

The Role of Ordering in the Loss of Shape Memory in some Copper-base Alloys

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Introduction

It is well known that copper-based β alloys exhibit the so-called 'shape memory effect' which is manifest as the ability of the material to regain its original shape when deformed and heated to above a particular temperature. This phenomenon is associated with the thermoelastic martensitic transformation of the β phase [1].

It has been observed by many workers that ageing plays an important role in affecting the degree of shape recovery in these alloys. Alloys, deformed and aged in the martensitic condition, show a progressive loss in the degree of recovery [2]. However, when the same alloys are given an intermediate anneal in the β phase (before transformation to martensite and deformation) the degree of recovery is not affected so markedly. This loss of recovery due to martensitic ageing in shape memory alloys given no intermediate anneal in the β phase, has been variously attributed to pinning of martensite boundaries by excess vacancies or to changes in the nature and degree of order [3-5]. A recent study [6] on Cu-Zn-Al alloys concluded that the loss of memory during martensitic ageing of alloys given no intermediate β anneal is directly related to disordering in the martensitic state during ageing.

The present study was undertaken to verify whether such is indeed the case not only in Cu-Zn-Al alloys but in other Cu-based systems such as Cu-Al-Mn alloys.

Experimental procedure

Two alloys were selected for investigation: a Cu-Zn-Al alloy with a nominal composition by weight of 26.1 zinc, 4% aluminium, the balance copper, while the other was a Cu-Al-Mn alloy with a nominal composition by weight of 11% aluminium, 6% manganese and the balance copper. Both these alloys were supplied in the form of 4 mm extruded wires by Delta Materials Research Ltd, Ipswich, UK.

The following experimental methods were employed in investigating the ageing behaviour of the selected alloys; differential scanning calorimetry (DSC) for determining the transformation temperature of the alloys, X-ray powder diffraction method for lattice spacing determinations and transmission electron microscope studies (TEM) for martensite structure determination.

(a) DSC Measurements:

The DSC measurements were made using a Dupont 990 thermal analyser. The alloys were quenched from the high temperature β phase, given an intermediate anneal in the β phase to remove excess vacancies and then

subjected to runs at a heating rate of 10 °C/min to determine the martensitic transformation temperatures characteristic of the alloys.

(b) XRD Measurements

Powder specimens of alloys were prepared and sealed in evacuated Quartz tubes and given high temperature β phase solutionising treatment for 10 minutes at the appropriate temperatures: 830 °C for the Cu-Zn-Al alloy and 700 °C for the Cu-Al-Mn alloy. These were then quenched in cold water to retain the β phase and given different post quenching treatments described below:

Cu-Zn-Al alloy specimens:

- (a) Ageing at room temperature directly after quench and
- (b) Ageing at room temperature after an intermediate anneal at 100 °C for 30 minutes.

Cu-Al-Mn alloy specimens:

- (c) Ageing at room temperature directly after quench
- (d) Ageing at 60 °C and 100 °C after quench and
- (e) Ageing at room temperature after an intermediate anneal at 180 °C for 15 minutes.

Powder diffractograms were obtained for all the specimens at different stages of martensitic ageing using filtered Cu-K radiation.

(c) Transmission Electron Microscope Studies

Specimens for TEM examination were prepared from 3 mm diameter discs that were thinned down mechanically to 0.3 mm thickness and electropolished in a Struers Tenupol-2 machine at -20 °C in a solution of 20% nitric acid in methanol. Specimens of both as-quenched and post-quench β phase annealed alloys were examined in a JEOL 200CX electron microscope operated at 160 kV.

Experimental Results

(a) DSC results

The M_s and M_f temperatures were measured as 36 °C and 30 °C respectively for the Cu-Zn-Al alloy. The M_s and M_f temperatures for the Cu-Al-Mn alloy were found to be 133 °C and 98 °C respectively. This meant that both alloys were fully martensitic at the chosen martensitic ageing temperatures.

(b) X-ray diffraction results

Typical powder diffractograms of the Cu-Zn-Al and Cu-Al-Mn martensites are shown in Figure 1 with peaks indexed corresponding to the M18R orthorhombic structure. The d-spacings for the diffracting planes were calculated and the spacing differences (Δd) between some selected pairs of diffracting planes satisfying the relation:

$$(h_1^2 - h_2^2)/3 = (k_2^2 - k_1^2)/n \quad (1)$$

were obtained after each selected interval of ageing. The variation of (Δd) as a function of ageing time in the martensitic state after different heat treatments are plotted in Figures 2 and 3 for Cu-Zn-Al

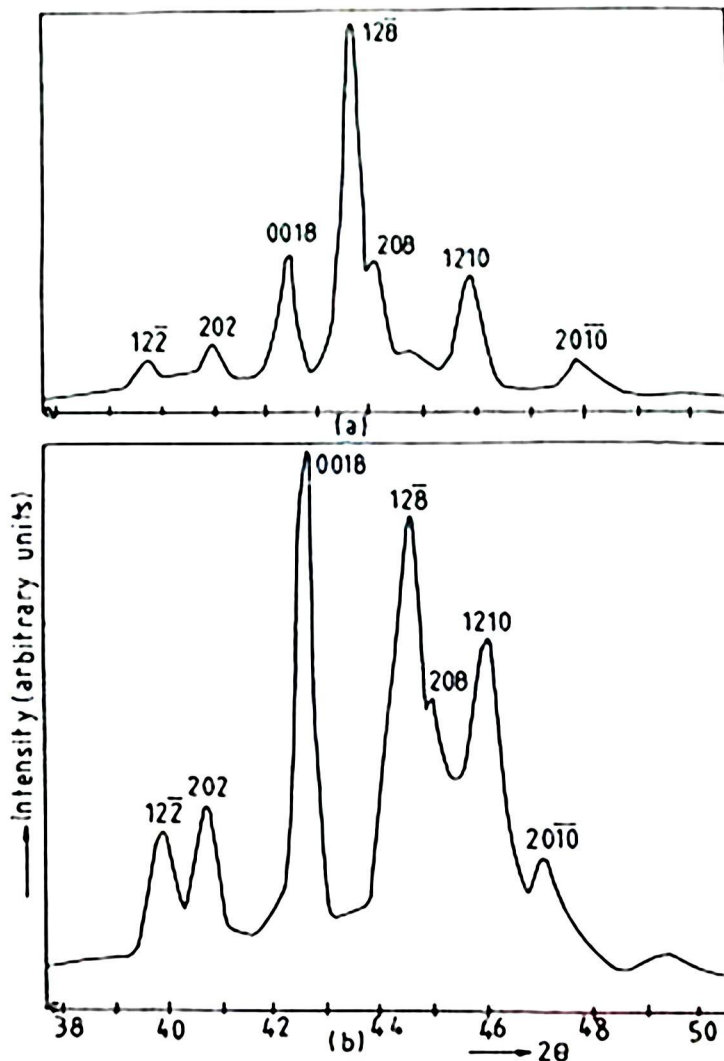


Fig. 1: X-ray powder diffractograms taken from the as-quenched (a) Cu-Zn-Al and (b) Cu-Al-Mn alloys.

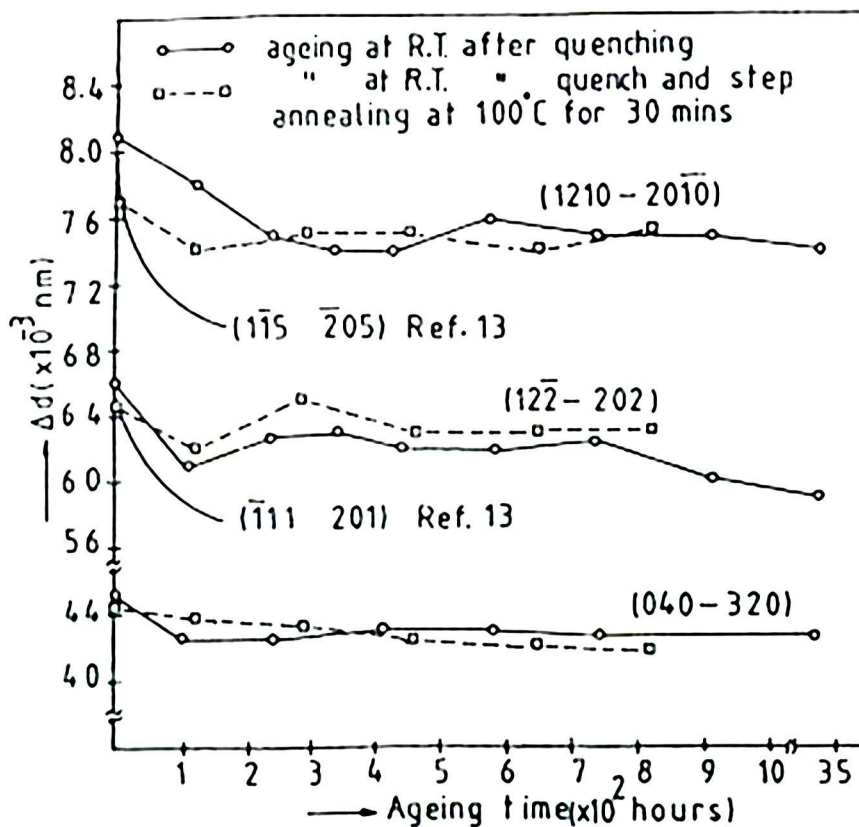


Fig. 2: The variation of Δd values of Cu-Zn-Al alloy samples against the holding time at room temperature.

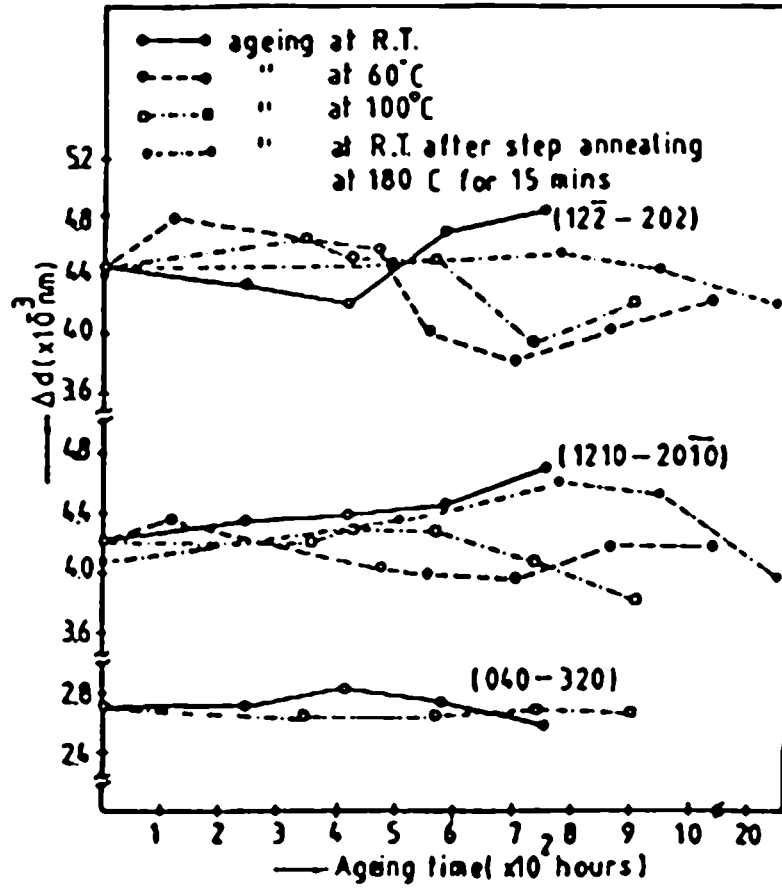


Fig. 3: The variation of Δd values of Cu-Al-Mn samples against the holding time at different ageing temperatures.

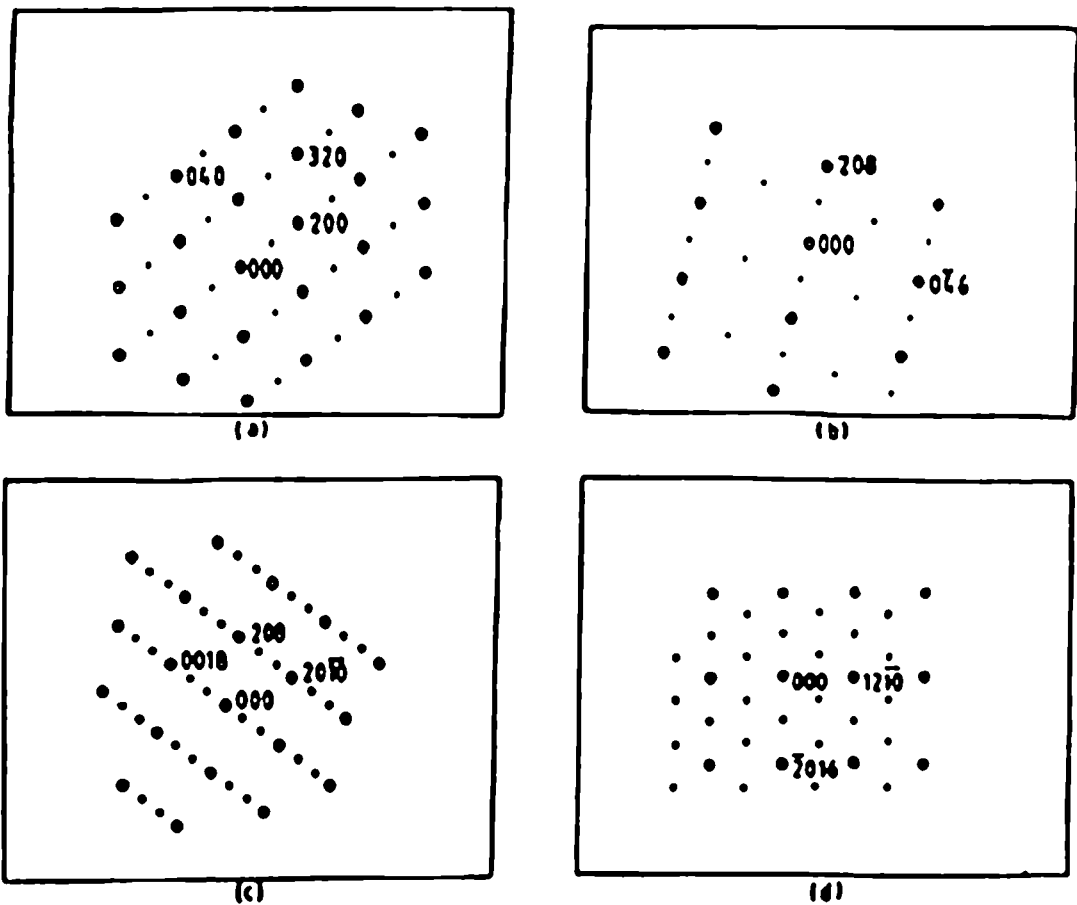


Fig. 4: Indexed key diagrams of the electron diffraction patterns.

alloys and Cu-Al-Mn alloys respectively. The reason for the choice of these pairs of planes and the relation between (Δd) and the degree of ordering in martensite are explained in the discussion part of the paper.

(c) Electron microscopy results

Electron diffraction patterns of as-quenched and post-quench β phase annealed alloys showed no readily observable difference between the differently treated specimens, which is consistent with the results of Scarsbrook et al [7]. Figure 4 shows the patterns indexed on the basis of the M18R structure.

Discussion

The relative positions of the different atom species in the (110) planes of the BCC matrix lattice remain unchanged when these planes become shear planes of the first strain during the transformation and are converted into the basal planes of the martensite [8]. If the constituent atoms are randomly distributed in the basal plane, the ratio a/b of the lattice parameters in the basal plane should equal $\sqrt{3}$ for 9R and $\sqrt{3}/2$ for 18R martensites respectively. However, as the parent phase is ordered and the basal plane consists of atoms of different sizes, the ratio a/b is less than $\sqrt{3}$ for 9R or less than $\sqrt{3}/2$ for 18R martensite. This deviation from the ideal value of a/b results in splitting of certain diffraction lines in the orthorhombic martensitic phase and can be used as a qualitative measure of the degree of ordering in the martensitic phase as shown by Qi Xuan et al [6].

The interatomic spacing ' d ' of crystal planes in an orthorhombic lattice is related to the lattice parameters a , b , c by the equation:

$$(1/d^2) = (h^2/a^2) + (k^2/b^2) + (l^2/c^2) \quad (2)$$

In the disordered case the lattice spacings of planes of type (h_1, k_1, l) and (h_2, k_2, l) will equal one another provided the indices of these planes satisfy the Equation 1 with $n = 1$ for 9R and $n = 4$ for 18R martensites. Under these conditions the diffraction lines from the planes (h_1, k_1, l) and (h_2, k_2, l) will coincide. On the other hand, when the martensitic phase is ordered, the lattice spacing of the plane (h_2, k_2, l) will not equal the lattice spacing of the plane (h_1, k_1, l) and the corresponding diffraction lines will separate. For example, the lines from the pair of planes $(12\bar{2})$ and (202) and the pair of planes $(1\bar{2}10)$ and $(20\bar{1}0)$ of the martensitic phase 18R satisfy Equation 1 and split in the ordered state. The splitting distance (Δd) of these pairs of planes can therefore be used as a measure of the degree of ordering in the martensitic phase 18R.

(a) Variation of the degree of ordering with ageing in Cu-Zn-Al alloys

The planes chosen for calculating the (Δd) differences for both the alloys were $(12\bar{2})$, (202) ; $(1\bar{2}10)$, $(20\bar{1}0)$; and (040) , (320) . Figure 2 shows the variation (Δd) with ageing time for the chosen pairs for a Cu-Zn-Al alloy with the M18R structure. Variations in (Δd) reported by Qi Xuan et al [9] for the pairs $(1\bar{1}5)$, $(\bar{2}05)$ and $(\bar{1}11)$, (201) of the M9R structure of Cu-Zn-Al alloy are also plotted for comparison. Such a comparison is legitimate because the (hkl) indices of the M9R structure

are related to the M18R structure by the relationship:

$$(hkl)_{gR} \rightarrow (h\ 2k\ 2l)_{18R} \quad (3)$$

It can be seen that the initial (Δd) values for the as-quenched specimens in the present case agree quite closely with the initial values of Qi Xuan et al [9]. The variation in (Δd) with ageing time also follows the downward trend reported by the same authors. However, the magnitude of the decrease in (Δd) in the present case is not as marked. Another interesting observation is that the post-quench β phase annealed specimens also show the same trend in (Δd) variations. Long-time ageing (500 hours or more) results in almost the same value of (Δd) for both types of specimens.

(b) Variation of the degree of order with ageing in Cu-Al-Mn alloys

Figure 3 shows the results of Cu-Al-Mn alloy samples aged in the martensitic state at different temperatures. The sample aged at room temperature actually shows an increase in the (Δd) value with ageing while those aged at 60 °C and 100 °C begin to show a decrease in (Δd) values after about 400 hours ageing. However, after about 1000 hours the (Δd) values in the two latter cases are almost equal to the initial value. This is also the case for samples aged after an intermediate anneal at 180 °C in the β phase.

Conclusions

Both the Cu-Zn-Al and Cu-Al-Mn alloy specimens studied here show progressive loss in shape memory due to martensitic ageing if no post-quench β phase anneal is given. On the other hand, specimens given a post-quench β phase anneal do not lose their memory so drastically. This is in keeping with the observations made by other workers [2-6].

The X-ray observations made in the present study indicate that the variation of degree of order during martensitic ageing is the same in both as-quenched specimens and specimens given post-quench ageing treatment in the β phase. The excess vacancies present in the as-quenched specimens seem to act only as a means of accelerating the change in degree of ordering concerned. There is no extra degree of disordering that can be solely attributed to the quenched in vacancies. This means that the reason for loss of reversibility in the as-quenched specimens during martensitic ageing is not solely disordering but some other special effect that needs excess vacancies.

References

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