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Formation of an 18R long-period stacking ordered structure in rapidly solidified $Mg_{88}Y_8Zn_4$ alloy

Gerardo Garcés [a,*], Guillermo Requena [b,c], Domonkos Tolnai [d], Pablo Pérez [a], Judit Medina [a], Andreas Stark [d], Norbert Schell [e], Paloma Adeva [a]

[a] Department of Physical Metallurgy, National Center for Metallurgical Research (CENIM-CSIC), Avda. Gregorio delAmo 8, 28040 Madrid, Spain
[b] Institute of Materials Research, German Aerospace Centre, Linder Höhe, 51147 Köln, Germany
[c] RWTH Aachen, 52062 Aachen, Germany
[d] Institute of Materials Research, Helmholtz-ZentrumGeesthacht, Max-Planck-Str. 1, 21502 Geesthacht, Germany
[e] Structural Research on New Materials, Helmholtz-ZentrumGeesthacht Outstation at DESY, Hamburg, Germany

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ABSTRACT

The formation of the long-period stacking ordered structure (LPSO) in a $Mg_{88}Y_8Zn_4$(at%) ribbon produced by melt spinning was studied using high energy X-ray synchrotron radiation diffraction during in-situ isochronal heating and transmission electron microscopy. The microstructure of the rapidly solidified ribbons is characterised by fine magnesium grains with yttrium and zinc in solid solution and primary 18R LPSO-phase segregated at grain boundaries. Using differential scanning calorimetry, a strong exothermal peak was observed around 300 °C which was associated with the development of the 18R-type LPSO-phase in the magnesium grains. The apparent activation energy calculated using the Kissinger model was 125 $KJmol^{-1}$ and it is related to simultaneous diffusion of Y and Zn through magnesium basal plane.

1. Introduction

The development of new magnesium alloy systems with thermally stable reinforcing phases is a strategy to improve the mechanical strength of Mg alloys, especially at intermediate temperatures.

Recent studies have shown that the presence of Long-Period Stacking Ordered (LPSO) structures in Mg-Y,RE-TM (RE = rare earth element, TM = transition metal) alloys results in an increase in the mechanical strength and creep resistance [1–12]. Furthermore, when they are processed by rapid solidification techniques it is possible to obtain superior performances with extremely high yield stress (600 MPa) and elongations of 5% at room temperature [13].

The LPSO-phase is a long-range stacking of basal planes with periodic enrichment of transition metals and yttrium or certain rare earth elements with chemical order. Different LPSO structures have been reported in the bibliography [13–16]. The 18R-type structure is commonly observed in the cast condition and it transforms to 14H at high temperatures [15–17]. This transformation is proposed to be a diffusional-displacive transformation controlled by the diffusion rate of Y and Zn atoms in the basal planes enriched in both elements [17].

The 18R-type structure is commonly observed as primary phase at grain boundaries and also as thin lamellar precipitates inside Mg grains. However, neither the formation of the 18R LPSO phase nor the diffusion energy values associated with the formation of LPSO structure have been reported. Recently, Shiratake et al. [18] have studied the formation of the LPSO phase in rapidly solidified (RS) $Mg_{85}Y_9(Zn,Ni,Cu)_6$ ribbons with an amorphous structure. The crystallization process at intermediate temperatures occurs in two stages: 1) Formation of magnesium clusters followed by 2) the development of the 18R-type LPSO-phase.

This paper studies the formation of the LPSO phase in rapidly solidified ribbons of the $Mg_{88}Y_8Zn_4$(at%) alloy. The formation of the LPSO-phase is analyzed using high energy synchrotron diffraction during in-situ differential scanning calorimetry (DSC) experiments and transmission electron microscopy (TEM).

2. Experimental procedure

A $Mg_{88}Y_8Zn_4$ (at%) alloy was melted in an induction furnace under inert atmosphere conditions using a graphite crucible coated with boron nitride and cast in a steel mould; the details of the procedure have been described elsewhere [19]. Small samples were re-melted for preparing melt spun ribbons, using a controlled atmosphere melt spinning apparatus. Helium at 1/3 atmospheric pressure was employed in the present series of experiments. Samples of the alloy, each weighing

* Corresponding author.
E-mail address: ggarces@cenim.csic.es (G. Garcés).

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approximately 5 g, were placed in a quartz crucible coated with a boron nitride to prevent reaction with the melt, and then inductively melted and forced by helium pressure on a rotating copper wheel. Melt spun ribbons were 22 μm thick and 2.4 mm wide, approximately and they had a smooth appearance.

Microstructural characterization of the ribbons was carried out by scanning and transmission electron microscopy (SEM and TEM) and high energy synchrotron radiation diffraction. Furthermore, the thermal stability of the ribbons was monitored by DSC experiments using heating rates from 10 to 40 $Kmin^{-1}$ under argon atmosphere in a Mettler Toledo 822 DSC apparatus.

Specimens for TEM observation were prepared by ion milling at liquid nitrogen temperature.

High energy synchrotron radiation diffraction was performed at the P07B – 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 DIL 805 A/D dilatometer (TA Instruments, Hüllhorst, Germany) which is modified for synchrotron radiation experiments. Two Kapton windows on the sides of the chamber and a hole in the DSC furnace 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 flat-panel detector with an array of 2048^2 pixel and an effective pixel size of $200 \times 200\ \mu m^2$. The beam energy was 100 keV, corresponding to a wavelength of 0.0124 nm. LaB_6 was used as a reference to calibrate the acquired diffraction spectra. The detector-to-sample distance was 1735 mm. Conventional line profiles were obtained by azimuthal integration of the Debye-Scherrer rings using the software FIT2D [20]. The heating rate of the DSC was 20 $Kmin^{-1}$.

3. Results and discussion

Fig. 1a shows the microstructure of the $Mg_{88}Y_8Zn_4$(at%) alloy in the as-cast condition. The microstructure consists of long LPSO-phase laths with a small volume fraction of α-magnesium islands (dark gray regions). This microstructure is in agreement with previous studies [19]. The crystal structure of the LPSO-phase in the as-cast alloy corresponds to the 18R structure as observed in the high energy synchrotron radiation diffraction pattern of Fig. 2. The magnesium island has a α-Mg hexagonal crystal structure. This structure is identified in the diffraction pattern by the diffraction peak located at $2\theta = 0.44°$ that corresponds to the (0003) plane of 18R-LPSO phase [21].

The ribbon in the rapidly solidified condition (RS) presents a microstructure characterised by α-magnesium grains (around 200 nm) with the LPSO-phase (primary LPSO-phase) segregated at grain boundaries (Fig. 1b). The cooling rate is not fast enough to avoid the formation of segregated LPSO phase at grain boundaries. The compositional analysis, made by EDX, showed that the magnesium grains are enriched by yttrium and zinc (4.5 ± 0.2 of Y and 1.6 ± 0.1 of Zn, at.%).

The X-ray diffraction pattern of the RS ribbon is considerably different with respect to the as-cast alloy, showing mainly the diffraction peaks corresponding to α-magnesium phase (Fig. 2b). Furthermore, the position of the α-Mg diffraction peaks is slightly shifted from their position of pure α-magnesium due to the increased solid solubility of yttrium and zinc, common in the rapidly solidification process. It is interesting to point out that small diffraction peaks corresponding to {42 $\bar{2}$10} planes of the 18R structure, arising from the primary LPSO phase located at grain boundaries, are also present.

The thermal stability of the RS ribbons was evaluated through DSC tests. Fig. 3a shows the evolution of the heat flow at heating rates of 10, 20, 30 and 40 $Kmin^{-1}$. A pronounced exothermal reaction is observed at intermediate temperatures. The amplitude and temperature

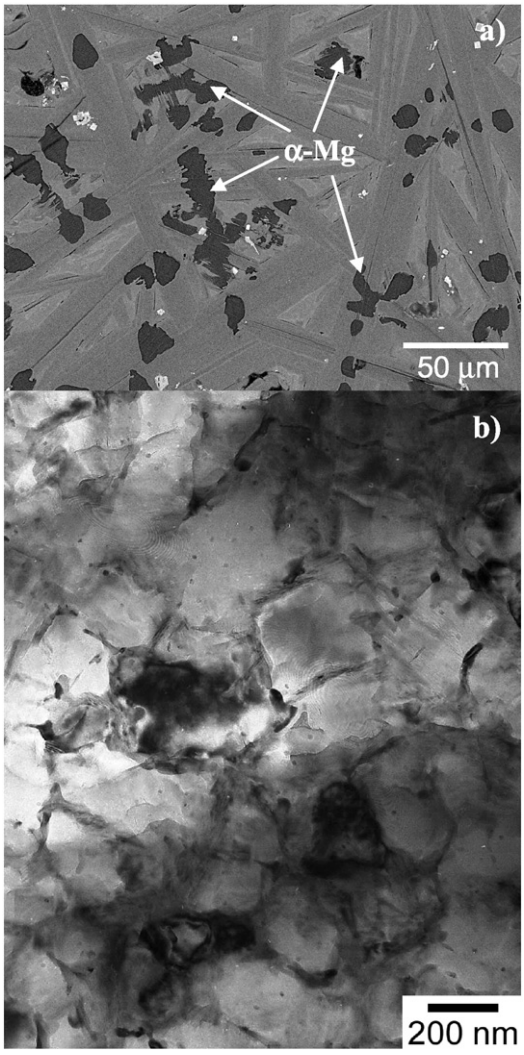

Fig. 1. Microstructure of the $Mg_{88}Y_8Zn_4$(at%) alloy in the a) cast and b) RS condition. Arrows in a) indicate the α-Mg phase.

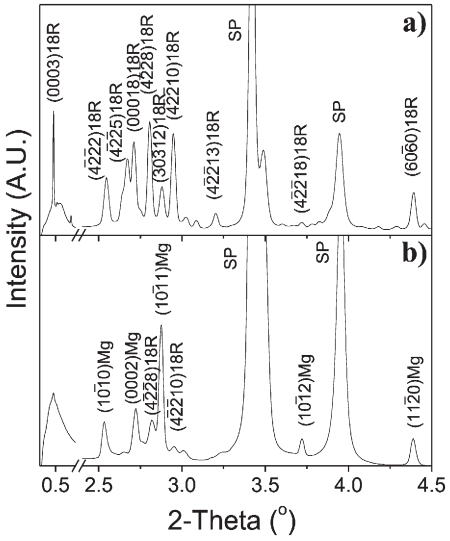

Fig. 2. High energy synchrotron radiation diffraction pattern of the $Mg_{88}Y_8Zn_4$(at%) alloy in the a) cast and b) RS condition. SP indicates diffraction reflexes of the stainless steel crucibles.