



Mechanical properties of martensitic Cu–Zn–Al foams in the pseudoelastic regime

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ABSTRACT

The mechanical properties of martensitic Cu–Zn–Al foams produced through molten metal infiltration of a leachable bed of silica gel were investigated. The novel porous shape memory alloy almost reversibly absorbs compression deformations up to 4%. Intergranular fracture occurs in the material along the test, similar to what is observed in polycrystalline solid samples. Despite its tendency to fracture at localized regions, the material is highly resilient, being able to stand several compression cycles. The Cu–Zn–Al foams showed excellent shape recovery after deformation (95%). This previous fact establishes it as a very promising candidate for interesting applications.

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1. Introduction

Porous metallic materials are the subject of numerous recent studies due to their ability to combine good mechanical and physical properties with low weight. There is a particular interest in developing porous materials based on shape memory alloys (SMAs) because they would be light materials able to almost reversibly stand large deformations while absorbing an important amount of energy. So far, this interest has almost exclusively been directed to the research and production of Ni–Ti-based porous and cellular materials with excellent shape memory properties at different temperature ranges [1,2]. However, Ni–Ti alloys suffer from high raw materials and production costs, which hinder their use in large engineering applications. For these reasons, alternatives to Ni–Ti are being explored. Among them, porous Cu-based SMAs such as Cu–Al–Mn or Cu–Zn–Al are promising candidates due to their very good shape memory properties, low costs and simple preparation. Recently, methods for producing porous Cu-based SMAs have been developed [3–6]. They benefit from the lower melting temperatures of these alloys which facilitate the production of porous structures by simple processes of molten metal infiltration of a leachable bed of particles [7]. Porous Cu-based SMAs display typical martensitic transformation temperatures and have good associated damping properties [3,6]. However, up to the authors' knowledge, the mechanical properties of porous Cu-based SMAs have never been studied. In consequence, the question on how these materials produced in porous form show their

shape memory behavior still remains open. Aiming at characterizing the compressive behavior of these new materials, a porous shape memory Cu–Zn–Al alloy was prepared. The results of compression testing are presented in this work. Our results present this new Cu–Zn–Al foam as a promising candidate for interesting applications such as damping materials.

2. Material and method of fabrication

A porous shape memory Cu–Zn–Al alloy was prepared by the method described in detail in references [3,8]. An 80 g starting alloy with a nominal composition of 75.9Cu–16.1Zn–7.9Al (wt.%) was melted from the pure elements in an evacuated Vycor capsule under Ar atmosphere. The alloy (electron concentration = 1.48) has been the subject of extensive studies and its shape memory properties are well known [9]. The starting alloy was re-melted in the pure graphite crucible of an induction furnace. By using a thermocouple, the temperature of the melt was recorded and kept at 100 K above the alloy's melting point. At this stage, dried SiO₂ (silica gel) balls with typical diameters in the range of 2 to 3 mm were pressed into the molten alloy. The volume of added SiO₂ is three times that of the Cu–Zn–Al bath. The mixture was left to solidify inside the crucible. A composite cylinder of Cu–Zn–Al in the β-phase embedded with SiO₂ balls was obtained. Afterwards, the SiO₂ balls were dissolved by immersing the composite in an aqueous solution of hydrofluoric acid which does not react with the metal. The resulting porous material has an open-cell structure with a density of 1921 kg/m³, which is lower than 25% of the starting alloy. Cylindrical samples for compression tests (height = 15.6 mm, diameter = 14.7 mm) were spark-eroded from the main porous material.

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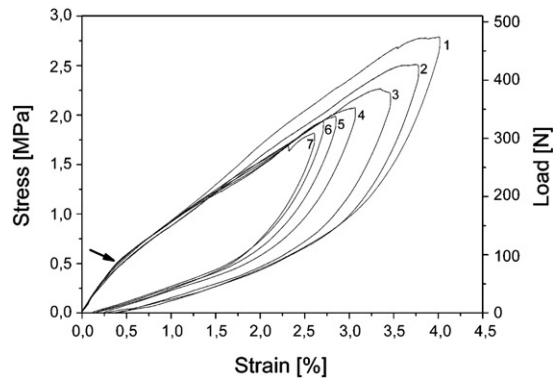


Fig. 1. Mechanical behavior of the porous Cu–Zn–Al SMA under compression. The first cycle corresponds to the outer curve, reaching a 4% compressive deformation. The final deformation was gradually reduced on each of the following cycles. Shape recovery is of about 95% in all cases. The arrow marks the point corresponding to the onset of stress-induced martensite formation.

Samples were cyclically deformed in compression at 0.1 mm/min by using an Instron 1123 mechanical testing machine. The bearing surfaces have been lubricated with a silicon grease to reduce friction effects. The deformation was measured by using an extensometer attached to the compression plates. Pictures along the deformation process of the tested samples were taken using a CCD camera with a macro lens. After the mechanical testing the deformed samples were also observed in a Philips 515 scanning electron microscope (SEM).

3. Results and discussion

The obtained foams are basically in the austenite phase at room temperature. To characterize the material the martensitic transformation temperatures were measured calorimetrically and resulted in $M_s = 288$ K, $M_f = 263$ K, $A_s = 273$ K, $A_f = 298$ K. At room temperature the material was found to be pseudoelastic, anyway a small amount of retained martensite could be present. Fig. 1 shows representative nominal stress–strain curves from several compression cycles. The first cycle corresponds to a maximum compressive deformation of 4% and appears as the outer curve in the figure. At 0.4% the slope of the typical stress–strain curve changes. The shape of this curve is similar to what has been previously observed in Cu–Zn–Al polycrystals under an applied load [10]. Thus the second stage can be related to the formation of stress-induced martensite in the sample. In this way we are absorbing a high energy amount by inducing the martensitic phase in the foam in the compressed state. After reaching the desired maximum deformation state, the compression load was gradually released. As a consequence, the stress decreased first rapidly and then

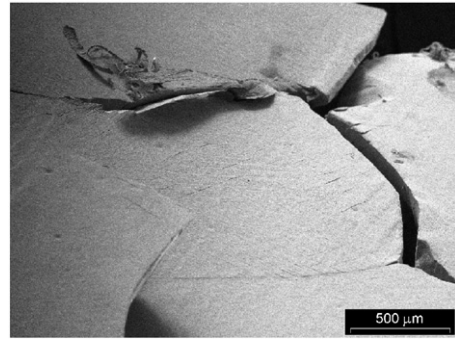


Fig. 3. SEM micrographs of the surface of a porous Cu–Zn–Al sample after several compression cycles. Intergranular fracture is apparent at several grain interfaces. Parallel lines crossing grains are due mechanical polishing during sample preparation.

at a lower rate, again in coincidence to what is observed in the recovery stage of polycrystals [10]. After this first cycle, a 0.25% deformation remained in the sample. The overall shape recovery can then be calculated as 95%. This is a remarkable recovery amount for a deformed material. The final deformation was gradually reduced down to 2.5% up to the 7th cycle. In all cycles, there is a small residual deformation, being the shape recovery ratio of 97% in the last cycle.

Fig. 2a shows the stress–strain curves of compression tests of a martensitic foam (solid line) and of a polycrystalline solid, with similar composition, M_s and grain size (dashed line). While the foam recovers around 95% of an applied 4% strain, the polycrystal recovers 79%. Fig. 2b and 2c show snap-shots taken in-situ at different stages during the foam compression test. Intergranular fracture occurring at several points can be clearly discerned in the picture (see, for example, the area pointed by an arrow in the picture). In this condition, the material stands 0.6 kN. When the applied load is reduced, the material almost returns to its original form. Notably, fractured struts returned to their original positions, resulting in a large shape recovery scenario.

A clearer view of intergranular fracture in these materials is presented in Fig. 3. These are SEM pictures of the porous SMA after several compression cycles. Grains in the images appear detached one from another. Intergranular fracture is a typical problem of Cu-based SMAs, being one of its main reasons the large grain size resulting from the preparation process and the high level of anisotropy of the stress-induced martensitic phase [9]. In our tested foams the grain size was about 3 mm. The origin of this problem is that non-transforming grains cannot accommodate the shape change of neighboring grains where martensite is being induced. In a typical Cu–Zn–Al polycrystalline solid sample, this process leads to the failure of the specimen. However, in the present case the material shows a remarkable resilience even though intergranular fracture occurs at several points. This behavior relates to

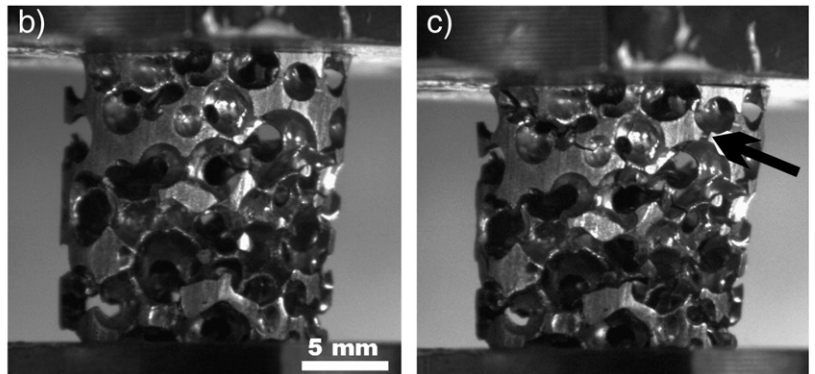
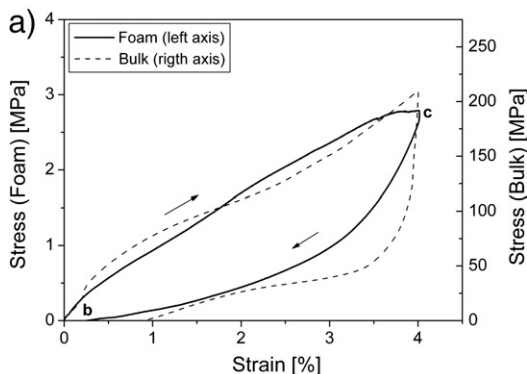


Fig. 2. Pictures taken during a compression test on a Cu–Zn–Al foam. (a) Stress–strain curve of the compression cycle for the foam (solid line). A compression test on a polycrystalline bulk material with similar composition, M_s and grain size (dashed line) is included for comparison. (b) Initial state (strain = 0%). (c) Maximum compression (4% strain). Signs of intergranular fracture are apparent (see place pointed by arrow).

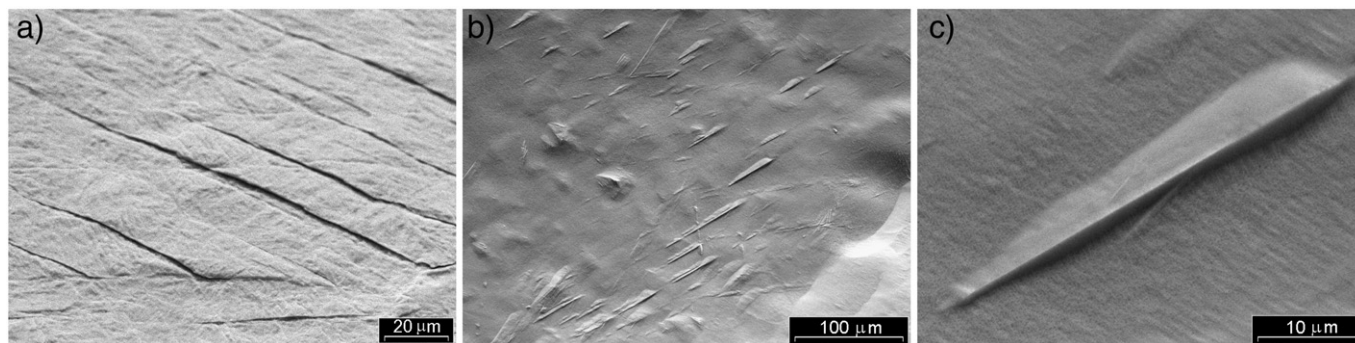


Fig. 4. SEM pictures of the surface of a porous Cu–Zn–Al sample after mechanical testing. (a) Traces of retained martensite on the surface. A small amount of martensite remains after testing. (b) and (c) Inner surface of a void showing secondary variants.

the nature of cellular materials. Fractured struts add voids to the total porosity. As the grains in the cellular material have adjacent pores, they have the advantage of not being completely constrained when transforming. As a result the material will retain its structural integrity as long as there are connecting paths between the transforming regions.

SEM observations of the mechanically tested samples also revealed zones with small amounts of retained martensite (Fig. 4). Traces of stress-induced martensite remain after testing because the A_f temperature of the alloy is slightly above room temperature and due to the presence of residual stresses. Fig. 4a shows evidence of parallel martensite plates. They can be easily distinguished from possible polishing lines, as those present in Fig. 3, because martensite plates stop at grain boundaries and present a typical surface relief. Observation of the inner surface of a void reveals a more intricate pattern with secondary martensite variants (Fig. 3b and c). These secondary variants partially accommodate the overall shape change inside a grain.

4. Conclusions

We conclude that porous Cu–Zn–Al foams produced by means of molten metal infiltration of a leachable bed of SiO_2 retains most of the shape memory properties of the polycrystalline solid material. The light porous material can almost reversibly absorb deformations of up to 4% while at the same time it remarkably recovers a 95% of the original shape. Intergranular fracture occurs in the material, similar to

what is observed in polycrystalline solid samples. Despite its tendency to fracture at localized points, the material is highly resilient being able to stand several compression cycles. Our experiments show this new material as a promising candidate for specific applications such as light damping structures.

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