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# 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 ($MgCu_4Gd$ and $Mg_2CuGd$) 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 $Mg_{65}Cu_{25}Gd_{10}$ [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 $Mg_{65}Cu_{25}Tb_{10}$ [10] the formation of quasicrystalline phases is reported, that transform to $Mg_2Cu$, $Mg_3Tb$ and unidentified phases during a second crystallisation stage. For $Mg_{65}Cu_{25}Y_{10}$ amorphous alloy, Murty and Hono [11] suggest the formation, as crystallisation products, of an Y containing $Mg_2Cu$, via polymorphic crystallisation. For amorphous $Mg_{60}Cu_{30}Y_{10}$, a eutectic crystallisation was suggested [12], with the formation of $Mg_2Cu$, MgY and MgCuY. $Mg_2Cu$ and $Cu_2Gd$ 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 exothermal 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 $T_g/T_m$, $T_g/T_l$, $\Delta T_x=(T_x-T_g)$ and $\gamma=T_x/(T_g+T_l)$ [13] suggests a high GFA (Tab 1).

**Table 1.** Thermal properties determined using DSC on amorphous samples ($T_g$, $T_x$, $T_m$, $T_l$, $\Delta T_x$ in °C).

| | $T_g$ | $T_{x1}$ | $T_{x2}$ | $\Delta T_x$ | $T_m$ | $T_l$ | $T_g/T_m$ | $T_g/T_l$ | $\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| $Mg_{60}Cu_{30}Gd_{10}$ | 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 |

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 $Mg_2Cu$, 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

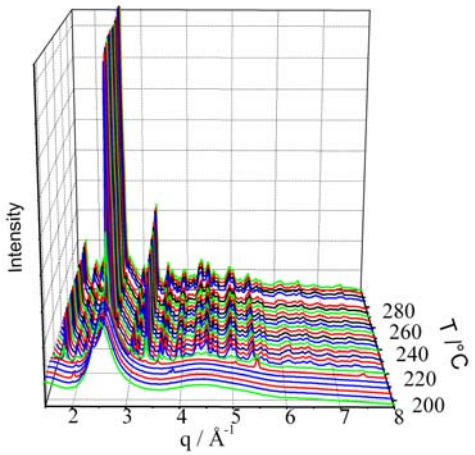


**Figure 1.** XRD patterns from *in-situ* heating experiments for $Mg_{60}Cu_{30}Gd_{10}$ amorphous alloy.

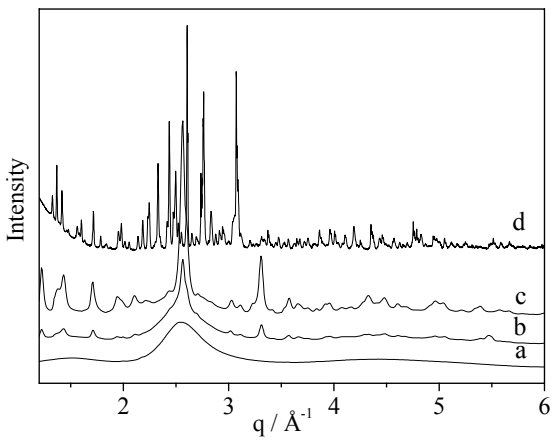


**Figure 2.** Selected XRD patterns from *in-situ* experiments for $Mg_{60}Cu_{30}Gd_{10}$ ribbon a) 40°C; b) 215°C; c) 300°C; d) $Mg_{60}Cu_{30}Gd_{10}$ annealed master alloy.

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).

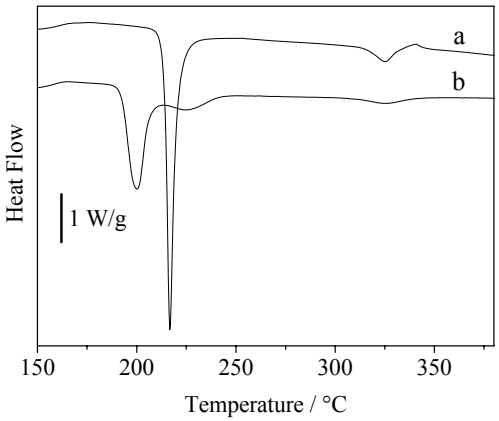


**Figure 3.** DSC traces of a) $Mg_{60}Cu_{30}Gd_{10}$; b) $Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5}$.

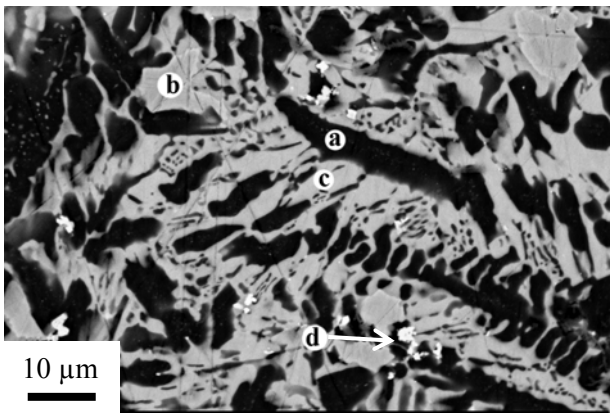


**Figure 4.** Backscattered SEM picture of $Mg_{60}Cu_{30}Gd_{10}$ annealed master alloy.

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 $Mg_{60}Cu_{30}Gd_{10}$ 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, $Mg_2Cu$ is easily recognised as the darkest phase in Fig. 4 (zone a). $MgCu_4Gd$ (zone b) and $Mg_2CuGd$ (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 $Mg_{37}Cu_{11}Gd_{52}$. Only two stable compounds are reported for the Mg-Cu-Gd system ($Mg_2Cu_9Gd$ and $MgCu_2Gd_2$) and no assessment is available for this phase diagram. So, a comprehensive analysis of the Mg-Cu-RE phase diagrams was carried out in

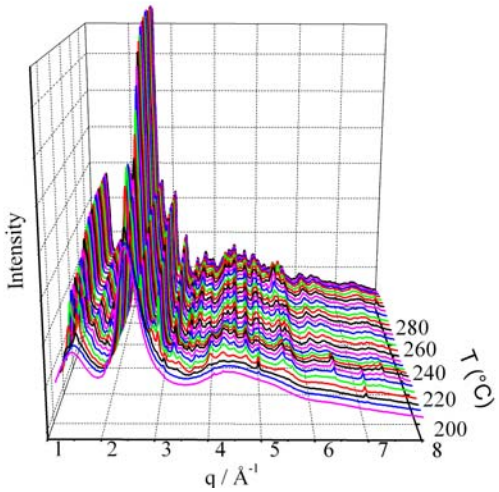


**Figure 5.** XRD patterns from *in-situ* heating experiments for $Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5}$ amorphous alloy.

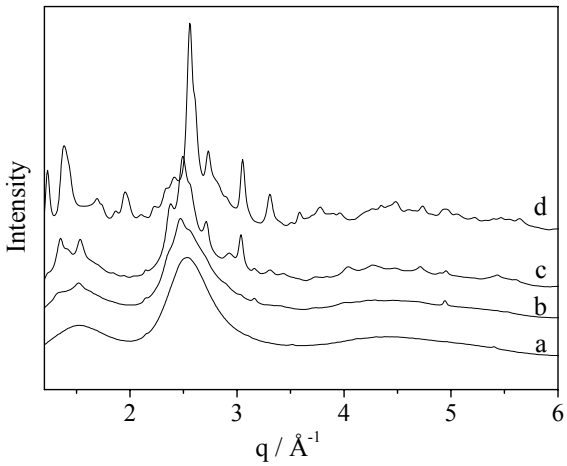


**Figure 6.** Selected XRD patterns from *in-situ* experiments for $Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5}$ ribbon a) 40°C; b) 198°C; c) 205°C; d) 300°C.

order to investigate on ternary compounds in similar systems [14-15]. $MgCu_4RE$ and $Mg_2CuRE$ 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 $Mg_{60}Cu_{30}Gd_{10}$ annealed master alloy (Fig. 2d). Concerning zone d, $Mg_{37}Cu_{11}Gd_{52}$ 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 $Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5}$ ribbons were also crystallized *in-situ* (Fig. 5) and corresponding selected XRD patterns are given in Fig. 6. The addition of Nd to the $Mg_{60}Cu_{30}Gd_{10}$ alloy produces a shoulder to the DSC crystallisation peak, as shown in Fig. 3b. The characteristic temperatures of $T_g$, $T_x$ and $T_m$ appear rather similar to those of $Mg_{60}Cu_{30}Gd_{10}$ (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 $Mg_{60}Cu_{30}Gd_{10}$ (Fig. 2c) and $Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5}$ (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 $Mg_{60}Cu_{30}Gd_{10}$ and $Mg_{60}Cu_{30}Gd_{1.5}Nd_{8.5}$ amorphous alloys was studied by DSC and *in-situ* synchrotron XRD. Crystallisation processes involved the formation of $Mg_2Cu$ compound, together with unknown phases. The existence of two new ternary compounds in the Mg-Cu-Gd system ($MgCu_4Gd$ and $Mg_2CuGd$) was suggested, based on SEM/EDS microanalysis on the $Mg_{60}Cu_{30}Gd_{10}$ 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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