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Manufacturing of Cu-based metallic glasses matrix composites by spark plasma sintering

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ABSTRACT

A preliminary study has shown that bulk metallic glasses of the CuZrAl type of large dimension may be manufactured from amorphous powders densified by a process of sintering such as spark plasma sintering (SPS). However, to remedy the lack of plasticity of these materials, the addition of ductile crystalline particles was carried out in the present study. The zirconium was chosen because its properties are close to those of the amorphous matrix. The same sintering parameters as those optimized for the metallic glass are also applicable for the production of the composite for the different zirconium volume fractions retained, respectively 5%, 10%, 20%, 30%, 40% and 50%. The materials obtained are dense. X-ray diffraction clearly indicates that only the amorphous matrix CuZrAl and the crystalline zirconium are present. Young's modulus as well as the elastic limit decrease only very slightly with the addition of crystalline particles. Decrease in hardness is more pronounced. On the other hand, the plastic deformation increases with the addition of zirconium, reaching about 4.9% for the alloy containing 50% zirconium. The analysis of the fracture surfaces clearly shows the role of the ductile crystalline particles, namely the deceleration of the shear bands. The influence of volume fraction and size of the crystalline particles and of matrix toughness is discussed from a mechanical point of view.

Therefore, SPS is a solution to solve both the problem of size and low ductility of amorphous metal, since it is possible to control microstructure and so to control mechanical properties.

1. Introduction

Bulk metallic glasses (BMGs) are considered as potential candidates in the structural engineering fields, due to their attractive mechanical properties. BMGs exhibit high strength, high hardness, high specific strength (strength/density), superior elastic limits (2%), high scratch and wear resistance [1–14]. However, most metallic glasses present no or limited plasticity, compared with crystalline materials, which limits their application at room temperature [15]. In the late 1990s, to bypass this problem, the strategy has been to introduce ductile crystalline phases in the glassy matrix. The presence of secondary ductile phase can absorb the shear strain energy of shear bands, confine their propagation before they can develop and become cracks, and significantly improve the plasticity [16].

Thus if amorphous alloy matrix composites containing ductile crystalline particles having sufficient ductility can be fabricated, the critical problems such as size limitation and poor ductility can be simultaneously solved while taking advantages of bulk amorphous alloys.

The development of composite materials and the characterization of the relationship between microstructure and properties, in particular mechanical properties, has been the subject of numerous publications. The metallic glasses which serve as a matrix for the composites are various: Ti–based [17–31], Zr-based [32–46], Cu-based [47,48], Ni-based [49], Fe-based [50,51], Mg-based [52–55]. The mechanical reinforcement can be obtained thanks to particles obtained by in-situ decomposition. The most obvious example is that of Ti- or Zr-based alloys, in which the formation of a ductile crystalline phase is obtained in the form of dendrites of the β phase (bcc) [19–21,23,27,29–31,34,35,38,41,48–50,54]. This technique offers two advantages: (i) it is fairly simple to produce (ii) interfaces are strong since they form during the quenching itself. However there are also drawbacks; (i) the possible chemical composition range is limited (ii) the resulting microstructure depends on the cooling rate and then depends on the sample size.

Another solution of the "in situ" type is the formation of nanocrystals, for example by carrying out appropriate heat treatments, [17,26,33,38,48,52]; the optimum is then the presence of CuZr B2 phase, which transforms into a martensitic phase of type B19 during

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plastic deformation. Other authors have made ex-situ composites by adding high-melting point particles that are not melted after the rapid quenching process in the injection casting or suction casting process [25,26,40,43,44,53,55]. Finally, other authors have shown the possibility of making ex-situ composites by mixing powders [16]: an amorphous powder and another crystalline powder; it may be metallic (W, Ta, Ti, TiNb) [24,39,42,43] or ceramic (WC, SiC, Al_2O_3, ZrO_2) [32,36,37,51]. A ceramic powder makes it possible to increase the modulus or the hardness, but these particles are more brittle and the expected improvement is not always achieved.

By powder metallurgy, large samples can be obtained. In a previous work, we have shown that sample with 30 mm in diameter can be manufactured by consolidation of CuZrAl amorphous powders; while by casting the same composition exhibits a critical diameter of only 3 mm [14]. Thus if amorphous alloy matrix composites containing ductile crystalline particles having sufficient ductility can be fabricated, the critical problems such as size limitation and poor ductility can be simultaneously solved while taking advantages of bulk amorphous alloys.

The increase in plasticity enables new applications of these materials. J.W. Qiao et al. [16] mentioned a lot of these applications, showing how complex shapes can be cast with Ti-based composites: bolts, washers, tubes, rods,… Hofmann et al. [20] described a semi-solid induction forging process by which complex components can be made, opening facilities for commercial and military hardware. A significantly enhanced drilling ability of the orthopaedic drill made of a Zr-based bulk metallic glass composite has been reported by T.H. Li et al. [43]. These examples clearly indicate the large interest in developing these new alloys.

In the present study, Cu-based amorphous alloy matrix composites were manufactured by spark plasma sintering (SPS) [56–66]. The principle is to apply in the same time an external pressure and an electrical field to densify the powder. The advantages are low sintering temperature, short sintering time and fast cooling rate. Microstructures and mechanical properties of the fabricated composites were investigated. The influence of volume fraction of zirconium crystalline particles on plasticity was studied.

2. Experimental

2.1. Materials

A glassy $Cu_{50}Zr_{45}Al_5$ powder (at%) was used in this study. The powder has been obtained by gas atomization in Tohoku University [16]. The particles have spherical shape and a smooth surface, and their average size is about 50 μm. T_g (glass transition temperature) and T_x (crystallization temperature) were determined and are 438 and 496 °C, respectively (see Section 2.2 for experimental details).

Table 1 gives some information on the features of the two powders (density, Young modulus, Poisson ratio and hardness). Fig. 1 displays the granulometry of the two powders. For the amorphous powder most of the particles are in the size range 20–80 μm and have an average size of 50 μm ($d_{0.9}$ = 78.6 μm). Smaller particles (in the range 1–10 μm) are also observed. So a large distribution exists, but particle size does not exceed 80 μm. Powder particles have a spherical shape as well as a smooth surface (Fig. 2). In contrast, crystalline particles have an irregular shape and a monomodal size distribution centered around 90 μm.

Table 1
Density (ρ), Young modulus (E), Poison ratio (ν), hardness (HV30) for CuZrAl bulk metallic glass and crystalline zirconium particles.

	ρ (g/cm^3)	E (GPa)	v	HV 30
CuZrAl BMG	7.22	97.3	0.371	503
Crystalline Zr (values from literature)	6.49	90.0	0.34	85–100

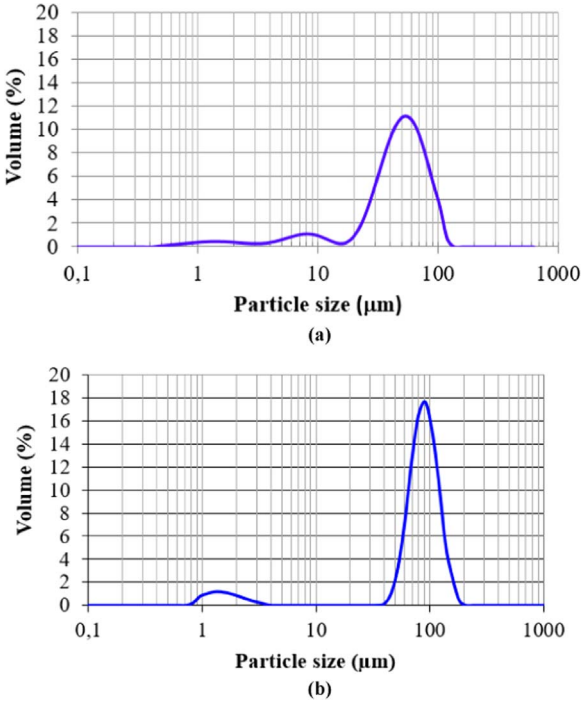

Fig. 1. Granulometry of the two powders: (a) CuZrAl amorphous powder; (b) Zr crystalline powder.

The amorphous powder was mixed with 5–50 vol% of pure crystalline Zr powder in a planetary ball mill. The micrograph shows the mixed powders before sintering; Zr particles are in white and amorphous powder in grey. We can observe that the Zr particles are well dispersed in the amorphous powder particles: a homogeneous mixing is obtained (Fig. 2).

The mixed powders were then consolidated under vacuum using a SPS system (FCT System HPD 25). The optimal conditions (sintering temperature 420 °C, holding time 10 min and pressure of 600 MPa) were established for monolithic amorphous alloy [14]. The detail of the processing parameters is shown on the graph (Fig. 3), the evolution of the temperature and the pressure are given as a function of time. The consolidated samples have a cylindrical shape, with a diameter of 10 mm and a thickness of 5 mm (Fig. 3).

2.2. Experimental techniques

The consolidated materials were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer, which produces the Cu-Kα radiation. The thermal stability was examined by DSC at a heating rate of 20 K/min using a standard commercial instrument (Pekin Elmer, DSC-7) under high purity dry nitrogen at a flow rate of 20 ml/min. Density of the consolidated samples was obtained using the Archimedean method. Specimens were observed using a Zeiss Axiophot optical microscope.

Young's modulus (E) and Poisson ratio (ν) were determined by ultrasonic measurement performed on a wave runner, using a pulser/receiver Panametric and two transducers (0.125 in., 5 MHz), for pulse echo and velocity measurement in longitudinal and shear modes.

Vickers hardness measurements were performed on mirror polished samples using a Testwell durometer. The load of 30 kgf was chosen since then the size of the indent is large enough to integrate both CuZrAl and Zr particles and then to represent the average value of the hardness of this composite material.

Consolidated alloys were machined into cylindrical specimens with a diameter of 3 mm and a height of 5 mm by electrical discharge machining and characterized by compression tests. Compression tests were