The stabilization of martensite in Cu-Al-Mn alloys

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The stabilization of martensite in Cu-Al-Mn shape memory alloys has been studied by measurement of the reverse transformation temperatures after various heat treatments and by positron annihilation spectroscopy. The martensite in the Cu-Al-Mn system rapidly stabilizes at room temperature after quenching from a high temperature in the β field. Positron annihilation measurements indicate the presence of excess quenched-in vacancies in the as-quenched sample. This vacancy excess is eliminated by heating in the β field just above the A_f temperature. Stabilization in the Cu-Al-Mn system, as in the Cu-Zn-Al system, thus arises either by pinning of the martensite plates by the quenched-in vacancies or by changes in configurational order, made possible by the increase in diffusion rate caused by the excess vacancy concentration.

1. Introduction

The increasing importance of shape memory effect (SME) alloys and in particular those based on copper which are being developed as lower-cost alternatives to Ni-Ti (Nitinol) has led to research on the factors which affect the stability of such alloys.

Among the factors which influence the thermal behaviour of SME alloys, stabilization of martensite which manifests itself as an increase in the start and finish transformation temperatures (A_s and A_f) of the reverse transformation (martensite to β) has received attention [1-3]. Early work on Cu-Zn-Al alloys attributed their poor shape-memory properties to the existence of residual internal stresses in the fine grain-size material. However, later work ascribed the poor shape memory to stabilization effects arising from the simultaneous action of two different phenomena [3-8]. These are the pinning of martensite by excess dislocations retained on quenching from a high temperature, and a change in the degree of ordering or configurational order of the martensite. As these changes in order involve the movement of atoms by diffusion, the rate of change of the degree of order is also enhanced by the excess quenched-in vacancy concentration present.

Stabilization of martensite has also been linked to precipitation phenomena occurring during the ageing of the alloy at a constant temperature or during prolonged successive thermal cycling [9, 10]. These precipitation phenomena also occur at a rate which depends upon the diffusion rate, which is itself increased by excess quenched-in dislocations as noted earlier.

The present paper reports the results of a study on the stabilization of martensite at room temperature in Cu-Al-Mn alloys which exhibit a thermoelastic martensitic reaction giving rise to pseudoelastic and shape memory effects [11-13]. The amount of stabilization was assessed by determining the martensitic transformation temperatures from resistivity measurements [13, 14] after different thermal treatments. A positron annihilation study was carried out concomitantly to ascertain the defect structure present after these thermal treatments.

2. Experimental procedure

The alloys were obtained by fusion of the constituent pure elements in a high-frequency induction furnace [14]. Their composition was determined by atomic absorption spectroscopy to an accuracy of ± 0.1 wt % (Table I).

Fig. 1 shows schematically the thermal treatment given to samples of Cu-10.6 wt % Al-7 wt % Mn. This treatment consisted of 10 min at 800° C followed by water-quenching to the stabilization temperature (25 $\pm$ 1° C). The samples were held at the stabilization temperature for various times, t_1, followed by thermal cycling, initiating always with the heating cycle, to determine the transformation temperatures by means of measurement of the variation of resistivity with temperature.

The other Cu-Al-Mn alloy compositions studied

TABLE I Composition of the alloys studied and the start and finish transformation temperatures of the martensitic and reverse reactions

Alloy	Composition (wt %)			Transformation temperatures (°C)			
	Cu	Al	Mn	A_s	A_f	M_s	M_f
A17	81.8	10.7	7.5	18	54	17	−10
A18	82.5	10.6	6.9	50	79	54	10
A22	82.4	10.6	7.0	50	93	52	15
A12	82.9	11.2	5.9	50	93	33	−10
A8	82.6	10.4	7.0	59	107	81	35
A16	83.5	10.6	5.9	74	119	107	59
A21	83.3	10.6	6.1	79	132	98	59

Figure 2 Variation of the A_s temperature as a function of the number of thermal cycles for various alloys studied.

were heat-treated in an identical manner, the only exception being that they were all held at the stabilization temperature for a fixed time of 3 days.

The positron lifetime spectra at room temperature were obtained for the Cu–10.6 wt % Al–7 wt % Mn alloy after various heat-treatments by means of a conventional coincidence system [15] with a resolution of 315 psec (full width at half-maximum). ^{22}NaCl evaporated on to a nickel foil was used as a positron source. After subtracting the source annihilations, one-component analysis gave satisfactory fits from which the average positron lifetime, which depends upon the type of defect present and the material, was determined.

3. Results and discussion

Fig. 2 gives the A_s temperature (A_{s_j}) as a function of the number of thermal cycles carried out after 3 days at the stabilization temperature (25°C) for various Cu–Al–Mn alloys. As can be seen, the value of the A_s temperature in the first heating cycle is considerably higher than in the second thermal cycle. The A_s temperature then decreases progressively with thermal cycling and reaches a stable value after 4 or 5 thermal cycles. These stable values of the reverse transformation temperature were designated A_s and A_f, while ΔA_s and ΔA_f correspond to the differences $(A_{s_i}-A_s)$ and $(A_{f_i}-A_f)$, respectively. Fig. 3 shows ΔA_s and ΔA_f as a function of stabilization time for the Cu–10.6 wt % Al–7 wt % Mn alloy. ΔA_s and ΔA_f reach maxima of ~24 and ~60°C, respectively, after 30 min at 25°C. Thus ΔA_f is considerably larger than ΔA_s. It should

also be noted that ΔA_s is within the range of (A_f-A_s) for this alloy. These alloys have a high rate of stabilization, which is in agreement with the results obtained by Ohta *et al.* [16] in similar alloys.

From Fig. 4 it can be deduced that the greater the A_s temperature, the greater is the stabilization obtained by quenching from 800°C.

Table II gives the thermal history of specimens of the Cu–10.6 wt % Al–7 wt % Mn alloy studied by positron annihilation spectroscopy. The values of the average positron lifetime, τ, are also included in this table.

On quenching this alloy from 300°C and holding at 25°C (Table II, Specimen (a)), the existence of only one major component in the defect structure of the martensite is revealed by positron annihilation spectroscopy. The value of $\tau^{Cu-Al-Mn}$ of 172 psec obtained is similar to that found for the martensite of a Cu–Zn–Al shape memory alloy quenched from 750°C [17] of 190 psec, and also close to the value for pure copper saturated with vacancies of 180 psec. This suggests
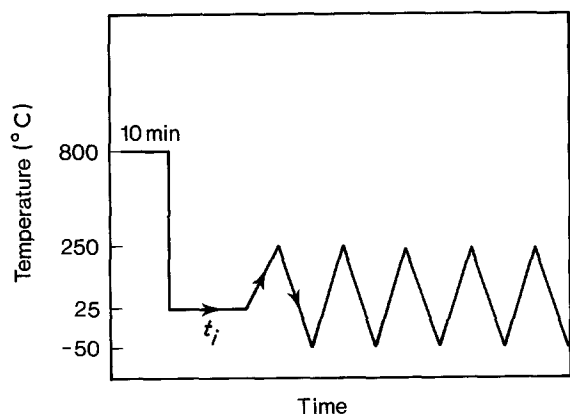

Figure 1 Thermal treatment given to samples of Cu–10.6 wt % Al–7 wt % Mn alloy in order to study the stabilization of the martensite. The stabilization time, t_i, is variable.
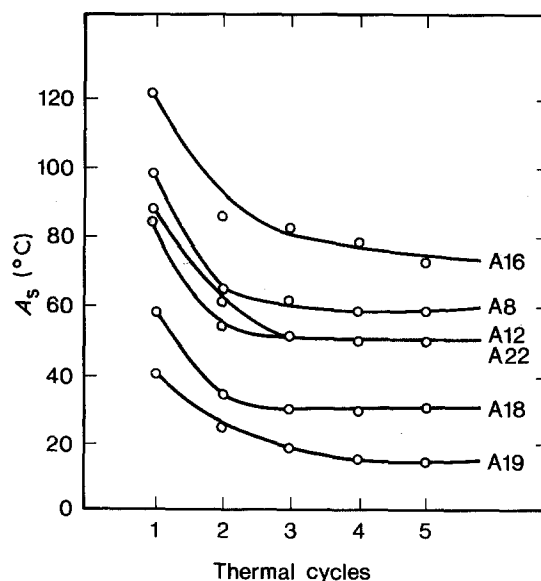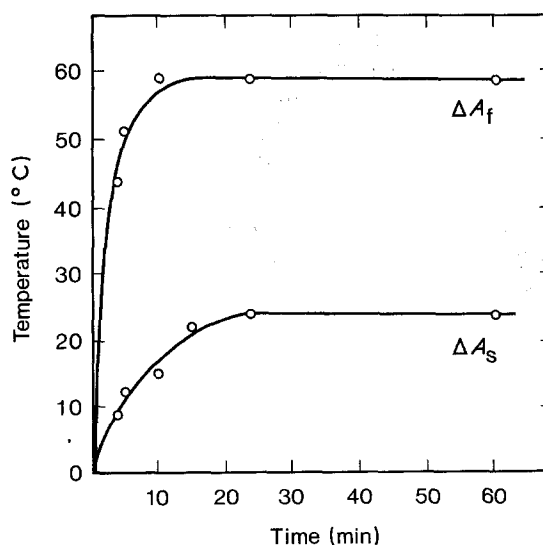

Figure 3 ΔA_s and ΔA_f as a function of the stabilization time for the Cu–10.6 wt % Al–7 wt % Mn alloy.

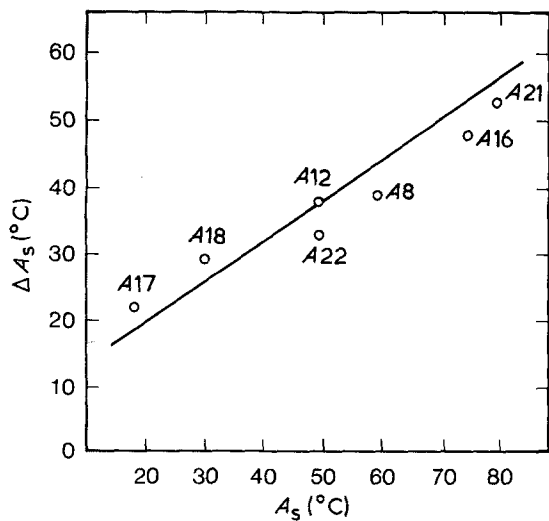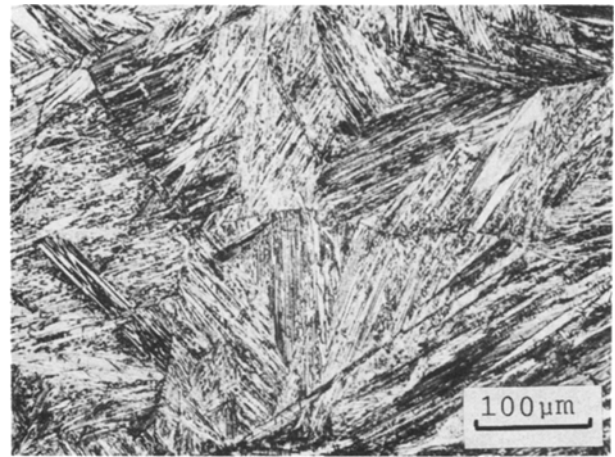Figure 4 ΔA_s as a function of A_s for the alloys studied.

Figure 5 Microstructure of the Cu–10.6wt% Al–6.1wt% Mn alloy. Note the very fine martensitic plates ($A_s = 79°$C).

that the defects in the stabilized martensite are mainly vacancies. Stabilization could then arise by the migration of excess vacancies retained by the quench towards the different types of defects and plate boundaries present in the martensite, pinning them and in that way hindering the reverse transformation. However, an excess vacancy concentration would also give rise to an increase in the diffusion coefficient, which would enable changes in configurational order to occur at the stabilization temperature and so in this way bring about an increase in A_s. Heating into the β-phase region allows the excess vacancy concentration to be eliminated, and thus the martensite subsequently formed from the β phase with an equilibrium vacancy concentration cannot undergo ordering changes or become pinned.

Fig. 4 indicates that the values of ΔA_s and ΔA_f increase with increase in A_s. Optical metallography revealed that the martensitic structure was finer for the alloy compositions necessary for the higher A_s temperatures (Figs 5 and 6). Thus the composition and detailed nature of the microstructure may also affect the amount of stabilization found. This has also been found in Cu–Zn–Al shape memory alloys [3]. However, the number of vacancies retained after quenching is known to depend upon the quenching rate. Van Humbeeck *et al.* [18] found that the change in quenching rate brought about by a difference in temperature of $21°$C of the quenching bath considerably affected the number of quenched-in vacancies. As the elimination of excess vacancies is much more rapid

in the β phase than in martensite [18], the time the specimen spends in the β-phase region during the quench obviously plays an important part in determining the number of quenched-in vacancies. During quenching from 300 to $25°$C, alloys with higher transformation temperatures will spend slightly less time in the β-phase region than alloys with lower transformation temperatures. This might also affect the number of vacancies retained sufficiently to cause a variation in the amount of stabilization found.

Stabilization can also be eliminated if, after quenching from $800°$C to the stabilization temperature, the specimen is given an isothermal heat treatment at a temperature slightly above A_{f_1} ($A_{f_1} + 15°$C). After this treatment no variation in the value of A_{s_j} was obtained, even after holding the specimen at room temperature for 3 months.

Positron annihilation spectroscopy revealed that only one major type of defect was present in the martensite at room temperature in the specimen which had been maintained at $170°$C for 90min (Table II, Specimen (b)), i.e. at $A_{f_1} + 15°$C. The value of $\tau^{Cu-Al-Mn}$ of 146 psec is considerably lower than that for the stabilized martensite, but is still higher than the average lifetime of a positron in a defect-free structure
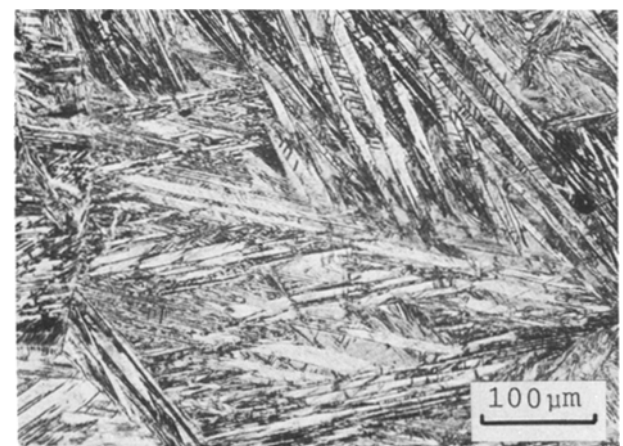
TABLE II Thermal history of specimens of the Cu–10.6wt% Al–7wt% Mn alloy used in the positron annihilation study, together with the average positron lifetime, τ, measured. All specimens were first heat-treated for 10min at $800°$C followed by quenching into water at $25°$C

Specimen	Isothermal heat treatment at $A_{f_1} + 15°$C	Number of thermal cycles to T_{max} of $A_f + 15°$C	τ (psec)
(a)	Not given	None	172
(b)	90 min	None	146
(c)	Not given	1	147
(d)	Not given	5	151

Figure 6 Microstructure of the Cu–10.6wt% Al–6.9wt% Mn alloy. Note that the martensitic plates are thicker than in the alloy shown in Fig. 5.

in copper ($\tau^{Cu} = 122\,psec$ [19]). As noted earlier, holding in the β-phase region leads to rapid elimination of the excess vacancy concentration, and thus neither pinning nor changes in configurational order can take place in the martensite formed on subsequent cooling. During the martensite transformation dislocations are generated, and thus the value of $\tau^{Cu\text{-}Al\text{-}Mn} = 146\,psec$ should be compared with the positron lifetime associated with dislocations. Values of 165 and 170 psec have been measured for this lifetime in pure copper [20, 21]. However, recent positron measurements in deformed aluminium have shown a decrease in the positron lifetime associated with dislocations as the impurity of the material increased, suggesting that impurities pinned to the dislocations can lower their open volume, leading to a decrease in the lifetime [22]. Hence the measured value of the positron lifetime in the martensitic defects of 146 psec may be associated with dislocations with impurity atmospheres.

When the specimen is thermally cycled just once after the stabilization treatment (Table II, Specimen (c)) the average positron lifetime drops from 172 to 147 psec, which is very similar to that after holding at 170° C for 90 min (Specimen (b)). Thus it would appear that the elimination of excess vacancies is very rapid in the β phase, and with just one thermal cycle practically all of the excess vacancies retained on quenching are eliminated. However, it should be noted that the A_{s_i} temperature only decreases progressively with thermal cycling and attains a stable value after 4 or 5 cycles, although it does decrease very markedly between the first and second cycles.

When the alloy is repeatedly cycled (Table II, Specimen (d)), a tendency for a slight increase in the value of $\tau^{Cu\text{-}Al\text{-}Mn}$ seems to be observed. This slight increase in $\tau^{Cu\text{-}Al\text{-}Mn}$ could be due to the generation of a dislocation substructure [22-26] which favours the reversibility of the martensitic transformation. Similar results have been reported in Cu–Zn–Al alloys [17].

4. Conclusions

The martensite formed in Cu–Al–Mn alloys on quenching from a high temperature in the β-phase region rapidly stabilizes upon holding at room temperature. This stabilization can be eliminated either by repeated thermal cycling through the transformation temperature range or by holding in the β phase at a temperature of $A_{f_i} \pm 15°\,C$.

Positron annihilation spectroscopy indicates that after quenching from a high temperature the mean lifetime of a positron is $\sim 172\,psec$, which is considerably higher than after repeated thermal cycling or holding at $A_{f_i} \pm 15°\,C$. This is consistent with the excess vacancies retained on quenching being eliminated when the alloy is heated into the β-phase region during thermal cycling or isothermal holding. Excess vacancies are then no longer available either

to pin martensitic boundaries or, by enhancing the diffusion rate, to bring about changes in configurational order, both of which give rise to stabilization.

The results found for Cu–Al–Mn shape memory alloys are broadly similar to those reported for Cu–Zn–Al alloys.

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