defects in the interior of the material. Preliminary direct determinations of released heats during stress - induced transformations would indicate that the dissipation of irreversible heat cannot be disregarded.

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