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## **Influence of Rare-earth addition on the Long-Period Stacking Ordered phase in cast Mg-Y-Zn alloys**

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### **Abstract**

The microstructure and thermal stability of the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$  (at.%) alloy, modified with the addition of 0.5 at.% of gadolinium or neodymium, have been examined by synchrotron radiation diffraction during in-situ differential scanning calorimetry. The microstructure of the three alloys consists of magnesium dendrites with the *Long Period Stacking Ordered* (LPSO) phase at interdendritic regions. Rare-earth atoms substitute yttrium atoms in the LPSO phase, promoting the formation of the 14H structure. Lattice parameters of the LPSO do not change significantly with the rare earth addition. However, they reduce the melting point of the LPSO phase, especially in the case of neodymium addition.

**Keywords:** Magnesium alloys; LPSO; Synchrotron diffraction.

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## 1. Introduction

Magnesium alloys combining yttrium/rare earth (Y, Gd, Nd, Dy, etc) elements and transition metals (Zn, Cu, Ni) are effectively strengthened by the presence of *Long Period Stacking Ordered* (LPSO) structures [1-8]. They can combine high strength with acceptable ductility and enhanced creep resistance. LPSO-phases are solid solutions of yttrium or rare-earth elements and transition metals in the magnesium lattice, where these atoms are arranged periodically in the magnesium basal planes forming ordered structures [9-12]. *Different LPSO crystal structures have been reported, i.e., 6H, 10H, 14H, 18R and 24R [13-15] depending on the thermal history of the material. The 18R structure is observed mainly in the as-cast condition. However, this structure is not stable at high temperature and is gradually replaced by a 14 H structure[11]. Recently, Egusa and Abe[12] have proposed crystal/order structural models for 18R and 14H phases formed in Mg–Zn–RE alloys. These phases can be rationalized by space groups  $C2/m$ ,  $P3_112$  or  $P3_212$  for the 18R type and  $P63/mcm$  for the 14H type. The characteristic ordered features are well represented by local  $Zn_6RE_8$  clusters, which are embedded in the fcc stacking layers in accordance with the  $L1_2$  type short-range order.*

A  $Mg_{97}Y_2Zn_1$ (at.%) alloy produced by warm extrusion of rapid solidified ribbons exhibited high yield strength, about 610 MPa, with 5% of elongation at room temperature[1]. Recently, Yamasaki et al.[4] have developed extruded  $Mg_{97}Y_2Zn_1$ (at.%) alloys that combine high yield stress (around 350 MPa) and acceptable ductility (around 8%) by controlling the cooling rate during the casting process and the extrusion parameters.

Optimization of the microstructure by developing fine lamella inside the magnesium grains can be achieved through an appropriate thermal treatment, resulting in additional

strengthening[8,16,17]. At room temperature, the hardening induced by these long plates is small. This fact is attributed to the crystallographic orientation of the precipitates within the magnesium matrix. Since they are located in basal planes, they have a low hardening effect on the basal slip system[18]. However, at high temperature, where non-basal slip systems are active, the lamellar structure increases the creep resistance of these alloys [8]. *In a recent review about precipitation and hardening in magnesium alloys[19], Nie concluded that precipitate plates formed on prismatic planes provide the most effective barrier to gliding dislocations and propagating twins in the magnesium matrix. The formation of this kind of precipitates has been reported in Mg-Y-RE systems, such a Mg-Y-Nd, Mg-Gd, Mg-Gd-Nd, etc. Moreover, Nie suggested that a higher strength can be achieved if a high density of strong plate-shaped precipitates with prismatic and basal habit planes and with a high aspect ratio can be introduced. Recently, it has been reported that the addition of rare-earth elements to the Mg-Y-Zn system containing LPSO phases promote the formation of plates in the prismatic and basal planes, preserving the LPSO phase in some conditions, and considerably increasing the strength of Mg-Y-RE-Zn(RE=Gd and Nd) alloys at room temperature[20-22].*

The presence of additional elements can modify the crystallography and thermal stability of the LPSO phase. Therefore, this paper explores the influence of the addition of 0.5 at.% of Gd and 0.5 at.% of Nd to the  $Mg_{97}Y_2Zn_1$ (at.%) alloy.

## **2. Experimental procedure**

Three alloys with nominal compositions  $Mg_{97}Y_2Zn_1$ (at.%),  $Mg_{96.5}Y_2Zn_1Gd_{0.5}$ (at.%) and  $Mg_{96.5}Y_2Zn_1Nd_{0.5}$ (at.%) were prepared by melting high purity elements Mg and Zn and Mg-22%Y(wt.%), Mg-20%Gd(wt.%) and Mg-22%Nd (wt.%) master alloys in an

electric resistance furnace. The three alloys were cast in a 12 mm diameter cylindrical steel mould. For comparative purposes, a fully LPSO alloy with composition  $\text{Mg}_{88}\text{Y}_8\text{Zn}_4(\text{at.}\%)$  was also prepared in an induction melting furnace using a graphite tube coated with boron nitride in argon atmosphere. The fully LPSO alloy was homogenized at 350 °C for 24 hours.

Microstructural characterization of the alloys was carried out by optical (OM), scanning (SEM) and transmission electron microscopy (TEM). Specimens for TEM observation were prepared by electrolytic polishing using a reactive mixture of 25% nitric acid and 75 % methanol at -20°C and 20V. Then, ion milling at liquid nitrogen temperature was used to remove the fine oxide film formed on the surface during electrolytic polishing.

The thermal stability of the three alloys was monitored by DSC experiments using heating/cooling rates of 10  $\text{Kmin}^{-1}$  under argon atmosphere in a Mettler Toledo 822 DSC equipment. The samples were subjected to one DSC heating/cooling cycle between RT and 570 °C.

Synchrotron radiation diffraction was performed at the P07 – HEMS beamline of PETRA III, at the DeutschesElektronen-Synchrotron (DESY) during in-situ DSC experiments. The samples were encapsulated in stainless steel crucibles during the measurement, using an empty crucible as reference. The DSC unit was placed inside the coil of a Bähr 805A/D dilatometer. The dilatometer and the DSC unit are modified for synchrotron experiments. Two Kapton windows on the sides of the chamber and a hole in the DSC pan allow the high energy X-ray beam to reach the sample and the detector without disturbance. The measurements were performed in argon flow. The diffraction patterns were recorded using an exposure time of 1 s by a Perkin-Elmer XRD 1622 flatpanel detector with an array of  $2048^2$  pixel, with an effective pixel size of  $200 \times 200 \mu\text{m}^2$ . The beam energy was 100 keV, corresponding to a wavelength of 0.0124 nm.

LaB<sub>6</sub> was used as a reference to calibrate the acquired diffraction spectra. The detector-to-sample distance was 1918.95 mm. Conventional line profiles were obtained by azimuthal integration of the Debye-Scherrer rings. The heating/cooling rate of the DSC was 40 Kmin<sup>-1</sup> and 10 Kmin<sup>-1</sup> below and above 400 °C, respectively. Similarly to the laboratory DSC scans, the samples were subjected to one DSC cycle between RT and 560 °C.

### 3. Results and Discussion

Figure 1(a-c) shows the microstructure of the MgY<sub>2</sub>Zn<sub>1</sub>(RE<sub>0.5</sub>) alloys in the as-cast condition. The microstructure consists of magnesium dendrites with the LPSO phase distributed at interdendritic regions. The volume fraction of LPSO phase is similar for the three alloys, about 22 vol.%. The Mg<sub>88</sub>Y<sub>8</sub>Zn<sub>4</sub>(at.%) alloy consists of long LPSO laths with a small volume fraction of magnesium islands (Figure 1d).

Figure 2 (a-h) shows the Debye-Scherrer rings obtained at RT for the alloys in the as-cast condition. It is interesting to note that diffuse scattering (streaking) is observed in the case of the LPSO phase in the MgY<sub>2</sub>Zn<sub>1</sub>(RE<sub>0.5</sub>) alloys. This is especially marked for the smaller diffraction ring that corresponds to (0003) reflex of the 18R LPSO phase. Okuda et al.[23], using SAXS, reported diffuse streaks connecting diffracted spots suggesting that 18R and 10H structures coexist in a coherent way in the same grains. However, in this case, these diffuse streaks are not observed connecting reflexes from other LPSO structures. On the other hand, similar diffuse streaking has been observed in diffraction patterns by TEM. Li et al.[24] showed diffuse streaking in the [0001] direction due to the formation of stacking faults (SFs) in the (0001) basal plane of deformed pure magnesium. Garces et al.[8] also observed diffuse streaking along the [0002] direction in the magnesium grains of MgY<sub>2</sub>Zn<sub>1</sub> alloys heat treated at high

temperature. This diffuse streaking was related to stacking faults in the basal plane due to the formation of long LPSO precipitates having the 14H structure. The fact that the streaking is radial to the diffraction ring indicates that the SFs are located parallel to the (0003) planes, namely in the  $c$  direction of the 18R LPSO lattice.

*The integration of the Debye-Scherrer rings to obtain the diffraction patterns as a function of  $2\theta$  has been carried out using the software Fit2D[25]. As an example, Figure 3 shows the indexed Debye-Scherrer rings and the  $2\theta$  diffraction patterns for the  $MgY_2Zn_1$  alloy. Figure 4 shows the integrated diffraction patterns obtained at room temperature for the four alloys in the as-cast condition together with the theoretical diffraction reflections of Mg and those of the 18R and 14H LPSO phase. The diffraction pattern of the 18R and 14H crystal structures were simulated using Carine 3.1[26] according to the structure described in[12]. The 18R type and 14H type crystal structures belong to the space groups  $P3_212$  and  $P6_3/mcm$ , respectively. It can be seen that the crystal structure of the LPSO phase in the four as-cast alloys corresponds mainly to the 18R structure.*

Lattice parameters of LPSO and magnesium phases can be calculated from the diffraction patterns of *Figure 4*. In all studied alloys, the use of a Rietveld fit is difficult due to the large overlapping exhibited by several reflexes of Mg and LPSO structures. Therefore, isolated peaks from each phase have been individually fitted using the software PeakFit[27]. Table 1 shows  $a$  and  $c$  values for the LPSO and magnesium phases, respectively. The lattice parameters of the LPSO phase are similar in all the cases and are in agreement with the literature[12]. The fitting errors in  $MgY_2Zn_1(RE_{0.5})$  alloys are larger than for the  $MgY_8Zn_4$  alloy because the intensity of diffracted peaks corresponding to the LPSO phase is smaller and the diffracted peaks are broader due to the diffusive scattering (Figure 2 e-g). The lattice parameter  $a$  of Mg shows an increase

with respect to pure Mg ( $a = 0.32089$  nm and  $c = 0.52101$  nm[28]). The magnesium phase in the  $\text{MgY}_2\text{Zn}_1(\text{RE}_{0.5})$  alloys contains a small amount of yttrium in solid solution which is reported to increase  $a$ , i.e. reducing the  $c/a$  ratio[29,30].

As described above, the diffuse scattering results in a very broad (0003) diffraction peak of the 18R structure, located at  $2\theta = 0.44^\circ$ . Furthermore, overlapping with a second peak at smaller angles seems to take, especially for the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloy. This may indicate the coexistence of 18R and 14H LPSO in the as-cast alloys. *Figure 5a* shows a detail of the lamellar structure corresponding to the LPSO phase in the as-cast  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloy. The contrast variation in the SEM image can be related to composition or crystallographic heterogeneities. *Figure 5b provides a two-beam bright-field image for the LPSO phase using  $g = 0002_\alpha$  diffraction vector in the  $\langle 11\bar{2}0 \rangle_\alpha$  zone axis in the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloy.* The 18R and 14H crystal structures can be identified through the selected area electron diffraction pattern (SAED) in the  $\langle 11\bar{2}0 \rangle_\alpha$  zone axis or by measuring the fringe spacing in the  $[0002]_\alpha$  direction formed when the  $\mathbf{g} = 0002$  is excited. The coexistence of 18R and 14H structures with a fringe spacing of about 1.6 and 1.8 nm, respectively, can be observed. This fact can be also observed in the SAED in the  $\langle 11\bar{2}0 \rangle_\alpha$  zone axis where the diffracted spots of both structures are overlapped. *Moreover, the SAED pattern shows weak streaks along  $[0001]$  direction and are visible through the  $\pm 1/2\{1100\}$  positions. Zhu et al.[11] indicated that the presence of these weak streaks provides important information on the ordered arrangement of Y and Zn in the 18R and 14H structures.*

Table 2 shows the composition of the LPSO phase determined by energy dispersive spectroscopy (EDS) for the three  $\text{MgY}_2\text{Zn}_1(\text{RE}_{0.5})$  alloys in the as-cast condition and after the DSC scan. The composition of the LPSO phase in the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1(\text{at.}\%)$  alloy is similar to that reported in a previous study[11]. Gadolinium and neodymium

additions have two different effects on LPSO phase composition. On one hand, zinc content slightly decreases with respect to LPSO formed in the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$  alloy. On the other hand, yttrium content decreases up to approximately 5 at.%, while the rare-earth content is around 1.5 at.% in both alloys in as-cast condition. The sum of yttrium and rare earth concentration in quaternary alloys is equal to the yttrium content in the ternary alloy, indicating that rare-earth atoms substitute yttrium atoms in the LPSO structure. Thus, an increase in the volume fraction of the LPSO phase in the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$  and  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloys may be expected due to the excess of yttrium. However, the volume fraction of the LPSO phase is similar in the three alloys (about 22 vol%) suggesting that the maximum volume fraction of the LPSO phase in the alloys is fixed by the zinc content. Therefore, the excess of yttrium and rare earth elements could favour the formation of new phases.

*Figure 6* shows laboratory DSC scans during heating and cooling for the three  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1(\text{RE})_{0.5}$  alloys. *It is important to note that the use of the term “laboratory” is used to distinguish from the DSC scans obtained in the in-situ experiments.* An endothermic peak is observed during heating and one or two exothermic peaks during cooling depending on the alloy. The endothermic and exothermic reactions are displaced to lower temperatures with the additions of rare earth elements. Neodymium results in a larger temperature displacement than gadolinium. During heating, the rare-earth-containing alloys show only one endothermic reaction, but two clear exothermic peaks can be observed during cooling. The separation between the exothermic reactions is larger for the alloy with Nd than for that with Gd addition. *Figure 7a* shows synchrotron diffraction patterns for the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1(\text{at.}\%)$  alloy at 400 °C during heating, at 560 °C (the temperature at the end of the endothermic peak) and at 400 °C during cooling. At 400 °C during heating, reflections corresponding to the magnesium matrix, the LPSO

phase with the 18R crystal structure and the stainless steel pan (SP) are observed. At 560 °C, right after the endothermic peak, the reflections of the 18R crystal structure disappear, remaining exclusively reflections from the magnesium phase and the steel pan. At 400 °C, during cooling, diffraction peaks corresponding to the LPSO phase reappear, but now with coexisting 18R and 14H structures. This indicates that the endothermic and exothermic reactions are related to melting and solidification of the LPSO phase, respectively. The addition of the rare-earth elements decreases the melting point of the LPSO phase, as it is evidenced in *Figure 6* by the displacement of the endothermic peaks of the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$  and  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloys to lower temperatures in comparison with the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$  alloy. Since the melting points of yttrium, gadolinium and neodymium are 1526, 1311 and 1010 °C[28], respectively, the highest melting point for the LPSO phase should be expected for the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ , followed by the Gd-containing and Nd-containing alloys, as observed in DSC scans. This agrees with the experimental data (end temperature of the endothermic peak: 561 °C, 556 °C and 542 °C for  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ ,  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$  and  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$ , respectively).

*Figure 7b* shows the synchrotron diffraction patterns at 400 °C during heating, at the highest temperature above the endothermic peak and at 400 °C during cooling for the four alloys in the  $2\theta$  range of 0.2-0.75°. In this  $2\theta$  range the diffraction peaks of the 18R and 14H crystallographic structures do not overlap considerably. The 18R structure is exclusively present in the alloys in as-cast condition since the cooling rate during casting was sufficiently fast to prevent formation of 14H structure[11]. However, while 18R and 14H structures coexist after the exothermic reaction during cooling in the three  $\text{MgY}_2\text{Zn}_1(\text{RE})_{0.5}$  alloys, the fully LPSO alloy only shows the 18R structure. The presence of the rare earth in solid solution in the LPSO phase has a strong influence in

its crystal structure during its formation in the course of solidification. *Figure 8* shows the diffraction patterns at low diffraction angle for the four studied alloys during cooling at the initial stage of the solidification of the LPSO phase. It must be pointed out that there is a difference of about +15 °C between the laboratory DSC and the in situ synchrotron diffraction experiments. This may arise due to the position of the thermocouple in the DSC unit of the Bähr dilatometer. This difference provokes a displacement of the temperature at which the reactions are measured but it does not influence the results. The temperature measured with the laboratory DSC equipment is more reliable and it must be considered as the correct one. Synchrotron diffraction data demonstrates that the 18R structure is formed first and then followed by the 14H one in the case of the  $\text{MgY}_2\text{Zn}_1$  and  $\text{MgY}_2\text{Zn}_1\text{Gd}_{0.5}$  alloys. However, in the  $\text{MgY}_2\text{Zn}_1\text{Nd}_{0.5}$  alloy, the 14H structure is rapidly developed and the intensity of the diffracted peak is even higher than that of the 18R structure. This is in agreement with the microstructure found in the as-cast condition, where the 14H structure is formed during solidification (*Figure 4 and 5*). These results indicate that the exothermic peak during cooling corresponds in fact to the overlapping formation of the 14H and 18R structures. However, the 18R structure is unstable and transforms into the 14H structure during heat treatments above 400 °C[11]. Therefore, the 14H structure can be expected for sufficiently slow cooling rates. However, recent work by Grobner et al.[31], which examine a phase diagram for LPSO and related phases in the Mg-rich corner of the ternary alloys, suggests a stable region in which 18R and 14H structures can coexist, as observed in this study. It is interesting to point out that in the case of the fully LPSO alloy, no 14H structure has been observed after cooling in the present work. The formation of 14H structure has been reported in the same alloy during a thermal treatment of 525 °C during 3 days[32]. Since transformation from 18R to 14H structures

is slow, it is expected that lower cooling rates are required to observe the appearance of the diffracted peaks corresponding to the 14H structure in the fully LPSO alloy.

*Figure 9* shows the microstructure of the  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy after the DSC scan. In the three alloys, the microstructure consists of magnesium and LPSO phases. The formation of a lamellar structure within the magnesium matrix is also found, identical to that reported previously in the  $Mg_{97}Y_2Zn_1$  alloy[8,16-17,33]. The chemical composition of the LPSO phase determined by EDS after the DSC scan is very close to that in as-cast condition for the  $Mg_{97}Y_2Zn_1$  and  $Mg_{97}Y_2Zn_1Gd_{0.5}$  alloys (see Table 2). However, the Nd content in the LPSO phase in the  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy falls almost 50 %. Moreover, a new quaternary intermetallic phase has formed during cooling. This phase appears at lower temperatures than the LPSO phase as evidenced by the last exothermic peak at about 505 °C for the  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy in *Figure 6*. Its composition is also listed in Table 2. The crystallography of this new phase is now under research. It has been reported that the LPSO phase forms in  $Mg_{97}RE_2Zn_1$  alloys when yttrium and gadolinium are added but not in the case of Nd[5]. Therefore, the amount of neodymium dissolved in the LPSO phase is lower, 0.8 at.% , than that of gadolinium. The excess of neodymium is free to promote the formation of the new intermetallic phase found in this work.

#### **4. Conclusions**

*The effect of the addition of 0.5 at.% of RE (Gd and Nd) on the microstructure and thermal stability of the LPSO phase in a  $Mg_{97}Y_2Zn_1$ (at.%) alloy has been studied. The microstructure of the as-cast alloy does not change significantly with the addition of Nd or Gd and consists of magnesium dendrites with the 18R LPSO phase distributed at interdendritic regions. RE atoms substitute yttrium atoms in the LPSO phase in the as-*

*cast condition and modified the crystallography of the LPSO phase, especially in the case of the addition of Nd which promotes the formation the 14H structure. Moreover, in this alloy, the LPSO phase is not stable and a new intermetallic phase is formed after the 14H and 18R LPSO phases during cooling from 570 °C at 10 Kmin<sup>-1</sup>.RE addition decreases the melting point of the LPSO phase. The lower the melting point of the RE the lower the melting point of the LPSO phase.*

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## Figure captions

Figure 1. Microstructure of the alloys in the as-cast condition. (a)  $Mg_{97}Y_2Zn_1$  alloy (OM), (b)  $Mg_{97}Y_2Zn_1Gd_{0.5}$  alloy (OM), (c)  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy (OM) and (d)  $Mg_{88}Y_8Zn_4$  alloy (SEM).

Figure 2(a-h) Synchrotron diffraction patterns obtained from the 2D detector. (a)  $Mg_{97}Y_2Zn_1$ , (b)  $Mg_{97}Y_2Zn_1Gd_{0.5}$ , (c)  $Mg_{97}Y_2Zn_1Nd_{0.5}$  and (d)  $Mg_{88}Y_8Zn_4$  alloys in as-cast condition. (e-h) Detail of the inner ring, which corresponds to the (0003) plane of the LPSO phase.

Figure 3(a-b) Synchrotron diffraction patterns (a) obtained from the 2D detector and (b) as a function of  $2\theta$  corresponding to the  $Mg_{97}Y_2Zn_1$ .

Figure 4. Synchrotron diffraction patterns as a function of  $2\theta$  corresponding to the  $Mg_{97}Y_2Zn_1$ ,  $Mg_{97}Y_2Zn_1Gd_{0.5}$ ,  $Mg_{97}Y_2Zn_1Nd_{0.5}$  and  $Mg_{88}Y_8Zn_4$  alloys. The diffraction patterns of the 18R, 14H and Mg crystal structures were simulated using Carine 3.1. SP designates diffraction reflexes of the stainless steel pan.

Figure 5. (a) Secondary electron image of the microstructure of the as-cast  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy. (b) Bright field TEM image of the LPSO phase in the as-cast  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy ( $B = \langle 11\bar{2}0 \rangle$  and  $g = (0002)$ ). (c) Selected area diffraction pattern of the  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy in the  $\langle 11\bar{2}0 \rangle$  zone axis.

Figure 6. Laboratory DSC scans (heating and cooling) recorded at  $10 \text{ Kmin}^{-1}$  for the  $Mg_{97}Y_2Zn_1$ ,  $Mg_{97}Y_2Zn_1Gd_{0.5}$  and  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloys.

Figure 7(a,b). (a) Synchrotron diffraction patterns at 400 and 560 °C during heating and at 400 °C during cooling for the  $Mg_{97}Y_2Zn_1$  alloy. (b) Synchrotron diffraction patterns at 400 °C during heating, after the endothermic peak during heating and at 400 °C during cooling for the  $Mg_{97}Y_2Zn_1$ ,  $Mg_{97}Y_2Zn_1Gd_{0.5}$ ,  $Mg_{97}Y_2Zn_1Nd_{0.5}$  and  $Mg_{97}Y_8Zn_4$  alloys.

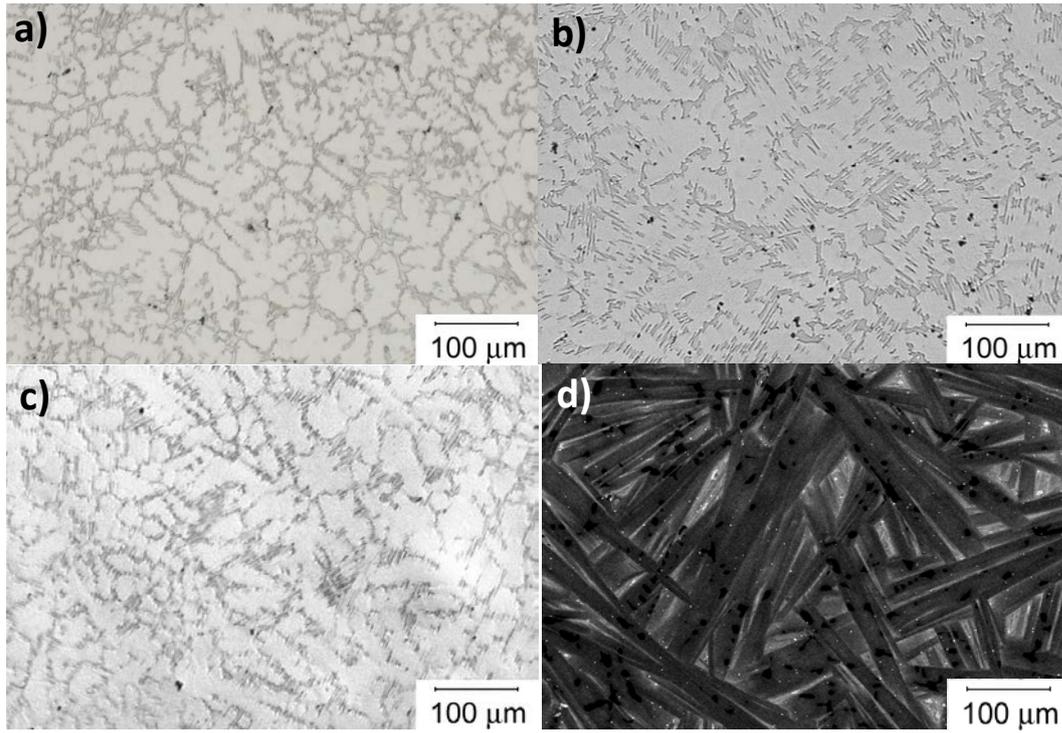
*Figure 8.* Synchrotron diffraction patterns for the (a)  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ , (b)  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$  and (c)  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloys during cooling from the solidification temperature of the LPSO phase.

*Figure 9.* Secondary electron image of the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloy after the heating/cooling scan.

### **Table captions**

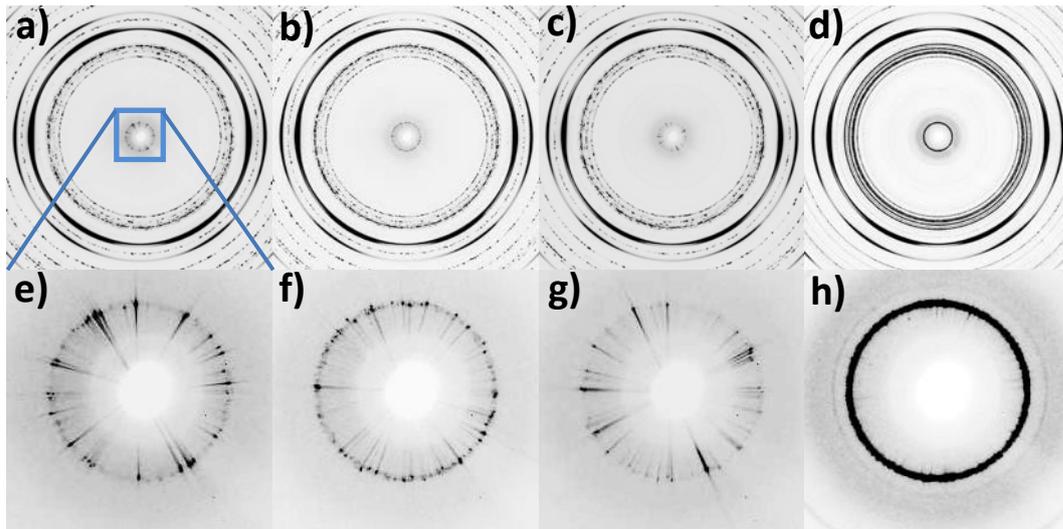
Table 1. Lattice parameters calculated from diffraction patterns of the magnesium and LPSO phases in the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ ,  $\text{Mg}_{96.5}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$ ,  $\text{Mg}_{96.5}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  and  $\text{Mg}_{88}\text{Y}_8\text{Zn}_4$  alloys.

Table 2. Composition of the LPSO phase (at.%) in the as-cast state and after the DSC scan in the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ ,  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$  and  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloys. The composition of a new Mg-Zn-Y-Nd intermetallic phase (NIP) is also given in the case of  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$ .



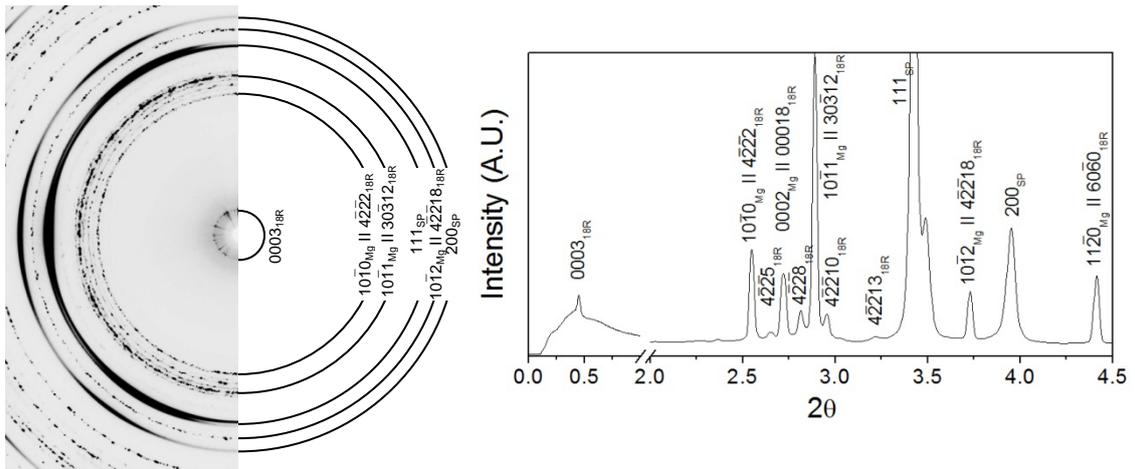
**Fig. 1**

Microstructure of the alloys in the as-cast condition. a  $Mg_{97}Y_2Zn_1$  alloy (OM), b  $Mg_{97}Y_2Zn_1Gd_{0.5}$  alloy (OM), c  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy (OM), and d  $Mg_{88}Y_8Zn_4$  alloy (SEM)



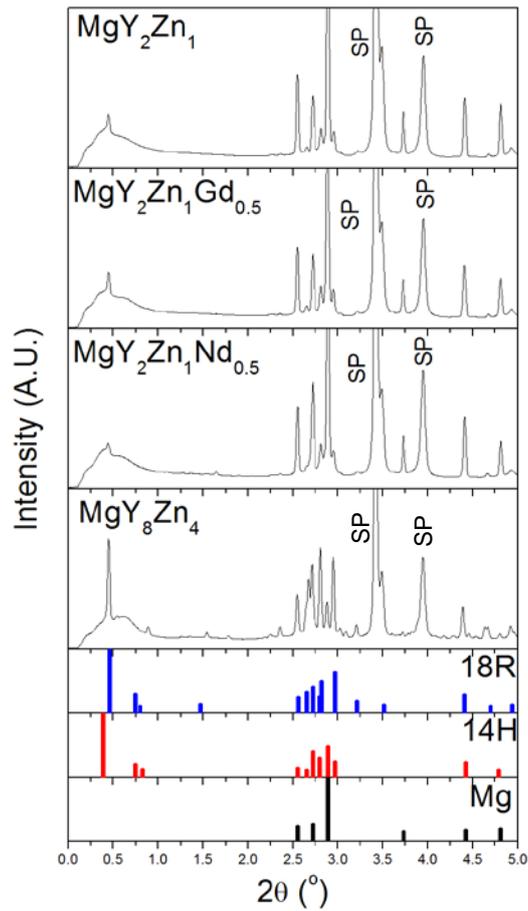
**Fig. 2**

Synchrotron diffraction patterns obtained from the 2D detector. a  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ , b  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$ , c  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$ , and d  $\text{Mg}_{88}\text{Y}_8\text{Zn}_4$  alloys in as-cast condition. e–h Detail of the inner ring, which corresponds to the (0003) plane of the LPSO phase



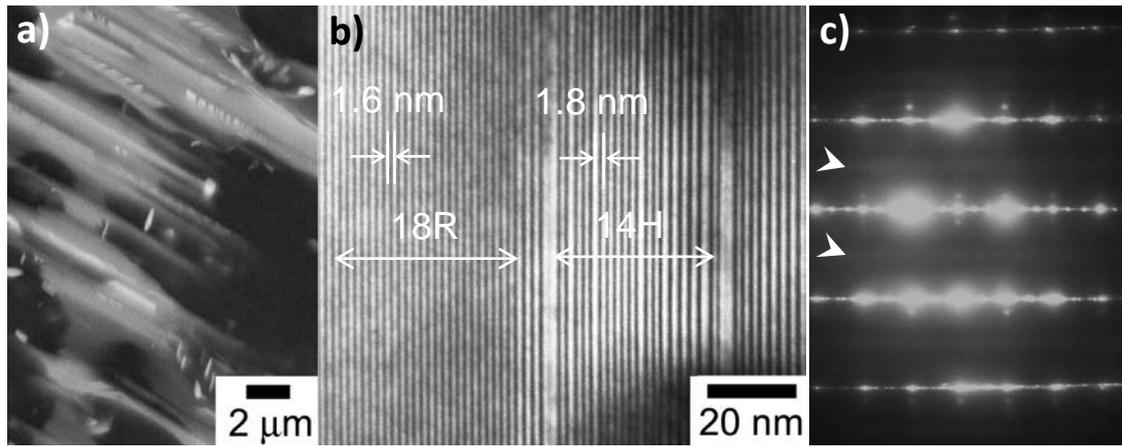
**Fig. 3**

Synchrotron diffraction patterns: a obtained from the 2D detector, and b as a function of  $2\theta$  corresponding to the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$



**Fig. 4**

Synchrotron diffraction patterns as a function of  $2\theta$  corresponding to the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ ,  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$ ,  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$ , and  $\text{Mg}_{88}\text{Y}_8\text{Zn}_4$  alloys. The diffraction patterns of the 18R, 14H, and Mg crystal structures were simulated using Carine 3.1. SP designates diffraction reflexes of the stainless SP

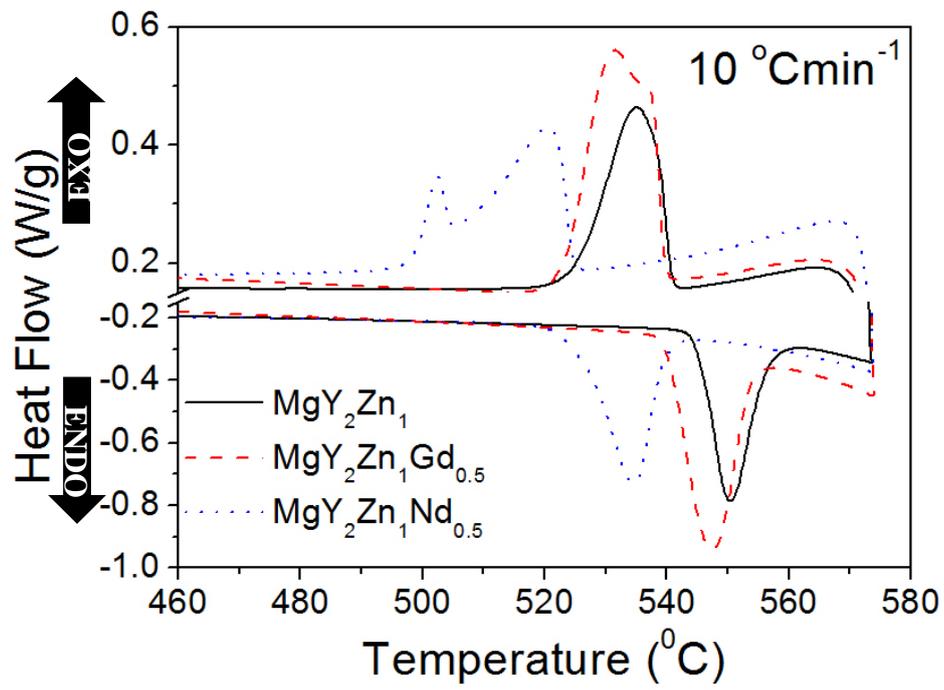


**Fig. 5**

a Secondary electron image of the microstructure of the as-cast  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy.

b Bright field TEM image of the LPSO phase in the as-cast  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy [ $B = \langle 112^- 0 \rangle$  and  $g = (0002)$ ].

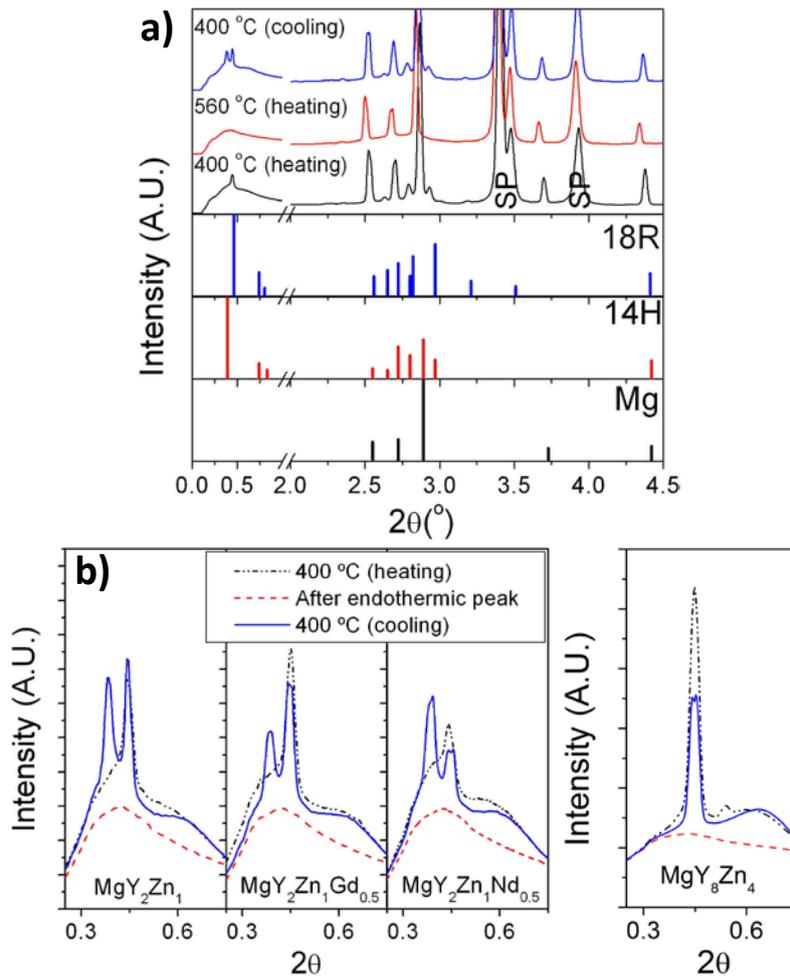
c Selected area diffraction pattern of the  $Mg_{97}Y_2Zn_1Nd_{0.5}$  alloy in the  $\langle 112^- 0 \rangle$  zone axis



**Fig. 6**

Laboratory DSC scans (heating and cooling) recorded at 10 K min<sup>-1</sup> for the Mg<sub>97</sub>Y<sub>2</sub>Zn<sub>1</sub>,

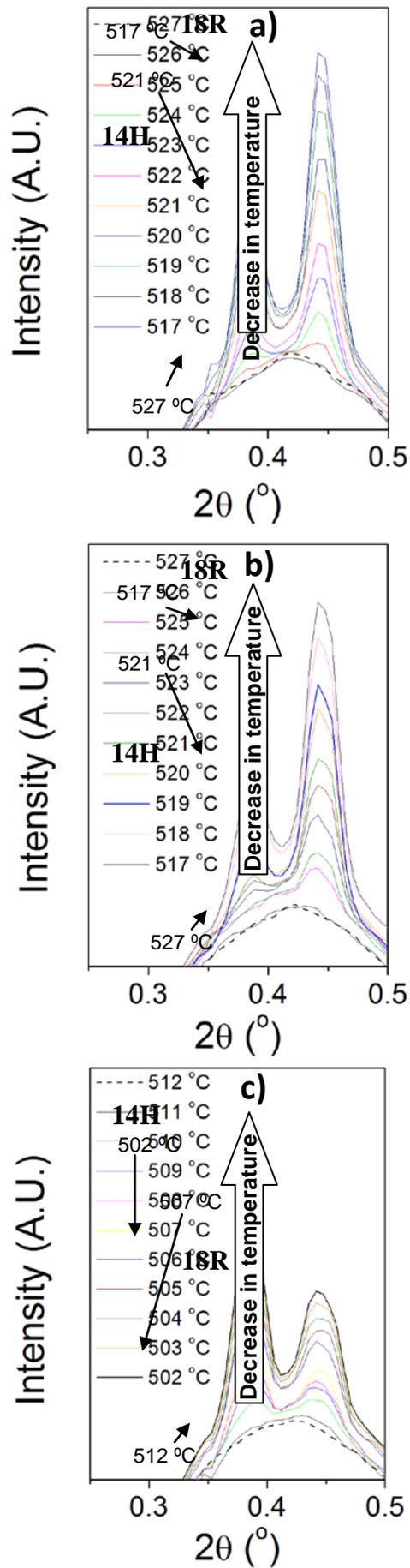
Mg<sub>97</sub>Y<sub>2</sub>Zn<sub>1</sub>Gd<sub>0.5</sub>, and Mg<sub>97</sub>Y<sub>2</sub>Zn<sub>1</sub>Nd<sub>0.5</sub> alloys



**Fig. 7**

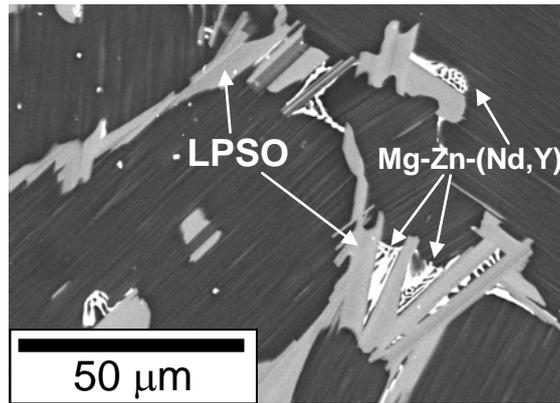
a Synchrotron diffraction patterns at 400 and 560 °C during heating and at 400 °C during cooling for the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$  alloy

b Synchrotron diffraction patterns at 400 °C during heating, after the endothermic peak during heating and at 400 °C during cooling for the  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ ,  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$ ,  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$ , and  $\text{Mg}_{97}\text{Y}_8\text{Zn}_4$  alloys



**Fig. 8**

Synchrotron diffraction patterns for the a  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ , b  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Gd}_{0.5}$ , and c  $\text{Mg}_{97}\text{Y}_2\text{Zn}_1\text{Nd}_{0.5}$  alloys during cooling from the solidification temperature of the LPSO phase



**Fig. 9**

Secondary electron image of the Mg<sub>97</sub>Y<sub>2</sub>Zn<sub>1</sub>Nd<sub>0.5</sub> alloy after the heating/cooling scan

**Table 1**

Alloy	LPSO		Mg	
	a(nm)	c (nm)	a (nm)	c (nm)
MgY <sub>8</sub> Zn <sub>4</sub>	1.111±0.003	4.72±0.07	--	--
MgY <sub>2</sub> Zn <sub>1</sub>	1.110±0.033	4.74±0.11	0.3221±0.0002	0.52067±0.0015
MgY <sub>2</sub> Zn <sub>1</sub> Gd <sub>0.5</sub>	1.111±0.020	4.73±0.16	0.3224±0.0002	0.52176±0.0013
MgY <sub>2</sub> Zn <sub>1</sub> Nd <sub>0.5</sub>	1.111±0.061	4.76±0.29	0.3221±0.0004	0.52013±0.0026

**Table 2**

<b>Alloy</b>		<b>Mg</b>	<b>Zn</b>	<b>Y</b>	<b>Gd</b>	<b>Nd</b>
MgY <sub>2</sub> Zn <sub>1</sub>	as-cast	87.2±1.2	5.2±0.2	7.3±0.2	--	--
	after DSC	86.9±1.3	5.5±0.4	7.6±0.3	--	--
MgY <sub>2</sub> Zn <sub>1</sub> Gd <sub>0.5</sub>	as-cast	88.6±1.2	4.5±0.1	5.5±0.2	1.4±0.1	--
	after DSC	88.5±1.2	4.7±0.1	5.5±0.2	1.3±0.1	--
MgY <sub>2</sub> Zn <sub>1</sub> Nd <sub>0.5</sub>	as-cast	89.4±1.4	4.4±0.1	4.7±0.3	--	1.5±0.1
	after DSC	88.6±1.5	4.5±0.1	6.1±0.4	--	0.8±0.1
	NIP	61.0±1.0	21.5±1.1	7.4±0.6	--	10.1±0.9