Microstructure and Mechanical Properties of a Rheo-Diecast Mg–10Zn–4.5Al Alloy

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High zinc content Mg–Zn–Al alloys have the potential to be used as high pressure die casting (HPDC) alloys for applications up to 150 °C. However, these alloys show high tendency to hot tearing and microporosity. Rheo-diecasting (RDC) is an innovative semisolid HPDC process, which can effectively eliminate the formation of primary magnesium dendrites and convert them into fine, globular particles. This very positive change in the morphology and distribution of the primary phase reduces the subsequent formation of various casting defects. In this study, a composition of Mg–10Zn–4.5Al was selected from the Mg–Zn–Al system and processed with both HPDC and RDC. It is shown that, samples produced by the RDC process exhibit substantially reduced hot cracks, few gas pores, and a nearly uniform distribution of fine, globular primary particles. These microstructural changes resulted in much improved strength and elongation, which are comparable to those of AZ91D, while the processing temperature is much lower. It is concluded that high zinc content Mg–Zn–Al alloys have good potential to be exploited as commercially useful alloys by the RDC process.

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1. Introduction

Aluminium (Al) and zinc (Zn) are two primary alloying elements in magnesium alloys. However, historically, Mg–Al–Zn alloys containing more Al than Zn have received much more attention than those alloys that contain more Zn than Al. Currently, in most commercial Mg–Al–Zn alloys, Zn is mainly used in combination with Al to improve the room-temperature strength, as Zn offers the required improvement with minimum loss in ductility compared with adding more Al.1) In these alloys, the Zn content is normally controlled at 1% or less (hereafter all concentration are in mass% unless stated otherwise). This is because Zn addition to Mg–Al type alloys increases hot tearing tendency and microporosity. The severe microporosity encountered in the old sand casting alloy of AZ63 (Mg–6Al–3Zn) was the major reason that eventually led to its replacement by AZ91.1) The drawbacks resulting from the use of a high Zn content have traditionally limited the use of Zn as a principal alloying element in magnesium alloys.

In the mid-1970s Foerster revisited the Mg–Al–Zn system with Al and Zn contents varying in the ranges of 0–10%Al and 0–35%Zn, respectively.2) It was found that, for a given Al content, there was a wide range of high Zn content alloys that were diecastable without showing severe hot tearing and microporosity, while the fluidity of some of these alloys was found to exceed that of AZ91D. More interestingly, these high Zn alloys showed improved creep resistance compared to AZ91D. However, owing to the inadequate interest in magnesium applications in the late 1970s, there were few follow-up studies on the Mg–Zn–Al system before the 1990s.

AZ91D is the benchmark alloy for the magnesium business. However, it is not suited to long-term applications at temperatures above 125 °C due to its poor creep resistance. The renewed interest in the Mg–Zn–Al system in the 1990s mainly arose from the demand for a low-cost, creep-resistant diecastable alloy, to bridge the gap between AZ91D and some creep-resistant but costly alloys. As a result, much effort has been taken in the past decade to investigate the processing ability, microstructure, mechanical properties and creep resistance of different compositions of Mg–Zn–Al alloys, with and without calcium additions.3–10) These studies led to the discovery of some promising Mg–Zn–Al alloys, most notably when the Zn content is around 10% and the Al content around 4%. It has been found that, Mg–Zn–Al alloys having such compositions generally show much improved creep resistance compared to that of AZ91D. On the other hand, both the castability and the room-temperature tensile properties of these alloys, including elongation, are acceptable or close to those of AZ91D.10) It is therefore likely that these alloys will evolve into a group of new alloys implying wide applications for both room temperature and elevated temperature purposes.

In this study, we are more interested in the room-temperature tensile properties and the castability of high Zn content Mg–Zn–Al alloys rather than their creep resistance. The major considerations are that high Zn content alloys can be cast at a much lower temperature than AZ91D alloy. This means easier melt handling and less loss of the magnesium metal. In addition, high Zn content generally enhances the corrosion resistance of magnesium alloys as measured by salt-water tests.1) Meanwhile, the densities of most of these high zinc alloys are still acceptable (less than 2.0 g cm⁻³). Therefore, if these alloys were made to have properties comparable to those of AZ91D, they would become commercially attractive.

Rheo-diecasting (RDC) is a new semisolid HPDC process recently developed at Brunel University,11,12) for manufacturing near-net shape components of high integrity from liquid metals. The process innovatively adapts the well-established high sheaf dispersive mixing action of the twin-screw mechanism, to the task of in situ creation of SSM slurry with fine and spherical solid particles, followed by shape casting using a conventional cold chamber HPDC
process. The twin-screw slurry maker used in the RDC process has a pair of screws rotating inside a barrel. Both screws have specially designed profiles that are co-rotating, fully intermeshing and self-wiping. The fluid flow inside the slurry maker is characterised by high shear rate and high intensity of turbulence. The basic function of the slurry maker is to convert the liquid alloy to high quality semisolid slurry, via solidification under high shear rate and high intensity of turbulence. During the slurry making process, there is an enormous amount of ever-changing interfacial area between the solidifying alloy, the twin screws and the wall of the barrel. This makes the slurry making process highly efficient because of the rapid heat extraction. In addition, the powerful convection effect inside the slurry maker during solidification leads to obvious grain refinement to the alloy, forming globular primary magnesium particles, compared with the coarse dendrites formed in a conventional HPDC process. Thus, in principle, it is anticipated that, application of the RDC process to high zinc content Mg–Zn–Al alloys should be able to further enhance their room-temperature mechanical properties.

The purpose of this investigation is to evaluate the effects of the RDC process on the microstructure, mechanical properties and castability of Mg–Zn–Al alloys, by comparison with the conventional HPDC process, and establish an experimental basis for rheo-diecasting of these alloys.

2. Experimental Procedure

The experimental alloy selected contains 10%Zn and 4.5%Al, which reportedly has a good combination of room-temperature mechanical properties and creep resistance at temperatures up to 150°C. The alloy was prepared using ingots of commercial grade AM50A and commercial purity Zn and Al metals, in an electrical resistance furnace at 670°C, under the protection of a cover gas consisting of 0.4%SF6 in N2.

During the RDC process, a predetermined dose of molten metal was poured into the twin-screw slurry maker, which was set at a temperature below the liquidus of the alloy. Depending upon the pre-set temperature, melt superheat and shearing intensity, the molten metal can be converted into semisolid slurry containing up to 50% of solid, typically in less than 30 s in the twin-screw slurry maker. The slurry is then released into the shot sleeve of a HPDC machine for shape casting. A 2,800 kN cold chamber die casting machine was employed for performing the casting tasks. Samples for tensile tests were cast using a specially designed die, which allows casting of four tensile samples each time. The die temperature was set at 230°C for all tests. The melt temperature used for the HPDC tests was 670°C.

Shearing intensity, shearing time and shearing temperature are the three most important factors that affect the microstructure and mechanical properties of a rheo-diecast magnesium alloy. Based on experience with rheo-diecasting of AZ91, AM50 and other magnesium alloys, the rotation speed of the twin-screws in the slurry maker was fixed at 800 revolutions per minute (min⁻¹). Three different shearing temperatures, 585, 575 and 570°C, and three different shearing times, 5, 20 and 35 s, were used to study the influence of melt shearing on the microstructure and mechanical properties of the alloy.

Tensile tests of the as-cast standard 6 mm diameter samples were carried out at room temperature on a Lloyd Instrument EZ50 tensile test machine with a crosshead speed of 1 mm/min. Samples for metallurgical examination were prepared from the tensile samples and etched using a solution of 60 vol% ethylene glycol, 20 vol% acetic acid, and 1 vol% concentrated HNO3. A Philips 1700 X-ray diffractometer was used to help identify the phases present in the alloy (CuKα radiation, operated at a voltage of 36 kV and an anode current of 26 mA).

3. Results

3.1 Microstructure of the Mg–10Zn–4.5Al alloy produced by the HPDC process

Figure 1 shows a cross-sectional view of the microstructure observed in a 6 mm diameter tensile sample produced by HPDC. The microstructure close to the surface is distinguished by fine primary magnesium crystallites. However, at about a fifth of the radius from the surface, coarse magnesium dendrites become visible, and exhibit an increased presence towards the centre, where a dominant presence of coarse dendrites is observed.

Fig. 1 Microstructure of the Mg–10Zn–4.5Al alloy from the cross-section of a HPDC 6 mm tensile sample.
Figures 2(a) and (b) are secondary electron images showing the eutectic structure formed in the HPDC sample. Similar to the \( \gamma_1/C_12 \) eutectic phase in an AZ91 alloy, a network-like second eutectic phase is present in the alloy. Casting defects, most notably microporosity and hot tearing, are visible in some samples, suggesting that under the present HPDC conditions microporosity and hot tearing are still a concern.

3.2 Microstructure of the Mg–10Zn–4.5Al produced by the RDC process

Figure 3 shows a similar cross-sectional view of the microstructure observed in a 6 mm diameter tensile sample produced by RDC, where the melt was sheared at 575°C for 35 s prior to casting. In contrast to the coarse dendrites shown in Fig. 1, a nearly uniform distribution of globular primary magnesium particles was observed throughout the sample, demonstrating a distinct difference between the RDC process and the HPDC process. No coarse dendrites were observed in any samples produced by RDC. There were two groups of primary phase particles in the RDC samples. The relatively large and spherical particles with an average particle size of 39 \( \mu m \) were formed inside the slurry maker, while the finer and irregular shaped primary particles were formed in the shot sleeve and fragmented during high pressure mould filling. In addition, no large pores due to gas entrapment were found in all samples produced by RDC. Only a few fine and isolated hot cracks were observed. The total porosity level was below 0.5 vol%.

There was little change in the eutectic structure in the samples produced by RDC. Figures 4(a) and (b) are secondary electron images showing the typical eutectic structure in these samples. As can be seen by comparing with Fig. 2, the eutectic structures look very similar. The RDC process has thus mainly altered the solidification of the primary magnesium phase in the Mg–10Zn–4.5Al alloy under the present processing conditions.

Figure 5 shows the X-ray diffraction (XRD) spectra of samples produced by both HPDC and RDC, analogous observations were obtained. In both cases, the \( \text{Mg}_{17}\text{Al}_{12} \) \( \beta \) phase, which is commonly present in low Zn content Mg–Al–Zn alloys, is no longer detectable. Instead, a \( \text{Mg}_{32}(\text{Al},\text{Zn})_{49} \) phase, which is the second eutectic phase shown in Figs. 2 and 4, was observed when it was indexed using the XRD databank JCPDS-ICDD (2002–2004). This is in agreement with the thermodynamic description of Mg–Zn–Al alloys of similar compositions.1)

Figure 6 shows typical results obtained from an EDS
(energy dispersive spectroscopy) line-scan across two globular primary magnesium particles in a sample processed by RDC. The compositions of Al and Zn in both particles were homogeneous; there was no evidence of the usually observed coring effect. This indicates that the solidification process inside the twin-screw slurry maker is close to equilibrium.

The influence of melt shearing time on the formation of the primary magnesium phase is shown in Fig. 7. The shearing temperature was fixed at 575°C in these tests. Increasing shearing time from 5 to 20 s resulted in an obvious increase in the primary magnesium phase, but a further increase in the shearing time to 35 s only led to a minor increase in the primary magnesium phase. Figure 8 shows the primary solid fraction as a function of shearing time, determined by Quantimet analysis. Also shown is the equilibrium solid fraction of the primary phase at 575°C, calculated using the Thermo-Calc software and the Mg-Data database. These results suggest that the volume fraction of the primary magnesium phase was approaching equilibrium after about 20 s of shearing at 575°C.

Table 1 summarises the average primary magnesium particle sizes in samples obtained under different melt shearing conditions. There was an obvious increase in the primary particle size when the melt shearing time was increased from 5 to 20 s, but the particle size remained largely constant for a further increase in the shearing time to 35 s. These results imply that, once the volume fraction of the primary phase approaches the equilibrium value, which is the case after about 20 s of melt shearing under the present conditions, growth of the primary particles will slow down due to the diminishing driving force. As a result, particle coarsening will become a major event.

The influence of shearing temperature on the formation of the primary magnesium phase is shown in Fig. 9. The
shearing time was fixed at 20 s in these tests. The dendritic forms of primary phase particles seen in Fig. 9(a) were mainly formed in the shot sleeve and most of them were fragmented dendrites, where the fragmentation occurred when the melt passed through the thin gate of the die cavity during high pressure mould filling. However, much fewer dendritic primary phase particles were found [Figs. 9(b) and (c)] when the melts were sheared at two lower temperatures, 575 and 570 °C. Figure 10 shows the volume fraction of the spherical primary particles as a function of shearing temperature, compared to the respective equilibrium solid fractions calculated using the Thermo-Calc software and Mg-Data database. These results provide further evidence that, after 20 s of shearing, the volume fraction of the primary magnesium phase was approaching the equilibrium level.

3.3 Mechanical properties

The mechanical properties of samples produced by HPDC and RDC are summarised in Table 2. The RDC process resulted in much improved tensile strength and ductility—on average, a 12% increase in UTS and a 78% increase in elongation, compared to the HPDC process. These results are encouraging, in that, the rheo-diecast Mg–10Zn–4.5Al alloy has shown even better mechanical properties than those reported in the literature for the benchmark alloy AZ91D.

4. Discussion

The RDC process delivered much improved mechanical properties to the Mg–10Zn–4.5Al alloy compared with the HPDC process, and these improvements made this high Zn content alloy comparable to AZ91D, while the casting temperature is much lower. The improved mechanical properties are mainly attributed to two factors: (1) the
elimination of large pores caused by gas entrapment during mould filling and the substantially reduced microporosity caused by solidification shrinkage, and (2) the formation of uniformly distributed fine and spherical primary particles, in contrast to the non-uniformly distributed coarse primary dendrites formed in a conventional HPDC process.

The fine and uniform microstructure is a direct result of the unique solidification behaviour of the alloy in the RDC process. The solidification in the RDC process occurs in two distinctive stages, the primary solidification inside the twin-screw slurry maker and secondary solidification in the shot sleeve and the die cavity of the HPDC machine. Owing to the large and constantly changing interfacial area between the liquid metal, the twin screws and the barrel of the slurry maker, the superheated liquid metal is quickly cooled to the preset barrel temperature of the slurry maker. As a result of the high shear rate and high intensity of turbulence provided by the twin-screw shearing mechanism, both the temperature and chemical composition of the melt will quickly get smoothed out. According to previous studies, this will result in enhanced effective nucleation and spherical growth, and eventually lead to formation of fine and uniform semisolid slurry, as shown in Figs. 3 and 7. The solid fraction in the slurry is dependent upon the shearing temperature (see Figs. 9 and 10). Owing to the favourable kinetic conditions inside the twin-screw slurry maker, the primary solidification process is close to equilibrium solidification, supported by the experimental results shown in Figs. 6 and 10. Solidification of the remaining liquid in the slurry starts when the slurry is transferred to the shot sleeve of

Fig. 9 Effect of shearing temperature on the primary phase formation in Mg–10Zn–4.5Al alloy samples produced by the RDC process. The twin-screw rotation speed was set at 800 rpm, and shearing time at 20 s. (a) 585 °C, (b) 575 °C, and (c) 570 °C.

Fig. 10 Measured solid fraction of spherical primary particles as a function of the barrel temperature. The shearing time was fixed at 20 s. The solid line represents the calculated equilibrium values using Thermo-Calc software and Mg-Data.

Table 2 Mechanical properties of samples produced by both HPDC and RDC processes.

<table>
<thead>
<tr>
<th>Processing condition</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPDC average</td>
<td>219</td>
<td>156</td>
<td>2.3</td>
</tr>
<tr>
<td>RDC average</td>
<td>245</td>
<td>159</td>
<td>4.1</td>
</tr>
<tr>
<td>RDC@575°C×5 s</td>
<td>254</td>
<td>169</td>
<td>4.2</td>
</tr>
<tr>
<td>RDC@575°C×20 s</td>
<td>254</td>
<td>156</td>
<td>4.7</td>
</tr>
<tr>
<td>RDC@575°C×35 s</td>
<td>251</td>
<td>171</td>
<td>3.7</td>
</tr>
<tr>
<td>RDC@585°C×20 s</td>
<td>253</td>
<td>159</td>
<td>4.3</td>
</tr>
<tr>
<td>RDC@570°C×20 s</td>
<td>249</td>
<td>159</td>
<td>4.6</td>
</tr>
</tbody>
</table>
the HPDC machine. This will result in the formation of further primary magnesium particles, usually with rosette morphology, in the remaining liquid in the shot sleeve. These rosette-like magnesium particles are fragmented into finer particles of irregular shapes when the slurry passes through the thin gate during mould filling under high pressure. The remaining liquid will subsequently solidify in the die cavity under a high cooling rate, resulting in fine and uniform microstructures.

The ultimate purpose of semisolid processing is to reduce or eliminate casting defects, such as large gas pores, hot cracks, oxide inclusions (dross and oxide skin from the ingots), microstructural non-uniformity, and chemical segregation, for improved mechanical properties. The RDC process produces semisolid slurry with a controlled volume fraction of fine and spherical primary particles that are uniformly present in a liquid matrix. In principle, by selection of an appropriate shearing temperature, the viscosity of the semisolid slurry can be controlled in such a way that, it is viscous enough to eliminate the gas entrapment, while it still has enough fluidity to achieve complete mould filling. According to the rheology of semisolid slurry, fine particle size, spherical morphology and good dispersion in the RDC semisolid slurry are in favour of achieving such a balance. This is the major reason why few gas pores were observed in the RDC samples. The use of a much lower melt temperature and the reduced volume fraction of the liquid metal arising from semisolid processing also contributed to the reduction in the porosity level, compared to casting from a superheated liquid state.

The substantially reduced hot cracks can be attributed primarily to the reduced casting temperature and the effective elimination of dendritic structures in the RDC process. In a conventional HPDC process, the casting temperature is typically around 670°C and the microstructure is characterised by coarse dendritic structures. By contrast, the casting temperature used in the RDC process is around 570°C and the microstructure is characterised by uniformly distributed fine and spherical particles. One possibility for hot tearing to occur is that, in the late stage of solidification, when the contraction strains pull the solid dendrites apart, the empty interdendritic area cannot be filled by the liquid due to restricted flow between the dendrites. This leads to open fractures or hot tears between the dendrites. The elimination of coarse magnesium dendrites is thus important in suppressing the occurrence of hot tearing. Lower casting temperatures give rise to less solidification shrinkage and therefore reduced tendency to hot tearing. In addition, the uniform solidification of the remaining liquid containing fine and spherical primary particles in die cavity also contributes to the reduced tendency to hot tearing. The overall effect is the substantially reduced hot cracks observed in the RDC samples.

Oxide inclusions due to mixing with the dross and the inclusion of oxide skin of the ingots are detrimental to the quality of castings produced by any casting process. This is a particularly important issue for processing liquid magnesium because of its high affinity with oxygen. Any improper protection during melting and casting can cause excessive oxidation. Detailed microstructural examination confirmed that, with appropriate protection, the RDC process does not increase the oxide content in the samples, despite the use of turbulent flow in the slurry making process. Neither clusters of oxide particles nor signs of oxide skin were found in rheo-diecast samples. This is attributed to the high dispersive mixing power of the twin-screw slurry maker. Agglomerates of oxide particles and oxide skin film, if any, are likely to be pulverised and dispersed by the intensive forced convection in the slurry maker.

Finally, the mechanical properties of the rheo-diecast Mg–10Zn–4.5Al alloy compare favourably with those reported in the literature of similar compositions produced by other processes. Figures 11(a) and (b) summarise the tensile properties of these alloys collected from the literature. The additions of Sr and Ca to the alloy of ZA105 (Mg–10Zn–5Al) were to refine the eutectic structure and improve the mechanical properties and creep resistance. As can be seen, both the tensile strength and the elongation of the Mg–10Zn–4.5Al alloy produced by the RDC process, are obviously higher than those of its similar alloys but produced by thixoforming, squeeze casting and permanent-mould casting. Of particular interest is that, the elongation property...
achieved for the as-cast samples of Mg–10Zn–4.5Al by the RDC process is equivalent to those obtained for the T4 heat-treated samples of ZA105 with Sr-modification. The comparisons provide further support to the advantages of the RDC process over other casting processes in improving the mechanical properties of high zinc content Mg–Zn–Al alloys.

5. Summary

(1) Rheo-diecasting can effectively reduce the occurrence of gas pores to a level below 0.5 vol% in the Mg–10Zn–4.5Al alloy and substantially ease the occurrence of hot hearing.

(2) The microstructure of the rheo-diecast high zinc content Mg–10Zn–4.5Al alloy is characterised by a uniform distribution of fine and globular primary magnesium particles, compared to the coarse dendritic structures achieved in a conventional HPDC process.

(3) The RDC process imparts much improved mechanical properties to the high Zn content Mg–10Zn–4.5Al alloy and makes the alloy comparable to the benchmark alloy AZ91D.

(4) The RDC process provides an attractive processing route for new alloy development.

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