2.1. Magnesium Alloys

Reduction in weight of vehicle, for increased fuel efficiency is a high priority for the automotive industry [19-20]. Due to its lower density, magnesium has been a potential candidate for a range of automotive components [21-24]. With replacing car parts made from aluminum, it is possible to save about 30% of the weight. The choice of magnesium for a particular application may be based not only on its lightweight, but also its easy machinability & adaptability to common methods of fabrication, and its high strength-to-weight ratio [25-26]. It is well proven that, through sensible alloying, the mechanical properties of magnesium can be improved without compromising its added density advantage [27-31]. Alloys of magnesium are available for both cast and wrought applications. The magnesium casting alloys almost fully belong to the Mg-Al series; mainly AZ91 (Mg-Al-Zn) and AM60 or AM50 (Mg-Al-Mn) [32-34]. Other common cast alloys include Mg-Al-Si (AS) and Mg-RE (rare earths, AE) series [35-41]. The Mg-Al alloys are widely used due to their reasonable mechanical properties and excellent castability. The magnesium wrought alloys are AZ31, AZ61 and ZK alloys (Mg-Zn-Zr). Among them, AZ31 is presently one of the most common Mg wrought alloy in use. Due to poor formability at room temperature caused by its hexagonal close packed (hcp) structure (limited amount of possible slip systems) AZ31 fabrication is mostly carried out using hot deformation processes like rolling, extrusion or forging.

2.2. Applications

2.2.1. Automotive Applications

The magnesium industry has made great efforts to educate the automotive industry on the benefits of utilizing magnesium to reduce vehicle weight, cost, and/or complexity [42]. Applications of magnesium in automobiles using the die casting approach has been in components such as instrument panels, steering wheels, steering columns and seat risers which take advantage of magnesium’s high strength-to-density ratio & excellent ductility combined with attractive energy absorbing characteristics. Magnesium parts in production include: accessory drive brackets (AZ91D), automatic transmission clutch piston and stator (AS41B), clutch housing (AZ91D), door mirror brackets (AZ91D), headlamp retainers (AZ91D), upper and
lower inlet manifolds (AM60B, AZ91D), oil filter adapter housing (AZ91D), power window regulator housings (AZ91D), seat frames (AM60B), steering wheel armatures (AM50 [Mg-5Al-0.3Mn], AM60B) and valve and cam covers (AZ91D) [42-45]. Fig. 2.1 shows some of the automotive components made from magnesium alloys.

![Major Magnesium Based Auto Products](image)

Fig. 2.1: Some of the major magnesium based automotive components [45]

### 2.2.2. Aerospace Applications

Magnesium has seen quite extensive use in both civil and military aircrafts. Some applications include the thrust reverser (for Boeing 737, 747, 757, 767), gearbox (Rolls-Royce), engines, and helicopter transmission casings, etc. Military aircraft, such as the Eurofighter Typhoon, Tornado, and F16, also benefit from the lightweight characteristics of magnesium alloys for transmission casings [46-47]. There is also widespread use of magnesium in spacecraft and missiles due to the requirement for lightweight materials to reduce the lift-off weight. This is coupled with its high specific mechanical properties, ease of fabrication, and other attractive features such as its capability to withstand (i) elevated temperatures, (ii) exposure to ozone, and (iii) bombardment of high-energy particles and small meteorites. Alloys such as ZE41 (Mg-4.2% Zn-0.7% Zr-1.3% MM), QE22 (Mg-0.7% Zr-2.5% Nd-2.5% Ag) and particularly WE43 (Mg-4% Y-3.25% Nd-0.5% Zr) are commonly used for
aircraft applications due to their improved corrosion and creep resistance. Fig. 2.2 gives some of the aerospace components made from magnesium alloys.

![Mg alloys in aerospace applications](image)

**Fig. 2.2: Some of the aerospace components made up of Mg alloys [47]**

### 2.2.3. Nuclear Industry

With natural uranium as a fuel, it is essential to conserve neutrons by only using materials in the reactor which will not absorb them readily. Natural uranium plants with operating temperatures suitable for power production essentially determine the general reactor design and limit the canning material to magnesium and the coolant gas to magnesium dioxide. The advantages of magnesium over competing materials are: (a) low tendency to absorb neutrons, (b) does not alloy with uranium, (c) adequate resistance to carbon dioxide up to the highest service temperatures envisioned, and (d) good thermal conductivity [48].

### 2.2.4. Medical Applications

Magnesium alloys were first introduced as orthopedic biomaterials in the first half of the last century [49]. However, due to its low corrosion resistance, a large amount of hydrogen accumulates around the implant during the *in-vivo* corrosion process, confining the widespread use of magnesium-based materials as biomaterials. Despite, magnesium still possesses many attractive characteristics that make
magnesium based materials potential candidates to serve as implants for load-bearing applications in the medical industry. Magnesium is also present as a natural ion in the human body, whereby approximately 1 mol of magnesium is stored in a 70 kg adult human body and an estimated amount of half of the total physical magnesium is present in the bone tissue [50, 52]. It also assists in many human metabolic reactions and is nontoxic to the human body. Magnesium has good biocompatibility and it is biodegradable in human body fluid by corrosion, thus eliminating the need for another operation to remove the implant. All these desirable features make magnesium-based material a promising implant material.

2.2.5. Sports Applications

The excellent specific strength and ability of magnesium alloys and magnesium composites to form intricate shapes resulted in many applications in sports-related equipment. For example, magnesium-based materials are used in the handles of archery bows, tennis rackets, and golf club heads. The lightweight and excellent damping characteristics of magnesium-based materials have also made them a popular material choice in bicycle frames and the chassis of in-line skates [51-52]. Fig. 2.3 gives some of the sports components made from magnesium alloys.

Fig. 2.3: Magnesium sports equipments: (a) golf club head, (b) in-line skates with magnesium chassis, (c) tennis racquet with magnesium head and (d) bicycle with magnesium frame [52]
2.2.6. Electronic Applications

In spite of automobile and aerospace components, magnesium also finds application in electronics items. Magnesium-based materials are used in housings of cell phones, computers, laptops, and portable media players. The ability to form magnesium alloys into complex shapes and the good heat dissipation and heat transfer characteristics of magnesium alloys also result in the use of magnesium alloys in heat sinks and the arms of the hard-drive reader [43, 51]. Other examples of the use of magnesium include the housings of cameras and digital image projection systems [52].

2.3. Limitations

Apart from the above said advantages and applications, there are some limitations, which restrict its full utilization in industry. Some of the challenges that are faced by magnesium for its acceptance in industrial applications are summarized in Table 2.1 [53-54].

<table>
<thead>
<tr>
<th></th>
<th>Limitations of magnesium alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High metal cost</td>
</tr>
<tr>
<td>2</td>
<td>Small supply base</td>
</tr>
<tr>
<td>3</td>
<td>High cost of recycling</td>
</tr>
<tr>
<td>4</td>
<td>Replacement of SF6 cover gas (melting difficulties)</td>
</tr>
<tr>
<td>5</td>
<td>Low high temperature properties</td>
</tr>
<tr>
<td>6</td>
<td>Corrosion problem</td>
</tr>
<tr>
<td>7</td>
<td>Poor workability</td>
</tr>
<tr>
<td>8</td>
<td>Lack of joining technologies</td>
</tr>
</tbody>
</table>

2.4. Melting Practice

2.4.1. Flux Melting and Refining

When magnesium and its alloys are melted, they tend to oxidize and explode. In order to solve these problems a number of methods were developed. Flux compositions were usually adjusted to melt below the melting point of the alloys. So that they spread-out and protect the solid metal from oxidation prior to melting.
Earlier, $\text{BaCl}_2$ was added to adjust the melting point, besides the addition of porous substances such as $\text{MgO}$ was performed to absorb the chlorides [55-57].

Later, the thickened (inspissated fluxes) consisting of $\text{MgCl}_2$ and thickening agents such as $\text{MgO}$ and $\text{MgF}_2$ were developed. The flux could provide a thin viscous protective layer on the melt surface and avoided the risk of chloride inclusions arising from the use of excess flux. The modern flux technique developed by Dow gave rise to a number of commercially available fluxes for magnesium. The composition could be varied high potassium flux (M134) has lower density, which made a better cover flux than high $\text{MgCl}_2$ (M-130).

The mechanisms behind the chloride flux in preventing oxidation and burning of magnesium melts involves the wetting of the underlying metal surface with very thin chloride films, thereby preventing the adsorption of oxygen molecules and consequent scale formation.

The function of flux is not only protecting against oxidation and burning but also refining (i.e., removing oxides and non-metallic inclusions) the melt [8]. This is achieved by appropriate use of fluid and inspissated fluxes. Nitride inclusions may also be found if the alloy has nitride forming elements such as sodium and barium. These oxide and nitride inclusions tend to settle to the bottom in fluxed melts.

Flux inclusions occur if unabsorbed protective flux remains on the metal surface, the flux is too fluid, there is brittle or powdery flux due to long handling, pouring is too fast or if there is incomplete removal of the flux adhering to the lip of the pot before pouring. Here stirring of the metal is needed to help the re-finining process. As the metal is stirred, the agitation of the metal brings the excess fluid flux, oxides, and inspissated flux together into a single thickened phase, which coalesces and settles to the bottom. When the balance of fluid flux, oxides and inspissated flux is correct, the melt will be left free of both oxide and flux and the settled phase will be pasty or custard-like. If too little flux is present the settled phase will be crumbly and dry in appearance. If the flux content is too high the settled phase will remain fluid and free flowing. In both, the melt is likely to remain contaminated by suspended flux-oxide inclusions.
2.4.2. Flux-less Melting

Although extremely effective in controlling oxidation, fluxes create corrosive fumes in the foundry and are difficult to separate from the metal, contributing to a high incidence of corrosive inclusions in magnesium casting parts. The quest for technology to protect magnesium from oxidizing without the negative ramifications associated with flux led to flux-less melting. Mixtures of \( \text{CO}_2 \), \( \text{CO}_2 \)-air, or air alone combined with 0.3 to 0.5\% \( \text{SF}_6 \) have been successfully used for melt protection in casting operations thus essentially eliminating the problems due to flux inclusions \[58\].

When melting in the absence of fluxes, the oxides formed tend to float at or near the surface due to their porous character and their association with the gases liberated during the melting operation. In most processes it is desirable to refine the melt by removing these oxides. Fluxless refining can be effectively achieved with standard Mg-Al alloys by flushing argon gas throughout the melt. This will accelerate the floatation of the oxides to the melt surface where they can then be removed \[8\].

The mechanism of melt protection with these gases is not completely understood. Sulphur or sulphur dioxide also provides protection but the role of sulphur gases is also poorly understood in relationship to providing a barrier to oxygen in the environment. \( \text{SF}_6 \), being a source of both sulphur and fluorine, provides a very effective barrier. Carbon dioxide has been used in a limited fashion in foundries, but it requires a continuous flow of fresh \( \text{CO}_2 \) onto the melt surface and strict temperature control. New gas protection systems are under development to address the environmental effects associated with the exceptionally high global warming potential (GWP) of \( \text{SF}_6 \) \[60\].

2.5. Casting Processes

Metal casting processes are used to design and manufacture a variety of components and finished products. Almost everything ranging from simple nails and fasteners to large machine parts and engine blocks can be cast using these casting processes. Normally the magnesium alloys are cast by die casting method \[61\]. This is to overcome the material cost disadvantages compared to aluminium alloys. All magnesium alloys development activities for different mechanical properties are thus...
focused with die-castability. Magnesium alloy containing Al as a major alloying element has high die castability compared to other Mg alloys. The most commercial and widely used die cast magnesium alloys are AZ91, AM60, and AE42 etc.

Selection of a particular casting method depends on many factors, e.g., the number of castings required, the properties required, dimensions and shape of the part and the castability of the alloy [42]. Despite, pressure die casting is predominantly used to produce many of the magnesium alloy components, other casting processes such as gravity and low pressure castings using sand and permanent moulds are also familiar. Investment casting process has also presently become popular in producing Mg alloy components. Magnesium alloy sand castings are used in aerospace applications because they offer a clear weight advantage over aluminum and other materials. Mg-Al and Mg-Al-Zn alloys are also easy to cast in gravity sand casting method; however they are limited in certain respects. They exhibit micro shrinkage when they are sand-cast, and the alloy is not suitable for applications in temperatures of above 120°C. The magnesium rare earth-zirconium alloys were developed to overcome these limitations. However these alloys are not suitable for die-casting application due to the poor die castability.

In general, the alloys that are normally sand cast are also suitable for permanent mould casting. The exception to this are the alloys magnesium-zinc-zirconium type which exhibit strong hot-shortness tendencies and are unsuitable for processing by this method. In addition, developments are well advanced with squeeze casting and semi-solid processing like rheo-casting and thixo-casting [62-66]. Components produced through these casting methods show less defects and porosity and they can be heat treated to get maximum mechanical properties. These casting methods are also suitable for thick and thin sections. Low Pressure Casting (LPC) is another casting technique used to produce magnesium castings with improved mechanical properties [67-69].

2.6. Major Alloy Systems

Although there is no international system for designating magnesium, the naming method used by the American society for testing, and materials (ASTM), is
the most commonly used for magnesium alloys. In this system the first two letters indicate the principal alloying elements according to the following code:

- A - Aluminum
- E - Rare earth metals
- H - Thorium
- K - Zirconium
- L - Lithium
- M - Manganese
- Q - Silver
- T - Tin
- Z - Zinc

The corresponding letters to the element present in greater quantities in the alloy is given first followed by number which represents the nominal compositions in weight percent of the principal alloying elements. Magnesium casting alloys may be classified into two major groups: zirconium containing alloys and zirconium free alloys.

### 2.6.1. Zirconium Containing Alloys

Zirconium is a very effective grain refiner for magnesium and can be used with all alloys except those containing aluminum or manganese. Zirconium cannot be used with the Mg-Al or Mg-Al-Zn alloys as it forms compounds with Al and Mn. Elements compatible with Zr include Zn, RE, Ag and Y. While binary Mg-Zn alloys show inferior mechanical properties and castability, the ability to refine the grains in Mg-Zn alloys with zirconium led to the introduction of ternary alloys such as ZK51 and ZK61. However, these alloys are susceptible to micro porosity and are not weldable; they have found little practical application [70, 71]. Mg-Zn-RE system (ZE and EZ alloys) have been the most important gravity cast magnesium alloy systems for automotive applications. Effective grain refinement by Zr, combined with additions of RE-elements to reduce microporosity, led to the introduction of alloys such as EZ33 and ZE41. An alloy belonging to this group offers moderate strength up to 150°C after ageing of the cast material. Better properties in terms of castability,
freedom from microporosity, strength, creep resistance up to 250°C can be obtained with EZ33 (2.5- 4% RE, 2- 3.1% Zn, 0.5- 1%Zr) [72].

In recent times, Mg-Y age hardenable alloy systems are developed to utilize the benefit of high solid solubility of yttrium in magnesium. A series of Mg-Y-Nd-Zr alloys have been produced, which provides high strength at ambient temperature and good creep resistance up to 300°C temperature [73, 74]. Maximum strength combined with an adequate level of ductility is found to occur in an alloy containing approximately 6% Y and 2% Nd and the commercially available alloy in this category is WE54 (Mg-5.25Y-3.5RE-0.45Zr).

Thorium additions also confer to increase creep resistance in magnesium alloys, and these alloys have been used in service temperatures up to 350°C. Ternary compositions such as HK31 (Mg-3Th-0.7Zr) is developed for high temperature applications. However, in spite of their application in missiles and spacecraft, the alloy usage is reduced because of environmental considerations. Silver also added to magnesium and Mg-Ag-RE-Zr alloys are developed with improved room temperature and high temperature mechanical properties [75]. The alloy QE22 (Mg-2.5Ag-2RE-0.7Zr) has been used for a number of aerospace applications including landing wheels, gear box housings and rotor heads for helicopters.

2.6.2. Zirconium Free Alloys (Mg-Al Alloys)

Most of the commercial magnesium alloys are based on the Mg-Al system, but most current compositions also contain small amounts of zinc and manganese and casting is currently the most commonly used production process for magnesium components [76]. Among the alloys used, AZ91, AM60 and, to a lesser extent, AM50 dominate [77]. The range of aluminium contents for the commercial alloys is 3-9 wt% Al, from AZ31, a wrought alloy composition cast as billet, to AZ91. This group alloys are relatively cheap compared to other group magnesium alloys available. They are readily castable, particularly by high-pressure die-casting, and exhibit good mechanical properties. An important feature of these alloys is that they can be cast into long and thin sections by high-pressure die-casting.

Alloys AS21, AS41 (Mg-Al-Si), which contain Si are developed for better creep properties compared to AZ91 [78, 79]. Later on, the beneficial effect of rare
Literature Review

Chapter 2

earth elements on the strength of magnesium alloys has been discovered and it is reported that 1% addition of RE in the form of mischmetal improved the creep resistance of Mg–Al based alloys, especially when the aluminium content is low (less than 4%) [80]. This led to the development of AE series alloys (AE41, AE42, and AE21) which contain 2–4% Al.

Calcium addition to Mg–Al based alloys for improved creep resistance is reported in a British patent in 1960 [81]. This patent discloses that calcium additions of 0.5–3% provide creep resistance to magnesium alloys containing up to 10% Al, up to 0.5% Mn, and a possible zinc content of up to 4%. However, the patent also reports that calcium containing alloys are prone to hot cracking during die casting. The patent has claimed that such a hot cracking tendency can be considerably reduced by increasing the iron content of the alloys to about 0.015–0.03%. Volkswagen [82] has attempted the use of Mg–Al–Ca alloys and claimed an improvement in creep resistance with the addition of about 1% Ca to magnesium alloy AZ81 (Mg–8Al–1Zn). However, the application of this alloy to die casting production of crankcases is not possible owing to die sticking and hot cracking. In recent years, the Mg–Al–Ca alloy system is revisited at the Institute of Magnesium Technology (ITM) in Canada [83]. An alloy known as AX51 (Mg–5Al–0.8Ca; X representing calcium) has been developed, which provides the creep resistance similar to AE42 and corrosion resistance similar to AZ91D.

2.6.2.1. AZ31 (Mg-3% Al-1% Zn-0.2% Mn) alloy

The wrought forms of Mg-alloys produced by thermo mechanical processing, like rolling or extrusion, possess their own position in the market. The pronounced temperature dependency on plastic deformation allows a wide range of mechanical properties by varying the processing temperature, which influences the product properties [84-85]. Wrought Mg alloys have the advantages of higher strength, ductility and formability than the cast form. The physical and mechanical properties of magnesium alloys are strongly affected by the amount of each alloying constituent added to the material. For example AZ31 (2.5-3% Al and 0.6-1.4% Zn, 0.2% Mn, % Mg in bal.) presents a good combination of strength and ductility resulting from solid solution hardening and grain refinement from Zn addition. AZ31 has a wide
application in extruded and sheet form. However, in order to compete with other lightweight materials, the processing has to be inexpensive. For example AZ31 can only be extruded at elevated temperatures of approximately 350°C, and at a relatively low rate of 10-20 m/min [8]. To overcome these drawbacks, thermo mechanical treatment should preferably start with improved feedstock from cast materials.

### 2.6.2.2. AZ91 (Mg-9% Al-1% Zn-0.2% Mn) alloy

The most common and commercially used cast Mg-Al based alloy is AZ91, which has a good combination of moderate strength and reasonable ductility [86-87]. Aluminum in this alloy offers mechanical, corrosion and foundry properties like castability. Zinc offers little solid solution strengthening and corrosion resistance. Manganese neutralizes the ill effect of Fe and hence provides corrosion resistance. However, the alloy exhibits a coarse and non-uniform microstructure and therefore offers poor mechanical properties.

### 2.7. Role of alloying elements in Mg-Al alloys

#### 2.7.1. Aluminium

Aluminium is the most widely used additive in magnesium alloys. The Mg-Al alloys are considered to have reasonable mechanical properties. The maximum solid solubility of aluminium in magnesium is 12.7wt% at 437°C [88]. Aluminium provides solid solution strengthening, and at greater than 2wt%, precipitation of the $\beta$ phase occurs which further enhances hardening. Al in this alloy also improves the castability and fluidity [89]. However, Al also increases the tendency for shrinkage micro porosity up to 9% and then reduces it [90]. The reason for the peak porosity at 9% can be related to the worst combination of mushy zone size, interdendritic feeding, permeability and eutectic volume friction. Aluminum also increases the corrosion behavior of Mg-Al alloys.

#### 2.7.2. Zinc

Zinc is often said to be added to Mg-Al alloys (the AZ system) to impart solid solution strengthening and improved fluidity [91-92]. But higher amount of Zn in Mg-Al alloys can lead to hot cracking problem. It is further reported that the addition of
Zinc reduces the ductility of the alloy. Zinc strongly affects solidification pattern of AZ91 alloy thereby forming micro-porosity. It is reported that addition of 2% Zn increases micro porosity in sand-cast magnesium alloys containing 2, 4, 8 and 10% Al \[34\]. It has also been reported that, zinc widens the two phase \(\alpha\)-Mg and \(\beta\)-Mg\(_{17}\)Al\(_{12}\) field which may result in a higher degree of precipitation and a corresponding increase in strength in age hardened alloys. Zinc may also have a role to play in accelerating the rate of precipitation in age hardening.

### 2.7.3. Manganese

Manganese is added to magnesium alloys in small quantities approximately 0.2wt\% to improve the corrosion resistance by removing cathodic impurities such as Fe through the formation of intermetallic compounds which are precipitated out of the melt prior to casting. This leaves the alloys far less sensitive to local galvanic corrosion. The exact amount of Mn addition into Mg-Al alloys is dependent on the chemical compositions and the casting conditions of each alloy. Manganese is predominantly present in the microstructure of Mg-Al alloys in the form of intermetallics such as Al\(_8\)(Mn,Fe)\(_5\) and \(\alpha\)-AlMnFe \[93\].

### 2.8. Strengthening Mechanisms of Metals

Strengthening mechanisms can be understood from the relation between dislocation motion and mechanical behaviour of metals. Since, the macroscopic plastic deformation corresponds to the motion of large numbers of dislocations; the ability of a metal to plastically deform depends on the ability of dislocations to move. Since hardness and strength (both yield and tensile) are related to the ease with which plastic deformation can be made to occur, by reducing the mobility of dislocations, the mechanical strength may be enhanced \[94\]. Greater mechanical forces will be required to initiate plastic deformation. In contrast, the more unconstrained the dislocation motion, the greater the facility with which a metal may deform, and the softer and weaker it becomes. Virtually all strengthening techniques rely on this simple principle: restricting or hindering dislocation motion renders a material harder and stronger. Strengthening of metals can be achieved in several ways, for example
by solid solution hardening, work hardening, precipitation hardening, dispersion strengthening, and grain refinement.

2.8.1. Solid Solution Strengthening

Alloying with impurity atoms that go into either substitutional or interstitial solid solution is a technique, which strengthens and hardens the metals. Accordingly, this is called solid-solution strengthening. Alloys are stronger than pure metals because impurity atoms that go into solid solution ordinarily impose lattice strains on the surrounding host atoms [94]. These lattice strain field interactions between dislocations and impurity atoms consequently, restrict dislocation movement.

2.8.2. Strain Hardening

Strain hardening is used for hardening/strengthening materials that are not responsive to heat treatment. The phenomenon where ductile metals become stronger and harder when they are deformed plastically is called strain hardening or work hardening. Strain hardening is used commercially to enhance the mechanical properties of metals during fabrication procedures. In addition to mechanical properties, physical properties of a material also changes during cold working. There is usually a small decrease in density, an appreciable decrease in electrical conductivity, small increase in thermal coefficient of expansion and increased chemical reactivity (decrease in corrosion resistance).

2.8.3. Dispersion Strengthening

Small second-phase particles distributed in a ductile matrix can hinder the dislocation motion and thus increase the strength of a material. Second-phase particles can be introduced by mixing and consolidation. In dispersion strengthening, hard particles are mixed with matrix powder and consolidated and processed by powder metallurgy techniques. Here second phase shall have very little solubility in the matrix, even at elevated temperatures. The degree of strengthening from second phase particles depends on particle distribution in the matrix. Particle dispersion along with the shape can be expressed by specifying the volume fraction, average particle
Literature Review

Chapter 2

diameter, and mean interspacing of particles which are interrelated. A simple expression for interspacing of particles is:

\[ \lambda = \frac{4(1-f)r}{3f} \]  

(2.1)

where \( f \) is the volume fraction of spherical particles of radius \( r \).

The spacing between second phase particles should be typically a few hundred angstroms. Optimum strengthening occurs once the right interspacing of particles is achieved.

2.8.4. Strengthening by Grain Size Refinement

The size of the grains, or average grain diameter, in a polycrystalline metal influences the mechanical properties. Adjacent grains normally have different crystallographic orientations and, a common grain boundary, as indicated in Fig. 2.4. During plastic deformation, slip or dislocation motion must take place across this common boundary, say, from grain A to grain B in Fig. 2.4.

![Fig. 2.4: The motion of a dislocation as it encounters a grain boundary, illustrating how the boundary acts as a barrier to continued slip. Slip planes are discontinuous and change directions across the boundary [94]](image)

The grain boundary acts as a barrier to dislocation motion for two reasons:

i. Since the two grains are of different orientations, a dislocation passing into grain B will have to change its direction of motion; this becomes more difficult as the crystallographic misorientation increases.
ii. The atomic disorder within a grain boundary region will result in discontinuity of slip planes from one grain into the other.

A fine-grained material is harder and stronger than one that is coarse grained, since the former has a greater total grain boundary area to impede dislocation motion. For many materials, the yield strength $\sigma_y$ varies with grain size according to

$$\sigma_y = \sigma_0 + Kd^{-1/2}$$  \hspace{1cm} (2.2)

In this expression, termed the Hall-Petch equation, $d$ is the average grain diameter, and $\sigma_0$ and $k$ are constants for a particular material.

It is important to note that the above relation is not valid for both very large grain and extremely fine grain sizes. Grain size reduction is technologically attractive because it generally does not adversely affect ductility and toughness, contrary to most other strengthening methods. According to the earlier studies grain refinement in Mg and its alloys leads improved mechanical properties, which includes the enhancement of both strength and ductility [95-98]. Grain size can be controlled by rate of cooling, addition of grain refiners and also by plastic deformation followed by appropriate heat treatment [99-107].

2.9. Mechanisms of Grain Refinement

2.9.1. Homogeneous and Heterogeneous Nucleation

Nucleation during solidification can be defined as the formation of a small crystal from the melt that is capable to grow. The rate of nucleation is dependent on the magnitude of the undercooling i.e. the difference between the equilibrium melting temperature $T_m$ and the freezing (solidification) temperature $T_f$. In general a higher undercooling results into an enhanced nucleation rate. Two nucleation theories may apply, homogeneous nucleation and heterogeneous nucleation.

Formation of a critically sized solid from the liquid by the clustering together of a large number of atoms at a high undercooling (without an external interface), it is said to nucleate homogeneously. The principal difficulty in the homogeneous formation of nuclei is that a surface is created when a second phase particle forms. Thus, for homogeneous nucleation to take place, a large driving force is required to
overcome the energy of the new surface created. Formation of a critically sized solid from the liquid on an impurity surface, it is said to nucleate heterogeneously.

The substrates can exist in various forms such as impurity particles suspended in the melt, the mould wall, or intentionally added inoculants. These substrates diminish the thermodynamic barrier required for nucleation, facilitating the nucleation event with a smaller amount of undercooling. Since the complete elimination of such substrates is practically impossible, heterogeneous nucleation occurs in most casting processes. The nucleation efficiency of a foreign solid substrate depends on the interaction between the solid surface and the melt, called wetting. Wetting is characterized by the wetting angle “θ” as shown in Fig. 2.5.

![Schematic representation showing the formation of a spherical nucleus of solid phase on the surface of a foreign substrate](image)

**Fig. 2.5: Schematic representation showing the formation of a spherical nucleus of solid phase on the surface of a foreign substrate [113]**

### 2.9.2. Growth

Once solid nuclei form, growth occurs as atoms are attached to the solid surface. The nature of the growth of the solid depends on how heat is removed from the system. Two types of heat must be removed: the specific heat of the liquid and the latent heat of fusion. The specific heat is the heat required to change the temperature of a unit weight of the material by one degree. The specific heat must be removed first, either by radiation into the surrounding atmosphere or by conduction into the surrounding mould, until the liquid cools to its freezing temperature. The latent heat of fusion must be removed from the solid-liquid interface before solidification is completed.
2.10. Solute effects in grain refinement

It is proposed that the addition of nucleant particles and the segregation of solute elements play an important role in grain refinement [108, 109]. The extent of segregation is measured in terms of growth restricting factor (GRF). In fact, the role of solutes as growth restricting elements has been realized earlier [110, 111] Maxwell and Hellawell [110] have shown that the number of grains per unit volume \((N_v^G)\) increases with the number of particles per unit volume \((N_v^P)\) only up to a critical value and reach saturation. This means beyond the critical value of \(N_v^P\), not all the particles added act as potent nucleating sites. This is due to the latent heat released by the growing grains, which raise the temperature of the melt above the heterogeneous nucleation temperature, thus suppressing further nucleation events. The rate of growth is known to be inversely related to the constitutional supercooling parameter \((GRF)\), \(mC_o(k-1)\), where \(m\) is the slope of the liquidus, \(C_o\) is the concentration of the solute in the melt and \(k\) \((=C_s/C_l\), where \(C_s\) and \(C_l\) are the solute concentration of the solid and liquid, respectively at the interface) is the equilibrium partitioning coefficient [112-114]. When this parameter is large, the rate of growth (and hence the latent heat evolved) is slow, thus allowing large number of substrates to act as nucleating sites. The reverse is true when the GRF is small. Thus the critical value of \(N_v^P\) depends strongly on the GRF.

2.11. Grain Refining Methods for Magnesium Alloys

Pure magnesium shows a coarse columnar structure when cast, hence grain refining processes are required to suppress the columnar structure. Various grain refining methods, therefore, have been developed for magnesium alloys, and quite different practices are required depending on alloy composition. The degree of grain refinement achieved is also very sensitive to the composition of the alloys. Magnesium alloys can be generally classified into two broad groups: aluminum free and aluminum bearing [10, 17].

2.11.1. Aluminium free alloys by Zirconium

Additions of zirconium in the range between 0.3 to 0.8wt% produce very fine grain structures in pure magnesium and in magnesium alloys containing zinc or rare
Zirconium has the same h.c.p. microstructure as such as Ag and Th [115,116]. The mechanism of grain refinement with zirconium in magnesium, and the lattice parameters of hexagonal $\alpha$ zirconium ($a = 0.323$ nm, $c = 0.514$ nm) are very close to those of magnesium ($a = 0.320$ nm, $c = 0.520$). Based on this, it is thought that zirconium particles may be powerful nucleants of $\alpha$-magnesium. The commercial practice of grain refinement of magnesium alloys with zirconium has been fundamentally based on the peritectic mechanism [117]. Consequently, the zirconium content dissolved in the melt needed to be greater than the peritectic composition, which was believed to be 0.601wt% Zr according to the Mg–Zr phase diagrams.

Recently, the solubility of zirconium in molten magnesium at the peritectic temperature has been reassessed to be 0.443% [118]. Since about 1960, addition of zirconium to magnesium has been achieved mainly through the use of Mg–Zr master alloys, however because of their low alloying efficiency, an excess of zirconium needs to be introduced in order to attain the full zirconium content for optimum grain refinement [119]. For example, when a Zirmax master alloy (Mg–33.3%Zr) is used, an addition of 7% of the master alloy, equivalent to adding 2.33% Zr, is necessary to ensure the 0.6% Zr content when starting from pure magnesium ingots. Therefore, if the 0.443% Zr solubility content can be established as a new basis for grain refinement with zirconium, it will help to reduce the cost of production of zirconium containing magnesium alloys. Recent work by Lee et al. [17] showed that small additions of zirconium ($\leq 0.32\%$) could reduce the grain sizes of pure magnesium samples cast under fast cooling conditions and the mechanism was attributed to the strong growth restriction effect of zirconium on magnesium.

It has been observed that the influence of combined addition of calcium and zirconium produces a strong grain refining effect than zirconium alone [120]. It is difficult to dissolve zirconium into the magnesium melt due to the formation of oxide film (MgO) which envelops the zirconium. The addition of calcium promotes the dissolution and dispersion of zirconium in the magnesium melt by forming CaO, which is a more stable oxide than MgO [120].
2.11.2. Aluminium Bearing Alloys

2.11.2.1. Superheating

In general, most of the metals and alloys should not be over heated above their liquidus temperature because of the associated problems, namely, oxidation, gas absorption, and grain coarsening [121]. However, Aluminum bearing magnesium alloys are an exception since they benefit from high-temperature treatment in terms of grain refinement. This high-temperature treatment is usually termed superheating and was first described in a British patent granted in 1931 [122]. Superheating process involves rapid cooling of the melt to the desired casting temperature after short holding time at an elevated temperature, generally between 180 to 300°C above the equilibrium liquidus temperature of the alloy [123]. The grain-refining effect of superheating is affected by alloy composition and process variables [10].

Aluminum is one of the major alloying elements for successful grain refinement by superheating. The degree of grain refinement is more in high aluminum content magnesium alloys (> 8 pct Al) than low aluminum content alloys [124]. Grain refinement by superheating is significantly affected by Fe and Mn. In general, high-purity Mg-Al alloys with low Fe and Mn contents are less susceptible to superheating treatment than alloys with high contents of Fe and Mn [125]. A small amount of silicon favors grain refinement by superheating. However, this effect disappears at high iron content [123]. The degree of grain refinement is suppressed with Be, Zr and Ti [126, 127].

According to Tiner [124], the required superheating temperature for the successful grain refinement of Mg-9Al-2Zn alloy is about 850 to 900°C and also stated that once sufficient treatment time is given to achieve a fine grain structure, there is no further refining effect to be gained through increasing holding time at the superheat treatment temperature or repeating the process.

Cao et al. [128] have confirmed that Fe is a grain refiner of high-purity Mg-Al alloys when added in the form of FeCl₃, due to the formation of Fe and Al rich intermetallic particles. Another theory proposed to explain the grain refinement by superheating is the temperature-solubility nucleation theory, which is based on changing particle size corresponding to a change in temperature. Particles present at normal melt temperatures are too large in size and too little in number for good grain
refinement, while at higher melt temperatures, they will dissolve into the melt and then re-precipitate as a large number of fine nucleation sites on cooling. In addition, the third approach is to attribute grain refinement to the formation of Al<sub>4</sub>C<sub>3</sub> particles from the Al in solution and carbon present on the surface of the steel crucible walls at high temperature [130]. Other mechanisms suggested for superheating process include the formation of clouds of magnesium oxide, aluminum oxide, or similar nonmetallic inclusions that act as nuclei during solidification. As the melt temperature increases for the superheating treatment, the possibility of forming such oxides is increased, resulting in a greater number of oxide particles available to act as nuclei or restrict crystal growth during solidification.

2.11.2.2. Elfinal Process

Effective grain refinement has been reported by the addition of ferric chloride (Elfinal process) in magnesium alloys containing aluminum and manganese [131]. The amount of grain refinement attained by the Elfinal process is somewhat similar to that achieved by superheating. However, the mechanism by which the grain refinement takes place by Elfinal process is still not clear. Nelson et al [123] have pointed out that the Elfinal process did not work for Mg-Al alloys containing no manganese. Emley apparently preferred the Al<sub>4</sub>C<sub>3</sub> hypothesis for the grain refinement [126]. Recent studies by Cao et al [128] have reconfirmed that the Elfinal process has lead to grain refinement when high purity Mg-Al alloys melted in carbon free aluminum titanite crucibles and suggesting that the Elfinal process has little to do with the Al<sub>4</sub>C<sub>3</sub> hypothesis proposed by Emley. However, due to the detrimental effect on corrosion resistance from the addition of Fe, the Elfinal process has not attracted industrial attention.

2.11.2.3. Agitation Method

Agitation method involves stirring the melt vigorously prior to casting and this process is successful when conducted with small melt volumes at high temperatures. Hultgren [132] observed grain coarsening in AZ92 alloy, when slow stirring by a large stirrer at temperatures below 760°C. In order to improve the grain refining performance by agitation, a combination of carbonaceous treatment and relatively
violent agitation action, which can be obtained by a small stirrer with high speed stirring, or by shearing the melt rapidly can be employed [123].

2.11.2.4. Native grain refinement

High purity Mg–Al alloys have naturally fine grain structure than the commercial purity alloys with the same chemical compositions, was first reported by Nelson [123]. This is referred to as native grain refinement. Tamura and co-workers [125, 133] further confirmed Nelson’s observations. The high-purity Mg-9% Al alloys used by Tamura et al. [125], have been prepared using of distilled pure magnesium (99.99 pct) and high-purity aluminum (99.99 pct), which contained 20 ppm of carbon. The observed native grain refinement is attributed to the Al$_4$C$_3$ particles existing in these alloys.

2.11.2.5. Carbon inoculation

Carbon inoculation involves the introduction of carbon containing agents into molten magnesium in various forms, including addition of graphite, paraffin wax, lampblack, organic compounds such as hexachloroethane (C$_2$Cl$_6$) and hexachlorobenzene (C$_6$Cl$_6$), carbides (Al$_4$C$_3$, SiC, CaC$_2$), and bubbling the melt with carbonaceous gases (e.g., CO, CO$_2$, CH$_4$) [123]. The addition of carbon to the melt (carbon inoculation) offers more practical advantages accompanied by lower operating temperatures, large melt volumes and less fading with long holding time. The elements Be, Zr, Ti, and RE (rare earth elements) are found to interfere with this process [126].

Similar to the superheating process, carbon inoculation is only effective for magnesium alloys that containing of aluminum [134-136]. Normally Mg-Al based alloys, which contain more than 2% Al can be effectively grain refined by carbon inoculation. A number of hypotheses have been proposed to explain the mechanism by which carbon inoculation methods cause grain refinement. One such mechanism is that aluminum carbide, Al$_4$C$_3$ is the compound responsible for the refining effect [137]. This hypothesis is further supported by a recent development that the addition of an Al-Al$_4$C$_3$-SiC master alloy to AZ31 and AZ61 results in significant grain refinement [138]. Further, Subramanian et al. [139] and Chen et al. [140] have also
observed $\text{Al}_4\text{C}_3$ particles in XRD. But there are literatures, which suggest that Al-C-O particles, probably in the form of $\text{Al}_2\text{OC}$, could be a much more potent nucleant than $\text{Al}_4\text{C}_3$ in terms of lattice match [137, 141]. Jin et al [142] have proposed a different theory for the grain refinement by C addition. The addition of carbon in the Mg-Al melt, segregate during the solidification and provide constitutional super cooling. This restricts the grain growth. However, recently, Qian et al [137] have rejected this hypothesis. Apart from that, recently some authors have proposed a duplex nucleation theory. Ding et al. [143] have demonstrated that the addition of Ni–C alloy in to Mg–3Al alloy leads to the formation of $\text{Al}_4\text{C}_3$ nuclei initially and subsequently they react with Al–Ni phase to form Al–Ni–C ternary compounds. These ternary compounds act as potent nuclei for $\alpha$-Mg and produce significant grain refinement. Similar observations are made by Nimityongskul et al. [144] when $\text{Al}_4\text{C}_3$ particles are introduced in to the AM60B alloy. The proposed duplex nucleation sequence is $\text{Al}_4\text{C}_3 \rightarrow \text{Al}_8\text{Mn}_5 \rightarrow \alpha$-Mg. Recently Kim et al. [145] have observed enhanced grain refining performance with carbon additions in presence of Mn in Mg-Al alloy systems when compared to the Mn free Mg–Al alloy systems. It is proposed that initially $\text{Al}_4\text{C}_3$ particles are formed in the melt from the reaction between carbon atoms and Al atoms, which in turn facilitates the formation of the $\text{Al}_8\text{Mn}_5$ phase in Mn containing Mg–Al alloys and subsequently the surface of polygonal $\text{Al}_8\text{Mn}_5$ phase nucleates $\alpha$–Mg. From the literature it is clearly understood that the presence of Mn enhances the efficiency of $\text{Al}_4\text{C}_3$ to facilitate significant grain refinement in Mg–Al alloys containing ≥6%Al and at the same time, $\text{Al}_4\text{C}_3$ itself is able to nucleate $\alpha$–Mg grains resulting in significant grain refinement in Mn free Mg–3Al alloy system [144, 146]. More recently all together a different grain refinement mechanism for the carbon inoculation is proposed, which suggested ternary carbide, not the binary carbide $\text{Al}_4\text{C}_3$, acts as a nucleation site for the magnesium grains [147, 148]. Y. Huang et al. [148] identified ternary carbide $\text{Al}_2\text{MgC}_2$ in XRD, and found that these carbides are highly reactive in water as like $\text{Al}_4\text{C}_3$, and hence observing these particles in microscope is much tricky. Therefore further studies are required to make clear the grain refining mechanisms of carbon containing agents in Mg–Al alloys.
For grain refinement of Mg-Al alloys, apart from the use of carbon or carbonaceous substances and FeCl$_3$, many other additives have also been tried. Yang et al [149] have reported that, as a result of Mg–10Sr master alloy addition to AZ31 magnesium alloy significant grain size reduction was observed due to growth restriction factor. In addition, Gruzleski et al. [150] have observed that addition of strontium in the range of 0.005wt% to 0.03wt%, to AZ91 alloy melt, reduced the grain size of the alloy from 225µm to 75µm-150µm. Recently, Wang et al [151] have studied the effect of Al–4Ti–5B master alloy on the grain refinement of AZ31 magnesium alloy and suggested that TiB$_2$ particles act as the heterogeneous nuclei of α-Mg. Further, Fu et al [152] have showed that AlN could grain refine Al containing Mg alloys. Recent study by Wang et al [153] has confirmed that the addition of Ti has lead to grain refinement in AZ31 Mg alloy. In addition to that, the grain refinement effect is explained in terms of the growth restriction factor (GRF) due to the constitutional undercooling generated by the Ti solute elements.

2.12. Shortcomings in Literature

The review of literature clearly reveals that the grain refinement of Mg and Mg-Al alloys has been investigated by many researchers. The grain refinement of magnesium alloys is reviewed with regard to two broad groups of alloys: alloys that contain aluminum and alloys that do not contain aluminium. The alloys that are free of aluminum are generally very well refined by Zr master alloys. However, the use of excessive zirconium often produces a large amount of sludge, leading to increased operating cost. Therefore, further work is required in this area to develop a cost effective alternative to it. On the other hand, the understanding of grain refinement in aluminum bearing alloys is poor and in many cases confusing probably due to the interaction between impurity elements and aluminum in affecting the potency of nucleant particles and the explained mechanisms are unclear. Besides, not much work has been carried out on the mechanical behaviour of grain refiners added to Mg and Mg-Al alloys. Hence, studies on understanding the grain refining mechanisms and the mechanical behavior of Mg and Mg-Al alloys with different inoculant additions (Al-4B and Al-5TiB$_2$ master alloys, Al$_4$C$_3$ and Charcoal particles) and the studies on the

---

28
effect of superheating on the grain refining mechanisms and the mechanical behaviour of AZ31, AZ91 Mg alloys without and with the addition of above mentioned inoculants are more valuable.