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# The effect of rapid solidification and grain size on the transformation temperatures of Cu–Al–Be melt spun alloys

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## Abstract

Copper base shape memory alloys were prepared by melt spinning technique at different wheel speed. The study was focused to investigate the effect of rapid solidification and grain size on characteristic $M_S$, $M_f$, $A_S$ and $A_f$ transformation temperatures. Changes on martensitic transformation temperatures in Cu–11.83 wt.%Al–0.48 wt.%Be melt spun ribbons were observed as grain size is reduced. A linear behavior curve of transformation temperatures as a function of grain size was observed. The transformation hysteresis grows as cooling rate increase. Results of optical microscopy and electrical resistivity were used to associate grain size with transformation temperatures.

*Keywords:* Shape memory alloys; Copper alloys; Rapid solidification; Martensitic transformation

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## 1. Introduction

Shape memory alloys (SMA) and their main characteristics as the superelasticity effect has been studied over the last 60 years. Most of these alloys have a high temperature cubic phase, which has a martensitic transformation, and this structural transformation is responsible of shape memory effect. The martensitic transformation temperature depends on the alloy composition. In copper based shape memory alloys this cubic phase is named β phase. It has been reported that the β phase of Cu–Al alloy is inadequate for most applications due to their high martensitic transformation temperatures (between 573 and 773 K) [1]. Furthermore, at this temperature the precipitation of α and γ phases takes place and the shape memory effect is lost.

Martensitic transformation temperatures can be reduced by the addition of a third element. At 4 wt.% of Ni addition the martensitic transformation temperatures decrease until 180 °C. Lower transformation temperatures can be obtained by adding higher Ni concentrations, but the alloy samples becomes brittle [2].

Addition of beryllium to Cu–Al alloy produces a shift of the martensitic temperature to lower temperatures, between 73 and 473 K [3,5,6]. On the other hand, the thermal stability of β-Cu–Al–Be alloy is at least as high as β-Cu–Al alloy [3,4].

The martensitic transformation temperatures are also sensible to the order degree of β phase in copper based alloys. The beta phase at high temperature is disordered

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with a bcc crystal structure A2 type, at lower temperature ordering process takes place and a B2 (CsCl type) structure is formed, and finally a further ordering produces a $DO_3$ or $L2_1$ structure. All those transitions are second order type. Those structures are shown in Fig. 1. Moreover, different heat treatments generate different phase ordered proportion, and different $M_S$ temperatures are then obtained. Actually, these order–disorder transitions depend on the vacancy diffusion [7]. In particular, β phase of Cu–Al–Be seems to undergo an ordering transition directly from A2 to $DO_3$ structure as reported by Jurado et al. [8], moreover, this transformation has been shown as a first order type.

In addition, the grain size seems to be an important parameter for determining the temperature transformation in these alloys [9].

The relationship between grain size and martensitic transformation temperature has been mentioned in other Cu-based shape memory alloys [10] but no research have be done for correlating these parameters. Moreover, it is important to control the grain size and texture because the high anisotropy of the β phase [11].

We have considered that growth of martensite variants are limited by grain boundaries. Thus, with decreasing grain size the length of variants will be reduced and the transformation energy should increase.

The aim of this work is to study the relationship between grain size and martensitic transformation temperature in Cu–Al–Be alloys. In order to attain a wide range of cooling rate and grain size, therefore melt spinning technique is considered a suitable preparation route for these alloys.

## 2. Experimental procedure

Melt spun alloy ribbons with composition Cu–11.83 wt.%Al–0.48 wt.%Be were obtained in a single roll type melt spinning apparatus, using a copper wheel at different tangential speeds, between 12 and 52 m/s. An induction furnace was used to melt the alloy in a quartz crucible with an orifice diameter of 1 mm. Argon gas was supplied with a 343 kPa of pressure to inject the melt on the copper wheel. The cooling was performed in air. It has been observed that an angle of 80° between the quartz crucible and the wheel tangent was optimal for our purposes.

Metallographic analysis on alloys samples was carried out with a 95 ml of Methanol, 2 g of $FeCl_3+2$ ml of HCl etching solution. Image analysis software (Quantimet 500) was employed for grain size measurements.

X-ray diffraction data were carried out in a D5000 Siemens Diffractometer with Cu-Kα radiation in order to verify ribbon crystallinity and phases obtained.

Transformation temperatures were measured by four probes electrical resistance technique. Liquid nitrogen was used as cooling agent and a helium atmosphere to improve thermal conductivity inside the chamber. Temperature cycles were ranged from −150 to 30 °C.

## 3. Results and discussion

Fig. 2 shows an X-ray diffraction pattern from a ribbon that confirms the $DO_3$ structure of β-Cu–Al–Be

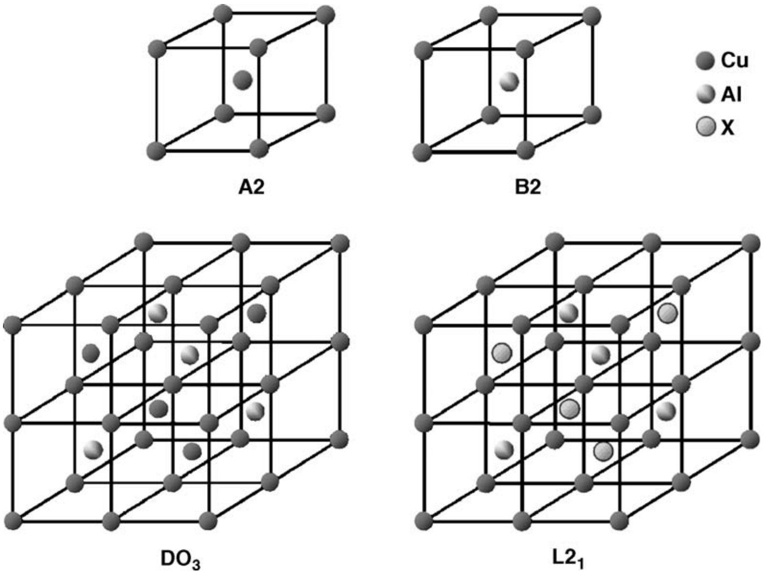

Fig. 1. Different ordered structures of beta phase in copper based alloys.

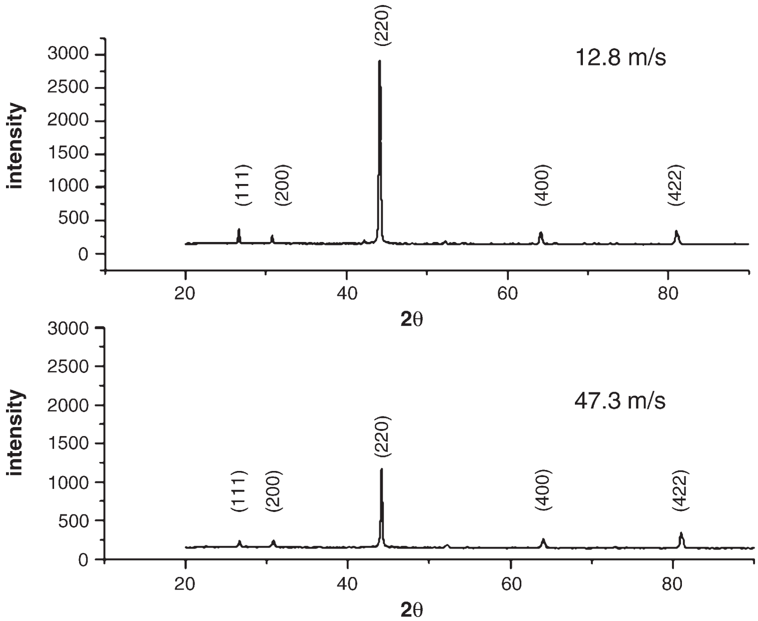

Fig. 2. X-ray diffraction pattern for a Cu–11.83 wt.%Al–0.48 wt.%Be ribbon obtained at 12.8 and 47.3 m/s.

alloy. The (111) reflection is characteristic of the ordered structure $DO_3$ type in this alloy [9] next reflection is common to $DO_3$ (200) and B2 (100) ordered structures. Third peak concerns to $DO_3$ (220), B2 (110), and A2 (110) disordered β phases. Differences associated with grain size (peak broadening effect) and texture (relative intensities may change slightly) have been observed in measured patterns at different wheel speeds.

Previous to the melt spinning process, we have observed a coarse grain size for the cast ingot (Fig. 3) which is expected for Cu-based alloys. On the other hand, Fig. 4 displays grain size for melt spun ribbons obtained at three different wheel speeds. No significant differences have been observed on the microstructure between contact wheel and free surface side. Grain sizes obtained were ranged from 60 to 380 $\mu m^2$. A grain size refinement is manifested for these ribbons compared with the cast ingot. The cross-section view of ribbons is shown in Fig. 5 at different wheel speeds. The increasing wheel speed results in reduced ribbon thickness and thus the heat transfer should be better at thinner ribbons. The ribbon thickness is irregular, this feature is inherent to the processing method as reported elsewhere [10,12,13]. The grain size histogram obtained from flat section samples is shown in Fig. 6, and presents a normal logarithmic distribution. Grains are equiaxed shape and only for higher rates they have some columnar morphology.

Fig. 7 exhibits grain area as a function of wheel speed. Three differential zones can be distinguished. Zone I, low speeds (up to 24 m/s), where there is no significant variation in grain size. Zone II where a strong dependence occurs, with a significant grain reduction (from 24 to 36 m/s). Finally, for zone III (40 m/s and higher) with a slower grain reduction.

Behavior in zone I may be attributed to an effect of lower wheel leads to a thicker ribbon which produces a

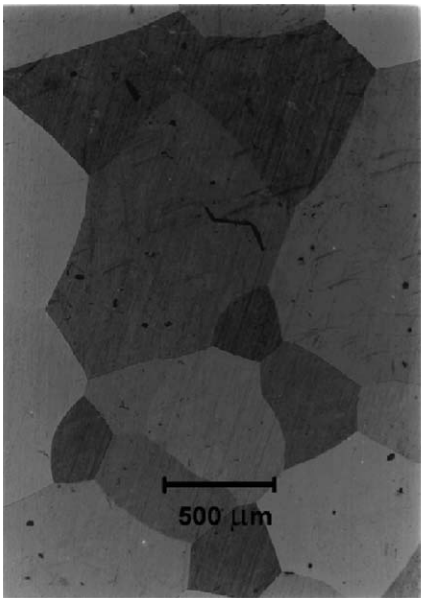

Fig. 3. Optical micrograph for the Cu–11.83 wt.%Al–0.48 wt.%Be alloys ingot, previous to melt spinning processing.

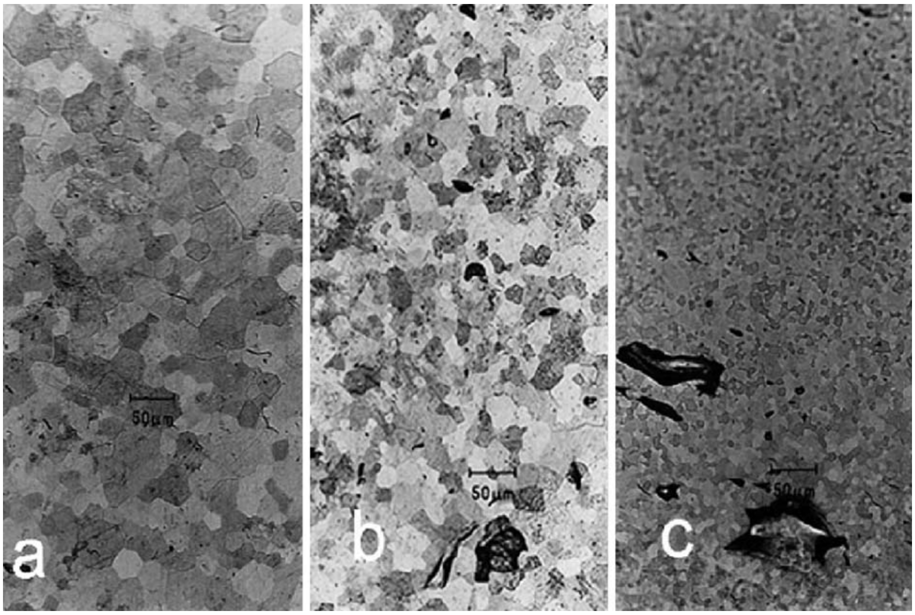

Fig. 4. Optical micrographs (20×) for melt spun Cu–11.83 wt.%Al–0.48 wt.% Be alloys using various wheel speeds; (a)12 m/s, (b) 36.1 m/s, (c) 47.3 m/s.

larger grain size. Within the second region, grain size decreases as a function of cooling rate. Finally, for zone III is related to a deficient ability of the wheel to extract heat from the ribbon.

Transformation temperature evolution ($M_S$, $M_f$, $A_S$, $A_f$) vs. $d^{-1/2}$ can be observed in Fig. 8, where a nearly linear behavior is shown. This result has been observed in other alloys [14], if cooling rate rises, the grain size, order degree, and $M_S$ temperature decrease; the last in agreement with thermodynamic calculations made in Cu–Al alloys [15]. On the other hand, experimentally martensitic transformation temperatures decrease with grain refining, as has been reported for other SMA [9,10,16].

Fig. 9 shows the hysteresis evolution, as grain size grows, the effect is probably due to a larger interaction between martensite variants and grain boundaries, i.e.

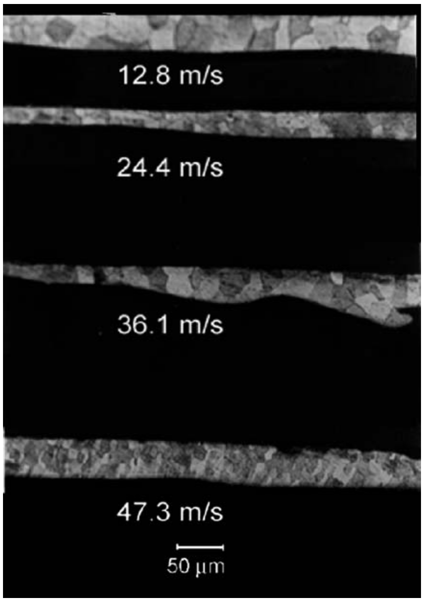

Fig. 5. Optical cross-sectional view of Cu–11.83 wt.%Al–0.48 wt.% Be alloys melt spun at various wheel speeds.

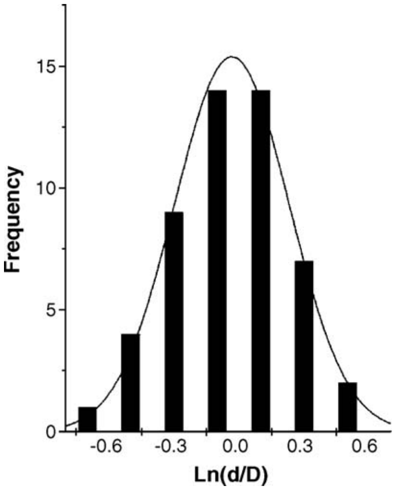

Fig. 6. Histogram of the surface samples spun ribbons.

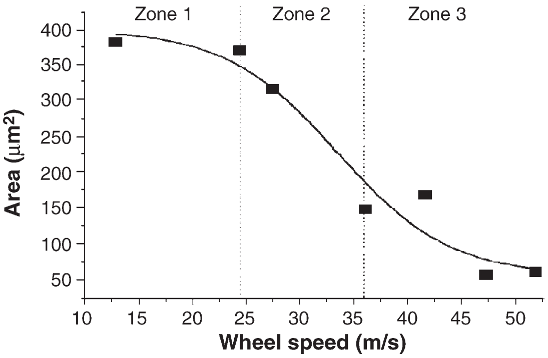

Fig. 7. Grain size average measured through grain area as a function of wheel speed.

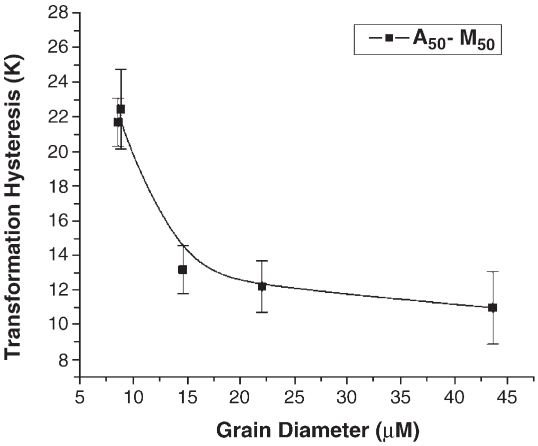

Fig. 9. Hysteresis ($A_{50}$–$M_{50}$) graphic as function grain size.

for a smaller grain more energy is involved during martensitic transformation.

In order to understand the observed behavior shown on Figs. 8 and 9 we have to consider the following mechanisms:

i. The residual stresses produced by fast cooling are mainly due to dislocations, which may produce many favorable sites for heterogeneous nucleation of martensite [17]. If we consider this mechanism isolated the expected change should be a higher transformation temperature from a sample with more residual stress, i.e., greater amount of defects can decrease the $\Delta T$ needed for martensite nucleation.

ii. Another mechanism is related to the grain size reduction which may limit the size of martensite twins. The strength to shearing of parent phase is inversely proportional to the grain size, and result in a $M_S$ temperature decrease. The interaction between martensite twins and grain boundaries may induce a larger hysteresis during martensitic transformation, increasing the gap between the $A_f$ and $M_f$ temperatures as observed in Fig. 8.

iii. Finally ordering process can take place during cooling, from A2 disordered phase to $DO_3$ ordered phase. At higher cooling rate a larger vacancy concentration is released and an ordering process takes place. Results in literature has demonstrated that order–disorder transition on martensitic transformation temperatures in copper based alloys can modify the transformation temperatures under different quenching conditions [18].

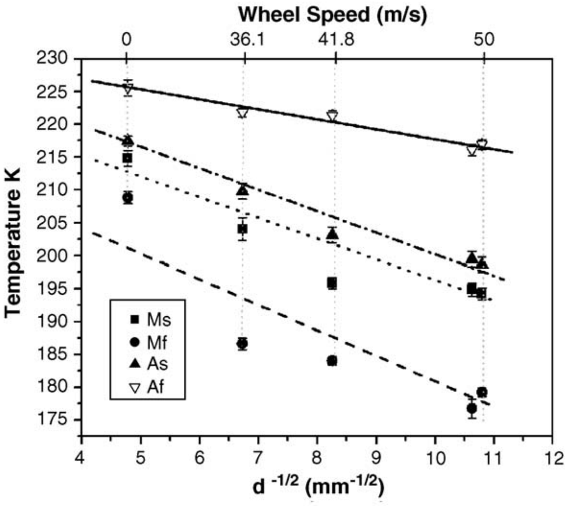

Fig. 8. Effect of the grain size on transformation temperatures $A_S$, $A_f$, $M_S$, $M_f$.

From these mechanisms we can say that behavior shown in Figs. 8 and 9, may be attributed to a mixture of the three phenomena mentioned before, in which the grain size effect and ordering process should have a major role.

Current experimental work is in progress, in order to elucidate the order transition in this alloy system. For instance, for Cu–Al–Be alloys, the order–disorder transition is a first order transformation, while for Cu–Zn–Al alloys a second order transition has been reported [9].

## 4. Conclusions

We have shown that in the Cu–11.83 wt.%Al–0.48 wt.%Be alloy, the transformation temperatures $M_S$, $M_f$, $A_S$ and $A_f$, decrease linearly with $d^{-1/2}$, as well as hysteresis, the last suggest a mayor role of grain boundaries on martensitic transformation, residual stresses and order–disorder transition effects may be also involved.

On the other hand, melt spinning technique has been useful to reduce grain size these alloys. The curve of grain size vs. wheel speed can be used as parametric curve for obtaining a desired grain size.

More work should be done for elucidate the influence of grain boundaries in martensite nucleation.

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