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# Friction and stored elastic energy in Cu–Zn–Al single crystals with pseudoelastic behaviour

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### Abstract

The stored energy has been calculated from the stress-strain curves, as the area under the curve when stress-induced martensitic transformation is complete and the friction energy as the area of the mechanical hysteresis, for four single-crystal Cu-Zn-Al alloys. Measurement results indicate that when the  $M_s$  of the alloy increases a decrease in stored energy can be observed. Also, the increase of the test temperature produces an increase in the stored energy. © 1997 Elsevier Science B.V.

Keywords: Cu-Zn-Al; Energy; Pseudoelasticity; Shape-memory; Superelasticity

# 1. Introduction

The thermoelastic martensitic transformation exhibited by Cu–Zn–Al alloys may be induced either by stress or by the effect of temperature. When the material in its  $\beta$  phase is quenched it transforms into a martensitic structure. Such transformation is initiated at a temperature  $M_s$  and completed at a lower temperature  $M_f$ . When the material is heated from a temperature below  $M_f$ , it transforms into a  $\beta$  phase. Such retransformation starts at a temperature  $A_s$  and is completed at higher temperature  $A_f$  which corresponds to the start of the martensitic transformation by cooling. The stress-induced martensitic transformation occurs because the external stress assists the transformation, which is easily understood by considering that

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the martensitic transformation is caused by the shearlike mechanism. The driving force of the pseudoelasticity is the free-energy difference between phases as a function of stress. What assures the recovery of strains on unloading is the crystallographic reversibility of the stress-induced transformation and the exclusion of slip during loading [1,2].

Under the influence of an applied stress the austenite transforms into stress-induced martensite and so a plateau will develop in the stress curve. As soon as the load is removed, the martensite transforms back to austenite and returns to its original shape. This all happens at a constant temperature. Stress hysteresis accompanies this phenomenon, the area of this hysteresis being the frictional energy. The shaded part under the returning stress curve represents the stored elastic energy as can be seen in Fig. 1. This elastic energy is released when the alloy is unloaded, because it is

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Fig. 1. Schematic stress-strain for a pseudoelastic alloy.  $\sigma^{\theta \to M}$ : critical stress to induced martensite, and  $\sigma^{M \to \beta}$ : critical stress for the retransformation.

extremely large as compared to the normal metals, since the strain is so high [3].

The effect of an applied stress on the martensitic transformation was first explored theoretically by Scheil [4] and discussed more quantitatively by Patel and Cohen [2].

# 2. Experimental

The study was carried out with four single-crystal alloys obtained by the Bridgman method [5], all with the same orientation (110). The chemical composition expressed as a weight percentage and the electron-to-atom ratio (e/a) are given in Table 1.

The samples, in the form of squat cylinders (diameter 5 mm and height 2 mm) with an average mass of 400 mg were subjected to a heat treatment for 10 min at 850°C followed by quenching in water at 20°C, when the structure remained as the  $\beta$  phase. Trans-

Table 1 Chemical composition in weight percentage and the electron-toatom ratio (e/a)

la
1.458
1.473
1.449
1.478
_

formation to martensite was carried out by cooling in a calorimeter 24 h after the initial heat treatment.

The flow calorimeter measured differential signals by means of Melcor thermobatteries, consisting of 32 thermocouples of P-N junctions made from Bi–Te– Se–Sb quaternary alloy connected in opposition, the working range of which is from -150 to  $100^{\circ}$ C. The temperature was measured by means of a standard Pt/ Pt–Rh thermocouple. All signals were digitized through a multichannel recorder and linked to a microcomputer [6,7]. The heating–cooling rate was  $1^{\circ}$ C min<sup>-1</sup>. The transformation temperatures obtained are shown in Table 2, together with the thermal hysteresis values defined as the difference between the martensitic transformation onset temperature and that at the end of the reverse transformation  $|T_h=M_s-A_f|$ .

The friction and stored elastic energies were studied at different test temperatures (10, 20, 30, 50 and  $70^{\circ}$ C). In order to carry out this study, compression tests were made on the single-crystal alloys. The compression tests were carried out using an Instron tensile machine on cylindrical samples 6.5 mm long and 5 mm in diameter.

The tests were performed at different temperatures by placing a container around the specimen in which a liquid at the required test temperature was present. The cross-head rate applied to the sample was constant  $(1 \text{ mm min}^{-1})$ . From the stress-strain curves, the stored energy was calculated as the area under the curve, when the stress-induced martensitic transformation is completed.

# 3. Results and discussion

The results of transformation stressing experiments  $(\beta \rightarrow SIM)$  are shown in Figs. 2 and 3 for each single crystal and test temperature in the direct and the

Table 2

Transformation temperatures of  $M_s$  (martensite start),  $M_f$  (martensite finish),  $A_s$  (austenite start),  $A_f$  (austenite finish) and  $T_h$  (thermal hysteresis) in °C

Alloy	Ms	M <sub>f</sub>	As	A <sub>f</sub>	T <sub>h</sub>
1	0	-39	-23	13	13
2	-5	-20	-11	10	15
3	14	-10	6	25	11
4	26	-6	12	37	11

reverse transformation, respectively. With increasing temperature a progressively higher stress is required to nucleate the martensite and the curves are displaced to higher stress levels. This is due to the stability of the  $\beta$  phase being greater as the temperature increases, so the stress has to be increased in order to overcome the increased thermodynamic stability. This increase in stress is linear according to the Clausius–Clapeyron equation [8], as can be seen in Table 3.

The differences in the stresses measured for the  $\beta \rightarrow SIM$  and  $SIM \rightarrow \beta$  transformations can be obtained from the results represented in Figs. 2 and 3 and are presented in Table 4 for the different specimens and test conditions. These results show, that within the range of test temperatures used there was no significant difference in the value of  $\Delta\sigma$  (the vertical width of the hysteresis loop), for each single crystal tested. These results confirm the Bornert studies, that the value of  $\Delta\sigma$  for the Landau model would show only a very slight increase with temperature [9–11].



Fig. 2. Transformation stress vs. test temperature.



Fig. 3. Reverse transformation stress vs. test temperature.

Table 3

Transformation stresses (in MPa) vs. test temperatures (T in  $^{\circ}$ C) equations

Alloy	Equation
1	$\sigma^{\beta \to \text{SIM}} = 33.68 + 2.26 T$
	$\sigma^{\text{SIM} \rightarrow \beta} = 18.21 + 2.35 T$
2	$\sigma^{\beta \rightarrow \text{SIM}} = 9.26 + 2.29 T$
	$\sigma^{\text{SIM} \rightarrow \beta} = -8.65 + 2.08 T$
3	$\sigma^{\beta \rightarrow \text{SIM}} = 7.12 + 2.66 T$
	$\sigma^{\text{SIM} \rightarrow \beta} = -1.34 + 2.68 T$
4	$\sigma^{\beta \to \text{SIM}} = -16.51 + 3.11 T$
	$\sigma^{\mathbf{SIM} \rightarrow \beta} = -45.16 + 2.10 T$

Table 4							
Mechanical	hysteresis	at	different	test	temperatures	in l	MPa

10	19	12	17	
25	25	28	26	
11	12	12	15	
36	33	42	52	
	10 25 11 36	10     19       25     25       11     12       36     33	10 19 12   25 25 28   11 12 12   36 33 42	10     19     12     17       25     25     28     26       11     12     12     15       36     33     42     52

The dissipated energy has a very important influence in the width of the hysteresis loop, but this energy may not be the only cause of hysteresis; hysteresis may also be due to lattice defects such as dislocations, elastic misfit of the phases and elastic interactions of neighbouring domains [7]. The area of the hysteresis cycle in the stress-strain diagram was calculated. This area gave the total energy dissipated, as shown in Fig. 4, for each test temperature and for the different alloys.

The area under the stress-strain curves has been evaluated; this area represents the energy density which the pseudoelastic alloy can store when the sample is loaded and transforms to released energy when the sample is unloaded. Fig. 5 shows the released energy per unit volume for each single crystal and each test temperature. The results indicate that as the  $M_s$  of the alloy increases a decrease in released energy can be observed. Moreover, when the test temperature increases, an increase in released energy can also be observed. The increase of released energy can be explained by the fact that the stability of the  $\beta$ phase is greater as the temperature increases. The stress has to increase so that the mechanical energy may overcome the thermodynamic stability.



Fig. 4. Dissipated energy in relation to test temperatures.



Fig. 5. Released energy in relation to test temperatures.

As can be seen from Fig. 5, the relationship between the released energy density vs. test temperatures is linear and follows the equations shown in Table 5.

The frictional-to-released energy ratio vs. test temperatures follow an exponential function, as can be seen in Fig. 6, the exponential equations being given in Table 6.

The released energy values for the Cu–Zn–Al single crystals studied exceed those of Ti-50.6 Ni (at%) alloy by 42 MJ m<sup>-3</sup> when subjected to a special thermomechanical treatment at 20°C [12]. The stored energy density of Cu–Zn–Al single crystals range from 50 to 93 MJ m<sup>-3</sup>, these results are about 42 times greater than those in elastic steel springs.

From the viewpoint of applications there are characteristics in the pseudoelastic transformation. The

#### Table 5

Linear equations between released energy density  $(E_{rel} \text{ in } MJ \text{ m}^3)$ and test temperatures (*T* in °C), *r* being the correlation coefficient

Alloy	Equation	r
1	$E_{\rm rel} = -20.15 + 3.05 T$	0.999
2	$E_{\rm rel} = -11.41 + 3.34 T$	0.996
3	$E_{\rm rel} = -23.06 + 3.09 T$	0.995
4	$E_{\rm rel} = -11.70 + 2.75 T$	0.988



Fig. 6. Frictional-to-released energy ratio for different test temperatures.

### Table 6

Exponential equations for the ratio of energies and test temperatures. ( $E_{tr}$ : Frictional energy,  $E_{rel}$ : released energy density, and T: temperature in °C)

Alloy	Equation
1	$E_{\rm fr}/E_{\rm rel} = 0.00284 + 0.00747 \exp(-(T - 12.73)/18.012)$
2	$E_{\rm fr}/E_{\rm rel} = 0.00459 + 0.05005 \exp(-(T-11.11)/7.073)$
3	$E_{\rm fr}/E_{\rm rel} = 0.00365 + 0.02308 \exp(-(T - 11.52)/12.064)$
4	$E_{\rm fr}/E_{\rm rel} = 0.00284 + 0.03178 \exp(-(T - 12.94)/8.266)$

first is the amount of recoverable strain. The second is the constancy of the stress during the transformation, this means that it is possible to make a spring which deforms without changing the stress. The third is the use of elasticity itself, in the region before the onset of the stress-induced transformation. An elastic strain as large as 2% is available in these alloys since, according to the Clausius-Clapeyron relationship, strain increases if the test temperature is raised relative to  $M_{\rm s}$ . This characteristic enables a spring with large elastic strain limit.

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