Journal of Alloys and Compounds 434–435 (2007) 84–87

Journal of ALLOYS AND COMPOUNDS

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Synthesis and mechanical behavior of nanocomposite Mg-based bulk metallic glasses

J.L. Soubeyroux [a,*], S. Puech [a,b], P. Donnadieu [c], J.J. Blandin [b]

[a] *Laboratoire de Cristallographie/CRETA, CNRS Grenoble, 25 Avenue des Martyrs, BP 166, 38042 Grenoble Cedex 9, France*
[b] *Génie Physique et Mécanique des Matériaux (GPM2), Institut National Polytechnique de Grenoble (INPG), UMR CNRS 5010, ENSPG, BP 46, 38402 Saint-Martin d'Hères Cedex, France*
[c] *Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques (LTPCM), Institut National Polytechnique de Grenoble (INPG), UMR CNRS 5614, ENSEEG, BP 75, 38402 Saint-Martin d'Hères Cedex, France*

Available online 17 October 2006

Abstract

Nanocomposites can be produced by partial crystallization of bulk metallic glasses (BMG). The introduction of such nanocrystals in an amorphous matrix can sharply change the mechanical behavior of the glass at room temperature. In the present study, the effect of crystals in Mg-based BMG is studied by partial crystallization of the $Mg_{65}Cu_{25}Gd_{10}$ and addition of 3 at.% of iron. Various techniques (DSC, DRX, TEM) are used to get data about the nature, the volume fraction or the average size of the crystals. Mechanical properties at room temperature are investigated in compression. The fracture stress is enhanced by iron addition, but no favorable effect of partial crystallization is observed for the $Mg_{65}Cu_{25}Gd_{10}$ BMG. These results are discussed in relation with the associated microstructures.

Keywords: Bulk metallic glasses; Magnesium alloys; Crystallization; $Mg_{65}Cu_{25}Gd_{10}$

1. Introduction

Bulk metallic glasses (BMG) exhibit particularly attractive mechanical properties like high stresses to fracture and large elastic strains (up to 2%). Among amorphous alloys, Mg-based BMG are of special interest since they can provide the possibility to obtain new light alloys for structural applications. Important efforts have been devoted to develop such Mg-bulk metallic glasses. Most alloys were focused on Mg–Cu–Y composition with various complementary element additions [1–8]. More recently, glasses based on Mg–Cu–Gd compositions have been elaborated [9,10] and present higher glass forming ability than Mg–Cu–Y alloys. Another interesting feature of BMG is the ability to nucleate by heat treatments nanocrystals inside the structure, and thus to produce nanocomposites. Despite some recent works on the Zr-based BMG, the mechanical properties of such nanocomposites remain quite poorly documented. It seems that partial crystallization may increase or decrease the mechanical properties of the BMG, depending on the volume fraction of the crystals, their composition, their size, their nature or their spatial distribution through the matrix [11–13]. Very few studies have dealt with mechanical properties of partially crystallized Mg-based alloys [14]. Another way to promote mechanical properties of Mg-based BMG is to add iron as it has been shown in the case of MgCuNiZnAgY + Fe [15]. For such compositions, the as-elaborated microstructure consists of a dispersion of Fe grains through the amorphous alloy.

In the present investigation, a $Mg_{65}Cu_{25}Gd_{10}$ alloy was elaborated and the effects of partial crystallization on the mechanical properties of the composite glass/crystal were investigated. The effect of iron addition was also investigated. Mechanical properties were studied by compression tests at room temperature.

2. Experimental procedure

Elements with purity better than 99.9% were used as starting materials. Cu–Gd or Cu–Gd–Fe as intermediate alloys were melted prior to be remelted with Mg to obtain the master alloy. The glasses of composition $Mg_{65}Cu_{25}Gd_{10}$ and $(Mg_{0.65}Cu_{0.25}Gd_{0.10})_{97}Fe_3$ were prepared by copper mould casting as cylinders of 4 or 6 mm diameter. The degree of amorphicity was characterized by X-ray diffraction (XRD) analyses. The thermal glass stability was determined by differential scanning calorimetry with an heating rate of 10 K/min (Perkin-Elmer DSC 7 and Netzsch DSC 404S). After each run, a second run was performed in order to estimate the baseline. From DSC

* Corresponding author. Tel.: +33 476889039; fax: +33 476881280.
E-mail address: soubeyroux@grenoble.cnrs.fr (J.L. Soubeyroux).

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doi:10.1016/j.jallcom.2006.08.297

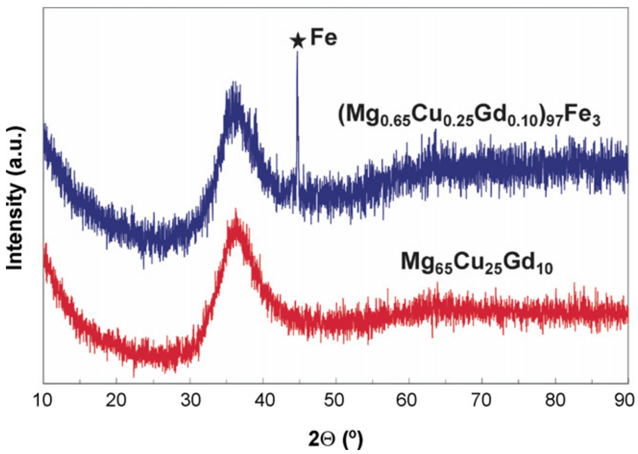

Fig. 1. XRD patterns of $Mg_{65}Cu_{25}Gd_{10}$ and $(Mg_{0.65}Cu_{0.25}Gd_{0.10})_{97}Fe_x$ BMG as-cast as 6 mm cylinders.

analyses, the characteristic temperatures T_g (glass transition temperature) and T_x (onset of crystallization) were measured. For crystallization experiments before compression tests, the samples were annealed at 438 K in oil bath, and the duration of heat treatment was deduced from isothermal DSC curves at the same temperature. In partially crystallized BMG, the fraction of transformed matter F_T associated to a peak in DSC was deduced from the ratio $H(t)/H_{tot}$ where $H(t)$ is the released heat flux at time t and H_{tot} for the complete transformation. The microstructures of the alloy were characterized by SEM and TEM observations. The mechanical properties were investigated at room temperature by compressive tests with an initial strain rate equal to $5 \times 10^{-4}\ s^{-1}$. Compression rods were 4 mm in diameter and 6 mm in length.

3. Results

3.1. Thermal stability

Fig. 1 displays XRD patterns taken from the cross-section of the rod confirming the amorphous structure of the as-cast alloys whereas Fig. 2 shows the corresponding DSC curves in continuous heating conditions. A glass transition temperature $T_g = 417$ K is measured, followed by a single crystallization peak with an onset crystallization temperature T_x equal to 472 K. These values are in relatively good agreement with those reported recently for a similar composition [10].

The effect of the alloying of $Mg_{65}Cu_{25}Gd_{10}$ with iron does not change the amorphous nature of the matrix as DSC events appear in the composite compound at exactly the same temperatures. In the diffraction pattern, the iron peak appears above the weavy diffuse scattering characteristic of the BMG. They present a (1 1 0) texture with very narrow peaks confirming the SEM observations of very well crystallized dendrites.

The crystallization kinetics was investigated at 438 K. Fig. 3 shows an isothermal DSC curve registered at this temperature, with the calculated percentage of transformed matter F_T. The vertical marks correspond to the selected durations of maintain of the samples for mechanical compression tests.

3.2. Mechanical properties

Fig. 4 displays the results of compression tests performed on amorphous and partially crystallized samples, annealed at

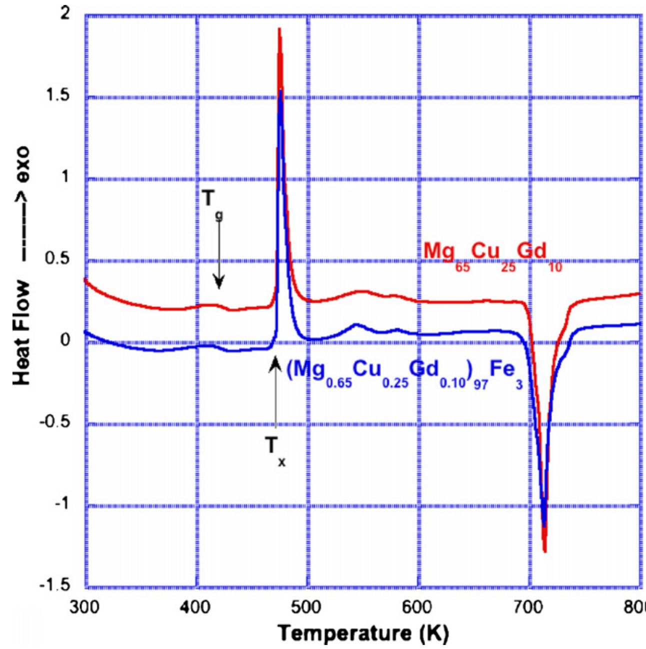

Fig. 2. DSC curves of $Mg_{65}Cu_{25}Gd_{10}$ and $(Mg_{0.65}Cu_{0.25}Gd_{0.10})_{97}Fe_x$ BMG as-cast as 6 mm cylinders.

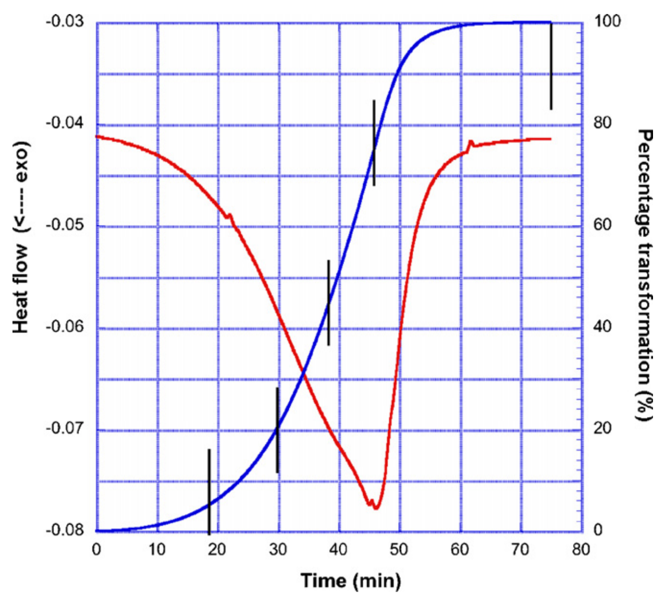

Fig. 3. Isothermal DSC curves of the $Mg_{65}Cu_{25}Gd_{10}$ BMG at 438 K.

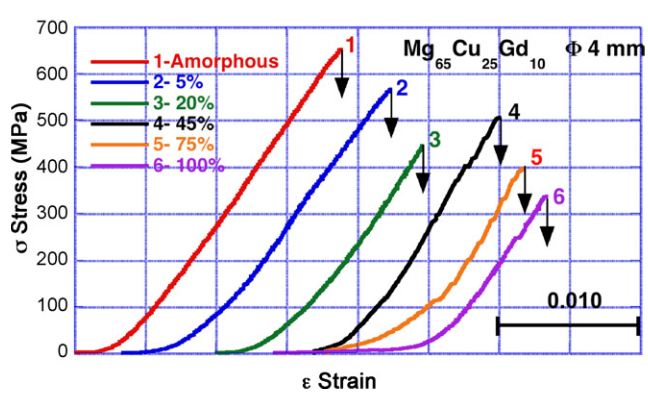

Fig. 4. Compression tests performed on the $Mg_{65}Cu_{25}Gd_{10}$ BMG.

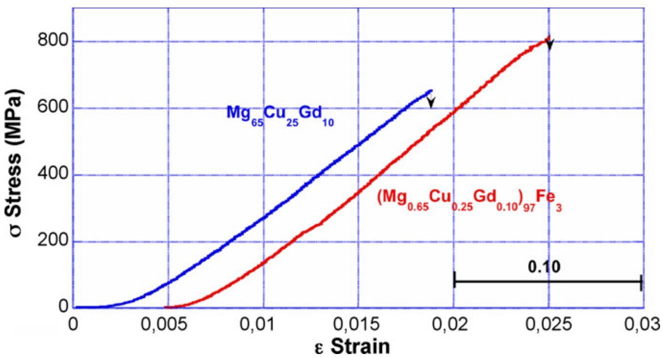

Fig. 5. Compression tests performed on the $(Mg_{0.65}Cu_{0.25}Gd_{0.10})_{97}Fe_x$ BMG.

438 K for various levels of crystallization. No signs of macroscopic plastic strain before failure are noticed. In the amorphous state, the fracture stress is about 650 MPa with an elastic strain of 0.014. Upon crystallization, the fracture stress decreases and falls to 335 MPa for the fully transformed state. These curves suggest that the effect of crystallization on the Young's modulus remains quite limited. Such effect of crystallization on the fracture stress differs to what has been reported in the case of other BMG for which the fracture stress increases up to a maximum (associated to a critical volume fraction of crystals nearby 40 vol.%) and then decreases [16].

Fig. 5 shows the effect on the mechanical behavior of the addition in the studied glass of 3 at.% Fe. Compared to the amorphous state, this addition does not modify significantly the Young's modulus but the fracture stress is increased to a value close to 800 MPa, leading to an elastic strain of about 0.02. These results are comparable with those obtained by Ma and coworkers [15], where the addition of 9 at.% of iron resulted in an increase of the fracture stress up to 990 MPa. However, in the latter case, significant plasticity was observed which is not clearly detected in the present investigation.

4. Discussion

4.1. Amorphous state

It was possible to elaborate a Mg-based BMG under the form of a 6 mm diameter rod. Glass forming ability is known to be favored by multi component systems with compositions close to deep eutectic ones, large differences in atomic sizes and negative heats of mixing between the solutes. These criteria are well satisfied in the case of the $Mg_{65}Cu_{25}Gd_{10}$ alloy since the atomic radii are respectively 0.160, 0.128 and 0.178 nm for Mg, Cu and Gd and the heat of mixing are −3, −6 and −22 kJ/mol for Mg–Cu, Mg–Gd and Cu–Gd [17].

4.2. Mechanical properties of Mg–Cu–Gd BMG + Fe

Fig. 6 displays a SEM observation of the Mg–Cu–Gd + 3 at.% Fe alloy. Iron forms dendrites typically in the range 10–20 μm in the amorphous matrix. XRD and DSC show clearly that the amorphous matrix in the composite and in the glass have the same characteristics. From a mechanical point of view, the fracture stress is significantly enhanced by the Fe addition, which may be probably related to the interaction between the dendrites and propagating shear bands through the glass. As already mentioned, in the case of the study on Mg–Cu–Y with Fe content between 9 and 13 at.%, plastic strain was observed, increasing with iron addition [15]. In the present investigation, the Fe amount (3 at.%) is probably too low to get such gains even if some very limited plasticity cannot be excluded on the stress–strain curve shown in Fig. 5. This observation is mainly based on the reduction of the (stress, strain) slope just before the fracture of the sample, knowing that such a reduction is not observed for the Fe-free samples. Work is under progress to increase the Fe content and also to promote the dispersion of the Fe crystals through the glass.

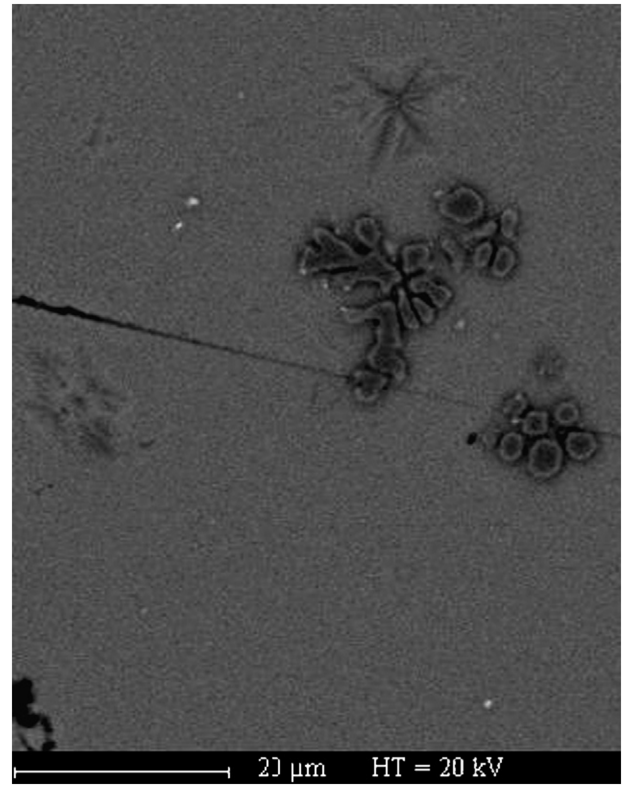

Fig. 6. TEM images of the $Mg_{65}Cu_{25}Gd_{10}$ BMG annealed at 438 K with 20% of crystallization. (a) Clear field image and (b and c) electron diffraction patterns of the selected areas for Cu_2Gd and Mg_2Cu, respectively.

4.3. Mechanical properties of nanocrystallized Mg–Cu–Gd

Nanocrystallization in the studied Mg–Cu–Gd amorphous alloy results in a decrease of the fracture stress, which differs from results reported in other BMGs [12,16]. The apparent specificity of the Mg-based BMGs may be related to the characteristics of the crystal population or their degree of relaxation of the glass before deformation.

The crystallization in the studied alloy was investigated by TEM. In the Mg–Cu–Gd studied in the present study, as illustrated by the TEM observations shown in Fig. 7, two populations of crystals can be observed in the annealed sample at 438 K with a volume fraction of transformed matter of 0.2. Rounded shaped

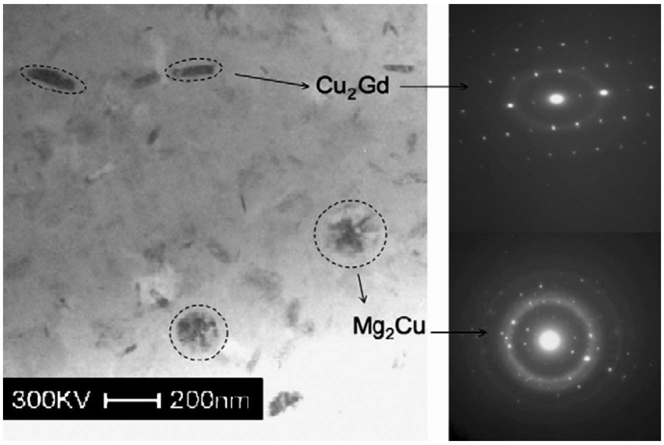

Fig. 7. SEM image of the $(Mg_{0.65}Cu_{0.25}Gd_{0.10})_{97}Fe_x$ BMG.

crystals with a size of about 100 nm were identified as Mg_2Cu, thanks to XRD and TEM diffraction patterns. These crystals reach quickly 100 nm size with relatively low growth kinetics during further annealing at 438 K. The second type of crystals, with a rod shape, was identified as Cu_2Gd. They grow quickly to a length of about 200 nm and diameter of about 50 nm in the first steps of crystallization and then keep a relatively constant size. In the case of Mg–Cu–Y BMG, it is generally assumed that only one kind of crystal (Mg_2Cu) nucleates and grows during primary crystallization [5,8]. The measured size of the crystals produced during the annealing at 438 K is significantly larger than that generally measured during nanocrystallization of Zr-based BMG for which nanocrystals diameter in the range 10–20 nm are often measured.

Another specificity of the Mg based BMG is related to the particularly low glass transition temperature which may results in significant relaxation of the amorphous structure nearby room temperature. The existence of medium range ordered zones even before nanocrystallization heat treatments has been recently reported [10]. In such a framework, a particular brittleness of the as-elaborated alloy can be expected.

5. Conclusions

The effect of crystals in a bulk amorphous Mg-based matrix was studied after partial crystallization of a $Mg_{65}Cu_{25}Gd_{10}$ BMG or addition of iron (3 at.%). The nanocrystallized composites are associated to relatively large sized crystals (>100 nm) of various natures (Mg_2Cu and Cu_2Gd), produced during the maintains at high temperature (438 K). In the second case, dendrites with micrometer sizes are dispersed in the glass. The effects on fracture stress of these two ways to elaborate a composite glass/crystals are opposite: nanocrystallization induces a reduction of the fracture stress whereas iron addition increases the fracture but without inducing significant plasticity.

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