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Mechanical cycles in multivariant martensitic single-crystal Cu–Zn–Al shape memory alloys

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The behaviour of Cu–Zn–Al single crystals with martensitic structure has been studied in relation to compression tests carried out at room temperature. Each sample was loaded at constant stress for different cycles and different stress values were used. Martensite stabilization was observed both in successive cycles and by increasing stress. This stabilization brought about a loss of shape memory recovery effect, on the one hand, and a training effect under stress, on the other, allowing the material total recovery in comparison with the previous cycle due to a two-way memory effect. This two-way memory effect appears at certain stress levels and/or determined cycles.

1. Introduction

A sample cooled to a temperature below M_f consists of self-accommodating variant groups of martensite; when a stress is applied, some variants grow at the expense of others [1]. According to the Bilby and Crocker's theory of deformation twinning [2], there are six twinning modes for 18 R type martensite, and any variant of growth can be accomplished by these deformation twinnings.

When the applied stress is released on the martensite, different types of behaviour can occur [3]: (1) the twin boundaries and martensite variants revert to their original positions before application of the stress (rubber-like behaviour); (2) the reverse movement of twins and variants does not occur upon unloading and the sample has apparently suffered a plastic deformation, its shape differs from its original shape; (3) a combination of the above mechanisms [3]. Which one of these three types of behaviour takes place depends on the stress level imposed during loading and on the detailed nature of the martensite plate interfaces.

The behaviour of Cu–Al–Mn polycrystals with martensitic structure in relation to compression loads has been studied by Mellor *et al.* [4].

2. Experimental procedure

A study was carried out on mechanical compression properties in two single-crystal alloys obtained by the Bridgman method [5] with the chemical composition (wt %) given in Table I. These single crystals are totally martensitic in structure at the experimentation temperature which remained constant for all the tests at 16 °C. The particular transformation temperatures (°C) are given in Table II.

In order to realize compression tests, a W-type Houndsfield testing machine was used. Alloy $Cu–Zn_{15}–Al_8$ underwent compression stress of 87, 174, 258, 345 and 388 $MN\,m^{-2}$ in five cycles for each stress, as did alloy $Cu–Zn_{15.6}–Al_{7.6}$ of 61, 183, 304 and 426 $MN\,m^{-2}$ five cycles for each stress. The error in measurement is $\pm 2\ MN\,m^{-2}$ in stress values.

For each stress a sample of approximately the same measurements was taken (5 mm diameter and 6.5 mm high) from one single crystal. The length was measured before beginning loading, l_0, after releasing the applied stress, l_2, and after submitting the sample to a shape recovery heat treatment, l_3, consistent with placing the sample in a furnace at 150 °C for 10 min and air cooled. The heat treatment does not cause ageing in the martensite. This process was carried out in each cycle and the following values were also calculated [6].

The corresponding strain at zero stress after unloading

$$\varepsilon_2 = \frac{l_0 - l_2}{l_0} \times 100 \qquad (1)$$

Final strain after heating

$$\varepsilon_3 = \frac{l_0 - l_3}{l_0} \times 100 \qquad (2)$$

The error in measurement of length values is 0.01.

The recovery of the shape memory defined from the strain is

$$R_2 = \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2} \times 100 \qquad (3)$$

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TABLE I Chemical composition of single crystal alloys

Alloy	Cu (wt %)	Zn (wt %)	Al (wt %)
$CuZn_{15}Al_8$	77.0	14.86	8.14
$CuZn_{15.6}Al_{7.6}$	76.7	15.68	7.62

TABLE II Particular transformation temperatures

Alloy	M_s	M_f	A_s	A_f
$CuZn_{15}Al_8$	43	25	30	46
$CuZn_{15.6}Al_{7.6}$	38	30	38	67

3. Results and discussion

3.1. ε_2 strain studies at different stresses

The results obtained for ε_2 are given for alloy Cu–Zn_{15}–Al_8 in Table III, and for alloy Cu–$Zn_{15.6}$–$Al_{7.6}$ in Table IV. First, it must be stressed that the first cycle has high strain values, both ε_2 and ε_3, and small shape recovery values, R_2. This is due to interactions between martensitic plates which grow in different preferential habit planes, these interactions bring about localized plastic strain and/or martensite which cannot be easily reversed, with plates pinned by defects. This leads to a permanent strain after unloading has taken place.

In general ε_2 strains, at the same stress, produce a slight decrease as the number of cycles increases. The strains increase as stress rises, as shown in Tables III and IV.

Figs 1 and 2 show these values for alloys Cu–Zn_{15}–Al_8 and Cu–$Zn_{15.6}$–$Al_{7.6}$, respectively. It can be observed that at stresses up to 250–300 $MN\,m^{-2}$. The strain grows in a straight line, producing a slower growth at greater temperatures and tending towards constant strains between 4% and 4.5%.

3.2. Studies of ε_3 strains and shape memory recovery

In Table III the values of ε_3 and the shape memory recovery are shown with different applied stress, together with the cycles for alloy Cu–Zn_{15}–Al_8. Table IV gives the results for alloy Cu–$Zn_{15.6}$–$Al_{7.6}$.

The values of ε_3 are always lower than those for lesser applied stress values ($\sigma = 87\ MN\,m^{-2}$ for alloy Cu–Zn_{15}–Al_8 and $\sigma = 61\ MN\,m^{-2}$ for alloy Cu–$Zn_{15.6}$–$Al_{7.6}$). It can be seen from the second cycle, that ε_3 strain is near zero and therefore shape recovery is 100%. Thus in the heat treatment carried out at temperatures greater than A_f, the martensite which has undergone strain becomes β, recovering its original shape; $\beta \rightarrow$ multivariant martensite transformation takes place on cooling the sample at room temperature.

For greater strain and in alloy Cu–Zn_{15}–Al_8 (174 $MN\,m^{-2}$ stress), there is total recovery until the seventh cycle, after which permanent defects are produced in the martensite and the plates remain pinned by them, preventing total martensitic transformation taking place when it is heated at a temperature above A_f. This partial transformation justifies the fact that shape recovery is only 85% for the tenth cycle.

TABLE III Strain and shape recovery values at different stresses and load cycles for single-crystal Cu– Zn_{15}–Al_8

Cycle	σ														
	87 $MN\,m^{-2}$			174 $MN\,m^{-2}$			258 $MN\,m^{-2}$			345 $MN\,m^{-2}$			388 $MN\,m^{-2}$		
	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)
1	6.90	5.9	14	6.10	5.30	14	8.47	6.82	20	12.50	7.90	37	12.10	8.30	31
2	0.96	0	100	1.32	0	100	2.65	0.25	91	6.00	0.10	98	4.30	0.04	99
3	0.85	0	100	1.42	0	100	2.40	0.13	95	5.80	0.19	98	3.50	0.10	97
4	0.68	0	100	1.10	0	100	1.77	0.13	93	3.10	0.40	89	4.00	0.48	88
5	0.82	0	100	1.12	0	100	2.41	0.25	90	3.52	0	100	3.50	0	100
6	0.82	0	100	1.10	0	100	2.03	0	100	3.43	0	100	4.10	0	100
7	0.82	0	100	1.10	0	100	2.03	0	100	3.50	0	100	3.87	0	100
8	0.82	0	100	1.70	0.20	88	2.70	0	100	3.49	0	100	3.83	0	100
9	0.86	0	100	1.61	0.30	82	2.40	0	100	3.40	0	100	3.83	0	100
10	0.82	0	100	1.30	0.20	85	2.50	0	100	3.32	0	100	3.83	0	100

TABLE IV Strain and shape recovery values at different stress and load cycles for single-crystal Cu–$Zn_{15.6}$–$Al_{7.6}$

Cycle	σ											
	61 $MN\,m^{-2}$			182 $MN\,m^{-2}$			304 $MN\,m^{-2}$			426 $MN\,m^{-2}$		
	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)	ε_2 (%)	ε_3 (%)	R_2 (%)
1	7.50	6.86	9	8.65	6.92	20	9.97	7.73	23	10.00	9.60	4
2	1.43	0	100	3.05	0.26	92	4.05	0.27	93	4.20	0.55	87
3	1.01	0	100	3.33	0.40	88	4.74	0.90	81	4.67	0	100
4	1.30	0	100	3.34	0	100	4.24	0	100	4.79	0	100
5	1.45	0	100	3.36	0	100	4.30	0	100	4.90	0	100

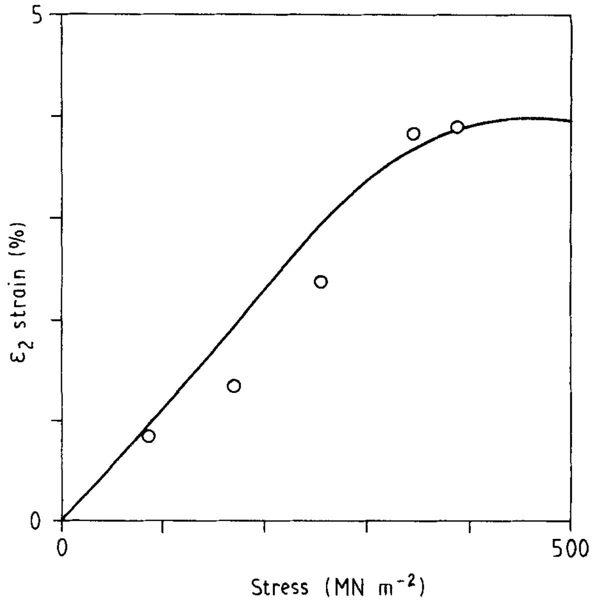

Figure 1 Strain ε_2 as a function of the applied stress for Cu–Zn_{15}–Al_8.

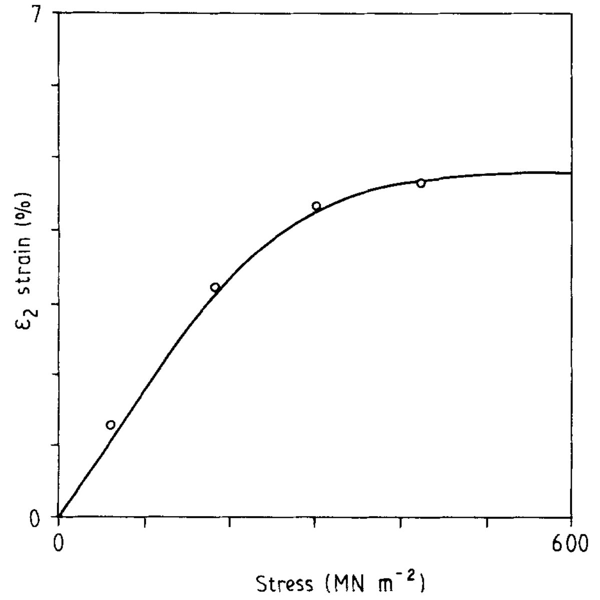

Figure 2 Strain ε_2 as a function of the applied stress for Cu–$Zn_{15.6}$–$Al_{7.6}$.

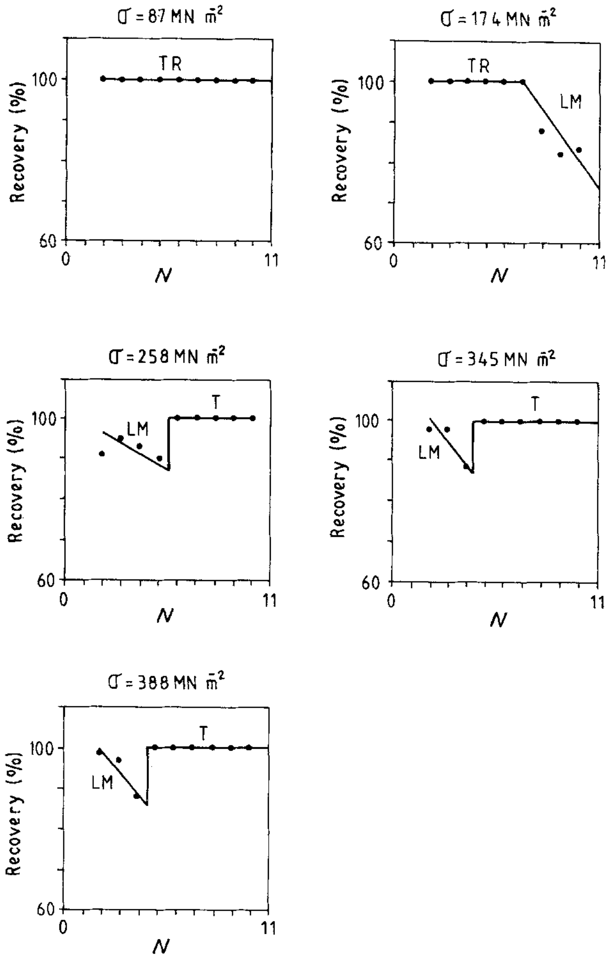

Figure 3 Shape memory recovery versus number of cycles, *N*, for different stress values applied to the single-crystal Cu–Zn_{15}–Al_8. TR, total recovery; LM, loss memory; T, training.

At greater strain values, such as those mentioned previously in both alloys Cu–Zn_{15}–Al_8 and Cu–$Zn_{15.6}$–$Al_{7.6}$, defects preventing total transformation can be observed.

As we increase the number of cycles there is a decrease in recovery values. However, this happens up to a cycle in which ε_3 strain is nil and, therefore, recovery is total for alloy Cu–Zn_{15}–Al_8 (Table III). For stress values of 258 $MN\,m^{-2}$ this occurs in the sixth cycle and for stresses of 345 and 388 $MN\,m^{-2}$ it is already produced in the fifth. For the alloy Cu–$Zn_{15.6}$–$Al_{7.6}$ (Table IV) this happens from a stress of 183 $MN\,m^{-2}$ being observed from the fourth cycle, as happens with a stress of 304 $MN\,m^{-2}$, being a stress of 426 $MN\,m^{-2}$ in the third cycle.

The explanation of this different behaviour is due to a training process which is created in the sample. In fact, when this stress is applied, strain in the martensite is produced and dislocations and permanent defects appear, favouring the appearance of some variants compared with 24 possible variants of thermal origin. When the sample is heated above the A_f temperature, it returns to β phase. This β phase inherits the defects which were brought about by stress in the martensitic structure, and on subsequent quenching martensite is obtained with stress-induced preferential variants.

When the quenched sample is measured, the initial length value of the first cycle in which training happens is obtained and not the original length value of the first cycle. Fig. 3 shows the shape memory recovery regarding the number of cycles and applied stress.

In order to confirm this, heat treatments of 10 min were carried out on samples at different temperatures (200, 300, 400, 500, 600 and 700 °C) to determine at what temperature the sample returned to the original dimensions of the first cycle. This is a clear sign that defects created in the sample have been eliminated, due to the temperature, and that the training process disappears. It was observed that all samples recovered their initial shape at 700 °C.

The metallographic study confirms that the structure produced by quenching from 700 °C has many variants, eliminating the preferential ones which had been previously trained by the cycling effect.

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