Effects of ageing treatments on transformation temperatures and precipitation kinetics in a Cu–Zn–Al shape-memory alloy

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The effects of ageing treatments on transformation temperatures, hardness, and precipitation kinetics in a Cu–14.2Zn–8.5Al (wt%) shape-memory alloy were investigated. Quench–ageing treatment temperatures varied from 100 to 500° C with times up to 200 h after the solution treatment. The martensitic transformation temperature, M_s, of the hot-rolled material was decreased from 55 to 51° C by the solution treatment. The temperature hysteresis ($A_f - M_f$) was 50° C for the hot-rolled condition, but was reduced to 30° C after the solution treatment. The maximum hardness for material aged at 500° C was lower than that for that aged at 300 or 400° C. The apparent activation energy for hardness increase in this alloy was 110 kJ mol^{-1}, compared with 72 kJ mol^{-1} for the similar copper-based shape-memory alloy Cu–21.2Zn–6.0Al. The ordering temperatures for B_2 and DO_3 superlattices were in the neighbourhood of 480 and 260° C, respectively. The tensile ductility and yield strength of this alloy were significantly reduced by the ageing treatment at 400° C.

1. Introduction

Copper-based shape-memory alloys are particularly interesting compared to other shape-memory alloys because of their lower cost and relative ease of processing [1, 2]. At elevated temperatures, the metastable beta-prime phases (9R, 18R, 2H martensites) and beta-1 phases (B_2, DO_3 superlattice) in the alloys transform to more stable structures by thermally activated processes [3]. It is therefore possible for these copper-based alloys to exhibit degradation of shape-memory capacity when thermally cycled [4].

The Cu–Zn–Al alloys reveal 9R or 18R martensite depending on the quenching conditions after solution treatment [5]. The effects of ageing on various properties in Cu–Zn–Al shape-memory alloys have been reported by several investigators [6–8]. For example, Kennon *et al.* [6] have recently reported the effect of ageing between 200 and 450° C for times up to about 280 h on hardness, shape-recovery capacity, transformation temperatures and lattice parameters in a Cu–21.2Zn–6.0Al (wt %) alloy. They showed that transformation temperatures (M_s, A_s, A_f) decreased with ageing time by the formation of alpha and gamma-2 precipitates in the alloy. They also predicted about 43 days of shape-memory life for the alloy with respect to the beta-phase stability at 100° C. Cook and Brown [7] also observed a decrease of M_s in a quenched Cu–26Zn–4Al alloy by ageing between 60 and 140° C. Schofield and Miodownik [8] reported a depression of M_s by ageing after solution treatment at 850° C in Cu–26.9Zn–3.9Al and Cu–33.0Zn–1.7Al (wt %) alloys.

Martensite transformation temperatures and precipi-

tation kinetics are very sensitive to zinc or aluminium content in Cu–Zn–Al shape-memory alloys [9]. Since the loss of shape memory is attributed to the formation of precipitates, the control of precipitation and its kinetics through alloy composition or processing is important in the increase of shape-memory life in Cu–Zn–Al alloys.

In this work, the effects of ageing treatments on transformation temperatures (M_s, M_f, A_s, A_f), microhardness, tensile behavior and precipitation kinetics in a Cu–14.2Zn–8.5Al (wt %) alloy were investigated. Ageing temperatures ranged from 100 to 500° C with time up to 200 h. The apparent activation energy was obtained from an Arrhenius plot of time to obtain 50% of maximum hardness against ageing temperature. The critical transition temperatures for B_2 and DO_3 orderings in the alloy were calculated using formulae given by Inden and Pitch [10] and interchange energies given by Rapacioli and Ahlers [11]. The tensile properties of the alloy were also measured before and after ageing treatments.

2. Experimental procedure

Alloy having a composition (wt %) of Cu–14.2Zn–8.5Al was melted in a graphite crucible under a reducing atmosphere using a high-frequency induction furnace. The 5 kg melt was poured into an iron mould of 5 cm × 5 cm × 17 cm. The ingot was subjected to a homogenizing heat treatment for 24 h at 800° C in an inert atmosphere. The homogenized ingot was hot-forged to 15 mm × 18 mm × 1000 mm plate after heating for 1 h at 900° C. The hot-forged plate was subjected to hot rolling in four passes after heating for

1 h at 850° C. The total reduction ratio in the rolling was 88%, with final thickness 1.6 mm.

Specimens for transition-temperature measurements had dimensions 4 mm × 1.6 mm × 130 mm. The specimens were solution-treated at 850° C and then quenched in iced water. In order to find the effect of solution treatment time on transformation temperatures, the solution treatment was varied from 5 to 35 min at 850° C. Low-temperature ageing treatments for 10 h at 100, 140, 180 and 220° C were conducted after the solution treatment (35 min at 850° C) and quenching. The martensitic transformation temperatures (A_s, M_s, A_f, M_f) and ordering temperatures (T_{B_2}, T_{DO_2}) were measured by electrical resistivity changes. The heating rate was $5°\,C\,min^{-1}$ and the cooling rate was $7.5°\,C\,min^{-1}$. For Vickers microhardness measurements, the solution-treated samples were aged for times up to 30 h at 300, 400 and 500° C. Tensile tests were performed at room temperature for samples aged for various times at 400° C. The ageing treatment was carried out in a salt bath containing 40% $NaNO_2$ + 60% KNO_3.

In order to analyse the precipitates formed, X-ray diffraction and energy-dispersive spectroscopic analysis (EDAX) were performed on the aged samples after polishing and etching with HCl + $FeCl_3$ solution. $CuK\alpha$ radiation was used at 30 kV and 20 mA for the X-ray diffraction.

3. Results and discussion

The effect of the solution treatment time at 850° C on martensitic transformation temperatures is shown in Fig. 1. M_s for the hot-rolled and subsequently air-cooled sample was 55° C. M_s decreased by 4° C with increasing solution treatment time at 850° C. M_s was stabilized at 51° C after about 30 min at 850° C. Typical curves of electrical resistance against temperature for hot-rolled material and solution-treated material are given in Fig. 2. The temperature hysteresis (A_f − M_f) was 50° C for the hot-rolled material, and that of solution-treated material was 30° C. M_s, M_f, A_s and A_f for the as-hot-rolled material were 55, 29, 58 and 79° C, while those for the solution-treated material were 51, 34, 42 and 64° C, respectively. The M_s of 51° C for solution-treated material was higher than the value of 45° C predicted by the relationship of Pops and Ridley [12].

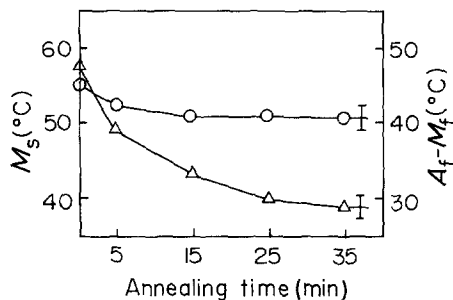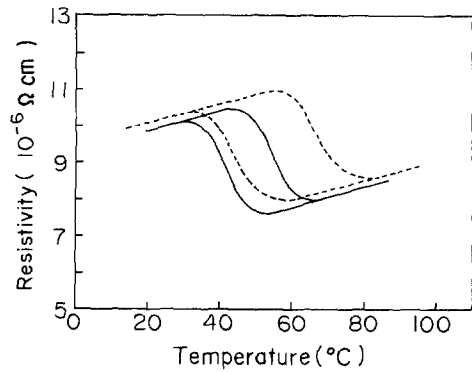The effect of quench−ageing treatment on transformation temperatures was studied after low-

Figure 2 Resistivity variation during martensite transformation: (— —) as-hot-rolled specimen, (—) specimen annealed for 35 min at 850° C.

temperature ageing. The variation of M_s and A_s at ageing temperatures of 100, 140, 180 and 220° C for 10 h is shown in Fig. 3. M_s and A_s decreased with increasing ageing temperature. For example, M_s decreased by 5° C upon ageing for 10 h at 220° C. The decrease of M_s by low-temperature ageing was consistent with the results for Cu−21.2 Zn−6.0 Al (wt %) obtained by Kennon et al. [6], and in Cu−26 Zn−4 Al by Cook and Brown [7]. Schofield and Miodownik [8] explained the shift of martensitic temperature in Cu−26.9 Zn−3.9 Al (wt %) shape-memory alloy by changes in the degree of long-range order present in the parent phase. The disordered beta-phase (A_2) present at high temperature transforms to beta-1 phases (B_2 and DO_3 superlattices) on cooling, and then transforms into beta-prime martensitic phases (9R or 18R type) on further cooling [3]. Schofield and Miodownik [8] proposed that the depression in martensitic transition temperature was attributable to residual quenched-in disorder from the B_2 to DO_3 ordering reaction.

Using the Bragg−William−Gorski model of long-range ordering theory and following the method of Indens and Pitch [10], the ordering temperatures of B_2 and DO_3 ordering were calculated using interchange energies by Rapacioli and Ahlers [11]. The ordering temperature of B_2 (T_{B_2}) was 500° C, while that of DO_3 (T_{DO_3}) was 280° C in this Cu−14.2 Zn−8.5 Al (wt %) alloy. The critical ordering temperatures were also measured by electrical resistivity changes in the present work. Fig. 4 shows the variation of resistivity with temperature. The experimental value of T_{B_2} was
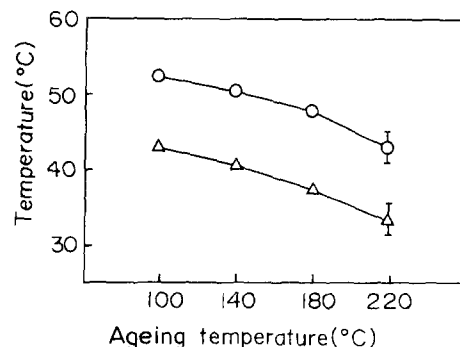

Figure 1 Variation of martensitic transformation temperature as a function of solution treatment time at 850° C: (O) M_s, (△) (A_f − M_f).

Figure 3 Variation of martensitic transformation temperature with ageing temperature (for 10 h at each temperature): (O) M_s, (△) A_s.
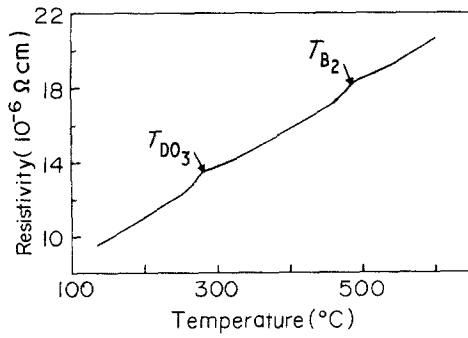
Figure 4 Variation of resistivity with temperature on cooling: T_{DO_3} = transition temperature for DO_3 superlattice, T_{B_2} = transition temperature for B_2 superlattice.

Figure 5 Variation of microhardness with holding time at different temperatures: ($\square$) 300, ($\triangle$) 400, ($\bigcirc$) 500°C.

480°C, and that of T_{DO_3} was 260°C. The agreement between calculated and experimental values was good. The ageing temperature of 220°C is below the transition temperature of B_2 to DO_3. However, a partially ordered structure exists at room temperature in the alloy since complete disorder cannot be obtained even by drastic quenching. During ageing treatments, a transition occurs from B_2 to DO_3 order by thermally activated motion of quenched-in vacancies, thereby changing the order parameter. The order parameter varies by an interchange of atoms, which is accomplished by the motion of quenched-in vacancies. Measurements on B_2 ordering in beta-brass [13] have shown that the Bragg–Williams ordering parameters change with temperature. Therefore, it was likely that
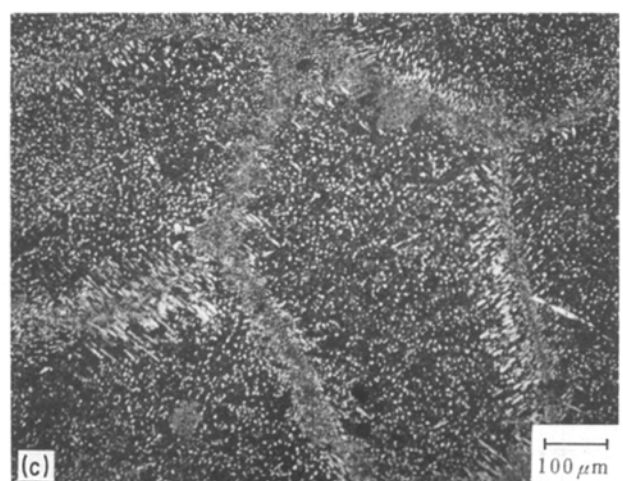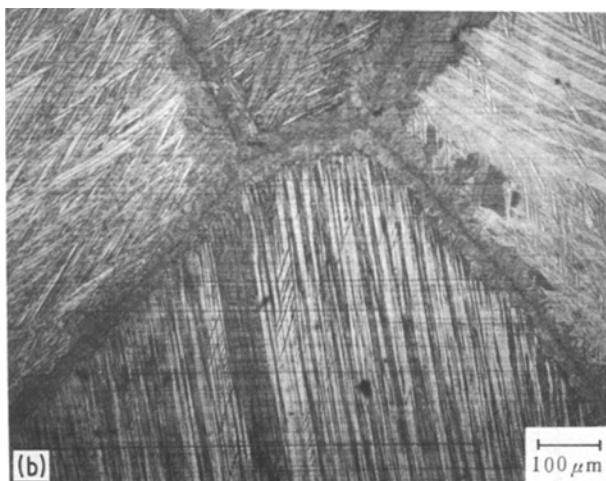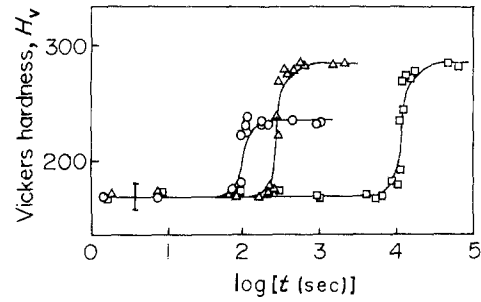
the change in the degree of order in the DO_3 phase also affected the change in M_s in the present work.

Samples for microhardness measurement were solution-treated for 35 min at 850°C, quenched, and then aged at 300, 400 and 500°C for times up to 30 h. The effect of ageing conditions on the Vickers hardnesses is shown in Fig. 5. Since the precipitation rate is dependent on temperature, the time to increase the hardness was shortest at 500°C, and was longest at 200°C. However, the maximum hardness produced at 500°C was lower than the maximum hardnesses at 300 and 400°C. One cause of the reduction in the maximum hardness at 500°C was the coarsening of precipitates at 500°C, which was confirmed by X-ray diffraction. It may also be attributed to a structural change of the matrix from ordered to disordered structure, since the ageing temperature of 500°C was near to the transition temperature of disordered A_2 to B_2 ordering.

X-ray analyses were performed to identify the nature of the precipitates formed during ageing treatments. Diffraction patterns from samples aged for 2 h at 300 and 400°C were consistent with those of alpha and gamma-2 precipitates observed in Cu–Zn–Ga alloy by Govila [14]. The lattice parameter of the alpha phase was 0.408 nm and that of the gamma-2 phase was 0.967 nm. It was also found that the X-ray diffractions of samples aged at 500°C were not different from those of samples aged at 300 and 400°C.

Figure 6 Optical microstructures of Cu–14.2 Zn–8.5 Al shape-memory alloy: aged for (a) 1 h at 300°C, (b) 15 min at 400°C, (c) 30 min at 500°C.
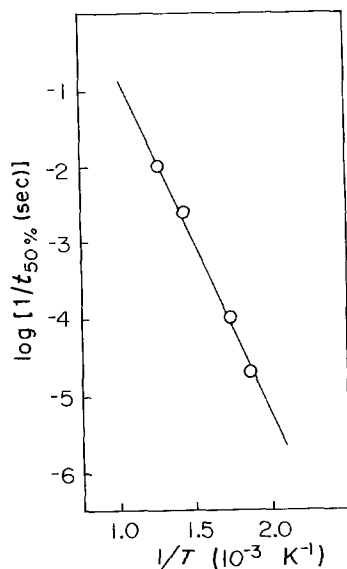
Figure 7 Arrhenius plot of the time to 50% of maximum hardness against temperature.

Figure 8 Variation of (O) yield stress and (□) tensile elongation with heat treating time at 400° C.

This result confirms the earlier interpretation of a reduction in hardness by precipitate coarsening at 500° C.

Fig. 6 shows the optical microstructures of samples aged for 1 h at 300° C (Fig. 6a), 15 min at 400° C (Fig. 6b) and 30 min at 500° C (Fig. 6c). They exhibited very coarse grains, about 2 to 3 mm in diameter. With increasing temperature and time, gamma-2 and alpha precipitates formed along grain boundaries as well as in the matrix. EDAX showed that the major grain-boundary precipitate was gamma-2 phase, while the intragranular precipitates were a mixture of alpha and gamma-2 phases. Hornbogen and Warlimont [15] reported that the initial product of isothermal transformation in beta Cu–Zn alloy was similar to the bainite in steel. The bainitic structure, containing stacking faults induced by a lattice-invariant shear, transformed to alpha-phase by a thermally activated process.

In order to estimate the apparent activation energy for increase in hardness, an Arrhenius plot of the time needed to obtain 50% of maximum hardness against ageing temperature was made, as in Fig. 7. The apparent activation energy was found to be 110 kJ mol^{-1}, which was significantly lower than the activation energy for diffusion, 150 to 200 kJ mol^{-1}, in similar copper alloys [16]. However, the apparent activation energy of this alloy, 110 kJ mol^{-1}, was higher than the reported activation energies in similar Cu–Zn–Al shape-memory alloys [6, 7]. Kennon et al. [6] reported an activation energy of about 72 kJ mol^{-1} in Cu–21.2 Zn–6.0 Al (wt %) shape-memory alloy, while an activation energy of about 65 kJ mol^{-1} was reported in Cu–26 Zn–4 Al by Cook and Brown [7]. The interpretation of our value for the activation energy is not yet clear. However, the fact that the apparent activation energy is significantly lower than the activation energy for diffusion may indicate that the thermally activated process was most likely enhanced by a super-concentration of quenched-in vacancies, as proposed by Clark and Brown [17].
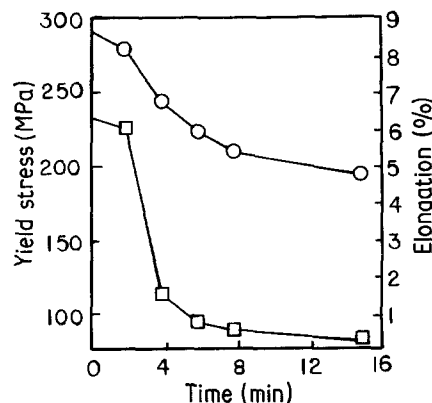
It is interesting to note that the time to increase hardness in this alloy is considerably longer than that of the similar copper-based alloy reported by Kennon et al. [6]. For example, the time to increase hardness appreciably in our alloy at 400° C was about 10^4 sec, compared with about 5 × 10^2 sec in Cu–21.2 Zn–6.0 Al [6]. The results obtained for Cu–21.2 Zn–6.0 Al by Kennon et al. [6] also showed that, at 300 and 400° C, the times to reach maximum hardness were about equal to the times to decrease the shape-memory effect, while at 200° C the time to reach only 50% of maximum hardness was about equal to the time to decrease the shape-memory effect. The effects of ageing treatment on shape-memory life in this alloy have not been studied. However, the fact that the time to increase hardness is considerably longer than that of the similar copper-based alloy [6] may indicate that this alloy possesses a longer shape-memory life than that predicted for other copper-based shape-memory alloys by Kennon et al. [6].

Tensile tests of samples aged at 400° C showed that the yield strength and tensile elongation were greatly reduced with increasing ageing time; the yield stress (0.2% offset) decreased from 290 to 193 MPa, and the elongation reduced from 5.5 to 0.2% after 15 min (Fig. 8).

4. Conclusions

1. The value of M_s for hot-rolled alloy (Cu–14.2 Zn–8.5 Al) was decreased from 55 to 51° C by solution treatment at 850° C for 35 min.

2. The temperature hysteresis ($A_f - M_f$) was 50° C for the hot-rolled condition, and that after solution treatment was 30° C.

3. M_s for the solution-treated condition (51° C) decreased by 4° C upon ageing for 10 h at 220° C.

4. The critical ordering temperature for B$_2$ was 480° C, and that for DO$_3$ was 260° C.

5. The maximum hardness of material aged at 500° C was lower than the hardness for ageing at 300 or 400° C, due to the coarsening of precipitates at 500° C.

6. The precipitates formed at 300, 400 and 500° C were alpha and gamma-2 phases.

7. The activation energy to increase the hardness was 110 kJ mol^{-1}, which was higher than that for Cu–21.2 Zn–6.0 Al alloy, 72 kJ mol^{-1}.

8. The time to increase hardness upon ageing was much longer than that for Cu–21.2 Zn–6.0 Al alloy.

9. Ageing at 400° C greatly reduced the yield strength as well as the tensile elongation.

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