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Microstructure of die cast and thixocast ZAEX10430 (Mg–10Zn–4Al–3Ce–0.3Ca) alloy

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ABSTRACT

The microstructure and phase composition of die cast and thixocast ZAEX10430 (Mg–10Zn–4Al–3Ce–0.3Ca) alloy were studied. Two intermetallic phases were identified in both the die cast and the thixocast specimens: the τ-phase doped with calcium $(Mg,Ca)_{32}(Al,Zn)_{49}$ (or τ′-phase) and the $(Al,Zn)_xCe$ isomorphous phase with Al_2CeZn_2 and Al_4Ce. In all of the specimens, the τ′-phase crystallized mostly as fine elongated particles and within a lamellar constituent. Needle-like $(Al,Zn)_xCe$ phase particles were visible in the die cast specimens, whereas coarse particles of various cross-sectional shapes (polygonal, elliptical, rod-like, etc.) were observed in the thixocast specimens. The difference in morphology of the intermetallic $(Al,Zn)_xCe$ particles in the matrix and the presence of large primary α-Mg grains in the thixocast specimens was used to explain the different creep behavior of die cast and thixocast ZAEX10430 alloy reported previously.

1. Introduction

Mg–Zn–Al (ZA) is a promising low-cost alloy system first developed in the 1970s by Foerster [1] to attain superior creep resistance and good castability [2,3]. ZA alloys exhibit a creep resistance that is superior to that of AZ91 alloy while maintaining similar mechanical properties at room temperature [1–4]. They also exhibit substantial age hardening during isothermal ageing at temperatures ranging between 100 and 200 °C [5]. Among the ZA alloys, ZA104 (Mg–10Zn–4Al) shows great potential due to the presence of a τ-phase $(Mg_{32}(Al,Zn)_{49})$ [6]. In order to further improve the creep resistance of ZA alloys, one approach involved the addition of rare earth elements and alkali metals to the Mg–Zn–Al system. Tardif et al. [7,8] showed that adding cerium and calcium significantly improved the creep resistance of these alloys. ZAEX10430 alloy, developed at Université Laval, was based on ZA104 alloy and the addition of 2.6 wt.% Ce and 0.3 wt.% Ca. The microstructure of this alloy was mainly characterized for specimens with a relatively coarse microstructure that were gravity cast in a permanent mold [7]. Recently, this alloy was produced by high pressure die casting and thixocasting [9]. In this paper, their microstructure is characterized in detail and compared.

2. Experimental Procedures

Table 1 presents the chemical composition of the ZAEX10430 alloy used in this study [7–9]. This alloy was prepared with ingots of magnesium, aluminum, and zinc of higher than 99.9% purity. Manganese, calcium, cerium, and beryllium were dissolved in a melt of commercial master alloys Al-25% Mn, Mg-35% Ca, Mg-20% Ce, and Al-5% Be (wt.%), respectively. Melting was carried out under the protection of a CO_2+0.5% SF_6 gas mixture and billets (diameter 7.5 cm, length 16 cm) were gravity cast in a permanent mold. These billets were then used to produce die

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Table 1 – Chemical composition (wt%) of ZAEX10430 alloy [7–9].

Zn	Al	Ce	Ca	Mn	Fe	Be	Mg
10.4	3.9	2.6	0.19	0.17	0.008	0.0005	Bal.

cast and thixocast experimental boxes in a Bühler SC N/53 (600 t capacity) cold chamber machine. Table 2 lists the die casting and thixocasting parameters [9]. Further details regarding the preparation procedure of these ZAEX10430 castings are provided in reference [9]. Metallographic specimens were taken from the boxes and prepared for microstructural and phase analyses.

Chemical composition analysis of secondary phase particles was performed by means of a Cameca SX 100 electron probe microanalyzer (EPMA) equipped with a wavelength dispersive spectrometer (WDS). Quantitative measurements were carried out only on particles larger than about 2 μm according to the spatial resolution of the instrument. Specimens used for EPMA analyses were molded in acrylic resin, subsequently mechanically ground with 2400 grit SiC paper, and polished successively with 6.0, 0.5, and 0.1 μm diamond pastes. The specimens were finally cleaned with distilled water and ethanol and dried in warm flowing air.

The chemical composition and crystallographic analysis of phases in the ZAEX10430 specimens were further analyzed by means of a Philips CM20 FEG TEM equipped with an Oxford energy dispersive X-ray spectrometer (EDS) and an INCA system analyzer. For the EDS analysis of a fine particle, the scanning mode (STEM) was set with a nominal probe size of approximately 1 nm. TEM specimens were prepared by dimple grinding followed by ion milling in a Gatan PIPS ion beam polisher. Characterization by TEM was carried out only for die cast specimens that exhibited relatively finer secondary phase particles.

3. Results

3.1. *Microstructure and Phase Analysis of the Die Cast ZAEX10430 Alloy*

Fig. 1 shows the backscattered electron image and elemental mappings for Zn, Al, Ce, Ca, and Mg in cross sections of polished die cast ZAEX10430 specimens. These maps reveal the fine microstructure of the α-Mg matrix with many intermetallic particles distributed in grains and at grain boundaries (Fig. 1a and f). Intermetallic particles were mostly present as fine elongated particles, although a lamellar constituent was also visible (Fig. 1a, red arrow). The lamellar particles contained mostly zinc and calcium (Fig. 1b and e). Other isolated aluminum- and calcium-rich particles were also present (Fig. 1c and e). Some aluminum-rich particles contained cerium and exhibited a rhombus cross section (Fig. 1c and d).

Table 2 – Die casting and thixocasting parameters of ZAEX10430 alloy [9].

Parameter	Die-casting	Thixocasting
Preheating temperature (°C)	680	573
Die temperature (°C)	200	200
Shot sleeve speed (m/s)	1.50	1.25
Injecting pressure (bar)	1200	1200

The composition of secondary phase particles in die cast ZAEX10430 specimens was determined with EPMA. Table 3 lists the phase composition of selected zones (spots 1–5), as shown in Fig. 2. The primary α-Mg grains consisted of a solid solution of Zn and Al in a magnesium-rich matrix (spot 1). Spot 2 shows lamellar Mg–Al–Zn particles with a low concentration of Ca and no cerium. Individual lamellae were too narrow to be analyzed with EPMA due to the interaction between the electron beam and the surrounding matrix. Spot 3 reveals a typical Al–Zn–Ce-rich particle with hollow hexagonal and rhombus cross sections, also visible in Fig. 1c and e. The measured composition of such particles was 50 at.% Al, 15 at.% Zn, 18 at.% Ce, and 16 at.%Mg. It was not possible to confirm whether the detected magnesium came from the particle itself or from the surrounding matrix. The magnesium concentration varied extensively and likely came from the matrix. Spots 4 and 5 correspond to the fine elongated intermetallic particles already apparent in Fig. 1a and consisting of $(Al,Zn)_xCe$ compound ($3.6<x<5.2$).

Numerous fine intermetallic particles in the die cast ZAEX10430 specimens were concurrently analyzed with TEM to determine their structure and chemical composition. The crystalline structure of the phases was indexed from selected area diffraction patterns (SAEDPs) (Fig. 3). From typical TEM micrographs, more than 24 spots on different particles were examined. The results listed in Table 4 indicate that many particles (spots 1 and 2 in Fig. 3a, spots 10–12 in Fig. 3b, and spot 23 in Fig. 3e) corresponded to the τ′-phase ($(Mg,Ca)_{32}(Al,Zn)_{49}$), with SAEDPs revealing a cubic structure (space group: Im3). Some τ′-phase particles were observed between α-Mg grains (spots 1, 2, and 23), while fine isolated τ′-phase particles ranging from 50 to 200 nm in size were distributed within α-Mg grains (spots 10–12). The higher magnesium content indicated a strong interaction between the electron beam and the α-Mg matrix. Most of the other fine particles analyzed with TEM (Fig. 3b,c and d) corresponded to the intermetallic $(Al,Zn)_xCe$ phase ($2.5<x<4.3$) and presented a common tetragonal structure (space group: I4/mmm) similar to that of Al_2CeZn_2, as confirmed, for example, with the SAEDP matching in spot 24 (Fig. 3e and f). A few CaO inclusions were also detected (Fig. 1e).

3.2. *Microstructure and Phase Analysis of the Thixocast ZAEX10430 Alloy*

Fig. 4 shows the backscattered electron image and elemental mappings for Zn, Al, Ce, Ca, and Mg in polished cross sections of the thixocast ZAEX10430 specimens. The large α-Mg grains correspond to the pre-existing solid phase present in the billet immediately prior to injection (Fig. 4a and f). These grains were surrounded by a finer microstructure solidified in the mold. Compared to the particles observed in the die cast specimens, the intermetallic particles in the thixocast specimens were more interconnected and formed a continuous network (Fig. 1a). The elemental mappings show that the fine microstructure was composed of primary α-Mg fine grains surrounded by small