

Effect of Grain Size on Transformation Temperatures in a Grain-Refined, Copper-Based, Shape-Memory Alloy*

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A Cu-20.6 wt.% Zn-5.7 wt.% Al alloy containing a small quantity of Zr was chosen for the study of grain-size effect on transformation temperatures in copper-based, shape-memory alloys. Various thermal treatments were performed to obtain a range of grain sizes. The transformation temperatures were determined using electrical resistance measurement and shape-change effects. All the transformation temperatures shifted to lower temperatures as grain size decreased, except for the temperature at which no further shape change occurred on cooling. For the grain-size range of 35 μm to a maximum of 50 μm , this corresponded to a shift of as much as 15°C in transformation temperatures. The effect of grain size on transformation temperatures has been found to follow the Hall-Petch relationship.

Introduction

Alloys exhibiting the shape-memory effect are now of commercial interest. Products using these alloys are being marketed, and other commercial applications for these alloys will likely be introduced in the future [1, 2]. Copper-based, shape-memory alloys are of particular interest compared with other shape-memory alloys because of their lower cost and relative ease of processing. However, the copper alloys generally exhibit poor mechanical properties with limited ductility. The brittleness of these alloys has been attributed to their high elastic anisotropy and large grain size [3]. Consequently, the poor mechanical properties in copper-based, shape-memory alloys reduces their potential commercial applications unless material or processing modifications can be made.

Recent investigations have indicated significant promise in improving mechanical properties by grain refinement without significant deterioration of the strain-memory properties [4, 5]. One method of grain-size control has been to use preferred thermomechanical processing [6, 7], but

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this is not a suitable means of controlling grain size. Another approach involves the use of powder metallurgy [8, 9] to produce alloys with grain size as small as 10 μm . Grain refinement by alloy additions also shows some promise in obtaining fine grain sizes. Effective grain refinement and improved shape memory properties were demonstrated in Cu–Zn–Al alloys containing vanadium additions [10] and in Cu–Al–Ni alloys employing additions of Ti or Cr, B, and Zr [11, 12].

The effects of grain refinement on the mechanical and the strain-memory properties has been extensively studied [5]. However, no detailed investigation on the influence of grain size on transformation temperatures has been made. The present investigation was undertaken with the purpose of studying the effect of grain size on transformation temperatures in a Cu–Zn–Al alloy that was grain refined with the addition of Zr.

Experimental Procedure

The alloy used in this study was a Cu–20.6 wt.% Zn–5.7 wt.% Al containing a small quantity of Zr. The alloy was prepared by induction melting, followed by hot extrusion and wire drawing. The drawing process was carried out at room temperature and a number of intermediate anneals were required to reduce 6-mm rod into smaller diameter wires.

Test specimens were cut from 1.5-mm wire into 200-mm lengths and solution treated in a vertical tubular furnace at selected temperatures and time periods. They were quenched into water and then aged at 100°C for 15 min.

Parameters pertinent to this study included the transformation temperatures and parent-phase grain size. Transformation temperatures were determined by two different methods as shown schematically in Fig. 1. The transformation temperatures M_s and M_f on cooling and the reverse transformation temperatures A_s and A_f on heating were measured by electrical resistance changes as a function of temperature (Fig. 1a). A constant current was passed through the wire and the voltage increase or decrease recorded. The other technique used is shown schematically in Fig. 1b. The temperatures T_{hs} and T_{hf} on heating and T_{cs} and T_{cf} on cooling were determined from deformation-shape change cycles as a function of temperature. The later procedure used wire specimens bent around a semi-circular jig with a radius of 63.5 mm. The angular deflection of the wire was measured by means of an angular displacement transducer as the wire was first heated and then cooled. In both procedures the wire was positioned in an environmental chamber that could be heated and cooled in a controlled manner. The deflection and voltage of the wire was continuously measured as a function of temperature. Each test was completed after two cycles.

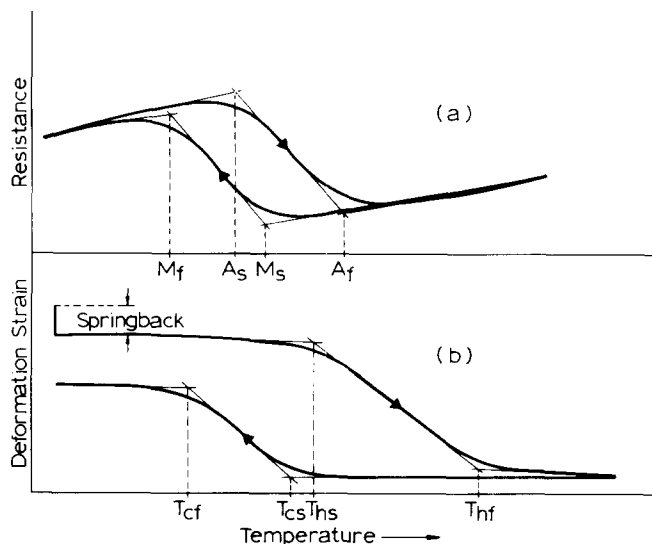


FIG. 1. Typical electrical resistance curve (a) and deformation-shape change cycle (b) as a function of temperature with characteristic temperatures indicated.

Finally, the microstructure of various specimens was examined after resistivity and deformation-shape change tests using optical microscopy. The specimens for metallographic examination were mechanically polished and etched. The etchant applied was 10 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in 100 ml water. Grain size was then determined by the linear intercept method [13], which was done directly at the microscope at appropriate magnifications. The average linear intercept measured in this manner is considered accurate to within $\pm 10\%$.

Results and Discussions

The parent-phase grain size as a function of solution treatment temperature and time are shown in Fig. 2. The grain sizes obtained are very fine, ranging from 35 μm to a maximum of 50 μm . A typical microstructure is shown in Fig. 3.

The addition of Zr in the Cu–Zn–Al alloy system is very effective in reducing grain growth during solution treatment. In previous work [14], the grain growth exponent has been commonly found in the range 0.08 to 0.20, a significant reduction compared to any ternary Cu–Zn–Al alloy.

Transformation temperatures M_s , M_f , A_s , and A_f for each solution treatment temperature and for each treatment time are shown in Fig. 4. All

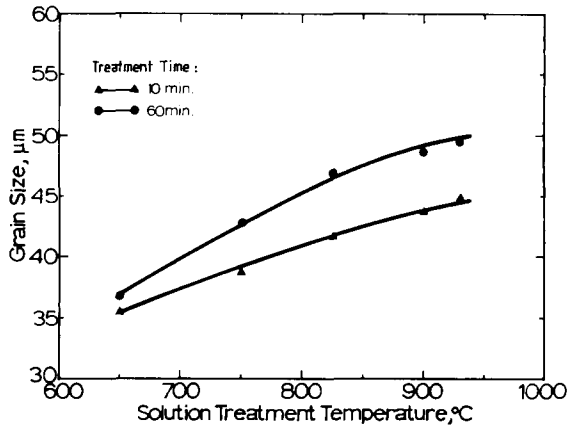


FIG. 2. Effect of solution treatment temperature and time on parent-phase grain size.

the transformation temperatures shift to higher temperatures as the solution treatment temperature is increased. An increase of as much as 15°C is generally achieved. Similar trends as shown in Fig. 4 are also obtained for the temperatures T_{hs} , T_{hf} , and T_{cs} (Fig. 5). In contrast, the T_{cf} temperature shifts to lower temperatures with increasing solution treatment temperature.

The sequence of transformation temperatures obtained from resistivity measurements (Fig. 4) is $M_f < A_s < M_s < A_f$, whereas the characteristic temperatures obtained from deformation-shape change tests (Fig. 5) following the sequence are $T_{cf} < T_{cs} < T_{hs} < T_{hf}$. Figures 4 and 5 also provide an indication that the extent of the reverse transformation during shape recovery is significantly enhanced to higher temperatures compared to the reverse martensite to parent-phase transformation obtained by the resistivity measurements. This is demonstrated by the difference in the characteristic temperatures: $(T_{hs} - A_s) = 7$ to 11°C , $(T_{hf} - A_f) = 22$ to 29°C , $(A_f - A_s) = 11$ to 15°C , and $(T_{hf} - T_{hs}) = 24$ to 31°C . In addition, the T_{cs} temperature is also found to be higher compared with the M_s temperature. The difference in these transformation temperatures may be attributed to the differences in the nature of thermoelastic martensite in as-quenched and deformed states as emphasized in papers presented at an international conference on the shape-memory effect in 1975 [15]. In the as-quenched structure, the martensite plates are randomly oriented, and each individual plate is internally twinned in a random manner. On heating this martensite structure reverts into parent phase, which is then transformed back to its original martensite structure during subsequent cooling. When a load is applied to the as-quenched structure, certain



FIG. 3. A typical micrograph showing the parent-phase grain boundaries and the martensite structure of a specimen after being heat treated at 750°C for 10 min, water quenched, and aged at 100°C for 15 min.

martensite variants and twin orientations are stabilized and begin to grow at the expense of others. Thus, the material is able to store, or accommodate, strain by a combination of detwinning and reorientation mechanism. When the as-quenched martensite structure is deformed by an amount sufficient to introduce or move dislocations, only part of the deformation can be recovered during heating. In this case, only a partial return to the deformed geometry is noted during subsequent cooling. This means the detwinned and reoriented martensite is formed on cooling and is not the original martensite structure; the presence of dislocations stabilizes the deformed martensite structure and may resist the reversal reaction during heating. The residual stress developed during prior defor-

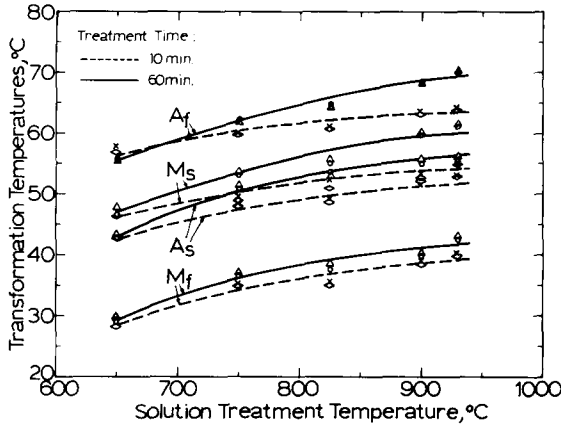


FIG. 4. Variation of M_s , M_f , A_s , and A_f temperatures as a function of solution treatment temperature for two different treatment times.

mation and heating cycle may assist the parent-to-martensite transformation on cooling.

The effect of austenite grain size on the M_s temperature in ferrous systems has been extensively studied [16, 17]. The studies indicate that the decrease in grain size is responsible for the observed depression of

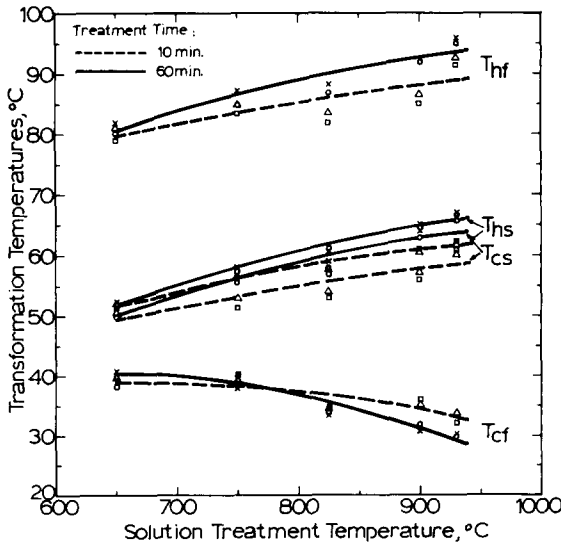


FIG. 5. Variation of T_{hs} , T_{hf} , T_{cs} , and T_{cf} temperatures as a function of solution treatment temperature for two different treatment times.

the M_s temperature. The same effect was also observed in some copper-based shape memory alloys [7, 18], but the scatter of results obtained was very large because coarse grain materials were used.

The present study shows that grain refinement of the parent phase causes not only the M_s temperature to shift to lower temperatures but also the other transformation temperatures A_s , A_f , and M_f . Grain refinement also suppressed the temperatures T_{hs} , T_{hf} , and T_{cs} but not the T_{cf} temperature. Instead, the T_{cf} temperature is found to increase with decreasing grain size. But irrespective of the grain size, the transformation temperature hysteresis as given by $(M_s - A_s)$ and $(T_{hs} - T_{cs})$ is about constant.

The transformation temperatures M_s , M_f , A_s , and A_f are plotted as a function of the reciprocal square root of the grain size in Fig. 6. The results show the reasonably good linear fits indicating the linkage of the transformation temperatures to a Hall-Petch relationship. The temperatures T_{hs} , T_{hf} , T_{cs} , and T_{cf} also followed a similar Hall-Petch relationship as shown in Fig. 7. All the line curves shown in Figs. 6 and 7, except for the T_{cf} temperature, show a negative slope with about equal value.

The Hall-Petch relationship is based on the barrier effect of grain boundaries to slip propagating from grain to grain and from the buildup of stress concentration due to dislocation pileups and increase in dislocation density. The work on Cu-Al martensite [19] has shown that the increase in 0.2% proof stress is due not only to increasing grain constraint but also to a decrease in martensite plate thickness with decreasing grain size. The Hall-Petch relation was also confirmed for grain-refined Cu-Zn-Al [4] and Cu-Al-Ni [5] shape-memory alloys. The Hall-Petch re-

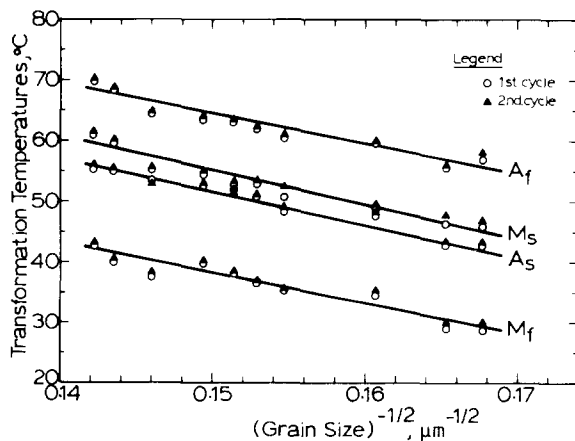


FIG. 6. Variation of M_s , M_f , A_s , and A_f temperatures with $(\text{grain size})^{-1/2}$.

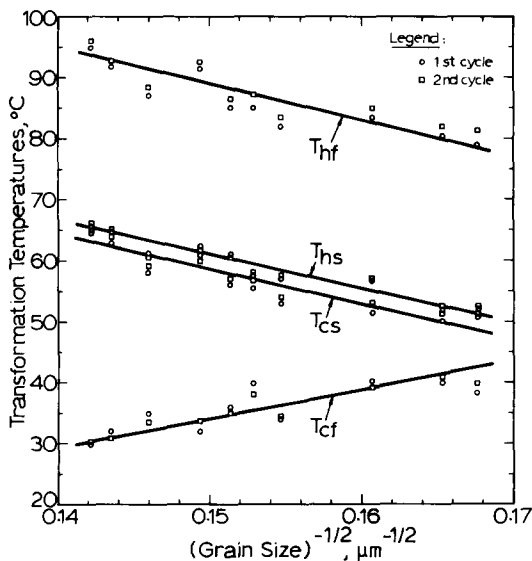


FIG. 7. Variation of T_{hs} , T_{hf} , T_{cs} , and T_{cf} temperatures with $(\text{grain size})^{-1/2}$.

lation found in these copper-based, shape-memory alloys was explained by the fact that martensite deformation by plate movement and variant reorientation becomes more difficult as grain size is reduced. When this happens the degree of grain constraint increases. Also with decreasing grain size, average martensite plate thickness decreases. Consequently, a higher stress is required to overcome the restraining factors inhibiting martensite plate movement.

In the present study, the Hall–Petch type relation in Figs. 6 and 7 may indicate that the formation of thermoelastic martensite is restricted by an increasing degree of grain constraint as grain size is reduced. As the grain size is decreased, martensite with a reduced plate thickness will form, giving rise to a higher stress required to produce the same amount of stress-induced martensite. This higher stress also indicates that greater energy is required for the martensite transformation to occur. This is consistent with the observed increase in the critical stress for stress-induced martensite with a lowering of the M_s temperature [14]. The T_{cf} temperature, at which the opposite effect is found compared with the effect at M_s , M_f , and T_{cs} temperatures, can be explained by the completion of martensite formation (which is accompanied by shape change), assisted by residual stress developed during previous deformation and heating cycles. The level of this residual stress is increased in constrained

grains due to a higher stress required to overcome the restraining factors inhibiting martensite plate movement of the previous deformation.

A lowering of the reverse transformation temperatures with decreasing grain size is also apparent in Figs. 6 and 7. This indicates that a lower driving force is required for the reversal reaction in constrained grains. This may be attributed by a lowering of resisting force within the martensite plate–parent phase interfaces during the reversal reaction due to the martensite plate thickness being decreased as grain size is reduced.

Conclusions

A Cu–20.6 wt.% Zn–5.7 wt.% Al alloy containing a small quantity of Zr was chosen as a model alloy for the study of grain-size effects on characteristic transformation temperatures in grain-refined, copper-based, shape-memory alloys. Varying the thermal treatments results in a range of grain size of 35 μm to a maximum of 50 μm , which corresponds to a shift of as much as 15°C in transformation temperatures.

The transformation temperatures measured by electrical resistance were different from those measured using deformation-shape change experiment. Irrespective of grain size, all the transformation temperatures differences are nearly constant, except for the difference in T_{cf} and M_{f} temperature, which is found to be dependent on grain size. In addition, the transformation temperature hysteresis as given by $(M_{\text{s}} - A_{\text{s}})$ and $(T_{\text{hs}} - T_{\text{cs}})$ is found very small in the range 2–4°C and independent of grain size.

Decreasing the grain size shifts all the transformation temperatures to lower temperatures, except for the T_{cf} temperature, which increases as grain size is reduced. This transformation temperature–grain size dependence has been found to be governed by the Hall–Petch relationship.

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