Optimisation of rebetatising time and temperature for lowering martensitic transformation temperature in Cu-Zn-4% Al shape memory alloy

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Cu-Zn-Al shape memory alloy (SMA) is a new class of smart engineering materials which can be incorporated in varieties of heat sensitive devices. Its martensitic transformation temperature is very sensitive to alloy composition which can be raised to some extent by incorporating a bias spring or by dezincification. However, lowering this temperature, once obtained, poses problems. The present paper reports that martensitic transformation temperature could also be lowered to some extent (∼ 20°C) without much adverse effect on the shape memory response in Cu-Zn-Al (4 wt % Al) shape memory alloys, by rebetatising the material at lower temperature.

Shape memory effect (SME) is an age old phenomenon and a unique characteristic exhibited by a number of alloy systems like Ni-Ti, Nb-Ti, In-Ti, Ni-Al, Cu-Zn-Ga, Cu-Zn-Al, Cu-Al-Ni and Cu-Zn-Sn. Such an alloy if deformed in the lower temperature martensitic state, completely regains its original underformed shape, on heating through the reverse transformation range. During this shape change, it exerts a usable force which can be used in many heat sensitive devices for warning, control, detection and regulation.

Research has been carried out on Cu-Zn-4 wt % Al alloy (α + β range) having a composition of approximately 70 Cu, 26 Zn and 4 Al (wt %) with a transformation temperature ∼ 65°C. Although this alloy has comparatively low strength and fatigue properties as compared to Nitinol, it is inexpensive and easier to fabricate. However, in Cu-Zn-6 wt % Al alloys (Fully β), the transformation temperature could be lowered to the extent of ∼ 70°C. But, we have concentrated on Cu-Zn-4 wt % Al alloys as it is easy to process by cold working in comparison to Cu-Zn-6 wt % Al alloy.

Experimental Procedure
The alloy was made by melting precisely the calculated quantities of commercially pure copper, zinc and aluminium, in an induction furnace, under a charcoal cover. The alloy was then cast into rods. These rods were then homogenised at 800°C for 2 h. The homogenised rods were hot groove rolled to ∼ 7 mm dia wires with necessary intermediate reheating at 800°C. These were annealed at 540°C for 2 h and furnace cooled to 480°C before cooling in air. The annealed wires were cold rolled in a groove rolling machine down to ∼ 4 mm dia in 3-4 stages with above mentioned annealing cycle, after every stage. These wires were then cold drawn to 1.5 mm dia wire through a series of tungsten carbide dies and using bull block wire drawing machine. During this cold drawing operation, wires were subjected to several intermediate annealings at 500°C for one and half hours and cooling in air. Between two annealings, the cumulative reduction was restricted to maximum 30%. The wires so obtained were first annealed and after cutting to the required
lengths were then given the desired shapes, i.e., formed into helical coils/springs. These coils were then betatised for inducing shape memory. The process flow chart is given in Fig. 1. The betatising (memorising) treatment consists of heating the material at 800°C for 10 min, quenching in hot water at ~80°C and keeping in it for 15 min before transferring these components into cold water. Quenching in hot water prevents the material from cracking, whereas soaking in hot water facilitates vacancy migration, i.e., prevents pinning effect, thereby, preventing stabilisation of martensite, thus reducing the aging effect. The microstructure of the betatised material was found to be
multioriented martensite with small volume fraction of α-phase at β grain boundaries (Fig. 2). The betatised material showed a recovery temperature (As) of ~65°C. For measuring recovery temperature, the alloy specimen was placed in a glass vessel containing water and the temperature of which was increased gradually by adding hot water. Temperature at which displacement (just start) of the specimen with reference to an index mark occurred, observed under a telemicroscope was measured as recovery temperature. The accuracy was within ±2°C. Out of these betatised coils, a few coils were then initially subjected to rebetatising treatments between 600-800°C with an increment of 50°C for various lengths of time, i.e., for 5, 10, 15, 20, 25 and 30 min, respectively. The temperature range for lowering of martensitic transformation temperature was then ascertained. It was found to be between 700-750°C. The remaining betatised coils were then rebetatised between 700-750°C with an increment of 10°C for the above said time intervals. Recovery temperature was determined, shape memory response and microstructures were evaluated at various stages (Figs 3-8). The rebetatised material at 720°C for 20-25 min showed a recovery temperature of ~45°C, which was ~20°C below the previously betatised material with a good shape memory response.

Results and Discussion
Rebetatising the previously betatised material between 750-800°C for various intervals, i.e., 5 to 30 min, showed good shape memory response but there was no significant decrease in the recovery temperature as the material was fully martensitic with a little feathery α-phase at the grain boundaries, rather there was slight increase in transformation temperature above 65°C probably due to the loss of zinc content at higher temperatures (Fig. 9). On rebetatising between 600-700°C for the above time intervals, sufficient volume fraction of α-phase was detected which remained undissolved even upto 30 min and there was hardly any visible martensite thus resulting in poor shape memory response. Further experimentation on rebetatising between 700-750°C with an increment of 10°C for 5-30 min, it was observed that transformation temperature could be invariably lowered for this particular alloy composition (4 wt% Al), inspite of being in α + β-phase range. The morphology of α-phase changes from needle shape to plate/lenticular shape and then to globular with rise of temperature and time interval upto 740°C for 10 min and, thereafter, the α-phase becomes feathery as observed by microstructure examination. It was also realised that at lower rebet-
Rebetatising temperature the rise in As is gradual with increase of time, whereas at higher rebetatising temperature the increase in As is spontaneous (Fig. 10). At 720°C for 20-25 min, the recovery temperature was found to be ~ 45°C (Fig. 11). This decrement in temperature could be realised from microstructures and Cu-Zn-4 wt % Al ternary diagram1 (Fig. 12), in which dashed line ×-× refers to the composition used. From the diagram, it could be seen that during heating at ~ 720°C the alloy composition is almost at the α + β and β-phase boundary region, which is a sensitive region in which there is a progressive dissolution of α-phase in β-phase, either with the rise of temperature or at constant temperature, but with more time. With prolonged heating, there is a danger of grain growth and coarsening of martensite plates, once α-phase fully goes into β-phase which is detrimental to properties. It was also observed that a little α-phase at the grain boundaries does not affect shape memory response, rather it gives a cushioning effect and prevents quench cracks. At 720°C for 20-25 min, a definite volume fraction of α-phase remains undissolved into β-phase, making the remaining β-phase richer in zinc contents which on quenching transforms into zinc rich martensite, responsible for lowering the transformation temperature by a few degrees and the material showed good shape memory. It has been seen that any increase in Zn/Al content decreases transformation temperatures whereas any increase in copper content raises the transformation temperature. It was also reported5 that slight shift in composition (Al, Zn, Cu) give rise to large change in martensitic transformation temperature. During experimentation it was also found metallographically that at 720°C for 5-15 min, enough volume fraction of α-phase remained undissolved in β-phase with hardly any visible martensite resulting in poor shape memory. On the other hand, on rebetatising at 720°C for 30 min, almost complete dissolution of α-phase was noticed and the material was fully martensitic.

Conclusion
It is concluded that martensitic transformation temperature could be lowered to some extent (~ 20°C) by rebetatising the material at slightly lower temperature in order to retain a definite volume fraction of α-phase in martensite which could be achieved by optimisation of rebetatising temperature and time. This retained α-phase has not much effect on shape memory response, rather it gives a cushioning effect and prevents quench cracks.

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