

## Calorimetric Study of Pseudoelastically Cycled Cu-Zn-Al Single Crystals

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### Introduction

When a Cu-Zn-Al single crystal is stressed at a temperature above  $A_f$ , the pseudoelastic effect takes place. The phase transformation  $\beta \leftrightarrow M$  which appears on loading/unloading shows irreversible effects which become more evident after a certain number of cycles (1 - 2). In each pseudoelastic cycle defects are created (dislocations, point defects); dislocations are accumulated in bands parallel to the habit plane of the transformation and to the basal plane of the formed martensite (3). These defects alter the following transformation cycles.

In this work the evolution of deformation curves during cycling is analyzed for Cu-Zn-Al single crystals of  $e/a = 1.48$ . Calorimetric measurements with simultaneous detection of acoustic emission are performed before and after mechanical cycling. Changes in thermal hysteresis and in thermodynamics of the transformation become noticeable.

### Experimental methods

Single crystals of a Cu-Zn-Al alloy (Cu, 15.74 Zn, 16.13 Al, at%) were grown by the Bridgman method. After thermal treatment, samples specially designed for tensile tests, were cycled under tension at a constant temperature,  $T_{exp}$  higher than  $A_f$ , with  $T_{exp} < M_d$  (pseudoelastic range). The cycling was performed in closed loop and in each cycle the sample was stressed until the transformation was completed.

After mechanical cycling, cylindrical samples A, B, C (central part) with faces perpendicular to the tensile axis, were cut from the pseudoelastically cycled samples 1 and 2. Another parallelepipedic sample D with two faces parallel to the tensile axis, was also cut from the original sample 3.

Transformation cycles were done in a calorimetric device (4 - 5) after mechanical cycling. It has to be pointed out that in samples A, B, C, the surface in contact with the thermobatteries is perpendicular to the tensile axis, while it is parallel in sample D. An appropriate thermal treatment allows us to recover the same conditions that the original sample had before mechanical cycling. So we will compare the mechanical and calorimetric results obtained before cycling and after cycling.

### Experimental results

Fig. 1 shows the  $\sigma$ - $\epsilon$  curves for the sample 1 corresponding to cycles 1 and 4213. The area enclosed in the  $\sigma$ - $\epsilon$  cycle is 1.2 J/mol for  $N=1$  and 2.8 J/mol for  $N=4213$ .

Fig. 2 shows the measured thermal effect (thermogram) for sample 1B corresponding to the direct transformation before and after mechanical cycling.

Fig. 3 shows the curves  $\int \delta Q/T$  (integrated between  $M_s$  and  $M_f$  for the direct transformation and between  $A_s$  and  $A_f$  for the reverse transformation) vs.  $T$  for sample 1C before and after mechanical cycling. In table 1 are presented the calorimetric results.

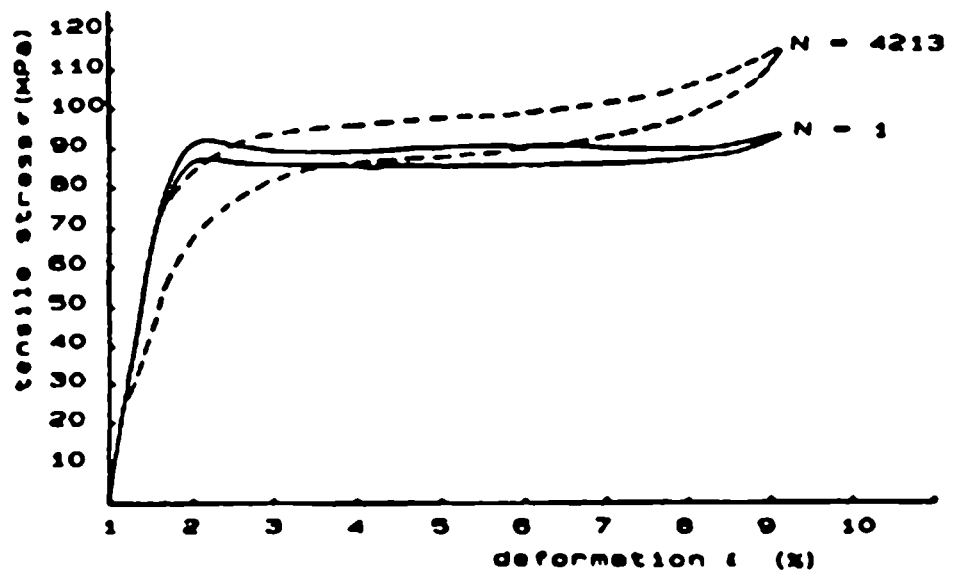


Fig. 1: Stress-deformation curves for the pseudoelastic cycles  $N=1$  and  $N=4213$ .

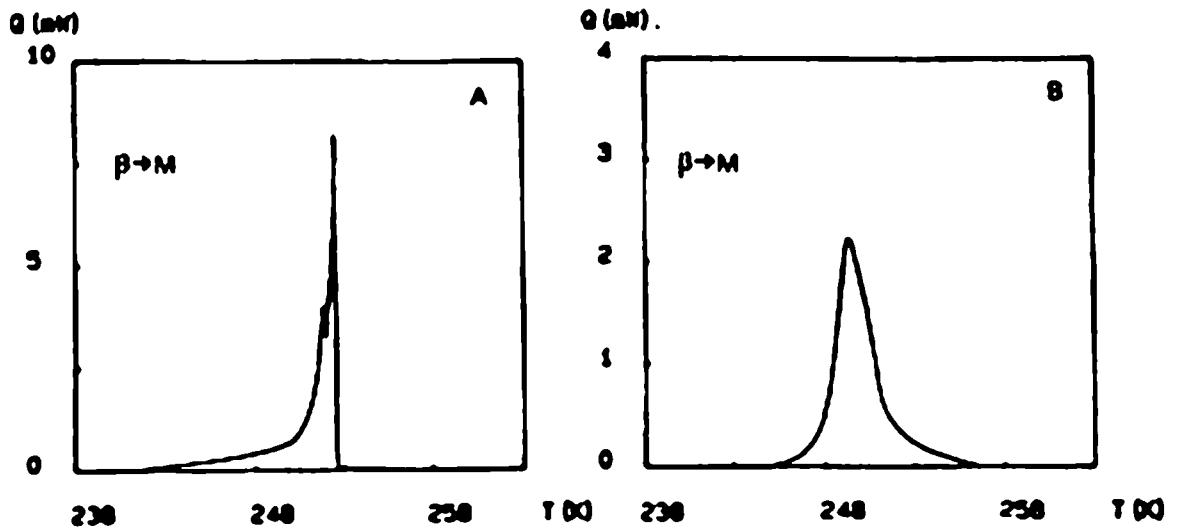


Fig. 2: Thermograms obtained for the direct transformation for sample TB. A) Before cycling; B) After cycling.

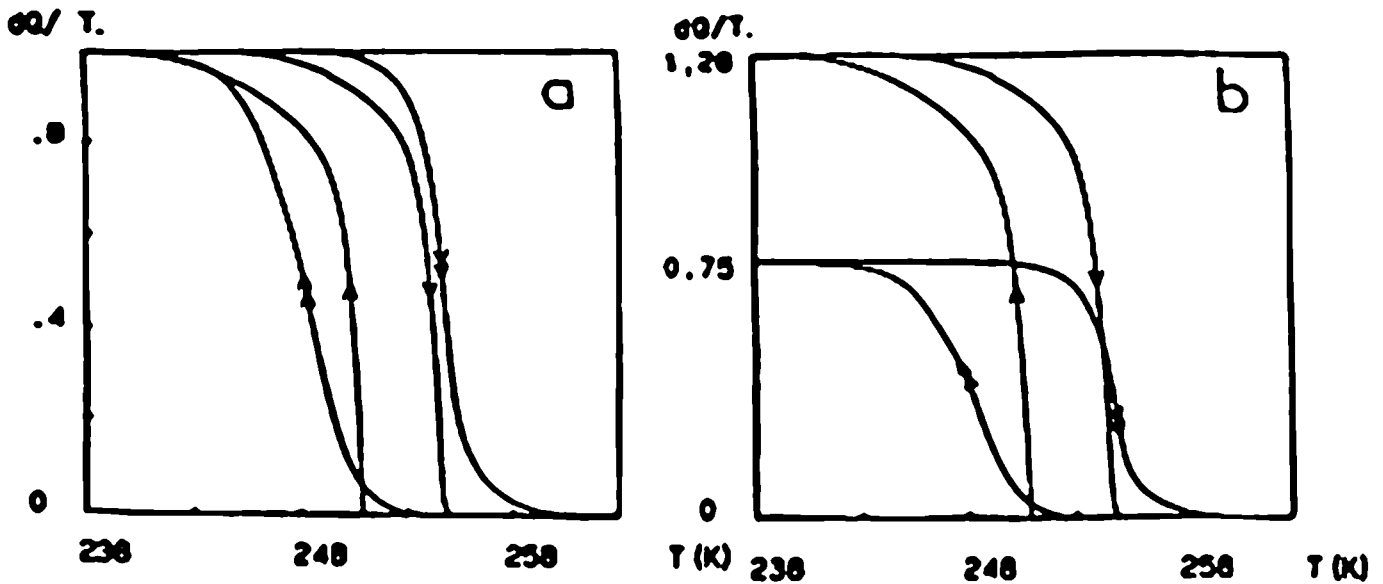


Fig. 3: a) Normalized curves  $f\delta Q/T$  vs  $T$  for sample 1C. b)  $f\delta Q/T$  for the same sample  $\rightarrow$  before cycling,  $\dashrightarrow$  after cycling.

Sample	$M_s$	$M_f$	$A_s$	$A_f$	$\Delta T(50\%)$	$Q_{\beta-M}$	$Q_{M-\beta}$	$f\delta Q_{\beta-M}/T$	$f\delta Q_{M-\beta}/T$	
2C	B.C.	255	247	255	261	4	368	357	1.45	1.39
	A.C.	255	243	251	262	7	120	135	0.48	0.53
3D	B.C.	256	245	252	260	3	370	363	1.45	1.41
	A.C.	258	242	248	261	5	349	353	1.38	1.37

Table 1: Transformation temperatures, hysteresis width ( $\Delta T(50\%)$ ), difference in temperature between the direct and reverse curve in  $f\delta Q/T$  vs  $T$  plot, corresponding to the 50% of the transformed material, measured heats and values of  $f\delta Q/T$  for samples 2C and 3D before (B.C) and after cycling (A.C). ( $T$  in K,  $\Delta T$  in K,  $Q$  in J/mol,  $f\delta Q/T$  in J/molK, absolute values). Estimated uncertainties:  $Q = \pm 10$  J/mol,  $T = \pm 1$  K,  $f\delta Q/T = \pm 0.04$  J/molK.

### Discussion

It is interesting to compare the changes detected in the  $\sigma$ - $\epsilon$  curves during cycling with those detected in the calorimetric curves:

- A softening at the start of the  $\beta \rightarrow M$  transformation is observed in both cases.
- A hardening effect: a higher  $\sigma$  is necessary to induce the same amount of transformation. Also an extra undercooling for the cyclod sample is necessary until the completion of transformation.
- A broadening in the hysteresis. The enclosed area in the  $\sigma$ - $\epsilon$  curves increases its value between 2 and 3 times for  $N > 3000$  cycles. In the calorimetric curves, the enlargement of the hysteresis width can be seen from the values of  $\Delta T(50\%)$ .

From this results, we can see that the information provided by the calorimetric system is consistent with that obtained from the mechanical curves, showing

evidency of equivalent roles of  $\sigma$  and  $T$  variables. Besides, the thermograms give additional information about the kinetics of the transformation which can not be detected from the  $\sigma$ - $\epsilon$  curves. The thermogram obtained after pseudoelastic cycling shows a smoother curve. From the local thermoelastic equilibrium condition  $\Delta G = \Delta G_{ch} - \Delta G_{el} = 0$ ; we can deduce that defects created during mechanical cycling allow the sample to reach this local equilibrium more continuously than without defects. This is also consistent with the observed decrease in the acoustic emission activity (a reduction factor of 3 in the number of counts) for cycled samples.

From values obtained for the measured heats in a thermal induced transformation we have observed a considerable decrease after mechanical cycling in all the cylindrical samples (A,B,C) studied (see for example sample 2C).

In order to explain the important decrease in the  $Q$  values after pseudoelastic cycling, we can consider changes in the amount of transformed material and also variations in the right hand side terms of Equ. 1 and 2 corresponding to the application of the first thermodynamic principle to the direct and reverse transformations (magnitudes in absolute values):

$$-Q_{\beta \rightarrow M} = -\Delta H_{ch} + \Delta H_{el} + W_{fr} \beta \rightarrow M \quad \text{Equ. 1}$$

$$Q_{M \rightarrow \beta} = \Delta H_{ch} - \Delta H_{el} + W_{fr} M \rightarrow \beta \quad \text{Equ. 2}$$

$Q_{\beta \rightarrow M}$  and  $Q_{M \rightarrow \beta}$ : measured heats during a thermal induced transformation.

$\Delta H_{ch}$ : chemical entalpy change (latent heat).

$\Delta H_{el}$ : elastic energy which is accumulated in the direct transformation opposing it and which favours the reverse transformation.

$W_{fr}$ : frictional energy which is not dissipated as heat.

a) Changes in the quantity of transformed material: In this case an important amount of the stabilized martensite around dislocations has to be produced to justify the decrease in the  $Q$  values. However, that high quantity of stabilized martensite required has not been observed (3).

b) A decrease in  $\Delta G_{ch}$  due to the high density of defects. Moreover, the small change in  $T_0$  ( $T_0 = 1/2(M_s + A_f)$ ), does not support the possibility of such a change in latent heat.

c) An increase in  $W_{fr}$  can be expected after the creation of defects by mechanical cycling. It has been shown (6) that considering a null entropy production in a whole cycle the enclosed area in a  $\Delta S$  vs  $T$  diagram represents the total  $W_{fr}$ . Calculations from this hypothesis would not explain a decrease in  $Q$  higher than 100 J/mol, considering the values of the areas in  $\Delta S$  vs  $T$  diagrams: 5 J/mol before cycling, 8 J/mol after cycling.

d) A high increase in the elastic energy stored during the transformation after pseudoelastic cycling. Assuming that  $W_{fr} \beta \rightarrow M = W_{fr} M \rightarrow \beta$  from the Equ. 1 and 2 we obtain:

$$\Delta H_{el} = \Delta H_{ch} - \bar{Q} \quad \text{Equ. 3}$$

where  $\bar{Q} = 1/2(Q_{\beta \rightarrow M} + Q_{M \rightarrow \beta})$

The expression in Equ. 3 allows us do the calculation of the elastic term before and after the pseudoelastic cycling. Taking  $\Delta H_{ch} = T_0 \Delta S$  where  $\Delta S = \int \delta Q/T$ , and considering that  $\Delta H_{ch}$  is not affected by pseudoelastic cycling, we obtain for samples 2C and 3D, for example, the values presented in table 2.

	$\bar{Q}$	$\Delta H_{el}$
2C	B.C.	362
	A.C.	127
3D	B.C.	366
	A.C.	351

Table 2: Measured heats and elastic energy for samples 2C and 3D before (B.C) and after (A.C) cycling. (both in J/mol units).

As can be seen from table 2, the  $\Delta H_{el}$  term increases in both samples after pseudoelastic cycling. This increase is much more important in sample 2C. The  $\bar{Q}$  value diminishes for sample 2C while it remains almost constant for sample 3D. Although the origin of this increase in the elastic term is not yet well understood, our results indicate that it can be related to the two-way memory effect induced by mechanical cycling which produces an increase in the length of the sample during thermal transformation to martensite.

The usual mounting routine in the calorimeter exerts a pressure on the sample that, in the case of cylindrical samples, avoids its elongation. So the preferential variant induced in the previous pseudoelastic cycling is impeded to grow freely and other different variants are formed.

Optical microscopy observations agree with this interpretation. The increase/decrease in length of the sample on cooling/heating have been measured and microscopical observations of the transformation with and without pressure confirm the presence of variants different from the preferential in that first case. That effect does not play an important role for sample 3D. In this case, the pressure exerted for the mounting routine is normal to the direction of enlargement of the sample. Therefore, in this conditions the preferential variant can grow without impediment. Additional calorimetric experiments done with samples 2B and 2C without pressure on them also confirm the previous hypothesis because no differences in the  $\bar{Q}$  values before and after mechanical cycling are detected.

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