Microstructure and mechanical properties of ZA104 (0.3–0.6Ca)
die-casting magnesium alloys

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Abstract

In this paper, the microstructure of die-cast and slowly cooled specimens of two new experimental magnesium alloys (ZA104 + 0.3Ca and ZA104 + 0.6Ca) is examined. Microanalysis of specimens has revealed the presence of α-Mg phase (matrix) and two intermetallic compounds containing calcium with different Zn/Al ratios. These compounds, which have a crystal structure close to that of ε phase [Mg32(Al,Zn)49], were also found in slowly cooled ZA104 + 0.3Ca specimens and identified as (ε′1 and ε′2). The microhardness of these intermetallic compounds has been obtained from specimens having the intermetallic composition and slowly cooled from the melt. The tensile and creep resistance of the two die-cast alloys (ZA104 + 0.3Ca and ZA104 + 0.6Ca) are also presented. Tensile properties are equivalent to those of the AZ91D reference alloy, but their creep deformation rate is significantly reduced by a factor 3.5–3.8 at 150 °C and 4.0–7.2 at 175 °C. Besides, it was found that the ultimate tensile strength and elongation of ZA104 + 0.3Ca alloy are superior to those of ZA104 + 0.6Ca alloy. It is then established that the intermetallic phases ε′1 and ε′2 containing calcium are harder than ε phase and improve substantially the creep resistance of these new ZA experimental alloys.

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Keywords: Magnesium alloys; ZA alloys; Die-casting; Creep; Microstructure

1. Introduction

Magnesium alloys are known for their light weight, specific stiffness, low heat capacity and castability which are greatly appreciated in high pressure die-casting. From its early development during 1920s in Germany until now, die-casting of magnesium alloys has been expanded, essentially for Mg–Al-based alloys. Actually, AZ91D (Mg–Al–Zn) and AM50B (Mg–Al–Mn) are used most widely by industry. However, because of their inadequate behaviour for structural applications, requiring enhanced creep resistance, many die-casting alloys have been developed in the last 30 years [1–5].

In the early 1970s, three experimental alloys (ZA124, ZA102 + 0.3Ca and AZ88) were developed by NL industries [6,7]. It was reported that ZA124 can offer a creep resistance similar to AS41 alloy and a good corrosion resistance and fluidity. It was found that a small amount of calcium added to zinc-rich alloys could significantly improve their creep resistance. Indeed, the creep resistance of ZA102 + 0.3Ca alloy was higher than that of ZA124 and similar to that of AS21. Moreover, no die sticking or hot cracking problems appeared when calcium was added in these alloys. However, details on microstructural effects, strengthening and creep mechanisms concerning the higher zinc alloy system were not specified in these reports.

Considering the high potential of Mg–Zn–Al and Mg–Zn–Al–Ca series of alloys revealed by Foerster [6,7], a systematic study has been undertaken by Zhang and coworkers [8–14] with the objective to understand the role of alloying elements in the crystallization of phases and more precisely determine the composition range for creep resistant alloys in these alloy systems. For practical and economical reasons, most of the development of these experimental alloys has been carried out with test specimens cast in
permanent mould [8–14]. By these experiments, Mg–Zn–Al and Mg–Zn–Al–Ca alloys having mechanical properties comparable to those of AZ91D alloy have been identified, some of them showing a superior creep resistance [8–12]. In addition, these studies have revealed the distribution of calcium among intermetallic phases and its key role in improving the thermal stability of creep resistant intermetallic phases $\gamma_1$ and $\gamma_2$ in Mg–Zn–Al–Ca series of alloys [13,14]. However, mechanical properties of high pressure die-casting alloys are usually superior to those cast in permanent mould, and their microstructure differs on many aspects [15]. In this paper, two experimental alloys, ZA104 + 0.3Ca and ZA104 + 0.6Ca, were prepared by using high pressure die-casting. Their microstructure and mechanical properties were studied in order to develop inexpensive alloys having tensile properties comparable to that of AZ91, superior creep resistance, good castability and low density (less than 2.0 Mg/m$^3$).

2. Material and experimental procedures

The ZA104 + 0.3Ca and ZA104 + 0.6Ca experimental alloys were prepared from commercially pure Mg, Al and Zn (>99.9%) and Mg–35%Ca master alloy. Small amount of Al–25%Mn master alloy was added to decrease the iron content since the later can be removed by precipitation and settling of intermetallic particles containing iron and manganese. Steel crucible and electric heated furnace were used for melting and alloying operations. A mixture of CO$_2$–0.5%SF$_6$ was used as protective gas. The chemical composition of the experimental alloys and AZ91 reference alloy, as determined by inductively-coupled plasma (ICP) spectroscopy, are given in Table 1. A 600-tonne Prince cold chamber die-cast machine was employed to prepare tensile and creep test specimens.

Casting temperature of the melt was kept at 650°C, and die surface temperature was maintained at 215°C by a Thermo-cast die heating unit. The dwell time was approximately 3 s. Fig. 1 shows the drawing of die-casting specimens used for tensile and creep tests following the ASTM standard B557M [16]. Real time X-ray radioscopy was used to detect internal defects such as shrinkage, pores and cracks in test bars. It is worthy to mention that less than about 5% of test bars were rejected due to casting defects (including all types of defects—inclusions, porosities and cracks).

In order to obtain large size intermetallic phases for easier microstructural analysis, ZA104 + 0.3Ca specimens were slowly cooled at 0.03°C/s from the melt state. Specimens having the same composition as the identified intermetallic compounds were also prepared for microhardness measurement. Pure metals and master alloy were melted in steel crucible, well mixed and cooled at 0.03°C/s.

X-ray diffractometer using Cu K$_\alpha$ radiation was employed for the identification of the crystal structure of phases. X-ray diffraction pattern were analysed with the software Jade (MDI) version 2+ with direct access to the JCPDS X-ray diffraction databank. Scanning electron microscope (SEM) was used to characterize the microstructure of alloys. Electron probe microanayser (EPMA) equipped with a wavelength dispersive spectrometer (WDS) was used to determine the composition of each phase, as well as the distribution of elements in the alloys. The detection limit (wt.%) for each

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Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zn</th>
<th>Al</th>
<th>Ca</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Be</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA104 + 0.3Ca</td>
<td>9.50</td>
<td>3.80</td>
<td>0.350</td>
<td>0.40</td>
<td>0.010</td>
<td>0.039</td>
<td>0.004</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>Balance</td>
</tr>
<tr>
<td>ZA104 + 0.6Ca</td>
<td>9.90</td>
<td>3.76</td>
<td>0.590</td>
<td>0.33</td>
<td>0.010</td>
<td>0.010</td>
<td>0.005</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>Balance</td>
</tr>
<tr>
<td>AZ91D</td>
<td>0.80</td>
<td>8.90</td>
<td>0.001</td>
<td>0.20</td>
<td>0.014</td>
<td>0.002</td>
<td>0.001</td>
<td>0.009</td>
<td>&lt;0.001</td>
<td>Balance</td>
</tr>
</tbody>
</table>

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Fig. 1. Die-casting specimens used for tensile and creep tests (ASTM standard B557M [16]).

Fig. 2. SEM micrograph of ZA104 + 0.3Ca die-casting alloy.
element was: 0.1 for Zn, 0.03 for Al, 0.04 for Mg and 0.016 for Ca, under analytical conditions.

Tensile properties were determined with a SATEC tensile testing machine (model T20000) equipped with a 12.5 mm extensometer and a 100 kN load cell according to ASTM standard B557M[16]. Ultimate tensile strength (UTS), 0.2% yield strength (YS), and fracture strain (\(\varepsilon_f\)) were averaged over six to eight tests. Creep tests were carried out on a SATEC creep/stress-rupture testing system (model GTU) in agreement with ASTM standard E139[17]. The creep testing parameters were kept at \(\sigma_c = 34.5\) MPa, \(T = 150 \pm 1\) °C or 175 ± 1 °C, and \(t = 100\) or 200 h. The creep properties were averaged over three tests. Vickers indenter was used for microhardness measurements of phases according to the ASTM standard E384[18]. Test load and its application time were respectively, 10 g and 15 s. The hardness value was averaged over eight measurements.

3. Results and discussion

3.1. Microstructure of ZA104 + 0.3Ca die-casting alloy

A SEM micrograph of ZA104 + 0.3Ca die-casting alloy is shown in Fig. 2. A very thin network of secondary phase (1–2 \(\mu\)m) is distributed along the grain boundaries. A backscattered electron image and a calcium X-ray mapping of ZA104 + 0.3Ca die-casting alloy are presented in Fig. 3. The mapping shows that the highest calcium concentration is found in secondary phases. It indicates the presence of two distinct phases in interdendritic zones (Fig. 3b). In spite of undesirable contrast variations induced by interactions of incident electron beam with narrow phases, the semi-quantitative linescan across a typical grain boundary confirms the presence of distinct phases containing different level of zinc, aluminum and calcium (Fig. 4). In one peak, labelled P1, the relative signal of zinc and aluminium is much higher than that found for neighbouring peaks, labelled P2 and P3, a result which cannot be explained only by electron-matter interactions.

The X-ray diffraction data for ZA104 + 0.3Ca die-cast alloy are given in Table 2. They show that, in addition to the structure of primary magnesium structure (hexagonal), only the crystal structure corresponding to phase \(\tau [\text{Mg}_{37} (\text{Al},\text{Zn})_{49}]\) was found, a ternary phase having 162 atoms per unit cell in \(T_{\text{h}}\) space group with a wide range of solubility and Zn/Al ratio [19–21]. The crystal structure of that phase was further studied by others [22,23]. In a previous paper about a Mg–10Zn–4Al–0.15Ca alloy cast in permanent mould two isomorphous phases designated as \(\tau_1\) and \(\tau_2\) were reported [13,14]. Since the cooling rate of alloys cast in permanent mould and die-casting are reasonably similar, it is suggested that the microstructure of die-cast ZA104 + 0.3Ca alloy consists mainly of a matrix (\(\beta\)-Mg) and two intermetallic phases (\(\tau_1\) and \(\tau_2\)). The presence of an intense X-ray peak at 0.278 nm suggests a surface texture in cast specimens. Such a surface texture was reported by Avishai et al.[24] for other die-cast magnesium alloys.

3.2. Microstructure of slowly cooled specimens

The size of secondary phases obtained from slowly cooled ZA104 + 0.3Ca specimens has permitted a precise analysis of intermetallic phases. For comparison purposes, and based on earlier observations on ZA104 + 0.15Ca cast in permanent mould and slowly cooled, the slow crystallization of intermediate phases was considered as having a comparable influence on hardness of isomorphous intermetallic \(\tau\) phases.
Table 2
X-ray diffraction data analysis for ZA104 + 0.3Ca die-casting alloy and phases

<table>
<thead>
<tr>
<th>Interplanar spacing “d” (nm) and peak intensity “I” (%)</th>
<th>ZA104 + 0.3Ca</th>
<th>phase a</th>
<th>ZA104 + 0.3Ca</th>
<th>phase b</th>
<th>α-Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.019 (3.7)</td>
<td>1.010 (90)</td>
<td>–</td>
<td>0.213 (3.8)</td>
<td>0.214 (4)</td>
<td>–</td>
</tr>
<tr>
<td>0.586 (2.3)</td>
<td>0.580 (45)</td>
<td>–</td>
<td>0.211 (2.2)</td>
<td>0.210 (70)</td>
<td>–</td>
</tr>
<tr>
<td>0.443 (1.6)</td>
<td>0.449 (35)</td>
<td>–</td>
<td>0.207 (2.2)</td>
<td>0.201 (85)</td>
<td>–</td>
</tr>
<tr>
<td>0.382 (2.6)</td>
<td>0.380 (55)</td>
<td>–</td>
<td>0.202 (5.6)</td>
<td>0.198 (20)</td>
<td>–</td>
</tr>
<tr>
<td>0.359 (2.6)</td>
<td>0.356 (6)</td>
<td>–</td>
<td>0.195 (4.9)</td>
<td>0.190 (15)</td>
<td>–</td>
</tr>
<tr>
<td>0.278 (68.2)</td>
<td>0.279 (6)</td>
<td>0.278 (25)</td>
<td>0.189 (0.6)</td>
<td>0.187 (2)</td>
<td>–</td>
</tr>
<tr>
<td>0.260 (14.1)</td>
<td>0.260 (6)</td>
<td>0.261 (36)</td>
<td>0.172 (1.3)</td>
<td>0.175 (8)</td>
<td>–</td>
</tr>
<tr>
<td>0.253 (6.4)</td>
<td>0.252 (2)</td>
<td>–</td>
<td>0.160 (12)</td>
<td>0.160 (12)</td>
<td>–</td>
</tr>
<tr>
<td>0.245 (100)</td>
<td>0.244 (100)</td>
<td>0.245 (25)</td>
<td>0.147 (16.9)</td>
<td>–</td>
<td>0.147 (16)</td>
</tr>
<tr>
<td>0.238 (5.2)</td>
<td>0.237 (30)</td>
<td>–</td>
<td>0.144 (2.8)</td>
<td>0.144 (25)</td>
<td>–</td>
</tr>
<tr>
<td>0.232 (7.1)</td>
<td>0.231 (100)</td>
<td>–</td>
<td>0.139 (5.3)</td>
<td>0.138 (6)</td>
<td>0.139 (2)</td>
</tr>
<tr>
<td>0.225 (3.5)</td>
<td>0.225 (6)</td>
<td>–</td>
<td>0.136 (15.4)</td>
<td>0.136 (20)</td>
<td>0.137 (13)</td>
</tr>
</tbody>
</table>

* Standard interplanar spacing and peak intensity from JCPDS [19].

Fig. 5. EPMA backscattered electron image (a) and calcium X-ray mapping (b) of slowly cooled ZA104 + 0.3Ca specimen.

Backscattered electron image and calcium X-ray mapping of this slowly cooled specimen are shown in Fig. 5. Two intermetallic phases (nos. 1 and 2) were identified in ZA104 + 0.3Ca alloy (Fig. 5a). The composition of these phases and the composition of magnesium-based matrix are given in Table 3. Phase no. 2 having a lower content in calcium than phase no. 1 (Fig. 5b). About only 0.5 at.% Ca is detected in phase no. 1 comparatively to 4 at.% Ca in phase no. 2. The composition of these intermetallic phases is close to that of intermetallic phases found in ZA104 + 0.15% Ca cast in permanent mould [13].

Table 3
Composition of different phases observed in slowly cooled ZA104 + 0.3Ca alloy (standard deviation in parenthesis)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>τ (τ₁)</td>
<td>40.3 (0.5)</td>
</tr>
<tr>
<td>No. 1 (τ₁)</td>
<td>43.6 (0.4)</td>
</tr>
<tr>
<td>No. 2 (τ₂)</td>
<td>39.1 (2.3)</td>
</tr>
<tr>
<td>Matrix (α-Mg)</td>
<td>97.0 (0.7)</td>
</tr>
</tbody>
</table>

Table 4
Microhardness of intermetallic phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Microhardness (HV 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ</td>
<td>249 ± (3)</td>
</tr>
<tr>
<td>τ₁</td>
<td>258 ± (5)</td>
</tr>
<tr>
<td>τ₂</td>
<td>320 ± (19)</td>
</tr>
</tbody>
</table>

3.3. Microhardness of intermetallic phases

Fig. 6 shows the backscattered electron images of two slowly cooled specimens (0.03°C/s) specimens having an average composition corresponding to that of the intermetallic phases τ₁ [(Mg, Ca)_2(Al, Zn)_10] and τ [Mg_2(Al, Zn)_10], respectively identified as specimens A and B. The two intermetallic phases (τ₁ and τ₂) were observed in specimen A (Fig. 6a) and only one phase (τ) in specimen B (Fig. 6b). The composition of phase τ, given in Table 3, is similar to that found in isomorphous phases containing calcium that have crystallized in ZA104 + 0.15% Ca alloy cast in permanent mould [13]. The microhardness of the three intermetallic phases τ, τ₁, and τ₂, measured in slowly cooled specimens, are listed in Table 4. These values demonstrate that phases τ₁ and...
Fig. 6. Backscattered electron images of two slowly cooled specimens A and B having respectively, the composition of $\gamma'$ phase (a) and $\gamma$ phase (b).

Table 5

<table>
<thead>
<tr>
<th>Alloy</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>$\varepsilon_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA104 + 0.3Ca</td>
<td>168 (6)</td>
<td>212 (7)</td>
<td>5.8 (0.8)</td>
</tr>
<tr>
<td>ZA104 + 0.6Ca</td>
<td>170 (5)</td>
<td>204 (10)</td>
<td>4.5 (0.8)</td>
</tr>
<tr>
<td>AZ91D</td>
<td>163 (4)</td>
<td>213 (10)</td>
<td>6.0 (0.6)</td>
</tr>
</tbody>
</table>

Standard deviation in parenthesis, approximately the average of seven tensile tests.

$\gamma'$ becomes harder than phase $\gamma$ with an increase in calcium content (see also Table 2). Calcium added to Mg-Zn-Al alloys tends to modify the intermetallic phase $\gamma$ which becomes harder and more stable at high temperature [13].

3.4. Tensile properties

The tensile properties including ultimate tensile strength (UTS), 0.2% yield strength (YS) and fracture strain ($\varepsilon_r$) of die-casting specimens are given in Table 5. As reference, the tensile properties of the AZ91D alloy die-cast in the same conditions are also listed. Within the margin of experimental error, and after using a simple two-tailed Student’s $t$-test at 95% level of significance, it can be showed that the yield, tensile strength and fracture strain of the two ZA experimental alloys are slightly affected negatively with an increase in calcium content. But generally, the tensile properties of the ZA104 + 0.3Ca alloy stay very close to those of the popular AZ91D alloy.

3.5. Creep properties

Typical creep curves of ZA104 + 0.3Ca, ZA104 + 0.6Ca and AZ91D die-casting alloys at 175 °C ($\sigma_c = 34.5$ MPa) are shown in Fig. 7. Total creep strain ($\varepsilon$) and minimum creep rate ($\dot{\varepsilon}$) of the two experimental ZA alloys and AZ91D reference alloy are listed in Table 6. At 150 °C, the ZA alloys

$$\begin{array}{|c|c|c|}
\hline
\text{Alloy} & \text{Creep behaviour ($\sigma_c = 34.5$ MPa)} & \text{At 150 °C} \\
\hline
& & 100 h & 200 h & 100 h & 200 h \\
\hline
\text{ZA104 + 0.3Ca} & 0.53 & 0.70 & 1.95 & 1.45 & 2.12 & 7.00 \\
\text{ZA104 + 0.6Ca} & 1.92 & 2.68 & 8.90 & 8.10 & 15.28 & 71.3 \\
\text{AZ91D} & & & & & & \\
\hline
\end{array}$$

* $\varepsilon$: Total creep deformation; $\dot{\varepsilon}$: minimum creep rate (d$\varepsilon$/dt).
have a total creep strain and a minimum creep rate averaging, respectively ~3.7 and 4.3 times lower than that of AZ91D alloy. The creep properties of ZA104 + 0.6Ca alloy are slightly better (3–5% for ε and 9% for ε′) than that of ZA104 + 0.3Ca alloy. At 175 °C, the total creep strains of ZA104 + 0.3Ca and ZA104 + 0.6Ca alloys are respectively ~4.9 and 5.6 times lower than that of AZ91D for the 100 h creep tests, and shift up to ~6.4 and 7.2 times lesser for the 200 h creep tests. The minimum creep rates (200 h) of ZA104 + 0.3Ca and ZA104 + 0.6Ca alloys are respectively ~9.1 and 10.2 times lower than that of AZ91D. It is clearly demonstrated that creep properties of ZA104 + 0.3Ca and ZA104 + 0.6Ca alloys increase with calcium content and surpass significantly the creep behaviour of AZ91D alloy, particularly at higher temperature. In these ZA104 + 0.3Ca and ZA104 + 0.6Ca alloys, the morphology, size and distribution of isomorphous phases were not significantly different from those found in calcium-free ZA alloys [29]. The presence of harder and more thermally stable intermetallic phases [13], particularly the phase τ2, could explain this important improvement.

4. Conclusions

The microstructural study of the two die-casting experimental alloys (ZA104 + 0.3Ca and ZA104 + 0.6Ca) have shown the presence of two new intermetallic phases distributed along the grain boundaries of the fine α-Mg grains (matrix). The two intermetallic phases, identified as τ1 and τ2 and having a crystal structure similar to the phase τ (\[\text{Mg}_2\text{Al}_3\text{Zn}_{0.5}\]), contain different Zn/Al ratio and quantity of calcium. The phase τ1 is harder than phases τ2 and τ, contains more calcium, and should be considered as a more stable phase at higher temperature.

Tensile properties of ZA104 + 0.3Ca die-casting alloy are comparable to those of AZ91D alloy. Ultimate tensile strength and fracture strain of the two ZA experimental alloys decrease while calcium increases. Total creep deformation and minimum creep rate of ZA104 + 0.3Ca and ZA104 + 0.6Ca alloys are significantly lower than that of AZ91D alloy, especially at 175 °C. Creep resistance of ZA104 + 0.6Ca is superior to that of ZA104 + 0.3Ca, particularly when creep tests are performed at 175 °C. The presence of the intermetallic phase τ2 at the grain boundaries can explain the better creep performances of ZA alloys containing calcium.

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References