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# Microstructural changes in an extruded Mg––Zn––Y alloy reinforced by quasicrystalline I-phase by small additions of calcium, manganese and cerium-rich mischmetal

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ABSTRACT

The effects of calcium, manganese and cerium-rich mischmetal additions on the microstructure and texture of the extruded Mg—6Zn—1Y (wt.%) alloy have been investigated. The microstructure of the alloys consisted of a magnesium matrix embedding second phase particles aligned along the extrusion direction. The nature and volume fraction of the second phases depended on the alloying element. Thus, Ce-rich mischmetal promoted the formation of T-phase while calcium additions resulted in the formation of a ternary Mg—Zn—Ca compound. Only, manganese additions did not affect the existence of the I-phase present in the ternary alloy. The texture was measured and it was found that calcium addition has a significant effect weakening the extrusion texture.

## 1. Introduction

Magnesium alloys have great potential for applications in structural parts as they are the lightest metallic structural material. However, their use is still limited because of their low ductility and insufficient strength at room temperature and at high temperatures, and poor corrosion resistance. Many efforts and attempts are being devoted to modifying the composition/microstructure of magnesium alloys to overcome such disadvantages. Thus, the strength of magnesium alloys can be enhanced by adding proper amounts of certain alloying elements and/or by controlling the thermomechanical processing. Accordingly, the mechanical strength of magnesium has increased through the development of a great number of alloy families like Mg—Al—Zn (AZ alloys), Mg—Al—Mn (AM alloys), Mg—Al—Si (AS alloys) or Mg—Al—RE (AE alloys) (RE denotes rare earth elements) [1,2]. More recently, new high-strength Mg—Zn—Y and Mg—Zn—RE alloys have been developed, whose hardening is attributed to the presence of ternary Mg—Zn—Y phases. Depending on the concentration Zn/Y ratio, different kinds of second phases are formed: Long period stacked ordered phases (so-called LPSO-phases), W-Phase ($Mg_3Zn_3Y_2$), I-phase ($Mg_3Zn_6Y$) and $Mg_7Zn_3$ [3–7]. Among these phases, the quasicrystalline I-phase with its quasiperiodic lattice structure has attracted a lot of attention because of its unique properties as high hardness, thermal stability, high corrosion resistance, low friction coefficient and strong bonding with the magnesium matrix [8–14]. Despite of the good properties of these new Mg alloys, an additional increase of strength is required to replace Al alloys in structural applications. A possible way for enhancing the mechanical properties of Mg—Zn—Y alloys containing the I-phase could be the addition of small amounts of a fourth element. Based on the effect on other magnesium alloys, calcium, manganese and cerium-mischmetal (CeMM) were chosen as alloying elements. Calcium and RE additions refine the microstructure of magnesium alloys and improve the strength at room and high temperatures through the formation of hard intermetallic phases [2,15–21]. Moreover, both elements contribute to randomize the basal texture [22]. The complete insolubility of manganese produces a fine dispersion of manganese particles in the magnesium matrix which strengthens the alloy through the refining of the grain size in magnesium alloys [23,24].

In the present work, the effect of Ca, Mn or Ce-rich mischmetal (CeMM) additions on the microstructure of extruded Mg—6Zn—1Y (wt.%) alloy has been investigated. Special emphasis has been dedicated to determine the nature and stability of the phases present as well as their influence over the texture of the extruded bars. In order to

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understand the nature of second phases of extruded alloys, characterization of as-cast alloys was at first done.

## 2. Experimental

The master alloy Mg—6Zn—1Y (wt.%) was prepared by melting pure magnesium, zinc and yttrium in an electric resistance furnace. This alloy was modified by the addition of small amounts of a fourth element: 1% Ca (wt.%), 1% Mn (wt.%) and 3.5% CeMM (wt.%). The CeMM has a RE content of 99.6 (at.%) distributed as follows: 51.88% Ce (at.%), 26.50% La (at.%), 5.22% Pr (at.%) and 16.41% Nd (at.%). It is interesting to remark that 1% Ca (wt.%), 1% Mn (wt.%) and 3.5% Ce-rich mischmetal (wt.%) additions correspond to around 0.5 at.% of each element. The alloys were obtained by casting in a cylindrical steel mould of 45 mm in diameter and 50 cm in length. Designations, nominal and chemical compositions of the alloys determined by micro X-ray fluorescence are listed in Table 1.

Billets were ground to 41 mm and directly extruded at 300 °C using an extrusion ratio of 18:1. Microstructural characterization of alloys was carried out by X-ray diffraction (XRD) as well as by optical microscopy (OM). Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope and transmission electron microscopy (TEM) was carried out on a Jeol-2010.

Thermal stability of as-cast alloys was performed by differential scanning calorimetric (DSC) experiments in Setaram SETSYS evolution equipment at a heating rate of 20 K/min under argon atmosphere. The samples were heated from room temperature up to 650 °C. Additionally high-energy X-ray diffraction (HEXRD) was performed at the P07 beam-line of PETRA III, at the Deutsches Elektronen-Synchrotron (DESY) during in situ DSC experiments. The samples were encapsulated in stainless steel crucibles. The DSC unit of a DIL 805A/D dilatometer was modified for synchrotron experiments, having a hole allowing the X-ray beam to reach the sample. The energy of the synchrotron X-ray source was 87.1 keV corresponding to a wavelength of 0.01424 nm. The diffraction patterns were collected using a 2D Perkin Elmer XRD1621 flat panel detector with an array of 2048 × 2048 pixels, with a $200 \times 200\ \mu m^2$ pixel size and located 2350 mm from the sample. $LaB_6$ standard powder sample was used as a reference to calibrate the acquired diffraction spectra. The samples were exposed to one DSC cycle from room temperature (RT) up to 700 °C with a heating rate of 20 K/min. The diffraction patterns observed as Debye–Scherrer rings were collected every 4 s and then integrated using Fit2D software in order to obtain the diffraction pattern as a function of 2θ. To distinguish between two DSC experiments, DSC measurements run in Setaram equipment will be designated as "conventional DSC experiments" while those obtained by synchrotron radiation will be called "in-situ DSC experiments".

X-ray diffraction was used for phase identification and texture analysis. Measurements were performed in a Siemens D5000 X-ray diffractometer (XRD) using Cu Kα radiation. Texture data were analyzed by TextEval software.

Phase characterization, determination of the volume fraction of second phases and grain sizes of all alloys were studied by OM, SEM and TEM and EDS microanalysis. Volume fraction of second phases was estimated by image analysis technique (OPTIMAS software). Statistical measurements of particle and grain sizes were calculated with the software Sigma Scan Pro using OM and SEM micrographs.

Micro-texture analysis of extruded alloys was also done by Electron Backscattered Diffraction (EBSD) technique attached to the SEM equipment. Data of EBSD were analyzed using Channel 5 EBSD software. The samples have a cylindrical symmetry where the reference directions are: ED (extrusion direction), TD (transversal direction) and ND (normal direction). For Orientation Image Mapping the scan size was set at 0.2–0.3 μm. High angle grain boundaries >10° and low angle grain boundaries >2° are represented by black and white lines, respectively.

Metallographical preparation of samples for optical and scanning electron microscopy observation consisted of conventional mechanical polishing, and finishing with a solution of colloidal silica. The grain structure was revealed with a solution of 0.5 g of picric acid, 0.5 ml of acetic acid, 0.5 ml of water and 25 ml of ethanol. Specimens for transmission electron microscopy were thinned by electrolytic polishing using the reactive mixture of 25% nitric acid and 75% methanol at −20 °C and 20 V. Then, ion milling at liquid nitrogen temperature was used to remove the fine oxide film formed on the surface.

EBSD samples required a very carefully metallographical preparation because of the high reactivity of magnesium. Thus, the specimens were ground with 320, 600, 1200 and 2000 grit SiC paper, polished with a solution of colloidal silica in ethanol and finally chemically etched.

## 3. Results

### 3.1. Characterization of as-cast alloys

The microstructure of all alloys consists of magnesium dendrites with different intermetallic phases at the interdendritic spaces resulting from solidification of the liquid enriched in alloying elements. The alloying addition determines the nature of the phases present in the interdendritic regions. The interdendritic regions are constituted by eutectic pockets of binary Mg + I-phase in the ternary alloy and in the Mn1 alloy, as can be seen in the backscattered electron images of Fig. 1a and b. In the case of Mn1 alloy, some fine particles inside the magnesium dendrites are also detected (see Fig. 1b). The volume fraction and nature of the second phases existing at the interdendritic space are different for Ca1 and CeMM3.5 alloys. Thus, two different phases can be clearly identified at the interdendritic regions (Fig. 1c), a predominant light grey phase and a bright minority phase close to it. The main phase corresponds to a Ca-rich phase without yttrium while the second one is a ternary Mg—Zn—Y compound with the stoichiometry of W-phase. Two phases can be also distinguished inside the interdendritic regions in CeMM3.5 alloy, as observed in Fig. 1d. A semiquantitative composition determined by EDS microanalyses reveals that the dark phase contains Mg, Zn, and Ce, while the bright phase, surrounding the mentioned Ce-rich phase is composed by Mg, Zn and Y with a composition close to that of the W-phase.

Fig. 2 compares isochronal conventional DSC curves. During heating the endothermic peaks can be associated with different transformations. The in-situ synchrotron diffraction patterns obtained at different points in the curve during the heating (see Fig. 3) allow identifying the evolution of the phases. Three transformations are detected in the curves. Temperatures of the different transformations are listed in Table 2. Common for all alloys is the last peak, also the most intense, which is produced by the melting of magnesium dendrites. The first

**Table 1**
Nominal composition (wt.%) and chemical composition determined by micro X-ray fluorescence (wt.%) and designation of Mg–Zn–Y alloys.

| | Nominal composition (wt.%) | | | | | | X-ray fluorescence results (wt.%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloy designation | Mg | Zn | Y | Mn | Ca | CeMM | Mg | Zn | Y | Mn | Ca | CeMM |
| 6-1 | 93.0 | 6.0 | 1.0 | – | – | – | 93.0 | 6.0 | 1.0 | – | – | – |
| Mn1 | 92.0 | 6.0 | 1.0 | 1.0 | – | – | 90.6 | 7.4 | 1.0 | 1.0 | – | – |
| Ca1 | 92.0 | 6.0 | 1.0 | – | 1.0 | – | 92.0 | 6.3 | 0.9 | – | 0.8 | – |
| CeMM3.5 | 89.5 | 6.0 | 1.0 | – | – | 3.5 | 89.5 | 6.6 | 1.0 | – | – | 2.9 |