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Phases formation during heating of Mg–Cu–Ag–Y bulk metallic glasses

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ABSTRACT

DSC and in-situ neutron diffraction have been used in order to find the phases formed under various heating treatments in the vicinity of the glass transition for Mg-based bulk metallic glasses (BMG). The first phase to crystallize in the $Mg_{58.5}Cu_{30.5}Y_{11}$ alloy, when the sample is hold at $T_g + 20$ K, is Mg_2Cu and a nanocrystallized phase. During continuous heating of the same sample, the main phases to crystallize are Mg_2Cu, MgY and Cu_2Y. The alloy $Mg_{55.5}Cu_{28.5}Ag_5Y_{11}$ has the best GFA parameters observed for Mg-based BMG ($\Delta T = 54^\circ$ and $\gamma = 0.415$) and presents a single event for crystallization. The phases formed by holding the sample at $T_g + 20$ K are the same than observed for the alloy without silver (Mg_2Cu and nanophase). During continuous heating of this sample the same phases as previously observed appear but with Ag_3Mg as extra phase. If ternary phases are present, they could correspond to tiny lines not refined, but they appear with a very low intensity. Mg_2Cu and Cu_2Y produce the main intensity lines. The appearance of nanocrystals during crystallization in the glass transition region could be at the origin of the plasticity observed in these alloys.

1. Introduction

Bulk metallic glasses (BMG) exhibit particularly attractive mechanical properties like high stresses to fracture and large elastic strains. Mg-based BMG are of special interest since they can provide the possibility to obtain new light alloys for structural applications. For shaping by hot deformation, it is important to produce alloys with a large temperature range between the vitreous temperature transition and the crystallization temperature (ΔT). It is also important to produce alloys with a high critical diameter (D_c) in order to produce thick pieces with the vitreous characteristics responsible of the good mechanical properties. Most of previous studies on magnesium-based BMGs were focused on $Mg_{65}Cu_{25}Y_{10}$ [1] or $Mg_{60}Cu_{30}Y_{10}$ [2,3]. Minor element additions is one of the simplest methods to enhance the glass forming ability (GFA) of BMGs. Improvement of GFA has been reported in $Mg_{65}Cu_{25}Y_{10}$ alloys where Cu is partially substituted with transition metals such as Ni, Zn, Ag, Pd [4–8]. Recently in the search for high GFA in magnesium alloys Ma et al. have proposed alloys with various Mg/Cu composition ratios and D_c of 16 mm and 25 mm were obtained on $Mg_{54}Cu_{28}Ag_7Y_{11}$ and $Mg_{54}Cu_{26.5}Ag_{8.5}Gd_{11}$, respectively [9] and $D_c \geq 11$ mm for mixed Y–Gd alloys also with various Mg/Cu composition ratios but without silver addition [10,11], however, none of these alloys show plasticity. Plasticity in Mg-based alloys has been clearly obtained by making composites with a BMG matrix containing ductile particles, for example with Nb [12], Fe [13] or TiB_2 [14] but also by nanocrystallization in monolithic alloys [15–17]. In these last alloys the plasticity is low and the mechanism is not well understood but we think that nanocrystallization may play the role of ductile particles. We have undertaken this study on the crystallization of $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{58.5}Cu_{30.5}Y_{11}$ with their silver substituted alloys, $Mg_{65}Cu_{20}Ag_5Y_{10}$ and $Mg_{55.5}Cu_{28.5}Ag_5Y_{11}$ in order to get new data to understand the links between plasticity enhancement and partial crystallization. In this paper, we present the sample synthesis with thermal and structural characterization and an in-situ neutron diffraction study of the crystallization. Mechanical properties will be presented in a forthcoming article.

2. Experimental procedure

Several compositions have been prepared by high frequency melting of pure metals with pre-melting of Cu + Y + (Ag) before long melting with magnesium and injection in a cylindrical copper mould (4 and 6 mm diameter samples) in order to have samples for neutron diffraction which need more volume (6 mm) and for compression test and thermal analysis, 4 mm cylinders were prepared. Differential scanning calorimetry (DSC) analysis was carried out on a Netzsch DSC 404S calorimeter under a flowing argon atmosphere, at a constant heating rate of 2 K/min (the heating rate used for neutron experiments). In order to determine glass transition (T_g), crystallization (T_x), melting (T_m) and liquidus (T_l) temperatures with the aim to calculate usual GFA indicators: $\Delta T = T_x - T_g$ and $\gamma = T_x/(T_g + T_l)$. Neutron diffraction experiments have been performed on the D1B-CRG diffractometer at Institut Laue-Langevin in Grenoble. This diffractometer is equipped with a 400 cells position sensitive detector, covers an 80° 2-theta range, and allows recording a pattern every 5 min. The experiments were performed in a dedicated furnace with a vanadium resistor under a secondary vacuum. The wavelength used was 0.2524 nm.

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Table 1
Results of thermal analysis with calculated GFA factors (ΔT, γ) on the $Mg_xCu_yY_z$ and $Mg_xCu_yY_zAg_5$ alloys measured at 2 K/min.

Glass	T_g (K)	T_{x1}	T_{x2}	T_m	T_l	ΔT	γ
$Mg_{65}Cu_{25}Y_{10}$	420	461	541	726	741	41	0.397
$Mg_{65}Cu_{20}Ag_5Y_{10}$	422	455	478	693	725	33	0.397
$Mg_{58.5}Cu_{30.5}Y_{11}$	424	476	559	734	756	52	0.403
$Mg_{55.5}Cu_{25.5}Ag_5Y_{11}$	428	482	517	713	733	54	0.415

3. Results and discussion

Table 1 reports the results of thermal analysis obtained from DSC experiments with GFA parameters. Fig. 1a and b show the DSC traces for the 4 mm diameter samples recorded at 2 K/min (0.033 K/s). Traces have also been recorded for 6 mm samples and show no difference. The samples with the higher yttrium content have the best GFA parameters (ΔT and γ), particularly the $Mg_{65}Cu_{20}Ag_5Y_{10}$ sample presents a lower ΔT range with a first crystallization event at a temperature lower than for the sample without silver. On the contrary the $Mg_{55.5}Cu_{28.5}Ag_5Y_{11}$ sample presents a single crystallization event and better GFA parameters than the sample without silver, in particular it has a very low melting temperature with a narrow transition indicating the proximity of an eutectic composition, it presents the higher γ parameter of all the Mg-based BMGs. In-situ neutron diffraction experiments have been done on the 4 samples and with 2 heating profiles for each sample. The first heating treatment was done at a constant speed of 2 K/min and a diffraction pattern was recorded continuously during the temperature change during 5 min (each pattern is a mean value on 10 Kelvin change) up to 623 K then cooling down at room temperature. The second heat treatment was a constant heating at 2 K/min up to T_g + 20 K, then a dwell at this temperature until crystallization was not evolving, then cooling down at room temperature. We present here only some results on the best GFA alloys with the higher yttrium content (Y = 11 at%), the results on the Y = 10 at% are quite similar. The Fig. 2 shows the constant heating experiment for the $Mg_{58.5}Cu_{30.5}Y_{11}$ sample represented such as the x-axis is the 2-theta angle, y-axis is the time (temperature) and z-axis is the neutron counts.

At the beginning of the experiment, the characteristic diffraction pattern of an amorphous phase with short-range order (bump maximum at 2-theta = 62.2°; d = 2.443 Å) is observed. At 480 K

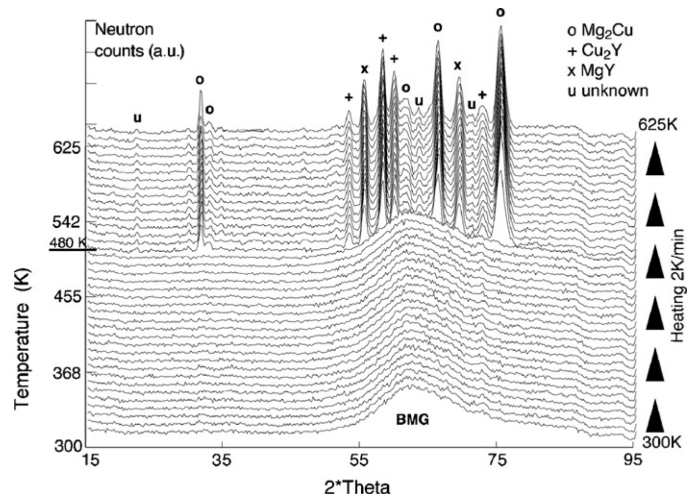

Fig. 2. Neutron diffraction constant heating experiment for the $Mg_{58.5}Cu_{30.5}Y_{11}$ sample.

(474 K in DSC experiment) the wavy pattern is transformed to Bragg peaks by crystallization of new phases. During further heating to 623 K, no transformation seems to occur (no new phase or intensity change on the main Bragg peaks are observed). The main phases observed are Mg_2Cu, MgY and Cu_2Y, they are marked by symbols on the Fig. 2. We have done a profile refinement of the neutron pattern recorded at room temperature at the end of the experiment. It is reported in Fig. 3, above some amorphous contribution remaining, the following phases have been refined using the Fullprof program, Mg_2Cu (orthorhombic, Fddd, a = 0.9123(3) nm, b = 1.844(1) nm, c = 0.5328(2) nm), MgY (cubic, Pm-3m, a = 0.38197(8) nm) and Cu_2Y (orthorhombic, Imma, a = 0.4321(5) nm, b = 0.6864(6) nm, c = 0.7289(5) nm); some tiny peaks marked with "u" have not been identified among the known binary and the new ternary phases proposed by Satta et al. [18]. The Fig. 4 shows the experiment for the $Mg_{58.5}Cu_{30.5}Y_{11}$ sample heated at 443 K and holds at this temperature for 7 h and cooled down at room temperature. After one hour held at 443 K, the sample starts to crystallize and the main phase is Mg_2Cu with a second phase with 2 very broad peaks at d = 2.630 Å and d = 2.459 Å respec-

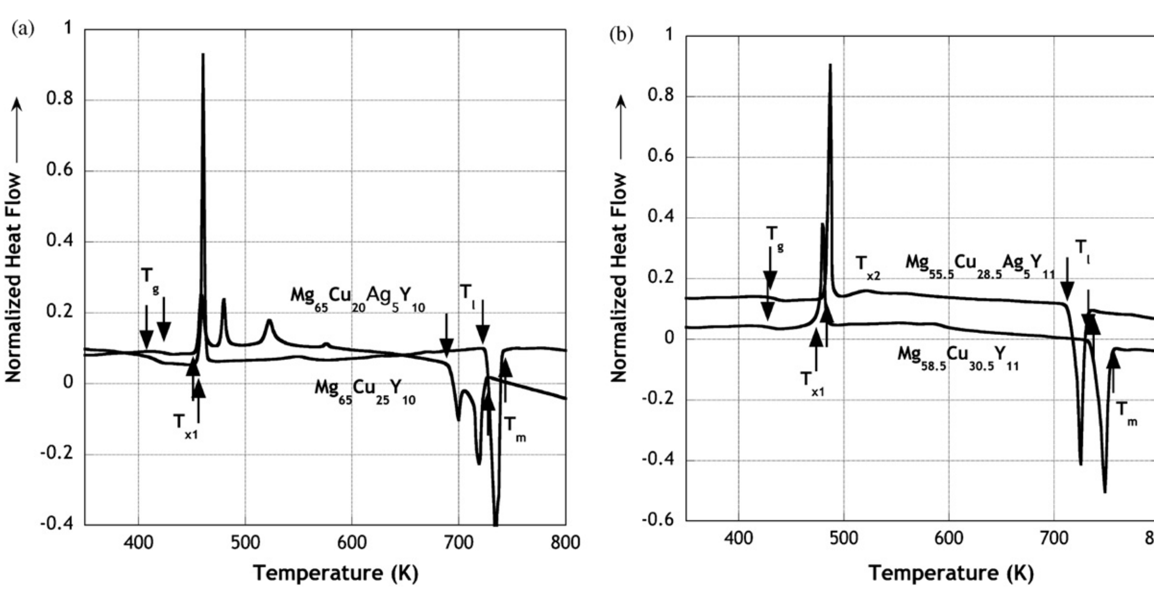

Fig. 1. DSC traces for the 4 mm diameter samples recorded at 2 K/min (0.033 K/s).

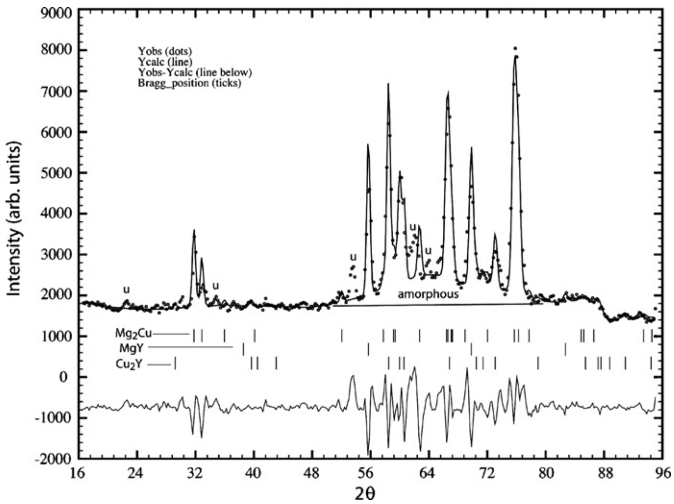

Fig. 3. Neutron profile refinement of the crystallized phases after heat treatment at 350 °C (623 K) and cooling down to room temperature.

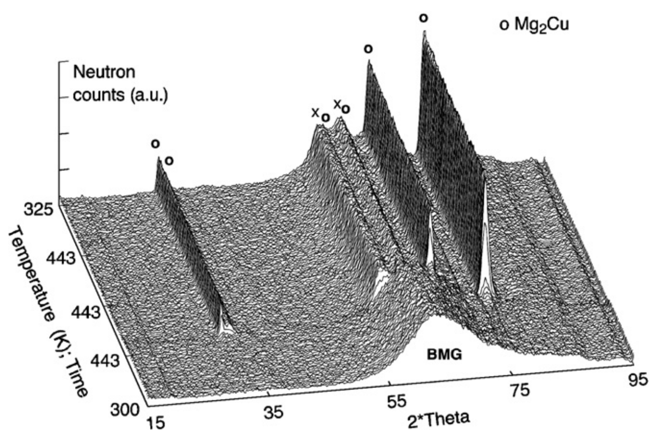

Fig. 4. Neutron diffraction experiment for the $Mg_{58.5}Cu_{30.5}Y_{11}$ sample after one hour held at 443 K.

tively, corresponding to a nanocrystallized phase which has not yet been identified. After longer annealing at this temperature no new phase appears. We have done a profile refinement of the neutron pattern recorded at room temperature at the end of the experi-

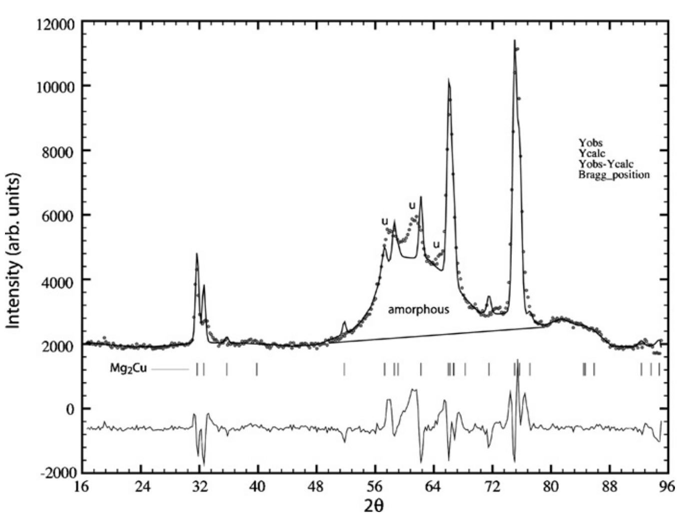

Fig. 5. Neutron profile refinement of the crystallized phases after heat treatment at 170 °C (443 K) for 7 h and cooling down to room temperature.

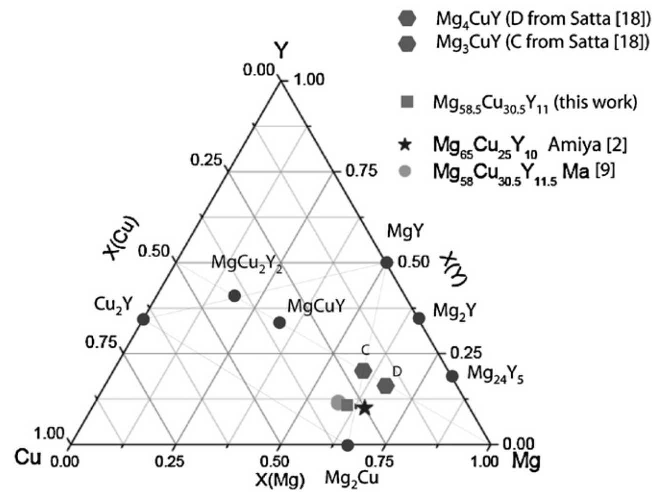

Fig. 6. Ternary Mg–Cu–Y phase diagram with known binary and ternary phases.

ment. It is reported in Fig. 5, above a large amorphous contribution remaining, the Mg_2Cu phase has been refined, (orthorhombic, Fddd, a = 0.9185(3) nm, b = 1.8487(7) nm, c = 0.5372(2) nm). The width of the peaks not refined corresponds to nanocrystals with 20 nm in size.

The position of the $Mg_{58.5}Cu_{30.5}Y_{11}$ phase is reported in the ternary phase diagram of Mg–Cu–Y (Fig. 6) with the known binary and ternary phases, this position is very close to the Amiya ($Mg_{65}Cu_{25}Y_{10}$) and Ma formula ($Mg_{58}Cu_{30.5}Y_{11.5}$). The closer very stable binary phase is Mg_2Cu, so it is logical to find this phase as the main crystallization product. The presence of ternary phases in the vicinity (C and D formulas of Satta) has been tested as possible phases but without success.

Plasticity induced by nanoparticle dispersion in bulk metallic glasses has been observed in Zr- and Cu-based alloys [19–23]. In the Mg-based BMG with gadolinium, we have shown that primary crystallization was producing large crystals of Mg_2Cu and Cu_2Gd (200 nm) [10,11] and that partial crystallization was reducing the stress fracture limit without any plasticity. In the Mg-based BMG with yttrium, the primary crystallization is different and involves the appearance of nanocrystals during crystallization in the glass transition region. This nanocrystals could be at the origin of some plasticity observed in these alloys. More observations by TEM are necessary to confirm these hypotheses.

4. Conclusion

The alloy $Mg_{55.5}Cu_{28.5}Ag_5Y_{11}$ has the best GFA parameters observed for Mg-based BMG with a single event for crystallization. The phases formed by holding the sample at T_g + 20 K are the same as for the alloy without silver. During continuous heating of this sample the same phases as previously observed appear but with Ag_3Mg. If ternary phases are present, they could correspond to tiny lines not refined, but they appear with a very low intensity. Mg_2Cu and Cu_2Y phases produce the main intensities in all crystallized samples. DSC experiments coupled with in-situ neutron diffraction are necessary to determine the nature and the size of the different phases crystallizing from the amorphous state. Holding the sample at a temperature in the ΔT range produces crystallization of the main phase (Mg_2Cu) and of another unknown phase but with the size of nanocrystals. These nanocrystals should be at the origin of the plasticity observed in this alloy.

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