Role of Lanthanum in Grain Refinement and Tensile Properties of Cast Mg–La–Zr Alloys

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In a previous investigation, a combined addition of zirconium and lanthanum was found to confer more marked grain refining than zirconium alone. The present experimental study confirmed this result. However, in this study, the microstructure was examined with more attention to the form of the zirconium-rich coring in the grain refined structures. It was concluded that although the average apparent grain size decreases with an addition of lanthanum, this is in part because grain growth takes place in the Mg–Zr alloy, while the suppression of grain growth occurs with an addition of lanthanum as small as 0.5%. [doi:10.2320/matertrans.M2012424]

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1. Introduction

Grain refining in casting offers many beneficial effects during solidification and subsequent secondary processes of cast products.1–5 For example, it provides better castability and lower susceptibility in hot tearing by delaying the dendrite impinging during solidification.3,5 It also provides more uniform cast structure, reducing chemical segregation and improving mechanical properties.6 Zirconium is an exceptional grain-refining agent for magnesium and its alloys. It readily reduces the grain size in the range of 30 to 90 µm.7–10 In earlier, it was realized that undissolved zirconium particles in the melt play an important role in grain refining, causing copious heterogeneous nucleation and growth.8,9 This view was further supported by more recent studies of Qian et al.11,12 The majority of active undissolved particles observed at the center of the cores of grains were in the range of 1 to 5 µm in size.10,13 In the previous investigation,9 a combined addition of zirconium and lanthanum was found to confer more marked grain refining than zirconium alone. The modification of dendrite structure into spherical morphology and the consequent uniform distribution of the eutectic Mg12La phase within the structure were achieved by an addition of lanthanum and zirconium. Apparent average grain size decreased significantly with lanthanum content. This aspect is reexamined in more detail in the present work through discussion regarding the morphology of Zr-rich cores, which was not discussed in previous investigations.9 Owing to the limited solubility of lanthanum in magnesium,14 almost all solute lanthanum solidifies as a thermally stable, hard eutectic Mg12La phase.15 Thus, the additional objective is to provide a detailed comparison of Mg–La–Zr and Mg–La alloys in order to highlight the effect of microstructure modifications through zirconium and lanthanum additions on room temperature mechanical properties.

2. Experimental Procedure

Mg–La, Mg–Zr, and Mg–La–Zr alloy ingots were prepared from 99.96% magnesium, 99.9% lanthanum (all in mass%) and Mg–33Zr master alloys (Magnesium Elektron Ltd.). To produce alloys, magnesium was first charged and melted using an electric resistance furnace under a flux cover in a stainless steel (SUS430 grade) crucible, coated with magnesium oxide to prevent the uptake of impurities from the crucible. Lanthanum and zirconium master alloys were added at a temperature of 750 and 720°C respectively. The temperature for the zirconium addition and the amounts were based on previous studies on grain refinement of magnesium casting.7,9 In these studies, a significant grain refinement in the alloys was observed with a soluble zirconium amount of 0.4–0.5%, a level which was attained with an addition of approximately 1–2% zirconium to the melt. In the present experiment, 1.5% zirconium was added to the melt charge. This addition provided a soluble zirconium amount of approximately 0.5% and a sufficient number of undissolved zirconium particles (insoluble Zr) that act as active heterogeneous nucleation sites, thus ensuring good grain refinement.8,9 The melt was also stirred to ensure proper mixing and good grain refining effect prior to pouring at 700°C into an open cast-iron mold with trapezoidal-cavity (18 mm top × 13 mm bottom × 10 mm high × 100 mm long) with a sufficient amount of riser to avoid shrinkage porosities in the cast bars for tensile testing. The melt was also poured to a bottom pour cast-iron mold with a cylindrical cavity (20 mm dia. × 100 mm high) to examine grain refining characteristics. During pouring, the melt was protected with a gas mixture of carbon dioxide and sulfur hexafluoride to prevent the ignition of magnesium. The tensile test specimens 6 mm in diameter with a gauge length of 30 mm were machined from the cast bars and tests were performed at room temperature with an initial strain rate of 6.67 × 10−4 s−1. Micro-structural examination of cast and tensile specimens was conducted by both optical and scanning electron microscopy. For micro-structural examination, specimens were lightly etched with a 2% solution of oxalic acid. For deep etching a 10% solution of nitric acid was used. The Vickers hardness test was carried out with a load of 49N and holding time of 15 s. The image analyser (Image Plus Pro ver. 4.5.1) was used to obtain the primary α–Mg grain size and area fraction of the eutectic. The chemical
analysis of alloys, obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES), is given in Tables 1 and 2.

3. Results and Discussion

3.1 Effect of lanthanum and zirconium on solidification structure

3.1.1 Addition of lanthanum to magnesium

Figure 1 shows the macrostructure of an Mg–2.1La alloy cast in a steel mold. Considering the cast structure of pure magnesium is essentially composed of columnar grains, lanthanum exerted some degree of grain refinement effect to magnesium casting. The macrostructure is entirely composed of equiaxed grains with an average grain size of 489 µm and the grain size further decreased to 425 µm at 3.3%La and 345 µm at 5.9%La. The degree of grain refinement effect of solute elements has been correlated by StJohn et al. in terms of grain growth restriction factor (GRF), which is an indicator of the initial rate of development of constitutional undercooling and expressed as

$$\text{GRF} = \frac{k}{m}$$

where $k$ is the slope of liquidus line, $m$ is the initial concentration of element $i$, and $k_i$ is the equilibrium distribution coefficient. Using this expression and taking the values of $m = -3.1$ and $k = 0.067$ by assuming the liquidus and solidus lines are straight in the Mg–La phase diagram given in the literature, the GRF for a 2.1% La addition yields the GRF value of 6.07 and the values for 3.3 and 5.9%La addition are 9.5 and 17, respectively. As shown in Fig. 2, comparing the plots of the $y$-coordinates of grain size (489, 425, 345 µm) and the $x$-coordinates (an inverse value of the GRF (1/$Q$)), which is 0.16, 0.1 and 0.06 for 2.1, 3.3 and 5.9%La, respectively, with the grain refinement effect of other additive elements presented in the literature, lanthanum lies almost on the coordinate line of aluminum, which is listed as a mild grain refiner for magnesium.

While the macrostructure of the as-cast binary magnesium alloys, containing 2.1, 3.3 and 5.9% lanthanum, exhibited a coarse spherical grain structure (Fig. 1), the microstructure within these grains, shown in Fig. 3, contained α-Mg dendrites, delineated by eutectic regions (dark areas). The eutectic area at higher magnifications revealed the two-phase eutectic structure composed of Mg12La and magnesium phases. In order to observe the morphology of the lanthanum intermetallic compound, a cast Mg–5.9% La alloy was sublimated to vaporize the magnesium dendrites and eutectic magnesium phase. As shown in Fig. 4(a), a skeletal structure magnesium–lanthanum compound left behind in the eutectic areas was all interconnected. XRDS analysis indicated that the compound was no longer Mg12La but was MgLa3 due to the vaporization of magnesium. Conversely, a micrograph in Fig. 4(b) shows the morphology of the eutectic magnesium phase left behind by etching the Mg12La phase away by a 10% solution of nitric acid.

3.1.2 Addition of lanthanum to Mg–Zr alloys

The grain refinement effect of lanthanum on Mg–Zr alloys is shown in Fig. 5 together with the microstructure of zirconium grain-refined pure magnesium (Fig. 5(a)) for...
comparison. It appeared that the combination of lanthanum and zirconium exerted a much greater grain refining effect in comparison with only a zirconium addition. The average grain size was plotted against lanthanum content in Fig. 6. Grain size decreased quickly from approximately 35 µm at 0% La to 25 µm at 0.87% La then decreased gradually beyond this point and dropped to about 19 µm at 4.7% La. An increase in the area fraction of the eutectic region with lanthanum content will also contribute to the reduction in primary grain size. The combined grain refining effect of lanthanum and zirconium appears to level off at about 1% La and the gradual linear decrease in primary grain size observed beyond this point, is most likely due to an increase in eutectic area. In Fig. 6, the values for grain size from previous works⁹,¹⁹ were also plotted for comparison. All agree that the grain size decreased with lanthanum content. Since the grains in the Mg–La–Zr alloys were finer than those of the Mg–Zr alloy and of greater number per unit area, it was previously thought⁹ that due to lanthanum’s lack of solubility in magnesium, there would be a buildup of solute lanthanum at the growth front, restricting the crystal growth. It was also thought that a combination of the greater growth restricting factor of zirconium¹⁶ with the available potent zirconium particles present in the melt⁹ would lead to an increase in the number of crystal formations as might have occurred in the Mg–La–Zr alloys, resulting in a much greater grain refinement effect. However, the grain growth in the Mg–Zr alloy might have taken place right after solidification, while it did not occur or was hindered in the Mg–La–Zr alloys due to the
presence of lanthanum. For example, while the average grain size of the Mg–La–Zr alloys are all in good agreement, despite the casting temperature, the dimension of molds and technique of pouring differ from one another, all of which cause differences in cooling rate, the average grain size of the Zr grain-refined magnesium without lanthanum seems to differ more widely. This suggests the possibility of solid state grain growth in the Mg–Zr alloy. If so, the slower the cooling, the greater the grain growth should take place. Figure 7 shows a plot of grain size of the Mg–Zr alloy of a similar zirconium content solidified in various types of distinctive vessels: (1) cast-iron mold, cast at 700–720°C,6,7 (present work); (2) shell-mold, cast at 720°C,7 and vessel 3: boron-nitride coated steel cone ladle, sampled at 680–730°C.20-22 The shell mold has slower cooling than mold 1 and mold 3 can be considered as the slowest of all, since the melt was sampled with the ladle and then solidified. The grain size differs accordingly from finer grains (30–50 µm) obtained with the cast-iron mold to coarser grains obtained with the ladle sampling (50–90 µm). However, from this figure alone it is not possible to confirm the greater solid-state growth in samples with a slower cooling rate, because the slower cooling rate may alter nucleation events in the melt (e.g. fewer nucleation and hence coarser grains). In order to confirm if this difference in grain size was indeed due to the result of solid state grain growth or difference with the nucleation event during solidification, in the following discussion, particular attention is given to the forms of zirconium-rich cores. Since undissolved zirconium particles contribute significantly to the grain refining of magnesium by acting as nucleants and also the subsequent formation of Zr-rich core structures occur due to a zirconium solute built-up in the liquid adjacent to growing grains during solidification, Zr-rich cores and their morphologies can be a good indicator for nucleation events and the growth history of grains associated with solidification conditions.

### 3.1.3 Zirconium-rich coring

Zr-rich coring structures are commonly observed in the grain-refined microstructures of zirconium-containing magnesium alloys and are well documented in the literature.8,21-23 They are easily visible with deep acid etching and particularly with an SEM in back scattered mode. Figure 8 shows an example of such cores (bright areas) observed in the Mg–Zr alloy from the present study. As described in the aforementioned literature, they were found not only in the center but at the edges of grains, and also along the grain boundaries. The grain boundaries often cut through the Zr-rich cores and large grains in the structure often contained more than one Zr-rich core. All of these aspects can be found in Fig. 8. It was noted8 that this is due to shifting of grain boundaries during cooling from the solidification temperature. In fact, the presence of multiple cores in the grain and other aspects described are the indirect evidence of grain growth after completion of solidification. Since the Zr-rich cores originate from the undissolved zirconium particles as nucleants, followed by a peritectic solidification process,8,11,12 each Zr-rich core observed in the microstructure must belong to the originally solidified individual grain.

The density of zirconium is much greater than magnesium; thus, zirconium particles in the magnesium melt tend to settle over time to the bottom of the holding vessel, leaving fewer nucleants at the upper portion of the melt. Consequently,
when the upper melt was poured to solidify after long holding, the crystallites formed from fewer available nucleants have more space to grow, allowing the change in the form of Zr-rich cores from a round form shown in Fig. 8 to the more developed form with the rosette pattern shown in Fig. 9. This naturally results in a microstructure of much coarser grains. Despite the fact that the melt was solidified in the cast-iron mold, the reported average grain size was 60 µm, which is significantly coarser than when the melt was poured right after stirring. Although there is some difficulty in judging from the micrograph (Fig. 9(a)), each Zr-rich core in rosette form tended to correspond to an individual grain. In addition, when the melt, after being kept for a long time, is stirred again to bring the settled particles up from the bottom of the holding vessel and is immediately solidified in the same cast-iron mold (same cooling rate), it once again produces the microstructure similar to the one shown in Fig. 8 with round Zr-rich cores with an average grain size of 30 µm.8) This is indicative that for the grain size of the solidification structure from the melt containing the grain refiner is significantly affected by the available active nucleants and also indicative that the round Zr-rich cores is associated with the formation of copious crystallites, suggesting that the original solidification grains are small, although the final structure depends on the cooling conditions which will affect the solid-state grain growth. From these, it can be said that coarser grains, associated with a rosette core pattern, were caused by solidification due to fewer numbers of crystallites originating in the melt and conversely, coarser grains, associated with a round core structure, experienced abundant crystallite formation. It is also noted that the flower-like form occurs when zirconium content decreases in the melt.7,23) Since the amount of soluble zirconium up to 0.4–0.5% in the melt is directly proportional to the amount of zirconium addition,7) the occurrence of the rosette form at lower soluble zirconium contents may be related to less available active zirconium particles in the melt. Nevertheless, the Zr-rich rosette patterns are a more progressed form of core structure, resulting from fewer crystals in the melt, while the presence of round Zr-rich forms is indicative of abundant crystal formation and may be called a stunted crystal growth due to the confined space. The rosette form of dendrite pattern was also observed in the cast microstructure of high purity AZ91 (Mg–Al–Zn) alloy with a resultant solidification grain size of approximately 60 µm.24)

The Mg–Zr alloy (0.4–0.5%Zr), solidified in various types of vessels right after stirring of the melt, produced apparent average grain sizes ranging from approximately 30 to 90 µm depending on the vessel types (Fig. 7). In the light of these observations stated above, it may be reexamined if the coarser grains indicated in Fig. 7 contain rosette or round forms of Zr-rich cores. As shown in Fig. 10, the micrograph of the melt solidified in a shell-mold contained round Zr-rich cores with an average grain size of 70 µm7) and for the melt solidified in boron-nitride coated steel cone ladle, the Zr-rich cores shown in the literature21,22) were also found to be circular or elliptical in form regardless of differences in grain size and grains appear to contain multiple cores, suggesting that the originally solidified grains are smaller in size.

3.1.4 Effect of lanthanum

Figure 11 shows Zr-rich cores observed in the Mg–La–Zr alloys. All Zr-rich cores exhibited a round form, the diameter of which was approximately 20 µm or less. This is indicative of copious crystal formations during solidification. Zr-rich cores in the Mg–Zr alloy (Fig. 8) also exhibited a similar round form and size. However, it was observed that the Mg–Zr alloy has more incidences of multiple Zr-rich cores within the grains than Mg–La–Zr alloys, whereas in Mg–La–Zr alloys (e.g. 0.42%La in Fig. 11(c)) each Zr-rich core tends to correspond to an individual grain, although they are not necessarily located at the center of the grains. This suggests that the grains in the Mg–Zr alloy experienced more grain growth than the Mg–La–Zr alloys (0.19%La and 0.42%La). In order to confirm if this is indeed due to the solid state grain growth in the Mg–Zr alloy and not due to the result of more nucleation during solidification in the Mg–La–Zr alloys, the numbers of the Zr-rich cores were counted. It was found that the cores in all micrographs are approximately 40 to 45 in number, suggesting that there is no significant difference in the nucleation event between Mg–Zr and Mg–La–Zr alloys. This implies that the grains in Fig. 5(a) (Mg–Zr alloy) would
have been as small as those in Fig. 5(c) or 5(d) (Mg-La-Zr alloy) or approximately 25 µm based on extension of the line in Fig. 6 to 0% La right after solidification if it had not been for subsequent grain growth. Table 3 shows the standard deviation of grain size obtained from the micrographs using image size analysis. The standard deviation of grain size for the Mg-Zr alloy is 2 to 6 times larger than those for the Mg-La-Zr alloys, indicating that a greater spectrum of grain size exists in the microstructure of the Mg-Zr alloy and indicating that significant grain growth has taken place. The optical micrograph of the Mg-0.47Zr alloy, shown in Fig. 12, exhibits evidence of grain growth.

The stronger tendency of solid-state grain growth in the Mg-Zr alloy than the Mg-La-Zr alloy discussed above is solely based on the morphology of Zr-rich cores which grew from undissolved active zirconium particles in the melt. Since these particles contribute significantly to the grain refining of the magnesium, Zr-rich cores and their morphologies are a good indicator of nucleation events. It may be that the lanthanum’s ability to suppress grain growth during solidification also extends to suppressing the grain growth after solidification.

A heat treatment of Mg-Zr alloy in moist argon gas or in hydrogen is known to transform solute zirconium in the alloy to zirconium hydride and form precipitates, which were found to inhibit grain growth by the pinning of the boundaries.25,26) However, zirconium itself does not appear to hinder the mobility of grain boundaries after solidification, allowing the solid-state grain growth in the Mg-0.5Zr alloy. As a result, the final grains often contain multiple zirconium-rich cores.7,22) On the other hand, when a small amount of lanthanum, as little as 0.5%, was added to the Mg-0.5Zr alloy, the grain growth was greatly suppressed (Fig. 6). These combined effects of lanthanum and zirconium may be the cause of the finer grain size of the Mg-La-Zr alloys than the Mg-0.5Zr alloy.

### Table 3 Effect of lanthanum content on primary α-Mg average grain size (d) with standard deviation (σ) in alloys containing approximately 0.5% soluble zirconium (Table 1).

<table>
<thead>
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<th>La (mass%)</th>
<th>Grain size, d/µm</th>
<th>Standard deviation, σ/µm</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>34.9</td>
<td>16.2</td>
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<tr>
<td>0.19</td>
<td>29.9</td>
<td>7.60</td>
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<tr>
<td>0.42</td>
<td>26.7</td>
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</tr>
<tr>
<td>4.75</td>
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<td>2.71</td>
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3.2 Mechanical properties

3.2.1 Hardness

Figure 13(a) shows an image of the eutectic areas of the Mg-2.6La-0.48Zr alloy exhibiting degenerated lamellar eutectic morphology. Despite the change in primary Mg grain morphology due to the zirconium addition, there was no apparent effect on eutectic morphology. The Mg12La eutectic is a hard phase with a hardness value of about 185 HV.15) As shown in Fig. 13(b), the eutectic area increases linearly with lanthanum content for both the Mg-La and Mg-La-Zr alloys. For this reason, alloy hardness increases with increasing lanthanum content (Fig. 14). Despite the significant differences in microstructure, the hardness values for Mg-La and Mg-La-Zr are very similar.
3.2.2 Tensile properties

Figure 15 shows the comparison of tensile properties between Mg–La alloys containing fine spherical primary \(\alpha\)-Mg dendrites and Mg–La–Zr alloys containing fine spherical primary \(\alpha\)-Mg crystals. The values of UTS and 0.2% proof strength for both alloys increased with lanthanum content due to an increase in the Mg\(_{12}\)La phase. However, these values for the Mg–La–Zr alloys are much higher than those of the corresponding Mg–La alloys despite their having similar average hardness values. The values of UTS and 0.2% strength increased approximately by 50 MPa over those of the Mg–La alloys, indicating that a contributing factor to these higher values is the grain refinement of the \(\alpha\)-Mg grains, which helped increase uniformity in microstructure. For example, the variation in the spread of hardness values in Fig. 14 in the Mg–La–Zr alloys containing fine spherical structures is almost half that of the Mg–La alloys, suggesting that the distribution of the eutectic area in the Mg–La–Zr alloys is much more uniform than that in the Mg–La alloys. The coarse grain structure in the cast Mg–La alloys will have fewer grains favorable to deformation in relation to tensile direction than a grain-refined structure.\(^9\) All of these aspects in the Mg–La alloys may lead to stress concentration in some areas of the microstructure and the accommodation of strain in coarse dendrite structures will be more difficult than in structures with fine spherical crystals as in the Mg–La–Zr alloys, resulting in earlier fracture.

3.3 Fracture characteristics

3.3.1 Mg–La alloys

Magnesium has limited ductility at room temperature except when the slip planes are favorably aligned with the stress direction. The tensile specimens show only about 7% elongation (Fig. 15) and, as shown in Fig. 16, the fracture surface of the tensile specimen exhibited rugged surfaces, indicating a trans-granular fracture characteristic.

The solidification structures of Mg–La alloys (Fig. 3) contained primary magnesium dendrites and a hard Mg\(_{12}\)La compound existed within the inter-dendritic areas forming the interconnected network of the eutectic structure (Fig. 4). The presence of the Mg\(_{12}\)La eutectic phase contributed to an increase in hardness, resulting in higher values of UTS and 0.2% proof strength, and also susceptibility to crack formation within the eutectic regions. Shown in Fig. 17 are backscattered images of longitudinal cross-sections at the fracture end of the tensile specimen of Mg–3.3La and 5.9%La alloys exhibiting cracks that formed within the eutectic areas and propagated along the magnesium dendrites (shown by arrows). Elongation values were reduced to less than 2% above 3.3%La. Although the fracture surface contained dendrite fractures, shown by a dark arrow in Fig. 18, it exhibited conspicuous eutectic fractures (areas around the white arrow).

3.3.2 Zirconium containing alloys

(1) Mg–Zr alloy

In contrast to the low-ductility fracture feature observed in the cast pure magnesium specimen (Fig. 16), the Mg–Zr alloy shown in Fig. 19(a) contained many dimpled surfaces, indicative of ductile fracture, in many of the fractured grains. The value of elongation to fracture of the Mg–Zr alloy increased dramatically to about 33% from 7% for pure magnesium. The longitudinal cross-section at the fracture end (Fig. 19(b)) contained twin formations and large voids of various sizes which may have originated along the twin boundaries.

The Mg–Zr alloy specimen contains undissolved zirconium particles 2–3 \(\mu\)m in size, which acted as nucleants and exist in the center of the Zr-rich cores in the grains (Fig. 8). Qian et al.\(^{13}\) noted that the majority of active zirconium particles in these cores were in the range of 1 to 5 \(\mu\)m in size. Zirconium particles are often associated with a single ring or concentric multi-rings (Fig. 8) of an increased zirconium concentration.\(^7,8\) By close observation of the micrographs...
shown in Figs. 20(a), 20(b) and judging from the size and form of the cores (~20 µm), some of the Zr-rich cores, as indicated by arrows in Fig. 20(a), appeared to be cut through by the fractured plane. Also as indicated by arrows in Fig. 20(b), there were particles 2–3 µm in size, most likely zirconium particles, at the bottom of the dimples, although not all dimples were associated with the particles. Since it takes a larger strain level to form voids from smaller particles.
than larger particles, a contribution by void formation to fracture due to particles of 2–3 µm may not be significant. Instead the dimples that originated from these small particles may have formed during the last stage of fracture.

(2) Mg–La–Zr alloys

With an addition of lanthanum to Mg–Zr alloys, eutectic consisting of Mg₁₂La and magnesium phases forms around the primary-Mg crystals. Due to the hardness increase with the increasing lanthanum content in the alloys, which solidified as the Mg₁₂La eutectic phase, the values of UTS and 0.2% proof strength increased over those of the Mg–Zr alloy and exhibited higher values than those of Mg–La alloys with similar lanthanum content. The ductility values also were much higher than those for the Mg–La alloys. However, zirconium did not exert any effect on the morphology of the eutectic structure, so the eutectic areas remained as a source of void formation and cracks, resulting in fracture from these areas and decreasing the ductility of the alloy with increasing lanthanum content. Examples of cracks and voids, indicated by arrows, formed within the eutectic area are shown in Figs. 21(a), 21(b). It appears that the initiation of voids occurs between the magnesium phase (either primary magnesium or eutectic magnesium phase) and the eutectic Mg₁₂La phase. For example, in Fig. 21(b), voids indicated by arrows 1 and 5 occurred between the primary magnesium and eutectic Mg₁₂La phase and those shown by arrows 2, 3 and 4 were formed between the eutectic magnesium phase and Mg₁₂La phase or due to cracks of the eutectic phases. Figure 22(a) shows the fracture surface of Mg–4.2La–Zr, which exhibited extensive eutectic fracture, skirting individual grains. Shown in Fig. 22(b) is a detail of a fracture surface exhibiting the exposed eutectic areas. In this photograph and also in Fig. 23, an enlarged photograph of the arrowed area in Fig. 22(b), decohesion between two phases is evident, an example of which is indicated by arrows. In the photograph (Fig. 23), a partly separated cylindrical phase is still in place (arrow 1) and at nearby location (arrow 2) only a cylindrical cavity remains.

4. Conclusions

In a previous investigation, the combined addition of zirconium and lanthanum was found to confer more marked grain refining than zirconium alone. The present experimental study, conducted in order to investigate the effects of lanthanum and zirconium, confirmed the previous result. In this investigation, particular attention was given to the form of the Zr-rich cores in the microstructure to provide further insight on this marked grain refining effect. The Zr-rich cores, originating from fewer nucleants, grew in the form of a rosette pattern associated with coarser grains, most likely owing to more available space in the melt. With the presence of abundant crystallites in the melt, growth is restricted and the Zr-rich cores remain in a small round form due to less available space to grow. However, the average grain size varies depending on the mode of cooling and lanthanum contents. Based on these findings, it is concluded that:

![SEM micrographs of the fracture surface of the tensile specimen of Mg-0.5Zr alloy: (a) revealing fractured Zr-rich cores (indicated by arrows) and (b) particles at the bottom of dimples (indicated by arrows).](image1)

![Initiation of voids and cracks, indicated by arrows, within the eutectic regions of (a) Mg–1.6La–Zr and (b) Mg–2.6La–Zr alloys.](image2)
Lanthanum in the Mg-Zr alloy suppresses grain growth after solidification while in the absence of lanthanum addition, grain growth takes place. The overall effect is that the average grain size decreases with an addition of lanthanum.

Lanthanum content as low as 0.5% hinders grain growth.

Owing to high hardness of Mg₁₂La eutectic network and change in morphology of primary magnesium phase from course dendrites to a fine spherical form, the values of 0.2 proof stress and UTS for Mg-La-Zr alloys significantly increased over those for Mg-La alloys with similar lanthanum content. Elongation values were also much higher due to the change in morphology.

Eutectic Mg₁₂La exists as an interconnected phase and fracture originated within the eutectic areas.

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