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The effect of thermal and stress cycling on thermoelastic martensite formation in Cu–Al–Mn alloys

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The effect of thermal cycling on the thermoelastic martensitic reaction and stress cycling on stress induced martensite formation and pseudoelasticity have been studied in alloys in the Cu–Al–Mn system. The martensite to high temperature phase start and finish transformation temperatures, A_s and A_f, of alloys quenched from 850° C were considerably higher than after repeated thermal cycling. The excess vacancy concentration present after quenching is postulated to enhance low temperature ordering reactions in these alloys through defect assisted diffusional mechanisms and so stabilize the martensite leading to higher A_s and A_f temperatures. Stress cycling of a β phase alloy increased pseudoelastic recovery and decreased the stress necessary to form stress induced martensite. Ageing specimens at room temperature after stress cycling was found to increase considerably the stress required to form stress induced martensite on subsequent stress cycling. Both pseudoelastic and shape memory recovery were observed in a martensitic alloy.

1. Introduction

In recent years shape memory and pseudoelasticity have been the subject of numerous publications and reviews [1–3] which have shown that the key to understanding these effects lies in the nature of the thermoelastic martensitic reaction which takes place in the vast majority of the alloys where these phenomena are registered. This reaction is characterized by the M_s, M_f, A_s and A_f temperatures where M_s and M_f are the temperature for the start and finish of the martensitic reaction, while A_s and A_f are the temperatures for the start and finish of the reverse process, martensite to high temperature phase. However it has been demonstrated that these temperatures depend, in part, on the previous thermal history of the specimen e.g. quenching temperature, rate of cooling, ageing at a temperature slightly above the M_s [3–7]. However the effect of thermal cycling on the thermoelastic martensitic reaction and the influence of stress cycling on pseudoelasticity has not been extensively studied and the present paper reports the results of a study of these effects on alloys from the Cu–Al–Mn system. In this system the β phase decomposes by a thermoelastic martensitic reaction [8] but there has been little published work on the details of this transformation in this particular alloy system. Alloy compositions were chosen by reference to the ternary phase diagram [9] so as to be in the β phase region down to a temperature of approximately 600° C. Below that temperature the β phase decomposes by a eutectoid reaction which has sluggish kinetics.

2. Experimental details

Alloys were prepared by melting high purity copper, aluminium and manganese in a high frequency induction furnace, followed by casting into a heated metallic mould. Specimens 4 mm in diameter and 6 mm long were subsequently machined. The composition of the alloys was determined by atomic absorption spectroscopy and is given in Table I.

The martensitic transformation temperatures were determined by passing a constant intensity direct current (6 A) through the specimen and measuring the variation of the voltage drop across the specimen with temperature, the apparatus drawn schematically in Fig. 1 being employed. Fig. 2 shows the voltage drop against temperature, from which the transformation temperatures could easily be determined. Specimens were cycled by repeatedly heating to a temperature of approximately 100° C above their A_f and cooling to $-160°$ C in liquid nitrogen vapour. The transformation temperatures were measured in each cycle.

The specimens were examined at room temperature by standard metallographic procedures to confirm the transformations indicated by the voltage drop measurements. Alcoholic ferrous chloride was used as an etch.

Stress cycling experiments were performed at room temperature on β phase alloys by registering the load–deformation curves on loading in compression and unloading the cylindrical specimens various times in a Chevenard micro-mechanical testing apparatus. Prior to these tests the transformation temperatures were determined by the previously described technique.

TABLE I The composition of the alloys studied together with their transformation temperatures, M_s, M_f, A_s, A_f after various thermal cycles

Copper (wt %)	Aluminium (wt %)	Manganese (wt %)	Cycle	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)
81.4	11.2	7.3	1	−89	−135	−96	−63
			2	−89	−135	−103	−60
85.0	10.9	4.0	1	161	98	186	223
			2	164	98	158	198
			3–5	164	98	158	198
82.2	11.7	6.0	1	22	−39	–	91
			2	22	−39	3	70
			3–11	17	−39	−3	70
83.0	11.7	5.3	1	52	−14	64	168
			2	52	−14	29	117
			3–6	52	−14	29	114

The specimens were examined metallographically after the cycling experiments.

The shape memory determinations were made by deforming a martensitic specimen a previously specified amount, removing the load and then heating the specimens for 15 min at 115° C (20° C above A_f). The dimensions of the specimen were determined before and after this heat treatment.

3. Results

3.1. Thermal cycling

Table I gives the transformation temperatures as a function of the number of times cycled through the transformation temperature region. Optical metallography carried out at room temperature on the different alloys confirmed that above the M_s temperature the structure was completely β phase (grain size $\sim 200\,\mu$m), while below the M_f temperature the structure was entirely martensitic. No α phase precipitation nor eutectoid was detected.

3.2. Stress cycling

Fig. 3 shows the stress–strain curves obtained at room temperature for a specimen with an initially β phase structure ($M_s = -91°$C, $M_f = -134°$C, $A_s = -99°$C, $A_f = -60°$C) during various loading and unloading cycles. The stress–strain curves are at first linear on loading, until, at a certain stress level they flatten out as the deformation proceeds (Region A). On removing the load, the stress falls rapidly and the curve then flattens out (Region B), before rising to a maximum from which the stress decreases almost lineally with strain. As can be seen, a hysteresis loop is formed by the loading and unloading cycles.

After the first cycle, the specimen is observed to have recovered almost all of the apparently plastic deformation received during the loading stage of the cycle, i.e. it has behaved pseudoelastically. Defining the pseudoelastic recovery, r_p as

$$r_p = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1} \times 100\% \qquad (1)$$

where ε_1 is the maximum strain and ε_2 the strain corresponding to zero stress on the unloading cycle, the values given in Table II are obtained for the pseudoelastic recovery values after various cycles. As is apparent from both Table II and Fig. 3 the pseudoelastic recovery increases notably after the first cycle and reaches 100%.

In the fourth cycle, when the specimen was subjected to a large deformation (44%) the pseudoelastic recovery was less, but part of the residual strain after the cycle was, in fact, recovered in the next cycle. The area of the hysteresis loop also increased as the maximum strain increased.

From the stress–strain curves, the stress corresponding to the onset of Region A was seen to fall slightly as cycling proceeded. As it was impossible to determine with exactitude when Region A started the stress at 10% deformation was measured and this, too, is given in Table II.

After six cycles, the specimen was allowed to remain

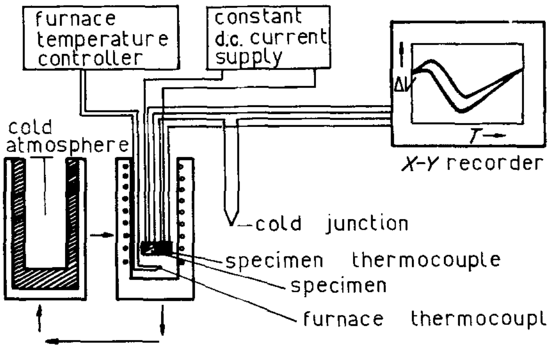

Figure 1 Schematic diagram of the apparatus used to measure the variation of voltage drop across a specimen as a function of temperature.

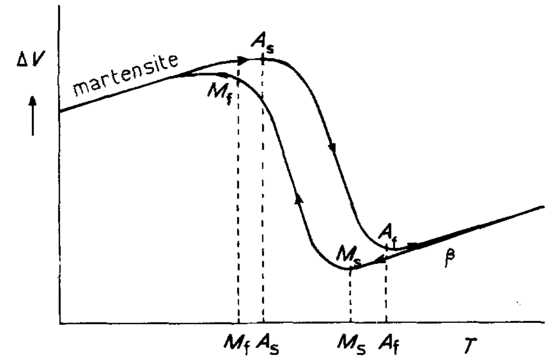

Figure 2 The voltage drop, ΔV, as a function of temperature, T.

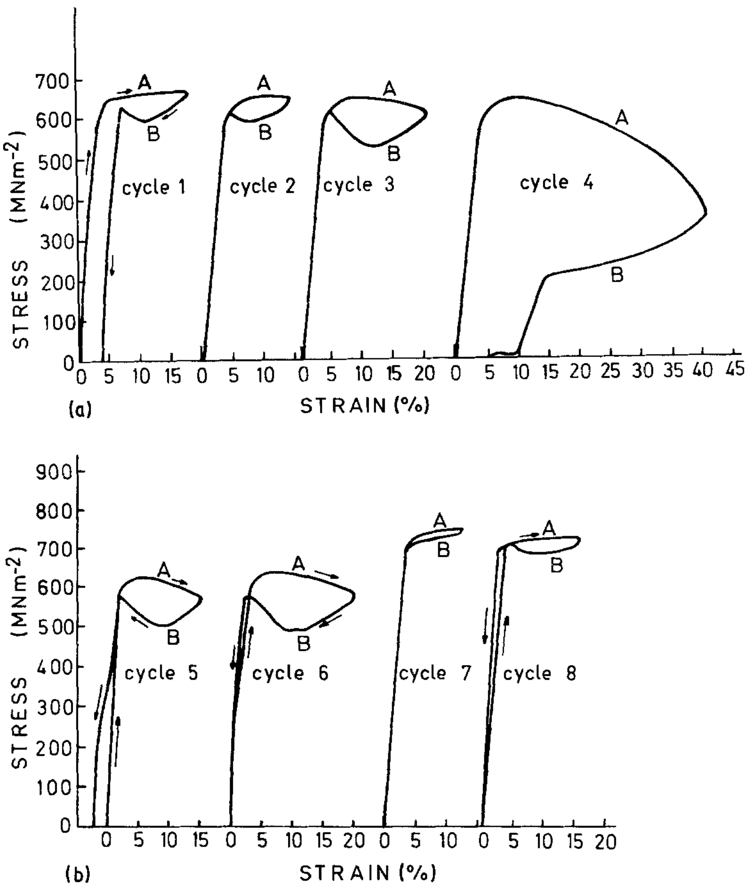

Figure 3 Stress–strain curves obtained at room temperature, for a specimen with an initially β phase structure, during various stress cycles.

at room temperature for 30 min and was then cycled again. Cycles 7 and 8 of Fig. 3 correspond to this new cycling sequence. Region A of the curve is now at higher stress levels than in Cycles 1 to 6, the area of the hysteresis loop is smaller, but the pseudoelastic recovery is still 100%.

Fig. 4 shows the microstructure of the specimen after this cycling treatment. Interlinked martensite plates were observed in certain parts of the specimen.

3.3. Shape memory

Fig. 5 shows the stress–strain curves of an alloy which is almost completely martensitic at room temperature ($M_s = 46^\circ$ C, $M_f = 20^\circ$ C, $A_s = 68^\circ$ C, $A_f = 92^\circ$ C) deformed to various pre-selected strain levels. The curves are practically linear, but on unloading some residual strain exists indicating that the deformation has been in part "plastic". The percentage of the strain recovered on unloading (pseudoelastic and elastic recovery r_p) was calculated and is given in Fig. 6 from which it can be deduced that on increasing the strain, the pseudoelastic recovery decreases.

TABLE II The mechanical properties of an alloy with an initially β phase structure during stress-cycling

Cycle	Maximum strain ε_1 (%)	Residual strain ε_2 (%)	Pseudoelastic recovery $\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1} \times 100\%$	$\sigma_{10\%}$ on loading (MN m^{-2})
1	18.8	3.6	80.8	670
2	16.2	0	100	660
3	22.8	0	100	650
4	44.0	3.7	91.5	650
5	17.7	−2.1	112	620
6	22.8	0	100	650
7*	13.9	0	100	740
8*	17.3	0	100	720

*Tested after ageing for ~30 min at room temperature.

On heating the specimens, the values for the shape memory recovery, defined as

$$r_m = \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_1} \times 100\% \qquad (2)$$

where ε_3 is the permanent strain after heating, given in Fig. 6 were obtained. The total recovery, $r_t = r_p + r_m$ is also shown in Fig. 6.

4. Discussion

Table I indicates that for alloys which are partially or completely martensitic at room temperature the M_s and M_f temperatures do not seem to change appreciably on thermal cycling. However there is a drop in the A_s and A_f temperatures between the first and subsequent cycles. The material used in the first cycle had previously been water quenched from 850° C and held at room temperature for various weeks prior to the cycling experiments which always began with the heating cycle. Quenching from 850° C will quench in nonequilibrium disorder and excess vacancies [6, 7]. It has been postulated [4, 6, 7, 10–13] for Cu–Zn–Al alloys that the higher diffusion rates available when excess vacancies are present enhance low temperature ordering reactions which stabilize the martensite leading to higher A_s and A_f temperatures. Heating the specimens to A_f + 100° C during the first heating cycle will reduce somewhat the excess vacancy concentration and thus the susceptibility of the martensite to stabilization will be reduced and the A_s and A_f temperatures will be correspondingly lower in subsequent thermal cycles. Low temperature ordering reactions are known to occur in Cu–Al–Mn

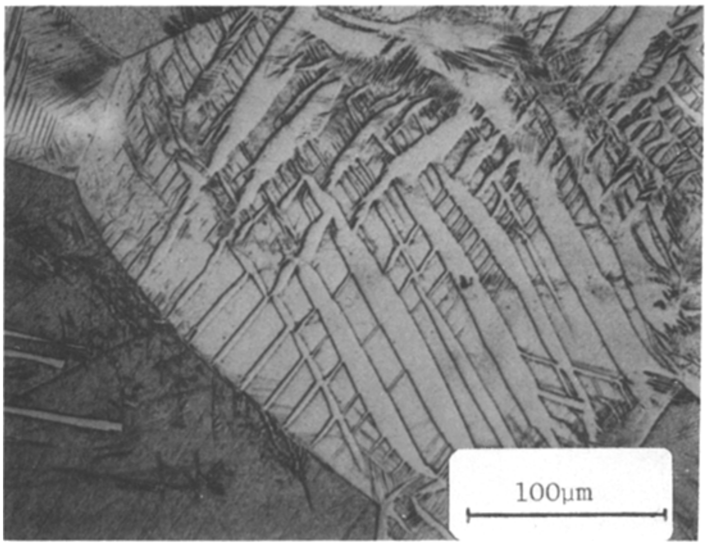

Figure 4 Microstructure of an initially β phase alloy after stress cycling.

alloys [14] so the interpretation proposed for Cu–Al–Zn alloys would seem to be relevant in the present study. The effect of ordering on martensitic transformation temperatures in Cu–Al–Mn alloys will be discussed in more detail in a subsequent paper [15].

The stress–strain curves for the alloy with an initially β phase structure show two clearly distinct regions, and in agreement with previous work [1–3] Region A is identified as being caused by the nucleation of stress induced martensite while on unloading the reverse process produces Region B. The exact nature of the stress–strain curves in the stress induced martensite region (A and B) is due to two factors which are the deformation of the specimen at a constant strain rate by the testing machine and the change in shape brought about by the formation and disappearance of stress induced martensite, and the combination of these two factors is thought to account for the observation of maxima and minima in the curves.

The pseudoelastic recovery was noted to be less on the first cycle than on subsequent cycles. During the first stress cycle the β phase will work harden and thus be more resistant to plastic i.e. non-reversible deformation during subsequent cycling to the same stress level, resulting in higher pseudoelastic recoveries.

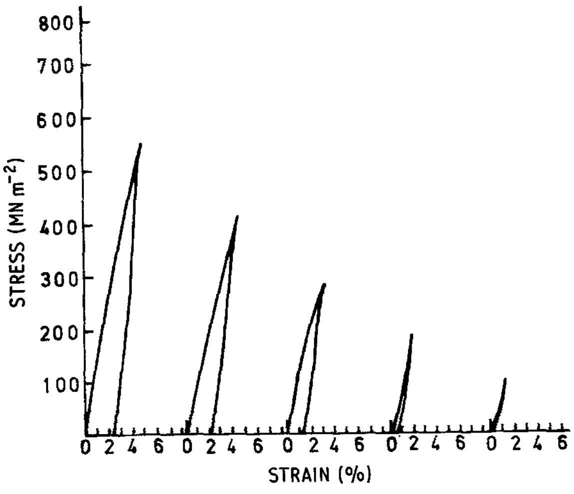

Figure 5 Stress–strain curves of an alloy with a martensitic structure.

The stress to nucleate martensite, represented by $\sigma_{10\%}$ was lowered slightly by stress cycling which suggests that cycling assists the nucleation of martensite. It has been postulated that the movement of martensite plates could activate suitably orientated defects, or induce the formation of other defects which could assist both the martensitic and reverse transformation, thus lowering the stress necessary for the nucleation of martensite in subsequent cycles [10, 16, 17]. Changes of degree of order in the β phase may also be enhanced by the high defect concentration introduced during stress cycling leading to a modification of transformation temperatures and hence stress to nucleate martensite [6, 7].

A room temperature ageing treatment on the specimen after cycling was found to give rise to an increase in the stress necessary to induce martensite. Cu–Al–Zn alloys aged at 100° C after quenching have been observed to exhibit a similar effect [5] and this was thought to be brought about by a change in long range order.

Further work is in hand to see if this is the case for Cu–Al–Mn or whether the ageing treatment after stressing modifies the dislocation arrays produced during previous stress cycles in such a way as to make the nucleation of stress induced martensite more difficult i.e. kinetic factors might be involved.

No apparent change was detected in the slope of the

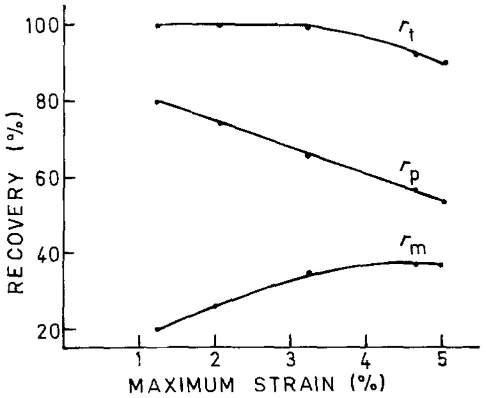

Figure 6 The pseudoelastic recovery, r_p, the shape memory recovery, r_m, and the total recovery, r_t, as a function of the maximum strain reached.

stress–strain curves for the initially martensitic alloy. This was probably caused by a lack of precision in the measuring apparatus. The pseudoelasticity detected in this alloy, by analogy with other systems [1–3] may be caused by the formation of some stress induced martensite or by a reorientation of martensite plates and/or their internal twins. On greater deformation, interactions occur between martensite plates to form a structure which is only reversible on heating (shape memory recovery). That is, pseudoelastic recovery will decrease and shape memory recovery will increase as the maximum strain increases as was found experimentally (Fig. 6). At even higher stress levels, plastic deformation takes place which is not recoverable even on heating i.e. r_t will fall when the maximum strain exceeds a certain value which is again in agreement with Fig. 6.

5. Conclusions

1. The effect of thermal cycling on the characteristic temperatures of the martensitic reaction has been studied by means of measurements of the variation of voltage drop across a specimen with temperature. The A_s and A_f temperatures after quenching from 850° C was higher than on subsequent cycling.

2. The higher diffusion rates possible when excess quenched-in vacancies are present are postulated to enhance low temperature ordering reactions which stabilize the martensite leading to higher A_s and A_f temperatures.

3. Stress cycling of an initially β phase alloy increases pseudoelastic recovery and decreases the stress at which stress induced martensite occurs. Work hardening of the β phase during the first cycle results in a strengthening of the β matrix which is thus more resistant to plastic deformation during subsequent cycles.

4. Ageing specimens at room temperature after stress cycling was found to increase the stress at which stress induced martensite nucleated on subsequent cycling.

5. Both pseudoelasticity and shape memory were observed in an alloy with an initially martensitic structure. The pseudoelastic recovery decreases as the maximum strain increases while the shape memory is constant at 100% up to ~ 3% maximum deformation and then decreases as the strain increases.

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