

## Characterization and Comparative Study of Pseudo-Elastic Cu-Zn-Al foams synthesized by two different methods

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**Abstract.** Low cost Cu-Zn-Al foams present, in specific composition ranges, good pseudoelastic properties associated with interesting damping capacities, which establish these materials as attractive from the point of view of structural applications. These foams are manufactured by infiltration of small SiO<sub>2</sub> spheres into the molten alloys. After alloy solidification the SiO<sub>2</sub> spheres are removed by immersing the material in a solution of aqueous hydrofluoric acid. In this work, we have investigated the effect of two different foam preparation techniques: inductive and resistive melting. The paper details both the physic-chemical and mechanical characterization of the foams synthesized with the two different methods. The purpose of this study is to determine the quality of each synthesis method in order to identify the best alternative.

### Introduction

The possibility of developing technological applications in the field of martensitic transformations is very promising. Recently, it has been reported the possibility of manufacturing pseudoelastic Cu-based foams [1-4]. In particular, Cu-Zn-Al foams present good pseudoelastic properties and they are potential candidates for damping applications [1-2]. The synthesis procedure for these foams is relatively simple, fast and inexpensive [5]. It consists in infiltrating a bed of SiO<sub>2</sub> small spheres into the molten alloys. Afterwards, the SiO<sub>2</sub> spheres are removed by immersing the material in a solution of water and HF acid [1,2,5]. As a result, a porous metal structure is obtained, where the pore size corresponds to the size of the SiO<sub>2</sub> spheres. Cu-Zn-Al foams showed a reasonable pseudoelastic behavior, even in the as-cast condition, up to thousands of compression cycles. They displayed a specific damping capacity up to 40% for 1.5% deformation amplitude at room temperature [2]. The damping capacity is related to the pseudoelastic hysteresis and has been found to be independent of the cycling frequency in the range between 0.01 Hz and 20 Hz.

In our previous works, the main focus was to characterize the mechanical behavior of pseudoelastic Cu-Zn-Al foams [1,2]. However, the foams could be produced by following different synthesis procedures. The aim of this paper is to identify a viable, low-cost procedure between two competing methods: resistive and induction melting. In order to compare these methods, we investigated the physic-chemical and mechanical characteristics of different Cu-Zn-Al foams.

### Manufacturing Methodology

**Foam synthesis.** Base alloys of composition 76.0Cu-16.1Zn-7.9Al wt. % were produced from pure elements in evacuated Vycor capsules using a vertical resistive furnace. The electron concentration of the base alloys is  $e/a=1.48$ . At room temperature the alloys present an ordered L2<sub>1</sub> structure in the beta phase. Base alloy pieces were produced in 80 g batches.

Afterwards, these base alloys were used to produce foams by applying two different methods. Basically the two methods present in common that small pre-heated SiO<sub>2</sub> spheres are pressed into the molten alloy. In order to do so, the alloys have to be melted in an open crucible. The main difference between the two investigated methods is the type of furnace used to melt the base alloys, previously to the infiltration procedure. For the sake of convenience, we will refer to these two different methods as MET A and MET B.

**MET A:** The pieces of base alloy were melted in an induction furnace in 25 mm diameter open graphite crucibles. The process temperature was kept 100°C above the base alloy melting temperature. At this point, SiO<sub>2</sub> spheres pre-heated up to 900°C were added and pressed into the melt with the help of a piston.

**MET B:** The base alloys were melted in a resistive muffle furnace in 25 mm diameter Vycor crucibles. Once melted, the alloys were withdrawn from the furnace and infiltrated with SiO<sub>2</sub> spheres in a similar way as described in MET A.

Under both situations the alloys infiltrated with SiO<sub>2</sub> were left to cool down to room temperature inside the crucibles. After that, the materials were retired from the crucibles. Finally, the specimens were machined to a final diameter of 22 mm and 22 mm in length, and SiO<sub>2</sub> spheres were dissolved by immersing the samples in a solution of 1:5 HF acid in H<sub>2</sub>O. SiO<sub>2</sub> particles of a foam cylinder with the final dimensions are dissolved after approximately 15 hours. This final procedure does not affect the Cu-Zn-Al foam structure.

**Physic-Chemical Characterization.** In order to test the compositional homogeneity the local M<sub>s</sub> transformation temperatures of samples taken from different zones of a foam were measured. This method is sensitive enough because small variations in composition produce noticeable variations in the transformation temperature. There are several expressions relating the M<sub>s</sub> temperature with chemical compositions for Cu-Zn-Al alloys. One that we found useful for alloys with e/a=1.48 is the following expression [6]:

$$M_s [^{\circ}\text{C}] = 2959 - 64 C_{\text{Zn}} - 90 C_{\text{Al}}. \quad (1)$$

In Eq. (1), C<sub>Zn</sub> and C<sub>Al</sub> are the concentrations of the respective elements expressed in atomic percentage (at. %). It can be seen that a loss of 1 at. % in C<sub>Zn</sub> results in an increment of 64°C in M<sub>s</sub>.

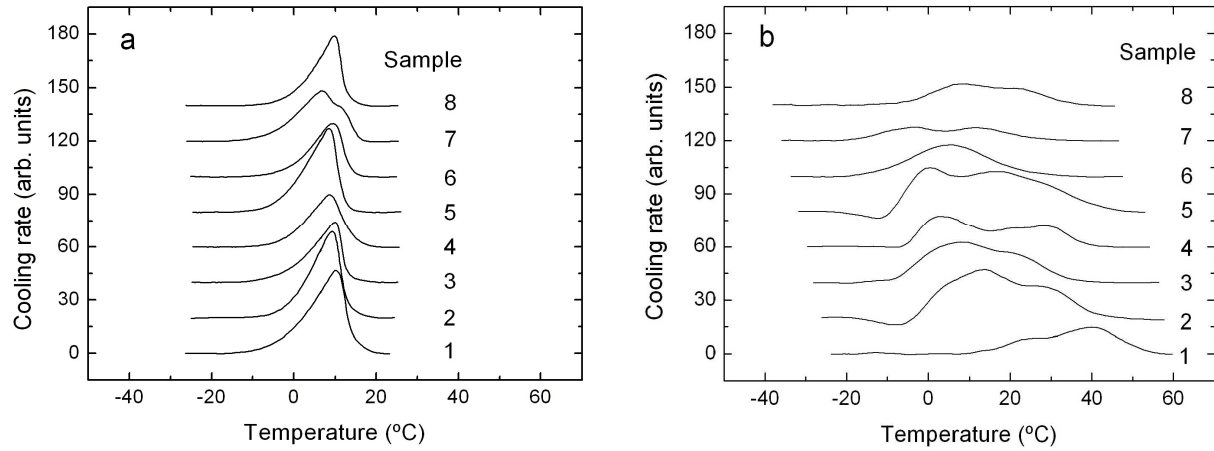
In order to determine the local composition homogeneity of foams manufactured by MET A and MET B, samples from different parts along the length of each foam specimen were taken. Each sample is a 2 mm thick transversal slice of a 22 mm diameter foam. Slices were numbered from 1 to 8 from top to bottom, respectively. In order to determine the M<sub>s</sub> of each sample, a thermocouple was welded to it. Afterwards, the temporal evolution of the temperature was registered while the sample is heated by a hot plate or cooled by liquid nitrogen vapor. Along the martensitic transformation, due to its first order character, heat is evolved proportionally to the mass of the sample. By registering the cooling or heating rates as a function of the temperature it is possible to determine the beginning and end of the transformation. This is basically a low cost calorimetric technique.

**Mechanical Characterization.** Cylindrical specimens of 22 mm in diameter and 22 mm in length synthesized by both methods were used to study their transformation behavior. In all cases, mechanical compression cycles were performed in an INSTRON 5567 testing machine with a temperature chamber. Compression cycles were performed at a rate of 0.2 mm/min for deformation ranges between 1% and 2%. The mechanical tests were performed at different temperatures in the range between 40°C and 120°C. For each temperature at least three compression cycles were done. The deformation was measured with the help of an extensometer attached to the compression plates.

## Results and Discussion

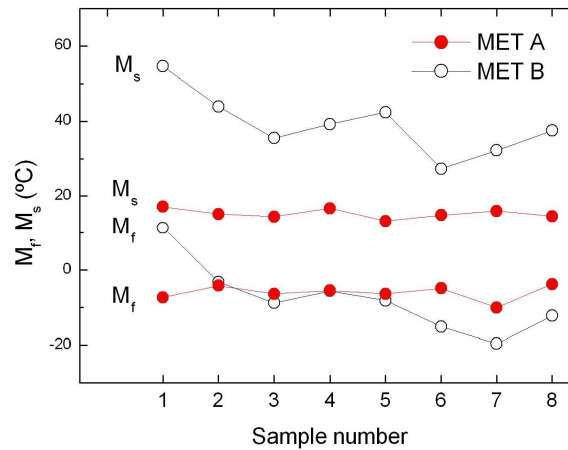
**Physic-Chemical Results.** Figure 1 shows the cooling rate as a function of the temperature. With the purpose of improving the visualization and to obtain a better determination of the M<sub>s</sub> and M<sub>f</sub> we eliminated the base line. Figures 1a and 1b show the cooling rates for MET A and MET B foams,

respectively. While peaks are relatively sharp and well defined for MET A foams, they appear broad and, in some cases, as multi-peaks in MET B indicating the presence of stronger inhomogeneities in the later case.



**Figure 1:** Cooling rate as a function of temperature for samples taken along the length of: a) foam prepared by induction melting (MET A), and b) foam prepared by resistive melting (MET B).

Figure 2 shows the  $M_s$  and  $M_f$  values obtained for MET A and MET B foams, as determined from the results presented in Figure 1. In the case of MET B, the transformation temperatures tend to decrease as the slice number increases. Considering Eq. (1), this trend indicates that the bottom part of the foam is richer in Zn, which is consistent with Zn evaporation through the top surface of the melt. The measured  $M_s$  values vary in the range from 55°C to 27°C. According to Eq. (1), there is a 0.4 Zn at. % difference from Slice 1 to Slice 6. Table 1 shows the average values obtained from these results. This information further support that MET A foams are of better quality.



**Figure 2:** Measured  $M_s$  and  $M_f$  values for samples taken along the length of MET A and MET B foams.

**Table 1:** Average of measured  $M_s$  and  $M_f$  values, and transformation width for MET A and MET B foams.

	$M_s$ [°C]	$M_f$ [°C]	Transformation width [°C]
MET A	$15 \pm 1$	$-6 \pm 2$	$21 \pm 3$
MET B	$39 \pm 8$	$-8 \pm 9$	$47 \pm 4$

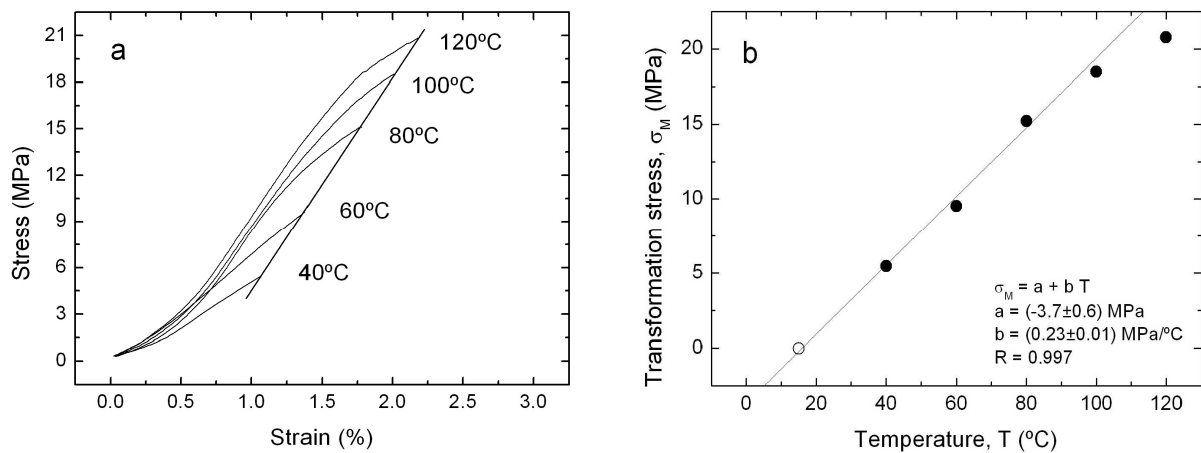
To rationalize the measured  $M_s$  values and main features of the calorimetric measurements for MET A and MET B foams considered the following factors. Due to the  $\text{SiO}_2$  infiltration step the crucibles have to be open in both methods. In the resistive furnace case (MET B) the manufacturing time is longer than for the induction melting procedure (MET A). Additionally, at temperatures

approximately 50% of the melting temperature, Cu-Zn-based alloys start to release zinc in a process known as dezincification. As the temperature increases approaching the alloy melting point, dezincification becomes more pronounced. Considering this fact and the prolonged melting time, dezincification is expected to be stronger in MET B, resulting in an altered nominal composition in relation to the base alloy.

A second factor that has to be considered is the stirring effect produced in the molten alloy by the induction furnace. Even considering some degree of zinc loss, the melt will remain homogeneous due to stirring. As a result, MET A foams display uniform and well defined transformation temperatures across their length. On the contrary, the melt produced by resistive heating is very still. Taking into consideration that zinc release occurs by diffusion through the top surface of the melt, a concentration gradient will develop for MET B. Although SiO<sub>2</sub> infiltration probably causes some mixing, the effect is not strong enough to homogenize the alloy resulting in larger transformation temperature variations and broader transformation ranges for each slice.

If we now consider both phenomena together, the larger Zn loss due to longer melting times and the poorer homogenization, we can rationalize that MET A foams are more homogeneous in composition than foams manufactured by MET B.

**Mechanical Characterization.** Figure 3a shows the beginning of the compressive stress-strain curves measured at different temperatures for a MET A foam up to the transformation stress. This transformation stress was determined for each curve as follows. First, the elastic behavior range was determined from the linear behavior found at the higher temperature cycle (120°C). Then, the point where each curve deviates 0.75% from the linear behavior was identified. These points are linked by the straight line in Figure 3a. We verified that these results are not fundamentally modified if close but different values are taken for the linear behavior deviation. The stress values obtained by applying this procedure correspond to the transformation stress and are presented in Figure 3b. In addition, the value corresponding to the  $M_s$  temperature under null applied stress has also been included in the figure.

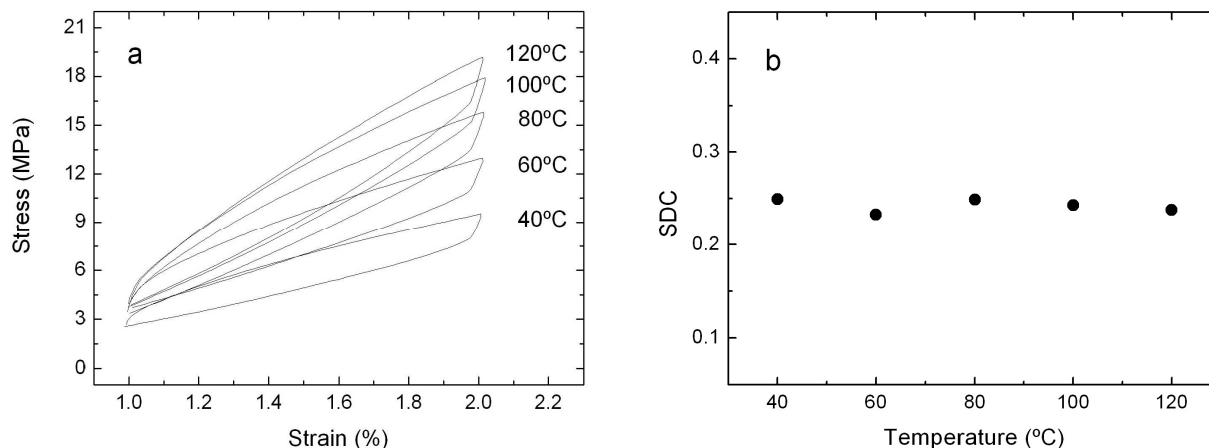


**Figure 3:** a) Beginning part of the stress-strain curves measured at different temperatures for a MET A foam. b) Transformation stress values. The open symbol at null stress level corresponds to the measured  $M_s$  temperature.

The transformation temperatures increase linearly with the increment of temperature at a rate of  $(0.23 \pm 0.01) \text{ MPa/°C}$ . At higher temperatures the measured transformation stress deviates from the linear behavior, evidencing the partial introduction of plastic deformation.

Due to its inhomogeneous character, similar results for MET B foam are difficult to analyze. In this case, the  $M_s$  temperature is considerably higher than room temperature (Figure 2). Then, some martensite remains retained after each compressive cycle, thus affecting the transformation level measured in the next cycle. Although a rate of change for the transformation stress with temperature has been determined at about  $1 \text{ MPa/°C}$ , the result is not conclusive.

Figure 4a shows the last of three compression cycles performed between 1% and 2% strain limits at different temperatures for MET A foam. Both, the transformation stress and the area enclosed in a cycle increase with increasing temperature. However, when considering the specific damping capacity (SDC) [2], we found that it remains almost independent of the temperature at a mean value of  $(0.24 \pm 0.01)$  (Figure 4b). This kind of behavior was also found in the case of MET B foam under similar conditions.



**Figure 4:** a) Transformation cycles measured between fixed strain limits for MET A foam. b) Specific damping capacity versus temperature for MET A foam, as determined from Figure 4a results.

### Conclusions and remarks

This paper presented a comparison of pseudoelastic Cu-Zn-Al foams manufactured by two different methods: induction and resistive melting. The results for foam homogeneity and thermo-mechanical transformation behavior allows establishing induction melting as the best option for manufacturing reliable Cu-Zn-Al foams.

A linear relationship between transformation stress and temperature was verified up to 100°C. In addition, the specific damping capacity related to the pseudoelastic hysteresis has been found to be independent of the temperature in the range between 40°C and 120°C. Foams dissipate 24% of the applied deformation energy in a 1% to 2% deformation cycle.

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