2.1 INTRODUCTION

The weight of the average family car has increased by 20% over the last 20 years [51]. Most of the increased weight is a result of increased average engine size and the additions of safety features. On the other hand, customer's awareness of fuel efficiency has been made more acute by increasing fuel prices and the popularity of environmental issues. So, weight reduction is an imperative task for automobile producers. The attractive benefit of reduction in automobile weight can be seen in terms of improved fuel efficiency as shown in Figure 2.1 [52]. “Concept cars” produced in recent years have been lightweight, for example, the Ford P2000, which weighs only 544.3 Kg [53]. The weight reductions have been made possible by the replacement of steel by light metal alloys, usually aluminum or magnesium. In production vehicles, the weight is saved through the use of lightweight metals, which have reduced the weight of cars by 10% since 1978, without compromising safety [54]. Earlier, aluminum alloys replaced most of steel or cast iron components in automobiles. But at this moment, the major aim and task of the researchers is to find suitable material, which is more efficient than aluminum so as to reduce the weight of automobile further. Magnesium and its alloys are one such promising material, whose light weight advantage could be used for the above said purpose.

Magnesium, with a density of 1.7 g/cc is the lightest of the structural materials. It is two third of its counterpart aluminum density (2.7 g/cc) and one third of steel density (7 g/cc). So, it has high specific strength properties over aluminum alloys. However, the total annual world consumption of magnesium at around 250 thousand tones is a fraction of the 20 million tones of aluminum used. Both metals were discovered in the early 19th century and industrial refining processes for each metal were announced in 1886. So, the lower usage of magnesium is due to different complex of factors. However, developments in magnesium refining and processing technology have coincided with new demands from many industries for high precision light-weight die-castings. Now the use of magnesium is growing at a faster
2.2 ADVANTAGES

Magnesium alloys has several advantages. Table 2.2 lists some of the key attributes of magnesium alloys that make them more attractive to automotive, aerospace and other industries [12]. The most important of these is light weight. This leads to relatively high specific stiffness and specific strength for magnesium alloys. Another very important advantage is the design flexibility and manufacturability. Typical magnesium die-casting alloys such as AZ91, AM50 and AM60 can be cast into larger, more complex shapes with thinner sections. Thus they lend themselves to produce large die cast components that, in a single-shot die casting, integrate the functions of structure that would otherwise be fabricated from a large number of pieces in several manufacturing steps.

2.3 APPLICATIONS

2.3.1 Aerospace Industries

Magnesium is employed extensively in aircraft engines, air frames and landing wheels [56]. The main factors dictating the use of magnesium in aircraft have been strength/density ratio in castings and stiffness/density ratio in wrought forms, combined, as required, with factors such as good elevated temperature, fatigue and impact properties, always with good machinability. 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.

2.3.2 Defense Industries

High specific strength and rigidity coupled with ease of fabrication are important for missile and space applications. EZ33 (Mg-2.7% Zn-0.7% Zr-3.2% MM) sand castings are used in the “Skylark” research rockets. ZK51 (Mg-4.5% Zn-0.7% Zr) and ZE41 castings have been used extensively for structural parts in British missiles [57].

2.3.3 Automobile Industries

Automobile industries are the latest beneficiary of magnesium, currently exploring its maximum usage. Table 2.3 gives a number of applications of magnesium that are currently being addressed by the automotive industry. Components at the top of this list, such as steering wheel armatures, cylinder head covers and instrument panel beams are already in significant production, while items at the bottom of the list require several years of intensive development before they can be implemented [12]. Figure 2.2 gives some of the automobile components made from magnesium alloys [58].

Table 2.2: Advantages of magnesium alloys [56]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Strength/Weight ratio</td>
</tr>
<tr>
<td>2</td>
<td>Excellent damping capacity</td>
</tr>
<tr>
<td>3</td>
<td>Non-magnetic, EMF shielding</td>
</tr>
<tr>
<td>4</td>
<td>Good heat dissipation</td>
</tr>
<tr>
<td>5</td>
<td>High castability</td>
</tr>
<tr>
<td>6</td>
<td>Complex, thin walled castings</td>
</tr>
<tr>
<td>7</td>
<td>Excellent machinability</td>
</tr>
</tbody>
</table>
Table 2.3: Some of the magnesium alloy automobile components [12]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Steering wheels</td>
</tr>
<tr>
<td>2.</td>
<td>Cylinder head covers</td>
</tr>
<tr>
<td>3.</td>
<td>Instrument panel beams</td>
</tr>
<tr>
<td>4.</td>
<td>Sear frames</td>
</tr>
<tr>
<td>5.</td>
<td>Door frames</td>
</tr>
<tr>
<td>6.</td>
<td>Transmission housings</td>
</tr>
<tr>
<td>7.</td>
<td>Grill opening reinforcements</td>
</tr>
<tr>
<td>8.</td>
<td>Structural supports</td>
</tr>
<tr>
<td>9.</td>
<td>Rear deck lid/engine hood</td>
</tr>
<tr>
<td>10.</td>
<td>Wheels</td>
</tr>
<tr>
<td>11.</td>
<td>Engine blocks</td>
</tr>
<tr>
<td>12.</td>
<td>Steering wheels</td>
</tr>
</tbody>
</table>

2.3.4 Nuclear Industry

With natural uranium as a fuel, it is essential to conserve neutrons by 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 [57]. The advantages of magnesium as a canning material 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 [57].

2.3.5 Sporting and Electronic Industries

Apart from transport and missile components magnesium also finds application in electronics and house holding items. Some of the examples are computer housing and mobile telephone cases, where lightness, suitability for thin wall casting and the characteristic of electromagnetic shielding are the particular advantages [57]. Figure 2.3 shows some of such applications [58].
2.4 LIMITATIONS

In spite of the above said advantages and applications, there are some limitations, which restrict its full utilization for industry applications. Some of the challenges that are facing magnesium in order for its wholesale acceptance for industrial applications are summarized in Table 2.4 [12].

![Figure 2.2: Some of the automobile components made up of Mg alloys [58]](image)

2.5 MELTING PRACTICE

2.5.1 Flux Melting and Refining

When magnesium and its alloys are melted, they tend to oxidize and explode, unless care is taken to protect the molten metal surface against oxidation. Molten magnesium alloys behave differently from aluminium alloys, which tend to form a continuous, impervious oxide skin on the molten bath and limits further oxidation. Magnesium alloys, on the other hand, form a loose, permeable oxide coating on the molten metal surface. This allows oxygen to pass through and support burning of melt below the oxide surface. The two main reasons that lead to the ignition of magnesium during melting process are given below [59];
Chapter 2: Literature Review

Figure 2.3: Magnesium parts used in communication engineering [58]

Table 2.4: Limitations of magnesium alloys [12]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></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>Lack of joining technologies</td>
</tr>
<tr>
<td>8.</td>
<td>Poor workability</td>
</tr>
</tbody>
</table>

1. The volume of magnesium shrinks after it is oxidized, and the structure of magnesia (MgO) is loose and many small holes appear on the surface thus become porous. So it cannot prevent the passage of oxygen and the oxidation of inner magnesium.

2. The heat formation of magnesia is too large so that the local area temperatures can even reach 2850°C by the heat generated in the oxidation process.
Two kinds of fluxes such as melting and refining fluxes are normally used during melting of Mg to overcome the above said problems [59, 60]. Melting flux is used to prevent the oxidation of magnesium during melting. It is added throughout the melting when ever the local burning occurs. The melting flux normally consists of various chloride and fluorides like MgCl₂, KCl, NaCl, CaF₂, etc. The requirements of a melting flux are: It should have a liquidus temperature below the solidus temperature of the alloy to be melted and sufficient fluidity and wetting power above this temperature to enable the flux to spread out on melt so as to form a complete protective layer over the metal. The flux melts first and form a protective chloride layer over the solid as well the liquid metal during melting [59-61].

Many non metallic inclusions suspends in the molten metal of magnesium. These inclusions have to be removed before pouring otherwise, would enter in to the casting and reduces the casting quality [60]. For this purpose an inspissated flux (Refining flux) is used. The removal of oxides by inspissated flux is known as "refining process". In this process, the flux is added into the melt while it is rigorously stirred. The refining flux disintegrates into globules, and is able to wet and absorb particles of suspended oxides, thereby becoming denser, so that they readily settle to the bottom of the crucible [59, 60]. 10-30 minutes, depend upon the size of the melt, should be given for settling inspissated impurities. The essential constituent of the inspissated flux is MgCl₂.

2.5.2 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 lead to flux-less melting. It is very effective way of melting in which, inert gases are used to protect the molten metal. The most common gas used in flux-less melting is SF₆ mixed with dry air and CO₂ [62]. To maintain an adequate and homogenous level of SF₆ at all area of the melt surface it is usually desirable to supply the protective atmosphere through a manifold with several outlets so as the gas
to spread out over the melt surface. The gas mixtures take away the oxygen out of the melting area and hence, provide an oxygen free atmosphere for melting.

The SF$_6$ based shielding gas is non-toxic, odourless and corrosion free. However, SF$_6$ is having a heavy green house effect. Its Global Warming Potential (GWP) is 23900 times higher than CO$_2$ and will be banned from industrial use [63]. Therefore, researchers in magnesium industries are trying to find the alternatives. Recently International Magnesium Association (IMA) found out suitable substitutes for SF$_6$. These are HFC-134, HFE-7100 and HFE-7200, Novec$^{\text{TM}}$ 612 (FKs) [64]. These alternatives are all fluorides and their protective effects are no less than that of SF$_6$ but their GWP values much less than that of SF$_6$[65].

2.6 CASTING PROCESSES

Normally the magnesium alloys are cast by die casting method. This is to overcome the material cost disadvantages compared to aluminium alloys [66]. All magnesium alloys development activities for different mechanical properties are thus also 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.

The choice of a particular casting method depends upon many factors, e.g., the number of castings required, the properties required, dimensions and shape of the part and the castability of the alloy [67]. Although 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. 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 $120^\circ$C. Magnesium alloys containing RE as a major alloying element are mainly produced in sand casting route for this purpose and they are used in
aerospace applications. However these alloys are not suitable for die-casting application due to the poor die castability.

In addition, developments are well advanced with squeeze casting and semi solid processing like Reho casting and thixo casting [68-74]. 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 [75-77]. Uniform filling rate throughout the casting in LPC eliminates turbulence and cold shut, which are inherent defects in gravity castings while making thin wall component castings [75].

2.7 MAJOR ALLOY SYSTEMS

The alloy designation system has been standardized by the American Society for Testing Materials (ASTM). 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 letters corresponding to the element present in the 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 in to two major groups: zirconium free alloys and zirconium containing alloys. Zr is an effective grain refiner for Mg alloys. However, in presence of Al, the
efficiency of Zr reduces because Al removes Zr from the solid solution to form Al-Zr based intermetallics. Hence in zirconium free alloys, Al presence as the major alloying element along with zinc and manganese (Mg-Al-Zn, Mg-Al-Si, Mg-Al-RE, etc.,) where as alloy systems like Mg-Zn-Zr, Mg-RE-Zr all are examples for zirconium containing alloys.

2.7.1 Zirconium Containing Alloys

The maximum solubility of zirconium in molten magnesium is 0.6%. As binary Mg-Zr alloys are not sufficiently strong for commercial applications, the addition of other elements is necessary. The ability to refine the grains in Mg-Zn alloys with zirconium led to the introduction of ternary alloys such as ZK51 (Mg-4.5Zn-0.7Zr). However, these alloys are susceptible to micro porosity and are not weldable, they have found little practical application [78, 79]. However, Zn along with RE addition provides high strength and finds many applications.

Magnesium forms solid solutions with a number of RE elements. The addition of cheaper mischmetal based on cerium or neodymium to magnesium gives good casting characteristics and mechanical properties. These properties are improved by adding Zr to refine grain size and further increases in strength occur if zinc is added as well. EZ33 (Mg-3RE-2.5Zn-0.6Zr) is one such alloy, which retains strength and creep resistance at temperatures up to 250°C [80].

Recently Mg-Y age hardenable alloy systems are developed to utilize the benefit of high solid solubility of yttrium in magnesium. 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 [81, 82]. 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).

Addition of thorium also confers 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 is also added to magnesium and Mg-Ag-RE-Zr alloys are developed with improved room and high temperature mechanical properties [83]. 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.

2.7.2 Zirconium Free Alloys (Mg-Al Alloys)

Aluminium is the principal alloying element to magnesium. The binary Mg-Al system is the basis for the first magnesium casting alloys but most current compositions also contain small amounts of zinc and manganese. The most widely used alloys in this group are AZ91 and AM50 [78]. These alloys have a wide range of mechanical properties and good castability and mostly used in die casting application. However, the draw back of using these alloys is its poor elevated temperature tensile and creep properties above 150°C. [15].

Alloys like AS21, AS41 (Mg-Al-Si), which contain Si in it are developed for better creep properties compared to AZ91 [66]. Later on, solubility of rare earth (RE) in magnesium led to the development of AE alloys systems, which contain less amount of aluminium and small percent of RE [84]. One such alloy system, AE42 (Mg-4Al-3RE-0.3Mn) has a good combination of properties including creep strength, which is superior to the Mg-Al-Si alloys [85]. The major drawback of these alloys is addition of RE increase the alloy cost drastically [66]. Recently, it is also found that the thermal stability of Al₄RE intermetallic in RE containing Mg alloys does not extend beyond 150°C and hence the AE42 alloy loses creep strength above this temperature.

The addition of calcium to Mg-Al based alloys for improved creep resistance is reported in a British patent [86]. This patent disclosed that calcium additions of 0.5-3% provide creep resistance to magnesium alloys containing up to 10% Al. However, the patent also revealed that calcium containing alloys prone to hot cracking,
Volkswagen attempted the use of Mg-Al-Ca alloys in the 1970's and claimed an improvement in creep resistance with the addition of about 1% Ca to magnesium alloy AZ81. However, the application of this alloy to die casting was not possible owing to die sticking and hot cracking. Later, a thorough investigation on the optimum amount of Ca addition to Mg-Al alloy to avoid these problems was carried out by Institute of Magnesium Technology (ITM) in Canada and General Motor [87, 88]. It is found that Mg-Al-Ca based alloys, which contain Ca more than 1%, are susceptible to the hot cracking problem.

Mg-Al-Sr (AJ) alloys are new addition to the creep-resistant Mg-Al based magnesium alloys [89]. Various alloy compositions such as AJ51 (Mg-5Al-1Sr), AJ52 (Mg-5Al-2Sr) and AJ62 (Mg-6Al-2Sr) have been developed. The creep resistance of these alloys is found to be better than many Mg-Al alloys [90, 91]. However still, the microstructure and its creep mechanism are not fully understood.

2.7.2.1 AZ91 (Mg-9% Al-1% Zn-0.2% Mn) alloy

AZ91 alloy is one of the old but most commercially used Mg-Al based alloys. Among 90% of Mg alloy components used in transport industries are made from AZ91 alloy [14]. Currently, this alloy is being used in manufacturing instrumental panels, steering column, steering wheel, seat frame etc in automotive vehicles. This alloy provides wide range of properties and castability. Of course, AZ91 is the benchmark alloy for castability compared to all Mg alloys.

AZ91 alloy contain 8.1-9.3% Al, 0.4-1% Zn, 0.3 % max Mn, other impurities like Si, Fe, Cu and Ni. 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, AZ91 alloy does not exhibit good creep resistance, which is a major setback [15].
2.8 FACTOR INFLUENCING THE STRUCTURE AND PROPERTIES OF Mg-Al ALLOYS

The physical and mechanical properties attainable in these alloys are strongly influenced by the alloy composition, impurity elements, solidification characteristics, and heat treatment.

2.8.1 Effect of Alloy Compositions

2.8.1.1 Aluminum

Aluminum is one of the major alloying elements to magnesium. Aluminum has a very good solid solubility in magnesium. The Mg-Al binary phase diagram is given in Figure 2.4 shows that the maximum solubility of Al in Mg at 437°C (eutectic temperature) is around 12.7% [92]. Figure 2.5 illustrates the effect of Al addition on the tensile properties of Mg-Al alloys [93]. The yield strength increases with addition of Al whereas UTS increase up to 6% and then decreases. However the ductility increases initially up to 3% of Al addition and then start to decrease steeply [93]. The solid solubility of aluminum in magnesium at room temperature is around 2%. So the excess aluminum forms Mg17Al12 intermetallic with Mg. This phase is hard and brittle and hence, acts as a strengthening element at room temperature. Al in this alloy also improves the castability [94]. However, Al also increases the tendency for shrinkage micro porosity up to 9% and then reduces it [95]. The reason 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.

2.8.1.2 Zinc

Zinc has very good solubility in Mg. The role of zinc in AZ91 alloy is to improve the strength of alloy by solid solution strengthening. Zinc also improves the fluidity of the alloy. But higher amount of Zn to 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 and thereby forming micro-porosity. Studies report that addition of 2% Zn increases micro porosity in sand-cast magnesium alloys containing 2, 4, 8 and 10% Al [96]. The
presence of zinc decides the type of eutectic (completely or partially divorced) during final stage of solidification.

![Figure 2.4: Phase diagram of Mg-Al binary alloy system [92]](image)

![Figure 2.5: Effect of aluminum on the mechanical properties of Mg-Al binary alloys [reproduced from ref. 93]](image)
2.8.1.3 **Manganese**

The main purpose of addition of Mn to AZ91 alloy is to improve the corrosion properties. The role of manganese in the improvement of corrosion resistance is twofold.

1. When manganese is added to Mg-Al alloys several types of AlMnFe intermetallic particles are formed [97]. These particles settle at the bottom of the melt, by which the iron content in the melt is reduced.

2. Manganese also renders the iron containing particles left in the melt during solidification less harmful by making them less efficient as cathodes, compared to the Al-Fe intermetallics, which are formed in Mn-free Mg-Al alloys.

2.8.1.4 **Impurities**

The heavy metal impurities like iron, nickel and copper in AZ91 alloy mainly affects the corrosion behavior. These elements form particles, which are highly cathodic to the matrix, and thus, leading to micro-galvanic corrosion. So, there exists a tolerance limit for these elements, above which the corrosion rate increases rapidly [98].

Nickel and copper are usually not create much problem due to the very low content of these elements in alloys from primary production. Iron is the most troublesome element in high purity alloys, as there always is a risk of iron pick-up form crucibles made of carbon steel.

2.8.2 **Solidification**

The solidification sequence of Mg-Al alloys starts with nucleation of primary magnesium (α- Mg) in the temperature range of 650-600°C, i.e. ranging from the melting point of pure magnesium to the liquidus temperature of Mg-9Al, covering the various aluminum contents used in commercial alloys. Later solidification reactions involve the formation of eutectic phases, with Mg-Mg$_{17}$Al$_{12}$ eutectic reaction occurring at 437°C [99]. Both these liquidus and eutectic (solidus) temperatures are cooling rate dependent. According to the phase diagram with equilibrium
solidification the liquidus and solidus temperatures of AZ91 is \( \sim 600^\circ C \) and \( \sim 500^\circ C \) respectively. But, in most of the casting practice the solidification never approach the equilibrium. Luo [99] reports the change in liquidus and solidus temperature of AZ91 at wide range of cooling rate and the data is presented in Table 2.5. The eutectic [Mg (\( \alpha \)) +Mg\(_{17}\)Al\(_{12}\) (\( \beta \))] of AZ91 is a divorced eutectic. In a slow cooled alloy, when casting cools from eutectic to the room temperature, the solid deformation takes place, in which the highly super saturated eutectic Mg decompose into alternative layers of solute deployed Mg and Mg\(_{17}\)Al\(_{12}\) phase.

2.8.2.1 Eutectic solidification

The eutectic solidification controls the size, shape and distribution of the more brittle Mg\(_{17}\)Al\(_{12}\) phase in the final microstructure, which, in turn, is likely to influence mechanical properties particularly ductility and creep strength of the alloy. Moreover eutectic growth affects feedability at a crucial stage when feeding is interdendritic and large pressure differentials are required to draw liquid through the dendritic network. [96]. The Mg-Mg\(_{17}\)Al\(_{12}\) eutectic in Mg-Al alloy, exhibits a wide range of morphologies depending on the alloy composition and cooling conditions. The Mg-33% Al (eutectic composition) alloy, exhibits a lamellar morphology and at low growth rates and a fibrous morphology at higher growth rates. However, in low aluminum content Mg-Al alloys such as AZ91 and AM60, the eutectic has different morphologies, described as either completely or partially divorced [96].

<table>
<thead>
<tr>
<th>Cooling Rate (dT/dt, °C/s)</th>
<th>0.03</th>
<th>0.06</th>
<th>0.4</th>
<th>7.8</th>
<th>20.6</th>
<th>41.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus (TL, °C)</td>
<td>600.2</td>
<td>600</td>
<td>599.5</td>
<td>598</td>
<td>595.5</td>
<td>593.8</td>
</tr>
<tr>
<td>Solidus (TS, °C)</td>
<td>435</td>
<td>435</td>
<td>430</td>
<td>328</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Both fully and partial divorced eutectic morphology is shown in Figure 2.6. In fully divorced morphology, as shown in Figure 2.6 (a), the two eutectic phases are
completely separated in microstructure. Each interdendritic region consists of a single β- \( \text{Mg}_17\text{Al}_{12} \) particle surrounded by eutectic \( \alpha \)-Mg. A partially divorced eutectic morphology, as shown in Figure 2.6 (b), is characterized by an ‘islands’ of eutectic \( \alpha \)-Mg within the \( \beta \)- \( \text{Mg}_17\text{Al}_{12} \) phase, but the bulk of the \( \alpha \)-Mg is still outside the \( \text{Mg}_17\text{Al}_{12} \) particle, i.e. the volume fraction of \( \alpha \)-Mg within the \( \text{Mg}_17\text{Al}_{12} \) particle is much lower than the proportion by the equilibrium phase diagram [96].

Figure 2.6: Microstructure of AZ91 alloy showing (a) fully divorced eutectic (b) partially divorced eutectic [16]

M.D. Nave et al [100] have shown that as the aluminum content of Mg-Al alloy increases, the eutectic progresses through the morphological sequence: fully divorced—partially divorced—granular—fibrous—lamellar. They also demonstrated that increase in cooling rates, increase the tendency towards divorced eutectic formation in a particular alloy. The effects of aluminum content, zinc content and cooling rate on eutectic morphology in permanent mould cast alloys are shown schematically in Figure 2.7 [96]. Hence the eutectic tends to become less divorced with increasing aluminum content, but more divorced with increases zinc content and cooling rate.
The morphology of the eutectic is strongly influenced by the morphology of the primary dendrites, which determines the size and degree of interconnection of the interdendritic regions, in which the eutectic solidifies. Some undercooling below the eutectic temperature is required before solidification of the eutectic can commence. As the primary Mg dendrites continue to grow below the eutectic temperature, the composition of the liquid is enriched in aluminum past the eutectic coupled zone and into the region of the phase diagram where the Mg\textsubscript{17}Al\textsubscript{12} phase grows faster than the coupled eutectic as shown in Figure 2.8. When nucleation of the Mg\textsubscript{17}Al\textsubscript{12} occurs, a halo of this phase is deposited on the primary dendrites. If the amount of undercooling is not great and the eutectic region is sufficiently large, the formation of this halo consumes the excess solute in the boundary layer adjacent to the dendrite and the composition come back to the coupled zone (T\textsubscript{1} in Figure 2.8). This leads to the lamellar growth. This situation occurs with high aluminum content and at slow cooling rates. The higher amount of aluminum ensures the quite large interconnected regions of liquid between the primary dendrites. However, if the amount of aluminum is less and the cooling rate is fast, the composition of the liquid could increase well past the eutectic composition before nucleation of Mg\textsubscript{17}Al\textsubscript{12} phase occurs. The entire pocket of the liquid could then become enriched to a composition, which is outside the coupled zone at that temperature. This leads to the formation of a partially or fully divorced eutectic.
Like aluminum content and the cooling rate, zinc also affects the morphology of the eutectic in Mg-Al alloys as shown in Figure 2.7 [101]. There are a number of possible ways in which zinc may affect the growth morphology of the eutectic. Zn, with a partition coefficient of 0.1 in Mg at 600°C, segregates more strongly to the liquid than aluminum (whose partition coefficient is 0.33 at 600°C). This increases the degree of constitutional undercooling ahead of the solid-liquid interface during the early stages of primary dendrite growth. The dendrites are therefore likely to grow with a more highly branched morphology. A more divorced eutectic is then favored because of the reduced size of the interdendritic spaces [101].

2.8.2.2 Solid state transformation

Solid state reaction takes place after the eutectic reaction when the cooling rate is slow. Normally this happens in gravity casting like sand and permanent mould cast AZ91 alloy. During this, the highly supersaturated eutectic α-Mg rejects the excess Al in the form of laminar kind of Mg$_{17}$Al$_{12}$ at grain boundary, known as discontinuous precipitates. An alternative layer of depleted α-Mg and Mg$_{17}$Al$_{12}$ precipitates form from the super saturated eutectic α- Mg during this reaction.

2.8.3 Grain Refinement

Grain refinement is an important practice used to improve the mechanical properties of castings. It is an essential and fundamental approach since grain size significantly influences the strength properties without compromising the ductility
much, and the grain size is usually determined at an early stage of solidification by nucleation of dendrites.

2.8.3.1 Effect of aluminum

Figure 2.9 shows the grain size change with increasing aluminum content in Mg-Al alloys [96]. A small addition of aluminum to pure magnesium leads to a morphological change of the primary phase from a cellular to a dendritic structure. Rosette-like globular equiaxed grains form with aluminum-rich solid solution between the dendrite arms. As the aluminum content increases further to 5%, dendrites with pools of eutectic phase between the dendrite arms start to develop and, when the aluminum content is further increase, a fully developed dendritic structure with sharp tips is observed.

The addition of small amounts of alloying elements such as zinc, manganese and rare-earths to Mg-Al alloys has little effect on nucleation of the primary phase since these elements are mostly segregated to form secondary phases well after the primary phase has nucleated [99].

2.8.3.2 Superheating treatment

Several methods of grain refinement have been developed. The first method of grain refinement is by a simple thermal treatment prior to casting, known as 'superheating treatment'. This method involves rapid cooling of the melt to the desired casting temperature after short holding time at an elevated temperature, generally between 150°C and 260°C above the equilibrium liquidus temperature of the alloy [102]. This method is only useful for Mg-Al alloys like AZ91, where as in other magnesium alloys refinement by the means described is marginal [103, 104]. Usually, superheating treatment is not much effective, owing to the small number of nucleation sites forms during this treatment [105]. It is assumed that superheating of Mg-Al alloys facilitate the formation of many intermetallic compounds, which serves as the nucleation site for α-Mg. One hypothesis is that hexagonal Al₄Mn forms as a result of the manganese content in the commercial alloys of the AZ series [106]. According to another theory the compound is of the type Al₄C₃, or iron Aluminide, both of which
has been observed experimentally [107]. The presence of these compounds can be justified with the fact that superheated Mg-Al alloy melt strongly dissolves crucibles made of iron or steel. Such dissolution, or the presence of organic impurities, could be the source of the iron or carbon necessary for inoculation. Despite the successful grain refinement achieved by the superheating method, this technique has several practical problems, mainly related to the higher operating temperatures involved [108].

2.8.3.3 Elfinal process

Successful grain refinement has been reported by the addition of ferric chloride (Elfinal process) in magnesium alloys containing aluminum and manganese [109, 110]. The amount of grain refinement achieved by the Elfinal process is somewhat similar to that achieved by superheating. The mechanism by which the grain refinement takes place by Elfinal process is still not clear. Partridge [111] has reported that a rusty mild steel crucible that loosely adherents rusty iron produced grain refining effect. Nelson et al [103] have pointed out that the Elfinal process did not work for Mg-Al alloys containing no manganese. Emley apparently preferred the $\text{Al}_6\text{C}_3$ hypothesis for the grain refinement [107]. Recent studies by Cao et al [112] 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 Al₄C₃ 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.

2.8.3.4 Carbon inoculation

The addition of carbon to the melt (carbon inoculation) offers more practical advantages accompanied by lower operating temperatures and less fading. Various carbon-containing agents such as organic materials like C₂Cl₆, CCl₄, SiC particles or granular graphite and carbon in the form of wax- fluorspar- carbon compound have been reported to produce successful grain refinement in Mg-Al alloys [111,113, 114]. Similar to superheating, carbon inoculation is effective only to magnesium alloys that contain aluminum [115-118].

A number of hypotheses have been proposed to explain the mechanism by which carbon inoculation methods cause grain refinement. Once such mechanism is that aluminum carbide, Al₄C₃ is the compound responsible for the refining effect [103]. But there are some literatures, which suggest that Al-C-O particles, probably in the form of Al₃OC, could be a much more potent nucleant than Al₄C₃ in terms of lattice match [119-122]. Qinglin Jin et al [123] 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, M. Qian et al [118] have rejected this hypothesis. Moreover, the efficiency of grain refinement with Carbon inoculation process is depending upon the holding time and temperature of the melt. Extending the time of interaction between inoculant and melt adversely affects the refinement, as illustrated in Figure 2.10 [124]. According to the figure, inoculation produces finer grains after much shorter holding times and at lower temperatures.
2.8.3.5 Thermo mechanical treatment

Mechanical working like rolling, extrusion, forging are other potential way of achieving grain refinement. Number of publications is available on the effect of these processes on the grain refinement of Mg-Al based alloys particularly wrought alloy AZ31 [126-128]. Ravikumar et al [129] have reported that 5μm grain size is obtained in AZ91 using hot extrusion at a temperature of 335°C. There are other studies, which reports on grain refinement of AZ alloys by severe plastic deformation processes like Equal Channel Angular Pressing (ECAP), Accumulative Roll Bonding (ARB), Large Strain Rolling (LSR) and hot multiple forging [130-133].
2.8.4 Heat Treatment

2.8.4.1 General behavior

The maximum solubility of aluminum at eutectic temperature (437°C) is around 12%, which reduces down to around 2% at the room temperature. This solubility variation provides AZ91 alloy system to be age hardenable. The precipitation processes in AZ91 alloy have been studied extensively [134, 135]. The precipitation in this alloy system is relatively simple; plates of the equilibrium phase, \( \text{Mg}_17\text{Al}_{12} \), are formed without any intervention of a transition phase. No evidence of G.P zones is so far reported in this alloy. The normal sequence of heat treatment is solution treatment at 410°C for 48 h and ageing at a temperature range from 150 to 250°C. During solution treatment, dissolution of eutectic \( \text{Mg}_17\text{Al}_{12} \) phase is slow mainly due to its massive size. With 24 h of solution treatment, complete dissolution of this phase takes place, however, 48 h of solution treatment is normally required to get completely homogenous microstructure of Al in Mg matrix [134]. Cold water quenching is followed by solution treatment to retain the aluminum in solid solution.

A typical ageing curve at different temperatures for AZ91 alloy after solution treatment is shown in Figure 2.11 [134]. In general, the ageing curve can be divided into four distinct regions as follows [136]:

1. A incubation period where the hardness is not increased with time
2. A rapid increase in hardness with respect to time
3. Slow down in the rate of hardening nearer to the peak hardness
4. Leveling off at the peak hardness

It can be seen from Figure 2.11 that a large decrease in peak hardness when the ageing temperature increases from 100 to 150°C and another large decrease in peak hardness observed between 250 and 300°C. The hardness for ageing at 200 and 150°C remained at the maximum value for a significant period before gradually decreasing. Ageing kinetic is increased with increases in ageing temperature. The ageing kinetic also increases with the amount of aluminum in the solid solution. S. Celotto et al [134] have reported that the higher peak hardness in shorter time obtained in AZ91 alloy compared with Mg-6Al alloy is due to the difference in
aluminum content. He also observed that the presence of zinc in the AZ91 alloy improves the hardness and ageing kinetics over its counter part Mg-9Al by reducing the solubility of aluminum in magnesium matrix [134].

![Typical ageing curve for AZ91 alloy at different temperatures](image)

Figure 2.11: Typical ageing curve for AZ91 alloy at different temperatures [134]

2.8.4.2 Continuous precipitate

The microstructural development of Mg-Al binary alloys and Mg-Al-Zn ternary alloys for a range of ageing temperatures has been investigated in a number of studies [134, 135]. During ageing the Mg$_{17}$Al$_{12}$ precipitates out in two forms: discontinuous (cellular) and continuous (intragranular) form. Discontinuous precipitation (DP) is the cellular growth of alternating layers of Mg$_{17}$Al$_{12}$ phase and near equilibrium magnesium matrix at high angle grain boundaries. Growth of the discontinuous precipitates regions ceases relatively early in the precipitation process. Then, continuous precipitation (CP) takes place in the remaining regions of the matrix that are not already occupied by discontinuous precipitation.

Clark [135] and Crawley and Lagowski [137] have reported that the continuous precipitates consist of relatively large plates on the basal plane of the matrix. The predominant orientation relationship (OR) between the β-phase plates and the magnesium matrix is reported to be the Burgers OR, namely: (0001)$_m$//(110)$_p$ and [12'10]$_m$//[11'1]$_p$ [137, 138]. Some precipitates have also been observed perpendicular to the basal plane of the matrix [139]. Two different ORs have been
reported for these precipitates: (0001) // (110)p, [12'10]m // [11'2']p by Crawley and Lagowski [137] and Crawley and Milliken [137]; and (12'11) // (11'0)p, [12'10]m // [11'2']p from Poter reported by Duly et al [139]. It is also found that dislocations acts as a nucleation site for continuous precipitation [135, 140]. Clark [135] has observed that introduction of dislocations by cold work prior to aging markedly improve the ageing kinetics and increase the peak hardness. Figure 2.12 shows the effect of 1% prior strain by cold work on the age hardening of Mg-9Al alloy. He found the density of continuous precipitates for a given time of aging in the pre-strained by the cold working is higher. He also observed that nucleation of continuous precipitates occurs most rapidly in the interfaces of, and within, {1012} twins.

It is continuous, not discontinuous precipitate, which is responsible for most of the age hardening in AZ91 alloy [141]. Lagowski and Crewley [138] have carried out a double stage (96 h for 100°C and 192 h at 140°C) ageing on AZ91 after solution treatment and observed increase in strength. It is found that the double stage aging leads to the formation of higher amount of continuous precipitation and the decrease in inter precipitates spacing. The hardening mechanism explained by Clark [135] suggested that the continuous precipitation suppresses the basal slip and {101'2} twinning and promotes cross slip in the prismatic plane. This generates complex dislocation tangle, which harden the alloy. However, the hardening response of AZ91 is generally less than that observed in many heat-treatable aluminum alloys. There are two reasons suggested for the poor hardening response of AZ91. The order of magnitude difference in the number of continuous precipitates per unit volume compared with many age-hardenable aluminum alloys. Another reason is the orientation of the precipitates with respect to the predominant slip plane of the matrix. The effectiveness of a single precipitate as an obstacle to dislocations is improved if it is oriented such that it intersects more operating slip plane. According to Celotto [134], the continuous precipitation, rod or lath-shaped precipitates lying perpendicular or at an angle to the basal plane are more effective than symmetric lozenge or lath-shaped precipitates lying parallel to the basal plane in preventing slip in the magnesium matrix.
2.8.4.3 Discontinuous precipitate

Discontinuous precipitation (DP) is a heterogeneous reaction, which leads to the formation of a lamellar structure behind a moving grain boundary [142]. The schematic diagram representing the discontinuous precipitation process is shown in Figure 2.13 [143]. Two phases (α, β) forms simultaneously from a supersaturated single α matrix. The moving grain boundary, called reaction front (RF), act as a short circuit path for the diffusion of the solute atoms [144-147]. DP is arrested when CP relieves the solute super-saturation in front of the advancing nodule. The nucleation of discontinuous precipitates are mainly depends upon grain size, initial solute content, temperature. Three main nucleation mechanisms have been identified for discontinuous precipitation:

1. A precipitate first nucleates at the grain boundary and then acts to pull it from its initial position; the movement is associated with a reduction of interfacial energy as proposed by Tu and Turnbull [148-150]
2. The initial displacement of the grain boundary is due to chemical forces (similar to the DIGM (diffusion induced grain boundary migration) driving force) as for steady state growth, as proposed by Purdy and Lange [151]
3. The force responsible for the initial grain boundary motion are capillarity forces, identical to those that act during grain growth or recrystallization, as proposed by Fournelle and Clark [152]

![Figure 2.13: Schematic diagram showing DP process [143]](image)

Duly and Brechet [153] studied the nucleation phenomena with respect to ageing temperature. It appears that at high temperatures (T>220°C) Clark’s nucleation mechanisms dominates where as at lower temperatures (T~140°C) Tu and Turnbull’s mechanism dominates. At intermediate temperatures it is found that Purdy and Lange’s mechanism is the one, which dominates.

Effect of discontinuous precipitation on the mechanical properties particularly creep properties of AZ91 are studied and reported [28, 154]. Since the discontinuous precipitation takes place at the grain boundary and the reaction associated with movement of grain boundary, it leads to the grain boundary sliding particularly in die cast alloy at elevated temperature exposure. This reduces the creep properties of AZ91 alloys [28].

2.8.5 Tensile Behavior

Tensile properties of AZ91 find scatter. This is because the tensile properties are highly sensitive to the microstructure. The tensile properties are mainly depends on grain size and volume and size of second phase [155, 156]. Porosity is another
Chapter 2: Literature Review

major factor, which affects the tensile properties much [157-160]. The tensile properties are also sensitive to temperature and strain rate.

2.8.5.1 Effect of temperature and strain rate

The tensile properties of AZ91 alloy at high temperatures are well documented in literature. A drastic reduction in both yield and Ultimate strength occurs while the ductility improves considerably. As far as AZ91 alloy is concerned the main room temperature strengthening element is Mg17Al12 intermetallics. But this intermetallic has a low melting point (437°C) and has a tendency to become coarsen at elevated temperature i.e. above 100°C and no longer act as a barrier for dislocations [161]. Moreover Mg17Al12 has a cubic crystal structure, which is incoherent with the hcp magnesium matrix. Therefore this phase leads to the poor elevated temperature properties of AZ91 alloy. It is also important to note that temperature has a great effect on the tensile properties at lower strain rate whereas at higher strain rate, the temperature effect is less significant [162].

Figure 2.14 shows the variation in flow stress of AZ91 as a function of deformation temperature for various strain rates. The flow stress for each strain rate is determined at a fixed strain of 0.1. It is noted that the decrease in flow stress with temperature at strain rate at 10^-3 S^-1 is far greater than that at a strain rate of 10^3 S^-1. It is suggested that climb controlled dislocation creep could be a dominant deformation process in the low strain rate range. However, the operating deformation mechanisms at high strain rates are suggested to be dislocation glide and twinning even at elevated temperatures [162].

2.8.5.2 Effect of grain size

Several studies have been made of grain size strengthening in magnesium and in several of its alloys. Due to the fact magnesium is basically a HCP materials, it is more sensitive to the grain size. In general, the yield strength as a function of grain size can be represented as Hall-Petch equation;
Figure 2.14: Typical tensile behavior of AZ91 alloy at different temperatures and strain rates (a) at strain rate $10^{-3}$ s$^{-1}$ (b) at $10^3$ s$^{-1}$ [162]

\[
\sigma = \sigma_0 + Kd^{1/2}
\]

where $\sigma$ is the yield stress, $\sigma_0$ is the yield stress of a single crystal, $K$ is a constant and $d$ is the grain size. The value of $K$ increases with increasing the Taylor factor [163]. The Taylor factor generally depends on the number of the slip systems. Because the slip systems are limited and the Taylor factor is larger for HCP metals than for FCC and BCC metals, HCP metals exhibit the strong influence of grain size on strength [164]. Reduction in grain size improves both strength and ductility. The higher strength and ductility obtained by thermo mechanical treatment and severe plastic deformation is due to the same fact that these processes provide fine grain size in the order of 1μm. Table 2.6 provides the room temperature tensile properties of as cast and hot extruded AZ91 alloy [164]. It can be seen that both strength as well as ductility is improved significantly. This is attributed to the fine grain structure obtained in hot extrusion. It is observed that intergranular fracture is occurred in magnesium alloy with a large grain size; however, intergranular fracture is limited in magnesium alloy with a small grain size [165], indicating that the fracture mechanism is changed by grain refinement. This is because the critical stress for crack propagation at grain boundaries increases with decreasing grain size [165].
Table 2.6: RT tensile properties of as cast and hot extruded AZ91 alloy [164]

<table>
<thead>
<tr>
<th>Materials</th>
<th>UTS, MPa</th>
<th>0.2% Proof stress (MPa)</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As cast</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ91 (F)</td>
<td>131</td>
<td>72</td>
<td>1-3</td>
</tr>
<tr>
<td>AZ91 (T6)</td>
<td>235</td>
<td>108</td>
<td>3</td>
</tr>
<tr>
<td>Extruded</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ91</td>
<td>341</td>
<td>244</td>
<td>13</td>
</tr>
</tbody>
</table>

The fine grained AZ91 alloy not only shows high strength and ductility at room temperatures, but also superplasticity at elevated temperatures. Recently, it has been reported that an extruded AZ91 exhibits a maximum elongation of 425% at a testing temperature of 250°C with a strain rate of $3 \times 10^{-4}$ s$^{-1}$ [166]. Y.H. Wei et al [167] have also reported that the rolled AZ91 shows excellent superplasticity with the maximum elongation to failure of 455% tested at 350°C and a strain rate of $10^{-3}$ s$^{-1}$.

The dominant deformation mechanism in high strain rate superplasticity is reported as grain boundary sliding (GBS). Moreover, recently it is reported that the AZ91 processed by ECAE (Equal Channel Angular Extrusion), shows superplastic behavior at even low temperatures of 175-200°C [168]. This is attributed to a very small grain size in order of 1 μm.

2.8.6 Wear Behavior

Wear properties are important especially when magnesium alloys are to be applied for critical automobile applications. Wear, in the broadest sense, may be defined as the removal of surface material of a component. There are several mechanisms of wear, which include seizure, melting, oxidation, adhesion, abrasion, delamination, fatigue, fretting, corrosion, and erosion [169, 170]. Wear may normally be reduced by using a lubricant with appropriate anti-wear additives or changing the materials and/or the operation parameters affecting the wear rate. There are few studies available on wear behavior of AZ91 alloy. H. Chen et al [171] have carried out a dry sliding wear testing on AZ91 alloy against AISI 52100 steel ring within a load range of 1-350 N and a sliding velocity range of 0.1 – 2 m/s. They observed two main wear regimes, namely a mild wear regime and a severe wear regime. In the mild
wear regimes, it is found that the volume loss due to sliding wear increased linearly with the sliding distance where as in the severe wear regimes, it is no longer linear. Oxidational wear and delamination wear is reported in mild wear regime. Sever plastic deformation induced wear and melt wear is observed in sever wear regime. Recently, Song et al [172] have investigated wear mechanism and wear rate of two magnesium alloys, AS21 and AZ91D under constant sliding and dry loading conditions and concluded that the wear rate of the alloy mainly depends on the alloy hardness. D.S Mehta et al [173] also have reports that AS21 alloy shows higher wear rate than the AZ91D alloy due to its lesser hardness. Peter et al [174] have conducted both unidirectional and reciprocation sliding motion wear test on die cast and thixomolded AZ91D alloy. In reciprocating tests, the thixomolded specimens have slightly lower wear rates than die cast specimens where as in unidirectional sliding, both have similar wear rates, indicating that the microstructural differences do not have a pronounced effect on wear when the direction of surface shearing remained the same for each pass of the slider [174].

2.8.7 Creep Behavior

Creep is time-dependent deformation occur at high temperature normally above 0.5T_m (T_m – melting temperature). While elastic-plastic deformation, strain is a function of stress only whereas, creep strain is a function of stress, time and temperature [175]. Figure 2.15 shows a typical creep-strain versus time curve for a metal, where three distinct regions can be observed [176]. After an initial and instantaneous restructuring of the metal, primary stage creep occurs with decreasing creep rate. Here, the work hardening is higher than the stress recovery (work softening). In the secondary creep stage (stead-state) the metal experiences a two-way balance between work-hardening and stress recovery resulting in steady-state creep (constant creep-rate). The tertiary creep stage exhibits increasing creep rate due to necking and cracking resulting finally in fracture.
2.8.7.1 Creep behavior of pure magnesium

The creep response of pure magnesium has been extensively investigated [177-181]. In the temperature regime of around 200°C, the creep response of pure magnesium is fully comparable to that observed in other pure metals, where creep is controlled by dislocation climb [181]. In these cases, the activation energy for creep is equivalent to that of self-diffusion (Q=Q₁), and the stress exponent in the conventional Norton equation is around 5. It is generally accepted that at temperatures below 300-330°C dislocation glide (<11'20> {0001} slip system) on basal planes is dominant, whereas slip on pyramidal systems, {101'1} or {112'1} in the <11-20> directions, is the rate controlling mechanism above these temperature [182].

2.8.7.2 Creep behavior of die cast AZ91

Number of creep studies have been published on die cast AZ91 Mg alloys [17-27]. But still the creep deformation mechanism is not clearly understood. Some authors found the dynamic precipitate occurs during creep exposure is a fine particles and it strengthen the alloy. Coarsening of these precipitates is the softening mechanism. But it is also stated by others, that discontinuous precipitate form during creep and leads to the grain boundary sliding.

Regev et al [183] have reported that the creep rates of AZ91 are found to be a few orders of magnitude lower than these of pure magnesium and elongation to
fracture is to be at least 1.5 times higher than the pure magnesium. Regev [183] also reported a stress exponent ‘n’ value of 6.9 at 150°C and 5.4 at 180 °C and related the creep mechanism to dislocation creep. Blum [184] conducted a compressive creep testing on AZ91 die casting in the temperature range of 70-150°C and reported that the dislocation creep is the dominant mechanism and no grain boundary sliding contribute to the deformation. William K. Miller [185] has found that AZ91 alloy is creeping even at room temperature under the stress level of 60-120 MPa. The measured stress dependency of the secondary creep rate suggests that diffusion driven dislocation climb may be the rate controlling creep mechanism.

M.S. Dargusch [28] observed grain boundary sliding in AZ91 alloy and suggested that it play a dominant role at least in low stress levels. Creep testing of die cast AZ91 at stresses in the range of 20-60 MPa and temperature in the range of 125-175°C, gives an ‘n’ value of 1.5 and a ‘Q’ value of 44 KJ/mol [28]. This value of Q is close to 30 KJ/mol determined for the apparent activation energy for the formation of discontinuous β precipitation in Mg-9Al alloy. As it is evident that DP normally forms at a grain boundary and migrates in to the nearby grains, it damages the grain boundary. This will lead to the grain boundary sliding and formation of cavities and subsequent failure. Indeed they observed grain boundary sliding in AZ91 alloy as shown in Figure 2.16 in which the splitting of marked line across the grain boundary is clearly seen.

2.8.7.3 Creep behavior of AZ91 against other Mg-Al alloys

The creep behavior of AZ91, AS21, AS41 alloys are compared by Dargusch et al [28, 186] and have found that under all stress conditions and temperatures, the relative behavior of the alloys is similar with the creep strength of AE42 and AS21 being considerably better than AZ91. The comparison creep curves of three alloys at 150°C and 50 MPa is shown in Figure 2.17.
The superior creep resistance by other alloys over AZ91 alloy is explained by the amount of dynamic β precipitates form during high temperature exposure [28, 186]. The cast microstructure of AS21 and AE42 contain less amount of supersaturated α Mg because of less aluminum content compared to AZ91 alloy and as a result, their microstructures are much more stable and considerably less discontinuous precipitates occurs during exposure at elevated temperatures. Moreover these alloys also contain strong stable intergranular phases, Mg₂Si, in the case of AS21 and Al₄RE in the case of AE42, which can be expected to pin grain boundaries and hinder both grain boundary movement.
On the other hand W.Blum [30, 31, 184, ] compared the creep behavior AZ91 die cast alloys with the other Mg-Al alloys like AS41, AS21 and AE42. From stress-strain curve obtained under compressive loading they found that AZ91 alloy has highest work hardening and has higher yield stress at all the testing temperature. They measured the maximum deformation resistance during compressive creep and represented in Z-σ plot, which is shown in Figure 2.18. AZ91 has a higher maximum deformation resistance at stress above 150 MPa and inferior to AS21 below this stress level. Apart from this, the values of AZ91 and AM60 lie on the one hand and AS21 and AE42 on the other hand. They showed that AZ91 alloy has the highest creep resistance of all alloys in the whole investigated range, with the exception of AS41 which becomes more creep resistant than AZ91 at stresses below 130 MPa. They attributed this behavior to high rate of work hardening of AZ91, combined with the precipitation hardening due to the dynamic precipitation of Mg17Al12. AZ91 alloy is expected to have highest super saturation of Al and subsequent precipitation of β during creep, strengthening the alloy. At low stresses, the alloys like AS21, AS41 exhibits good creep behavior because of the Mg2Si precipitates, which is more stable than Mg17Al12 phase. The same author has proved this precipitation hardening in AZ91 alloy by conducting creep test on annealed, which exhibited higher creep resistance [187].

2.8.7.4 Creep behavior of ingot cast AZ91

There is not much creep studies are available on the gravity cast AZ91 alloy. However, a detailed work on the creep behavior of ingot AZ91 alloy carried out by Regev et al [29, 188] suggested that no grain boundary sliding contribute to the creep deformation. The creep mechanism observed is either dislocation creep or dislocation glide. Dynamic precipitation is also observed in ingot casting. It is suggested that creep induced precipitates are strengthening the alloy against creep.
The precipitation hardening is verified by conducting creep testing on AZ91 alloy ingot casting at various tempered conditions i.e., as cast, solutionized and aged [188]. Superior creep resistance of solution treated ingot AZ91 alloy castings over the as cast and aged alloy is observed as shown in Figure 2.19. The minimum creep rate of the solution-treated specimens is lower than that of the as cast specimen tested under the same condition (0.135%/h at 100 MPa compared with 0.05%/h for the as cast). It is also observed that the aged specimens showed higher minimum creep rates than the as cast specimens (0.11%/h at 50 MPa and 150°C compared with 0.025%/h for the as cast). Moreover, that the minimum creep rate occurred app.2/3 of the time to failure in as cast and solutionized specimens where as in aged specimens, the minimum creep rate is attained at the earlier stage. This behavior is attributed to the β-Mg17Al12 precipitates formation during high temperature exposure. According to Regev [188], in the solutionized samples the hardening process starts with solid solution hardening as more aluminum in the solid solution and then changes to precipitation hardening whereas in aged sample neither solid solution nor precipitation strengthening takes place. The poor performance of the aged specimens is due the softening effect takes place because of the precipitates coarsening straightway. This indicates that submicron precipitates formed during creep exposure in ingot casting strengthens the alloy.
While comparing the creep behavior of die and ingot cast AZ91, Regev et al [189] have found that the minimum creep rate was reached approximately two thirds of the time to rupture in the ingot specimen compared to one third of that time in the pressure die-casting as shown in Figure 2.20. Apart from that, the minimum creep rate at given test parameter is much higher in the pressure die casting than in ingot. These behaviors are related to the difference in hardening mechanisms due to the dynamic precipitation process involved during creep. Due to the faster cooling rate, the die cast alloy contains more amount of eutectic $\beta$-Mg$_{17}$Al$_{12}$ and less amount of Al in $\alpha$-matrix. On the other hand, due to the slow cooling rate in gravity ingot casting, more amount of Al goes into the $\alpha$-Al matrix. The higher content of Al in the matrix leading to prolonged precipitation until steady state is reached in ingot casting. This leads to the slow creep rate in ingot casting. In contrast the precipitation process comes to end at earlier in the die casting and coarsening of precipitates takes places, which degrade the microstructure [189, 190].

S.Spigarelli [191] also compared the creep behaviour of AZ91 alloy processed by die casting and thixo casting with the ingot casting at 150°C with an initial stress of 100 MPa. Similar kind of results are observed as the creep behaviour of die-cast and the thixo-formed samples exhibited a similar response, characterized by a relatively short primary stage followed by a short minimum-creep-rate range rather than by a secondary regime, and by a prolonged tertiary region. The ingot exhibited a longer
primary stage. Rupture in this case occurred abruptly after a short tertiary stage and exhibited the greatest creep strength as shown in Figure 2.21. The higher creep resistance of the ingot alloy is attributed to the extended precipitation of fine particles during creep exposure and marked difference in grain size with the die and thixoformed alloy samples.

![Figure 2.20: Creep curves of ingot and die cast AZ91 alloy at 150°C [189]](image)

Figure 2.20: Creep curves of ingot and die cast AZ91 alloy at 150°C [189]

![Figure 2.21: Comparison of creep behaviour of AZ91 alloy processed through different Casting processes [191]](image)

Figure 2.21: Comparison of creep behaviour of AZ91 alloy processed through different Casting processes [191]

### 2.8.8 Corrosion Behavior

Poor corrosion resistance is a recognized property of magnesium. Hence, this property is playing a prominent role in preventing more widespread use of magnesium, especially in aerospace applications. Of course, magnesium is the most active metal used in engineering applications and corrodes so readily in some
environments where magnesium alloys often serve as sacrificial anodes on structures such as ships’ hulls, buried pipelines, and steel piles [192].

The standard electrochemical potential of magnesium is -2.4 V (NHE), and even though in aqueous solutions it shows a potential of -1.5 V due to the formation of Mg(OH)₂ film. Consequently, magnesium dissolves rapidly in aqueous solutions by evolving hydrogen below pH 11.0, the equilibrium pH value for Mg(OH)₂ [193, 194]. The reaction is relatively insensitive to the oxygen concentration. The overall reaction is described as

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \]

As corrosion proceeds, the metal surface experiences a local pH increase because of the formation of Mg(OH)₂, whose equilibrium pH is about 11. The protection supplied by this film is highly dependent on the conditions of exposure. For example, magnesium is very resistant to corrosion in small volumes of water that are free of species aggressive to the film. In the atmosphere, Mg reacts further with carbon dioxide, forming magnesium carbonate, which acts as a sealer for the hydroxide film. High purity magnesium therefore has the potential to be extremely better in the atmosphere than iron [195]. Problems arise when impurity elements are present at levels that promote micro galvanic cell action, when the metal or alloy is galvanically coupled to an effective cathode materials, or when the nature of the environment prevents formation or maintenance of a protective film.

2.8.8.1 Corrosion behavior of AZ91

The corrosion behavior of AZ91 alloy is very sensitive to the microstructure. As mentioned already the AZ91 alloy consists of three microstructural constituents in the cast microstructure. These are primary α, eutectic α and β-Mg₁₇Al₁₂ intermetallic. The primary α phase normally contains much less aluminum compared to that of eutectic α and β phase. The β phase reported to have more cathodic potential than that of α phase [33]. Thus, α and β phases when in contact will easily cause galvanic corrosion. Song et al [34] by examining the individual phases, have shown that in
chloride solution, the rest potential of the β phase (-1.6 V) is some 300 mV positive to α phase (potential, -1.3V). Lunder et al [33] also found that the positive drift of the rest potential of Mg₁₇Al₁₂, which could be attributed to the passivation of this phase.

That way in AZ91 alloys, size and distribution of β phase together with the coring of α phase makes the alloy surface electrochemically heterogeneous. The corrosion behavior of the material thus depends on how these microconstituents interact when it is exposed to aqueous environment. The above said parameters changes with processing route, gives rise of different corrosion behaviors for materials prepared by different processing routes.

2.8.8.2 Effect of micro constituents

(i) α-Mg

The α phase plays an important role in the corrosion behavior of AZ91 [36], and its corrosion performance determines corrosion behavior of the alloy. The composition of α should be crucial to its corrosion behavior. In general, within α grain, the composition distribution is not always uniform. It has been shown that the aluminum concentration can vary from a few percent in the grain interior to 10% in the vicinity of the β phase [35]. The effect of aluminum on the corrosion behavior of Mg alloys has been subject to many investigations [98, 196, 197]. It has been generally agreed that the presence of aluminum is beneficial in improving the corrosion behavior of magnesium. Later it is found that for effective protection an optimum level of aluminum is required. Ambat et al [36] observed the region preferentially corroded is one with less than 8% aluminum. Lunder et al [33] also reported that this quantity is about 8% where as Warner et al [198] using TEM studies on rapidly solidified ribbons of composition Mg-9Al, arrived at the conclusion that it is >5%. Hehmann et al [199] studied corrosion behavior of rapidly solidified ribbons with aluminum concentration varying between 9 and 62.3%. They observed a decrease in the corrosion rate and E_{corr}, from 9.6 to 23.4% Al in aerated 0.01 M sodium chloride solution. Daloz et al [197] have reported that the increase in aluminum content in the material shifts the potential towards anodic side. But many authors find the corrosion initiates in α – Mg where the aluminum content is lesser.
This discrimination is explained by the presence of zinc in the solid solution. It is also reported that in Mg-Al alloys, presence of Zn influences the $E_{\text{corr}}$ of both matrix and precipitates and has a beneficial effect on the corrosion resistance of the alloys [197].

(ii) $\beta$-Mg$_{17}$Al$_{12}$

The $\beta$-Mg$_{17}$Al$_{12}$ phase is cathodic with respect to the matrix and exhibits a passive behavior over a wider pH range than either of its components Al and Mg. $\beta$-Mg$_{17}$Al$_{12}$ is found to be inert in chloride solutions in comparison with the surrounding Mg matrix and could act as a corrosion barrier [200]. It is reported that the resistance of $\beta$-Mg$_{17}$Al$_{12}$ to corrosion is due to the presence of a thin passive film on its surface.

However, literature also suggests that $\beta$ phase serves dual role in corrosion; the $\beta$ phase can acts either as a barrier or as a galvanic cathode [37, 201-203]. If it is present as a small fraction, it serves mainly as a galvanic cathode, and accelerates the overall corrosion of $\alpha$ matrix. However, if its fraction is high, then it may act mainly as an anodic barrier [35].

If the $\alpha$ grains are very fine, the $\beta$ phase fraction is not too low, and the $\beta$ phase is nearly continuous like a net over the $\alpha$ matrix, then the $\beta$ phase particles don not easily fall out by undermining. Instead, in this case the $\alpha$ matrix is much more easily corroded and even undermined because many more $\alpha$ grains are completely separated by the $\beta$ phase net. Therefore, it can be expected that $\beta$ fraction increase with time during corrosion, and finally the fraction becomes high enough to make the $\beta$ phase become nearly continuous. The corrosion rate should be low after this steady state surface condition is reached. Hence, if $\alpha$ grains are fine, the gaps between $\beta$ precipitates are narrow and the $\beta$ phase is nearly continuous, the corrosion is greatly retarded [201, 202]. Figure 2.22 provides a schematic illustration of change of surface composition of die cast during corrosion. This kind of behavior normally observed with die cast AZ91 alloy.

On the other hand, if $\alpha$ grain size is large, the $\beta$ phase is agglomerated and the distance between the $\beta$ phase is large then at the final stage of the corrosion, the $\alpha$
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Phase is not effectively blocked either by β phase or by the corrosion products deposited between the β phase and α phase. In an even worse case, the β can be undermined instead of α phase. In this case β fraction decreases with time during corrosion and the corrosion rate increases with time. This is what happens during corrosion of gravity cast AZ91 [37].

Figure 2.22: Schematic presentation of change of surface composition during corrosion (a) initial surface (b) final surface [201]

2.8.8.3 Effect of impurities

Another important factor, which affects the corrosion behavior of AZ91 alloy, is the kind and level of impurities presence in the alloy. Fe, Ni, Co, Cu are the impurity elements that have negative effect on corrosion resistance [204]. The tolerance limits for these elements are defined by the ASTM standards [205]. Iron is the most critical element since it reacts with aluminum forming a binary intermetallic compound Al3Fe. This compound segregates at grain boundaries and it acts as an active cathodic phase relative to the magnesium rich matrix. One of the first observations by Hanawalt and co workers [98] was the effect of purity on the corrosion rate of pure magnesium, as measured by weight loss in 3% sodium chloride. The commercially pure metal (99.9%) has a corrosion rate of 5-100 mg/cm²/d (410-8300 mpy), while the corresponding rate for high purity magnesium (99.994%) is about 0.15 mg/cm/d (12mpy). The generalized curve in Figure 2.23 illustrates schematically the effects of common impurity elements observed in the Hanawalt study [98]. The curve shows a well defined impurity level, above which the corrosion rate increases dramatically. For high purity magnesium, these values are 170, 1000, and 5 ppm for iron, copper and nickel respectively.
Reichek et al [206] also showed that the salt water corrosion performance of the AZ91 alloy is a direct function of the alloy purity. They are able to define the specific tolerance limits of the three common contaminants of Mg alloys, i.e., Fe, Ni and Cu with respect to corrosion behavior. By keeping the respective limits of these contaminants to values below the defined values (Fe=3.2%Mn max.; Ni=50 ppm max.; and Cu=400 ppm max.), they found that AZ91 consistently exhibited a better salt spray corrosion performance than pressure die cast SAE 380 (Al-4.5% Cu-2.5% Si) and cold rolled steel. [206].

![Figure 2.23: Generalized curve showing the effect of impurities on corrosion rate of magnesium [98]](image)

To reduce the effect of iron in Mg-Al alloys, manganese is generally used. Manganese, combine with iron and improve the corrosion behavior in two possible ways: either removing iron by settling at the bottom of the melt, or forming intermetallic compounds with iron, which apparently have no negative effects. It has been shown by several authors that the corrosion rate of Mg-Al castings is better correlated to the Fe/Mn ratio of the alloy, rather than the absolute Fe content [198].

### 2.8.8.4 Effect of heat treatment

The effect of ageing on corrosion resistance of die cast AZ91 also reported in literature. Suman [207] showed that ageing at temperatures up to 230°C for 36 h has little effect on corrosion resistance. However, ageing at a temperature above 230°C significantly reduces the corrosion resistance of die cast AZ91 under a salt spraying
condition. Lunder et al [33] reported that the alloy exhibits an improved corrosion resistance in the artificially aged condition (T6) compared to as cast and homogenized (T4) state.

Recently Song et al [208] have carried out a detailed study on the effect of ageing at 160°C on the corrosion behavior of die cast AZ91 alloy. It was found that the corrosion rate of the alloy decreases with ageing time in the initial stages and then increases again at ageing times greater than 45 h. The dependence of the corrosion rate on ageing time is related to the changes in microstructure and local composition change during ageing. The β precipitates occurred during ageing treatment at the grain boundary acts as a barrier, resulting in a decreasing corrosion rate in the initial stages of ageing. In the later stages, the decreasing aluminum content of α grain makes the matrix more active, causing an increase in the corrosion rate. They also reported that the continuous rod shaped precipitates, which occur in the later stage in the grain, do not act as an effective barrier for the corrosion.

In contrast, Singh Raman [209] studied the ageing effect on corrosion of gravity cast AZ91 and reported that T4 (solution treated) treated specimen exhibit superior corrosion resistance. On the other hand, the aged specimen (16h and 19h) and as cast shows higher corrosion rates. He observed that the corrosion is highly localized in the region of β phase and the surrounding eutectic α phase. It is said that the cathode to anode area ratio is one of the prime factors governing the severity of the galvanic corrosion. The increase in corrosion rate with increase in ageing time is attributed to the increase in the precipitates volume, which in turn increases the cathode to anode area ratio, leading to more galvanic corrosion (ref Figure 2.24).

2.8.8.5 Corrosion protection coatings

There are two different ways to improve the corrosion resistance of magnesium alloys. The first one is to purify the alloy from impurities like Fe, Ni, Cu, etc. the second method is to form a protective coating on the magnesium alloys. Various surface treatments have been used to generate protective films or surface coating [210-213]. These techniques basically classified as two types. The first one is
to produce a protective film by chemical or electrochemical conversion treatments. The second one is a coating usually containing organic materials like paint. Chemical conversion coating, electrochemical anodizing, chemical plating, electro plating are comes under the first type. The chemical treatments usually involve the dipping of the magnesium alloy into acidic or nearly neutral solutions containing Cr compounds, which form a passive oxide layer on the surface of the metal. In electrochemical process like anodizing, film composed of MgO containing Cr compounds are produced on the surface [214].

![Figure 2.24: Schematic diagram illustrating the cathode-anode area change during ageing of AZ91 alloy (a) T6-16h (b) T6-19h [reproduced from ref. 209]](image)

Among the various electrochemical techniques, anodizing treatment is become most promising methods for magnesium even though this treatment is quite expansive compared to the chemical treatment [215]. Different process like DOW 17, HAE and MGZ has been developed. These coating has environmental problem as most of the electrolyte used in these process contain dichromate and phosphoric acid [216]. Recently, due to the health and environmental pressure, some new coatings such as Anomag and Tagnite have been developed [210, 211, 217]. These coating methods have less hazards and more effective in terms of corrosion resistance over HAE and DOW17 [218].

Laser treatment is another surface modification technique in which, formation of metastable solid solutions as promoted at metal surfaces by laser annealing where cooling rates as high as $10^{10}$ Ks$^{-1}$. This is also a kind of rapid solidification technique
in which only surface layer melt and solidifies [214]. Akavipat et al [219] studied the effects of thin layers of Al, Cr, Cu, Fe and Ni on the pitting resistance of AZ91C and found that improved breakdown potential for all cases. This improvement is attributed to the surface structure consists of mixture of amorphous mixed oxides. C. Padmavathi et al. [220] have reported that pulsed Nd:YAG laser melting treatment on AZ91C alloy improve its corrosion behavior because of its fine microstructure and redistribution of β- phase.

2.9 ROLE OF MINOR ALLOYING ADDITIONS

Surface active elements like Sb, Ca, Bi, Sr, RE, etc., are added to the AZ91 alloy to improve its mechanical and corrosion properties [221-224]. These elements mainly form intermetallics either with Mg, or with Al, which is high thermally stable than the Mg17Al12, thereby improve the creep properties. Some elements like Ca and Sr are effective in refine the grain size of AZ91 alloy. Ca and RE is also found to improve the corrosion resistance of AZ91 alloy.

2.9.1 Antimony

Qudong Wang et al [42] and Guangyin et al [44] studied the effect of Sb on the microstructure and mechanical properties of AZ91 alloy. Addition of small amount of Sb (0.5 to 2%) lead to the microstructure of AZ91 alloy with needle shaped Mg3Sb2 particles at the grain boundary and refinement of Mg17Al12 precipitates to some extent [221]. Since the melting point of Mg3Sb2 is around 1228°C, it is thermally stable at high temperature. Maximum tensile properties are observed with 0.5% Sb added alloy. Improved creep properties at 150°C with 50 MPa initial stress is also observed [221]. With addition of 0.4% Sb, the minimum creep rate of AZ91 alloy is reduced from 5.6×10^{-8} to 1.5×10^{-8} s^{-1}. The total strain for 100 h is also reduced from 2.4% to 1.2% [222]. The hard and stable Mg3Sb2 precipitates pin both the grain boundary and dislocations at high temperature and thus improves the creep resistance. The microstructural analysis on the creep tested samples indicates that Sb rich particles hindering the dislocation movement and lead to the formation of dislocation tangles during creep process (ref Figure 2.25) [221]. However the problem associated with Sb addition is that if the addition exceeds 0.5% the number of Mg3Sb2 phase also
increases and the needle shape morphology of this intermetallic brings down the properties.

![TEM micrograph showing dislocation pileups around the Mg₃Sb₂ intermetallics in Sb added AZ91 alloy crept at 200°C][221]

Figure 2.25: TEM micrograph showing dislocation pileups around the Mg₃Sb₂ intermetallics in Sb added AZ91 alloy crept at 200°C[221]

2.9.2 Calcium

Wang Qudong et al [41] added up to 2% Ca to AZ91 alloy and studied its microstructure and mechanical properties. Ca addition found to refine the microstructure and reduce the quantity of Mg₃Al₁₂ phase by forming new Al₂Ca phase. Addition of Ca is also effective in reduction in grain size of AZ91. Hirai et al [222] reported that the initial grain size of as cast AZ91 alloy is reduced from 65 μm to 20 μm when 1% of Ca is added. However, when the amount of added Ca is more than 1%, no change in grain size is observed. Peijie Li and S.S. Li also [223, 224] reported that the grain refinement efficiency is high with initial additions of Ca up to 0.4% and then the degree of grain size reduction decreases with further additions.

The addition of Ca improves the ambient temperature yield strength but ultimate tensile strength and ductility are found to reduced [41, 223]. The improvement in yield strength is attributed to the grain refinement effect of Ca but the Al₂Ca phase forms at grain boundaries is brittle and face centered cubic structure that may deteriorate the bond strength and result in worse UTS and elongation [223]. However, Ca addition confers elevated temperature strengthening of this alloy because at high temperature, the Al₂Ca phase is thermally stable compared to
Mg$_{17}$Al$_{12}$ precipitates and acts as an effective dislocation barrier [41]. In addition to that, increase in the stability of Mg$_{17}$Al$_{12}$ intermetallic is also observed with Ca addition. Part of the added Ca dissolves into the Mg$_{17}$Al$_{12}$ phase, which raises its thermostability, consequently, strengthen the alloy at elevated temperatures [225]. Improvement in corrosion resistance of AZ91 alloy with Ca addition is also reported [48]. This is due to the reduction in volume fraction of Mg$_{17}$Al$_{12}$ phase and formation of less harmful Al$_2$Ca intermetallic.

Hot-crack problem is noticed with Ca addition. Figure 2.26 shows the effect of Ca on the hot-crack grade of AZ91 alloy [223]. It could be understood from the figure that 1% of Ca addition greatly affects the hot-crack property of AZ91. Bi Tang [226] studied the hot crack mechanism of Ca added AZ91 alloy and reported that the Ca addition elevates the tendency of the divorce eutectic and forming the new Al$_2$Ca phase, which is distributed as a net-shape on the grain boundary and debases the boundary tension of the liquid film, deteriorating the filling capacity and lowering the hot-crack property of magnesium alloy [224].

![Figure 2.26: Effect of Ca on the hot-crack grade of AZ91 alloy [223]](image)

2.9.3 Bismuth

Bi addition to AZ91 alloy forms a hard compound Mg$_3$Bi, which has a melting point of 823°C. Compared to Sb, Bi addition has, only little effect on the improvement of creep properties of Mg alloy. But when it combines with Sb, the effect is appreciable [43]. Microstructure observations reveal that the additions of
bismuth refines the Mg$_{17}$Al$_{12}$ precipitate in the as cast alloys and effectively suppresses the discontinuous β-Mg$_{17}$Al$_{12}$ precipitation during the aging process [43].

2.9.4 Rare earth

Rare earths are important alloying elements to magnesium alloys, which can improve casting characteristics, high temperature properties and corrosion resistance [227-230]. With addition of rare earth elements a rod-like Al$_{11}$RE$_3$ intermetallic forms at the grain boundary. Due to the formation of Al$_{11}$RE$_3$, the Al available for the formation of Mg$_{17}$Al$_{12}$ phase reduces. The effect of RE addition on the tensile properties of AZ91 alloy is scatter in the literature. Y. Lu [45] has reported that RE has little effect on the UTS of AZ91 at ambient temperature but greatly increase the high temperature tensile strength and elongation. Fan [46, 47] has reported a sharp increase in both UTS and ductility with the addition of La and Ce to AZ91 alloy. On the other hand, G. H. Wu et al [48] have found that with increasing RE additions, the UTS increases but the elongation decreases. S. Lee et al [231] have reported that addition of Y and Nd improves hardness and fracture toughness of AZ91. He observes planer slip bands and transgranular crack propagation along these slip bands. When planer slip bands are forms, a heavier load is requires for fracture than in the case of intergranular fracture, thereby yielding an overall improvement of mechanical properties [231].

G. Pettersen [232] indicates that RE could reduce the range of crystallization temperature of magnesium alloy, and hence the Mg-RE eutectic has good fluidity. However, Y. Lu [45] has reported a decrease in fluidity up to 2% RE addition and then it increase with higher percentage addition to AZ91 alloy. Qudong et al [233] observed the fluidity of RE added alloy is depending on the mould section thickness also. The fluidity decreases with increase in RE addition in mould section thickness under 2 mm whereas it decrease first with section thickness above 2 mm when RE content increases from 1 to 2% and increase when RE content increases from 2 to 3% to AZ91 alloy.
Wang et al [234] studied the effect of RE on hot tearing susceptibility. Small quantity of RE additions have little effect on the hot susceptibility coefficient (HSC) of Mg-9Al alloy, while RE content is exceeded 1.6%, HSC increases notably. The increase in HSC is attributed to the formation of rod-like Al₄RE precipitates, which has high latent heat. During the formation of this phase, much heat is given out, which slow down the temperature decrease at the initial stage of solidification.

Rear earth addition has a significant role on corrosion behavior of Mg alloys. Lunder [235] found that the Al₁₁%M₃ (MM refers to misch metals, a mixture of rare earth metals) intermetallic phase in AE42 magnesium alloy is nobler than pure Mg. Its micro-galvanic corrosion is not severe since the Al₁₁%M₃ phase behaves as a passive cathode over a wide pH range. As a result, it is not expected to have a detrimental effect on the corrosion resistance of the alloy. Mercer [236] considered that the advantage of RE in magnesium alloys can be attributed to trapping deleterious elements and decreasing the activity of cathode. Nordlien et al. [237] indicated that the coexistence of aluminum with RE is an essential condition for improving the passivity of Mg-Al-RE alloy, suggesting a synergistic effect between these elements. Recently Fan et al. [46, 47] studied the effect of Ce and La addition on the corrosion behavior of AZ91 alloy and found improved corrosion behavior. They attributed the improvement is the ability of these elements to refine the β phase and thereby forming a continuous β network along the grain boundaries. Rosalbino et al [50] added erbium (Er) to AM50 alloy to improve it corrosion behavior. Electro chemical investigations revealed that the surface layers formed on Mg-Al-Er provide a better protective layer than the magnesium hydroxide or aluminum hydroxide layer normally form on AM60 in borate buffer solution. Zhou Xuehua et al [49] studied the corrosion behavior of holmium (Ho) added AZ91 alloy in 3.5% NaCl solution saturated with Mg(OH)₂ and reported that Ho enhanced the corrosion resistance of AZ91. The addition of Ho reduces the amount of β phase by forming Ho containing phase with Al and Mg and they are easily oxidized and passivated. They also reported that the corrosion product films on Ho added alloys contain more Al, which is more compact and stable [49].
2.9.5 Strontium

Not much studies available on the effect of Sr to AZ91 alloy. S. Lee [231] has reported a grain reduction of 82 µm to 48 µm with addition of 0.5% Sr to AZ91. The grain refinement obtained is attributed to the modified precipitation behavior observed with Sr addition [238]. With Sr addition, it is found that more amounts of Mg17Al12 phase are precipitates along the grain boundary. This can hinder the movement of grain boundaries and the subsequent grain growth leading to the greater effect of grain refinement. K. Hirai et al. [222] have noticed a grain reduction of only 65 µm to 40 µm with 0.5% Sr to AZ91 alloy. Moreover, when it is added along with 1% Ca, the grain size greatly reduced to 17 µm. It is also reported that the combined addition of Sr and Ca improves the room and high temperature properties due to the reduction in stacking fault energy [222]. However, low hardness and fracture toughness is obtained with 0.5% Sr added AZ91 alloy by S. Lee et al. [231]. This is due to the presence of coarse needle-shaped Sr based precipitates, which is mainly distributed on grain boundaries, beside the discontinuous Mg17Al12 precipitates. When load is applied, micro cracks are formed initially in these particles, and then are immediately connected to grain boundaries, causing intergranular fracture. Thus its mechanical properties are reduces despite the fine grain size.

P. Zhao et al [239] studied the Sr effects on the tensile and creep properties of AM50 alloy. It is observed that trace additions of Sr to the alloy has a beneficial influence on the mechanical properties of Mg-5Al alloy, especially on UTS and elongation. The tensile properties increases with increasing Sr content when the Sr addition is lower than 0.1%. However, greater amount of Sr, deceases the UTS and elongation whereas increases the yield strength. He also observed the creep properties are increased with increase in Sr content.

2.10 SHORTCOMINGS IN LITERATURE

The creep behavior of die cast AZ91 alloy is extensively dealt in literature. In general two contradictory findings are reported: (i) dynamic discontinuous precipitate forms during creep leads to the sliding at low stress level. (ii) in contrast, continuous fine precipitates occurred at the same temperature and stress region provides
precipitation hardening and finally, coarsening of these precipitates at the later stage is the softening mechanism. Moreover, not much literature is available on the ingot cast alloy. Available literature, which deals the creep behavior of ingot AZ91 alloy, suggests dislocation creep is the dominant mechanism and no substantial grain boundary sliding contributes to the creep. In addition, most of the literature, which deals improvement in creep behavior of gravity cast AZ91 alloy by minor alloying addition suggests that the formation of thermally stable intermetallics and suppression of discontinues precipitates due to the additions are the reasons for the improvement. However, most of the studies are not provided the microstructural evidence for such a claim. Detailed post creep microstructural examination is hence, needed to understand the deformation mechanism of gravity cast AZ91 alloy added with various elements.

Moreover, most of work on AZ91 alloy is focused on its creep behavior and considerable effect has been put to improve its creep properties, particularly modify the alloy composition slightly through different alloying addition. While, considering the industrial application of magnesium alloys, particularly AZ91, creep is not the only concern. There are other properties like ageing behavior, tensile properties and corrosion properties, which are all important in practical applications. In specific, the corrosion behavior is another major concern, which restricts it wide spread application as a structural material. AZ91 alloy exhibit excellent corrosion resistance due to the high percentage of Al in the alloy. When alloy modification takes place to improve its high temperature performance, the microstructure changes considerably. Mainly these additions introduce various high temperature stable intermetallics in the microstructure. Since the corrosion behavior of this alloy is highly sensitive to microstructure, these intermetallics definitely play an important role. Hence studies on corrosion behavior of AZ91 alloy with different alloying additions are more valuable.

Even though the effect of elements like Sb, Ca, Bi, and RE addition on the tensile and creep properties of AZ91 is studied to certain extend and reported, there are other elements like Si, Sr whose influence on above said properties are not investigated in detail.
2.11 SCOPE OF THE WORK

The increase in the demand to reduce the weight of a passenger car thereby increase the fuel efficiency oblige the auto industries to paying more attention to discover the lighter material with high specific properties. It is not surprise that magnesium is one of the potential candidates as it is one of the lightest structural materials with a density of 1.77 g/cc. Since the material cost of magnesium is slightly higher than aluminum, die casting is always preferred for magnesium alloy castings. The magnesium alloys containing considerable amount of aluminum (6-9%) provides excellent die castability. AZ91 alloy, which containing 8-9%Al in it, is considered as a bench mark alloy for castability of Mg alloys. More over this alloy offer wide range of room temperature properties. In the as cast condition, the strengthening phase is the massive Mg_{17}Al_{12}, which is known as eutectic phase. However in the aged alloys, a fine and evenly distributed continuous form of Mg_{17}Al_{12} precipitates in the basal plane strengthen the material according to Orowon theory of precipitation hardening. However, this alloy does not have adequate high temperature tensile and creep properties, which hamper its usage above 100°C. Literature said that the presence of higher amount of aluminum in this alloy not only increase the brittleness but also impair the creep properties. The coarsening of β-Mg_{17}Al_{12} at elevated temperature, due to its low melting point (437°C), is said to be the cause for the poor creep properties. Due to this fact, it is believed that it does not act as a barrier for dislocation and grain boundary movement. Moreover, it is found that the structure is not stable at high temperature. Dynamic precipitation of Mg_{17}Al_{12} occurs at the grain boundary. Hence, alloys with less amount of Al are developed for high temperature applications. These alloys containing only 2-4%Al along with third element results in no or fewer Mg_{17}Al_{12} precipitates, in addition to the thermally stable intermetallics. Hence these alloys exhibit superior creep resistance over conventional AZ91. However, fewer amount of aluminum and presence of certain other elements like Ca and RE create die casting problem for these alloys.

Since AZ91 is still a work horse magnesium alloy system for automobile industries, even a slight improvement in its mechanical properties, particularly the creep, would be very much appreciated. Previous studies proved that addition of
minor alloying elements to AZ91 alloy is a successful way of improving its mechanical behavior. Surface active elements like Sb, Ca, Bi, RE and etc are added to Mg-Al alloys like AM60 and AZ91 alloys and noticed improvement in high temperature tensile and creep properties. This improvement is attributed to following reasons:

1. Introduction of intermetallics like Mg$_3$Sb$_2$, Al$_2$Ca, Mg$_3$Bi, and AlRE
2. Suppression of discontinuous Mg$_{17}$Al$_{12}$ precipitates at the grain boundaries
3. Increase the stability of Mg$_{17}$Al$_{12}$ precipitates

Corrosion is another concern of Mg alloys, which has been a major obstacle to its growth in structural applications. Magnesium with a standard electrochemical potential of -2.4 V (NHE), dissolves rapidly in aqueous solutions by evolving hydrogen below pH 11.0, the equilibrium pH value for Mg (OH)$_2$. As a consequence, researchers all over the world have shown much interest to study the corrosion behavior of Mg alloys and to develop protective measures. The corrosion behavior of AZ91 is highly sensitive to the microstructural features like, volume fraction and size of Mg$_{17}$Al$_{12}$ phase, amount and distribution of Al in the matrix, grain size, porosity etc. The alloying elements, which are added with the intention to improve the creep properties might changes the corrosion behavior of AZ91. Hence it is imperative to study the effect of intermetallics on the corrosion behavior of AZ91 alloy. So, the objectives of the present research work are:

1. To study the effect of individual and combined additions of Si, Sb and Sr on the microstructure, aging behavior and tensile properties of AZ91 alloy
2. To investigate the effect of additions on the creep behavior and understand its strengthening mechanism.
3. To estimate the change in corrosion resistance and behavior of existing AZ91 alloy in presence of various intermetallics.