

ON THE INHIBITION OF STABILISATION OF MARTENSITE IN Cu-Zn-Al ALLOYS

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Introduction

A shape memory device, and thus the alloy, when not operating is generally held in the martensitic condition. Also the shape memory effect depends on the retransformation of the martensite to the parent phase (1). Use of an alloy in a temperature controlling device, therefore, demands reliability and reproducibility of this retransformation temperature with shape memory cycles and more particularly, with time of hold in the martensitic condition before the device is operating at any given time. Notably, the latter aspect is known to be a weakness of Cu-Zn-Al shape memory alloys, as they are vulnerable to ageing which shifts the retransformation temperature to higher values (2-4). The martensite is thus stabilised relative to the parent phase and a shape memory device where the martensite is stabilised is unreliable. This poses a problem in utilising Cu-Zn-Al alloys in applications requiring high retransformation temperatures, as ageing in martensite is more pronounced the higher the temperature.

Several methods have been used to contain the stabilisation of martensite in Cu-Zn-Al alloys. The latter, being the result of a diffusional process, is accelerated by the presence of an excess, non-equilibrium concentration of vacancies quenched into the martensite from a higher temperature. Resorting to a step quench (5), wherein the alloy is first quenched into the parent condition and held for sufficient time at this temperature reduces the vacancy concentration substantially. When subsequently transformed to martensite, the tendency to stabilise with ageing is lowered considerably, if not totally inhibited. Alloying additions to Cu-Zn-Al can also improve its resistance to stabilisation. Manganese additions, in particular, have been reported (6) to exhibit such beneficial effect, though it is not clear whether the effect is strong enough to inhibit stabilisation. The most interesting finding to date, however, on inhibition of stabilisation, has been reported by Duan and Stobbs (7). These authors have shown that hot rolled Cu-Zn-Al alloys are much less prone to stabilisation than step quenched alloys. They have demonstrated this effect in a hot rolled alloy which was subsequently aged at room temperature for 1.5 years in the martensitic condition.

Lately, efforts are being made to develop shape memory alloys for applications with operating temperatures at around 473 K. There is an obvious reluctance to consider Cu-Zn-Al alloys for such applications because of the stabilisation problem. Yet, it would be interesting to explore in the wake of Duan and Stobbs' (7) finding on the inhibition of stabilisation, whether the usable temperature of these alloys can be raised by appropriate thermomechanical treatments. This would require some more systematic investigation. As a first step, we consider here the effect of deforming at different temperatures and to different extent at the same temperature, on the ageing in martensite and any consequent

stabilisation. The results will be discussed both from a practical aspect on the conditions relevant to obtaining inhibition of stabilisation, as also from a fundamental aspect on the reason / mechanism of stabilisation.

### Experimental

The alloys used in this investigation had a nominal composition of 76.99 % Cu, 14.77 % Zn and 8.24 % Al (all in at%). The as received material was in the form of hot extruded bars, 6 mm in diameter. Several 15 cm lengths of the bar were solution treated in the  $\beta$  condition at 1123 K for 6 hours and then taken out of the furnace and cooled in air to room temperature. They were subsequently hot rolled at 1073, 973, 823 or 673 K to final thicknesses of 4 or 3 mm. The lower rolling temperatures were always reached by heating the material first to 1073 K and then transferring to another furnace maintained at 973, 823 or 673 K, where they were left to equilibrate for 600 seconds before being rolled. As it came out of the rolls, the material was immediately quenched into hot water at 368 K and left to cool slowly to room temperature followed by dipping into liquid nitrogen to ensure complete transformation to martensite. After ageing at room temperature for over 3 months, the material was cut into suitable sizes for transformation experiments in a differential scanning calorimeter (DSC).

The DSC experiments were carried out in the following manner. The sample was introduced into the DSC at room temperature, then cooled to 243 K, after which it was subjected to heating cooling cycles at 20°/ minute while the retransformation and transformation were recorded. The maximum and minimum temperatures during cycling were generally set to 393 K and 243 K respectively.

Optical microscopy of the aged samples was carried out, after electropolishing, using polarised light.

### Results

The results of transformation cycling the samples rolled at different temperatures and aged subsequently at room temperature are given in figs. 1 to 6. Figures 1 to 3 show the results obtained with samples reduced to 4 mm from 6 mm, while in figs. 4 to 6 are presented the results obtained with samples reduced to 3mm from 6mm. The transformation cycles shown in each figure correspond to the first and second heating cycle, as also the second and third cooling cycles. The first cooling cycle corresponding to transformation on cooling the as rolled material could not be measured in any of the samples.

The following observations can be made from the data presented in the figures. In all cases, complete retransformation of martensite to the parent  $\beta$  phase in the first heating cycle occurs at a higher temperature compared to that in subsequent heating cycles. This difference corresponds to the martensite stabilisation due to ageing before the first heating cycle.

For a given deformation temperature, the material that is deformed more is less prone to stabilisation.

For a given amount of deformation, the material that is deformed at a lower temperature suffers lesser stabilisation.

The nominal transformation temperatures, as seen in the second heating or cooling cycle, of the more heavily deformed samples are slightly lower when compared to those of the less deformed sample.

There was not any appreciable difference either in the  $\beta$  grain size or martensite plate size of the aged but yet untransformed samples, subjected previously to different conditions of deformation.

### Discussion

The results presented above establish that inhibition of stabilisation is promoted by lower rolling temperatures and higher amounts of deformation. The most suitable choice of the amount of deformation and temperature would, however, be dependent on the quality of the rolled material, as judged by any tendency for cracking along the grain boundaries. For the alloy investigated here, the quality of the rolled material was good even after rolling at 823 K. In the material rolled at 673 K precipitates of  $\gamma$  phase were observed along with grain boundary cracking after rolling.

In seeking the reasons for the inhibition of stabilisation of martensite, one has to consider the mechanism/s of stabilisation. Several mechanisms proposed in this respect can be broadly divided into two groups (8). In one, atom relaxations and resulting strain energy changes near interfaces and defects in the martensite are considered to be the cause. This mechanism is often referred to in the literature as "pinning of interfaces or defects". The other possible mechanism considers configurational changes in the martensite volume occurring during ageing as responsible for the relative stabilisation of martensite with respect to the parent.

It has been argued recently (7,8), that experimental evidences, to date, do not support the pinning mechanism. For example, both transformation cycling a specimen several times and deforming a sample in the  $\beta$  phase lead to martensite plate size refinement and thus an increase in the number of interfaces, as also an increase in the amount of dislocations inherited by the martensite, with the consequent increase in the number of non-basal stacking faults within it. Stabilisation, however, is inhibited in such cycled or deformed samples and not promoted as would be expected if the pinning mechanism were the reason for the stabilisation. Neither can the mere presence of the dislocations in the martensite be the reason for its stabilisation. If such were the case, stabilisation should be independent of time of ageing in the martensitic condition, which runs contrary to the observed behaviour. Besides, as reported in the previous section, there is a tendency for the transformation temperatures to be shifted down (and not up as in martensite stabilisation) with increasing deformation or equivalently with increasing number of dislocations.

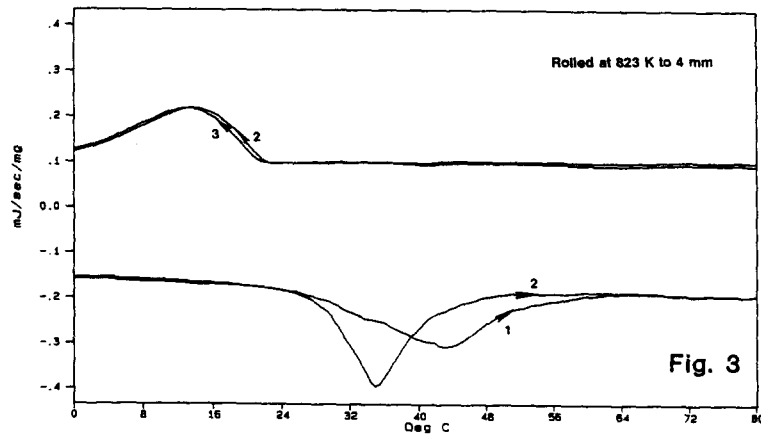
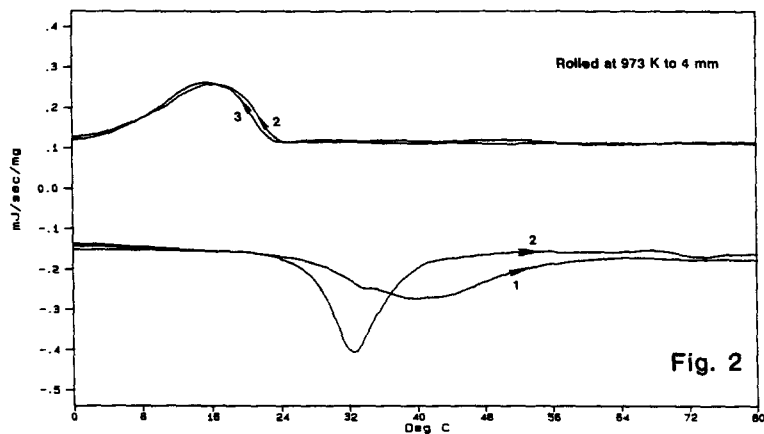
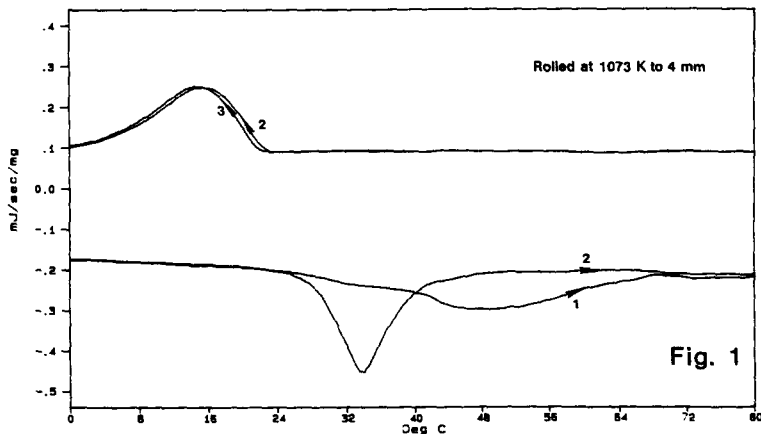
Stabilisation as already mentioned is due to a time - temperature dependent diffusional process, whose rate is enhanced in the presence of excess quenched in vacancies. Diffusion leads to configurational changes in the martensite disordering it relative to the unstabilised state. Experimental evidence at least in single variant stress induced martensite (9) supports this mechanism. The role of dislocations in such a mechanism has been considered by Duan and Stobbs who attribute the inhibition of stabilisation in the presence of dislocations to the latter providing high mobility pathways and sinks for the vacancies. But, in the experiments conducted in the present investigation, the concentration of vacancies before transforming the  $\beta$  phase to martensite was anyway minimised in all cases by step quenching into water at 368 K after rolling. Thus it is believed, that there must be another aspect of the dislocations inherited by the martensite, which retards subsequent diffusion. This would be considered as contrary to normal behaviour in metals and alloys, where dislocations often enhance the diffusion rate. Possibly, the answer to this strange behaviour lies in the crystallography of the dislocations specifically introduced by rolling. Duan and Stobbs' (7) remark that only dislocations introduced by rolling and not by other methods, such as fatigue, inhibit stabilisation effectively might support the present view. Besides, it is known that for binary Cu-Zn alloys, dislocations with specific Burgers vectors are predominant after deformation at different temperatures (10). Cu-Zn-Al alloys are known to undergo a first neighbour and subsequently a second neighbour ordering reaction (11). It would thus be worthwhile examining the crystallography of the dislocations in these alloys introduced after rolling at different temperatures and possibly the type of disorder that they introduce. These experiments are currently in progress and the results will be reported soon.

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Figs. 1-3: DSC curves showing the retransformation - transformation behaviour in alloys aged in the martensite condition after rolling previously to 4mm at temperatures indicated

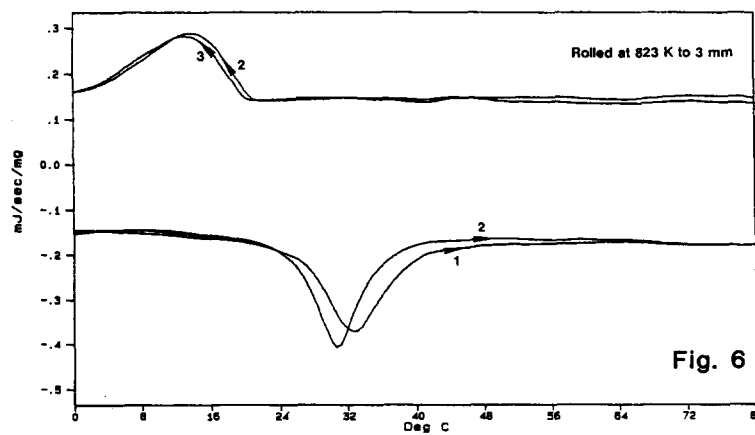
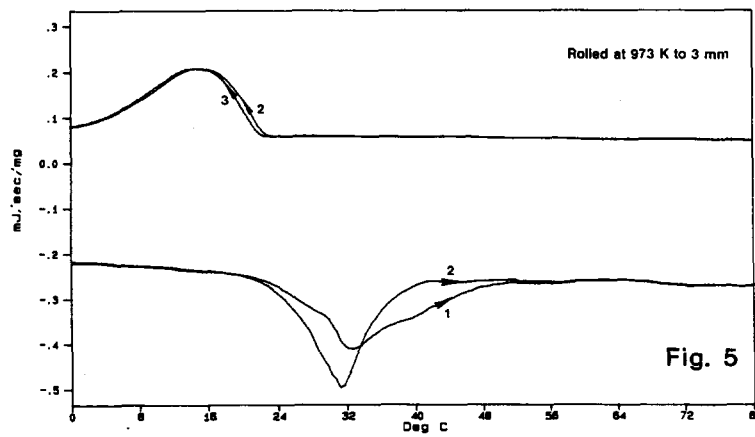
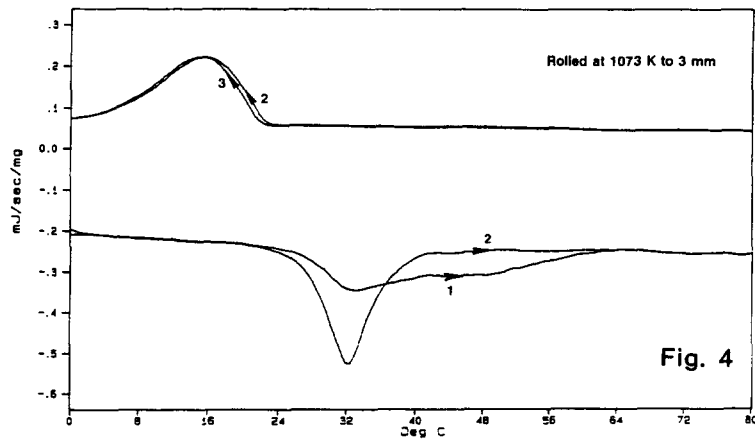


Fig. 4-6: DSC curves showing the retransformation - transformation behaviour in alloys aged in the martensite condition after rolling previously to 3mm at temperatures indicated