Crystallisation process in Mg$_{60}$Cu$_{30}$Gd$_{10-x}$Nd$_x$ (x = 0, 8.5) amorphous alloys

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Abstract. Mg$_{60}$Cu$_{30}$Gd$_{10}$ and Mg$_{60}$Cu$_{30}$Gd$_{1.5}$Nd$_{8.5}$ ribbons were obtained by melt spinning. For both compositions, a fully amorphous phase was found and a clear Tg was observed. In-situ XRD measurements were carried out during heating of ribbons at the ID11 synchrotron beamline of ESRF, Grenoble (France). In order to identify the crystallisation products, an annealed Mg$_{60}$Cu$_{30}$Gd$_{10}$ master alloy was analysed by SEM/EDS and XRD. The existence of new ternary compounds (MgCu$_4$Gd and Mg$_2$CuGd) in the Mg-Cu-Gd system is suggested.

1. Introduction

Mg-Cu-RE (RE = Rare Earth) amorphous alloys have attracted attention because of their high strength-to-weight ratio and low glass transition temperatures. Among these systems, the Mg$_{65}$Cu$_{25}$Y$_{10}$ alloy exhibits high glass forming ability (GFA) [1-3]. A significant improvement of GFA was reached with the substitution of Y with Gd, obtaining Mg$_{60}$Cu$_{25}$Gd$_{10}$ [4], or by adding other elements to the ternary composition [5,6]. The Mg-Cu-Y and Mg-Cu-Gd bulk metallic glasses have a tensile strength exceeding 600 MPa [7,8] but samples appear to be brittle. In some cases, the presence of nanocrystals in the amorphous matrix can enhance the strength of the material [9], so it is of interest the study of the early crystallisation stages in order to determine the crystalline phases involved. For Mg$_{60}$Cu$_{25}$Tb$_{10}$ [10] the formation of quasicrystalline phases is reported, that transform to Mg$_2$Cu, Mg$_3$Tb and unidentified phases during a second crystallisation stage. For Mg$_{60}$Cu$_{25}$Y$_{10}$ amorphous alloy, Murty and Hono [11] suggest the formation, as crystallisation products, of an Y containing Mg$_2$Cu, via polymorphic crystallisation. For amorphous Mg$_{60}$Cu$_{30}$Y$_{10}$, a eutectic crystallisation was suggested [12], with the formation of Mg$_2$Cu, MgY and MgCuY. Mg$_2$Cu and Cu$_2$Gd were identified in Mg$_{65}$Cu$_{25}$Gd$_{10}$ by Soubeyroux et al. [9]. So, the crystallisation process in Mg-Cu-RE amorphous alloys seems to be strongly dependent on composition.

In this paper, Mg$_{60}$Cu$_{30}$Gd$_{10}$ alloy was selected as a starting composition for studying crystallisation and GFA. An effect of Nd addition on crystallisation process was observed for Mg$_{60}$Cu$_{30}$Gd$_{1.5}$Nd$_{8.5}$ amorphous alloy. In order to identify the crystallisation products, a careful analysis of equilibrium compounds in the Mg-Cu-Gd system has been carried out.
2. Experimental

Mg_{60}Cu_{30}Gd_{10} and Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5} master alloys were prepared by arc melting suitable amount of Cu, Gd and Nd pure elements. The ingots were then remelted with Mg in an induction furnace under argon atmosphere. Ribbons with thickness of about 40 µm were prepared by melt spinning. Structural information were obtained performing both conventional X-Ray diffraction (XRD) analysis with Cu Kα radiation and high-flux high-energy XRD in monochromatised synchrotron light at ID11 ESRF, Grenoble. In-situ annealing was performed with heating rate of 40°C/min and an acquisition time of 10 s per pattern, by using Linkam THMS600 heater, from room temperature to 300°C. Crystallisation and melting behaviour were checked by differential scanning calorimetry (DSC) by using a heating rate of 20°C/ min. Scanning Electron Microscopy (SEM) coupled with Energy Dispersion Spectroscopy (EDS) was used to study the microstructure of an annealed master alloy.

3. Results and discussion

The results of the XRD in-situ experiments for Mg_{60}Cu_{30}Gd_{10} ribbon are reported in Fig. 1, where the development of crystal phases from the amorphous halo is clearly evidenced. Selected XRD patterns from the in-situ experiment are reported in Fig. 2. The corresponding DSC trace of crystallisation is shown in Fig. 3a. T_g is evident at 151°C, followed by a main crystallisation peak starting at 212°C. A second exothermic event is observed at 314°C. Thermal data for crystallisation and melting are collected in Tab. 1. For Mg_{60}Cu_{30}Gd_{10}, the values of empirical parameters T_g/T_m, T_g/T_l, ∆T_x=(T_x-T_g) and γ=T_x/(T_g+T_l) [13] suggests a high GFA (Tab 1).

|                | T_g | T_x1 | T_x2 | ∆T_x | T_m | T_l | T_g/T_m | T_g/T_l | T_x/T_m |
|----------------|-----|------|------|------|-----|-----|---------|---------|---------|
| Mg_{60}Cu_{30}Gd_{10} | 151 | 212  | 314  | 61   | 425 | 482 | 0.61    | 0.56    | 0.41    |
| Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5} | 147 | 191  | 309  | 44   | 434 | 480 | 0.59    | 0.56    | 0.39    |

Figure 1. XRD patterns from in-situ heating experiments for Mg_{60}Cu_{30}Gd_{10} amorphous alloy.

Figure 2. Selected XRD patterns from in-situ experiments for Mg_{60}Cu_{30}Gd_{10} ribbon a) 40°C; b) 215°C; c) 300°C; d) Mg_{60}Cu_{30}Gd_{10} annealed master alloy.

and γ=T_x/(T_g+T_l) [13] suggests a high GFA (Tab 1).

The amorphous phase (T=40°C; Fig. 2a) remains stable up to 213°C, in good agreement with the DSC data (Fig. 3a). The first pattern showing crystalline diffraction peaks (T=215°C; Fig 2b) evidences the presence of Mg_{2}Cu, together with an unidentified phase. After heating up to 300°C (Fig 2c), a limited amount of amorphous phase is still present. An enlargement of the diffraction peaks with respect to the instrumental function (obtained with LaB_6) is observed. For example at q=1.709 the half
width at half maximum (HWHM) is 0.039 Å⁻¹ and the instrumental function is 0.00585 Å⁻¹, so the presence of nanosized crystal phases at this temperature can be inferred. From the comparison of the XRD patterns b and c in Fig. 2, it is evident that the phase structure remains unchanged, suggesting a eutectic crystallisation mechanism, as confirmed by the single peak in the DSC trace (Fig. 3a).

In order to identified the diffraction peaks remained unassigned, a study of the phase mixture in the master alloy was carried out, assuming that stable phases can be present in the crystallised sample. The SEM micrograph of the Mg₆₀Cu₃₀Gd₁₀ master alloy, after an isothermal treatment at 380°C for one week, is reported in Fig 4. From the contrast in the electron backscattered image, four crystal phases are clearly evidenced, suggesting that this composition can hardly reach the equilibrium conditions. From the EDS analysis, Mg₂Cu is easily recognised as the darkest phase in Fig. 4 (zone a). MgCu₄Gd (zone b) and Mg₂CuGd (zone c) average compositions are also identified. A fourth phase, with higher Gd content, is observed in the SEM image (lightest crystals, zone d), with more scattered compositions, corresponding to an average value of Mg₃₇Cu₁₁Gd₵₂. Only two stable compounds are reported for the Mg-Cu-Gd system (Mg₂Cu₉Gd and Mg₂Cu₂Gd₂) and no assessment is available for this phase diagram. So, a comprehensive analysis of the Mg-Cu-RE phase diagrams was carried out in

**Figure 3.** DSC traces of a) Mg₆₀Cu₃₀Gd₁₀; b) Mg₆₀Cu₃₀Gd₁.₅Nd₈.₅.

**Figure 4.** Backscattered SEM picture of Mg₆₀Cu₃₀Gd₁₀ annealed master alloy.

**Figure 5.** XRD patterns from in-situ heating experiments for Mg₆₀Cu₃₀Gd₁.₅Nd₈.₅ amorphous alloy.

**Figure 6.** Selected XRD patterns from in-situ experiments for Mg₆₀Cu₃₀Gd₁.₅Nd₈.₅ ribbon a) 40°C; b) 198°C; c) 205°C; d) 300°C.
order to investigate on ternary compounds in similar systems [14-15]. MgCu₄RE and Mg₃CuRE compounds exist and their structural data are available in literature, therefore the identification of diffraction peaks corresponding to these phases was possible in the XRD pattern of the Mg₆₀Cu₃₀Gd₁₀ annealed master alloy (Fig. 2d). Concerning zone d, Mg₃₇Cu₁₁Gd₅₂ composition lies on the line joining MgGd and CuGd phases, that have the same crystallographic structure (CsCl type), suggesting the existence of a region of solid solution between these phases. From the comparison of the XRD patterns of the annealed master alloy and crystallised ribbons (Fig. 2c and 2d), it appears that none of the ternary phases indexed in the master alloy were formed in the early stages of crystallisation. Amorphous Mg₆₀Cu₃₀Gd₁₅Nd₈.₅ ribbons were also crystallized in-situ (Fig. 5) and corresponding selected XRD patterns are given in Fig. 6. The addition of Nd to the Mg₆₀Cu₃₀Gd₁₀ alloy produces a shoulder to the DSC crystallisation peak, as shown in Fig. 3b. The characteristic temperatures of Tₕ, Tₙ and Tₘ appear rather similar to those of Mg₆₀Cu₃₀Gd₁₀ (Tab. 1), suggesting that the addition of Nd doesn't improve the GFA of this alloy. The fully amorphous alloy (T=40°C; Fig. 6a) begins to crystallize with the formation of an unknown phase (T=198°C; Fig. 6b). At higher temperatures, in correspondence to the shoulder in the DSC peak, a progressive growth of crystalline diffraction peaks is observed (T=205°C; Fig. 6c). After heating up to 300°C, the XRD patterns of Mg₆₀Cu₃₀Gd₁₀ (Fig. 2c) and Mg₆₀Cu₃₀Gd₁₅Nd₈.₅ (Fig. 6d) show the same diffraction peaks, suggesting that the phases involved at this stage of the crystallisation are the same.

4. Conclusions

The crystallisation of Mg₆₀Cu₃₀Gd₁₀ and Mg₆₀Cu₃₀Gd₁₅Nd₈.₅ amorphous alloys was studied by DSC and in-situ synchrotron XRD. Crystallisation processes involved the formation of Mg₃Cu compound, together with unknown phases. The existence of two new ternary compounds in the Mg-Cu-Gd system (MgCu₄Gd and Mg₃CuGd) was suggested, based on SEM/EDS microanalysis on the Mg₆₀Cu₃₀Gd₁₀ master alloy, heated up to 380°C for one week. For both alloys, the early stages of crystallisation lead to a metastable phase mixture, without any evidence of equilibrium ternary compounds.

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