Magnesium extrusion alloys: A review of developments and prospects

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Magnesium (Mg) alloys have received significant interest in the past 20 years, owing to a non-linearly increasing demand for lightweight structural materials in transportation and a surge in portable electronics. The suitability of Mg-alloys for what is undoubtedly an emerging market of Mg extrusion products remains to be realised. Magnesium extrusions alloys to date have had lower industrial uptake than their counterpart aluminium extrusion alloys, predominantly due to lower extrudability, lower formability, tension-compression yield asymmetry and no clear advantage in the specific strength of magnesium extrusion alloys produced to date. Any improvement in extrusion alloy strength and extrudability requires a better understanding of the effects of alloy composition and processing conditions; and how these dictate the final alloy microstructure. Microstructural factors, such as the presence of second phase particles, grain size, twins and texture, are critical to balance strength, formability and extrudability. This review sheds insightful information on the processing-microstructure-property relationships of extruded magnesium alloys - which have previously not been apparent or appreciated - on the basis that the review presents several uniquely compiled and consolidated plots. Historical and recent progress in magnesium extrusion alloys, based on the magnesium-aluminium, magnesium-zinc, magnesium-rare earth, magnesium-tin and magnesium-lithium alloy systems, are critically reviewed; including the advances in extrudability, mechanical properties and microstructural characterisation. It is demonstrated that high strength extrusion alloys with negligible tension-compression yield asymmetry can be developed, whilst extrudability can be significantly improved in relatively dilute alloys containing tin, calcium, manganese, or rare earth elements. The challenges associated with the ‘gap’ in properties between the high-performance magnesium extrusion alloys and aluminium extrusion alloys are identified, and a number of critical points discussed regarding the ready prospects for development of next generation magnesium extrusion alloys with high extrudability, high specific strength and negligible yield asymmetry by utilising conventional alloy and processing design.

\textit{Keywords:} Magnesium, extrusion, mechanical properties, grain size, precipitation
1. Introduction

Magnesium (Mg) is the lightest structural metal. The density of Mg is 1.74 g/cm$^3$ at 20°C, which is approximately two-thirds that of aluminium (Al) and a quarter that of steel. Magnesium is an abundant element, being the 8th most abundant element in earth’s crust and the 3rd most abundant ion in sea water. Since 1808 when the first Mg was produced in quantity, the purity of commercially available Mg now exceeds 99.8%. Some useful characteristics of Mg include high stiffness, Young’s modulus about 45 GPa at room temperature, high specific heat about 1.05 kJ/(kg·°C), and a low melting temperature (~650°C)\textsuperscript{1}. Products produced from Mg and its alloys are readily manufactured by near-net shape casting. As early as 1909, a Mg crankcase was presented at the International Air Transport Fair in Frankfurt \textsuperscript{2}. In 1924, Mg alloys were used in the automobile industry for the first time to produce pistons by die-casting \textsuperscript{2}. Although Mg alloys have been industrially used since the early 20th century, their wider applications remain limited, predominantly because the cost-effective commercial Mg alloys have inadequate properties such as yield strength, ductility, formability, and corrosion resistance \textsuperscript{3, 4}. Since the late 1990s, a renewed interest in Mg alloys has been stimulated by the requirement of weight-saving in the automotive, aerospace and portable electronics industries. In the transportation industry, the improvement of energy efficiency, and reduction of greenhouse gas emissions is becoming increasingly important, where Mg alloys are regarded as an important material to achieve light-weighting.

Despite the emerging and critical significance of Mg alloys as a class of engineering materials, Mg extrusion alloys have had only very minimal usage and industrial penetration to date; which can also be generally said of wrought Mg alloys (including sheet and forgings) \textsuperscript{3}. Mg extrusion products account for less than 1.5% of the annual output of Mg production in 2004, and remains at <3% in 2013 \textsuperscript{5, 6}. In contrast, ~25% of semi-finished Al-alloy products are produced by extrusion, and widely adopted in infrastructure, automotive and aerospace applications \textsuperscript{7}. There are principally three major issues that have restricted the wider uptake of Mg alloy extrusions.

The first issue is the properties of the extrudate, with Mg extrusions having lower strength than Al extrusions, poor formability, and tension-compression yield asymmetry (compressive yield strength / tensile yield strength < 1) \textsuperscript{8}. Table 1 reveals the tensile properties and tension-compression yield asymmetry of commercially available Mg extrusion alloys \textsuperscript{5, 9}. In general, the strength of extrusion alloy is represented by the yield strength; whilst a proxy for formability is represented by the reported elongation (given formability is not typically reported); whilst it should be noted that tensile ductility does not fully represent alloy formability as relevant to metal forming, because formability in the context of plastic deformation of metals is the ability of a metal piece to be biaxially stretched, deep drawn, stamped or bent without failure \textsuperscript{5}. None the less, it is readily observed that the tensile properties of commercial Mg extrusions are inadequate relative to counterpart Al alloys. Commercial Mg extrusion alloys also have significant tension-compression yield asymmetry. The yield strength in compression test is about 0.4 – 0.8 of that in tension, which is not the case for Al extrusion alloys.
The second issue is commercial viability, with some Mg alloys being expensive (depending on alloying elements) and with only few Mg alloys capable of being extruded at high enough speeds to be viable. The die exit speeds reported for Mg are in the 20 – 30 m/min range for basic profiles of the so-called easy-to-extrude alloys, such as Mg-3Al-1Zn-0.3Mn (AZ31) and Mg-2Zn-1Mn (ZM21). These extrusion speeds are about five to ten times slower than a typical Al alloy \(^{10,11}\). For the difficult-to-extrude Mg alloys, such as Mg-6Al-1Zn-0.3Mn (AZ61) and Mg-6Zn-0.6Zr (ZK60), or for the complicated section in any extruded profile, the extrusion speed of Mg alloys nominally drops by a factor of ten or more \(^{10}\). Therefore, the realisation of Mg alloy extrusions to date has been accompanied by significantly lower production rates and lower cost-effectiveness of extruded products compared to Al alloy extrusions.

The third issue is the poor corrosion resistance of Mg extrusion alloys. Whilst Al alloys have good corrosion resistance, in contrast, nearly all Mg alloys have intrinsically low corrosion resistance. The low electronegative potential of Mg and its alloys renders them prone to galvanic corrosion when in contact with any other engineering alloys. Additionally, the oxide/hydroxide layer that forms on Mg and its alloys does not adequately protect the metal surface from corrosion, and is not stable in most aqueous environments \(^{12}\). The corrosion rate of Mg alloys, in general, is predominantly influenced by

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### Table 1. Typical tensile properties of selected commercial Mg and Al extrusion alloys \(^{8,9}\).

<table>
<thead>
<tr>
<th>Designation</th>
<th>Compositions wt.%</th>
<th>Temper*</th>
<th>YS MPa</th>
<th>UTS MPa</th>
<th>Elongation %</th>
<th>Tension-compression yield asymmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Pure Mg</td>
<td>F</td>
<td>87</td>
<td>185</td>
<td>5</td>
<td>0.51</td>
</tr>
<tr>
<td>M1</td>
<td>Mg-1.5Mn</td>
<td>F</td>
<td>189</td>
<td>255</td>
<td>12</td>
<td>0.46</td>
</tr>
<tr>
<td>AZ10</td>
<td>Mg-1.5Al-0.2Zn-0.2Mn</td>
<td>F</td>
<td>155</td>
<td>240</td>
<td>10</td>
<td>0.45</td>
</tr>
<tr>
<td>AZ31</td>
<td>Mg-3Al-1Zn-0.3Mn</td>
<td>F</td>
<td>200</td>
<td>260</td>
<td>15</td>
<td>0.49</td>
</tr>
<tr>
<td>AZ61</td>
<td>Mg-6Al-1Zn-0.3Mn</td>
<td>F</td>
<td>230</td>
<td>310</td>
<td>16</td>
<td>0.57</td>
</tr>
<tr>
<td>AZ80</td>
<td>Mg-8Al-0.5Zn-0.1Mn</td>
<td>T5</td>
<td>275</td>
<td>380</td>
<td>7</td>
<td>0.88</td>
</tr>
<tr>
<td>HM31</td>
<td>Mg-3Th-1Mn</td>
<td>T5</td>
<td>270</td>
<td>300</td>
<td>10</td>
<td>0.63</td>
</tr>
<tr>
<td>ZK21</td>
<td>Mg-2Zn-0.6Zr</td>
<td>F</td>
<td>195</td>
<td>260</td>
<td>4</td>
<td>0.69</td>
</tr>
<tr>
<td>ZK60</td>
<td>Mg-6Zn-0.5Zr</td>
<td>F</td>
<td>260</td>
<td>340</td>
<td>11</td>
<td>0.88</td>
</tr>
<tr>
<td>WE43</td>
<td>Mg-4Y-3RE</td>
<td>F</td>
<td>214</td>
<td>296</td>
<td>14</td>
<td>~1</td>
</tr>
</tbody>
</table>

*F: As-fabricated

T3: Solution heat treated and naturally aged to a substantially stable condition

T5: Cooled from an elevated temperature shaping process and then artificially aged to a substantially stable condition

T6: Solution heat treated and artificially aged to peak hardness

O: Annealed

T751: For Al extrusions: solution heat-treated, stress-relieved by controlled stretching and then artificially overaged in order to achieve a good exfoliation corrosion resistance. The products receive no further straightening after stretching.
alloy chemistry, i.e. dictated by the specific elements with which Mg is alloyed\textsuperscript{12}. The corrosion mechanisms of Mg extrusion alloys are the same as those of Mg alloys prepared in other forms, e.g. cast alloys, rolled sheet, die cast alloys, etc. A comprehensive treatise of how alloying additions affect the corrosion of Mg, and the associate electrochemical mechanisms, have been demonstrated in other recent reviews \textsuperscript{4, 12}. At present, protective coatings remain the most effective (and the most widely-employed) means to increase the corrosion resistance of Mg alloys \textsuperscript{13}. However, the topic of coatings is beyond the scope of this review, as it is not related to the alloying and processing design of Mg extrusion alloys; therefore in the present review the specific effect of the extrusion process on the subsequent corrosion performance of in Mg and its alloys is documented below.

Owing to the basic features of Mg alloy extrusions described above, and driven by the increasing market demand for light alloy extrusions, the property ‘gap’ in properties between Mg and Al extrusion alloys has sought to be bridged by considerable research over the last decade. More than 10000 papers have been published in the past 10 years on the topic of Mg extrusion alloys; with the number of papers in 2016 being twice as many as that in 2007 (Fig. 1) \textsuperscript{14}. Considering the significant increase in the total number of papers in the (overall) research field of Mg in the past ten years, the ratio between articles when using the search keywords “magnesium extrusion alloy” and “magnesium alloy” is also plotted against years. It is shown that in the past ten years, the fraction of papers related to magnesium extrusion alloys amongst the papers published overall on Mg, increased from 20.8% in 2007 to 24.1% in 2016.

\textbf{Fig. 1.} Number of articles published in the past 10 years when searched using the keywords “magnesium extrusion alloy”, and the fraction of journal articles when using the search keywords “magnesium extrusion alloy” and “magnesium alloy”, according to Google Scholar \textsuperscript{14}.

In order to provide a framework for which recent works have reported considerable improvements in the extrudability and mechanical properties of Mg extrusion alloys, the schematic in Fig. 2 is presented.
Fig. 2. Schematic diagram showing the trends and significant research directions of Mg extrusion alloy development to date.

The tensile yield strength of Mg extrusion alloys has increased from <300 MPa before 2006, to present yield strengths of over 400 MPa for rare earth (RE) element free alloys $^{15,16}$ and ~500 MPa for RE containing alloys $^{17,18}$. The ductility of Mg extrusion alloys has also increased from < 20% elongation to >40% $^{19,20}$ following years of alloy development. Notably, highly formable pure Mg extrusions, which can be compressed, rolled, and bent even at room temperature, has been developed $^{21}$. With respect to extrusion speed, the maximum extrusion speed of some dilute Mg alloys can be as high as that of Al extrusion alloy $^{22,23}$. Recently, a “stainless” Mg extrusion alloy was developed, which exhibited excellent corrosion resistance $^{24}$. However, formability, extrudability and corrosion resistance are generally inversely correlated with strength, and to date, it is still difficult to optimise all these properties simultaneously.

Facilitated by advances in alloy characterisation and the emergence of new analytical techniques, such as electron backscattered diffraction (EBSD), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and increased collection efficiency of 3-dimensional atom probe tomography (APT), more insights have been provided in a composition-processing-microstructure-property relationship. Such insights can serve as the basis for future alloy and processing design for Mg extrusion alloys. Despite the aforementioned studies on Mg-alloys, including a number of broad topic monographs and focused review papers $^{25,26}$, none have specifically focused on the development of Mg extrusion alloys. The purpose of this article is to provide a comprehensive review on the development of Mg extrusion alloys with a focus on the 21st century, which includes a review of the key factors that affect the extrudability and mechanical properties. The present review also uses the insights gained to discuss prospects and potential future alloy considerations to enable further enhancement in extrudability and mechanical properties.

2. Extrudability of Mg alloys

The property of “extrudability” refers to the multivariable processing window of an alloy during extrusion. This window is determined by the press limit (left lines in Fig. 3a) and the limit for hot
cracking (right lines in Fig. 3a). For a material with good extrudability, it can be extruded under low extrusion load and high extrusion speed, having good surface finish and tight dimensional tolerance without defects. Compared to Al extrusion alloys, Mg alloys have much lower extrudability, i.e. they must be extruded at lower speeds and within a narrower range of extrusion temperatures (Fig. 3a). This so-called low extrudability leads to a lower production efficiency and higher cost than Al extrusion alloys. For some Mg alloys such as AZ61, ZK60 and high RE-containing alloys, it has low extrudability, simply because they are hard and the extrusion machine cannot press them through a die at low temperature, and thus they have to be extruded at higher temperature with low speed. When the extrusion speed is beyond the right limit of the appropriate processing window, cracking, also known as hot shortness, forms on the surface of the extrudate (Fig. 3b). Hot shortness is formed when the local temperature in the die exceeds the solidus temperature of the alloy and/or the melting temperature of any second phase (if it exists). Another factor for the occurrence of transverse cracks in the peripheral zone is the tensile stress on the surface of extruded bars. In extrusion, the material in the die is under three-dimensional compression, and thus crack formation is suppressed. Only when a material has passed through the die will tensile stress be developed close to the surface. Given that the tensile strength of Mg alloy decreases significantly with the increasing temperature, transverse cracks will form if the tensile stress on the extrusion surface is higher than the hot strength of Mg alloy (as seen in the lower image of Fig. 3b).

Fig. 3. (a) Extrusion limit diagrams of some commercial Mg alloys and the Al alloy AA6063. (b) Photos showing surface of as-extruded Mg alloy AZ31 processed with a ram speed of 2.6 mm/s, 6 mm/s and 14.7 mm/s at 375°C (4 mm-diameter of extruded rods).

Several methods have been applied to enhance the extrudability. With respect to alloy design, it is noted that a lower alloy content, generally results in better extrudability (which may also be judged by Fig. 3a). Firstly, the Mg alloy with lower alloying concentration is generally softer during extrusion and thus lower extrusion temperature and higher speeds can be tolerated before the press capacity is reached. Pure Mg can be extruded at 80°C, but our unpublished result has shown that
lowest extrusion temperature for Mg-1Zn alloy is 150°C, when pure Mg and Mg-1Zn samples with same dimension were extruded at 0.1 mm/s using a 100-tonne extrusion machine. Secondly, hot cracking is increasingly difficult to occur with the decreasing concentration of alloying elements, such as Zn which is known to decrease the alloy solidus temperature and lead to the formation of low melting temperature second phases. For example, the decrease in Zn concentration from 6.8% to 3.8% increased the maximum extrusion speed by 3 times. By removing Zn from the alloy AZ31, the eutectic Mg-Al-Zn phase with low melting temperature, ~338°C, does not form, therefore resulting in an increase in the maximum extrusion speed by ~20%. Extrudability can also be enhanced by adding the alloying elements that increase the solidus temperature, such as zirconium (Zr) and manganese (Mn). It has been shown that the addition of 0.8 wt.% Zr to Mg-6Zn increased the maximum extrusion speed by 10 times, which is considerable; whilst the alloy Mg-1Mn presents high extrudability and a processing window similar to that of Al-alloy AA6063 (Fig. 3a). Recently, several Mg-Ca and Mg-Sn based alloys have been researched, capable of being extruded at comparatively high speed, which are discussed in §5.

With respect to thermomechanical processing, a homogenisation treatment (where homogenisation refers to a high-temperature soak usually at the solution heat treatment temperature and sustained for a suitable duration) of Mg-alloy billets prior to extrusion can improve extrudability. For example, homogenised AZ31 billets present a larger processing window than as-cast AZ31 billet. Furthermore, proper lubrication in extrusion can reduce friction and tensile stress on the surface of extruded bars, and help mitigate temperature rise caused by the friction between the billet and its container and the extrusion die, in an effort to avoid hot shortness. Molybdenum di-sulphide and combination of grease, oil, and graphite are often used as lubricants, as they can form a lubricating film, and have relatively low thermal conductivity.

3. Processing-microstructure-mechanical properties of Mg extrusion alloys

During extrusion, the microstructure of Mg changes significantly, which include changes such as dynamic recrystallization, static recrystallization (after exiting extrusion die), alignment of crystalline orientation (strong basal texture), refinement of second phases, and also dynamic precipitation. This process is schematically illustrated in Fig. 4a.

Dynamic recrystallization results in replacement of coarse grains in the cast ingot by fine recrystallized grains during hot extrusion. For example, large grains of about 380 μm in diameter in as-homogenised AZ80 alloy are refined to about 1 μm after extrusion (Figs. 4b and c). Moreover, during extrusion of homogenised AZ80, solute atoms that are dissolved in Mg matrix during homogenization treatment can lead to dynamic precipitation, forming fine Mg17Al12 particles with a diameter of 200 – 400 nm (Fig. 4d). Hot extrusion also results in the fragmentation of comparatively large sized eutectic phases that are nominally present along grain boundaries (Fig. 4e), making the refined second phase more uniformly distributed with the alloy (Fig. 4f). The significant change in microstructure and re-distribution of alloying elements during extrusion greatly affects the mechanical properties of Mg alloys, with an attendant influence on corrosion properties.
3.1. Effect of extrusion temperature and speed on mechanical properties

The mechanical properties of extruded alloys – which are dictated by alloy composition and microstructure – are significantly affected by extrusion temperature and speed. Other factors, including the extrusion ratio\(^{44-47}\), pre-extrusion ageing\(^{48,49}\), cold pre-extrusion deformation\(^{50}\), double extrusion\(^{51-54}\) and post-extrusion severe plastic deformation\(^{55}\), have all been investigated for their effect on the resultant mechanical properties of Mg extrusion alloys. Such additional processing steps have had limited industrial uptake, as they have proved to be either impractical for industry, have a limited effect on the mechanical properties, or don't provide properties relative to cost that outperforms competitor materials. Post-extrusion ageing is an effective way to improve the strength, but it is dependent on alloy composition, and will be reviewed in §5.

The effect of extrusion temperature on tensile yield strength (YS), ultimate tensile strength (UTS), and elongation of selected Mg extrusion alloys are summarised in Fig. 5\(^{56-62}\). The alloys in Fig. 5 have widely varying compositions, but on this basis of comparing compositions, the alloys presented have been subject to the same extrusion ratio and speed, and plotted against their extrusion temperature. This compilation allows the reader to gain an initial high-level appreciation of the processing-property space that existing Mg extrusion alloys occupy. Such a compilation of data also allows one to observe the general trend that the yield strength of an extruded alloy generally decreases with the increase in extrusion temperature (Fig. 5a). For example, the tensile yield strength of Mg-3Zn-0.2Ca-0.5Y was 309 MPa when extruded at 150°C, and significantly decreased to 160 MPa when extruded at 300°C\(^5\). Such a result is representative of most of Mg alloys, demonstrating that a higher yield strength is more likely to be achieved with low extrusion temperatures. As shown in Fig. 5b, the ultimate tensile strength of an extruded Mg alloy decreases or changes only subtly with an increase in extrusion temperature. Also, in the classical paradox for metallurgists, the elongation of extruded alloys is enhanced with an increase in extrusion temperature. For example, when the extrusion temperature was increased from 300°C to 400°C, the elongation of the Mg-0.2Zn-0.3Ca-
0.14\text{Mn} markedly increased from 20.6\% to 32\%\textsuperscript{57}, whilst the increase in elongation of Mg-1Zn-0.5Ca alloy was much more significant, from 8\% to 44\% (Fig. 5c)\textsuperscript{58}.

\textbf{Fig. 5.} Variation of (a) tensile yield strength, (b) ultimate tensile strength and (c) elongation as a function of extrusion temperature for Mg-extrusion alloys processed with the same extrusion speed and extrusion ratio\textsuperscript{56-62}. 
Figure 6 represents a compilation of results from tensile testing, allowing a comparison between tensile yield strength, ultimate tensile strength and elongation of Mg extrusion alloys, subject to different extrusion speed, with a constant extrusion temperature and ratio.

An increase in extrusion speed is seen to generally result in a decrease in yield strength (Fig. 6a). For example, when increasing extrusion speed from 1 mm/s to 9 mm/s, the yield strength of Mg-1Zn-1Mn-0.5Ce alloy decreased quite significantly from 317 MPa, to 135 MPa. Even in the case of heavily-RE-alloyed Mg alloys, the yield strength was also equally sensitive to extrusion speed. When Mg-9Gd-3Y-1.5Zn-0.8Zr alloy was extruded at 0.1 mm/s, the yield strength was 333 MPa, however, when the extrusion speed was increased by 3 times to 0.3 mm/s, the yield strength was decreased to 267 MPa. As such, independent of alloy compositions explored to date, high strength extrusion alloys are more likely to be produced by low-speed extrusion. Concomitantly, increased extrusion speed also leads to a decreased ultimate tensile strength (Fig. 6b). Interestingly, how extrusion speed affects alloy elongation was unique on a case-by-case basis (Fig. 6c). For alloys such as Mg-1Zn-1Mn-0.5Ce alloy, increased extrusion rate resulted in an increased alloy ductility, whilst for other alloys, such as Mg-7Sn-1Zn-1Al and ZK60 alloys, elongation was almost unchanged or even decreased with an increase in extrusion speed.
Fig. 6. Variation of (a) tensile yield strength, (b) ultimate tensile strength and (c) elongation as a function of extrusion speed for extrusion alloys subjected to same extrusion temperature and ratio 20, 63-68.

3.2. Grain size effect

Inspection of the microstructures in Mg alloys extruded at different temperatures or speeds has revealed that the grain size of extrusion alloys increases with an increase of extrusion temperature and extrusion speed, as shown in Fig. 7 20, 56-68.
Moreover, the higher extrusion temperature or speed also leads to a larger fraction of recrystallized grains, and weaker basal texture. For example, in Mg-0.2Zn-0.3Ca-0.14Mn extruded at 300°C, the fraction of recrystallized grains in the sample was about 60%, with the average grain size of ~2.3 µm (Fig. 8) ⁵⁷. Meanwhile, this alloy had a high texture intensity of about 14 mrd (multiples of random texture distribution). The concepts of crystallographic texture have not been presented in detail herein thus far, however as will be elaborated in the following sections, the crystallographic texture of Mg alloys is a critical microstructural feature produced by the given extrusion processing conditions. When extrusion the temperature of Mg-0.2Zn-0.3Ca-0.14Mn was increased from 300°C to 400°C, the fraction of recrystallized grains was increased to 98% and texture was weakened to 2.1 mrd (Fig. 8). The complete recrystallization and grain growth led to a decreased yield strength but significantly enhanced ductility.

![Diagram](image.png)

**Fig. 7.** Variation of grain size as function of extrusion (a) temperature with fixed ram speed ⁵⁶-⁶², and (b) ram speed with fixed temperature ²⁰, ⁶³-⁶⁸.
Fig. 8. EBSD maps and corresponding inverse pole figures of Mg-0.2Zn-0.3Ca-0.1Mn extruded at (a) 300°C, (b) 350°C and (c) 400°C. The texture intensity in the inverse pole figures is in the unit of mrd.

Increased extrusion speed increases the effective extrusion temperature, since adiabatic heating and friction on the die walls both serve to raise the local temperature of the billet at the die. Therefore an increase in extrusion speed will have similar effects on the microstructure and texture of as-extruded alloys that may arise from an increase in the extrusion temperature. Such effects include an increase in the fraction of recrystallized grains and the accelerated growth of recrystallized grains in alloys subject to higher extrusion speeds. Changes in microstructure and texture due to an increase in extrusion speed, will lead to a decrease in the yield strength of the extruded alloys.

The grain size and yield strength of more than 100 extruded alloys from the published literature have been summarised in Fig. 9.

Although the alloys presented in Fig. 9 are based on diverse alloy systems including (a) Mg-Al, (b) Mg-Zn RE-free, (c) Mg-Zn-RE, (d) Mg-RE and (e) Mg-Sn extrusion alloys (and extruded under...
different conditions) it is apparent that the data points are clustered, and can be generally described by the Hall-Petch relationship. As different alloys have different coefficients in the Hall-Petch equation, it is difficult to fit a line to multiple alloys. However, rudimentary inspection of Fig. 9 suggests that grain refinement is (universally) likely to be an effective strengthening method for Mg extrusion alloys. Inspection of the data from the numerous studies in Fig. 9 have indicated that irrespective of alloy composition, that alloy yield strengths have rarely been demonstrated to exceed 200 MPa, when the grain size of extruded alloys was larger than 10 μm. When the grain size was reduced to about 1 μm, the yield strength of extruded alloys could be doubled, to about 400 MPa. The scattering of the data in Fig. 9 is rationalised by factors other than grain size effect alone, which include differences in solute type, particle (precipitate) size, shape and distribution, fraction of recrystallized grains, crystallographic texture, and possibly even variations in grain size measurement depending on the various methods adopted in the open literature.

In the exploitation of grain refinement and the Hall-Petch effect for Mg alloys, there has been a report in the literature indicating that when the average grain size of Mg-Y-Zn alloys was refined to 100 – 300 nm, the yield strength was ultra-high, in the range of 500 – 610 MPa (Fig. 9f). However, such a grain refined alloy was produced by gas atomisation and powder metallurgy. To date, the highest reported yield strength of an extruded Mg alloy produced by conventional ingot metallurgy is ~480 MPa. An ultra-high-strength Mg extrusion alloy (with YS > 500 MPa) has not yet been demonstrated. Production of ultra-high strength extrusion alloys that can be adopted by industry, via grain refinement of the submicron scale, is indeed a promising research area. To achieve such an aim, alloying elements would be required to effectively suppress the grain growth during extrusion at the given processing temperature. Alloying would be required to contribute to fine and dense precipitates, and effectively pin grain boundaries during hot extrusion. Low extrusion temperatures and low extrusion speeds may also limit grain growth, and potentially even lead to grain refinement, but this would require alloys with excellent low-temperature (i.e. < 300°C) extrudability. These concepts are revisited following a critical review of the Mg extrusion alloys reported to date by alloy type.
Fig. 9. A compilation of the tensile yield strength as a function of grain size (d) for (a) Mg-Al, (b) Mg-Zn RE-free, (c) Mg-Zn-RE, (d) Mg-RE, (e) Mg-Sn, and (f) data points in Figs (a-e) against the strength-grain size of ultra-high-strength Mg-Y-Zn alloys produced by powder metallurgy.

Whilst grain refinement is known as a strengthening mechanism for Mg alloys, it is also noted that grain refinement also increases the compressive yield strength, which has the attendant effect of significantly decreasing the tension-compression yield asymmetry (Fig. 10). Such yield asymmetry is a typical characteristic of most Mg alloys and is nominally problematic for designers wishing to work with Mg. The occurrence of tension-compression yield asymmetry is caused by easier plastic
deformation via twinning during compression, than during tension where slip is dominant. The response of slip and twinning to changes is grain size is not identical, twinning is more grain size sensitive than slip. As a consequence, grain refinement can effectively suppress twinning, and thus minimise tension-compression yield asymmetry of extruded alloys — which is a concept that can be also be gleaned from the consolidated empirical data compiled herein (Fig. 10).

3.3. Texture effect

Tension-compression yield asymmetry can be particularly problematic for extruded material owing to the possibility of a strong texture being produced (by extrusion) — stronger textures leading to higher tension compression yield asymmetry. Such inevitably developed texture corresponds to the basal (0001) plane of most grains being essentially parallel to the extrusion direction, which is illustrated by the basal pole figure (Fig. 11a).

With strong basal texture, the Schmid factor for basal slip and extension twinning is low, such that when an extruded alloy is tensile tested along the extrusion direction the result is higher strength, but low work hardening and ductility. When an extruded alloy is tensile tested perpendicular to the extrusion direction, extension twinning is easier to operate, leading to lower yield strength but enhanced work hardening and ductility. Such yield anisotropy in tensile testing is observed in rolled Mg sheet alloys, such as Mg-Zn-Ca or Mg-Zn-RE sheet which possesses a TD-spread texture. When extruded alloys with strong basal texture are compression tested along the extrusion direction, compression along the basal plane readily allows deformation twinning to operate, leading to low strength (Fig. 11b). As such, a significant tension-compression yield asymmetry is often observed in the extrusion of pure Mg and alloys with a strong basal texture, such as M1, AZ31, ZM61 and ZK21 alloys.

Fig. 10. Tension-compression yield asymmetry for variations in grain size of extruded Mg alloys.

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5. See text for detailed discussion.

The yield asymmetry realised for different loading directions may be illustrated by yield loci, such as that shown in Fig. 12a \(^{128}\).

For the extruded alloy ZM61 with strong basal texture (texture intensity > 7 mrd), the tensile yield strength along the extrusion direction is higher than that along the transverse direction, with a much higher compressive yield strength along both extrusion and transverse directions (Figs. 12a and 12b). Texture weakening can decrease the yield asymmetry \(^{129}\), as the weaker basal texture leads to plastic deformation more readily during tension. As shown in Figs. 12c and 12d, the extruded Mg-3Y alloy has weak basal texture (texture intensity ~ 2). Such weakened basal texture results in a smaller difference in the operation of slip and twinning, in cases when the extruded Mg-3Y alloy is subjected to different loading directions. It is noted that in many experimental studies, obtaining clear data to validate the texture effect on yield asymmetry is complicated by additional factors that includes grain size effects and the presence of precipitates. However, crystal plasticity modelling (visco-plastic self-consistency) confirmed the effect of texture on tension-compression yield asymmetry (Fig 13), where it can be seen that all things being equal (grain size and stress required to activate the individual deformation modes) a decrease in the texture strength minimized the yield asymmetry \(^{130}\).
Fig. 12. Yield loci and (0002) pole figures of extruded (a, b) Mg-6Zn-1Mn (ZM61) and (c, d) Mg-3Y alloys, reproduced from Ref. 128.

Fig. 13. Visco-plastic self-consistency simulated tension-compression yield asymmetry for variations in texture of extruded AZ31 alloy with the same grain size, reproduced from Ref. 130.

Figure 14a shows that the extruded Mg-0.2Ce alloy exhibits improved ductility (> 30%) with respect to the extruded pure Mg sample. Microstructural characterization revealed that the extruded pure Mg and Mg-0.2Ce alloy have similar grain size, but significantly different texture (Figs. 14b and 14c). With the weaker basal texture in the extruded Mg-0.2Ce alloy, basal dislocation slip and extension twining are expected to be more operative so that they can accommodate larger plastic strain. Therefore, weakened basal texture is identified to be important for the enhanced ductility of the extruded Mg-0.2Ce alloy. In addition to texture weakening, the addition of RE elements or Ca was also reported to increase the operation of non-basal slip during plastic deformation and possibly enhance grain boundary coherence, both of which contribute to enhanced ductility and formability.
Extrusion conditions and alloy composition are the two major factors that dictate the texture of Mg extrusion alloys. As shown in Fig. 15, higher extrusion temperatures and extrusion speed results in a decrease of texture intensity, due to faster recrystallization. In the hot deformation process of Mg alloys, plastic deformation and recrystallization generally occur simultaneously. A strong basal texture is developed during plastic deformation, dominated by preferential growth of deformation twins with strong basal texture. During recrystallization, the recrystallized grains replace their deformed parent grains, with the orientation of recrystallized grains deviating from the orientation of their parent grains. Apparently, higher extrusion temperature and ram speed accelerate recrystallization kinetics and thus weaken basal texture. Compared with extrusion temperature and speed, the extrusion ratio is reported to have an insignificant impact on the texture and ductility of extruded Mg alloys. In order to develop a highly ductile and formable Mg extrusion alloy, a high extrusion temperature and speed is normally required to allow a fully recrystallized microstructure.
Fig. 15. Variation of basal texture intensity as function of extrusion (a) temperature with fixed ram speed 57, 58, 60, and (b) ram speed with fixed temperature 64-68.

Whilst high extrusion temperature and speed can weaken basal texture by accelerating the recrystallization kinetic, the equilibrium texture intensity at full recrystallization is dictated by the alloy composition. When the deformed pure Mg or AZ31 alloy is fully recrystallized (equilibrium state), the texture intensity is lower than that in the as-deformed state, but texture distribution is still a basal texture—most grains having their basal plane nearly parallel to the extrusion direction 137-139.

In contrast, the addition of rare-earth (RE) elements such as Ce, Nd, Gd and Y 87, 140-147 or the combined addition of Ca and Zn 88, 148-150 not only significantly weakens texture intensity, but also changes the texture distribution—the basal planes of most recrystallized grains tilted away from the extrusion direction. Such significant differences in texture and ductility between RE-containing and non-RE-containing extrusions are shown in Fig. 14 131.

Whilst the phenomenon of RE and Zn-Ca additions on texture weakening is a widely observed phenomenon, the mechanism by which such texture weakening occurs is somewhat controversial. Several explanations related texture weakening have been proposed and can be categorised into two groups: randomised nucleation and randomised grain growth. With respect to the randomised nucleation theory, RE and Zn-Ca additions are posited to randomise the orientation of nucleus of recrystallized grains, and thus lead to the occurrence of the weakened texture at full recrystallization. Specifically, the randomised orientations of nuclei are likely to be caused by particle stimulated...
nucleation (PSN)\textsuperscript{151-154}, shear band induced nucleation (SBIN)\textsuperscript{137, 155, 156} and deformation twin induced nucleation (DTIN)\textsuperscript{157, 158}. This is because particles, shear bands and deformation twins\textsuperscript{141, 148, 159} provide considerable heterogeneous nucleation sites for recrystallized grains with randomised orientations in Mg alloys. The addition of RE elements promotes the formation of particles, shear bands and contraction and secondary twins. Therefore, PSN, SBIN and DTIN are considered to be the dominant factors for the development of weakened recrystallization texture in the RE-containing alloys. However, texture weakening is also observed in dilute Mg extruded alloys that contain essentially no second-phase particles\textsuperscript{127, 160}. Therefore, PSN is not likely to be the cause of texture weakening. With respect to SBIN and DTIN mechanism, shear bands and twins are also observed in RE-free magnesium alloys such as AZ31\textsuperscript{161} and Mg-1wt.\%Zn alloy\textsuperscript{143}, but these alloys have strong basal texture after recrystallization. Therefore, the effectiveness of SBIN on texture weakening is still under question.

In the randomised grain growth theory, texture weakening is related to the growth of recrystallized grains of randomised orientations at a similar growth rate\textsuperscript{162, 163}. At the early stages of recrystallization, recrystallized grains in conventional Mg alloys (such as Mg-1Zn) and Mg-Zn-Ca alloys have similar basal texture. During subsequent recrystallization, the preferential growth of recrystallized grains with their c-axis nearly parallel to the ND is dominant in pure Mg\textsuperscript{164}, Mg-1Zn\textsuperscript{136} and AZ31 sheet\textsuperscript{165, 166}, which would lead to the formation of a strong recrystallization texture. In contrast, the preferential grain growth is suppressed in Mg-RE or Mg-Zn-Ca alloys. The recrystallized grains with randomised orientations grow equally, leading to the occurrence of weakened basal texture\textsuperscript{136}. Rare earth elements, Zn and Ca have some solubility in Mg and significant misfit in atomic size to Mg, and therefore the observed segregation of RE, Zn and Ca atoms to grain boundaries can reduce grain boundary energy\textsuperscript{134, 136, 167-170}. It is hypothesised that RE, Zn and Ca solute atoms segregate or co-segregate more strongly to high-energy boundaries of the recrystallized grains that would otherwise grow preferentially. Subjected to the solute segregation, high-energy grain boundaries are likely to significantly reduce their mobility by reducing grain boundary energy and enhancing the solute drag effect, which could lead to a more uniform growth of recrystallized grains\textsuperscript{136}.

Although some success in increasing formability has been achieved by texture weakening, the improvement in formability is still limited. This is because even though the texture is weakened by alloying additions, the major deformation modes (basal slip and extension twinning) are not fundamentally altered\textsuperscript{8}. Recent studies have shown that despite possessing a strong basal texture, pure Mg extrusions, which are intrinsically brittle at room temperature\textsuperscript{171}, can be tensile tested to more than 100% in elongation\textsuperscript{172}, and cold-rolled to by 96% thickness reduction, and the resultant cold-rolled sheet can be further formed\textsuperscript{21}. The super-plasticity and super-formability of extruded pure Mg at room temperature are caused by grain size reduction to the order of one micron or submicron by low-temperature extrusion. This ultra-fine grain size allows the inter-granular mechanisms such as grain boundary sliding and dynamic recrystallization to be the dominant deformation modes, rather than usual slip and twinning\textsuperscript{21, 172-175}. Whilst the super-plasticity and super-formability at room temperature are observed in the extruded pure Mg extruded at low speed (ram speed of 0.1 mm/s), they have not been realised in pure Mg extruded at higher speed or any Mg alloys yet.

4. Corrosion of magnesium extrusion alloys

The extrusion process does not fundamentally change the corrosion mechanism of Mg alloys; however a significant refinement in grain size and second phase particle size can occur, along with the re-distribution of alloying elements during extrusion (shown in Fig. 4). Such local microstructural
(namely micro-chemical) alterations can affect the corrosion properties of Mg alloys. Without any alloying addition, the refinement in grain size of pure Mg enhances its corrosion resistance. If the specimen is fully recrystallized with uniform equiaxed grains during the extrusion process, the as-extruded sample will show slightly better corrosion resistance than the as-cast sample. The improved corrosion resistance is speculated to be caused by the formation of more coherent oxide/hydroxide layer in fine-grained Mg, and this explanation has been adopted in several search papers. If the specimen is partially recrystallized, then the heterogeneous microstructure may have resulted in the formation of a somewhat more heterogeneous film on the alloy surface, although the range of variation in corrosion rates simply by alteration of grain size is minimal relative to the changes observed when alloy chemistry is altered. Although several studies relate the corrosion of Mg and its alloys to the properties of any developed surface film, the effectiveness of surface films on the corrosion resistance of Mg is still rather insignificant. To date, the only coherent surface film that has been demonstrated to provide corrosion protection to an underlying Mg alloy was observed in an extruded Mg-Li alloy with a body centered cubic structure (owing to <10 wt. % Li addition). Although somewhat counter-intuitive, as Li is more chemically active than Mg, the significant addition of Li to Mg leads to the formation of a uniform and insoluble lithium carbonate (Li₂CO₃) film, which effectively restricts the alloy corrosion rate. Mg-Li-based alloys are promising candidates for future development of light-weight and corrosion-resistant extrusions.

Aside from the influence of surface films, the corrosion resistance of Mg may also be influenced by microstructural changes (namely arising from microstructural refinement due to extrusion) having an attendant influence on the ability to sustain anodic or cathodic kinetics. The enhanced corrosion resistance in the fine-grained Mg extrusions has also been previously attributed to reduced intensity of microgalvanic coupling between grain interiors and grain boundaries, or due to the increased density of grain boundaries, which may also reduce kinetics of corrosion, as opposed to a thermodynamic tendency to influence corrosion. Although (electrochemical) polarization testing reveals some difference in the corrosion current between cast and extruded pure Mg, the longer term immersion testing of pure Mg has revealed that the longer-term corrosion rate of extruded pure Mg is only marginally lower than that of cast pure Mg. This observation again demonstrates that chemistry, rather than microstructure, is the dominant effect on the corrosion resistance of Mg alloys.

With respect to Mg alloys with intermetallic particles, the corrosion rate of Mg alloys is predominantly affected by the amount, type and distribution of intermetallics. Different types of intermetallics have unique electrochemical potentials (in isolation), and they can be either anodic (more reactive) such as Mg±Ca or cathodic (nobler) such as Mg₁₇Al₁₂ with respect to the Mg matrix in which they are present. For example, Mg₁₇Al₁₂ in AZ91 is polarized (at the equipotential of the alloy) to a greater electrochemical potential difference than say, Mg₃Nd in Mg-Nd alloy. The distribution of intermetallics may be significantly affected by extrusion. For cast alloys, the intermetallics generally form along grain boundaries and have a large particle size. If the intermetallics are so called ‘anodic’, then the corrosion initiated at the intermetallic phases in the eutectic structure occurs rapidly and continuously along the grain boundaries. For example, a net-like distribution of the Mg±Ca phase promotes extensive localized corrosion, leading to rapid mass loss. If the intermetallics are so called ‘cathodic’, then the secondary phases will enhance corrosion of nearby matrix. Irrespective of whether the intermetallics are either anodic, or cathodic the occurrence of localised corrosion in cast Mg alloys increases the surface roughness and is concomitant with large mass loss. In contrast, if intermetallic phases are refined, they may be discontinuously and uniformly distributed in an alloy following extrusion. Therefore, the so-called intensity of microgalvanic coupling may influenced such that corrosion rates (dictated by localised corrosion) can be reduced, which may also lead to an apparently more uniform and shallow corrosion morphology.
second phases, the corrosion rate is decreased after extrusion – as shown in Fig. 17, from which data are collected from Refs. 43, 180, 182, 188, 192-194. Similarly, any manipulation of extrusion conditions that can lead to finer and more homogeneous distributions of the intermetallic particles, such as increasing extrusion ratio, will decrease the corrosion rate195. It should however be noted that whilst this trend of lower corrosion rates with microstructural refinement is nearly universal, it is also stated that the change in corrosion is confined within a range of the original (unrefined) alloy. In other words, a different Mg alloy of different bulk chemistry will have a different corrosion rate, with a different window of corrosion rate alteration with microstructural refinement. On this basis, it is still the alloy chemistry overall that dictates corrosion rate more so that microstructural refinement as imparted by extrusion.

Fig. 16. Scanning electron microscopy images shown surface after immersion test of (a, c) Mg-2Ca and (b, d) Mg-3Gd-2.7Zn-0.4Zr-0.1Mn alloy in the (a, b) as-cast state and (c, d) as-extruded state 180, 182.

Fig. 17. Corrosion rates of selected alloys before and after extrusion in immersion test 43, 180, 182, 188, 192-194
Apart from grain refinement and redistribution of intermetallics, dislocation density may also have some effect on the corrosion rate of Mg alloys. After extrusion, a bimodal microstructure may occur. The high dislocation density in the deformed grain having previously been reported to encourage the corrosion process \(^{191}\), with one study claiming deformed grains are sensitive to the reacting with electrolytes and corrosion reaction may preferentially occur at such sites \(^{196}\). The experimental results show that corrosion rate of as-annealed (below the recrystallization temperature) pure Mg samples is lower than as-deformed pure Mg samples, which contain a higher density of dislocations \(^{196}\). Therefore, realising a fully recrystallized microstructure by proper extrusion processing design may potentially enhance the corrosion resistance of Mg extrusion alloys – however again, the review of the literature reveals that chemical heterogeneities are the dominating factor in dictating Mg alloy corrosion rates overall. In this context, whilst the texture of Mg specimens has also been reported to influence corrosion rates, the texture effect is confined to the changes within a window of corrosion rates relevant to the bulk alloy composition being studied. In the case of pure Mg, it has been reported that the surface that has strong basal texture is more corrosion resistant in 5 wt.% NaCl \(^{197}\) and simulated body fluid (SBF) at 37 °C \(^{198}\). This phenomenon has been speculated to be related to the lower surface energy of (0001) plane than that of \{10\overline{1}0\} and \{11\overline{2}0\} planes \(^{199}\). After extrusion, the stronger basal texture may somewhat influence corrosion rate, however such studies are scarce and require further verification.

5. Extrusion alloys

5.1. Mg-Al-based alloys

Aluminium is the most commonly used alloying element in Mg and the majority of commercial extruded alloys are based on the Mg-Al alloy system, such as AZ31, AZ61 and AZ80 alloys. Mg-Al based alloys have good extrudability and are cost-effective among the Mg extrusion alloys. Al has the added advantage of having a low density, therefore the large alloying addition of Al do not compromise the low density of the alloy. Aluminium has a large solubility in Mg, about 12.9 wt.% (11.8 at.%) at the eutectic temperature of 437°C, and it decreases to about 3.3 at.% at 200°C \(^{40}\). Mg\(_{17}\)Al\(_{12}\) precipitates form during ageing treatment. The compilation of tensile yield strengths and elongations of Mg-Al-based extrusion alloys is shown in Fig. 18 \(^{15, 16, 22, 38, 49, 50, 59, 69-72, 120-123, 200}\).

![Fig. 18. Tensile yield strengths and elongations of Mg-Al-based alloys](image-url)
Among Mg-Al-based alloys, Mg-Al binary alloys have low strength and moderate ductility, and are rarely used in engineering applications. For example, the yield strength of Mg-3Al alloy is only ~103 MPa, and its total elongation ~17.3%. Zinc and Mn are commonly added to Mg-Al-based extrusion alloys. Zinc is added as a solute strengthener, but the principle role of Mn is to increase the corrosion resistance if the alloy by removing trace amounts of Fe from the alloy. The concentration of Zn and Mn are generally about 1 wt.%. Most alloys in the AZ series can be homogenised to form a single phase solid solution microstructure at 400°C, and they have the potential to form Mg_{17}Al_{12} precipitates at lower temperatures. The strengthening effect of these precipitates in the lean Mg-Al based alloys (such as AZ31) is reportedly negligible, predominantly because of the low volume fraction and relatively coarse distribution of precipitates. For the more concentrated alloys such as AZ80, precipitation leads to an age hardening response of about 30 MPa.

The strongest Mg-Al based alloy that has been reported is Mg-3.5Al-3.3Ca-0.4Mn (wt.%), developed by Xu et al. The as-extruded alloy has a high yield strength, about 410 MPa, which is currently the highest reported tensile yield strength of any RE-free Mg alloy. This high strength alloy has a moderate tension-compression yield asymmetry of ~0.8. The microstructure of this alloy shows a high volume fraction of recrystallized grains (~70%) with an average size of ~1.2 μm in diameter. Plate-shaped and spherical precipitates were found in the as-extruded microstructure. Both the small grain size and the precipitate population contribute to the high strength of this Mg-Al-Ca-Mn alloy. However, the strength of Mg-Al-Ca-Mn extruded alloy is significantly affected by the cooling rate during casting. The direct chill (DC)-cast Mg-3.6Al-3.4Ca-0.3Mn alloy is about 100 MPa stronger than the permanent mould (PM)-cast alloy (Fig. 19), because the higher cooling rate in DC-casting results in the formation of much finer eutectic phases and higher density of mono-layer GP zones.

**Fig. 19.** Tension and compression stress-strain curves of Mg-3.6Al-3.4Ca-0.3Mn alloys subjected to direct chill casting and permanent mould casting.

Recently, dilute Mg-Al-Ca-Mn alloys were found to have excellent extrudability. A dilute Mg-0.3Al-0.2Ca-0.5Mn alloy was successfully extruded with the ram speed of 50 mm/s (corresponding to the die exit speed of 60 m/min) at 350°C – 500°C (Fig. 20). In contrast, subjected to the same extrusion condition, a large amount of surface cracks were observed on the surface of AZ31 extruded bar. This is because the Mg-0.3Al-0.2Ca-0.5Mn alloy has a higher solidus temperature than that of AZ31. In addition to high extrudability, this alloy showed well-balanced strength and ductility. The tensile yield strength and elongation were 207 MPa and 29%, respectively.
Similar to Ca, strontium (Sr) is another alkali-earth element that can be added to Mg-Al alloys, however the addition of Sr in reports to date has tended to lead to low ductility. For example, the total elongation for Mg-4Al-2Sr-0.3Mn wt.% and Mg-4Al-2Sr-1Ca-0.3Mn wt.% alloys were 6.2% and 3.2%, respectively. Therefore, Sr-containing extrusion alloys have not attracted significant interest to date. Rare earth elements, such as Ce, have been examined as alloying elements in the Mg-Al family of alloys. For the case of Ce, and most likely all of the RE elements, the Ce, Al and Mg atoms form Al₁₁Ce₃ and Mg₁₂Ce particles during casting. These particles have little strengthening effect on the alloy, and solute strengthening is lost due to the entirety of the RE content being bound inside coarse precipitates. Consequently, the improvement in the mechanical properties of Mg-Al based extruded alloy, due to the RE additions, is insignificant.

5.2. Mg-Zn-based alloys

In addition to Al, Zn is another cost-effective and thus commonly-added alloying element. In Mg-Zn-based alloys, Zn is the major alloying element. The maximum solubility of Zn in Mg is 6.2 wt.% (2.4 at.%) at a eutectic temperature of 340°C. The equilibrium solid solubility of Zn in Mg decreases substantially with temperature, to ~2.6 wt.% (1 at.%) at 150°C. During ageing, the supersaturated solid solution decomposes and precipitates form. The precipitation sequence in Mg-Zn alloys is more complex than that in Mg-Al alloy, which includes a sequential formation of GP zone, [0001]ₐ rod-shaped β₁' phase, [0001]ₐ plate-shaped β₂ MgZn₂ phase and equilibrium β MgZn phase. The [0001]ₐ β₁' rods and β₂ [0001]ₐ plate can pin mobile basal dislocations, and therefore provide a substantial strengthening effect. In most cases, minor alloying elements are also added to Mg-Zn extrusion alloys, as Mg-Zn binary alloys still have inadequate strength and ductility for commercial
applications. These elements can be categorised into two groups: RE elements and non-RE elements. The following sections summarise the effect of additions of these minor elements on the properties of Mg-Zn-based extrusion alloys.

5.2.1. RE-free alloys

Figure 21 shows the yield strength and ductility of some Mg-Zn-based RE-free alloys reported in Refs. 19, 44, 52, 55, 57, 58, 60, 66, 73, 74, 76, 78-81, 83-85, 205-207.

![Graph showing tensile yield strengths and elongations of Mg-Zn-based RE-free alloys.](image)

**Fig. 21.** Tensile yield strengths and elongations of Mg-Zn-based RE-free alloys 19, 44, 52, 55, 57, 58, 60, 66, 73, 74, 76, 78-81, 83-85, 205-207.

Mg-Zn binary alloys have moderate ductility (10% - 30%) but low strength normally < 150 MPa. Zirconium and Mn are commonly added to the Mg-Zn series of alloys. Zr is added as a grain refiner during the casting process, and Mn is added to improve corrosion resistance as well as the precipitation response. **Fig. 21 reveals that** the tensile yield strength of as-extruded ZK60 alloy is typically in the range of 250 – 265 MPa, which is about 80 – 90 MPa higher than that of as-extruded Mg-6Zn (Z6) binary alloys 24. When ZK60 and Z6 alloys were subjected to extrusion at 350°C, the Z6 alloy developed a fully recrystallized microstructure, but in contrast ZK60 alloy was only partially recrystallized (Figs. 22a and b). Moreover, after hot extrusion, a large proportion of Zn-Zr containing precipitates were observed in ZK60, but no observable precipitates formed in the clean Z6 alloy (Fig. 22c). These precipitates were identified to be Mg(Zn, Zr) precipitates, rather than Zn-Zr binary intermetallic phases or MgZn precipitates 24, 85. The rod-shaped Mg(Zn, Zr) [0001]a precipitates which formed in ZK60 are about 48.9 ± 25.8 nm in length and 11.6 ± 5.6 nm in width (Fig. 22d) 24, but dimensions might vary depending on the extrusion conditions.
Apart from a difference in dynamic precipitation during extrusion, the other difference between ZK60 and Z6 is the post-extrusion age hardening response, with hardening of ZK60 not as significant as that of Z6 binary alloys. For ZK60 the ageing treatment only led to a strength increment of about 20 – 30 MPa \(^74\), whereas the age strengthening of Mg-6Zn alloy was as high as 80 MPa. This difference is due to the precipitation sequence. ZK60 tends to form precipitates during extrusion and post-extrusion treatment simply coarsens these precipitates – whilst Z6 is commonly extruded as a single phase alloy and therefore shows a large strengthening increment on post-extrusion ageing.

Compared to Zr, the addition of Mn to the binary Mg-6Zn alloy improves not only the strength of as-extruded alloy, but also the age hardening response, as shown in Fig. 23 \(^74, 76, 84, 206\).
Fig. 23. Tensile yield strength of Mg-Zn-based RE-free alloys before and after ageing treatment 74, 76, 84, 206.

The tensile yield strength of as-extruded Mg-Zn-Mn and Mg-Zn-Mn-Si alloys ranged from 200 to 240 MPa 76. Single step ageing increased the strength of these alloys by as much as 80 MPa. When subjected to a two-step ageing treatment at a low temperature (70 – 90°C) followed by a slightly higher temperature (160 – 180°C), the tensile yield strength of this alloy family was further increased to 338 – 350 MPa 76 (Fig. 23). The larger strengthening effect observed after the two-step ageing process is the result of the formation of closely spaced GP zones during step one, and these act as heterogeneous nucleation sites for [0001]αβ′ rod precipitation during the second step. Consequently, the number density of [0001]αβ′ rods in the Mg-6Zn-1Si-0.5Mn subjected to the two-step ageing treatment is about 17 times more than that subjected to the single step treatment. Although the peak aged Mg-Zn-Mn based alloys showed excellent strength levels, the ductility was inadequate for most applications, only being between 5% and 10%. This has therefore limited the use of this particular alloy class to date.

Mg-Zn-Ca-based alloys have attracted considerable interest in the literature because Ca has some solubility in Mg (1 wt.% at 500°C) and a much larger atomic radius than Mg. When the larger solute atoms such as Ca and smaller solute atoms such as Zn are combined added to Mg, weakened basal texture will occur during recrystallization 136. The texture weakening caused by strong co-segregation of Zn and Ca to grain boundaries, which exerts a more significant drag effect on grain boundary migration than the individual segregation of Zn or Ca to grain boundaries 136. The mechanism has been reviewed in §3.3. In particular, all of Mg, Ca and Zn are biocompatible elements 208. The tensile yield strength of Mg-Zn-Ca-based alloys ranges from 100 MPa to 300 MPa. More importantly, it is possible for dilute Mg-Zn-Ca ternary alloys such as Mg-1Zn-0.5Ca to achieve exceptionally high elongations of up to 44% 19.

In Mg-Zn-Ca alloys, addition of Zr and Mn can improve the strength of extruded alloys 80. When 0.8 wt.% Zr was added to a Mg-6Zn-0.2Ca alloy (ZX60), the tensile yield strength was increased significantly from 148 MPa to 310 MPa 200. Firstly, the Zr addition suppresses recrystallization during extrusion, which is similar to the Zr addition in Mg-Zn binary alloy 74. Furthermore, the addition of Zr leads to a much denser distribution of smaller precipitates. The average diameter and number
density of the precipitates were measured to be 33 nm and 1.3×10^{21}/m^3 in the Mg-6Zn-0.2Ca-0.8Zr (ZKX600) extruded alloy, and 132 nm and 4.9×10^{18}/m^3 in the Zr-free equivalent alloy. Therefore, in both ZK60 and ZKX600 extruded alloys, the combination of the smaller grain size and higher density and finer precipitates result in a much higher strength, compared to the Zr-free equivalent. When the Mg-5.25Zn-0.6Ca alloy with and without an additional 0.3Mn was compared, the addition of Mn led to a 52 MPa increase in yield strength in the as-extruded condition, due to grain size refinement. Different to Mg-Zn-Zr based alloys, Mg-Zn-Mn alloy has significant post-extrusion ageing. The yield strength of Mg-6Zn-1Si-0.2Ca-0.5Mn was increased from 200 MPa in the as-extruded condition to 330 MPa in the peak-age state.

With the dilute additions of Zn, Ca and Mn, a quaternary Mg-Zn-Ca-Mn alloy has shown an excellent balance of yield strength and ductility. After extrusion at 300°C with a ram speed of 1 mm/s, the Mg-0.2Zn-0.3Ca-0.14Mn alloy had a high yield strength of 309 MPa. This is slightly higher than T6-treated ZK60, and interestingly, is also higher than more concentrated alloys of the same family. In addition to these good strength levels, this alloy had a ductility of about 20% total elongation, which is again better than more concentrated alloys. Decreasing the alloying concentration also reduces the cost, minimises alloy density and thus maximises specific strength. Consequently, this low cost, low density, and dilute Mg-Zn-Ca-Mn alloy is expected to be competitive in future industrial applications.

The addition of silver (Ag) to Mg-Zn alloys has been demonstrated to improve the age-hardening response and thus the strength of the Mg-Zn system, predominantly due to the refinement of β′ precipitates during post-extrusion ageing at 160°C. However, the addition of Ag will significantly increase the cost of any alloy, and will increases its corrosion rate. Therefore Ag-containing extrusion alloys remain unlikely to be adopted in favour of other Mg-alloy systems. In addition to Ag, other micro-alloying elements such as Ba, Cu, Co, Cr, V, and Al have been tested in the Mg-Zn-based alloy system. These elements have all been found to improve the age hardening response to some degree, but have typically been tested in the as-cast or solution treated condition rather than after extrusion.

5.2.2. **RE-containing alloys**

In Mg-Zn-based extrusion alloys, the rare earth (RE) elements such as Ce, Gd, Y, La, and Nd are commonly added to improve the mechanical properties (strength and ductility) of Mg extrusion alloys. Similar to dilute Ca additions, micro-alloying additions of RE elements to Mg wrought alloys can weaken basal texture. Mg-Zn-RE-based alloys with dilute RE additions have been widely investigated in Mg sheet and extrusion alloys, since the weakened basal texture results in a significantly enhanced ductility and formability. With the increase in the concentration of Zn and RE, some extrusion alloys show increased strength due to the formation of strengthening particles, but the ductility generally drops significantly.

The compilation of tensile yield strengths and elongations of Mg-Zn-RE-based extrusion alloys selected from Refs. is shown in Fig. 24.
Among the Mg-Zn-RE-based extrusion alloys, Mg-Zn-Ce-based alloys have attracted considerable research interest, due to their high ductility and formability. The ductility of Mg-2Zn-0.2Ce extruded alloy has been reported to be ~27%, which is ~10% higher than the ductility of AZ31 alloy subjected to the same extrusion conditions. When the Zn concentration of Mg-Zn-Ce was increased to more than 5 wt.%, the ductility dropped significantly (by about half), however the yield strength remained largely unchanged (Fig. 24). In order to improve the strength and ductility of alloys with higher Zn concentrations (5–6 wt.%), Zr is often added. In these quite heavily alloyed materials (Mg-Zn-Ce-Zr), where the Zn content is high (5–6 wt.%), yield strengths in the range of 247–330 MPa can be achieved, with the total elongations being between 17% and 27%.

It is informative to consider the effect of Ce in the Mg-Zn-Ce-Zr alloys by comparing them to the similar ZK60. Both alloys contain about 0.5 wt.% Zr and ~6 wt.% Zn. When extruded under the same conditions, the addition of Ce resulted in a strength increase of 5–75 MPa. This has been attributed to the Ce addition significantly refining the size of precipitates, and increasing their density in the as-extruded condition (Fig. 25).
Fig. 25. TEM micrographs of as-extruded (a) ZK60, (b) Mg-6Zn-0.5Zr-0.5Ce, (c) Mg-6Zn-0.5Zr-1Ce, and (d) Mg-6Zn-0.5Zr-1.5Ce alloys. 

Aside from enhancing dynamic precipitation, Ce additions to ZK60 also significantly improve extrudability (Fig. 26). These photographs reveal that when ZK60 and Mg-6Zn-0.5Zr-1Ce was subjected to the same extrusion speed of 6.7 mm/s (corresponding to die exit speed 20 m/min) at 250°C, the extruded ZK60 bar was severely cracked, whilst the surface of Mg-6Zn-1Zr-1Ce alloy was defect-free, and had no visible cracks (Fig. 26).

Fig. 26. Photos showing surface quality of (a) ZK60 and (b) Mg-6Zn-0.5Zr-1Ce alloys extruded at 250°C with a ram speed of 6.7 mm/s.
Combined additions of RE and Ca have been found to further improve strength, relative to individual additions of Ca. The tensile yield strength of Mg-2.5Zn-0.2Ca-0.4La and Mg-5.3Zn-0.2Ca-0.5Ce alloys were about 325 MPa and 268 MPa, respectively, higher than those of Mg-Zn-Ca or Mg-Zn-Ce alloys extruded under similar conditions [87, 88]. The examination of microstructures in Mg-Zn-Ca or Mg-Zn-Ce alloys have shown that the aforementioned alloys contained a dense distribution of small Mg-Zn and Mg-Zn-Ca precipitates. The authors postulated that the addition of Ce or La to Mg-Zn-Ca alloy increased the number density of precipitates that formed during hot extrusion, and this resulted in alloy strengthening [87, 88].

Gadolinium (Gd) additions have also been demonstrated to improve alloy extrudability and mechanical properties [225]. The yield strength of as-extruded Mg-Zn-Gd is generally 200–300 MPa. When the Mg-2Zn-1.5Gd and Mg-2Zn-0.5Ce alloys were subjected to the same extrusion conditions, the yield strength of Mg-2Zn-1.5Gd alloy was about 50–60 MPa higher than that of Mg-2Zn-0.5Ce [20], predominantly due to the much higher solubility of Gd than Ce in Mg matrix and the more effective suppression of dynamic recrystallization caused by Gd. Among the Mg-Zn-Gd alloys, a lower concentration of Gd and Zn leads to the enhanced strengthening effect. For example, the yield strength of Mg-5Zn-0.5Gd alloy was about 291 MPa, higher than that of Mg-6.8Zn-2.8Gd alloy of 228 MPa, when both alloys were subjected to the same extrusion condition [51]. In another study, the Mg-2Zn-Gd alloy had much higher yield strength than the Mg-5Zn-Gd alloys (Fig. 27) [226].

![Fig. 27. Tensile yield strength of Mg-2.5Zn-1Ce(Gd) and Mg-5.5Zn-1Ce(Gd) alloys subjected to different extrusion temperature from 250°C to 500°C.](image)

This phenomenon in both cases [51, 226] was reportedly caused by the formation of thermally stable second phases that cannot be dissolved during homogenisation treatment in more concentrated alloys. Such second phases, including the icosahedral quasi-crystalline phase (I-phase), are coarse and deplete the matrix of solute atoms, and therefore reduce the maximum attainable precipitate volume fraction. The depletion of solute atoms in the matrix also results in the formation of large grains during dynamic recrystallization, due to lack of solute pinning.

The chill cast Mg-14Zn-3Y alloy extruded at 250°C had a high yield strength of 386 MPa [61]. Such high strength has been speculated to be caused by the small grain size of about 1 µm in diameter and
the dispersion of I-phase particles and [0001] β₁ rod-shape precipitates. However, in an earlier study the tensile yield strength of permanent mould cast Mg-15Zn-3Y that was also extruded at 250°C was only ~213 MPa, which was ~170 MPa lower than the yield strength of Mg-14Zn-3Y alloy reported in Ref. 61. Therefore, the high yield strength of the Mg-14Zn-3Y alloy in Ref. 61 is more likely to be caused by microstructural refinement due to the chill casting, rather than the occurrence of I-phase. In the Mg-Zn-Y-based alloys with lower alloying concentration, such as Mg-5Zn-0.9Y-0.16Zr, Mg-6.4Zn-1.7Y and Mg-5.5Zn-0.7Y-0.4Zr, the I-phase particles were also observed, and the yield strength of these alloys ranged from 260 – 320 MPa, with the ductility in a range between 10% – 16%, which are similar to the tensile properties of ZEK600, and ZKX600 extrusion alloys.

5.3. Mg-RE-based alloys

Mg-RE-based alloys have been developed to be high strength, age hardenable and creep-resistant alloys 84. To date, the strongest magnesium extrusion alloy is based on Mg-RE alloy system (Mg-Gd-Y-Zn-Zr), whose yield strength was reported ~480 MPa 17, 18. In the high-strength Mg-RE-based alloys, many different types of intermetallic particles and precipitates have been observed, which contribute to the high strength. The compilation of tensile yield strengths and elongations of Mg-RE-based extrusion alloys is shown in Fig. 28 17, 45, 53, 63, 92-95, 97-100, 103-105, 228-235.

![Fig. 28. Tensile yield strengths and elongations of Mg-RE-based alloys 17, 45, 53, 63, 92-95, 97-100, 103-105, 228-235.](image)

The high strength Mg-RE-based extrusion alloys are categorised into two groups: Mg-Y-Zn-based and Mg-Gd-based alloys. In some cases, Gd, Y and Zn are added together in order to achieve enhanced strength. However, the Mg-RE-based alloys are typically difficult to extrude, with high RE
concentrations necessitating high temperatures and low speed, resulting in a high cost for industrial production.

5.3.1. Mg-Y-Zn-based alloys

In 1997 the Mg-10Y-2Zn alloy produced by rapid solidification and hot-extrusion was reported to have a high ultimate tensile strength of ~520 MPa. In 2001, using the similar method, the hot-extruded Mg-6.7Y-2.5Zn alloy has been reported by Kawamura et. al to be the strongest Mg alloy. The tensile yield strength of the as-extruded alloy was exceptionally high ~610 MPa, resulting in its specific strength being even higher than those of conventional titanium alloy (Ti-6Al-4V) and high-strength aluminium alloy (7075-T6). Examination of microstructure has shown that the grain size was small of 100 – 200 nm in diameter. Moreover, a long-period stacking ordered (LPSO) phase particles with a size of 7 nm in diameter were homogeneously dispersed in the Mg matrix. Since that time, Mg-Y-Zn-based alloys containing LPSO phases have attracted great interest of research on the structure of LPSO phase and on the effect of LPSO phase on mechanical properties. With the advances in the HAADF-STEM technique, the structures of the LPSO phases have been identified. As shown in Figs. 29a and b, the two most commonly observed LPSO structures in Mg-Y-Zn alloys are 14H and 18R. Both 14H and 18R LPSO structures have the same building block, whose structure is similar to γ’ phase (Fig. 29c). The γ’ phase has a disordered hexagonal structure (space group P3m1; a = 0.321 nm and c = 0.780 nm), which is perfectly coherent with the Mg matrix.

![Fig. 29](image)

**Fig. 29.** HAADF-STEM images showing the structure of (a, b) 14H and 18R LPSO phases and (c) γ’ precipitate in Mg-8Y-2Zn-0.6Zr alloy. Electron beam is parallel to [2110]α.

After Kawamura et. al. reported a yield strength of 610 MPa in the Mg-6.7Y-2.5Zn alloy in 2001, any yield strength exceeding 600 MPa was not reached in subsequent studies. Even when the Mg-6.7Y-2.5Zn alloy was produced by a similar rapid solidification, powder metallurgy and hot extrusion methods, the yield strength of Mg-6.7Y-2.5Zn alloy was reported to be about 480 MPa. For the Mg-Y-Zn alloys produced by conventional casting and hot extrusion, the tensile yield...
strengths of as-extruded alloys are found to be even lower, in the range between 200 MPa and 400 MPa \(^{93, 228-230}\). Therefore, the strengthening effect caused by the LPSO phases is not as significant as expected. In the cast Mg-Y-Zn alloys, large blocks of LPSO particles are distributed along Mg grain boundaries. Once formed during casting, the LPSO phase is unlikely to be dissolved in Mg matrix by solution treatment. During extrusion, the LPSO phase is deformed by kinking (Fig. 30) \(^{240, 241}\). After extrusion, the grain size of Mg is around several to tens of microns, which is similar to those of extruded Mg-Al-Ca, Mg-Zn-(Ca/RE)-Zr alloys. Extruded Mg-Y-Zn alloys generally have low ductility, below 10%, because of the existence of coarse LPSO phase particles in the extruded Mg-Y-Zn alloys. The high cost and density, moderate strength and low ductility of Mg-Y-Zn extrusions has to date limited their adoption in industry.

![Fig. 30. SEM images showing LPSO phases in Mg-6.7Y-5Zn alloy (a) before and (b) after extrusion (c, d) HAADF-STEM images showing kink bands in deformed LPSO phase in a Mg-Y-Zn alloy. Electron beam is parallel to [2110]_α in (c, d).](image)

5.3.2. Mg-Gd-based alloys

In addition to Mg-Y-Zn alloy system, the Mg-Gd-based system has also attracted significant research interest for developing high-performance extrusion alloys. The equilibrium solid solubility of Gd in Mg is high (23.49 wt. % or 4.53 at. %) at the eutectic temperature of 548°C. The equilibrium solid solubility decreases exponentially with temperature to approximately 5.0 wt. % (0.81 at. %) at 250°C,
and to 3.82 wt. % (0.61 at. %) at 200°C\textsuperscript{14}. Due to the large solubility of Gd in Mg, the precipitation hardening response is not significant when the Gd concentration is less than 10 wt. % in Mg-Gd binary alloys\textsuperscript{242,243}. The precipitates in Mg-Gd binary alloys include $\beta''$, $\beta'$, $\beta_1$, and $\beta$ phases, and their structures and strengthening mechanisms have been reviewed in Ref. \textsuperscript{31}. These precipitates can provide a significant age strengthening effect during post-extrusion ageing treatment, as shown in Fig. 31, with data from Refs. \textsuperscript{17, 18, 53, 95, 97, 99-101, 103, 232, 233}. As a result, the heavily-alloyed Mg-Gd-based system remains a suitable candidate for developing high strength Mg extrusion alloys\textsuperscript{17,18}, bearing in mind the high cost.

![Graph](image)

**Fig. 31.** Tensile yield strength of Mg-RE-based alloys before and after ageing treatment\textsuperscript{17, 18, 53, 95, 97, 99-101, 103, 232, 233}.

A comparatively high extrusion temperature of 350 – 500°C is required to extrude Mg-Gd-based alloys, owing to such alloys being nominally difficult to extrude. Consequently, the high extrusion temperature leads to lower tensile yield strength in the as-extruded condition, because of the significant grain growth and insignificant precipitation during extrusion. For example, the yield strength of Mg-14Gd-0.5Zr alloy is \~190 MPa\textsuperscript{97}. A similar value of yield strength of \~164 MPa was obtained in the extruded Mg-8Gd-0.4Zr alloy\textsuperscript{98}. These as-extruded alloys contain fully recrystallized grains with a grain size of 10 – 20 μm. For the Mg-14Gd-0.5Zr alloy extruded at 505°C, dynamic precipitation was unlikely to occur, and the as-extruded alloy is comprised of an essentially supersaturated solid solution (single phase) after the extrudate exits the die and is water quenched. Subjected to post-extrusion isothermal ageing treatment at 200°C for 36 hours, the extruded bar contains a large amount of $\beta'$ precipitates. The precipitation during ageing resulted in about 115 MPa increment in tensile yield strength, from 190 MPa to 305 MPa\textsuperscript{97} (Fig. 31).

Micro-alloying of Zn was found to effectively enhance the age hardening response of Mg-Gd-based alloys. For example, the Mg-6Gd binary alloy displayed a negligible age hardening response during isothermal ageing at 250 °C. With the addition of 1 wt.% Zn, the age hardening response was
significantly enhanced. During isothermal ageing of this alloy at 250 °C, γ" basal precipitates (space group P62m, \( a = 0.556 \) and \( c = 0.444 \)) formed at the early stage, and were gradually replaced by γ' basal precipitate plates - which have a crystal structure identical to those in Mg-Y-Zn alloys. Depending on the concentration of Gd and Zn (and ageing temperature), 14H LPSO phase and β', β1, and β phases can also form in Mg-Gd-Zn alloys. In as-extruded Mg-Gd-Zn-based alloys such as Mg-14Gd-2.3Zn, Mg-Gd particles and 14H LPSO phase have been observed. The densely dispersed 14H LPSO phase was considered to be the main contributor to alloy strength. In addition, the growth of recrystallized grains was reduced so that the grain sizes were found to be small of 200 – 500 nm in diameter. The tensile yield strength and ductility of the Mg-14Gd-2.3Zn alloy were 345 MPa and 6.9%, respectively.

In addition to Zn, another commonly-used alloying element in Mg-Gd alloys is Y, owing to the potential of Mg-Gd-Y-based alloys to achieve higher strength and better creep resistance. Mg-Gd-Y alloys have been demonstrated to have a significant precipitation hardening response during ageing, predominantly due to a dense distribution of precipitates. In the peak-aged condition, the second phase particles are mostly lenticular β' precipitates, which are similar to those in Mg-Gd alloys. The yield strengths of Mg-Gd-Y-Zr alloys, extruded at 350 – 400°C, were reportedly in a range of 190 – 270 MPa. Following isothermal ageing to peak hardness, the tensile yield strengths of these Mg-Gd-Y-Zr alloys are about 300 – 350 MPa. With micro-alloying of Zn and/or Nd to Mg-Gd-Y-Zr alloys, the yield strength of as-extruded alloys is increased substantially. For example, an as-extruded Mg–10Gd–5.7Y–1.6Zn–0.7Zr alloy revealed a high yield strength of 419 MPa. After isothermal ageing at 200°C for 64 hours, the as-extruded alloy reached peak hardness, and the yield strength of the peak-aged sample was impressively high of 473 MPa with moderate elongation of 8%. This is actually a record for Mg alloys produced by conventional casting and extrusion. Such high strength in the as-extruded condition was postulated to be caused by a dense distribution of β1, and β precipitates that provide precipitation hardening and restrict the growth of dynamic recrystallized grains. The further increment in yield strength during ageing was speculated to be the formation and dense distribution of β' precipitates.

5.4. Mg-Sn-based alloys

The addition of Sn to Mg enhances alloy extrudability and provide age-strengthening during isothermal ageing, and therefore the Mg-Sn-based alloys have received attention in recent years for developing extrusion products. Tin has a large solid solubility in Mg of 14.5 wt.% (3.35 at.%) at the eutectic temperature (561°C), and decreases to about 0.49 wt.% at 200°C. The equilibrium precipitate in Mg-Sn binary alloy is β-Mg2Sn (space group Fm3m, \( a = 0.68 \) nm). However, the β-Mg2Sn precipitates formed during ageing in Mg-Sn binary are much coarser than the precipitates in other precipitation hardenable Mg alloys.

The compilation of tensile yield strengths and elongations of some Mg-Sn-based extrusion alloys is provided in Fig. 32. The Mg-2Sn and Mg-6Sn binary alloys reveal low yield strengths of ~157 MPa and ~191 MPa, respectively. To enhance the strength of extruded Mg-Sn-based alloys, Zn and Al are added. The highest yield strength of Mg-Sn-Al-Zn alloy is about 370 MPa (Fig. 32).
Fig. 32. Tensile yield strengths and elongations of Mg-Sn-based alloys.

Mg-Sn-Al-Zn alloys generally have good extrudability; for example, the Mg-7Sn-1Al-1Zn (TAZ711) alloy had a smooth and shiny surface when it was extruded at 350°C with a ram speed of 9 mm/s (corresponding to die exit speed of 27 m/min), as seen in Fig. 33.

The enhanced extrudability of Mg-Sn-Al-Zn alloys results from the formation of the thermally stable Mg2Sn phase. By comparison, severe surface cracking was observed in AZ80 when it was extruded with a much lower ram speed of 2 mm/s (or 6 m/min die exit speed). However, the Mg-7Sn-1Al-1Zn alloy extruded at high speed has a relatively low yield strength of 180 MPa. Subjected to extrusion at low temperature (200°C) and speed (0.1 mm/s), the yield strength of Mg-Sn-Al-Zn alloy can be markedly improved to above 300 MPa.

Fig. 33. Photo showing the surface quality of AZ80 and TAZ711 samples extruded at 350°C. The numbers in parentheses indicate the exit speeds of the extruded bars.
In order to further improve the strength of extruded Mg-Sn-Al-Zn alloys, ageing treatments have been explored—but were found insignificant. The tensile yield strengths of peak-aged alloys are normally only 10–40 MPa higher than those as-extruded samples, as shown in Fig. 34 48,107,108.

In order to improve the age hardening response, sodium (Na) can be added to Mg-Sn-Al-Zn alloys 108. The ageing treatment of Mg-5.4Sn-4.2Zn-2.0Al-0.2Mn-0.1Na at 160°C resulted in a strength increase of 100 MPa. In contrast, without Na additions, the age-hardening response of Mg-5.4Sn-4.2Zn-2.0Al-0.2Mn was negligible. The trace addition of Na to Mg-Sn based alloys formed Sn-Na co-clusters in the early stages of ageing. The presence of Sn-Na clusters provides heterogeneous nucleation sites for Mg2Sn precipitates, and thus enhanced the precipitation hardening response. However, the Na atoms in the Mg-Sn-based alloys segregated to the grain boundaries, and this process ‘embrittled’ the alloy—significantly decreasing ductility 246,247. Hence, the Mg-Sn-Al-Zn-Na-based alloys are unlikely to be widely used. It would be desirable to find an alternative alloying element that replaces Na, which can also enhance age-strengthening but will not decrease the ductility.

Another way to enhance the age hardening response of Mg-Sn-Al-Zn alloys is to subject them to a two-step heat treatment after extrusion and solution treatment. Subjected to pre-ageing at 70°C for 150 hours and ageing at 140°C for 30 hours, the extruded Mg-6.6Sn-5.9Zn-2.0Al-0.2Mn alloy showed high yield strength of 370 MPa, which is about 123 MPa higher than that of as-extruded alloys 108. During the pre-ageing treatment at 70°C, a large number density of GP zones were formed, acting as heterogeneous nucleation sites for MgZn2 precipitates. Similar to the case of the Mg-Zn-based alloys 76, two-step ageing led to the formation of higher density of finer precipitates after the second heat treatment step.

5.5. Mg-Li-based alloys

The advantage of Mg-Li-based alloys is their ultra lightweight. Lithium is the lightest metal, whose density is only 0.533 g/cm³. In addition, Li has significantly solubility in Mg. The maximum solubility
of Li in Mg is 5.5 wt.% (17 at.%) at eutectic temperature of 588°C, and solubility of Li in Mg almost does not decrease with the decreasing in temperature. With the concentration of Li is between 5.5 wt. % and 11 wt. % (30 at. %), the alloy is comprised of an α-Mg (hcp) phase and β-Li phase (body centred cubic structure, space group Im3m, a = 0.351 nm) \(^{16}\). When the concentration of Li is more than ~11 wt.%, the alloy is composed of single β-Li phase. The high atomic concentration of Li leads to decrease of alloy density to 1.4~1.5 g/cm\(^3\) (and below, depending on precise composition).

The compilation of tensile yield strengths and elongations of Mg-Li-based alloys from Refs. \(^{24, 46, 248-255}\) are shown in Fig. 35.

It can be seen that the yield strength of Mg-Li binary alloys is generally in the range between 60 MPa and 140 MPa. However, their ductility differs substantially. In the α-Mg phase regime of the phase diagram, the Mg alloys reveal a low ductility. With the increase in the Li concentration to β-Li phase regime, the strength is decreased but the ductility is significantly improved. The ductility of Mg-11Li-3Zn extruded alloy predominantly composed of β-Li phase was as high as 55\% \(^{249}\).

![Fig. 35. Tensile yield strengths and elongations of Mg-Li-based alloys \(^{24, 46, 248-255}\).](image)

In order to enhance the strength of Mg-Li extrusion alloys, Zn and Al are commonly added to Mg-Li alloys. The main intermetallic compounds in these alloys are MgLi\(_2\)Al, MgLi\(_2\)Zn, AlLi and MgLiZn, however such intermetallic compounds do not provide appreciable strengthening. To further enhance the strength of Mg-Li-based alloys, RE elements are also often added to form some second phase particles during casting and strengthening precipitates during hot extrusion. Depending on the ratio between Zn and RE, the second phase that provides strengthening effect can be icosahedral quasicrystal phase or long-period stacking order structure, which is identical to that in Mg-Zn-Y and Mg-Y-Zn alloys \(^{253}\). To date, the highest yield strength of Mg-Li-based extrusion alloys is reportedly 263 MPa in the Mg-5Li-3Al-2Zn-1.5Cu alloy \(^{250}\). The reason for the relative high strength among Mg-Li-based alloys in such alloys is yet fully not clear but is possibly related to the formation of Al-Cu precipitates during extrusion.

5.6. Comparisons amongst Mg extrusion alloys

Dilute Mg-Al-Ca-Mn and Mg-Sn-Al-Zn alloys have been consistently reported to have high extrudability, and can also be extruded at high (industrially relevant) extrusion speeds.
Mg-Al-Ca-Mn alloy can be extruded as fast as Al alloys, 60 m/min in die exit speed, and this extruded alloy displays a balanced strength (~200 MPa) and ductility (29%) \[120\]. For the Mg-Sn-Al-Zn alloy, the highest extrusion speed reported is 27 m/min \[64\], lower than that of the Mg-Al-Ca-Mn alloy. However, it is still unknown that whether such an alloy can be extruded at higher speed, e.g. 60 m/min. Compared to the dilute Mg-Al-Ca-Mn alloy, the advantage of the Mg-Sn-Al-Zn alloy is that it may have significant age-hardening in response to double ageing treatment. Therefore, if the alloy composition is properly designed, the Mg-Sn-Al-Zn alloy extruded at high speed and double-aging is potentially more than 350 MPa \[169\].

To date, if high strength (YS > 400 MPa) is required from Mg alloy extrusions, then alloys are required to be extruded at low speed, and so far only heavily alloyed Mg-Al-based and Mg-RE-based alloys meet the criterion of high strength (Fig. 36). However, the high-strength AZ80 (YS of 403 MPa) was extruded at low temperature with a very low speed, which is likely to be industrially impractical. The Mg-3.5Al-3.3Ca-0.4Mn alloy reveal the highest yield strength among RE-free alloys, of 410 MPa, however the ductility is comparatively low at ~5.6%. Given that the Mg-Al-Ca-Mn alloys have exhibited high ductility more rapid extrusion (e.g. die-exit speed > 20 m/min), it may be possible for a Mg-Al-Ca-Mn alloys to achieve high strength (YS > 400 MPa) and acceptable ductility (> 10%) simultaneously - if the alloy composition and extrusion conditions are optimised.

The appreciable addition of RE elements (i.e. > 6 wt. %) presently remains the apparently most effective approach to improve the strength of Mg extrusion alloys, compared to the alloying additions of other alloying elements. This is because RE additions not only lead to higher strength in as-extruded alloys, but also provide a significant age-strengthening response. The peak-aged Mg–Gd–Y–Zn–Zr extrusion alloy has the highest record of yield strength among Mg alloys, ~480 MPa \[17\]. By comparison, several 7xxx Al extrusion alloys, such as 7001-T6 and 7055-T751, have high yield strength exceeding 550 MPa \[5\] – with a higher density.

Compared to high strength Mg-Al and Mg-RE based alloys, none of the Mg-Zn-based alloys reported to date present a yield strength above 400 MPa (Fig. 36). However, the Mg-Zn-based alloys have a
more balanced strength and ductility. Some Mg-Zn-based alloys have tensile yield strengths exceeding 200 MPa with an elongation > 25% \cite{53, 56, 60, 65, 99, 120, 250}, which is comparable to some 3xxx, 5xxx and 6xxx Al extrusion alloys \footnote{1}. Furthermore, the alloying elements such as Zn, Ca and Mn are comparatively cheap (compared to RE elements). Therefore, these cost-effective alloys with balanced strength and ductility are expected to be potential candidates for industrial applications. Similar to Mg-Zn-Ca-based alloys, Mg-Zn-RE-based alloys also reveal a balanced of strength and ductility. When the RE elements are limited to low concentrations, the addition of RE elements will not significantly increase cost.

Of the Mg extrusion alloys researched to date, a number of Mg-Al, Mg-RE and Mg-Zn-RE alloys have revealed a higher specific yield strength than Al alloy AA7001 (Fig. 37). Whilst Mg-Li-based extrusion alloys may be expected to have the high specific strength, due to their ultra-lightweight \footnote{24}, as noted from Fig. 37 the specific yield strength of Mg-Li based alloys is still lower than other high-performance Mg alloys.

![Fig. 37. Specific tensile yield strength and elongations of extruded Mg alloys, and 7001-T6, 6061-T6 Al alloys.](image)

To further take the cost-effectiveness into consideration, the specific yield strength of the high-performance Mg alloys reviewed herein have been normalised by the price of the alloying elements (Fig. 38) (price of alloying elements obtained from Ref. \cite{256}). Fig. 38 reveals that the Mg-Al-based alloys are the most cost-effective among the high-performance Mg extrusion alloys. Such outstanding cost-effectiveness is predominantly caused by the major alloying addition of Al, which is both cheap and light-weight. Due to the high-cost of RE elements, the high-performance Mg-RE-based alloys are essentially much less cost-effective than the Mg-Al-based, Mg-Zn-based and Mg-Sn-based extruded alloys. Furthermore, Li is an expensive element, about 50 times more expensive than Al. Moreover, production of Mg-Li alloys requires special precautions due to Li being chemically active, adding to the overall alloy cost. Therefore, Mg-Li-based alloys have amongst the poorest cost-effectiveness among the Mg extruded alloys.
Fig. 38. Specific tensile yield strength normalised by price and elongations of extruded Mg alloys, and 7001-T6, 6061-T6 Al alloys.
6. Summary, perspectives and outlook

Considerable advances in the development of Mg extrusion alloys with improved extrudability, higher strength and ductility, and improved tension-compression yield asymmetry, have occurred in the last two decades. To date, several extruded Mg alloys have been reported to exhibit a good balance of strength and ductility, with tensile yield strengths exceeding 200 MPa and elongation more than 25%, which are comparable to those of 3xxx, 5xxx and 6xxx Al extrusion alloys. Moreover, some Mg extrusions based on the Mg-Zn, Mg-RE, and Mg-Sn alloy systems reveal negligible tension-compression yield asymmetry. Despite such advances, Mg extrusion alloys, as a class of engineering materials, are still inferior to counterpart Al alloys in terms of extrudability and strength. The highest extrusion speed of Mg alloys reported was 60 m/min, which is still lower than the extrusion speed used to process Al extrusion alloy (> 100 m/min). The highest tensile yield strength is reportedly 410 MPa for a RE-free Mg-alloy and ~480 MPa for a RE-containing Mg-alloy. In order to compete with Al extrusions commercially, further enhancement of extrudability and mechanical properties of Mg extrusion alloys is required, which requires a comprehensive understanding of the interplay between processing variables, alloy composition, microstructural development, precipitation, and mechanical response. The following viewpoints are raised, based on the review herein:

a. To date, it remains unknown whether the extrusion speed of Mg alloys may be improved to achieve speeds as high as those for Al alloys (> 100 m/min). In order to achieve high extrudability, alloying elements that can increase the solidus temperature of the alloy, such as Ca, Mn, Sn and RE-elements are required. Conversely, elements such as Zn, that decrease the solidus temperature of the alloy or induce the formation of second phase particles with low melting temperature, need to be minimised. It can be concluded that the pursuit of high-performance extrusion alloys with dilute alloying is a promising research direction, as dilute alloys are more likely to be processable by high-speed extrusion, however, the concentration and ratio of alloying elements requires optimisation. In the future studies, extrusion processing maps as a function of alloy composition, if established, will reveal the prospects for optimisation of alloy composition for high-speed extrusion. Moreover, in order to develop new highly extrudable Mg alloys, efforts are required to provide an insightful understanding how the factors important in extrudability, such as solute species and distribution, and particle size and distribution, affect local melting and cracking during the extrusion process. Such aspects described are to date principally explored empirically; the complexity of the multitude of variables relating alloy design, to microstructure and texture, remain to be appropriately modelled. The inability to accurately model metallurgical systems from design through to properties (when complex processing and complex alloying exists) remains a difficult nexus in the field.

b. The development of ultra-high-strength Mg extrusion alloys (YS > 500 MPa for RE-free alloys and YS > 550 MPa for RE-containing alloys) also appears promising. To achieve this aim, the microstructure of any ultra-high-strength Mg extrusion alloy need to be tailored, so to contain uniform submicron grains and dense and fine precipitates. As evidenced in the review herein, submicron grains and dense and fine precipitates would provide the significant strengthening effect. To date, uniform submicron grain size has been achieved in the extruded alloys produced by powder metallurgy rather than bulk (ingot) metallurgy. However, production of ultra-high-strength extrusion alloy using cost-effective conventional bulk metallurgy is critical for adoption by industry. It is foreseeable that production of the ultra-high-strength and submicron grain size extrusion alloy might be easier at low extrusion temperature and low extrusion speed, but the real challenge is how to produce the submicron grain size extrusion alloy at high extrusion speed and the moderate temperatures widely used in the existing extrusion industry. Achievement of this aim needs new discoveries in Mg alloy design.
c. Regarding improvements in properties achieved from grain refinement to the submicron scale, it concomitantly remains a challenge with regards to balancing the ability to also permit precipitation strengthening. For example, the size, shape and distribution of precipitates in many emerging Mg alloys remains poorly understood; furthermore it would be ideal if a high density of fine precipitates (nanometre scale) could be uniformly distributed within the submicron grains. At present, such an ideal microstructure has proven difficult to achieve in Mg extrusions, principally owing to the lack of knowledge of precipitation (and manipulation of precipitate size, distribution and morphology) coupled with a lack of understanding relating to how precipitates interact with dislocations, twins, and grains during dynamic recrystallization. To address such issues, a comprehensive understanding surrounding (i) the effects of alloying composition and extrusion conditions on the structure, morphology and distribution, formation and growth mechanism of precipitates during extrusion, and (ii) the interactions between precipitates and crystal defects, such as dislocations, as these defects will have significant effect on the nucleation and growth of precipitates during hot extrusion and post-extrusion ageing. The complexity of precipitation in Mg alloy systems has been highlighted only recently by the advent of ultrahigh resolution microscopy, where aspects such as a periodic segregation or aggregation of solute atoms (to single atomic columns) have been demonstrated. Phase transformations in Mg alloys will require computational (kinetic) modelling, as opposed to solely conventional thermodynamic assessment.

d. The ductility and formability of magnesium extrusion alloys can be enhanced by texture weakening, which has been empirically evidenced by appropriate additions of RE and Ca. However, the mechanism of texture weakening in Mg alloys still remains somewhat controversial. Although several recent studies have provided some direct observation of texture evolution during deformation and/or recrystallization in Ca- and RE-containing alloys, the fundamental mechanism of texture weakening caused by RE and Ca additions is still incomplete; predominantly due to limitations in EBSD resolution and limitations of in-situ TEM and in-situ EBSD observations may provide more insightful information regarding recrystallization behaviour, and therefore assist in revealing the origins of weakened basal texture. In addition to texture weakening, triggering the operation in inter-granular deformation mechanisms, such as grain boundary sliding, is another effective means for enhancement of ductility and formability of Mg extrusions - now already having been demonstrated whereby the operation of intergranular mechanisms successfully making intrinsically brittle Mg super-plastic and super-formable at room temperature. However, to date, the research in the latter field has not been widely published, and has great potential for further improvement in ductility and formability – in addition to providing a more comprehensive understanding of inter-granular deformation mechanisms that operate at room temperature. The super-formability of pure Mg at room temperature is only realised when the pure Mg is extruded under low speed (ram speed 0.1 mm/s), which is impractical for industrial production. Obviously replicating the super-formability in more industrially favourable operating conditions (larger ingot size and faster extrusion speed) is important for its wider applications. Moreover, the super-plasticity and super-formability at room temperature have only been reported in pure Mg, and not yet realised for Mg alloys. It is foreseeable that if pure Mg extrusion alloys can be tailored to be super-formable, that such alloys would possess higher strength and super-formability simultaneously, significantly promoting the application of Mg extrusion alloys in industry.

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