

Review

The role and significance of Magnesium in modern day research-A review

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Received 15 December 2020; received in revised form 26 April 2021; accepted 14 May 2021

Available online 24 June 2021

Abstract

Magnesium is one of the largely available elements in the earth's crust. It has a low structural density with high specific strength. This unique material property has forced an increase in the use of magnesium and its alloys in various applications pertaining to industrial sector, automobiles, aerospace and biomedical. Since magnesium is a highly reactive metal, it is prone to higher rate of corrosion as compared to its counterparts. Thus, it is essential to analyze the corrosion behavior of magnesium and its alloys in its applications. An appropriate process is to be followed in the design and development of magnesium alloys which overcome the limitations of magnesium and enhance the desired material properties in accordance to their applications. This review paper summarizes the importance of magnesium and its material properties. The influence of various alloying elements on the mechanical properties of magnesium is reviewed. The broad classification of Mg alloys and their behavioral trends are detailed. The corrosion behavior of magnesium and the influence of corrosion products on the material characteristics of magnesium, in aqueous medium, are discussed. The manufacturing techniques of magnesium alloys along with the secondary techniques are also covered. The various applications and the limitations of magnesium in these applications are covered. A complete section is dedicated towards detailing the recent trends of magnesium (Mg) alloys, i.e., the biodegradable nature and applications of Mg alloys. The influence of biocorrosion on Mg alloys and techniques to overcome it have been deliberated. This paper provides a thorough review on recent developments of magnesium with respect to engineering applications.

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Peer review under responsibility of Chongqing University

Keywords: Magnesium alloys; Biodegradable alloys; Magnesium corrosion; Biocorrosion.

1. Introduction

1.1. Lightweight materials “Need of the Hour”

The major concern in our realm has always been the optimum use of the limited available resources. Across the globe, the rising levels of carbon dioxide (greenhouse gas emission), in the recent past and increase in the global temperature has created a sense of awareness among the manufacturers, in taking precautionary measures towards reducing the

carbon dioxide emissions, to benefit the atmosphere. Apart from this, a tremendous rise in the crude oil prices over the last two decades has become a worry to industrialists. From the data obtained in statistical website [1], a graph has been plotted as shown in Fig. 1. The graph shows an escalating average annual crude oil prices per barrel for the last 18 years. The rules against greenhouse gas emission have also become very stringent. These issues revolutionized the thought process in the manufacturing sector and provided impetus to search for alternatives. This stimulated a need for lightweight materials in the form of composite materials, which would replace the conventional materials. Composites having lighter weight and better strength would have enhanced performance

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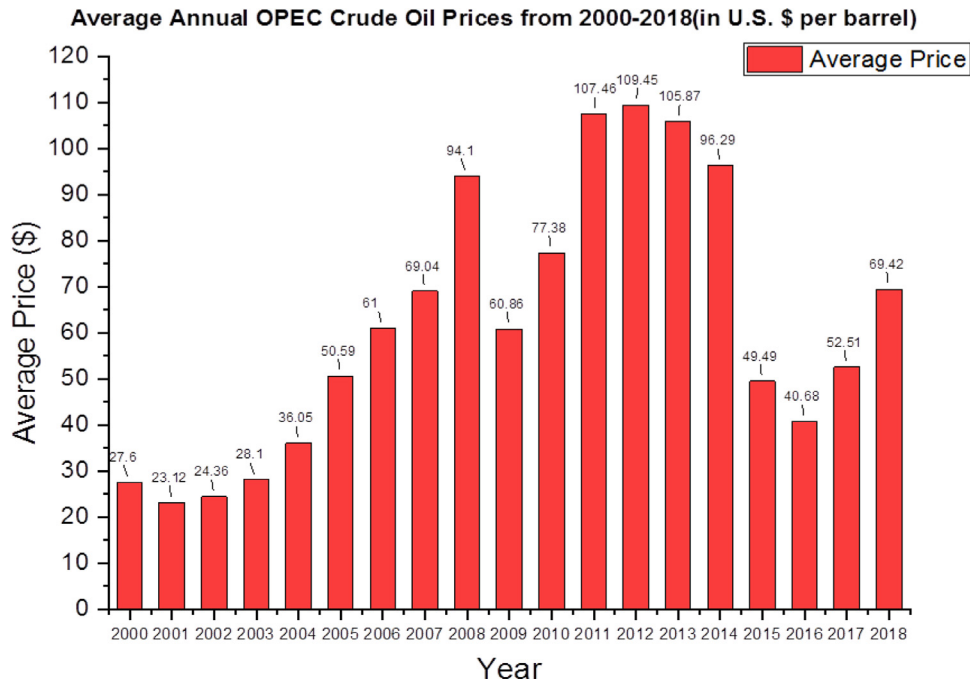


Fig. 1. Average annual crude oil prices for the last 18 years in U.S. dollars per barrel.

across diverse testing conditions, in various engineering applications.

The lightweight materials in structural applications are an excellent alternative as they can enhance the efficiency of the automobiles and also reduce the carbon dioxide emissions. This is achieved through reduction of an automobile mass. The improved efficiency is economical to the consumer as it reduces the fuel consumption thus reducing the burden on the limited resources.

As an illustration, if the weight of a passenger car is reduced by approximately 10%, fuel savings of 20% to 30% can be achieved without any major modifications in the vehicle design [2]. Light weighting, therefore, has become an integral part of an automobile design and manufacture. For light weighting, a noteworthy factor is the selection of material and its application. Among various advanced materials, magnesium alloys are the lightest in comparison to their counterparts, i.e., high strength steels and aluminium alloys. Hence magnesium is being used in various structural applications like steering wheels, instrument panel beams, from a long time [3]. Although need of magnesium and its alloys have increased, the evolution has not been as expected. This is due to the low capability of magnesium to resist corrosion.

1.2. Magnesium “the one-off metal”

Magnesium, a lightweight metal, is currently utilized in various engineering applications. It represents 2.7% of earth’s crust, making it the eighth most abundant element available [4]. Magnesium doesn’t exist in its elemental form, only magnesium compounds are found. MgCO_3 (magnesite), $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (carnallite) and $\text{MgCO}_3 \cdot \text{CaCO}_3$ (dolomite)

Table 1
Physical Properties of Mg [5].

S.No.	Material Property	Numerical Value
1	Density (at 20 °C)	1.738 g/cm ³
2	Melting Point	(650 ± 1) °C
3	Boiling Point	1090 °C
4	Thermal Conductivity (at 27 °C)	156 W m ⁻¹ K ⁻¹
5	Specific heat capacity (at 20 °C)	1.025 kJ kg ⁻¹ K ⁻¹
6	Latent heat of fusion	360 to 377 kJ kg ⁻¹
7	Latent heat of vaporization	5150 to 5400 kJ kg ⁻¹
8	Latent heat of sublimation (at 25 °C)	6113 to 6238 kJ kg ⁻¹
9	Heat of combustion	24.9 to 25.2 MJ kg ⁻¹
10	Linear coefficient of thermal expansion	29.9 × 10 ⁻⁶ °C ⁻¹

are the most common compounds [5]. The crystal structure of magnesium is hexagonal close packed (HCP). With that structure, the physical properties of magnesium are a matter of interest. Some of the physical properties at ambient temperature are listed in Table 1.

Magnesium, lightest among structural metals, has 1.74 g/cm³ density. The low density and high specific strength (approximately 130 kNm/kg) of magnesium-based materials make them widely useable for weight-critical applications. However, its other properties such as ductility, corrosion and creep are yet to be completely researched [6]. Some of the mechanical properties of pure magnesium are presented in Table 2. The hardness values represented are at 500 kg load using a 10 mm diameter ball. All the denoted values in Table 2 are studied at room temperature (20 °C).

After steel and aluminium, magnesium stands third in its usage as the structural element. Magnesium is the most active of all engineering materials [10, 11]. The use of magnesium is limited in many applications due to its ability to corrode, es-

Table 2
Mechanical Properties of pure Mg at room temperature (20 °C) [5, 7–9].

Mechanical Property	Annealed Sheet	Hand Rolled Sheet	Sand Cast	Extruded
Compressive Yield Strength (MPa)	69 to 83	105 to 115	21	34 to 55
Tensile Yield Strength (MPa)	90 to 105	115 to 140	21	69 to 105
Ultimate Tensile Strength (MPa)	160 to 195	180 to 220	90	165 to 205
Hardness (HB)	40 to 41	45 to 47	30	35

pecially in applications where there is exposure towards aqueous solutions like *in vivo* and aggressive environments [12]. But magnesium and its alloys have a lower rate of corrosion than its steel and aluminium counterparts [10, 11]. Galvanic corrosion is the most influencing factor because magnesium corrodes when coupled with materials like steels, SS (stainless steels), Cu alloys (copper alloys), Al alloys (aluminium alloys), Ti alloys (titanium alloys). High purity magnesium (Mg) has the lowest rate of corrosion because it has alpha Mg in its microstructure. This alpha magnesium (Mg) is formed by normal cooling from the melt of Mg having impure elements like iron, nickel, copper, cobalt, less than the tolerance limit [12].

The benefits of magnesium and its alloys have created a reputation among the researchers. The alloys of magnesium are also under intense scrutiny as biodegradable implants due to the biocompatibility of magnesium with good mechanical and physical properties [13–16]. The density of magnesium is nearer to the cortical bone (1.75 to 2.1 g/cm³) [17]. Moreover, the biocompatibility promotes bone formation [18]. Magnesium alloys are less susceptible to hydrogen porosity and are extremely fluid. Hence their castability is better than aluminium and copper [19]. As compared to aluminium, magnesium can be die cast at 50% higher rate. Electromagnetic shielding and versatility (can be processed through extrusion, rolling) are the other unique properties of magnesium [5, 20]. The energy of any material is absorbed by magnesium due to its outstanding damping capacity. This makes it suitable for load enduring applications [5]. Magnesium has high machinability (ease of machining), hence, intricate designs can be easily machined with acute dimensional accuracy [21]. This is an essential aspect for medical applications [22–24]. Magnesium has a higher thermal conductivity than polymers and is completely recyclable, unlike polymers [25]. In fact, the heat dissipation is 100 times better in magnesium than plastics.

Even with the above-mentioned benefits, the usage of magnesium and its alloys is restricted. The major cause is the high degradation rate of magnesium. The material properties can be enhanced and tailored as desired by adding various alloying elements but there is always a certain compromise in terms of corrosion resistance [26]. This aspect has to be carefully monitored depending on the application. Magnesium burns in air due to rapid oxidation. Magnesium powder is pyrophoric in nature [6]. The as-cast pure magnesium has a low strength (20 MPa) with high rate of corrosion. Also, the release of hydrogen gas when in contact with the air, results in corrosion of magnesium [27]. Hence the manufacturing process of

magnesium alloys becomes complicated. Moreover, the selection of the appropriate alloying element becomes a precarious aspect of manufacturing.

1.3. The Review in brief

The discussions in the article so far converge to the fact that magnesium has all the benefits to replace the existing alloys of steel, aluminium in various structural applications. The moderate cost per unit volume of magnesium can make it one of the most sought-after lightweight materials across various engineering applications like the automobile sector, aerospace industry, medical field etc. This is not the case, as low corrosion resistance is a major hindrance. Furthermore, the volatile nature of magnesium complicates the manufacturing process of components using magnesium and its alloys. Additionally, a fitting alloying element is to be considered to enhance the material properties of magnesium alloy. If not, the adverse effect will lead to an enhanced corrosion rate in the alloy.

Therefore, the present review is aimed at a comprehensive analysis of all the aspects associated with magnesium and its alloys which will help in better understanding of this unique metal. The negative effects of corrosion, its cause, the types and the various techniques to measure corrosion are broadly discussed. A detailed explanation of various manufacturing techniques suitable for the preparation of alloys is conversed. The secondary manufacturing techniques necessary for the betterment of material properties are briefly discussed. The alloying elements compatible with magnesium are briefed and the effect of each alloying element on the material properties is widely elaborated. The different types of alloys that can form with magnesium are elucidated. Lastly the role of Mg and its alloys in the area related to automobiles, aircrafts (structural applications) are discussed. Advancements in the use of magnesium alloys in battery are also discussed. Moreover, an in-depth discussion of magnesium alloys in the medical field as biodegradable implants is carried out.

An attempt in this review paper has been done to compile all the information related to magnesium and its alloys. The problematic areas and the solutions pertaining to any issues related to magnesium have been specified. Details of pros and cons on all the debatable areas where further research is necessary have been provided. The current advancements related to this field have also been covered. An important feature of this wide-ranging review is to provide a learning medium where the researchers can access all the information related to magnesium and its alloys which shall stimulate better ideas

for future development. This will provide an opportunity to identify the research gaps in this field and probably further advancements, shall ensure, broader applications of this unique material. Lastly, magnesium, a cost-effective material, with admirable properties but very restricted usage can be termed as an excellent future scope in this field of research. A break-even point is to be arrived at, where the demerits of magnesium are completely wiped out and this lightweight element finds a larger share in the industrial sector, especially at a critical time where light weighting has become necessary.

2. Magnesium Alloys

2.1. Influence of alloying elements on Mg alloys

As-cast magnesium has poor strength and excessive degradation rate [28]. The material properties, hence, can be enhanced by appropriate alloying and processing technique. Chemically active magnesium forms intermetallic compounds by reacting with alloying compounds [29]. It is these intermetallic phases, observed in magnesium alloys, influence the microstructure, thereby impacting the material properties [30]. Mechanical properties are strengthened directly by the alloying elements through precipitation hardening, grain-refinement strengthening and solid-solution strengthening [31]. Elements having high temperature-dependent solubility are to be alloyed with magnesium to strengthen its matrix. The element's atomic size w.r.t magnesium, its valence are the key parameters influencing solubility [5, 32]. The HCP (hexagonal close-packed) structured Mg (magnesium) ($c/a = 1.624$) and 0.320 nm atomic dia. ensures the formation of solid solutions with various elements [32]. The most common alloying elements and their effects on magnesium alloy are mentioned briefly in Table 3.

The influence of each of these alloying elements can be associated with the number of alloying elements and the percentage of the alloying element. A certain important aspect in relation to the alloying elements are to be noted.

2.1.1. Aluminium

It has the most positive influence on magnesium. The strength of an alloy is enhanced by 180 MPa due to the presence of aluminium. Hence, it's the most commonly alloyed in Mg (magnesium) alloys. The heat treatment of an alloy can be carried out if it has more than 6% weight of aluminium [5]. The solubility of Al in magnesium is about 12 wt.% but this is influenced by the temperature. aluminium is less soluble at ambient temperature in alloys rich in Al content. More than 3 wt.% of Al enhances the corrosion rate by increasing the cathodic reaction [33]. Below the boundary of solubility, the kinetics at anode are reduced when Al is added to Mg. Al enhances the vulnerability towards stress corrosion cracking in alloys with significant quantity of β -phases [34].

2.1.2. Arsenic

It has the ability to reduce the rate of corrosion by hampering the occurrence of the cathodic reaction. Hence, arsenic

Table 3

Some alloying elements and their effect on Mg [26].

Alloying element	Influence on material properties of mg alloys
Aluminum (Al)	increases hardness, strength and castability
Beryllium (Be)	Reduces surface melt oxidation
Calcium (Ca)	Improves corrosion resistance, creep resistance and grain refinement
Cerium (Ce)	Increases elongation and work hardening rate. Reduces yield strength
Copper (Cu)	Increases ambient temp., high temperature strength. Reduces ductility
Iron (Fe)	Harmful to corrosion resistance
Lithium (Li)	Increases ductility and decreases strength
Manganese (Mn)	Improves salt water corrosion resistance
Molybdenum (Mo)	Increases hardness, young's modulus and ductility
Nickel (Ni)	Improves YS and UTS. Reduces corrosion resistance
Neodymium (Nd)	Strength is increased
Silicon (Si)	Improves fluidity
Silver (Ag)	High temp. strength, creep resistance is elevated
Strontium (Sr)	Enhances creep and corrosion resistance, grain refinement. Increases bone mass
Thorium (Th)	Creep strength is enhanced up to 370 °C. Increased weldability with zinc in alloys.
Tin (Sn)	Ductility increases with Al in Mg. Enhanced corrosion resistance, compressive strength
Titanium (Ti)	Increased ductility and yield strength
Yttrium (Y)	Improved creep resistance and high temperature resistance.
Zinc (Zn)	Yield stress is enhanced and corrosion resistance is improved
Zirconium (Zr)	Excellent refiner of grain structure

is also termed as cathodic poison since it stops the recombination of hydrogen. Adding 0.37 wt.% of arsenic will lead to the formation of Mg_3As_2 which reduces the rate of corrosion [34].

2.1.3. Bismuth

Addition of bismuth aggravates the reactions at both cathode and anode leading to enhancement in corrosion. It improves the creep and tensile characteristics by restricting the sliding of grain boundaries [34, 35].

2.1.4. Beryllium

Small quantities of beryllium (less than 30 ppm) are added which coarsen the grains. A higher amount of it will lead to a negative effect on magnesium as it is detrimental on the corrosion resistance. Beryllium controls the oxidation of the Mg melt at the time of casting. The solubility of beryllium is low in the alloys of Mg.

2.1.5. Calcium

In equilibrium conditions, calcium is 1.34% soluble in magnesium [28]. It improves the mechanical and thermal properties of magnesium alloy [36, 37]. In casting magnesium alloys, during heat treatment, calcium reduces oxidation process. Better rollability of magnesium sheets can be achieved by calcium but if the percentage is more than 0.3 then, during welding, the sheet will develop cracks [5]. In biomedical

applications, only 1 wt.% is the acceptable levels of biocompatibility for adding calcium to magnesium [28]. Beyond the limit of solubility (around 1.34 wt.%), the rate of corrosion in Mg alloys is extremely high.

2.1.6. Copper

Copper has a negative influence on corrosion resistance as it has less solid solubility in magnesium [4, 5]. Copper forms Mg_2Cu with magnesium. The usual tolerance limit of copper in Mg is 0.1 wt.% but in the presence of Al and Mn in the alloys, the tolerance limit reduces to 0.01 wt.% [34].

2.1.7. Iron

Up to a percentage of 0.005 of iron, is acceptable for corrosion resistance in magnesium beyond which it is harmful. It is commonly found in Mg alloys as an impurity. The extremely low soluble nature of Fe in magnesium (about 0.001 wt.%), allows it to be in pure state.

2.1.8. Lithium

Lithium has a low density of 0.54 g/cm^3 and is highly soluble in magnesium [4]. Research on Li suggests that it can influence the ductility of a material by modifying the crystal structure.

2.1.9. Manganese

The addition of manganese (Mn) to magnesium is reduced due to its low solubility (2.2 wt.%) in magnesium. But adding Mn as a binary element in the alloys of Mg (up to 5 wt.%), exhibited no significant change in the rate of corrosion. Hence manganese is used along with other alloys like aluminum. Manganese is an important element in human body which is crucial for a healthy bone structure. Manganese plays a vital role in prevention of osteoporosis as it helps in bone formation and bone metabolism [28]. In the Mg alloys, to alleviate the influence of Fe, Mn should adhere to the Fe/Mn ratio of 0.032 (maximum limit) beyond which the corrosion rates enhance radically [38]. Recent studies emphasize on the encapsulation of Fe by Mn in the aluminium free alloys of Mg. This is a promising aspect as Mn can be extremely influential in the sequestration of Fe even when Al is absent [39].

2.1.10. Molybdenum

Molybdenum does not alloy with magnesium as it is insoluble in it [4]. But adding 0.1 wt.% of Mo at micro level, to the AZ91E alloy, enhanced the corrosion current density of the alloy.

2.1.11. Nickel

The solid solubility of Nickel is limited in magnesium [4]. The Mg_2Ni intermetallic is formed due to incorporation of nickel in magnesium [40].

2.1.12. Cerium

The REE (rare earth elements) improve high thermal strength, corrosion and creep resistance in magnesium. The freezing range of magnesium alloys is also reduced by rare

earth elements [30]. The anti-corrosion property of Mg alloys (magnesium alloys) is reduced if the silicon is added along with iron.

Only 0.2% of cerium is to be added to magnesium for a significant elongation. Enhanced plastic deformation capability is observed at recrystallization temperature due to the presence of cerium in magnesium alloys, in extruded rods [41]. In binary alloys of Mg-Ce, the rate of corrosion is enhanced by the presence of cerium. The reason for this is $Mg_{12}Ce$ compound which improves the cathodic kinetics [42]. The wrought alloys of Mg don't have the combination of RE and Al because Al_xRE_y compounds are formed which hamper the ductility of the alloy. According to previous studies, Ce enhances the surface layer stabilizing the hydroxide of Mg [43].

2.1.13. Erbium

Much research hasn't been done on Er. According to previous studies, adding 2 to 3 wt.% of Er reduced the rate of corrosion in the alloys of Mg-2 to 3 Al wt.%, over AM60 in the buffer solution of borate [44].

2.1.14. Gadolinium

It is highly soluble (more than 10 wt.%) in Mg. When Gd is added to Mg-Al alloys, the phases of Al-Mn-Gd and Al_2Gd are formed which consume Al and the volume fraction of the $Mg_{17}Al_{12}$ is diminished [45]. This, therefore, might reduce the reaction rate at the cathode [46]. This phenomenon is usually observed in the Mg-Al alloys containing RE elements. The influence of Gd is complicated in the alloys of Mg because heterogeneous mixtures are obtained and the content of Al is reduced. Hence, the corrosion tests carried out in the long term indicate higher rate of corrosion in the alloys of Mg which constitute of Gd. Also, previous studies support that Gd is usually unfavorable for corrosion [34].

2.1.15. Holmium

There hasn't been much research done on the influence of Ho in Mg alloys. But based on the studies done so far, Ho reduces the corrosion rate when added in quantities of 0.24 wt.% and 0.44 wt.% to the alloy of Mg-Al (AZ91D). The intermetallic compounds of Ho and the reduced volume fraction of $Mg_{17}Al_{12}$ are the reason for this. One of the previous studies suggest that Ho in Mg-Al alloy marginally reduced the rate of cathodic reaction but the rate of mass loss was 10 times lower than the base alloy. This might decrease the strength of alloy and have a similar impact as that of reduction of Al content within the alloy. Ho also adds to the uniformity and compaction to the corrosion layer due to higher amount of Al present. But more research is to be done to ascertain this statement.

2.1.16. Lanthanum

Adding Lanthanum (3 to 5 wt.%) above its limit of solubility to the alloys of Mg, enhances the corrosion rate due to the formation of $Mg_{12}La$ phase which increases the cathodic activity [42]. But La, when added fundamentally, to the alloys

of Mg-Al, brings a microstructural change in the alloy (similar to Ce), producing needle shaped phases of Al-La. It also modifies the $Mg_{17}Al_{12}$ into continuous fine polygon shaped structure. Previous studies support the reduction in the rate of corrosion of AZ91 alloy in 3.5 wt.% of NaCl, upon addition of 0.5 wt.% La. Microstructural refinements and higher shielding corrosion films have been considered to be the reason for reduced corrosion rate [47]. In the alloys of Mg-Al, adding La above its limit of solubility will decrease the resistance against corrosion due to the formation of rough phase of Al-La [34].

2.1.17. Neodymium

The formation of Mg_3Nd phase in the binary alloys of Mg-Nd increases the rate of corrosion as Mg_3Nd is a better cathode than Mg in pure form leading to the increase in corrosion kinetics as the concentration of Nd is elevated. But corrosion rate increase is lower in case of Nd, as compared to La or Ce. Resistance against corrosion is enhanced in Mg-Al alloys by Nd because, it reduces the galvanic coupling occurring in Nd free alloys of AZ or AM. Moreover, Nd influences the production of a shielded oxide layer on the surface comprising of Mg and rare earths. But this theory has to be further investigated to be cemented.

2.1.18. Yttrium

Adding yttrium (around 2 to 18 wt.%), to the binary alloys of Mg-Y increases the rate of corrosion due to the increased volume fraction of $Mg_{24}Y_5$ and improved kinetics of corrosion [48]. Studies suggest that Y in AZ91 alloys enhances the corrosion properties when added in quantities of 0 to 0.8 wt.% [49]. This is due to the reduction and enhanced homogeneous dispersion of $Mg_{17}Al_{12}$. The microstructural refinement contributed towards the reduction in the rate of corrosion. High solubility of Y resulted in the existence of hardenable alloys making Y an important element in the commercial WE43 and WE54 alloys.

2.1.19. Silver

Silver in magnesium alloys, is used along with rare earth elements [30]. The addition of silver in Mg has a tolerance of around 0.5 wt.%, beyond which the rate of mass loss has a monotonous increase. The intensity of improvement in corrosion rate by silver is similar to that of calcium. There was a significant enhancement in strength of Mg-RE-Zr alloy because silver (less than 2 wt.%) improved the response of age hardening. Adding Ag to AZ91 increased the hardness without losing the corrosion characteristics due to the interaction among $Mg_{17}Al_{12}$ and silver [34].

2.1.20. Strontium

Strontium is a vital element in human body. It prevents bone resorption by supporting the growth of osteoblasts. Similar to silver, strontium is also used with other alloys in magnesium. Strontium is 0.11 wt.% soluble in magnesium [28]. Sr has the ability to form $Mg_{17}Sr_2$ when alloyed as a binary element along the boundaries of grains. The corrosion rate is

extremely high in Mg when strontium is added, as it boosts the corrosion potentials and overall rate of corrosion.

2.1.21. Tin

Tin is nontoxic but tin salts may be carcinogenic. Tin is believed to be useful for health in humans but function for tin has not been identified. The biological role of tin is still undefined and unidentified [28]. Tin forms Mg_2Sn about the boundaries of the grains and there is an increase in the volume fraction of Mg_2Sn with increasing quantity of Sn [34].

2.1.22. Zinc

Mg alloys with zinc, have enhanced weldability by alloying thorium. But it is replaced by another element due to its radioactivity. Tin reduces cracking in forging of Mg alloys. The mutual solubility of magnesium and titanium is very limited [4]. Zinc is most effective and common in magnesium alloys [50]. It is used along with aluminium to improve the strength. Zinc overcomes Ni and iron impurities to improve corrosion resistance of Mg alloys (magnesium alloys) [30]. The tolerance limit for zinc in Mg is 2.5 wt.% [34]. But reports suggest higher corrosion rates with increase in concentration of Zinc from 1 to 3 wt.% [51]. Further increase in concentration of zinc exhibited an inclination to stress corrosion cracking [52]. In the human body, zinc is the most essential nutrient. The bones and muscles contain more than 85% of Zn. 6.2 wt.% of zinc is soluble in magnesium [28]. In biocorrosion, zinc reduces the hydrogen evolution [50]. Though the zinc alloys have similar strength as that of magnesium alloys, their higher young's modulus might have a negative effect on healing process in biomedical implants due to non-uniform transfer of load between implant and bone [28].

2.1.23. Zirconium

It is an excellent refiner of the grains when used with the alloys of rare earth metals, or zinc, or thorium and their combination. It forms stable compounds with aluminium and manganese. Therefore, zirconium cannot be used with these alloying elements. Zr results in the purification of alloys of Mg as it combines with iron to form Fe_2Zr , allowing it to settle at the below the molten metal by the action of gravity. This produces purer castings of high quality. In the magnesium melt, it also combines with the hydrogen, carbon, oxygen and iron to form stable compounds [28]. There are no intermetallic compounds formed since zirconium is least soluble in Mg. Studies conclude that Zr is detrimental to corrosion but the impact is unique [39]. Zr has the ability to promote the reactions at anode which would have a negative impact on the surface film. Hence the quantity of Zr should be apt in order to prevent the harmful effects of it on the corrosion.

2.2. Classification of Magnesium alloys

The nonferrous alloys of titanium, aluminum and magnesium have wide applications in the areas of technology. They

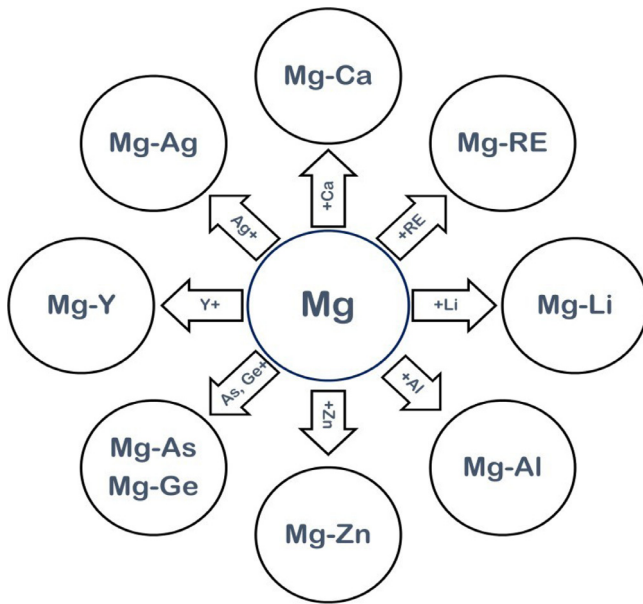


Fig. 2. Common magnesium alloys [6].

are considered as the best suited alternatives to steel in structural applications due to their unique properties [53]. Among these (Ti, Al, Mg), magnesium and its alloys are the lightest structural metals. Hence, with the advancement in technology, the use of Mg alloys (magnesium alloys) has increased in the recent past in structural and biomedical areas. In the formation of alloys, the compatibility of Mg is to be studied along with its alloys in other engineering materials.

The classification of Mg alloys based on their processing technique can be categorized as, cast magnesium alloys (Mg alloys), wrought magnesium alloys, for applications of engineering, R&D (research and development). Magnesium alloys produced through die and other casting techniques are cast alloys. In the recent past, cast alloys have been used for commercial and industrial applications [54, 55]. But the applications of cast magnesium alloys have been limited to areas where the moderate mechanical properties are in demand [56]. The wrought alloys of magnesium are the ones that are produced through secondary manufacturing processes like extrusion, forge pressing, rolling, SPD (severe plastic deformation) and ECAP (equal channel angular pressing). Apart from grain refinement, plastic deformation and severe plastic deformation (SPD) are also the effective ways of grain size refinement in the microstructure [57]. The mechanical properties of wrought Mg alloys are superior in comparison to cast Mg alloys. Uniform microstructural composition and well-defined grain refinement without pores are the main reasons behind this [58]. Some of the common alloys of magnesium (cast alloys and wrought alloys) are shown in Fig. 2. The alloys may be binary, ternary or quaternary depending on the number of phases present in the alloy and also it depends on the number of alloying elements existing.

2.3. Cast and extrusion alloying systems of magnesium

2.3.1. Mg-Al Based alloys

The solubility of aluminium in Mg is very high (12.7 wt.%) at 437 °C (eutectic temperature). The α -Mg and

γ -Mg₁₇Al₁₂ phases are formed when Al dissolves Mg matrix, leading to solid-solution strengthening. The castability of Mg–Al-based alloys is excellent but has mediocre mechanical properties. It shows good resistance to corrosion which improves with increasing amount of aluminium [31, 59]. Zinc and manganese (Mn) are the common additions to Mg–Al-based extrusion alloys with a concentration of 1 wt.%. The major series of Mg–Al based alloys are AZ, AM and AE [58] among these AZ31, AZ61, AZ81, AZ91 [59] and AM60 are the most investigated as biodegradable materials. In AZ31, alphabets A and Z represent the alloying components aluminium and zinc. The numbers 3 and 1 represent the % composition of each alloying element in the order of their appearance (3% Al and 1% zinc). AM series alloys of AM30, AM40, AM50, AM60 come under the alloys of Mg inclusive of Al, Mn but with higher amount of aluminium (Al) [60, 61]. The AM alloys exhibit higher extrudability and mechanical properties than AZ alloys as Zn-containing eutectic ternary phases is absent [62]. In the Mg alloys, zinc is added to strengthen the solute whereas Mn improves anti-corrosion properties by removing traces of Fe from the alloy [63]. The age hardening due to Mg₁₇Al₁₂ is negligible in Mg–Al alloys like AZ31 due to low volume fraction and rough precipitate distribution but higher in case of AZ80 [64, 65]. The as-extruded Mg–3.5Al–3.3Ca–0.4Mn, is the strongest among Mg–Al alloys with a yield strength of 410 MPa having the highest tensile yield strength of an RE free alloy [66]. Around 70% of the grains in the microstructure have been recrystallized with an average grain size of 1.2 μ m. This is due to the small grain size and precipitate population [67].

AZ Series. The strength and creep of Mg–Al alloys increases with the addition of calcium (Ca), as it forms a stable Al₂Ca phase with a melting temperature as high as 1352 K [68]. There was a significant grain refinement when 1.7 wt.% Ca was added to an extruded Mg–2.32Al alloy. This improved the UTS (ultimate tensile strength), YS (yield strength) and elongation to 324 MPa, 275 MPa and 10.2%, respectively. The optical images in Fig. 3 clearly justify this where the presence of sharply broken Al₂Ca phase is noticed [69]. Hence the enhanced mechanical properties are obtained.

When AZ31 alloy containing Ca was compared with AZ31 alloy without Ca, the AZ31 alloy containing calcium performed better with higher ductility and finer grains after thermomechanical processes. Moreover, the investigations of hot compressive behavior done on extruded 0.5 wt.% Ca–AZ31 alloy by Kwak et al. suggested that Ca refined the grains and produced a more homogeneous structure [70]. Though the alloy had better formability at high temperatures, the formability was poorer at low temperatures. This is due to the dispersion of Al₂Ca phase in the matrix at higher temperatures promoting dynamic recrystallization and hampering the coarsening of grains.

Lithium (Li) added to Mg–Al alloys, has the potential to optimize its microstructure. This is due to low density of Li which promotes cross slip and non-basal slip [71, 72]. Due to high solubility of lithium in magnesium alloys (5.5 wt.%)

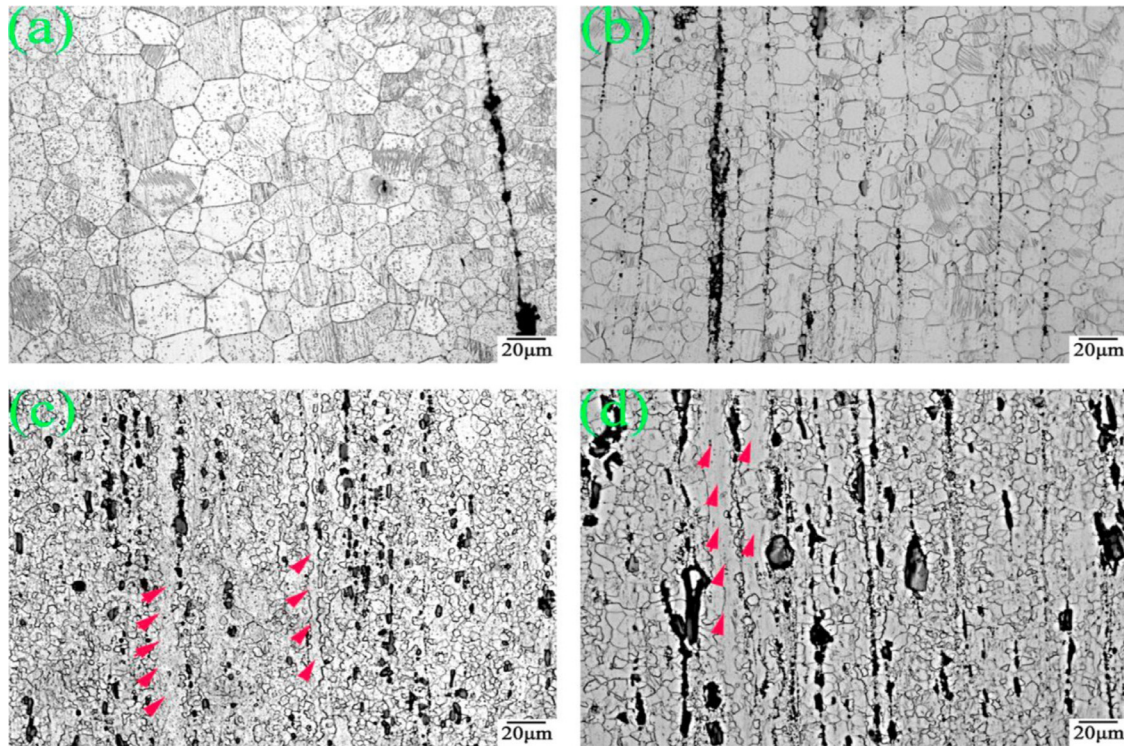


Fig. 3. Optical images of the as-extruded alloys: (a) Mg-0.61Al-0.46Ca; (b) Mg-1.34Al-1.03Ca; (c) Mg- 2.32Al-1.70Ca; (d) Mg-3.74Al-2.52Ca [69].

at room temperature), the lattice parameters of magnesium solid solutions are altered [73]. With the increase in the addition of lithium, the rotation of basal poles increased in transverse direction and the basal structure intensity got reduced which is generally high in as extruded AZ31 sheet. Further, the orientation of the grain boundaries also became random. Further lithium enhanced the ductility and reduced the planar anisotropy of AZ31 alloy due to this modified structure and recrystallized grains but no significant influence on the tensile strength is seen. High tensile strength (233.38 MPa) and elongation (9.2%) were observed by Meng et al. in as-rolled Mg-1Al-1Zn-8Li with high level of lithium content [74].

The high temperature mechanical properties of Mg-Al alloys are enhanced due to the addition of strontium (Sr) because it forms a stable Al_4Sr having a high melting point of 1013 K [75]. A study on double hot extruded AZ80, addition of 0.02 wt.% strontium lead to the increase of UTS and elongation to 355 MPa and 13.2% respectively [76]. But another contrasting study also suggested that Sr reduces the aluminium's solubility in magnesium alloys as it hinders the formation of $\beta\text{-Mg}_{17}\text{Al}_{12}$. This negatively effects the mechanical properties at high temperatures [77].

In Mg-Al alloys, $\beta\text{-Mg}_{17}\text{Al}_{12}$ is both discontinuous and continuous precipitates [78]. The previous research on the influence of tin (Sn) content on AZ91 precipitates suggested that increasing tin (Sn) content could substantially restrict the discontinuous $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitates production [79]. However, more addition of Sn (up to 4 to 5 wt.%) not only reduces

discontinuous precipitates but also improves the mechanical property in comparison to Sn free AZ91 alloys. This is due to increased density of plate shaped fine continuous precipitates [80, 81]. The Mg-Al alloys exhibit superior mechanical properties at higher temperatures because the melting point of β phase is much lower than Mg_2Sn phase [82, 83]. The ductility of Mg-Al based alloys is enhanced by adding Sn as it may also reduce the stacking fault energies in the alloy [84]. Results of Wu et al. suggested that in high ratio hot extrusion, the grains in AZ91 are refined considerably by addition of tin (Sn). The restriction of small Mg_2Sn precipitates on grain boundaries migration is the reason behind this. With the addition of 3 wt.% Sn, the UTS and elongation of as-extruded AZ91 became 380 MPa and 8% respectively [85].

The rare earth elements (RE) are usually added to Mg-Al based alloys to accelerate the formation of thermally stable (Mg, Al) xREy phases. Due to this, the mechanical properties of wrought magnesium alloys are improved at elevated temperatures [86]. Pan et al. conducted experiments on as-extruded AZ31 to study the influence of yttrium (Y) on the mechanical properties and its microstructure. High yield strength (YS) of 209 MPa was observed when 0.5 wt.% Y was added. The formation of Al_2Y phase could have been the reason for this high yield strength [87]. Similarly, in the hot-rolled AZ61, Al_2Y phase increased and $\text{Mg}_{17}\text{Al}_{12}$ phase decreased when Y content was increased. For 0.9 wt.% of Y, the optimal mechanical properties of 258.9 MPa (yield strength), 371.9 MPa (tensile strength) and 7.33% (elongation) were obtained. The fine refined grains of Al_2Y are

responsible for the exceptional mechanical properties. But coarse and brittle Al_2Y phase was detected in 1.4 wt.% of Y content. This reduced the tensile strength of the alloy [88]. In Mg–Al–Gd alloy, processed by high frequency induction melting, needle-like precipitations were seen which included LPSO phases and Mg_5Gd post heat treatment [89]. These needle-like precipitations formed on the surface, improve corrosion resistance in heat treated alloys of T4 and T6 in NaCl (1 wt.%) [90]. But aluminium is toxic towards the neurons and might lead to increase in Alzheimer's disease. Accumulation of aluminium in the brain and alteration in the amino acids is the reason behind neurotoxicity of aluminium [91]. The direct influence of aluminium depends on the binding of aluminium with different cells in the brain, but astrocyte interaction obstructs Na^+ , K^+ and Ca^{2+} ATPase leading to cellular changes and also death.

AM Series. The alloys in AM series like AM50, AM60 have balanced properties like ductility, room temperature strength, and high corrosion resistance. Their applications are in instrument panels and steering wheels which require properties like ductility and toughness. But, due to their modest mechanical properties during elevated temperatures, their application is confined to temperatures of 120 °C. Precipitation of rough phase of $\text{Mg}_{17}\text{Al}_{12}$ within the eutectic area of inter dendrites is the reason behind their low mechanical properties at high temperatures [92]. The mechanical properties of AM series alloys can be enhanced by the addition of rare earth elements. With a constant 1.2 wt.% of RE, investigation on AM50–1RE alloys was done. The influence of La–Ce ratio on mechanical properties and microstructure was analyzed [93]. It is suggested that lanthanum (La) or cerium (Ce) can improve the ultimate and yield tensile strengths without any compromise on the elongation. The grain size in AM50–1La alloy suggested at a better strengthening of lanthanum (La) than Ce. But, adding both La and Ce together to AM50 alloy, decreased its mechanical properties. It formed a coarse and reduced $\text{Mg}_{17}\text{Al}_{12}$ phase. In the analysis of as-cast, hot rolled Mg–3Al–0.5Mn–0.5Zn–1 metal matrix (AM30–0.5Zn–1 MM) alloy, a significant improvement in the grain size (from 240 μm to 7 μm) was seen after hot rolling [94]. The rough $\text{Al}_{11}\text{RE}_3$ and $\text{Al}_{10}\text{Ce}_2\text{Mn}_7$ phases formed due to addition of Ce were broken into smaller sections. The hot rolling process prominently enhanced the mechanical properties with an ultimate tensile strength of 300 MPa and yield strength of 230 MPa. The strengthened grain boundaries, the dislocation slip with improved second phases and enhanced dislocation density are the primary reasons for improved properties. The AM50–2Nd alloy was hot rolled to enhance its mechanical properties by adding 2 wt.% of Nd. It exhibited good thermal stability as no rough grains were seen even at 250 °C during annealing process [4].

The scarcity and expense of REE (rare earth elements) forced for alternative alloying elements such as Ca (calcium), tin (Sn). The refinement of grains is possible by adding Ca. It improves the property of ignition proof whereas Sn enhances the creep resistance. Investigations were done on as-extruded Mg–Al–Mn–Ca for its mechanical properties at ambient and

elevated temperature [57]. It exhibited high mechanical properties at elevated temperatures with modified yield anisotropy when at increased temperature of 150 °C. Fine and thermally stable Al_2Ca and Al–Mn phases with activated non-basal slip are the main reasons for this.

The as-extruded AM30–1Sn–xLi alloys exhibited a significantly increased elongation from 16% to 35% when the lithium content was increased from 5 wt.% to 11 wt.% but a marginal decrease in its ultimate tensile strength was noticed. The change of its structure of crystal from HCP to BCC is the reason [95].

2.3.2. Mg–Zn Based alloys

Zinc (Zn) is another efficient alloying element barring aluminium due to which it has a frequent use. Contrasting to aluminium, zinc is biocompatible as it is one of the key elements present in the body. Hence it is also used for biomedical application. It has a major portion among all the alloying elements in Mg–Zn alloys. The major constituents of Mg–Zn alloys are α -Mg matrix and γ -MgZn phases [96]. At 340 °C (eutectic temperature), Zn has the highest solubility in magnesium (6.2 wt.%) but, at 150 °C this solubility drastically reduces to approximately 2.6 wt.% [97]. The increase in zinc content increases YS (yield strength) of Mg–Zn alloy but the max. UTS (216.8 MPa) and 15.8% of elongation are obtained only at 4 wt.% of zinc [97]. The mechanical properties of Mg–Zn based alloys can be enhanced by the addition of alloying elements like calcium, zirconium, yttrium, strontium, silicon and manganese [98].

Mg–Zn–Ca alloys. The researchers have shown interest on Mg–Zn–Ca alloys as they are cost effective and they portray outstanding mechanical properties. Also, calcium is a good refiner of grains in Mg based alloys [98, 99]. The disadvantage with calcium is that mechanical properties of Mg alloys decrease with the increase in Ca content beyond 1%, as its solubility in Mg alloys is only 1.34 wt.%. The alloy of Mg–1Zn–0.5Ca, in hot extruded state, indicated excellent mechanical properties at ambient temperature. This is due to refined grains and weakened basal texture. The material had 44% elongation, 105 MPa YTS and 205 MPa UTS. Interestingly, with increase in extrusion temperature, the alloy's ductility increased but its strength decreased [100]. At 583 K, the highest UTS (300 MPa) was recorded due to partial recrystallization of its microstructure and development of sharp basal texture. Experiments with low Ca and Zn content (1 wt.% of each) were conducted on extruded Mg–Ca–Zn–Zr alloy. It had an elongation of 11% but a higher strength of 306 MPa [101]. Dynamic recrystallization and Zener pinning of fine precipitates refined its microstructure. The strength of extruded Mg–Zn–Ca alloys increases by adding Zr and Mn [102]. In Mg–6Zn–0.2Ca alloy (ZX60), addition of 0.8 wt.% of Zr showed a major increase in its tensile yield strength from 148 to 310 MPa [102]. In the extrusion, the recrystallization is suppressed by Zr by which smaller precipitates will have a denser distribution [103]. A high yield strength (309 MPa) was seen in the extruded Mg–Zn–Ca–Mn quaternary alloy at 300 °C with the speed of ram being 1 mm/s. It exhibited a balanced

ductility and yield strength when zinc, manganese and calcium were added in diluted state [104]. The extrudability of the alloy is improved by maximizing its specific strength. This is possible by low alloy density which can be done by a low concentration of the alloy. This cost-effective technique of diluted Mg–Zn–Ca–Mn alloy provides a bright scope for industrial use [67].

Mg–Ca–RE Alloys. Since calcium forms the major part of the bone, it refines the grains in magnesium. It also enhances the tensile properties and resistance towards corrosion in the alloys of magnesium. Thus, adding rare earth elements can further enhance the mechanical properties of magnesium alloys. Yttrium was added to magnesium alloys, to produce a novel Mg–1Ca–1Y alloy which had an enhanced elongation (up to 15.9%) and reduced resistance to corrosion [105]. The strength of Mg–Ca–Y–Zr alloy significantly got enhanced when yttrium was added. The yield strength increased to 120 MPa, ultimate tensile strength increased to 191 MPa and the elongation increased to 8.3% [106].

Mg–Zn–Mn alloys. The alloys of Mg–Zn–Mn have excellent resistance towards corrosion along with high strength and ductility. The Mg–5.99Zn–1.76Ca–0.35Mn alloy in extruded state has exceptional mechanical properties with 289 MPa yield strength and 16% elongation [107]. The alloy when extruded at 350 °C has high yield ratio approximately equal to 1 which is the reason behind high precipitation density of $\text{Mg}_6\text{Zn}_3\text{Ca}_2$ and its weak texture. When 0.3% Mn was added to Mg–Zn–Ca alloy, its tensile yield strength had an increase of 50 MPa [108]. Addition of around 2 wt.% manganese to extruded wrought Mg–2 Zn alloy enhanced its ductility and yield strength. The fine Mn precipitates, further refined the grains and increased the base plane's slip resistance in the process of hot deformation. The ductility and strength of pure magnesium significantly increased when manganese was added to it. Correspondingly its tensile strength and elongation were also enhanced to 204.3 MPa and 38.8% respectively [109]. Adding Mn to extruded Mg–6 Zn alloy improved its strength and age-hardening response [110]. The alloys of Mg–Zn–Mn and Mg–Zn–Mn–Si have YTS (yield tensile strength) of about 200–240 MPa. aging process by one step enhanced their strength by 80 MPa. The YTS of these alloys was further improved by two-step aging. The two-step treatment was carried out at a low temperature range of 70 °C to 90 °C and then succeeded by a higher temperature range of 160 °C to 180 °C. This further enhanced the YTS to a range of 338–350 MPa [67]. The insufficient ductility of peak-aged Mg–Zn–Mn-based alloys for various applications restricted its use irrespective of its excellent strength.

Mg–Zn–RE alloys. The Mg–Zn extruded alloys are combined with rare earth elements to enhance their properties like ductility and strength (mechanical properties). The basal structure of these alloys (Mg–Zn alloys) becomes feeble when dilute RE elements are added [110]. This weak basal surface is the reason behind high mechanical properties like formability and ductility [111]. Increasing the RE and zinc concentration levels in the alloy leads to enhanced strength as strengthening particles are formed but there is a sharp decline in its

ductility. The extruded Mg–Zn–Ce alloys have been primarily researched as they possess properties of high formability and ductility. The extruded Mg–2Zn–0.2Ce was observed to have ductility of approximately 27%. Under the same conditions of extrusion, the ductility of Mg–2Zn–0.2Ce proved to be about 10% higher to AZ31 alloy [112]. With more than 5 wt.% Zn added, the ductility of Mg–Zn–Ce reduced to half but the yield strength was not affected. Hence, to counter that, zirconium is added to such alloys with more than 5 wt.% zinc (Zn) content to enhance ductility and strength.

The Mg–Zn–Ce–Zr alloys, with high amount of Zn (5 to 6 wt.%), exhibits yield strength of about 247–330 MPa and elongation within the range of 17–27% [113]. The comparison of extruded Mg–Zn–Ce–Zr alloys and ZK60 alloys, with 0.5 wt.% Zr and 6 wt.% Zn each, showed that the alloy with added Ce has an improved strength of 5 to 75 MPa. The added cerium (Ce) improved the density and refined the precipitates size during extrusion as shown in Fig. 4 [113].

Cerium (Ce) also enhanced the extrudability of ZK60. Both the alloys were exposed to an extrusion velocity of 6.7 mm/s at 250 °C. The images in Fig. 5 show multiple cracks on ZK60 but a defect less Mg–6Zn–1Zr–1Ce alloy under the same extrusion conditions.

Rare earth elements and calcium (Ca) together have improved the strength of alloys, as compared to Ca alone. The results of extruded Mg–5.3Zn–0.2Ca–0.5Ce and Mg–2.5Zn–0.2Ca–0.4La alloys exhibited higher yield tensile strength (268 MPa and 325 MPa respectively) than extruded Mg–Zn–Ce or Mg–Zn–Ca alloys for analogous conditions [113], [114]. The microstructural study of Mg–Zn–Ce and Mg–Zn–Ca alloys revealed denser precipitate distribution of Mg–Zn and Mg–Zn–Ca alloys. A strong alloy was developed in hot extrusion when cerium (Ce) or lanthanum (La) is added to Mg–Zn–Ca alloy as precipitation density improved [113], [114].

Gadolinium improves the mechanical and extrusion properties of alloys [115]. In general, Mg–Zn–Gd alloy has a yield strength of about 200–300 MPa. For equal extruded conditions, Mg–2Zn–1.5Gd alloy has better yield strength (YS) of 50–60 MPa than Mg–2Zn–0.5Ce, since, gadolinium (Gd) is more soluble in magnesium than cerium (Ce) [116]. In the alloys of Mg–Zn–Gd, lower Gd and Zn content enhances their strength. For similar extruded conditions, Mg–5Zn–0.5Gd alloy has better yield strength (291 MPa) over Mg–6.8Zn–2.8Gd (228 MPa) [117]. Other research implies better yield ability of Mg–2Zn–Gd alloy in comparison to Mg–5Zn–Gd alloys due to the thermally stable second phase which doesn't dissolve in homogeneous treatment of high concentration alloys [118]. The Mg–1.8Zn–0.2Gd alloy had low rate of corrosion of less than 0.28 mm per year. With a cell viability of more than 80% in vitro for L929, MG63 and VMSC cells it showed no signs of cytotoxicity. The structure was intact for the first two months within the body. *In-vivo* tests exhibited few residuals after six months duration which confirmed that the alloys of Mg–Zn–Gd are very good as biodegradable implants [119]. The investigations on Mg–2.4Zn–0.8Gd show

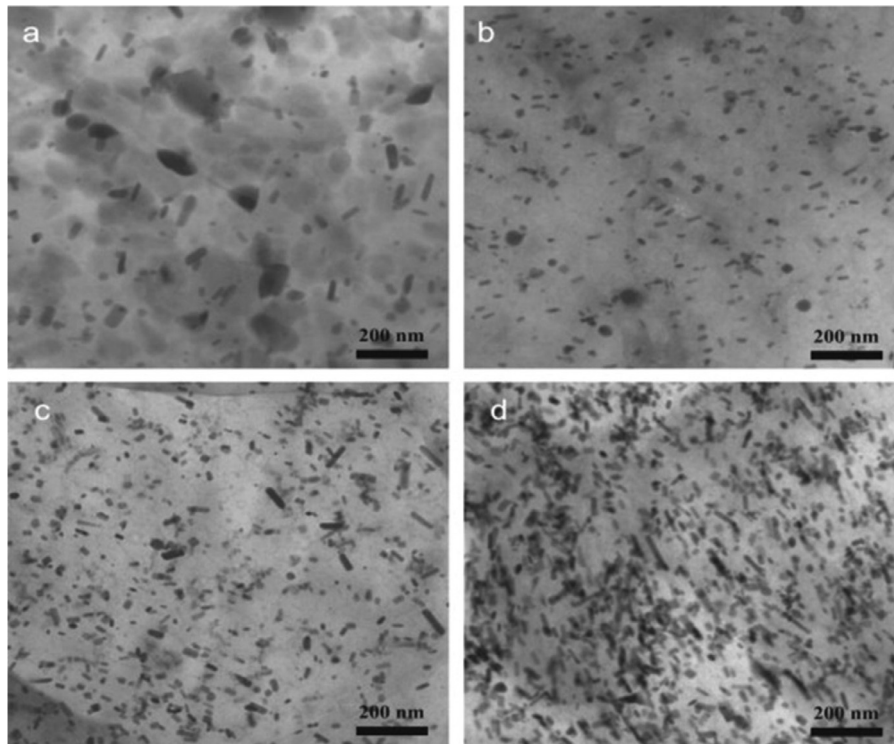


Fig. 4. TEM micrographs of as-extruded (a) ZK60, (b) Mg-6Zn-0.5Zr-0.5Ce, (c) Mg-6Zn-0.5Zr-1Ce and (d) Mg-6Zn-0.5Zr-1.5Ce alloys [113].

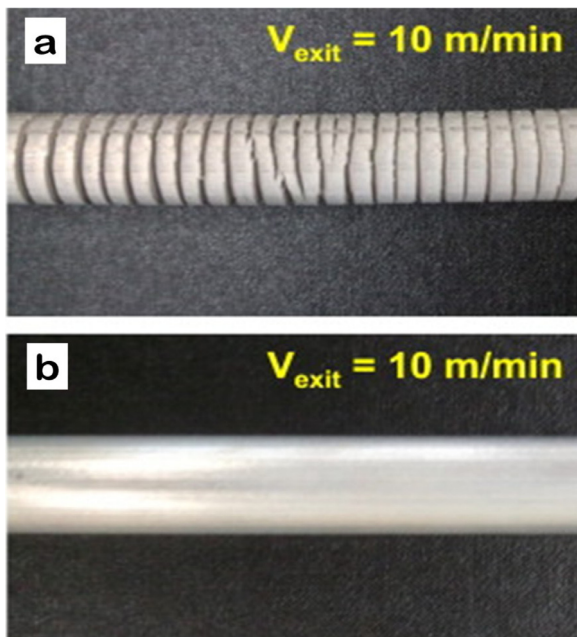


Fig. 5. Images representing the surface quality of (a) ZK60 and (b) Mg-6Zn-0.5Zr-1Ce alloys extruded at 250 °C with a ram speed of 6.7 mm/s [113].

the tolerance of the alloy towards solution treatment. Further extruding the alloy enhanced its mechanical properties (284 MPa YS, 338 MPa UTS and 24% elongation) and also its resistance towards corrosion improved in Hank's solution. Homogeneous microstructure with uniformly sized grains and distributed secondary phases are the reason for enhanced mechanical properties [120].

In the alloys of Mg-Zn-Y, LPSO phase was observed with moderate ductility and high strength [121]. Investigations on WZ21 (2 wt.% of Y, 1 wt.% of Zn) extrusion micro alloyed with Zr (zirconium) indicated that LPSO phase is the reason for its high strength and low rate of corrosion. This confirmed the suitability of this alloy in biodegradable implants [122]. Investigations on Mg-Zn-Y casting and extrusion alloys revealed that high content of yttrium reduced the grain size but enhanced the strength [123]. The alloys having single I-phase of $\text{Mg}_3\text{Zn}_6\text{Y}$ (second phase) had the lowest rate of corrosion of less than 0.1 mg per cm^2 per hour. The *in-vivo* results of ZX50 and WZ21 showed osteogenesis around the implant and longevity of WZ21 (longer than four weeks) [124]. Hence, WZ21 is suitable for biodegradable applications. It is highly biodegradable with the addition of yttrium.

Study on Mg-5.6Zn-0.55Zr-0.9Y alloy showed that alloying yttrium with enhanced corrosion resistance of Mg-Zn alloys (1.7% loss in mass after 242 h in simulated body fluid) [125]. The excellent mechanical properties of ZEK100 (1 wt.% of zinc, 0–0.5 wt.% zirconium, 0–0.5 wt.% of RE) promote bone growth making it a suitable material for biodegradable implants. Research on ZEK100 exhibited pathological effects on tissue after total degradation. Also, after implantation (*in vivo*), reduced weight (around 7.5%) and decrease in pull out forces (reduction to 44%) were noticed. This proves that the initially stable ZEK100 with a positive rate of degradation is perfect as biodegradable implants [126], [127]. Neodymium enhances the mechanical properties and resistance against corrosion in magnesium alloys. The mechanical properties and resistance to corrosion of JDBM al-

loy (Mg- (2.0–4.0) Nd-(0.1–0.5) Zn-(0.3–0.6) Zr, wt.%) are outstanding in simulated body fluid [128]. With the average rate of corrosion of 0.122 mm/year, the JDBM alloy may be absorbed in 18 months *in-vivo* [129].

2.3.3. Mg RE based alloys

Formability and strength enhancement are the primary interests in the use of Mg RE wrought alloys in various applications [130], [131]. Studies reveal that the texture of magnesium alloys diminishes and deformability is enhanced when RE elements are added. But the magnesium alloys are also significantly strengthened by precipitation hardening when Rare Earth (RE) elements are added [56], [132]. The most commonly used RE elements in magnesium (Mg) alloys are lanthanum (La), yttrium (Y), gadolinium (Gd), holmium (Ho), erbium (Er), ytterbium (Yb), cerium (Ce), neodymium (Nd), dysprosium (Dy). The Mg-RE alloys possess excellent strength at room temperature as well as high temperature [133]. Apart from good strength, these alloys have great resistance against creep and age hardenability properties. Researches have concluded that Mg-Gd-Y-Zn-Zr (Mg-RE alloy) is the strongest extrusion alloy of Mg (magnesium) with approximately 480 MPa yield strength [134]. Multiple precipitates and intermetallic particles are the reason behind this high strength. The Mg-RE-alloys having high RE content cannot be extruded easily, as they require extreme temperatures and low velocity. This involves higher production expenses.

In case of the magnesium rare earth (Mg-RE) castings, age hardening is the reason for elevated strengths. This age hardening process consists of, (i) High temperature solid-solution treatment, (ii) Quenching in water for obtaining a solid-solution of single-phase of α -Mg in supersaturated state and (iii) Followed by low thermal aging to get metastable precipitates in the matrix of magnesium (Mg). The precipitation quality influences the age hardening. This precipitation quality can be evaluated in terms of size, density, orientation, morphology and structure. It is the constituents in the alloy and the methods of processing (internal and external factors respectively) that influence the properties (mechanical) of alloys of magnesium (Mg). The literature suggests that control in preparation process including casting, heat treatment and plastic deformation is very much essential in enhancing the properties of the alloys. The alloys of magnesium and rare earth elements include Mg-Y, Mg-Gd and Mg-Nd. It is only the castings of magnesium with high amounts of gadolinium (Gd) have an ultimate tensile strength greater than 350 MPa [135].

Mg-Y-Zn alloys. The ultimate tensile strength (UTS) of hot extruded and rapidly solidified alloy of Mg-10Y-2Zn high is approximately 520 MPa which was manufactured in the year 1997 [136]. In the early 2000's another alloy of magnesium (Mg-6.7Y-2.5Zn) was formulated which had an outstanding yield tensile strength of about 610 MPa and this was considered as the strongest one [137–138]. This yield strength is higher than that of aluminium of high strength (7075-T6) and titanium alloys (Ti-6Al-4V). Microstructural analysis revealed small sized grains with diameters of 100–200 nm and

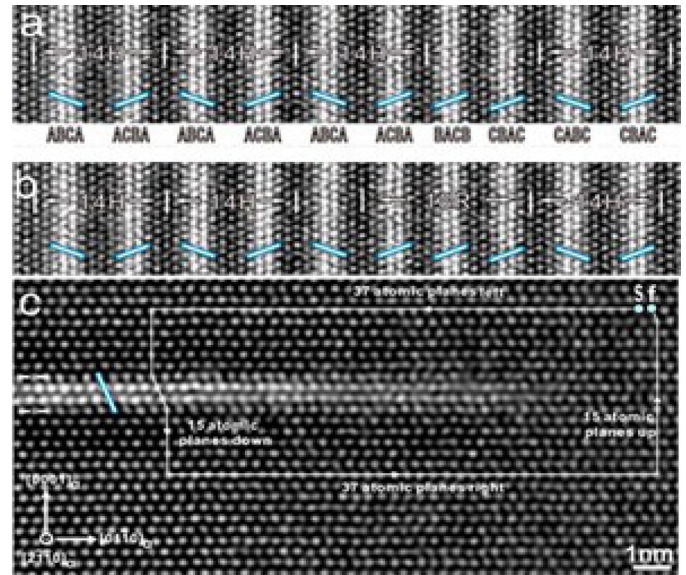


Fig. 6. AADF-STEM images of the structure of (a, b) 14H and 18R LPSO phases and (c) γ^I precipitate in Mg-8Y-2Zn 0.6Zr alloy [141].

homogeneous distribution of LPSO (long period stacking ordered) phase (7 nm sized particles) in the matrix of magnesium [139]. This focused the research on LPSO phase structure of Mg-Y-Zn alloys and its influence on the mechanical properties [140]. The most common LPSO phases in Mg-Y-Zn are 18R and 14H whose structure is same as γ^j phase (disordered hexagonal structure). This γ^j phase is entirely in coherence with the matrix of magnesium [141]. Fig. 6 shows STEM images of both the LPSO structures (18R and 14H) and the γ^j phase of Mg-8Y-2Zn 0.6Zr alloy.

However, the subsequent research on Mg-6.7Y-2.5Zn alloy could not produce the 610 MPa yield strength under the same conditions of hot extrusion and rapid solidification. Yield strength of only 480 MPa was possible [142]. The regular casting and extrusion (hot) of Mg-Y-Zn alloys have lesser YTS range of 200 and 400 MPa which proves that LPSO phase doesn't have a high influence on the strength of an alloy [143]. The particles of LPSO are found at the grain boundaries of magnesium. Upon treating by solution, the LPSO phase that forms in casting will not dissolve in the matrix of magnesium. Kinking deforms the phase of LPSO in extrusion. The magnesium's grain size is in several microns and equivalent to the alloys of Mg-Al-Ca, Mg-Zn-Ca-Zr or Mg-Zn-RE-Zr in the extruded state. The ductility of such extruded Mg-Y-Zn alloys is low (<10%) due to the presence of LPSO phase. The highly dense and expensive Mg-Y-Zn alloys have limited use due to their disadvantages of low ductility and modest strength.

WE system alloys. Yttrium positively influences, the corrosion resistance and strength when alloyed with magnesium for biodegradable applications [144]. It enhances the resistance of WE43 (4 wt.% of yttrium and 3 wt.% of RE) alloy towards corrosion. Many processing techniques have been employed in the production of WE43 implants. Numerous tests have been conducted to analyze the sustainability of WE43

alloys in the biomedical field. Investigations were done on heat treated WE43 alloys to evaluate their resistance against corrosion *in vitro*. The WE43 alloy which was polished and annealed showed a parabolic behavior in simulated body fluid (SBF) [145]. A decrease in degradation rate was observed because of the deposited corrosion products on the surface. When the alloy was annealed at a temperature of 500 °C, Y_2O_3 layer was formed on the surface which is the reason for higher resistance towards corrosion in case of the thermally oxidized sample. The resistance against corrosion increases in the heat-treated alloy due to the interactions of finely distributed precipitates and also the corrosion reactions [146]. It was observed that in phosphate-buffered saline (PBS) solution, there was a decrease in the rate of corrosion (0.9 mm per annum to 0.4 mm per annum) for extruded and heat treated WE43 alloys. This is due to the transformation in extrusions from diffusional corrosion to uniform corrosion [147].

An increase was observed in the yield strength (YS), ultimate tensile strength (UTS) and elongation to 190 MPa, 282 MPa and 37% respectively. The areas with high yttrium content in WE43 casting reduced the growth of corrosion thereby decreasing the rate of corrosion because of homogeneously distributed yttrium particles [148]. The mechanical properties of hot extruded WE43 processed by subsequent HPT (high pressure torsion) were analyzed by Liu et al. [149]. A decrease in the initial grain size (12 μm) was observed along with increased ultimate tensile strength (256 MPa) after 5 HPT (high pressure torsion) cycles. In the corrosion fatigue behavioral analysis of AZ91D casting and WE43 extrusion in simulated body fluid, it was observed that WE43 extrusion exhibited a higher limit of corrosion fatigue than AZ91D casting (40 MPa and 20 MPa respectively) [150].

Multiple surface modification techniques have been employed for enhancing the corrosion resistance and biocompatibility of magnesium rare earth alloys (Mg-RE). Research was carried out on the behavior of WE43 alloy towards corrosion in simulated body fluid along with DMEM (cell culture medium) [151]. The analysis was to check the influence of zirconium (Zr) and N plasma immersed, ion implantation on the alloy of WE43. In the simulated body fluid, the treated WE43 had very low (12 times lower) corrosion current density (29.8 μA per cm^2) than the untreated one (368 μA per cm^2). In DMEM corrosion current density of treated WE43 was 71 times lower than the untreated WE43 which indicates that this technique enhances resistance towards corrosion. There was a substantial increase in the resistance towards corrosion and biocompatibility in the investigations on WE43 alloy in the neodymium implantation (self-ion) technique [152]. A protective layer of Nd_2O_3 was formed of 70 nm thickness. The *in vitro* investigations on PE (plasma electrolytic) coated WE43 showed no gas release for four to eight days duration following which at 0.2 ml per cm^2 per day rate, gas was released. The uncoated samples *in vitro*, initially released gasses at a rate more than 1 ml per cm^2 per day but after four to five days, the gas release rate reduced to around 0.3 ml per cm^2 per day [153]. On an average, the coated plates lost weight at 15 mg/week whereas the uncoated plates

lost weight at 20 mg/week. According to the *in vivo* reports, large gas bubbles were present around the uncoated plates but no such bubbles were seen around coated plates in the initial week. At the end of fourth week, gas bubbles around uncoated plates disappeared but small gas pockets were seen around coated plates which remained till the entire lifetime. These results indicate enhanced resistance against corrosion for coated alloys of WE43. Polypyrrole (PPy) is a polymer that is extremely biocompatible and with electrical conduction. This recently has found use in biomedical applications like artificial muscle development, biosensors, controlled release of drugs and neural recording stimulation of nerve regeneration [154]. The influence of Polypyrrole (PPy) coating on WE43 alloy against corrosion was studied in m-SBF (modified simulated body fluid) solution. A protective layer was formed after it was immersed for 24 h. It could absorb carbon dioxide and hamper the transfer of charge. This reduced the rate of corrosion in WE43 magnesium alloy. Treating with phosphate is also an efficient method to enhance the bio-compatibility and resistance against corrosion in WE43 alloys [155]. The immersion test of phosphate coated WE43 alloys indicated lower hydrogen evolution (1 ml per cm^2 per day) in comparison to the uncoated alloys (more than 4 ml per cm^2 per day). The coated alloys also had a higher viability of L-929 cell (96.21%) than the uncoated ones (34.80%) [156].

A novel, rapidly solidified alloy of magnesium, EW62 (Mg-6% Nd-2% Y-0.5% Zr) was investigated in simulated fluids for the stress corrosion cracking [157]. Two kinds of immersion tests were conducted, short term (1 day) and long term (>10 days) respectively. The short-term tests showed much lower rate of corrosion in the rapidly solidified alloy in comparison to the conventional casting (0.5 mm per year vs. 2.1 mm per year). The long-term tests also indicated lower corrosion rate in the rapidly solidified alloy than the casting (0.078 mm per year vs. 0.152 mm per year). The rapidly solidified alloy had better ultimate tensile strength value in the test of stress corrosion over the conventional casting (274 MPa in air to 223–262 MPa in corrosive environment and 181 MPa in air to 141–178 MPa in corrosive environment, respectively). Hence, the rapidly solidified EW62 is a better biodegradable implant.

Mg-Gd alloys. The alloys of Mg-Gd have developed a great interest in the field of research in the production of extruded alloys that perform well in extreme conditions. The solubility of solid gadolinium at equilibrium is high in magnesium (23.49 wt.%) at 548 °C (eutectic temperature). This property (solid solubility at equilibrium) has an exponential decrease w.r.t. temperature having around 5.0 wt.% solubility at 250 °C, which reduces to 3.82 wt.% for a temperature of 200 °C [4]. Since Gd is highly soluble in Mg, lower Gd content (<10%) doesn't majorly influence the response of precipitation hardening [158]. The excellent age strengthening of Mg-Gd alloys is due to the precipitation of β , β^I and β^{II} in them. Thus, confidently it can be stated that the heavy alloys of Mg-Gd are ideal for producing extrusions of magnesium alloys which have great strength [134]. But the high cost has to be considered as Mg-Gd alloys are hard

to extrude and require relatively higher temperature range of 350–500 °C. This high thermal range results in yield strength (tensile) that is low for the extruded alloy. The noticeable growth of grains and negligible precipitation are the reason for this low tensile yield strength of the alloys. The alloys of Mg–8Gd–0.4Zr (164 MPa yield strength) and Mg–14Gd–0.5Zr (190 MPa yield strength) can be taken as examples for this case [159], [160]. These extrusions have grains that are completely recrystallized with 10–20 μm grain size. The dynamic precipitation for Mg–14Gd–0.5Zr extrusion (505 °C extrusion temperature and quenched with water), was dubious, as there was a single phase of solid solution which was supersaturated. The extrusion consists of huge quantity of β^j particle precipitation when it was exposed to treatment of isothermal aging after extrusion for duration of 36 h and 200 °C temperature. These β^j precipitates increased the yield tensile strength of the alloy by 115 MPa through aging. The yield tensile strength of the alloy increased to 305 MPa from 190 MPa [159].

The response of age hardening in Mg–Gd alloys is significantly improved when zinc is alloyed at micro level. Considering the binary alloy Mg–6Gd as an example, it was observed that, isothermal aging of the alloy at a temperature of 250 °C showcased a trivial response of age hardening. But when 1 wt.% of zinc was added, there was a substantial improvement in the response of age hardening. The isothermal aging replaced the initially formed basal precipitates of γ^{ij} with γ^j precipitates. The structure of γ^j precipitates crystal is same as the alloys of Mg–Y–Zn [64]. In Mg–Gd–Zn alloys, factors like zinc, gadolinium concentrations along with aging temperature decide the formation of the phases of 14H LPSO, β , β^j and β_1 .

Yttrium is the next most common element apart from zinc that is alloyed with Mg–Gd alloys as the alloys of Mg–Gd–Y exhibit better mechanical properties like resistance to creep and strength. The dense precipitate distribution in Mg–Gd–Y alloys is the reason behind substantial response to hardening in precipitation during aging [161], [162]. The yield strength of extruded Mg–Gd–Y–Zr alloys has a tremendous increase when elements like zinc or Nd or both are alloyed. When isothermal aging was done, these extruded alloys achieved maximum hardness at conditions of 64 h cycle and 200 °C temperature. For the above aging conditions, Mg–10Gd–5.7Y–1.6Zn–0.7Zr extrusion, at peak hardness, exhibited 473 MPa yield strength (from 419 MPa) and 8% elongation [163]. This is very high for the typical magnesium cast alloys and extrusions. The suggested theory behind this abnormal strength has mentioned the cause as densely distributed β and β_1 precipitates restricting the growing recrystallized grains.

2.3.4. Mg Sn alloys

The extrusions of Mg–Sn alloys have gained popularity in the field of research because tin improves extrusion properties of magnesium alloys. The isothermal aging of these tin based magnesium alloys enhances their age strengthening [164]. At 561 °C (eutectic temperature), the solubility of tin in solid



Fig. 7. Photo shows quality of surface in AZ80 and TAZ711 extrusions (350 °C) [169].

state is high (3.35 wt.%), in 14.5 wt.% of magnesium. But at a temperature of 200 °C this decreases to about 0.49 wt.% [4]. The coarse β -Mg₂Sn precipitate in Mg–Sn binary alloys is the equilibrium precipitate formed during aging process. In comparison to the precipitates in other hardenable magnesium alloys, the precipitates in Mg–Sn binary alloys are coarser [64]. The binary alloys of Mg–2Sn, Mg–6Sn display yield strengths of approximately 157 MPa and 191 MPa, respectively which is low [165], [166]. Hence, zinc and aluminium are alloyed with Mg–Sn-based alloys to improve their extrusion strength. The Mg–Sn–Al–Zn alloy has yield strength of 370 MPa which is the highest [167], [168].

The extrudability of Mg–Sn–Al–Zn alloys is usually good. This is very evident in Fig. 7 which shows extruded TAZ711 (Mg–7Sn–1Al–1 Zn) alloy. At an extrusion temperature of 350 °C, the alloy possessed a shiny surface which is also smooth. For extrusion, the speed of the ram is 9 mm per second and the corresponding die exit speed is 27 m/min [169]. The thermally stable phase of Mg₂Sn formed during extrusion is the reason behind excellent extrusion properties in Mg–Sn–Al–Zn alloys. In contrast, severely cracked surface was detected in AZ80 at a low ram speed of 2 mm per second (6 m per minute exit speed through die). But the yield strength of high-speed Mg–7Sn–1Al–1 Zn extrusion is comparatively low (180 MPa) [169]. The yield strength of Mg–Sn–Al–Zn alloy can be enhanced reasonably (above 300 MPa) under the conditions of lower extrusion temperature of 200 °C and 0.1 mm per second extrusion speed.

Though the process of aging was attempted to enhance the strength of Mg–Sn–Al–Zn extrusions, it did not have much influence on the alloys. The alloys at peak age had a yield tensile strength that is only 10 MPa to 40 MPa higher than the normal extrusions [168].

Adding sodium is a technique to enhance the response towards age-hardening in the alloys of Mg–Sn–Al–Zn [168]. The alloy Mg–5.4Sn–4.2Zn–2.0Al–0.2Mn–0.1Na exhibited an increased strength of 100 MPa at 160 °C aging temperature. Conversely, its response towards age hardening became negligible without sodium (Na). The initial phases of aging showed

co-clusters of Sn–Na when sodium traces are added to alloys of Mg–Sn. These clusters provide a heterogeneous nucleation for the precipitates of Mg_2Sn . This is the main reason behind improved response towards precipitation hardening. But the atoms of sodium in the alloys of Mg–Sn are separated towards grain boundaries. This reduced the ductility of the making it brittle [170, 171]. Thus, the alloys of Mg–Sn–Al–Zn–Na are undesirable with limited use. There is a necessity to look for a substitute for sodium which doesn't reduce the ductility and also improve age strengthening. The response of Mg–Sn–Al–Zn alloys towards age hardening can also be enhanced by two stage heat treatment subsequent to the extrusion and treatment with solution. The alloy of Mg–6.6Sn–5.9Zn–2.0Al–0.2Mn exhibited high yield strength (370 MPa) when exposed to a temperature of 70 °C for duration of 150 h (Pre aging) followed by exposure to 140 °C temperature for 30 h (aging). The obtained yield strength is 123 MPa higher than conventional extrusions [168].

2.3.5. Mg–Li alloys

The magnesium lithium-based alloys (Mg–Li) are extremely light since lithium, with 0.533 g/cm^3 density, is lightest among metals. The solubility of lithium at eutectic temperature (588 °C) is also high (5.5 wt.% at 17 wt.%) in magnesium. The solubility isn't affected when the temperature decreases. The alloy composition is of α -Mg and β -Li phases for lithium concentration of 5.5 to 11 wt.%. Alloy with a lithium concentration above 11 wt.% has single phase of β -Li. High lithium concentration reduces the alloy density to 1.4 to 1.5 g/cm^3 .

The binary alloys of magnesium-lithium (Mg–Li) have a yield strength ranging between 60 MPa to 140 MPa but there is a significant variation in ductility. The ductility is low in the α -Mg phase but with increasing levels of lithium concentration (β -Li), ductility increases notably. Though the ductility is high, the strength reduces in β -Li phase.

The extrusions of Mg–Li are alloyed with elements like aluminium and zinc so that their strength improves. Some of the important intermetallic compounds formed are MgLiZn , MgLi_2Al and MgLi_2Zn which do not have a radical change in their strength. Hence, Mg–Li alloys are alloyed with rare earth elements to improve their strength. The formation of second phase particles leads to the improved strength in casting and extrusion processes. The LPSO or icosahedral quasicrystal phase in the secondary phase is the reason behind the strengthening. So far 263 MPa yield strength in Mg–5Li–3Al–2Zn–1.5Cu alloy is the highest observed in Mg–Li extrusions [172]. There isn't enough clarity on the abnormal strength in such extrusions of Mg–Li. It might be due to the precipitation of Al–Cu in the process of extrusion.

The use of Mg–Li alloys has also been considered in the biomedical field. The focus has been on LAE442 (4 wt.% of Li, 4 wt.% of Al, 1.3 wt.% of Ce, 0.37 wt.% of Nd and 0.5 wt.% of La) [173]. In vitro and in vivo analysis was done on gravity castings of LAE442 and AZ91D (Mg–9Al–1Zn) [174]. The *in vitro* tests indicated higher corrosion resistance in AZ91D than LAE442 (0.267 mm/year and

5.535 mm/year respectively). Conversely, *in vivo* tests suggested higher resistance to corrosion in LAE442 over AZ91D ($1.205 \times 10^{-4} \text{ mm/year}$ and $3.516 \times 10^{-4} \text{ mm/year}$ respectively). Research was also done on MgF_2 coated and uncoated LAE442 extrusions for their resistance towards corrosion [175]. The *in vivo* results presented a lower rate of corrosion in LAE442 extrusion (0.4 mm/year). The MgF_2 coating enhanced the resistance towards corrosion by 0.2 mm/year. The mechanical properties and degradation were analyzed and compared in WE43 and LAE442 extrusions for duration of 6 months, *in vivo* [176]. In a measure of degraded volume, it was observed that the degradation rate was slower in LAE442 implants than WE43 (22.4% and 33% respectively). Initially WE43 implants exhibited lower strength (238.05 N) than LAE442 (255.67 N). The rate of loss in strength was constant after 6 months. This suggests it is best suited for weight bearing applications in bones. A comparative study on Mg–Li–Al ternary and Mg–Li–Al–RE quaternary alloys in terms of biocorrosion, biocompatibility and mechanical properties suggested that rare earth elements improved the strength. But the corrosion resistance was reduced by the dispersed intermetallic compounds in the matrix of magnesium [177]. Investigations on extruded LAE442 nails by cyclic fatigue tests in distilled water and HBSS resulted in 5 broken implants. This proves that LAE442 might not be suitable for load bearing applications within the human body [178]. The influence of ECAP (equal channel angular pressing) on LAE442 alloy for degradation *in vitro* test was analyzed. Also, the rate of corrosion of ECAP (12 passes) processed was found to be 2.49 mg per cm^2 per day in 0.1 M of sodium chloride (NaCl) and 0.18 mg per cm^2 per day in SBF, respectively. The cytotoxicity tests for 7 days duration showed 80% viability of ECV304 cells and VSMC cells. Hence, ECAP is a significant process to be implemented for obtaining outstanding resistance against corrosion in LAE442 alloy.

3. Magnesium Composites

The materials formed by combining two or more different components which act in synergy to generate a material having superior properties to that of either of the components are called composite materials. Though advanced techniques are adopted to fabricate magnesium alloys with highly pure Mg, there are a certain area of application where the alloys of magnesium (Mg) are not suitable. Low temperature stability, high vulnerability to thermal expansion, high rate of corrosion and lack of certain properties at higher temperatures are some of the limitations of magnesium alloys which hamper their use. These limitations led to the development of magnesium metal matrix to be used in Mg MMCs (magnesium metal matrix composites). These magnesium metal matrix composites are developed to overcome the limitations in magnesium alloys. The necessity of lightweight materials in various fields of engineering, such as, automotive and aeronautical to conserve energy, has also been a factor contributing to the enhancement of magnesium matrix composites [179]. The aluminium matrix composites are being re-

Table 4
Properties of commonly used ceramic reinforcements [180].

Ceramic Particulates								
Oxides			Carbides		Nitrides		Borides	
Properties	Al ₂ O ₃	Y ₂ O ₃	B ₄ C	SiC	TiC	AlN	BN	TiB ₂
Melting Point (°C)	2050	2425	2450	2300	3140	2300	3000	2900
Crystal Type	Hex	Cub	Rhomb	Hex	Cub	Hex	Hex	Hex
Density (g/cm ³)	3.9	5	2.5	3.3	4.9	3.2	2.2	4.5
Young's Modulus (GPa)	410		450	480	320	350	90	370
CTE(μ/ °C)	8.3	8.1	5to 6	4.7 to 5	7.4	6	3.8	7.4
Heat Conductivity(W/m °C)	25	27	29	59	29	10	25	27

placed with magnesium composites in structural applications (lightweight) since their properties are similar. According to the earlier findings, magnesium (purest form) and alloys of magnesium have an array of material reinforcements. Some of the reinforcements include Al₂O₃ (aluminium oxide whiskers or particulates), B₄C (boron carbide particulates), SiC (silicon carbide whiskers or particulates) and Y₂O₃ (yttria particulates). The reinforcements normally are fibers, particles or whisker for metal matrix composites. Satisfying the following conditions will provide optimized end properties of the composite

- Selecting the reinforcement with sufficient strength and stiffness
- The reinforcement and the metal matrix should be compatible of reinforcement with the matrix material
- Dispersion of the reinforcement within the matrix
- The matrix-reinforcement interface integrity should be good
- Porosity should be less.

Some of the manufacturing techniques for these composites are conventional casting, powder metallurgy, mechanical processing, melt infiltration. Ceramic reinforcements are commonly used for magnesium matrices. Table 4 shows the properties of some commonly used ceramic reinforcements [180]. The magnesium matrix can be reinforced with ceramics which are particles continuous fibers or whiskers.

The composites of magnesium reinforced with ceramic fiber exhibit enhanced strength and modulus of elasticity but the direction of the load applied determines the end properties of magnesium composites [181]. Thus, particles and whiskers of ceramic reinforcements are essential. The dispersion of whiskers in the magnesium matrix is difficult due to their tendency of accumulation even though they give minimal defect density [179]. Despite this, the ceramic particles have economical manufacturing techniques providing isotropic composite properties [181]. The reinforced ceramic particles can be categorized into borides, carbides, nitrides and oxides. The negative influence of particulate structured ceramic composites (magnesium) on ductility and toughness is restricting their development irrespective of their mechanical properties [180, 182]. The material ductility determines the formability of the structure. It is the reinforcements in the second phase that

significantly reduce magnesium's ductility [183]. But the latest studies suggest that adding reinforcements of ceramics in the nanoscale enhances the ductility of magnesium. The ductility of magnesium nanocomposites is higher in comparison to microscale composites. The nanoscale composites of magnesium also exhibited outstanding mechanical properties with reduced weight due to exceedingly fine distribution of secondary reinforcements [184, 185]. The matrix is strengthened through reduced size of grains. The reinforcement is to be selected with some precaution after analyzing the material properties. The metal matrix, manufacturing technique and the required material properties determine the choice of reinforcement. The following are the properties on which reinforcements are chosen [179].

- Sufficiently low density to assist the critical characteristic of weight-saving
- Bond ability of the reinforcement with the matrix material
- A difference in CTE to minimize the influence of thermal stresses
- Wettability
- Superior mechanical properties
- Availability and ease with which it can be manufactured
- Low corrosion
- Economical

Though the ductility has been enhanced, the manufacturing cost of magnesium composites is high. Hence, these can only be used if the manufacturing costs are economical. This led to the implementation of a new technique to create a new section of composites with spasmodic reinforcement called hybrid composites. The hybrid composites have two or more types of reinforcements in the form of particles whiskers or fibers with different sizes added parallel to the base matrix. The magnesium matrix containing different kinds of reinforcements acquires the benefits of every added reinforcement phase. The hybrid composites have been remarkable prospect for magnesium composites in extremely short duration leading to multiple studies related to these materials. The hybrid composites are important as they provide ideal material properties for the magnesium composites. The other benefits of hybrid composites are, (a) optimizing the properties of microstructure and mechanical characteristics, (b) enhancing reinforce-

ment's wettability, (c) mass production provisions and (d) reinforcement of local regions. Economical techniques can be employed in the manufacturing of hybrid composites which are conventional or innovative. There has been scarce literature on magnesium hybrid composites.

The AZ91 was reinforced with graphite and silicon carbide combined together and it was investigated for enhanced wear behavior. Investigations revealed lower wear in hybrid composite than the monolithic material [186]. The nanoscale reinforcements of carbon Nano tube and silicon carbide enhanced the stability of magnesium composite at elevated temperatures but there was a drop in the coefficient of thermal expansion with higher concentration of the reinforcements [187].

The bioactive and bioinert ceramics produce composites with strength (mechanical) and bioactivity. Bioactive ceramics also are used for manufacturing bio absorbable composites with customized properties. The application of ceramic materials in the field of medicine is associated with manufacturing of biomaterials used for implants [188]. Bioceramics is the term given to ceramics used in biomedical applications. These bioceramics have high strength (compressive) and are carbides, oxides or inorganic silicates with multi crystals. The bioceramics are further classified as, biodegradable, bioactive and bioinert materials. In the biological medium, the biodegradable materials disintegrate and get absorbed. The bioactive materials have high toughness and are extremely resistant to wear. Under stress induced conditions, these transforms and obtain tougher properties. The properties (mechanical and physical) of bioinert ceramics are retained in the biological medium. Phosphates and bioceramics are extremely biocompatible with similar properties of bone hence they are ideal for manufacturing biomaterials. Bioceramics are almost chemically inert and thus have biocompatibility which is their benefit. Inertness is the reason for the initial use of Al_2O_3 and ZrO_2 as implants. The exceptionally slow reaction rate is their principal property which makes them almost inert. The bioactive ceramics chemically react with physiological fluids forming a reaction that aids in bone formation. The process of ceramic coating of metals is complicated as the durability and quality at the boundary depends on various factors like purity, chemical composition, particle size, thickness of coating along with the substrate of surface morphology. The release of ions is reduced drastically when a metallic implant is coated with ceramic material. The ceramics obstruct and reduce the diffusion of metal ions towards the body. Ceramics like calcium phosphate and hydroxyapatite are being used for bone defect filling and enhancing the hip joint prostheses bond respectively. Hydroxyapatite isn't toxic, has excellent biological properties and doesn't lead to any immunological reactions. Hence, the use of ceramics in biomaterials is in coating metal implants and filling defects in bone.

3.1. Types of reinforcements in biological applications

3.1.1. Alumina (Al_2O_3)

Alumina is extremely hard and has excellent resistance towards abrasion. It has a smooth surface and surface en-

ergy which give it outstanding friction and wear behavior. The structure of Alumina (Al_2O_3) is hexagonal and has the ions of aluminum at octahedral interstitial sites. The alumina ceramic has its application in bone and dental implants as it is chemically inert and has excellent strength and abrasion resistance.

3.1.2. Carbon

The versatility of carbon is very high as it has a number of allotropes. It does not have any fatigue as in the case of polymers or other ceramics. But due to its low tensile strength and brittle nature, its applications in load bearing areas have been limited. It is used in biomaterials in areas having blood contact hence it is important to analyze its compatibility with blood.

3.1.3. Calcium Phosphate ceramics (CPCs)

The use of ceramics manufactured with calcium phosphate in bone tissue replacement and augmentation is familiar. β -Tricalcium phosphate and hydroxyapatite are the most common bioceramics in use. In body fluid and dry or wet air (up to 1200 °C), hydroxyapatite with a hexagonal structure, is the most stable among other calcium phosphate phases. It is bioactive due to its resorbable nature and doesn't decompose.

3.1.4. Zirconia (ZrO_2)

Zirconia has excellent strength (mechanical) and fracture toughness which gives it a wide scope as a biomaterial. The transformation toughening property of its microstructure provides an added advantage to zirconia over other ceramics. The same property is evident in the components made of zirconia.

3.1.5. Other reinforcements

Silicon nitride finds its use in spine surgery as an orthopedic implant that helps in bone synthesis. It also is used as bearings that enhance the life of prosthetic knee or hip joints. Its charge is hydrophilic negative, which assists the bone-cell bonding, leading to the integration of the implant with the surrounding bone.

The Carbon Nanotubes (CNTs) have a wide application in implants made of hard tissue, scaffolds and micro catheters. They also are used in neuronal growth disorder substrates. Titanium is hard, biocompatible and extremely resistant to corrosion. Apart from this it also possesses great tribological properties which make it suitable in load-bearing areas. Titanium carbide (TiC), titanium nitride (TiN) and titanium diboride (TiB_2) are some titanium reinforcements used as biomaterials.

3.2. Magnesium Composite trends

Composite of magnesium (Mg (5 wt.%, 10 wt.% and 15 wt.%) and hydroxyapatite particulates (HAP) were manufactured using powder metallurgy followed by extrusion (hot). Its microstructural and mechanical properties were analyzed. As seen in Fig. 8, size of the grains decreased showing an

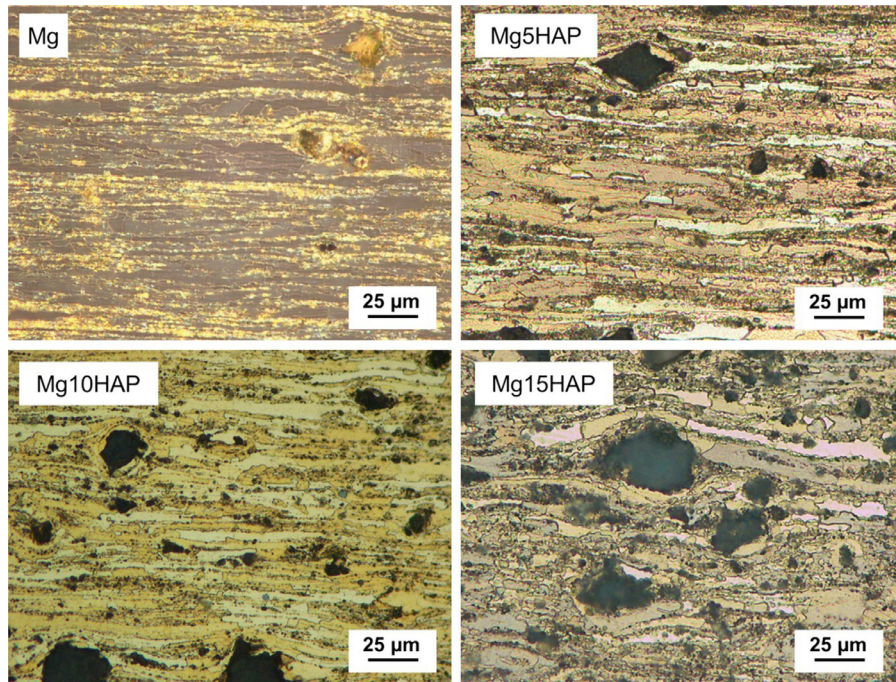


Fig. 8. Optical microscopy images of Pure Mg and Mg-HAP with wt.% of (5, 10 and 15) [189].

equiaxed structure of grains. The increase in HAP content resulted in maximum compression strength and hardness. The change in texture intensity and porosity level increased the corrosion resistance of Mg-5HAP [189].

The nanocomposites of Mg-TiO₂ were manufactured by the process of disintegrated melt deposition and then extruded in hot conditions. In the magnesium matrix, size of the grains decreased by adding TiO₂ (1.98 percentage of volume). There is an increase of about 37%, 9% and 31% in the stress (proof), UTS and fracture strain respectively after adding 2.5 percentage volume of TiO₂. The microstructure of pure magnesium and magnesium composites is seen in Fig. 9 [190].

The Mg-HA-TiO₂-MgO mixture was alloyed and then annealed at the temperatures of 500 °C and 630 °C, respectively to form a magnesium metal matrix composite. The nanocomposite of magnesium matrix was substituted with HA, CaTiO₃ and Mg(OH)₂ phases. The milled samples had MgTiO₃ after one hour of annealing at a temperature of 500 °C. The decomposition of HA took place after one hour duration at 630 °C annealing temperature. Hence, the retention in CaTiO₃ and Mg(OH)₂ phases was seen in large quantities. In the simulated body fluid, corrosion tests showed that the rate of corrosion decreased when the quantity of HA and milling times was increased [191].

The AZ91 magnesium alloy was investigated for its mechanical behavior and performance against biocorrosion when reinforced with FA (flurapatite) in quantities of 10 wt.%, 20 wt.% and 30 wt.% respectively. There was reduced ductility with increased FA reinforced quantities due to the dislocation movement while twinning leading to limiting effect in the matrix deformation. The presence of hard ceramic particles at the boundaries enhanced the hardness as they blocked

the deformation at the time of indentation. Also improved resistance towards corrosion was seen with increasing quantity of flurapatite (FA) [192].

The composite of Mg-2Zn-0.5Ca/ β TCP subjected to four passes of equal channel angular extrusion (ECAE) had uniformly dispersed particles of β TCP and highly refined grains in the magnesium matrix as seen in Fig. 10 [193].

The strength of Mg-40 vol percent bredigite composites manufactured by the technique of PM (powder metallurgy) has its strength nearer to the cortical bone. There was a 24-fold reduction in the magnesium's rate of biodegradation when the particles of bredigite were added to the matrix [194]. There were refined grains and enhanced mechanical properties similar to the cortical bone in the composites of Mg-20 vol percent of silicon dioxide (SiO₂). There was also exhibition of good damping properties feasible for implant related applications [195]. The rate of degradation decreased when pearl powder (PP) was added to Mg matrix. It also assisted in cell proliferation and adhesion required for bio implants [196]. Magnesium has enhanced mechanical properties; reduced evolution of hydrogen and also it shows biocompatibility when bio glass is added to it [197].

4. Inclusions in magnesium alloys

To enhance the properties of magnesium alloys, it is important to enhance the quality and cleanliness of magnesium melt. The quality of melt can be done by the following methods:

- (i) Controlling the trace elements
- (ii) Reducing the amount of gasses dissolved in the metal
- (iii) Removing the melt inclusions

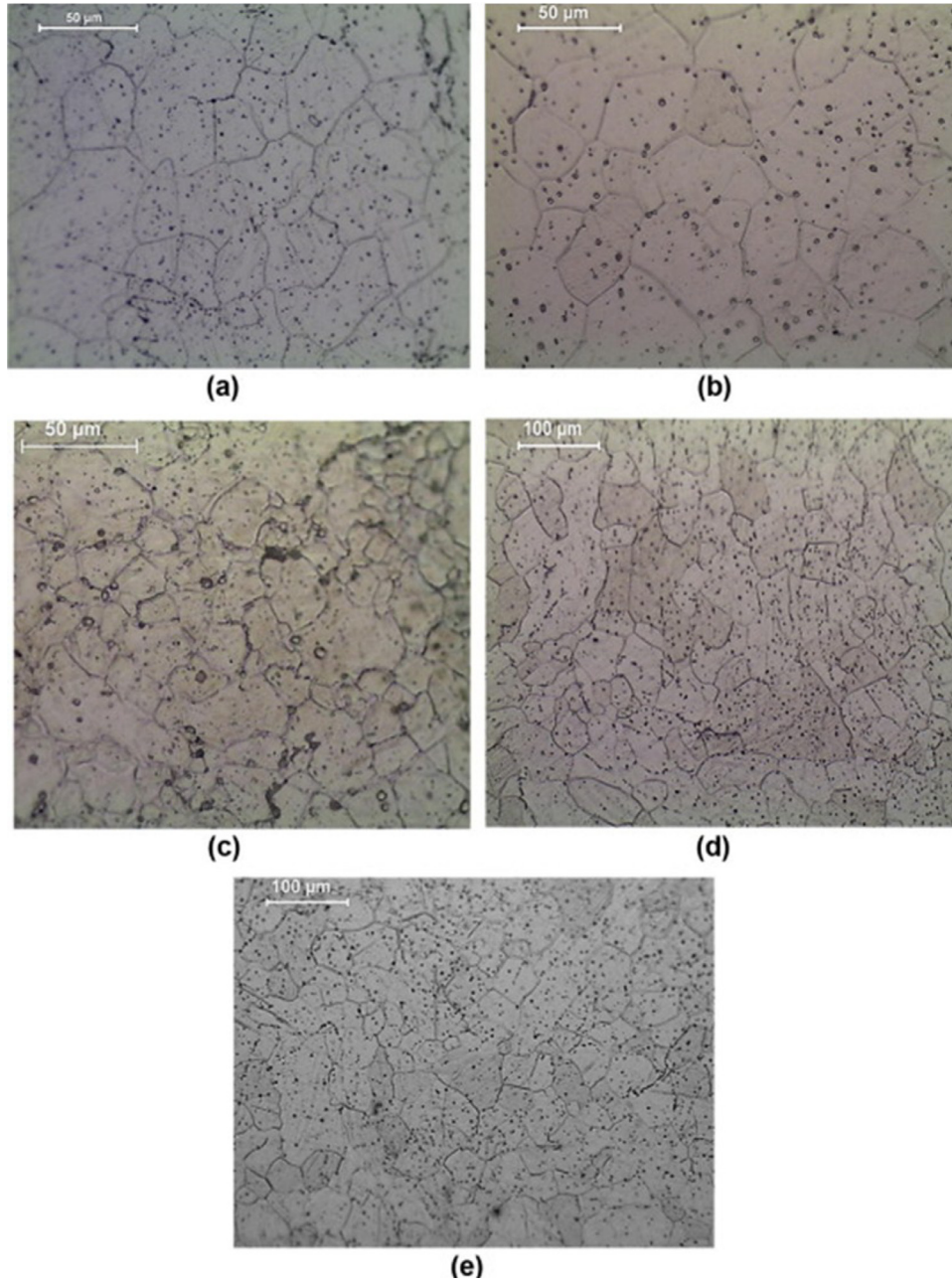


Fig. 9. Optical Microscopic images of (a) pure magnesium, (b) Mg0.58TiO₂, (c) Mg0.97TiO₂, (d) Mg1.98TiO₂ and (e) Mg2.5TiO₂ [190].

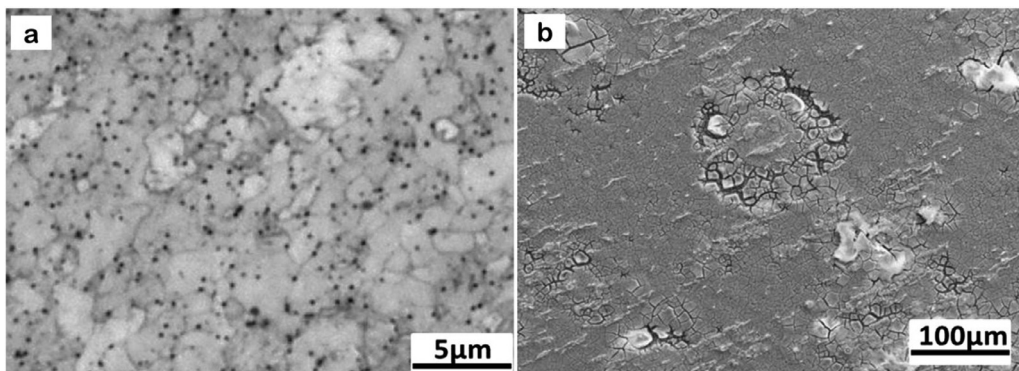


Fig. 10. a) Optical micrograph of Mg-2Zn-0.5Ca/βTCP composite (b) SEM microstructure of corroded Mg-2Zn-0.5Ca/βTCP composite [193].

Alloys with varied chemical composition and defective parameters will have a low level of homogeneity which in turn negatively influences the quality of the end product. The mechanical characteristics and the surface quality are affected [198]. It is an accepted fact that traces of compounds like cobalt, copper, iron and nickel are harmful for magnesium alloys [199].

The most familiar impurity in the magnesium alloy is iron whose source is the crucibles of steel in which the melting takes place. The immersion of the high stainless steels of nickel in the melt of magnesium gives rise to the contamination of nickel. The presence of copper bushings contaminates the recycled parts. The impurity in the form of cobalt is not common in the alloys of magnesium but it might rise from the paints of cobalt [199]. It is needed to eliminate these elements to ensure a quality product. These heavy metals can be minimized by alloying techniques, raw material selection, equipment and tool handling. Adding manganese to molten magnesium eliminates iron.

For the magnesium alloys, hydrogen is more soluble in the liquid state than the solid state. Therefore, higher hydrogen concentration over the specified solid solubility (15 to 20 cm³ per 100 g) leads to the pore formation in the casting after solidification. The mechanical properties and the quality of casting surface are compromised due to this [198]. In the process of casting, a porous, free film is formed by the Mg alloys which do not have the ability to prevent the further oxidation of melt. Without proper precautions, air contact of magnesium in molten state will lead to swift burning because of oxidation [198]. Inclusions in Mg alloys reduce mechanical properties, are detrimental to surface finish increase porosity and exhibit a tendency to increase corrosion [200]. The classifications of inclusions in magnesium melt are [201] a. Non-metallic inclusions: The non-metallic inclusions comprise of the nitrides and oxides. The most common non-metallic inclusions are oxides and then the nitrides. The other inclusions are chlorides of magnesium, potassium and sodium, carbides of calcium and aluminium, magnesium sulphide (MgS), magnesium fluoride (MgF₂) and magnesium sulphate (MgSO₄). b. Intermetallic inclusions: The intermetallic inclusions are precipitated when iron is removed. Iron is present in most of the intermetallic inclusions.

Both these inclusions negatively influence the tensile strength, resistance towards corrosion and elongation of the alloys of magnesium.

4.1. Origin of inclusions

4.1.1. Reaction with air

Magnesium oxide is formed when magnesium combines with oxygen during the process of melting upon exposure to atmosphere [201]. Also, reaction of magnesium melts with moisture in air leads to the formation of hydrogen and magnesium oxide. This can lead to an explosion or fire. Hence, before immersing in the melt, all the tools should be preheated or kept dry. There is always a certain amount of melt turbulence in casting which traps inclusions resulting in exposure

of new surface of melt to the atmosphere. This enhances the inclusions in the molten magnesium. Various factors which support the formation of oxides are gating design, pouring, stirring, poor venting. The length and thickness of oxide films may be around 50 µm and 0.5 µm respectively. The oxide clusters are formed with 50 µm diameters. The surface to volume ratios of clusters as well as the oxide films is high so melt settling can't remove them [198].

The nitrides of magnesium (Mg₃N₂) are seen along with clusters of oxides when magnesium reacts with nitrogen. The nitrides of magnesium are not formed until there is extremely low partial pressure of oxygen [198]. There are no signs of the inclusions of nitrides that are independent of the oxide particles.

4.1.2. Flux Reactions

Fluxes shield the molten magnesium from getting oxidized and also remove the inclusions. Fluxes like CaCl₂ or MgCl₂ are formed due to an unabsorbed shielding layer on the surface of the metal as the flux is not viscous. Long handling or incomplete flux removal from the pot lip leads to the formation of brittle, powdery flux [202]. Castings contain magnesium oxide formed by the reaction of magnesium chloride with water and oxygen present in the atmospheric air. The fluxes which contain boride form FeB inclusions in the magnesium melt. Hence, protective environments are being used to avoid loss in melt and entrapped fluxes.

4.1.3. Protective Gas reactions

The use of protective environments prevents oxidation and help in the reduction of melt inclusions. The oxide film is modified by the shielding gasses so that vaporization of magnesium doesn't occur and the reactive gasses are eliminated. Fluorinated ketones (FKs), hydrofluorocarbons (HFCs), sulphur hexafluoride (SF₆) and sulphur dioxide (SO₂) are some of the shielding gasses used. SO₂ and magnesium react to form MgSO₄, MgS or MgO. Magnesium reacts with SF₆, HFC and FK to form MgO, MgF₂ [198]. The melt inclusions are formed by all of the above compounds when they go into the melt. Though inclusions are formed by shielding gasses, without the presence of protective gasses the magnesium alloy properties are degraded. Hence the inclusions can only be minimized by following the right techniques during pouring, melting and handling.

4.1.4. Casting Reactions

High turbulence and entrapped oxides can be observed in casting if the gating system has a poor design. These entrapped oxides consist of folded MgO films which are double oxide film defects [203, 204]. While pouring, MgO film is formed that thickens quickly as magnesium is highly reactive. This thick MgO film forms an oxide tube that doesn't get trapped in the molten metal. The formation of inclusions can also be due to oxidation in the shot sleeve, trapping of air in casting and lubricant absorption on the surface of die. The turbulent flow in sand casting leads to the detachment of sand grains from mold walls and get trapped in the molten

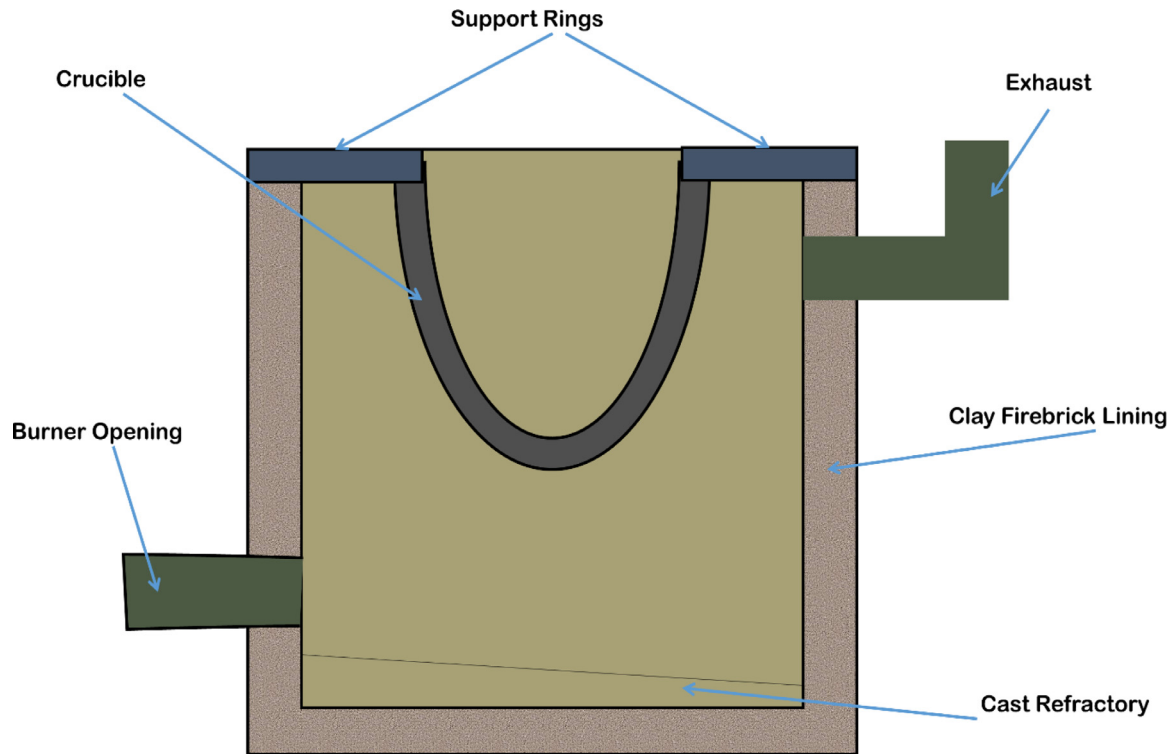


Fig. 11. Fuel-fired furnace for open crucible melting [5]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

magnesium. The sand inclusions in molten magnesium are known as ‘reacted sand inclusions’ [201].

4.1.5. Reactions during alloying and melt treatment

Adding manganese to magnesium melt can lead to the formation of intermetallic particles of iron, aluminium and manganese. These are the inclusions in the iron removal process. The process of degassing and refining grains also results in the formation of inclusions when alloy elements or calcium cyanamide (CaNCN) and hexachloroethane (C_2Cl_6) are added [201].

4.2. Control of inclusions in magnesium alloys

Inclusions can be reduced by employing best foundry practices. Precautions have to be taken in skimming the slag, selecting the charge, the gating design and the conditions of melting. The turbulence has to be minimized and the temperature of the process needs to be controlled to reduce the intermetallic precipitation. Refining methods like non-metallic inclusion separation or adding alloys reduces the inclusions in the molten magnesium.

4.2.1. Adding Flux

In this refining process, initially certain amount of flux (1 wt.% of the total mixture) is laid at the crucible’s base for preheating to red hot temperature [5]. The process is carried out in a fuel fired furnace (Fig. 11). Later, flux is added to a heated molten metal at 705 °C and thorough stirring is done.

Sludge is formed after the oxides in melt are absorbed by flux. The sludge settles at the bottom of the crucible post stirring following which the pure melt can be separated out. MgCl_2 , CaF_2 , KCl , NaCl are some of the fluxes added to refine magnesium. Of late, TiO_2 (30 wt.%) flux is being added to molten Mg which removes iron particles. The reaction of TiO_2 with iron forms Ti-Fe which settles at the base of crucible.

4.2.2. Fluxless Refining

The refining without the use of salt is fluxless refining. The melt inclusions either float on the surface or stick to the walls and base of the crucible. This way they are eliminated before casting [202]. Flotation, sedimentation and interception are the techniques employed in refining without adding flux.

4.2.3. Protective atmospheres

The inclusions decrease in a melt if protective atmosphere is employed because it averts the oxidation process in molten magnesium. Oxide film modifiers and non-reactive gasses are the shielding gas atmospheres. Burning is avoided by gasses like argon and nitrogen which are non-reactive but they cannot be used in practical applications as the vaporization of magnesium is not suppressed and this might lead to loss in melt. Vaporization of magnesium leads to the formation of pyrophoric particles on the furnace surfaces that are cool.

The alternative melt protection technique uses gasses which suppress the vaporization by modifying the MgO film on the melt surface. SF_6 has been widely used to shield magnesium as it has the ability to form thick layer of

MgO [205] and MgF_2 on the melt surface which averts further vaporization and oxidation of magnesium [206]. The colorless, odorless and non-corrosive nature of SF_6 makes it a popular choice for Mg. Only 0.1 to 0.2 vol percent of SF_6 is the ideal concentration and anything above that will severely corrode the crucible. But SF_6 is very harmful for the atmosphere as it is a strong greenhouse gas and also it is extremely expensive. The issues related to the environment had the industries in pursuit of a substitute cover gas. SO_2 (1.5% in air) was sufficiently protective of magnesium but its toxic nature led to the corrosion of crucible. The magnesium melt was efficiently shielded by CO_2 as well until CO_2 was not polluted with air quantities.

BF_3 , solid CO_2 , FKs and HFCs are some of the other substitutes that have a potential of covering molten magnesium. The shielding mechanisms of HFCs and SF_6 are similar as the compounds of MgO and MgF_2 are formed [207]. The capability of global warming in HFCs is lower than SF_6 . Though BF_3 has good shielding properties, it is costly and also toxic. Special storage conditions are needed for BF_3 as it has to be stored at high concentration and compressed at high pressure to avoid the dangers of explosion. BF_3 can be safely dispensed by the developed MagShield system. By decomposing KBF_4 , BF_3 gas was manufactured by in situ process. The thermal decomposition of FKs on the surface of Mg melt gives rise to CO_2 and MgF_2 . Their impact on global warming is same as CO_2 and they protect at concentrations much lower than SF_6 . A special nozzle was designed to inject CO_2 into the chamber of furnace to use the ice pellets of CO_2 for the protection of magnesium. Precipitation of CO_2 pellets on the melt surface reduces the vaporization tendency of magnesium. CO_2 that sublimates, expands the gas of CO_2 displacing the entire oxygen from the surface area of bath. It is essential to confirm that the gasses are free of moisture and continuous supply of new shielding gas is as required.

4.2.4. Filtering Inclusions

Reduction of turbulence of the molten metal decreases the inclusions in the casting. Turbulence at higher levels leads to the growth of oxide films and trapped gasses in the mold which further multiplies the inclusions. The melt flow and its turbulence are reduced by the use of filters in casting. The required properties of filters include inertness, rigidity, thermal stability and thermal shock resistance. The ideal position of the filter is closest to the casting, in the gating system. There are usually three metal filtering stages [208], a) Initial surge in which the temperature of the filter is made equivalent to the melt temperature by the metal entering through the filter pores, b) Normal flow in which flow of the metal through the filter is constant, c) Filter blockage where the filter gets blocked and the flow of the metal halts. Usually, two kinds of filters are used.

Ceramic Foam Filters: These filters have structure similar to foam with multiple open cells arranged. They are used for reducing the number of inclusions in molten alloys of steel and aluminium. These filters may react with molten magnesium and pollute the melt.

Stainless Steel Mesh Filters: These are ideal for filtration of molten magnesium as they are non-reactive with magnesium, readily available and inexpensive.

4.2.5. Sparging

Gas sparging is a refining technique in which inert gas is used for floating the inclusions on the melt surface for them to be filtered away. The most common gasses used for gas bubbling are CO_2 and argon. The efficiency of gas bubbling is influenced by the factors like the time of bubbling, the rate of gas flow, size of the bubble and temperature of the melt [209]. There was an enhancement in the mechanical properties when the time of bubbling, rate of flow and removal of inclusions were elevated. Excess bubbling resulted in porosity thereby hampering the strength and elongation of the casting. The usual parameters considered for argon in sparging are, 30 min of bubbling time, 1.8 liters per minute rate of flow and 740 °C temperature of molten metal [209]. The inclusions with a size less than 80 mm were significantly removed by argon bubbling but it was ineffective with inclusions more than 800 mm. This restrained efficiency in the process has led to the necessity in determination of ideal process parameters.

4.2.6. Degassing

The levels of hydrogen gas in molten magnesium can be reduced by using reactive gasses like Cl_2Cl_6 or Cl_2 . Though Cl_2Cl_6 refines the melt grains, it emits chlorinated hydrocarbons which are harmful to the environment. Both the gasses form MgCl_2 which can eliminate the inclusions but there is a danger of MgCl_2 becoming an inclusion itself while pouring.

4.2.7. Ultrasonic Purifying of melt

The magnesium melt can be treated with an ultrasound to quicken the process of separating inclusions from it. The acoustic radiation in an ultrasonic treatment exerts forces on inclusions which agglomerate and settle at the bottom [210]. This technique of reducing melt inclusions is still at a budding stage but initial studies revealed a lot of potential. The studies suggest that the agglomeration of smaller particles is time consuming for a specific ultrasonic power [211]. There is a homogeneous and finer spread of inclusions in the molten magnesium if cavitation bubbles are formed by the ultrasonic treatment as the waves (ultrasonic) will crumble the large inclusions [212].

4.2.8. Electromagnetic Separation

The process of removing the inclusions that non-conducting by electronic separation so that they float on the melt surface is called electromagnetic separation. This is one of the latest inclusion separations techniques for molten magnesium. The analytical studies suggest an increase in the efficiency of inclusion removal with increased current density and reduced size of the channel [213]. But this has been simulated only for a laminar flow under steady state conditions in rectangular channel that is vertical. The capability of the electromagnetic field to separate the inclusions reduces with increased melt

velocity [213]. Hence further analysis is needed on this process for practical applications.

4.2.9. Adding Alloys

The reaction of oxides with air, while melting magnesium is appalling and porous. Alloying elements like beryllium (Be) and Ca enhance the protection ability of the oxide film which enhances the ignition temperature of magnesium alloy [214]. The resistance against ignition and oxidation of molten magnesium are so significantly enhanced by adding CaO, that no shielding gas is needed [215]. It is assumed that reducing the oxidation potential might reduce the inclusions in molten magnesium.

4.2.10. Sedimentation of melt

In the molten metal, allowance of enough settling time will eliminate certain high density intermetallic compounds of silicon, iron, lead and silicon. Factors like crucible size, type of furnace and size of the intermetallic compounds will determine the settling time.

5. Manufacturing Mg alloys and Mg composites

The alloys of magnesium have distinctive characteristics related to the metal solidification. They are extremely fluid and their vulnerability towards hydrogen porosity is very low therefore the magnesium alloys are more castable than their counterparts like copper or aluminium [216]. This has made casting the most commonly employed production technique for magnesium. In case of the composites of magnesium, the metal matrix and reinforcement decide the manufacturing process of composite because composites can be produced in different ways. The final material properties of the composite are determined by the combination of metal matrix, reinforcement and the processing method [217]. Apart from these, the reinforcement dispersion also influences the composite properties and homogeneous dispersion is necessary for ideal properties [2]. The following techniques are employed in the production of magnesium composites.

- I. Liquid Phase Processing: It includes casting techniques like pressure casting, squeeze casting, stir casting, compo-casting, melt infiltration and DMD (disintegration melt deposition) [179].
- II. Solid Phase Processing: Methods like powder metallurgy, CVD, PVD, hot rolling, mechanical alloying diffusion bonding comprise of solid phase manufacturing techniques [179].
- III. Dual Phase (solid or liquid) Processing: Spray atomization [218] and rheocasting [219] encompass the dual phase manufacturing processes.
- IV. Processing through Special Methods: FSP (friction stir processing), flux-assisted synthesis, reactive hot pressing, SHS, rapid solidification and reactive spontaneous infiltration are some of the special production methods of composites [179].
- I. Liquid Phase Processing:

The most common process for the fabrication of magnesium alloys and composites is the liquid phase processing. The prime elements of liquid phase processing include the penetration of reinforcements into the molten metal followed by crystallization producing slurry that is homogeneous in nature. The composite mixture can be achieved by using techniques like injection or centrifugal distribution [220]. Depending on the methods of reinforcement infiltration, the liquid phase processing methods vary. The composite mixture is casted using conventional or various special techniques of casting. Though this processing technique is cost effective, there may be issues like inadequate reinforcement wettability resulting in non-uniform dispersion, melt rejection with segregated particles with unwanted reactions.

5.1. High Pressure die casting

The process of high pressure die casting is more accommodating in terms of designing and production of light weight metals. The properties of magnesium like die filling are extremely favorable for this process. Hence, this is a cost-effective technique for manufacturing large castings with complicated structures and thin walls. Both thin and thick-walled casting of magnesium can be produced as per the desired application. In thin-walled magnesium castings, stiffness can be balanced by using ribs without tampering with thickness of the wall. Shorter casting cycles and improved die lives is due to the low latent heat of solidification and low iron affinity of magnesium [221]. The high pressure die casting can be classified as hot chamber die casting and cold chamber die casting.

5.1.1. Hot chamber die casting

The hot chamber die casting, as seen in Fig. 12, encloses the molten metal in a steel crucible in a conservative environment [222]. Metal flow into the immersed gooseneck is regulated by a valve. This molten metal is injected into the die cavity with a nozzle. The nozzle is preheated and maintained at a temperature of 400 °C to 500 °C in order to avoid melt freezing.

In between shots, the nozzle is always filled by molten metal to reduce the cycle time. The metal oxides are not formed in the hot chamber die casting as there is no contact between the air and molten metal. The melt is held in a sealed crucible and shielded by a shielding gas till it reaches the die. This is one of the main advantages of this process. Moreover, magnesium is very compatible with steel hence it can be enclosed in steel vessels. Hence, crucibles and ladles for casting magnesium are made of carbon steel or stainless steels (400 series). But 300 series stainless steels are not advised because they contain cobalt and nickel. If these elements dissolve in magnesium, its corrosion resistance is hampered. The injection pressure of molten metal is lower in hot chamber casting than cold chamber casting and this restricts the size of the manufactured components by this process. The high working temperature of the nozzle is the reason. The hot chamber die

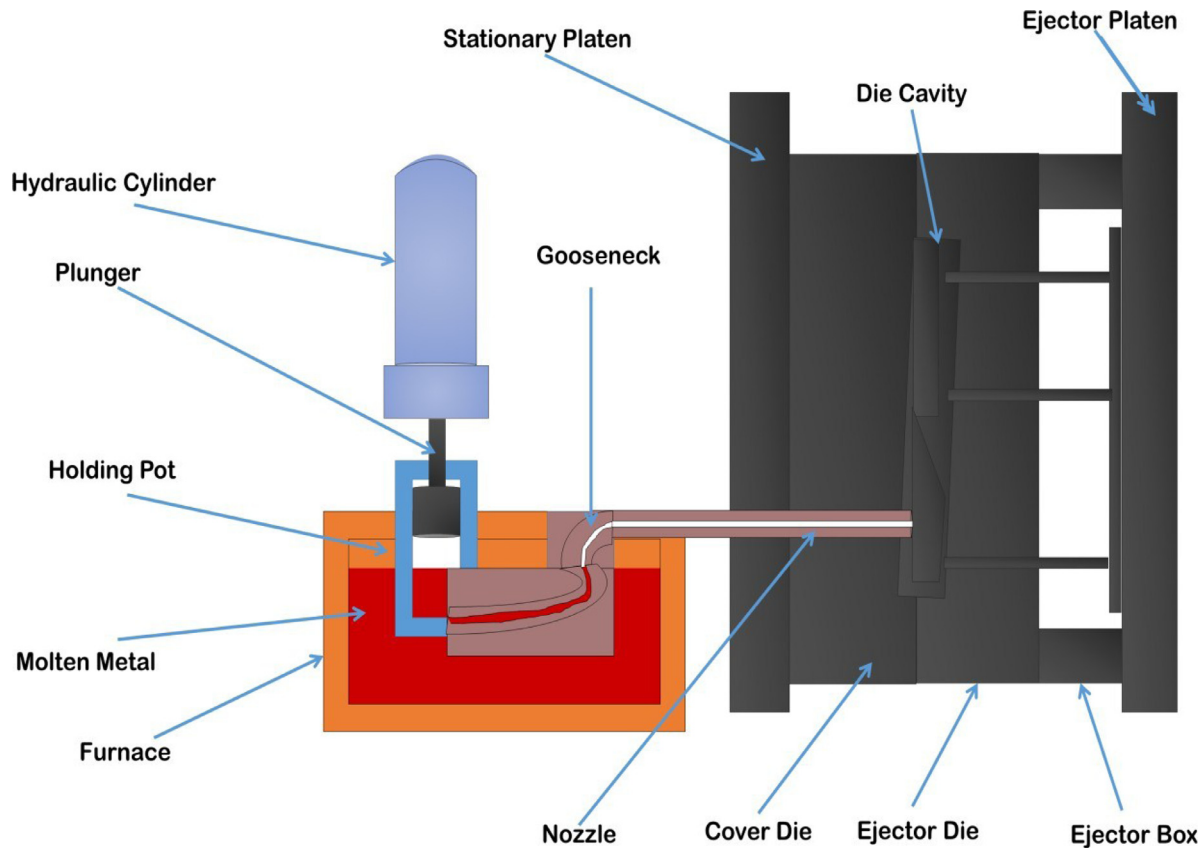


Fig. 12. Hot Chamber Die Casting [222].

casting is ideal for smaller components as it has short cycle times.

5.1.2. Cold chamber die casting

As seen in Fig. 13, in the cold chamber die casting, the shot cylinder feeding of magnesium melt, is done by a ladle (manually or automatically) or a pump [222]. The molten magnesium is quickly injected into the cavity with a plunger in which it solidifies taking the die shape at a high pressure of 35 to 140 MPa. The ejected casting and the gating system are then separated by trimming. The cycle time of the entire process is about 1 min. This process of die casting (cold chamber) is extremely beneficial for casting magnesium.

- It is economical for mass production in industries due to its high-volume generation.
- The metal reaction with air and metal contact with die are reduced due to its short cycle time.
- Magnesium is non-reactive to the steel containers thus increasing the die or crucible life.
- Large parts having thin cross sections can be manufactured due to the quick filling and injection of molten metal into the die.
- Fine grains are produced in the skins due to its higher rate of solidification (100 °C to 500 °C per second).

Most of the magnesium components in automobiles are manufactured using this process for the above reasons. Some of the important components include, beam of instrument panel, seat frames, radiator supports, transmission case, oil pan and engine cradles.

5.1.3. Vacuum die casting

The trapped gasses in the castings because of high injection velocity results in high levels of porosity which is the biggest disadvantage of high pressure die casting. In casting thin walls, the mechanical properties are obtained due to fine grains and skins without grains. Hence, porosity isn't a serious issue. But in case of thick walls, strength and stiffness are necessary for structural applications for which porosity becomes a serious issue as it is detrimental for material properties. Vacuum die casting is an alternative advanced manufacturing process in which less porous castings can be obtained. Low pressure is created inside the injection chamber and the die just before the metal gets injected which eliminates the possibility of entrapped gasses inside the casting. As a result of which, thin-walled casting can be produced with higher mechanical properties. The castings produced by this process are further heat treated for enhanced material properties. Hence, the vacuum die casting is a more beneficial process as compared to the typical casting but it is also cost effective [222].

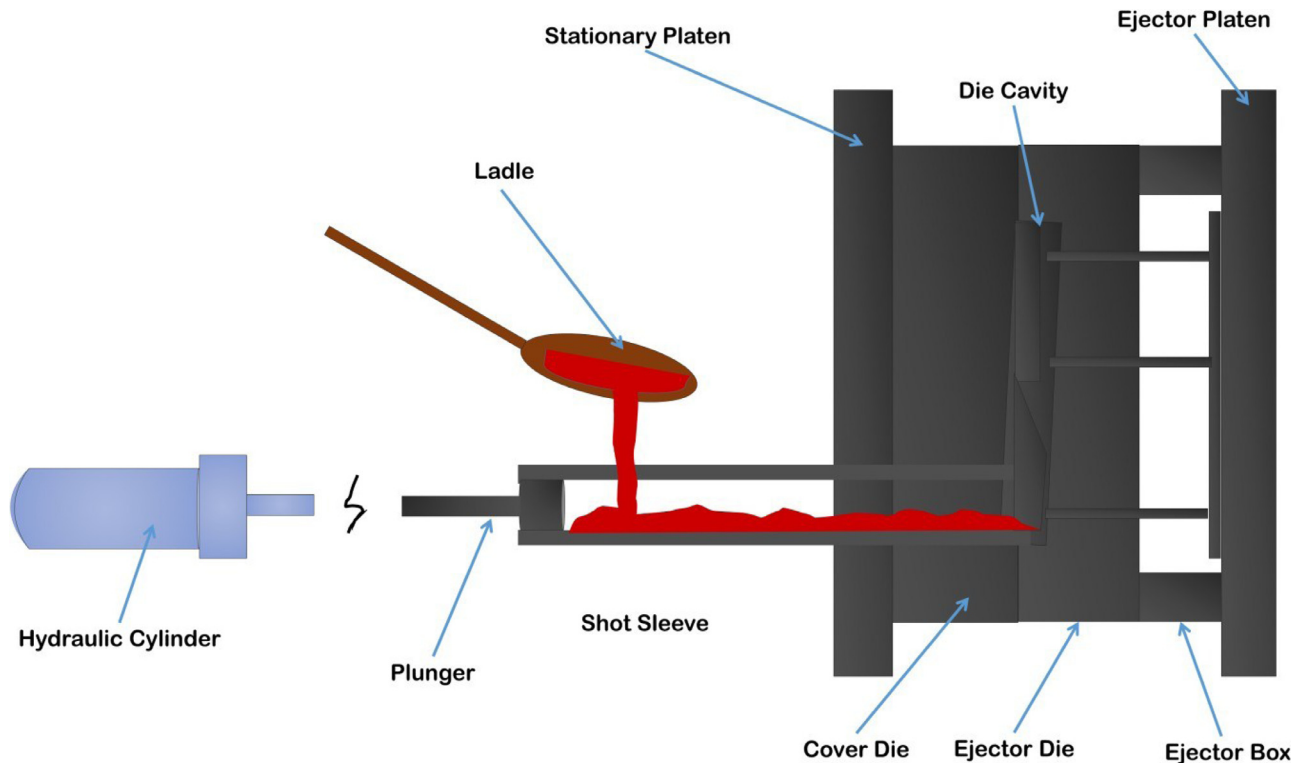


Fig. 13. Cold Chamber Die Casting [222].

Vacuum assisted die casting. The air from all cavities and feeding channels is removed in this process by vacuum. Then the required quantity magnesium melt is drawn into the cylinder of the injector by the transfer tube. The initial plunger movement restricts the metal flow thereby putting a control over the metal quantity within the cylinder. The metal is then injected into the vacuum die cavity. This eliminates the possibility of air within the casting. In the vacuum, a high pressure is exerted on the die to solidify the metal after which the casting ejects automatically. The porosity of magnesium castings can be reduced by a basic vacuum system in this process [221]. The components casted by the normal high pressure die casting cannot be heat treated as the entrapped air will expand forming blisters. This isn't a problem in vacuum assisted casting because no blisters are formed due to heat treatment. Casting in the absence of air will not form gas pores to expand on heat treatment.

Super Vacuum Die Casting. For magnesium die casting, an advanced vacuum system has been fostered to obtain superior levels of vacuum and also to monitor the intensity of vacuum in the whole filling process. The super vacuum die casting houses a dominant vacuum system with progressive vacuum controls and inspection systems along with distinctive gating designs [223]. The yield strength of components casted by super vacuum die casting is influenced by the size of grains and the nature of alloying. Hence marginal improvement is observed in the yield strength. But in the super vacuum die casted alloys of AZ91D and AM60B, large variation in ductility and UTS is seen than high pressure die castings. The

reason for this large variation is the decrease in porosity of the castings.

5.2. Gravity Casting

Excellent castability of magnesium in dies and high productivity are the reasons for dominance of high pressure die casting. But the gravity sand casting and permanent mold casting techniques are also used for manufacturing components required in various structural applications.

5.2.1. Sand Casting

The sand casting uses green sand, resin or silicate bonded sand for mold preparation. Castings of magnesium till 1400 kg weight can be sand casted. In magnesium sand casting, appropriate inhibitors have to be used in the mixtures of sand and cores to check the metal reactions. Inhibitors like sulphur, $(\text{NH}_4)_2\text{SiF}_6$, BF_4K can be used in combination or solely [5]. Wooden pattern is commonly used in sand casting but for high dimensional accuracy metal or plastic patterns of accurate tolerances are used. Magnesium has extreme tendency to oxidize and low density. Hence to reduce the turbulence in flow and for sequential solidification, the gating system is to be carefully designed.

5.2.2. Permanent Mold casting

The basic difference between permanent mold casting and sand casting is that a metal mold is used here. The process of permanent mold casting will either have a metal mold (permanent) or a breakable sand core (semi-permanent). The perma-

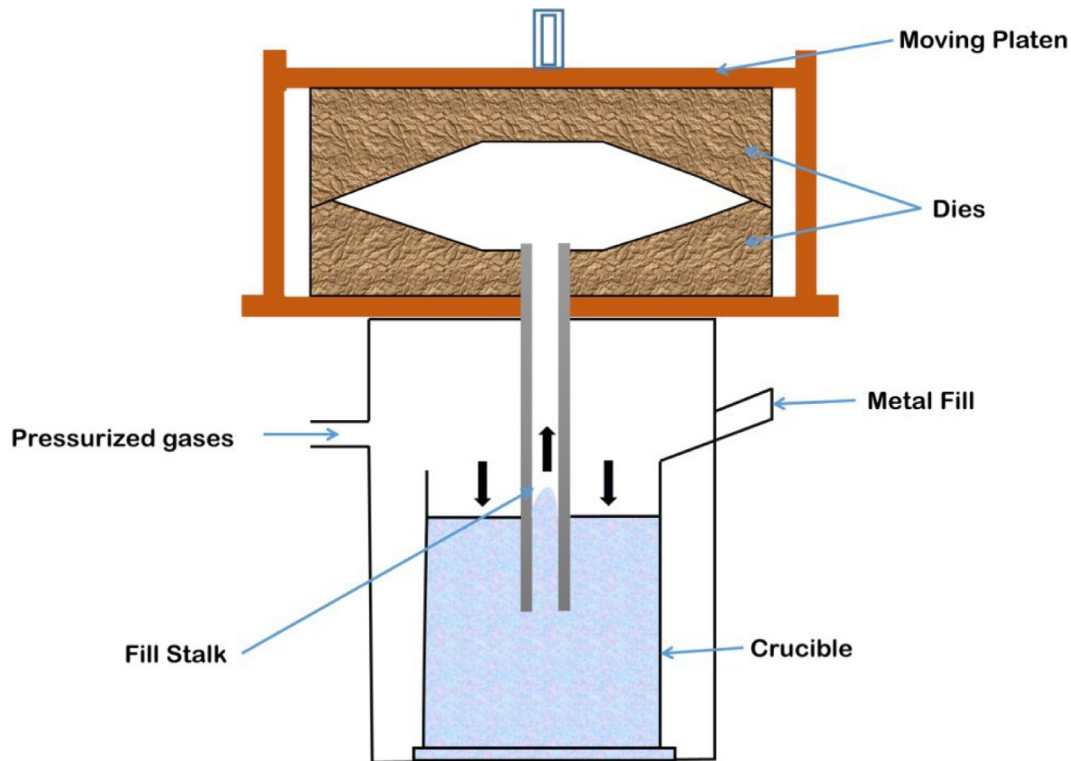


Fig. 14. Low Pressure Casting Machine [224].

nent mold casting is advantageous in terms of the dimensional accuracy, the surface finish and enhanced mechanical properties. In permanent mold casting, there are certain restrictions in the casting of complex shapes. The factors influencing the quality of permanent mold casting may be outlined as [221]:

- Cleaning the mold cavity with shielding gasses like SF_6 or CO_2 before pouring will eliminate the trapped oxygen and enhance the quality of casting.
- In casting magnesium, C_2Cl_6 is an efficient degasser.
- Adding fluoride like NaF to mold will form MgF_2 resulting in enhanced quality of casting and reduced oxidation.
- For low production volumes, cast iron can be the die material due to low melting point of magnesium and H13 steels for high production volumes.
- Inclusions due to oxidation will hamper the interdendritic feeding resulting in decreased wettability of interdendritic fluid. This will negatively affect the hot tearing.
- Alloys with wide freezing ranges are vulnerable to hot tearing. Interdendritic feeding is great for alloys having fine grains. It is the high surface tension of inter dendritic liquid that enhances hot tear resistance.

5.3. Low Pressure casting

There is a crucible under pressure placed below the mold table in a low-pressure casting machine. A riser or feed tube runs from the crucible to the lower half of the mold cavity as seen in Fig. 14 [224]. The dry gas pressurizes the melt

surface with a pressure low enough to create a capillary affect in the feed tube so that the molten metal rises to fill the die cavity. To balance the solidification of casting, the pressure is increased for the melt supply to continue within the riser.

After complete solidification, the external pressure is relieved and the excess melt flows into the crucible. The obtained casting is free of pores due to a dormant filling process and complicated internal passages. The disadvantages of low pressure casting over high pressure die casting are its long cycle times (2 to 4 times) and inability to produce thin walled (below 3 mm) castings of magnesium. But unlike in high pressure die casting, hollow castings can be obtained in low pressure casting process. Hollow castings are needed for their efficient structures. Thick, non-porous castings (thickness around 10 mm) can be produced by low pressure die casting and the castings can also be heat treated for further property enhancements. The YS and UTS of low pressure die casted AZ91 when heat treated improved respectively by 50% and 24% but its elongation decreased. The T6 heat treatment was carried out initially at 420 °C temperature for 18 h, quenched in hot water and finally heated again at 175 °C for 16 h duration. The grain size in low pressure die casting is higher than high pressure die casting process as the rate of cooling is higher in the posterior process. In the process of low pressure die casting, to enhance the strength of the component, grains have to be refined without disrupting its excellent ductility [221].

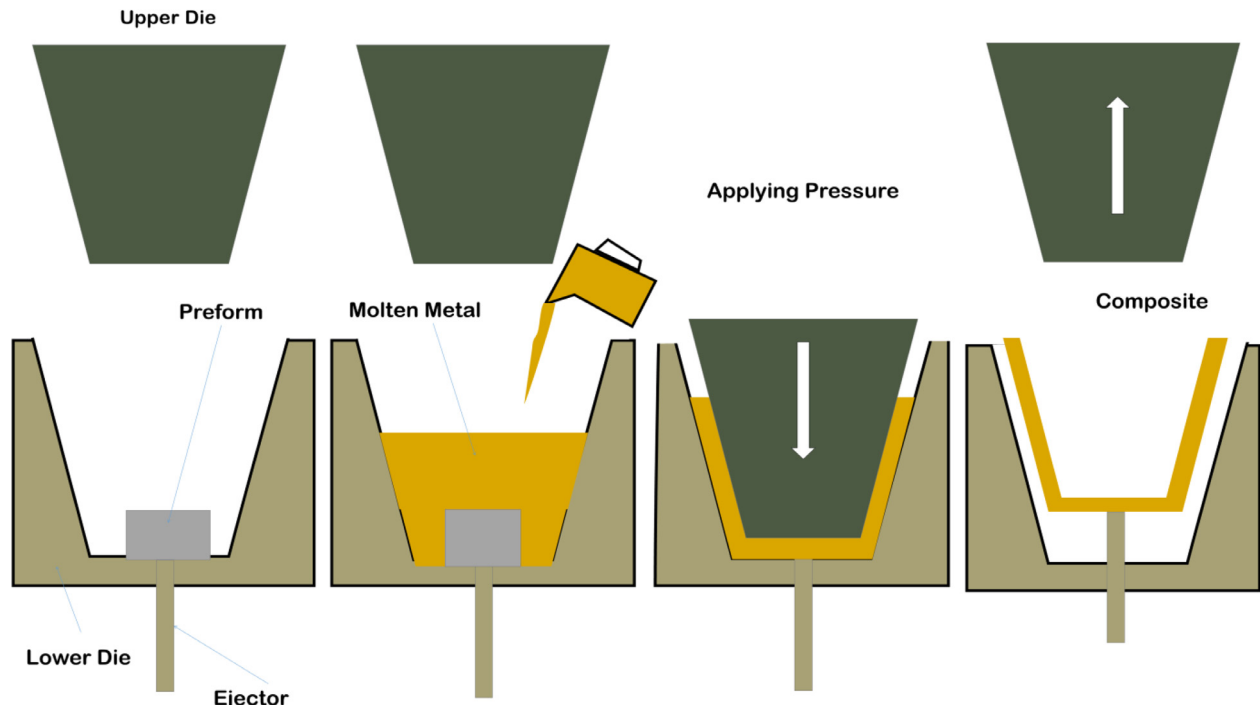


Fig. 15. Process of Direct squeeze casting of Mg composite [179].

5.4. Squeeze Casting

The squeeze casting technique came into existence in the year 1931. The processes of squeeze casting may be classified as direct squeeze casting and indirect squeeze casting. Molten metal, under high pressure (100 MPa) and with low turbulence is injected into a reinforced die cavity where the solidification of the molten metal takes place in closed dies. In case of composites, a reinforced preform is placed in the die and the molten metal is injected into the preform. The molten metal seeps into the preform pores and thus after solidification a composite is formed.

5.4.1. Direct Squeeze casting

The process of direct squeeze casting has an alternative name of liquid metal forging. Fig. 15, shows molten metal being poured into a pre heated die through reinforced preform placed in the bottom half [179]. The molten metal seeps through the reinforced preform under optimal pressure conditions forming a composite. The processes of vacuum or press forming are used to prepare the preform of reinforcement. The molten metal should have enough wettability and must have low viscosity for ideal infiltration [225, 226]. This is then forged in the hot condition by applying pressure. The pressure is continued till the solidification of the whole casting. The casting is ejected upon solidification.

This process is suitable for magnesium castings or composites which have low melting points. Squeeze casting can produce low porous castings with finer grains that have lower shrinkage. Hence excellent mechanical properties can

be achieved with higher reinforcement volumes (less than 50%) [179].

- Optimal pressure is to be applied in the process of squeeze casting because higher pressures can have adverse effects on magnesium castings mentioned as follows:
- The casting of magnesium will get oxidized resulting in entrapped gasses due to the turbulence of the molten metal.
- The reinforcement phases might be damaged resulting in lower mechanical properties of the final casting.

Hence utmost care has to be taken in the pressure control during the process of squeeze casting. The process of squeeze casting is not suitable for large scale production as there are dimensional and shape related constraints in squeeze casting [227]. Currently the process of squeeze casting of magnesium alloys or composites is being carried out in two stages (infiltration at low pressures and solidification at high pressures) to avoid the adversities related to casting at high pressures [228].

5.4.2. Indirect Squeeze casting

The process of indirect squeeze casting is similar to the high pressure die casting having horizontal as well as vertical machines. In this, the molten metal is shifted through a closed tube into a shot sleeve from which through a series of large gates gets injected into the die cavity as seen in Fig. 16a). The velocity of injection is very low and is below 0.5 m/sec. The molten metal inside the cavity of die solidifies under the high, indirect pressure applied by the piston

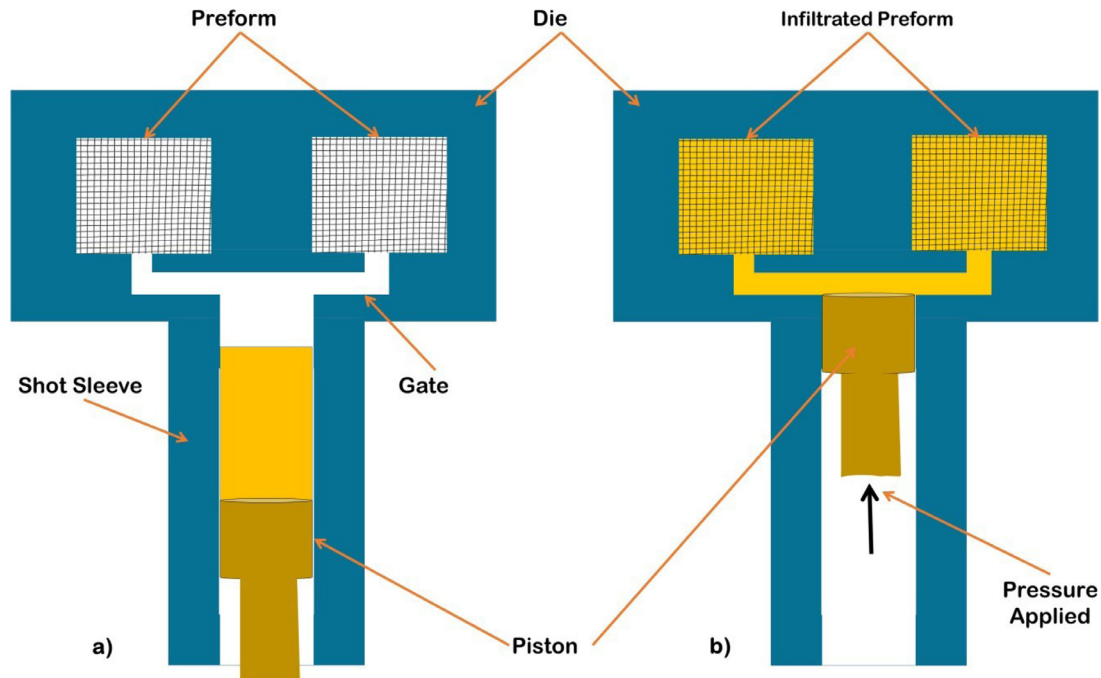


Fig. 16. Indirect Squeeze casting a) transfer of melt through shot sleeve b) melt solidification under indirect pressure [229].

as seen in Fig. 16b) [229]. The low injection velocity ensures planar melt filling inside the die cavity thereby removing the possibility of gas entrapping within the casting.

In the process of squeeze casting, lack of melt turbulence and high pressure eliminate porosity in the final castings. The porosity while shrinking is also minimized in squeeze casting because low superheat is used in the molten metal. This is feasible in squeeze casting because fluidity of molten metal isn't needed for die filling, instead it is done by high pressure. For heavy castings, where the possibility of shrinkage porosity is high, due to the high pressure, molten metal is squirted from hot spots to emergent shrinkage pores. This completely eliminates the pore formation in castings. The movement of the molten metal is feasible in metal alloys which have wide range of freezing. This enables high quality castings at low pressures. The squeeze casting is an extremely good alternative for magnesium castings with thick walls.

5.5. Lost Foam casting

The process of lost foam is carried out in two stages. In the first stage, a molded foam pattern coated with a refractory inclusive of the gating system is placed inside a flask contained by unbounded sand. This is then vibrated for establishing maximum compaction of sand about the pattern assembly. Next, molten metal is poured over the refractory coated pattern so that the polystyrene pattern vaporizes. This leaves the casting which is identical to the shape of the foam pattern. At the time of vaporization of pattern, the formed gasses escape through the vents of the flask, sand and the coating. High dimensional accuracy can be achieved through lost foam casting. The eliminated binders, sand cores and parting lines

are a major advantage of this process. Other significant advantages of lost foam process include part consolidation and easy cleaning of the castings. Automation of the lost foam process can attain high yields. In casting magnesium through this process, the major hurdle lies in the chemical reactivity of Mg with the coating, foam and particles of sand. The low heat content of magnesium has made it difficult to displace the foam patterns. Presently magnesium is being casted at higher temperatures with suitable gating systems besides the use of sand inhibitors to surmount these hurdles [221]. The sand inhibitor is a combination of sulphur with potassium fluoroborate. Coatings like semcoperm M70 or M66L and foams like probead 70 are used in magnesium castings for defect free castings. It was observed that in a vacuum of 40 kPa good castings were obtained.

5.6. Ablation Casting

In the process of sand casting, the turbulence in mold cavity filling can be reduced but this will result in poorer material properties of the final casting. Moreover, the casting solidification leads to contraction away from the walls of the mold while the mold cavity also expands, this creates an air gap between the two. The cooling rate, mechanical properties and the refinement of the microstructure are influenced by the air gap.

Ablation means erosion by the process of dissolution. In the process of ablation casting, the sand mold, held with an eco-friendly binder is eroded when water is impinged [230]. Ablation takes place which leads to impingement of the water right on the casting as seen in Fig. 17. The mold and the internal cores are easily removed by the ablation process

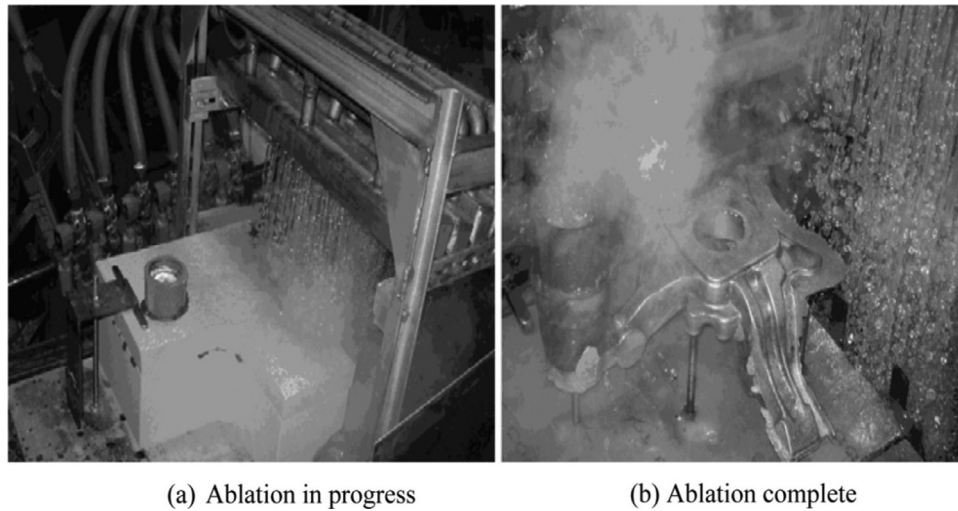


Fig. 17. Ablation process for Magnesium Castings [230].

resulting in higher rate of cooling for the casting. The advantages of ablation are clearly seen in the alloys of magnesium. Interestingly, magnesium alloys (AM60, AZ91) are passive to ablation which is essential for manufacturing good quality castings.

5.7. Stir Casting

The stir casting process is extremely popular due to its cost effectiveness and suitability for mass composite production. In the process of stir casting, reinforcements are added to the metal matrix in the molten state through continuous stirring. The process of continuous stirring ensures uniform dispersion of the reinforcement particles in the molten metal matrix. Mechanical stirring at vigorous speeds and elevated temperatures averts particle agglomeration. Conventional casting techniques are employed to solidify the molten composite mixture after desired mixing. The porosity of stir casted components is reduced by carrying out secondary operations which results in uniform dispersion of the reinforcements [231]. Composites up to 30% volume fraction of reinforcement can be manufactured using the process of stir casting. Fig. 18 represents the general steps involved in the process of stir casting [232].

Stir casting is the most cost-effective fabrication technique for large scale manufacturing of composite materials. It can also be combined with other fabrication techniques like SHS in the production of magnesium metal matrix composites [233].

The non-uniform reinforcement dispersion can lead to permanent casting failure. Hence uniform dispersion is absolutely necessary for good strength of the composite. But this isn't accomplished in the process of stir casting [234]. Another disadvantage of stir casting is the reinforcement agglomeration on the melt surface or sedimentation while pouring or casting. The reinforcement dispersion is influenced by the factors like strength of mixing, rate of solidification, relative density and wettability [234, 235]. Hence the optimum process parameters

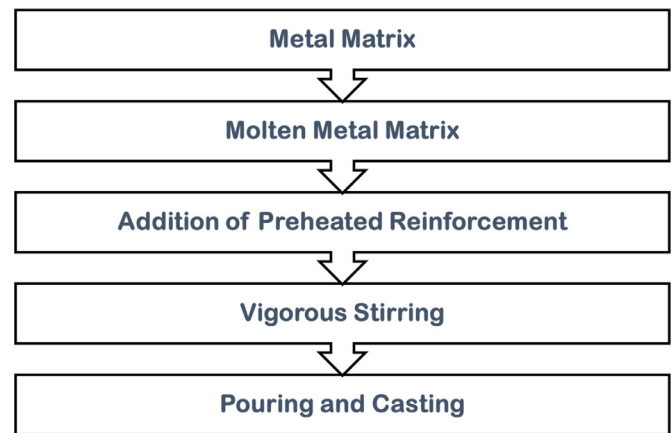


Fig. 18. Flow Chart representing the steps in Stir Casting Process [232].

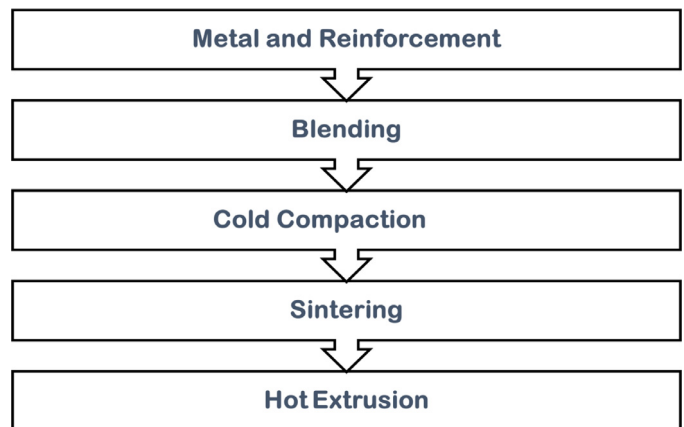


Fig. 19. Process of Powder Metallurgy [238].

are to be selected for acceptable reinforcement dispersion. The probability of gas entrapment and unnecessary inclusions is excessive in the process of stir casting due to vulnerability

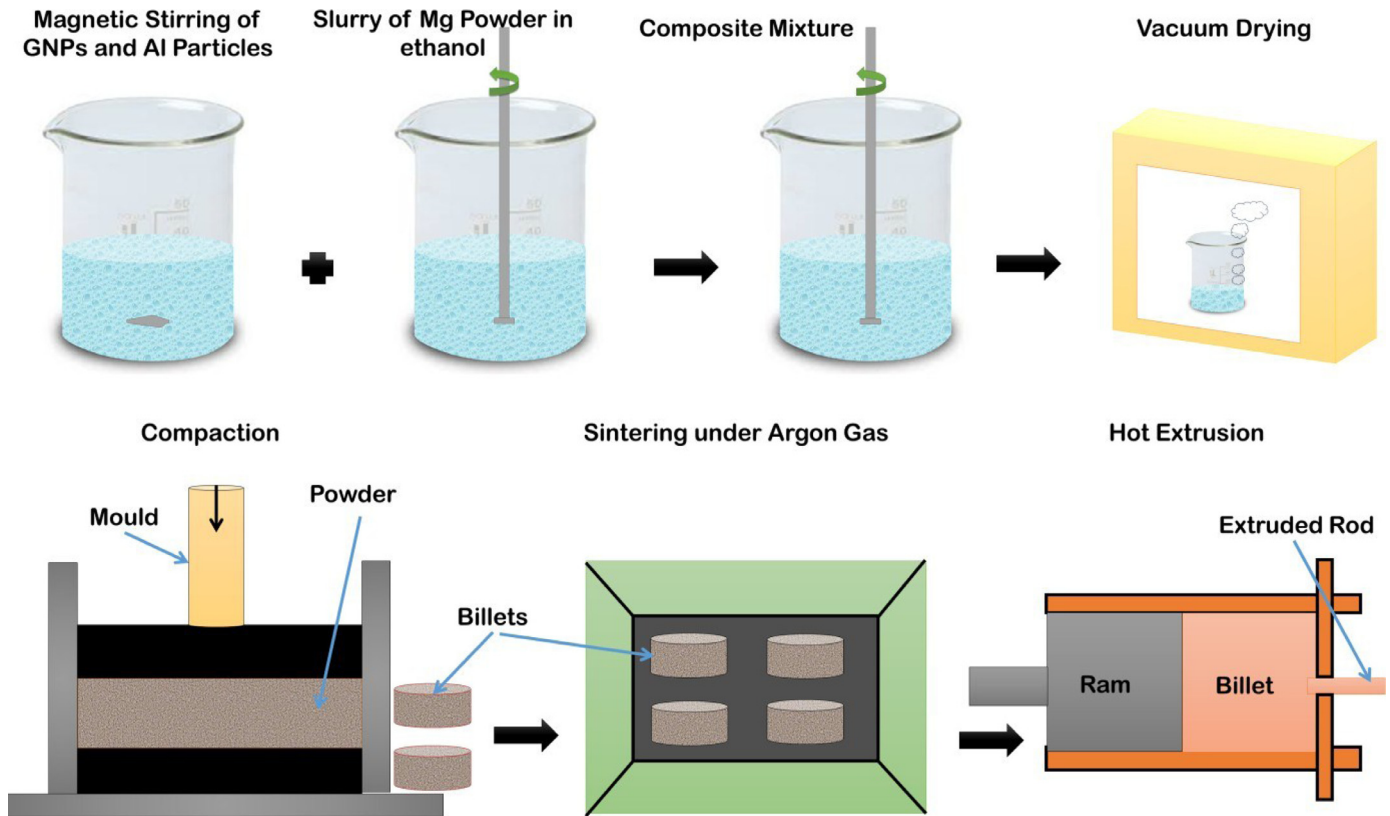


Fig. 20. Semi powder metallurgy process [241].

of magnesium towards oxidation. Hence a cautious effort is to be put in while stirring magnesium composites by maintaining high viscous and well stirred portions of the molten metal.

Currently, the process of stir casting is being employed by using a two-stage mixing process where initially, the metal matrix after heating above the points of liquidus and solidus is in a semisolid state. Next the semi-solid melt is added to reinforcements that are pre heated and they are thoroughly mixed for getting a pour ready mixture [235]. The high viscosity of the initial semi-solid melt ruptures the gas layer on the particle surface to enhance the mixing ability in the secondary molten state. Further research is necessary on the two-stage process of stir casting in the production of magnesium metal matrix composites.

5.8. Disintegrated Melt Deposition (DMD)

The inception of DMD started in the year 1800. It is regarded as blend of conventional casting and spray forming. Low impinging velocities of gas jet and elevated superheated temperatures are included in the process of DMD. In DMD, graphite crucible containing heated ($> 650^\circ\text{C}$, superheated state) turnings of magnesium and reinforcements are kept in a heating furnace controlled by argon. The reinforcements and turnings of magnesium are organized in a multi layered pattern. The mixture is stirred by a twin blade impeller (mild steel) at the superheated temperature for duration of 5 min at 450 rpm. This stirring ensures uniform temperature and

uniform dispersion of the reinforcements. The mild steel impeller is coated with Zirtex 25 to avoid contamination of iron from it. Zirtex 25 has a composition of ZrO_2 86%, Y_2O_3 8.8%, silicon dioxide 3.6%, potassium and sodium oxides of 1.2% and 0.3% of inorganic traces. The molten metal escapes through the orifice placed below crucible and gets deposited on a metal substrate. This deposition happens after fragmentation by two argon gas jets which are at right angles to the melt flow. This forms composite preforms. Secondary processed like extrusion (hot) or machining are carried out on castings in DMD to get the finished product [236, 237].

Equiaxed grains with uniform reinforcement dispersion are obtained in the process of DMD. Sudden solidification process yields lower casting pores. This leads to high quality composites with enhanced material properties. The wastage of material is less as almost the entire material deposits can be turned into extrusions. But stirring and uniform reinforcement is difficult in DMD due to the high viscous molten metal. Hence, adding large reinforcement quantities (more than 30% for micro size and more than 3% for nano size) is not advisable for DMD while stir casting.

II Solid Phase Processing

To obtain a homogeneous microstructure in the liquid phase processing techniques, extreme control is necessary in the dispersion of reinforcement. Interfacial reactions of reinforcement and metal matrix are bound to happen due to the involvement of extreme temperatures. This will result in

adverse composite properties. The above factors contributed in the acceptance of the solid-phase processing as a superior alternative. These techniques are correlated to lower temperature, lesser interface reactions and lower rates of diffusion. The metal matrix and the reinforcement are in the form of powder or particles (discontinuous). The powders are thoroughly combined to form a composite after going through various processes. Powder metallurgy, diffusion bonding and high energy forming with high rate are some of the illustrations of the processes in solid phase processing.

5.9. Powder Metallurgy

Out of the various processes in the solid phase processing, the powder metallurgy (PM) technique of blend press sinter is the most known and the oldest technique for manufacturing the metal matrix composites. Particulates or whiskers are the nature of reinforcements considered. In the beginning of the PM, metal matrix and reinforcements in the powdered form are blended together. After blending, the powder mixture under high pressure is compacted within a mold. The obtained compact is sintered at a temperature below the melting point of the matrix so that the constituent's bond by solid diffusion process. Sintering is carried out in controlled environment to avoid oxidation following which secondary operations are done on it. The end product is obtained after the secondary operations following which it is ready to be utilized for its desired application.

Fig. 19 shows generalized process of powder metallurgy [238]. The metal and reinforcement are blended mechanically and this is followed by cold compaction which is carried out under high pressures. Next is the process of sintering which induces diffusion of atoms in solid state. This leads to lesser porosity and mechanical integration inside the composite. Factors like time, the temperature of sintering, rate of heating and the surrounding conditions influence as to how effectively the sintering is carried out. An advanced technique known as hybrid microwave sintering has recently become popular. It is regarded as a combination of standard heating and microwave techniques. This is a quick sintering method in the material fabrication which is assisted by a microwave [239, 240]. The heating elements generate heat in a typical sintering process by the principles of conduction or radiation through the furnace. Energy of the microwave is transmitted to the material by electromagnetic fields which are the reason for molecular interactions in hybrid microwave sintering. The molecular interaction quickens the volumetric heating thereby reducing the time of sintering and the temperature of sintering. This eliminates the need for reheating. It is also observed that there is enhanced density in the process of hybrid microwave sintering.

Semi powder metallurgy technique (Fig. 20) was adapted for manufacturing the composites of magnesium. It involved combining ethanol to the powdered magnesium and separately with reinforcements [241, 242]. Mechanically the magnesium powder was stirred and magnetic stirrer was used for stirring the reinforcements.

Reinforcement –ethanol mixture was added in the form of drops to magnesium ethanol mixture so that a homogeneous mixture is formed. This mixture was then converted into powder by filtering and drying in vacuum. This was the modification to the conventional PM technique. After obtaining the powder, the regular PM steps were followed. Dense Mg composites were obtained with better mechanical properties. Different reinforcement quantities can be used in the PM process but this is not applicable for complicated shapes. The binder removal in the powder metallurgy process causes complications. The binder is used to collectively hold the reinforcement and the metal matrix.

III Dual Processing

5.10. Thixomolding

The process of Thixomolding is semi-solid in nature and produced net shaped parts of magnesium. The granules of magnesium are fed from the feed stock at room temperature which is seen in Fig. 21. The granules are fed into the heat barrel and the modified setup of injection molding consisting of a screw. The temperature is increases to semisolid region due to high rate of shear mixing [243].

The semi-solid mixture consists of solid particles floating in molten liquid which is injected into a metal mold that is preheated. Less porous castings with enhanced fatigue strength are obtained [243]. Thin-walled castings (0.5 to 1 mm) can also be produced and similar nature of working as plastic injection molding has made it popular. But high cost of magnesium granules and non-availability of molding machines of large size have hampered the applications of Thixomolding. The applications of Thixomolding include mobile casings, camera and computer casings.

5.11. Rheocasting

The processing of semi-solid metal has proved to be one of the most sought after alternatives to regular casting methods, especially in the production of complex Mg castings. The mold filling in this process has laminar flow of molten metal due to high viscous semi-solid metal [244]. Hence good castings with enhanced material properties are produced due to absence of entrapped gasses. The rheocasting process is a subset of semi-solid metal processing in which less porous castings with good strength are attained with optimum control in temperature [245]. The rapid slurry process or the rheometal process is the ideal process for slurry preparation in rheocasting method. The molten metal is converted into slurry by the process of rheometal. The exchange of internal enthalpy takes place at lower superheat between the solid metal at the stirrer and the molten metal converting it into slurry. Studies suggest that combining the processes of rheocasting and rheometal, magnesium castings of superior quality are obtained with reduced defects alleviating the atmospheric properties of magnesium [246].

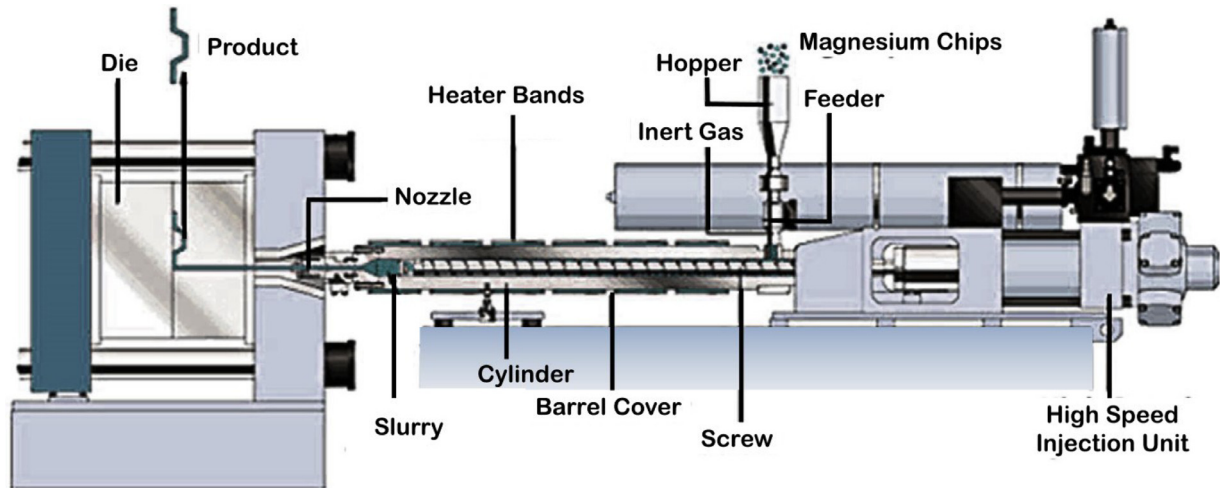


Fig. 21. Thixomolding Machine [243].

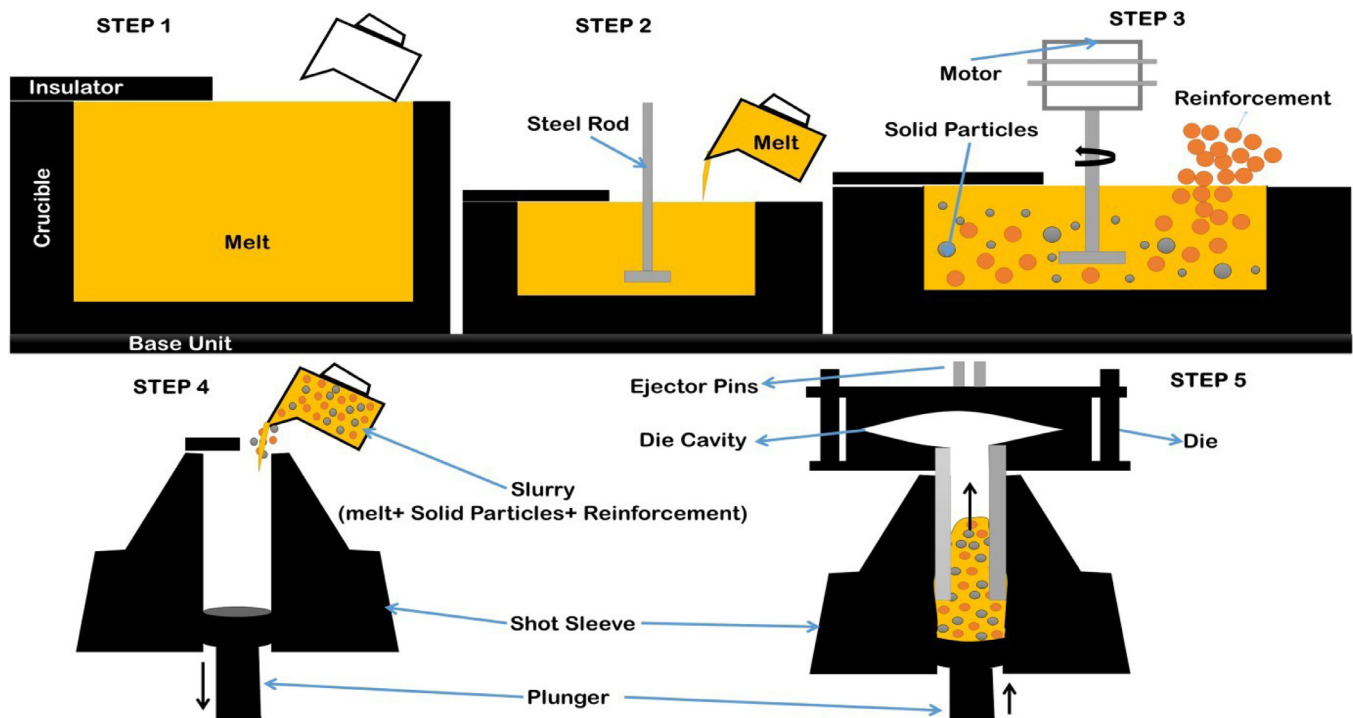


Fig. 22. Rheocasting Process [244].

Fig. 22 represents the rheocasting process of AZ91D and AM50 metal alloys of magnesium. Initially, magnesium melt beyond its liquidus temperature is prepared in the crucible [244]. The slurry preparation was done by rheometal process in which molten metal was reinforced with the particles of silicon carbide particles. Steel rod of EEM (enthalpy exchange material) was casted. The molten magnesium was allowed to cool and the casted rod was immersed resulting in further melt cooling. During this process of melt cooling EEM quickly melted forming homogeneous slurry. This slurry was poured into shot sleeve where the final alloy was casted at high pressure.

IV Other Casting Processes

5.12. Friction Stir Processing (FSP)

The evolution of processing through friction stirring is from the process of friction stir welding. The FSP initially was used for manufacturing composites with reinforced surfaces [248]. The present use of FSP has been in the production of nanocomposites on a large scale by the addition of nanoparticles into the matrix of metals. The schematic representation of the FSP (friction stir processing) is seen in Fig. 23 [247]. The FSP comprises of a tool with pin and shoulder that rotates. A groove of desired dimensions filled

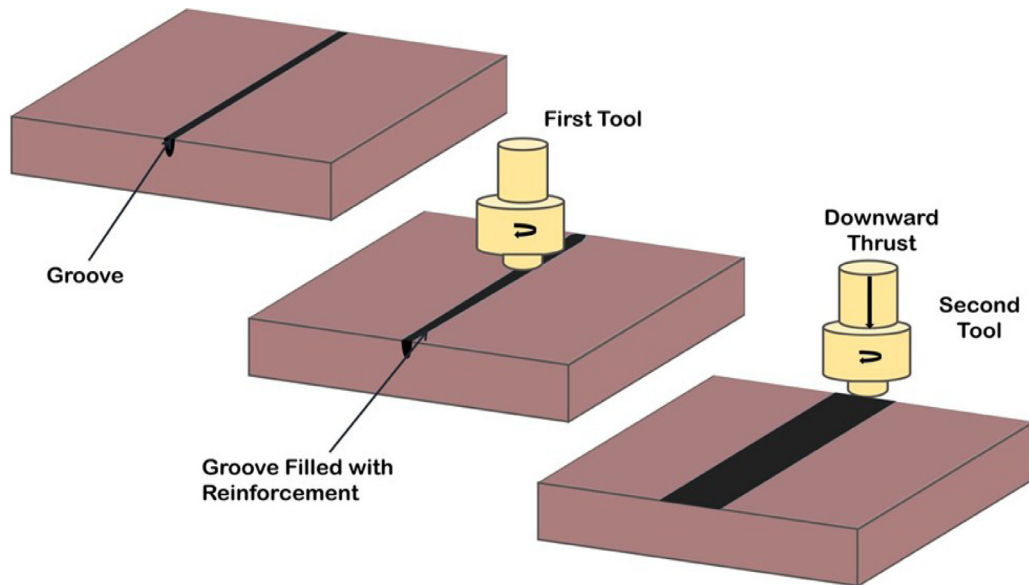


Fig. 23. Friction Stir Processing [247].

with reinforcements is made on the work surface. The rotating tool that advances into the groove generates heat due to friction and also applies thrust force. The surface bonding takes place due to high thermal softening and plasticization of the material (below the tool) [247, 249, 250]. This results in a composite with enhanced properties and an effective microstructure [250, 251]. Uniform reinforcement distribution and facilitating the material thickness have been some of the issues in this process as the process is still under research.

Though FSP is a process for grain refinement, it is ideal for composite production. Extensive research is yet to be done in FSP for the manufacturing of magnesium composites (hybrid). There are two methods of adding reinforcement in the composite preparation. Mix the reinforcement particles with a solvent like methanol that is evaporative and apply on the matrix forming a thin layer. Complete the manufacturing process later by FSP. This is the surface metal matrix composite [252]. The limitation of this process lies in the insufficiency and non-uniformity of the reinforcement substrate. In the alternative method of composite preparation, groove is cut along the direction of FSP for filling of the reinforcements. Composite having thick layer is formed after subsequent friction stir process [253]. In the FSP, proper tool design can assist in obtaining the desired mechanical and metallurgical properties of a given material especially when the FSP does not consume much time.

5.13. Reactive infiltration technique

The reactive infiltration process is an innovative and a viable process which has come into existence which is in-situ in nature. It is a process without any pressure and is an integration of the in-situ technique. The preform of reinforcement is prepared from different powders in elemental form that are capable to readily form a reaction with infiltration metal. When heat is supplied, reaction between the mixture of reinforce-

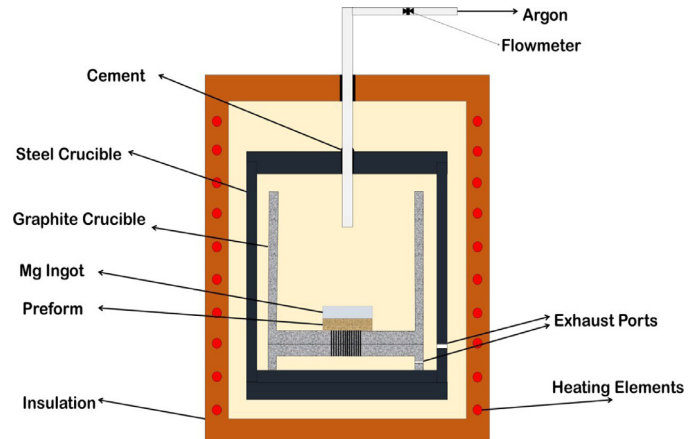


Fig. 24. Diagram of reactive infiltration process [254].

ment and the melt takes place resulting in the infiltration of metal within pores forming composite that is dense. Ceramic reinforcement of large volume fraction is needed to form the required composite [234].

Studies suggest that homogeneous reinforcement dispersion is achieved in composites that are approximately net shaped having excellent interface between matrix and reinforcement. This will result in improved material properties [255]. But initially preform pores have to be restricted as this influences the quality of the composite. There is also a possibility of macrosegregation of the grains owing to the combined effect of the reactions and the flow of the fluid. Fig. 24 shows the diagram of reactive infiltration process.

5.14. Self-propagating high-temperature synthesis(SHS)

The exothermic reaction between igniting powder reagents and spontaneous transformation into products is the principle of SHS process. The discovery of SHS was in the later part of

1960s. The self-sustaining reaction is the key feature of this process. The alternative names of the SHS process are self-propagating exothermic reaction or the combustion synthesis. The SHS process is extremely popular in the manufacturing of refractory materials due to its benefits like less duration, high purity, cost effectiveness and energy [256, 257]. The following requirements are to be fulfilled for the SHS reaction to be self-sustaining:

- (a) The reaction of SHS must be extremely exothermic in nature.
- (b) In order to facilitate the flow of reactant in fluid phase towards the reaction front, phase of one of the reactants must be either vapor or liquid.
- (c) The quantity of heat dissipated should be lower than the heat generated [258].

Ceramics were manufactured by the process of SHS in 1990s. But the application of SHS in the manufacturing of magnesium composites is limited due to the damping influence of magnesium matrix composites on the combustion wave. TiB_2 and TiC are stable in the matrix of magnesium and also are capable to generate reactions that are exothermic. Hence, they are the most sustainable reinforcements in for the magnesium composites manufactured through the process of self-propagating high-temperature synthesis [179].

5.15. Advanced Manufacturing techniques for high strength

5.15.1. Equal Channel angular processing (ECAP)

Presently, to produce high strength Mg alloys, the technique of severe plastic deformation (SPD) is being applied in which the alloys are subjected to extreme strains resulting in micro or nano scale of grain sizes [259]. There would be significant impact on the alloy strength by the refined grains which is in adherence to the Hall-Petch (HP) relation. It is known that for hexagonal close packed (HCP) structured Mg alloys; the value of HP slope is generally large [260, 261]. Hence it is important to elevate the mechanical characteristics of the RE free Mg alloys by SPD processes. ECAP and high-pressure torsion (HPT) are the generally employed SPD techniques. Previous literature on Mg-Zn binary and ZK60 ternary alloys supports the production of higher refined grains through the HPT process [262, 263]. But ECAP can be carried out for larger samples of huge volumes and therefore be applicable in the industries if multi pass facilities can induce large strain within one pass of extrusion [264]. ECAP on AZ91 in the year 1996 exhibited ultra-fine grains with super plasticity at low temperatures [265]. Subsequently Yamashita et al. achieved 3–4 times higher UTS through ECAP on pure Mg and Mg-0.9Al alloy [266]. The mechanical characteristic is also enhanced by ECAP. Studies on AZ31 suggest that ECAP at 200 °C can produce highly refined grains of sizes 0.5 μm to 0.8 μm and sometimes, grain sizes of 100 nm are also achieved. It is believed that low ECAP temperature restrains the growth of grains resulting in finer grains and enhanced YS (increment about 210 MPa) [267]. An appealing fact is that, higher strength can be achieved if Mg alloys with

adequate quantity of dispersive second phases undergo ECAP. The dynamic recrystallization (DRX) is endorsed by the second phases through particle simulated nucleation (PSN). This restrains the growth of α -Mg grains and leading to the formation of grains that are ultra-fine. The Zener pinning mechanism is the mechanism behind the production of ultra-fine grains. The YS is enhanced by the fine size of grains due to the hardening of refined grains and the alloy is strengthened due to precipitation hardening of the second phases. This theory motivated Yan et al. who experimented on Mg-6Zn-2Al and achieved UTS of 340 MPa [268]. The Mg-5.2Zn-0.6Ca alloy processed by ECAP possesses the highest YS and UTS of 246 MPa and 332 MPa respectively. Refined grains are the reason for such exceptional values of strength [269]. Different alloys of Mg processed through different routes of ECAP will have different textures. It is both the texture as well as refined grains that decide the ultimate mechanical properties of alloys.

5.15.2. Advanced Extrusion/Rolling

High Ratio Differential Speed Rolling. The process of differential speed rolling (DSR) is an improvisation of the conventional rolling and is also an asymmetric rolling process. In this, the material deformation occurs due to different rotational velocities of the above and below set of rollers. Factors like the different roll diameters, the non-similar roll materials (different coefficient of friction on either side of the material surface) or the different roll velocities cause asymmetry in the process of rolling. It is easier to maintain the asymmetry by varying the roll velocities. Therefore, DSR induces different velocities of rolling for the material on either side of its surface. The prime parameter of DSR is the rolling ratio which is taken as the velocity of upper rolls to the lower rolls.

In the high ratio differential speed rolling (HRDSR), enormous amount of shear strain is brought on the alloy due to asymmetric rolling with high-speed rolling ratio greater than 2. This causes significant refinement in grains [265]. HRDSR on AZ91 plate generated a sheet having grains of submicron sizes. The sheet possessed 327 MPa YS and 11% elongation (tensile) [270]. Similar results were obtained in ZK60 and Mg-Al-Ca alloys [271, 272]. High grain refinement having submicron or nano sized grains with uniformly distributed MgZn_2 or $(\text{Al}, \text{Mg})_2\text{Ca}$ precipitates was observed. This yielded in enhanced strength. The strength of 382 MPa in HRDS rolled AZ31 alloy is extremely high [273]. This indicates that high strength is possible through refined grains alone which is in adherence to the earlier studies having high value of HP slope. The high work hardening can be achieved through the precipitates which produce the desired elongation [274]. In an alloy, the rate of deformation, its working temperature and the shear stress/strain distribution are dependent on roll speed ratio, working temperature and roll speed in HRDSR. The morphology and distribution of the end precipitate is influenced by these factors.

High Strain-Rate Rolling. The formability of Mg is poor so the sheets of Mg alloys are rolled in multiple passes with

small strain for each pass. This makes the process of rolling inefficient and expensive. Thus, the behavior of Mg alloys deformation was analyzed by Zhu et al. over various rates of rolling and proposed high strain rate rolling (HSRR) of Mg alloys [275]. It has been observed that at low strain rates of 3.9 to 6.8 per second, multiple cracks propagate along the actual grain boundaries. But the twin densities and DRX improve with increasing rates of strains. At higher strain rates (7.8 per second) higher portions ultra-fine DRXed grains are produced ultimately hampering the micro-cracks. Hence HSRR is feasible for ZK60. The strain energy stored as twins supplies adequate drive for DRX to dispel the energy during deformation thereby liberating the concentration of stress. The significantly refined grains and weak texture resulted in UTS of 371 MPa with 28% elongation. The HSRR of ZK60 and AZ31 in different temperature ranges (250 °C to 400 °C) resulted in microstructures of fine grains at high temperatures (above 250 °C) due to DRX [276, 277]. The ZK60 and AZ31 alloys thus exhibited high UTS of 371 MPa and 340 MPa respectively. But at low temperatures of 200 °C, the retardation of DRX nucleation resulted in cracking along the grain boundaries.

Asymmetric Extrusion. Yang et al. was motivated by DSR and produced Mg sheets through a unique differential speed extrusion process or asymmetric extrusion (ASE) [278]. The change in orientation of (0002) basal plane in the extrusion direction and weak texture in AZ31 resulted in enhanced mechanical characteristics. An improvement of 24.5% in ductility was achieved by Yang et al. through progressive ASE [279, 280]. Subsequently they also succeeded in enhancing the strength and ductility together through severe strain asymmetric extrusion (SASE) [281]. For AZ31 the obtained UTS were about 355.7 MPa with 21.1% elongation. A unique technique combining extrusion with a random asymmetric deformation is an appealing prospect. On the similar lines, Orlov et al. followed up the extrusion process with ECAP on ZK60. Exceptional mechanical characteristics were achieved a microstructure that is extremely fine [282]. Another exceptional finding report that ZK60 alloys undergoing the process of extrusion and ECAP exhibit outstanding resistance against corrosion [283]. Apart from this the ZK60 alloys also possess excellent fatigue strength which is determined by the dispersion and refinement of Zn/Zr solutes [284].

Pre-aging extrusion. Previous studies emphasize upon improved mechanical characteristics of materials treated prior to extrusion. Aging before extrusion of Mg-7.6Al-0.4Zn resulted in increased strength and elongation of the alloy [285]. This is due to the precipitation of fine Mg₁₇Al₁₂ phases. These restrict the growth of DRXed grains. Aging prior to extrusion (APE) on Mg-7Sn-1Al-1Zn having thermally stable phase of Mg₂Sn resulted in high UTS of 361 MPa and excellent grain refinement [286]. The second phase precipitation also increased.

6. Corrosion in Magnesium

6.1. Broad View of Mg corrosion in aqueous medium

The modest resistance of Mg and Mg alloys against corrosion is due to the influence of two primary factors.

The high electronegativity of magnesium supports corrosion even when there is oxygen deficiency due to the dominating reaction of cathodic water reduction at the potential of negative charge.

The modest shielding characteristics of the films developed on the surface of magnesium due to the solubility of the hydroxide layers in aqueous conditions. Moreover, the layers are defective and do not completely shield the surface of the metal beneath [34].

The process of film formation on the surface of magnesium is as follows. The instantaneous reaction of Mg with oxygen (air) at ambient temperature gives rise to MgO. This reaction takes place in dry conditions without the presence of water. The pyrophoric nature of the Mg powders is due to the high exothermic nature of the reaction.



According to the investigations on the development of oxide layers (MgO) on the surface of Mg (humid conditions), the process undergoes in three stages [287]. The initial two stages respectively comprise of adsorption of dissociated water and development of MgO islands. In the final stage, crystalline layer of MgO (4 nm) covers the entire surface of the metal which has gradually growing thickness with inverse logarithmic kinetics.

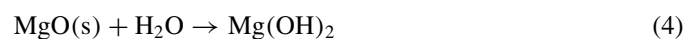
In dry conditions at room temperature, Mg exhibits good resistance to corrosion due to the presence of MgO film. This is analogous to the properties exhibited by other metals in similar conditions. The research on chemisorption of water on magnesium oxide suggests that process favours the surface of MgO (111) [288]. The process of protolysis occurs in which the disintegration of water molecules takes place resulting in the formation of H⁺ and OH⁻. The surface of MgO is thus hydroxylated.



Equivalently:



MgO in solid form reacts with water forming brucite (solid magnesium hydroxide). This reaction is possible due to the thermodynamics of equilibrium at lower water vapour concentrations (greater than 1 ppm H₂O).



The reason for non-protective nature of the layer is solubility of MgO and Mg(OH)₂ in water. Hence, in aqueous solutions of both acidic as well as neutral, the layer developed

on the surface of Mg fails to shield the metal beneath. The electrolyte's pH value increases when the hydroxide film dissolves in the aqueous solution. Also, the solubility of MgO is higher than brucite resulting in supersaturation of the surface water layer w.r.t Mg hydroxide [280]. This leads to the brucite precipitation. Studies suggest that the layer of MgO dissolves converting into precipitates of solid Mg hydroxide which is the corrosion mechanism of magnesium. The precipitation of brucite reduces the thickness of MgO layer which triggers the metal-fluid reaction thereby aggravating corrosion. When the metal is immersed in liquid (water), the quasi-passive layer of MgO or Mg(OH)₂ dissolves which exposes the metal to the liquid medium. Also, the secondary phases, the noble impurities do not have the double layer shielding and when they are polarized, they increase leading to localized corrosion.

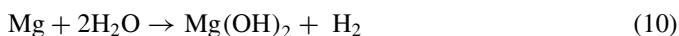
The process of corrosion in metals in electrochemical in nature where the metal transforms its oxidation state when it interacts with the environment. Electrons are released when electron transfer occurs at the electrode interface when the atoms inside the metal oxidize to form ionic species. The oxidation (anodic) half reaction for Mg is as follows:



The liberated electrons should be accepted by alternative groups in order to sustain electroneutrality. Thus, a cathodic (reduction) reaction follows the oxidation process. The nature of reactions that occur is influenced by the medium in which the reaction occurs. But primarily HER and ORR reactions occur which have different forms in acidic and alkaline mediums.



In acidic mediums, the reactions 6, 7 occur and in alkaline and in neutral mediums, reactions 8, 9 occur. Though oxygen plays a pivotal role in corrosion, these reactions are independent of the oxygen content dissolved within the aqueous medium. For Mg exposed to atmosphere, the primary reduction reaction is reduction of water known as HE. This is evident from the above reactions. Thus, the complete Mg corrosion reaction can be given as follows.



6.2. Mechanism of corrosion in magnesium

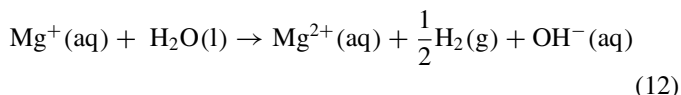
6.2.1. Anomalous HE on surface on Mg polarized anodically

A report on the excess HE on polarized surfaces of magnesium is essential to comprehend the corrosion process. This is a significant property in the electrochemistry of magnesium and its alloys which requires a definite consideration. In the process of corrosion in magnesium, the HER is the principal reduction reaction which occurs instantaneously on unpolarised Mg. But anodic polarization of Mg or Mg alloys results in higher dissolution rate which further enhances the

HE rate. This occurrence is termed as anomalous HE [6]. The presence of anomalous HE makes it impossible to predict the quantity of dissolved Mg when polarized anodically solely by the electrochemical techniques. This is because; the liberated electrons in the oxidation reaction are absorbed by HER on the surface of magnesium electrode instead of passing through the potentiostat towards the opposite electrode. This absorption keeps the electrons unnoticed [289,290]. The high electronegative potential of Mg polarizes it atomically in applications that endorse galvanic interfaces. Hence, understanding the mechanism of HE is extremely important to develop effective tactics in prevention of corrosion.

6.2.2. The concept of univalent magnesium (Mg⁺)

The theory of univalent Mg is based on the hypothesis that Mg⁺ exists in the form of intermediate when Mg dissolved anodically. This is a two-stage process in which initially dissolution of a portion of Mg occurs within a solution forming Mg⁺. This Mg⁺ reacts homogeneously with water forming Mg²⁺ and hydrogen. The corresponding reactions are shown below. This process suggests that with increasing rate of dissolution of Mg, higher Mg⁺ is formed resulting in higher rate of HE.



There has been a lot of debate on the existence of Mg⁺ and this concept has been considered hypothetical. But experimental findings of Petty et al. support the theory Mg⁺ as the reason behind anomalous HE. The existence of Mg⁺ may be used to explain the increasing rate of HE with amplified potential or current. However, there exists no direct evidence supporting the presence of Mg⁺ in aqueous medium. Had there been Mg⁺ existing it would have been highly reactive with very low life span (<μs) [282]. Until direct evidence of Mg⁺ is obtained, this concept remains to be considered hypothetical.

6.2.3. Influence of the corrosion layers and surface enhancement of impurities

The corrosion on newly formulated surface of Mg in aqueous solution occurs at the edges where the corrosion patches are developed due to the deposited corrosion products [291,292]. The exhibition of catalytic action in the direction of HER by the Mg corrosion product is remarked [290], [293]. In unpolarised conditions, at the time of corrosion in magnesium, the liberation of hydrogen at the corrosion film is quicker compared to non-corroded areas. Initially this isn't seen due to resistance of the thick oxide and hydroxide films. The corrosion layer developed on the surface of Mg consists of an outer layer (combination of magnesium oxide-hydroxide) above the inner layer having abundant MgO. Previous research suggests higher rate of HE on surfaces of Mg coated with magnesium hydroxide than pristine surfaces

of Mg (approximately 2–3 times higher) [294]. In an open circuit potential (OCP), the performance of Mg against corrosion was analyzed and it showed that dark regions spread quickly along the surface of Mg due to the corrosion. The analysis was done in a solution of NaCl by collecting hydrogen integrated with optical imaging at the time of potentiodynamic polarization. The cathodic activity was advanced in the corroded areas as compared to the non-corroded areas. This makes it evident that dark layer formed is the principal region for reduction reaction in magnesium dissolution at OCP. The increment in the polarization spreading enhanced the cathodic activity displayed by Mg at the time of anodic dissolution [293]. But ascribing the spreading corroded areas to the process of anomalous HE is possible only till these components are capable to promote HER.

Though the inclination of corrosion layer is towards HER and there is increase in the area of corrosion with progressing film of corrosion, the technique employed to evaluate HE rate by collecting hydrogen is frequently constant vs. time instead of improving w.r.t time. The anodic density of current influences the rate of HE. HE rate is independent of the amount of area corroded. The concept of the areas of dark corrosion being the principal source of HE (anomalous) is not supported by these results.

There is a possibility that the dark products of corrosion might include other residuals apart from magnesium hydroxide. Any metal impurities or alloying components are noble in comparison to Mg due to its extreme active nature. The influence of more noble impurities on corrosion of Mg is renowned [295]. The dissolution in Mg in the order of preference during unpolarised or polarized conditions might cause the impurities (like Fe) in the entire material to gather within or beneath the corrosion layer developed on the surface. This would enhance the impurities concentration at the surface over the entire metal. But research by Cain et al. articulates the uncertainty in the entrenched noble impurities within a film of modest conductance leading to exhibition of higher rates of HE when the metal is polarized anodically [296].

The presence of enriched impurities beneath the layer of corrosion electrically contacting the metal is practical enough to improve HE through gathered noble impurities. But previous findings support low efficiency of enrichment [297]. Similarly, findings of Birbilis et al. illustrate significant enhancement in the surface impurities but with very low enrichment efficiency (< 1%). The conclusions were made after analyzing the enriched impurities on the surface at the time of dissolution of Mg [298]. Though it is known that corroded layers endorse HE as compared to the non-corroded surfaces in unpolarised conditions, the overall influence towards the total rate of HE when polarized anodically is very less [299].

Studies on the influence of pH on anomalous HE in case of anodically polarized Mg suggest significant impact of altered pH in the area of dissolved magnesium [300]. For the analysis, the experimental setup consisted of a flowing cell combined with ICP-MS system along with measurements of collected HE over a range of solutions (buffered and unbuffered) with varying pH of 3 to 10.5. The results for low currents in

anode showed no HE in neutral buffers. But for unbuffered solutions (0.1 M sodium chloride) with high pH and high currents in anode anomalous HE was detected. Hence, change in the pH value of the Mg surface is an important parameter to be considered in the evolution of anomalous HE [300].

Therefore, the phenomenon of Mg dissolution is an intricate procedure as it involves multiple parameters like the anodic sections, the development of corrosion products and the noble impurities beneath the corrosion layer which influence the corrosion process in magnesium. Previous studies claim that the hydrogen evolution at anode is overshadowed by the areas in which the anodic reactions take place. Hence, further research needs to be done in order to completely comprehend the impact of all the included parameters in the process of magnesium corrosion and HE.

6.3. Influence of composition on corrosion in the alloys of Mg

Magnesium in pure state doesn't have the desired physical characteristics to be directly used for structural or engineering applications. Hence it has become inevitable to alloy magnesium in order to achieve better properties and stronger alloys. All the attempts to produce stronger magnesium alloys are slightly lacking in the aspects of handling the issues of corrosion in magnesium. Relatively, the emphasis on producing alloys of magnesium with good resistance against corrosion is limited. But in recent times, the influence of alloy elements in the corrosion of magnesium has been extensively studied across the world.

6.3.1. Material Solubility in magnesium

In the process of corrosion in magnesium, to understand the impact of alloying elements on corrosion it is necessary to employ the metallurgical perspective to clearly comprehend the characteristics of Mg as a system of alloy. Magnesium is extremely special considering the fact that very few elements are soluble in it. With the majority of elements having solubility less than 0.05 wt.%, they can generally be categorized as insoluble in magnesium [34]. Different types of insolubility are seen when Mg is alloyed.

- Complete insolubility (Mg-Nb, Mg-Ge, Mg-Fe)
- No solubility with Mg-X intermetallic compounds (Mg-Si)
- Minor solid solubility with subsequent total insolubility (Mg-Zr)

All of the above scenarios are unique considering the fact that solid solubility followed by intermetallic (as in Mg-RE) is included in conventional alloying process. From the corrosion point of view, elemental insolubility is challenging in Mg alloys because alloying in Mg cannot be done just to enhance corrosion resistance like adding Cr to Fe to form stainless steel [301]. Also, since majority of elements are "more noble" and Mg with high electrochemical activity might lead to the formation of localized anodes and cathodes resulting in higher rates of corrosion. The summary of maximum solid solubility

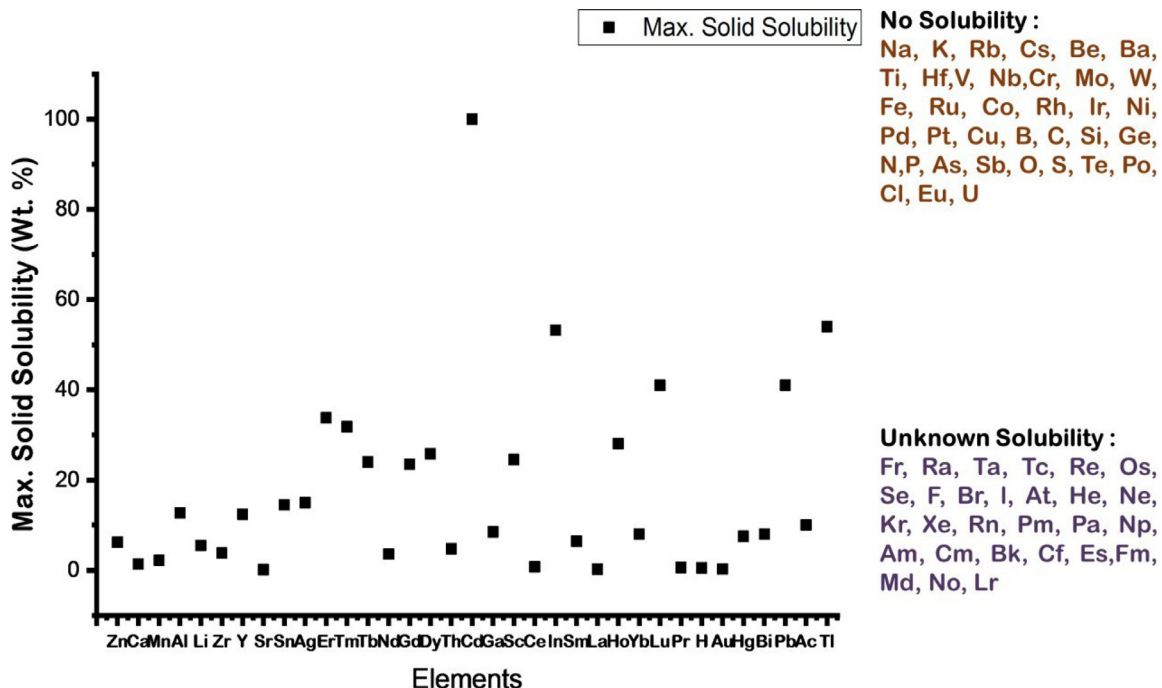


Fig. 25. Solid solubility (maximum) of elements at all temperatures in Mg [6, 57, 302, 303].

of all the elements is represented in Fig. 25 [6, 57, 302, 303]. Majority of the represented elements are either insoluble in magnesium or haven't been explored.

It is clearly evident that very few elements are considerably soluble in Mg with more than 1 wt.% solubility. Among these soluble elements, large number of them is highly dense and by alloying these with Mg is meaningless because then the overall density of the alloy shall be higher than its associates. The alloys of Mg for structural applications are made with the following properties.

- a The alloys have particles of second phase.
- b The overall load of alloys is less than 10 wt.%.
- c The alloying is usually done with Al for achieving lower density.
- d The alloying is done with RE elements in alloys free of Al to achieve good strength.

6.3.2. Tolerances of metals (impurities in Mg)

It is a well-known fact that Mg with impurities has a higher rate of corrosion. Hence, the concept of having certain limit of tolerance to such impurities came into existence. But the focus has always been on restricting the content of iron in Mg since it is widely available [38, 304]. Research has empirically concluded that the limit of tolerance of iron is 170 ppm after which the rate of corrosion increases significantly [38]. This limit of tolerance is also applicable to other elements like copper, nickel, cobalt, chromium and molybdenum. Studies on the influence of various impurities on the corrosion of magnesium were carried out and the tolerance limits have been decided as 170 ppm for iron, 5 ppm for nickel and

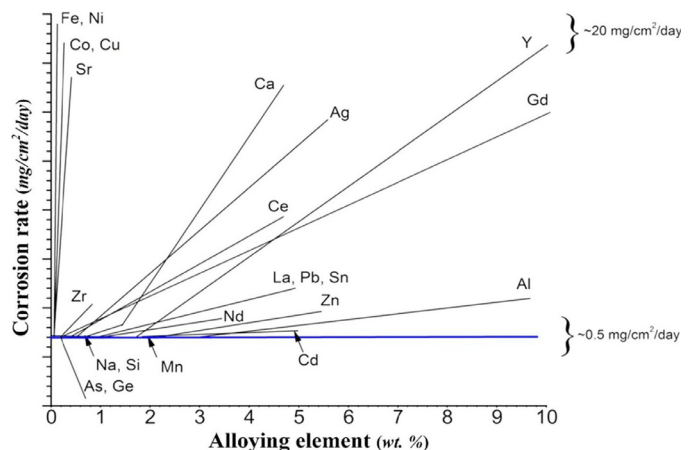


Fig. 26. Influence of alloying elements on corrosion rate of binary Mg-alloys in NaCl electrolytes represented in mg/cm²/day [6].

1000 ppm for copper. The corrosion rate past these limits enhanced [304].

The complied statistics in Fig. 26 represent the corrosion rate in the alloys of Mg, in the units of mg/cm²/day, as, the units of corrosion in mm per year are proven to be wrong assumption [305, 306]. The harmful influence of it is clearly visible from the Fig. 26. It shows that majority of elements are able to significantly enhance the rate of corrosion as the loading increases. It is inclusive of the elements like Ca [307], Sr [306] and RE elements (Y) [306, 308]. Low amount of Zr has a negative influence on corrosion [39]. In the alloys of Mg, elements like zinc, manganese and aluminium moderately influence corrosion. Among various binary additives, only As and Ge improve the corrosion resistance of Mg [309, 310].

According to previous studies, addition of Mn to Mg-Al alloys enhances corrosion resistance due to the formation of an intermetallic ($\text{Al}_x\text{Mn}_y\text{Fe}_z$) with Mn and Al [63]. This intermetallic compound confiscates the impure iron radically reducing the rate of corrosion. This is called the “Mn-effect”. Recently when analysis was done to study the “Mn-effect” on alloys of Mg-Al and also alloys that are free of aluminium then Fe “encapsulation” phenomenon was observed. This concept of Fe encapsulation was formerly never reported but was witnessed and justified based on rejected solute of manganese from iron when the melt was solidified [311]. Such findings signify the presence of impurities in the alloys of Mg which further suggest that their interface is complex. Further, research has to be done to confidently characterize the Mn-effect for its use in the alloys of Mg.

6.4. Corrosion Behavior of Mg-MMCs

The MMCs of magnesium consist of metal or reinforcements. Apart from that, they also consist interfacial reaction compounds which might be unstable thermodynamically. These compounds degrade the mechanical characteristics and the resistance against corrosion of the magnesium composites. Previous studies suggest that deprived wettability of ceramic particulates within the melt is the reason behind the generation of interfacial products of reaction. The wettability can be enhanced by employing pre-processing techniques like preheating, coating the particles etc. Also, in MMCs, the interfacial compounds production is hampered when the reinforcements (SiC) are pre oxidized. In case of semisolid and solid MMC processing techniques, the reactions at the interface can be reduced by low temperatures and shorter contact times. Due to the formation of interfacial compounds and the effect of reinforcements, properties of corrosion are complex in MMCs of magnesium in comparison to the alloys. The causes for lower resistance against corrosion in the MMCs of Mg are discussed in detail.

6.4.1. Micro-galvanic corrosion amongst the metal matrix and its reinforcement

The micro-galvanic corrosion is very familiar concept in the previous studies on MMCs of magnesium [312]. The particles of SiC, conventionally used in MMCs of magnesium, do not trigger galvanic corrosion but exceptions exist [313], [314]. Previous researches do support the galvanic corrosion by SiC particles in MMCs of magnesium [315]. A shift in cathodic branch in the direction of high density of current was seen in Mg MMCs indicating increase in the cathodic activity of SiC particles [316]. But this need not be always true for the particles of SiC because their electrical resistivity relies on the quantity of existing impurities and differs accordingly [312]. One of the instances of this case can be derived from the work of Kamieniak et al. which focuses on the influence of pure and impure SiC on corrosion of AM50 MMC [317]. In the galvanic corrosion of matrix-reinforcement (SiC), the quantity of oxygen dissolved within the solution influences the rate of corrosion [318]. But the galvanic corrosion wasn't

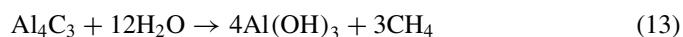
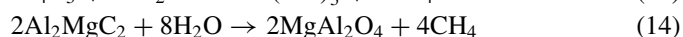
seen when Al_2O_3 or ZrO_2 are used as reinforcements. The insulation properties might be the reason behind this. However, when these were segregated compositionally, galvanic corrosion may be prevalent [319]. In AS31 (alloy of Mg and Al), the micro-galvanic corrosion is due to the presence of Mg_2Si but the compounds like MgO and MgAl_2O_4 have a minor influence on the electrochemical process. Due to poor conductance, Al_4C_3 might not influence corrosion [320].

6.4.2. Changes in the microstructure due to the reinforcement

Adding reinforcement to MMCs of magnesium certain changes in the microstructure are induced like refined grains, change in porosity, adulteration. SiC endorses the formation and refinement of $\beta\text{-Mg}_{17}\text{Al}_{12}$ due to which there is enhanced galvanic corrosion in MMCs of Mg [321]. Also, high levels of porous MMCs will have degraded resistance to corrosion [313].

6.4.3. Degradation of the reinforcement

The reinforcements or the interfacial compounds might degrade forming micro-crevices at the interface of matrix or reinforcement (similar to the ones in AMMCs) when they come in contact with moisture or aqueous solutions [322]. This isn't too harmful but the interfacial disintegration might enhance the region of cathodic reinforcement thereby enhancing galvanic corrosion. The process of degradation involves hydrolysis of Al_2MgC_2 or Al_4C_3 in composites of carbon reinforcements. The reactions of hydrolysis are represented in Eqs. (13) and (14) which show release of methane in MMCs of aluminium [323, 324].



It is alleged that methane is the reason for the existence of cracks, crevices and pores enclosing the reinforcement as seen in Fig. 27 [324]. Since carbon is chemically stable within the aqueous solution, no degradation is seen in the reinforcements of TiC, SiC, ZrO_2 and Al_2O_3 . But previous studies talk of the conversion of graphite into CO_2 when polarized anodically resulting in crevice generation for a few MMCs of magnesium [325].

Hence, in the production of MMCs of magnesium, the factors like active reinforcements, interfacial phases generated due to matrix-reinforcement reactions influence corrosion of the composites. Controlling the interfacial reactions can control the corrosion in Mg. For instance, a new research suggests that generating a layer of SiO_2 (silica glass) which insulates the surface of SiC reinforcements would reduce the cathodic activities. The layer of SiO_2 can be generated by pre-oxidizing the particles of SiC. It has also been proven that the layer of silica glass enhances the wettability thereby reducing the interfacial reactions. Due to this, MMCs of Mg are produced with lower pores which could reduce corrosion. An alternative technique to reduce corrosion would be by using reinforcements that don't react with Mg melt and that aren't cathodically active. But the issue is that there are very few

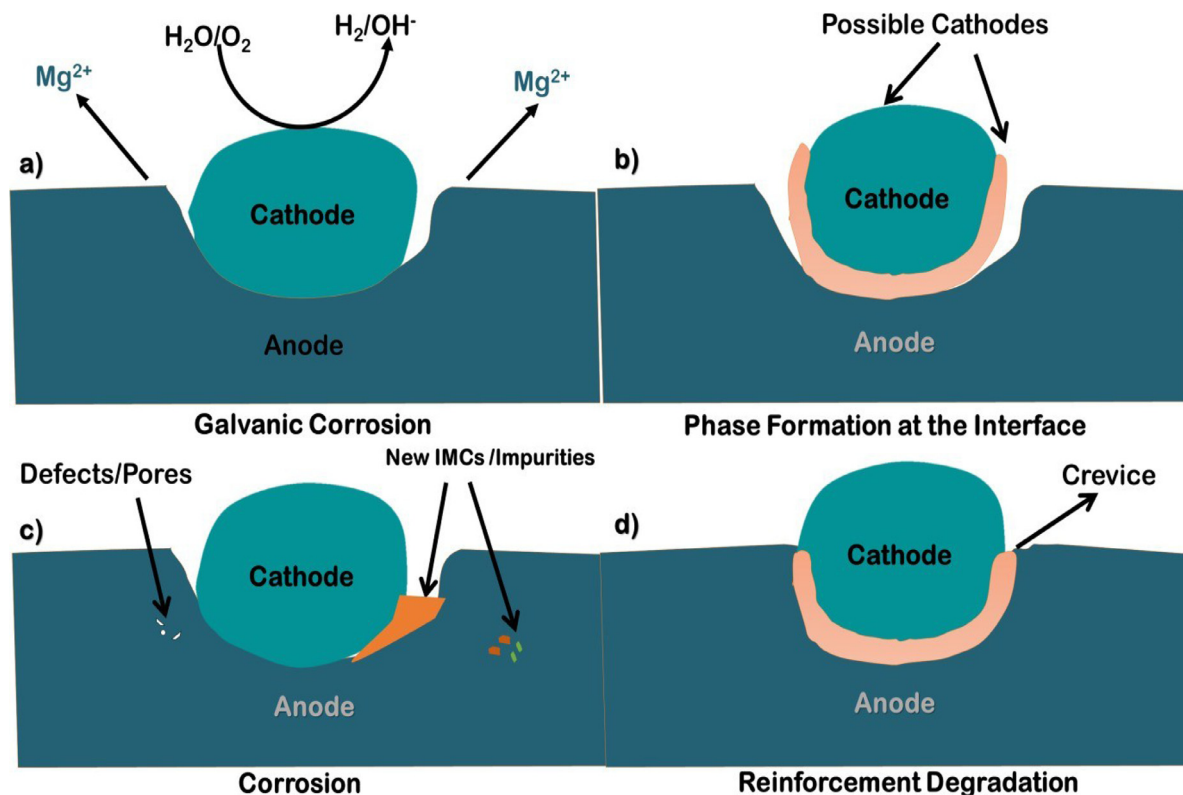


Fig. 27. The process of corrosion in Mg MMCs. (a) Galvanic couple among matrix and reinforcement, (b and a), interfacial reaction of matrix-reinforcement, discontinuous surface film and changes in the microstructure about the reinforcement, and (d) reinforcement degradation and corrosion of crevice [6].

compounds (Y_2O_3 , Al_2O_3 and ZrO_2) that are nonreactive to Mg. Therefore, it will be an interesting prospect of research to investigate the influence of surface coatings on the corrosion of Mg composites as it has been in the case of alloys of magnesium [326].

7. Biodegradable Mg alloys

The alloys of magnesium possess exceptional properties like low density; low modulus of elasticity, biocompatibility and it promotes osteogenesis [327]. Apart from these, Mg also has poor resistance against corrosion [328]. Mg isn't toxic by nature and it disintegrates wholly within the human body [329]. Hence, the alloys of magnesium are ideal as medical implants that are biodegradable. The applications include cardiovascular stents, implants (fixtures) in orthopedics which are present within the body for the duration of healing [330]. Bioabsorption of the implant within the body would eliminate the secondary operation of removing the temporary implant [331]. It is not suggestible to leave a foreign implant within the human body after its necessity is complete as it might lead to complications and negative effects. Basically, the evolution of biomaterials happened through three generations [332]. Initially, the biomaterial implants only replaced the tissues that were impaired or damaged. For this purpose, inert compounds like alloys of cobalt, Al_2O_3 and stable polyurethane were used. The issues of these biomateri-

als were that the implants loosened [329]. This gave rise to the next generation of biomaterials which responded specifically with the tissues around them and also capable of bonding with the bone. These biomaterials are bioactive ceramics (hydroxyapatite) with chemical structure equivalent to the minerals of the bones in human [328]. The present or the third generation of biomaterials include a novel strategy of regeneration in which the biomaterials are the temporary structures which degrade in the biological environment. Promotion of the tissue growth, integration and ultimate replacement of the implants is observed in this generation of biomaterials [327]. The third generation of the biomaterials include alloys of Mg, degradable polymers (PLA, PGA) and bio glasses that are biodegradable [333].

Initially due to the lack of comprehensive knowledge on the corrosion mechanism of Mg alloys, their use in bioimplants did not fetch success. It is only in the last decade that the use of Mg as biodegradable implants has resurged. Theoretically, any element which isn't toxic with corrosion ability in aqueous mediums is suitable for this application but focus is been primarily on the alloys of Mg. Due to the similarity in elastic modulus of Mg and the cortical bone, the stress shield effect is reduced [334]. Though conceptually it seems simple to use corroding alloys in temporary implants, the actual process of corrosion in the alloys of Mg is complicated and dependent on various factors. Further research on the corrosion mechanism of Mg alloys in the body environments is nec-

essary. Moreover, the side effects of Mg dissolution like HE and alkalization are still an apprehension [327, 335]. Novel alloys with biocompatible coatings are required as some of the Mg alloys exhibit extremely high corrosion rates initially within the body. Moreover, thorough study on the complex interactions between the implants and body fluids within the body is needed.

7.1. Corrosion of Mg from the perspective of biomedical applications

It is known that the oxidation reaction in Mg alloys is followed by reduction reaction at the cathode, which liberates hydrogen gas by reducing H^+ from H_2O . This is a major worry from the perspective of biomedical applications. The perils of liberated hydrogen gas are influenced by the rate and distribution along the space. For low rate of hydrogen production, there is a possibility to avoid local build up by transporting the gas away from the area of production. Factors like the type of alloy, the environmental conditions and the treatments on the surface influence the production of hydrogen. These factors also influence the rate of corrosion.

The alkalization of the surface is the other area of apprehension when the dissolution of magnesium occurs. The incomplete hydrolysis of Mg^{2+} enhances the alkalinity (pH 10–12) of non-buffered solution. A marginal increase in the alkalinity is possible in case of buffered solutions like body fluids as well. The hydrolysis reactions are influenced by the alloy composition and the nature of cations released during the alloy corrosion. This is the reason behind variation in pH for various alloys. But this change in alkalinity is advantageous for different applications of Mg alloys because it makes the surface passive due to the generation of stable layers of magnesium hydroxide.

The corrosion in Mg is seldom uniform as the alloys of Mg have multiple phases (heterogeneous). The intermetallic compounds will be the local cathodes while the Mg matrix acts as anode. This happens due to the presence of impurities and also because the Mg is lesser noble than the elements in the alloy. Combining with nobler surfaces aggravates the process of Mg dissolution giving rise to a morphology that isn't uniform. The mechanical integrity of the devices may be lost due to a corrosion process that isn't uniform. This also makes it difficult to forecast the lifetime of the material in case of non-uniform dissolution.

7.2. Corrosion of Mg in simulated body fluids

The human body solution includes 0.14 M sodium chloride and various inorganic ions like Ca^{2+} , HCO_3^- and PO_4^{3-} [336]. Corrosion is due to the existence of ions of chloride and 37 °C temperature within the body which aggravates the process of corrosion. The development of shielding layers of corrosion products is due to the presence of carbonates and phosphate ions. The body temperature also impacts the formation of different kinds of calcium phosphate ions

from the fluids within the body. It is the temperature that determines how soluble the phosphates of calcium are. Apart from this, the reactions in corrosion are further impacted by a number of inorganic substances like cells, biomolecules, proteins and bacteria. It is these factors and their interactions with Mg surface that complicate the corrosion processes. The processes and its interactions are represented in the Fig. 28.

The best simulated environment for the conditions of *in vivo* hasn't been devised so far. Depending on the type of SBF used, there is a noticeable variation in rate of corrosion of Mg alloys [337, 338]. Hence it is not possible to directly compare information available in literature. But previous literature does suggest that complex products of corrosion like phosphates of Mg or Ca, carbonates are precipitated in SBFs as compared to simple alkaline solutions. The rate of corrosion is influenced by the corrosion products. The implant degradation shall not happen wholly if there is presence of partially soluble products of corrosion. Due to this, the material of the metal slowly converts into the products of corrosion.

The variation of resistance against corrosion is impacted by the various layers formed on the surface of Mg in SBF and DMEM. The DMEM solution is a buffer of amino acids, inorganic compounds and glucose. The surface of Mg becomes passive in DMEM when the readings are taken in solutions open to the air (external to the incubator) [339]. The increase in pH is noticed when readings are done external to the incubator as the carbon dioxide existence buffers the complete solution. A compact layer of corrosion develops on the surface of Mg due to reduced dissolution of Mg and reduced liberation of hydrogen gas. The reason behind this is the increase in pH value of the solution. The amino acids in DMEM have the ability to impact the process of corrosion through the reactions of chelation of the metal cations [340]. Previous studies support degradation of pure magnesium due to the existence of glucose in DMEM [341]. The conversion of glucose into gluconic acid leads to corrosion of Mg due to reduced pH. Glucose also impacts the development of corrosion layer in Mg organizing with the ions of Ca^{2+} within the solution.

7.3. Influence of proteins and cells on Mg corrosion

Proteins are biomolecules that impact corrosion. But there has been a conflict of interests when investigations were carried out on the protein influence on the corrosion of Mg alloys. The behavior of dissolution is surely impacted by proteins but the influence is dependent on particular type of alloy or protein [342]. The effect of protein on the rate of dissolution of Mg varies with time. The corrosion might initially be restrained but later aggravated. The cations in the metal are made complex by the presence of proteins which may aggravate the process of dissolution, thereby corrosion. The adsorbed cations on the surface of Mg can decrease the corrosion as they develop a shielding layer [343]. Since the type of metal surface and the protein influence the generation of

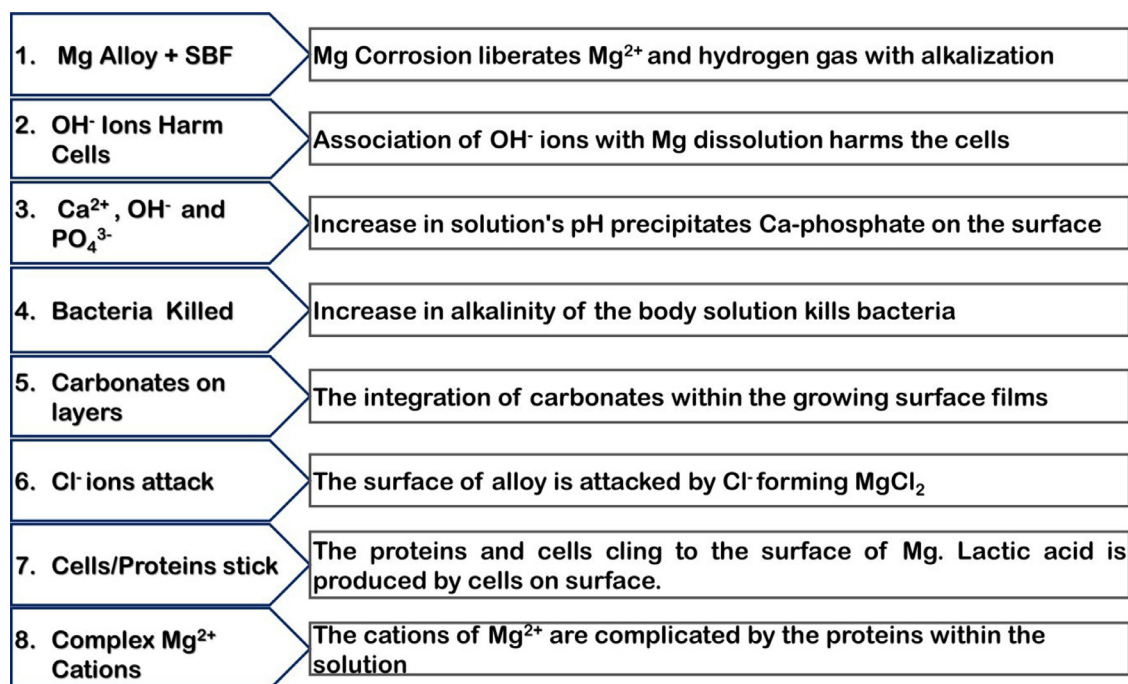


Fig. 28. The process of interactions between Mg and aqueous solution of the SBF [6].

cations, it is quite natural to obtain divided results regarding the protein's influence on the Mg corrosion.

The cell growth and adhesion on the surface of magnesium, is dependent on the products of corrosion like increased pH, liberated gas of hydrogen and Mg^{2+} [344]. The rate of Mg corrosion is dependent on the products of Mg dissolution. The layers of cell adhesion have the tendency to reduce the corrosion rate in Mg [345]. Previous studies support the change in pH beneath the layers of the cell, on the surface of metals [346]. The change in pH may be attributed to the products of cell metabolism, which reduce the pH due to generated lactic acid. The reactions of infection or/and the reactions of hydrolysis (due to dissolved cations) also influence the pH change (decrease pH). It can be justified that complex interactions occur between the cells and the alloy when discussed about the cell influence on Mg corrosion. Some evidence exists that corrosion is reduced due to the shielded surface due to cell layers. But the possibility of increase in the corrosion rate also exists due to the products of cell metabolism.

In case of *in vivo*, the scenario is further complicated especially with the lack of sufficient information on the performance of Mg alloys *in vivo*. According to previous research in all alloys of Mg, the rate of corrosion is lower (1 to 5 times) for *in vivo* than *in vitro* tests [347]. The lower corrosion rates, *in vivo*, may be attributed to the existence of lower concentration of chloride within the plasma of blood than synthetic solutions. The implant location and the surgical process may also be considered as important factors for the implant degradation. Therefore, incomplete information hinders the understanding of varying rates of *in vivo* corrosion. The research conducted on long term *in vivo* and *in vitro* Ca-phosphate coated Mg alloy degradation showed uniform

corrosion *in vitro* but localized and non-uniform corrosion *in vivo* [348]. The reason behind this was considered to be the interaction between the implant and tissue which resulted in slower, *in vivo* diffusion.

7.4. The effect of corrosion products on biocompatibility

The biocompatibility of Mg alloys is affected by the corrosion products of Mg like the Mg^{2+} cations, OH^- , alloying elements, hydrogen gas as well as the solid products of corrosion. The cations of Mg^{2+} not being toxic are advantageous for the growth and movement of endothelial cells [349]. The liberated gas of hydrogen, at the time of corrosion in Mg, is detrimental for medical applications of magnesium [350]. High rate of H_2 liberation through corrosion, surrounds the implants producing harmful gas pockets, which would influence the H_2 liberation, if attempts are made to regulate the rate of Mg dissolution.

It is also a known fact that alkalized solution containing corroding alloys of Mg is harmful for the biological surroundings. Shift in the pH of the alkaline solution influences the activities of protein and also kills the cells [351]. Recent research on the influence of pH on Mg-Ca binary alloys, *in vitro*, showed convincing levels of pH variations (> 3 units) in between the areas of cathode and anode [352]. This indicates, exposure of Mg implants to extreme alkaline environment having local variations. A contrasting theory speaks of Mg inheriting antimicrobial characteristic due to shift in pH and alkalized surfaces. During corrosion, Mg exhibited antibacterial characteristics *in vitro*, due to enhanced pH of the solution and not because of the liberated Mg^{2+} cations [353].

Insoluble compounds such as $Mg(OH)_2$, phosphates/carbonates of Ca or Mg are precipitated as surface

Table 5
Toxicity limits of elements related to the alloys of Mg [57].

Element	Maximum allowable dosage per day(mg)
Beryllium (Be)	0.01
Yttrium (Y) *	0.016
Nickel (Ni)	0.6
Titanium (Ti)	0.8
Tin (Sn)	3.5
Cerium (Ce) *	4.2
Lanthanum (La) *	4.2
Neodymium (Nd) *	4.2
Praseodymium (Pr) *	4.2
Rare Earth (RE)	4.2
Strontium (Sr)	5
copper (Cu)	6
Aluminum (Al)	14
Zinc (Zn)	15
Iron (Fe)	40
Magnesium (Mg)	400
Calcium (Ca)	1400

* The total quantity of these RE elements together shouldn't exceed 4.2 mg per day.

layers during corrosion of Mg alloys due to which the biocompatibility is affected. These insoluble products obtained from pure Mg and Mg-RE alloys during corrosion, were very harmful for the cells [354]. The adsorption of protein on the surface and cell adhesion in Mg is affected due to the formation of surface layers. This is due to the changed morphology and surface chemistry. The degradation is also reduced by the surface layers.

7.5. Cytotoxicity

Testing the cytotoxicity is an essential parameter for evaluating the biocompatibility of a given alloy. There are no theories supporting the unlimited consumption of metals within the body. The alloying elements have the tendency to generate toxic reactions beyond their limit of tolerance [51]. The quantity of elements liberated during reactions impact the biocompatibility of a given alloy within the human body. The rate of corrosion of a given alloy is also dependent on the reactions that take place inside the aqueous solution. Mg is extremely compatible with the human body, but, beyond the serum level of 1.05 mmol per liter, results in paralysis in the muscles, hypotension and respiratory problems. Extremely high serum levels (6 to 7 mmol per liter) might also cause cardiac arrest. The limit of toxicity of certain important elements for the alloys of Mg is represented in Table 5 [57].

It is clearly evident from Table 5, that the highest value for maximum allowable dosage per day is for calcium with 1400 mg and then it's for Mg with 400 mg. Beryllium has the least limit of maximum allowable dosage per day with 0.01 mg. The dosage of maximum allowable limit for elements is certainly related to the biodegradable implant alloys of Mg but the limits of toxicity might vary with that existing within the biodegradable implants. The implant location and the techniques handling the products of corrosion influence the limits of toxicity. For instance, the products of corrosion

may be different for stents within the blood than for the orthopedic implants [57].

7.6. Methods to monitor Mg corrosion in biomedical applications

Plenty of research has been dedicated towards monitoring the process of biodegradation in the alloys of magnesium. Focus has been on the development of new alloys and surface modifying techniques which would exhibit optimum performance against corrosion for the given application. The new alloys can be obtained by carefully alloying Mg with various elements compatible and which do not have a negative influence on biocompatibility. Different processing techniques, heat treatments and the nature of microstructure also determine the type of alloy produced. Likewise, the surfaces can be modified by applying coatings of single or multiple layers to overcome the problem of corrosion [355]. One of the key parameters to be considered for good performance of the coating is the adhesion of the coating to the surface of the metal [356]. Thickness of the coating depends on the area of application of the particular magnesium alloy.

7.6.1. Alloying

The alloys for the application of biodegradable implants should possess ideal mechanical properties, exceptional biocompatibility, bioactivity and controlled degradation. Though alloys with exceptional performance *in vitro* and *in vivo* are developed, there isn't an alloy with ideal characteristics and optimum performance. This is due to the inability to rank the behavior of corrosion in biodegradable materials and compare their characteristics *in vivo*. One of the most favourite system alloys for biodegradable applications is Mg-RE alloys containing Y and Zr. Apart from this, alloys like Mg-Ca, Mg-Ca-Zn, Mg-Mn-Zn and Mg-Nd-Zn-Zr have also been considered for biodegradable implants [357].

The corrosion rates of some important compounds for biomedical applications has been compiled in Fig. 29 [57]. This gives an idea as to how the alloying influences corrosion rates. It can be deciphered from the Fig. 29 that the resistance against corrosion has a radical increase for the alloys that have undergone secondary processes. Mg in the purest form exhibits extremely low rate of degradation *in vivo* and *in vitro*, with similar results in either of the cases [375].

The elements like Al, Li, Ca, Y, Mn, Zn, Zr and rare earths have been alloyed with Mg to enhance the alloy characteristics [328]. The mechanical properties of the Mg alloy are enhanced by the following [376]:

- Refined structure of grains.
- Enhanced resistance against corrosion.
- Formation of intermetallic compounds which improve the strength.

But the use of above elements was not in applications where biocompatibility was primarily the desired factor. Hence, to reduce cytotoxicity, it has been suggested to use

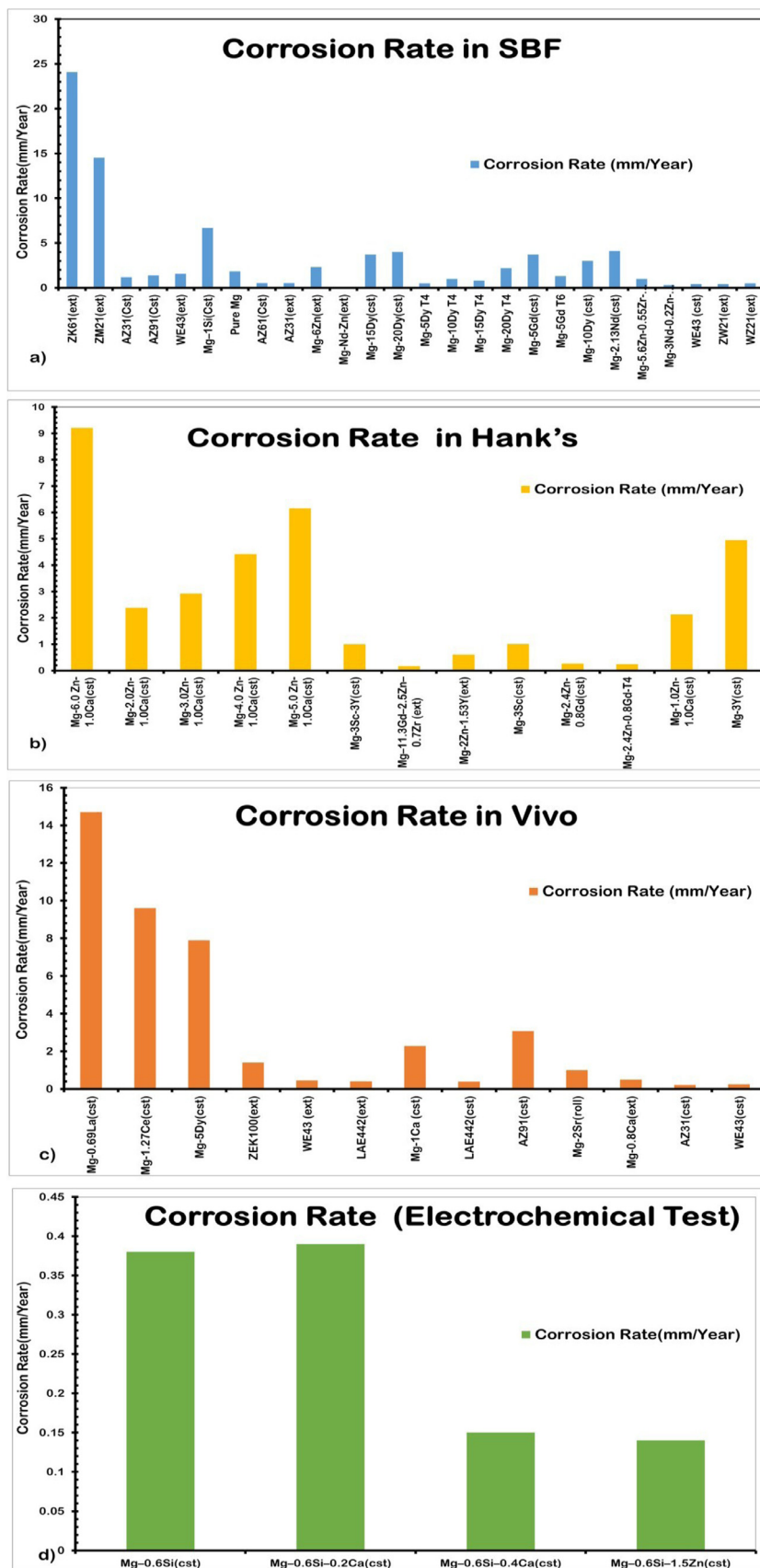


Fig. 29. Corrosion rates of typical biodegradable Mg-based alloys. (cst) is designated as As-cast, (ext) is designated as-extruded and (roll) is designated as-rolled [57, 59, 120, 123, 173, 176, 303], [358–374].

elements like Ca, Sr, Zn and Zr which are within the body also which endorse recovery/regeneration of the tissue [376].

Several techniques have been employed to enhance the biodegradation nature of Mg alloys simultaneously enhancing the mechanical characteristics. This is possible by tweaking with the microstructure of the alloy since it plays a vital part in modifying the material characteristics along with the resistance against corrosion. Reduction in the size of grains by the method of SPD (severe plastic deformation) results in the formation of alloys with ultra-fine grains which positively influence both the mechanical properties as well as corrosion resistance. Much literature is not available on Mg alloys processed by SPD in biomedical applications [377, 378]. The available literature speaks of the advantages of refined grains in Mg alloys processed through ECAP on resistance against corrosion and mechanical characteristics. The positive influence on corrosion properties is due to the reduced size of particles in the second phase and homogeneous microstructure which hindered the localized corrosion.

7.6.2. Surface Treatment of Mg alloys

The modification of surfaces can be carried out by applying coating on the surface to enhance the material properties. The process of coating is extremely challenging in Mg alloys due to their high reactive nature. To reduce the corrosion process in Mg and also to enhance the adhesion of the coating, it is important to carry out pre-treatments at the time of coating. For the biodegradable applications, it is essential for the coating to be compatible with surgical processes, biofunctional if possible, biocompatible and should have organized degradation behavior. These factors add to the complexity of surface modification in Mg alloys. Since, non-permanent implants comparatively have shorter degradation times (few months to maximum a year), the necessity to produce a coating with perfect shielding isn't there. An ideal coating is primarily expected to avert the initial high degradation of newly inserted implants and then facilitate gradual, organized degradation of the implant till the implant completely dissolves within the body solution. The ideal coating should also dissolve into the body solution along with the dissolved implant leaving no harmful products. It is possible for some coatings to avert the initially high but they fail to preserve the biological characteristics in the alloys of magnesium. The duration of degradation depends on the desired application. But one major shortcoming in the coating design is the lack of relative information regarding the degradation of the implant, *in vitro*, conditions and the actual rate at which the implant degrades *in vivo*. The adhesion of coating on the Mg surface is an important parameter that is usually neglected. Improper coating adhesion results in delaminated and a destabilized coating which results in filiform corrosion. Filiform corrosion is observed in thin coatings on Mg surfaces where randomly dispersed filaments resembling threads are formed. This is a major issue in polymeric coatings in the alloys of magnesium. To avoid improper adhesion, multi layered coatings may be applied. The process of surface treatment is possible through various techniques as represented in Fig. 30 [328]. Depending on the

type of application, different surface modification processes are employed. Some of the coatings techniques are coatings of Ca-P/HA, single and multi-layered self-assembled coatings (SMAs), laser cladding, micro arc oxidation and alkaline heat treatment [328].

The process of fluoride conversion coating involves the formation of conversion layer of MgF_2 upon direct treatment by fluoride salt [379]. Constant layer thickness was obtained after the treatment time was enhanced [380]. The rate of corrosion is reduced by the formed layer of MgF_2 . For treatments in alkaline medium, coated layers of MgO or Mg(OH)_2 are obtained which decrease the rate of corrosion.

Ceramic coatings which are biocompatible and bioactive are produced on the surfaces of Mg alloys by the micro arc oxidation (MAO) process. The special characteristics of the developed coatings include excellent corrosion resistance, inner strong adhesion of the film and outer porosity [381]. Research on the corrosion performance of MAO in SBF reports good resistance to corrosion and enhanced adhesion of cells on the Mg-Ca alloys [382]. The comparative studies of Mg-Sr casting and extrusion with/without MAO coating, *in vivo*, indicate high rate of H_2 evolution in both Mg-Sr casting and extrusion without MAO coating [383]. But Mg-Sr alloys with MAO coating exhibited no H_2 gas.

The electrochemical technique of EPD (electrophoretic deposition) involves alleviation of dispersed colloidal particles within the aqueous medium to be deposited on the electrode by applying electric field (electrophoresis). The process is economical and carried out at ambient temperature using simple setup. The duration of coating is relatively shorter than other coating processes and the coating of sufficient thickness is uniformly deposited [384]. The process of coating may be carried out on a series of structures with various shapes.

Physical coating technique like ion implantation makes use of various passive components which are bombarded to form a layer a metal oxide. But using the passive elements like Zn, Cr and Ti help in galvanic corrosion which enhances the rate of corrosion [328]. Another complication in physical coating process is that increased layer thickness leads to increased hardness of the surface. This might enable formation and propagation of cracks as the degradation increases in the alloys [385].

The polymer-based coatings which are organic and degradable are assumed to reduce the initial high degradation rate enhancing the cell growth and adhesion in Mg alloys [386]. The SMAs modify the wettability of the surface in Mg alloys thereby modifying the topography and roughness of the surface [387]. The biocompatibility increases in Mg alloys by the self-assembled layers which enable the growth of cells in the applications related to bone tissues.

Lastly, the laser assisted surface treatment like the laser cladding has developed recently due to its exceptional advantages. The process of laser cladding is a multidisciplinary technique which integrates the concepts of laser, computer aided manufacturing and control systems [388]. A laser heat source is used for depositing preplaced materials on a substrate that is in motion. An operating system can monitor

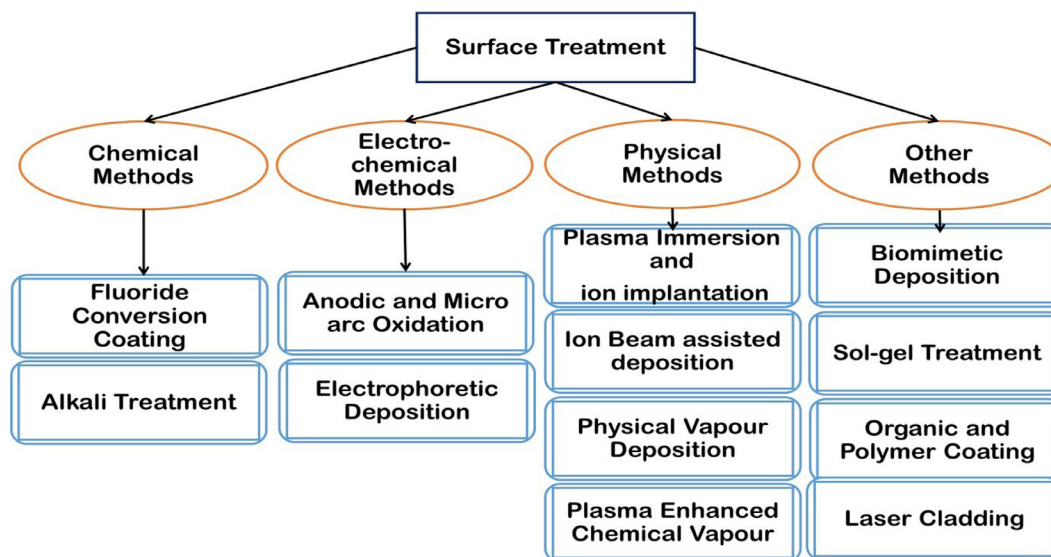


Fig. 30. Various Surface Treatment techniques [328].

the substrate's motion. The laser cladding process produces coatings with strong adhesion on the substrate with a thin heat affected zone. The higher rates of cooling or heating lead to a formation of microstructural uniformity. The inter-metallic compounds and the strengthened non-molten phases enhance corrosion resistance [388]. Further research is needed for increased implementation of the laser cladding process in various applications.

7.7. Machining of biodegradable implants

It is of utmost necessity that the bioimplants possess high accuracy in its dimensions and sound integrity of its surface so that the adhesion of cells is enhanced. The implants should also have good mechanical stability with least affinity towards the occurrence of inflammatory reactions [389]. The machining process influences the surface properties of bimetallic components thereby influencing the bio-functionality and life of fatigue of the implants used in the field of biomedicine [390]. Apart from these, the surface characteristics also influence the rate of corrosion and the composition of the implants. Therefore, selection of proper machining technique is needed for biodegradable implants.

It is not possible to use conventional machining techniques, as they are not suitable for applications which require surfaces without burrs and with high integrity. In the regular machining processes, incorrect machining parameters might result in excessive friction leading to ignition of Mg [391]. Lower speeds with ideal cutting parameters are needed for better machinability of the material. The process of cryogenic machining refines grains and helps in achieving high surface integrity with robust basal structure [392].

Though there are number of additive manufacturing techniques such as electron beam melting, selective laser melting which produce close tolerances and implants with high precision but due to high manufacturing costs, these haven't

been used for commercial purposes [393]. Machining processes without contact have better advantages in terms of lower wastage of materials and the feasibility to machine intricate geometries. The non-contact machining processes include laser beam machining (LBM) and electric discharge machining (EDM). The LBM is used for machining sheets of metal in vascular stents production with intricate geometries and micro sizes in medical applications. But highly generated heat is a major issue in LBM which detrimental to the process of corrosion *in vivo* [394]. Plasma of high energy has the tendency to thermally damage the alloy of Mg.

EDM is a cost-effective machining technique for materials that are conducting in nature. Hardness isn't a concern in the process of EDM. Repeated sparks of high heat generated in between the electrode (tool) and work melt the material eventually evaporating it. EDM and wire EDM may be used to machine desired contours with required topology of the surface in the preparation of implants. The surface modification in EDM might endorse growth of tissues and cell adhesion in biodegradable orthopedic implants thereby influencing the biocompatibility and rate of corrosion [395]. Monitoring the process parameters in EDM, the extent of surface modification can be controlled over numerous micrometers. The process of electrical discharge drilling can be used to drill interconnected holes of micro sizes in an implant that is solid [396]. This generates a porous structure suitable for growth of osteoblast and helps in the fixation of implant [397].

8. Applications of Mg alloys

Magnesium being the lightest structural metal with its exceptional properties like low density, biocompatibility and low resistance to corrosion finds itself being used in various applications requiring light weights. It finds itself in the fields of aerospace technology, automotive industries, and power tools.

The applications also are extended in the fields of communication, computers, hydrogen storage and consumer applications.

8.1. Aerospace Applications

The use of Mg in the aerospace field is limited to the engine, the castings of transmission systems and landing gears. Magnesium finds a lot of scope in the helicopter industry in the production of gearboxes and various non-structural parts. Though Mg has low density, it is not preferred for structural applications by the manufactures of Airbus and Boeing [221]. This is due to the low corrosion resistance of magnesium.

8.2. Automobile Applications

One of the primary techniques to conserve fuel is to adapt to lightweight vehicles. Magnesium, with its low density, is an exceptional prospect in the automobile sector. This has become a major aspect of researchers throughout the world. But magnesium has a low electrochemical potential which is the main reason for the vulnerability of Mg towards galvanic corrosion [398]. This galvanic corrosion has been a prime factor limiting the use of Mg in the field of automobiles. Using Mg in the structural applications in automobiles has certain practical issues. The prior designs of steel or Al are not suitable for Mg as the problem of corrosion does not arise in them. Using the same design for Mg might lead to the failure of the products due to galvanic corrosion. Although isolating the components can lessen the problem of galvanic corrosion, this technique induces extra cost and weight to the Mg making it expensive and also the concept of light weighting is nullified. The practical problems may be dealt with if the following aspects are researched [3].

- a Extensive and a methodical study are needed on the compatibility of the alloys of Mg with other materials.
- b Developing a suitable coating to modify the Mg surface in averting corrosion. This has to be done for short term duration.
- c Mg alloys with exceptional resistance against corrosion is to be produced which would have approximately the rate of corrosion superior to its counterparts (Al alloys).

Hence, Mg has found majority of its applications in the automobile interiors where corrosion isn't an issue. Components like instrument panels, dashboards, steering wheels, components of steering wheel columns are manufactured across the world using magnesium. In the areas of power trains, the transfer cases of 4 wheel drive trucks are manufactured using Mg in North America. Certain areas in Europe are producing engine blocks with the recently produced creep resistant alloys of Mg. The manufacturing of chassis and the vehicle body products using magnesium presently is restricted [221]. Apart from this the other applications of Mg composites in the automotive field are listed in Table 6. With developments in the corrosion resistance of Mg, the wide scope for Mg

is clearly evident in the automotive applications in the near future.

8.3. Electronic Applications

Apart from the aerospace and automobile sectors, Mg has found scope in power tools and electronics. The heat dissipation in Mg is 100 times better than plastics. Apart from this the recyclable nature of Mg, excellent vibration damping, electromagnetic shielding and machinability has given it a lot of scope in the field of electronics [399]. The applications of Mg in the consumer industry include audio-video players, mobiles, cameras, laptops, radars, rechargeable batteries [400] etc. The good strength of Mg with a low density is enforcing the manufactures to use it in the customer related electronic components to make them thin, light and portable [221].

8.4. Power tool applications

The Mg die casted products have excellent durability, are easy to handle with lighter designs. Hence the products of die casted Mg is widely suitable for power tool application to withstand the long working shifts especially in the construction area [221].

8.5. Biomedical Applications

Magnesium is biocompatible and it promotes osteogenesis. The density of Mg is similar to the human bone. Mg isn't toxic by nature and it disintegrates wholly within the human body. Hence, the alloys of magnesium are ideal as orthopedic implants that are biodegradable. The biocompatibility and less cytotoxic nature of Mg make it an important material in the preparation of cardiovascular stents [356]. Apart from this, the easy machinability of Mg is extremely useful in the manufacturing of stents or implants having intricate shapes or smaller sizes [401]. Though the issues of localized corrosion exist, by employing suitable alloying as well as coating techniques, the rate of corrosion can be controlled thereby enhancing the sustainability of biodegradable implants throughout the duration of healing or regeneration. The primary importance of biodegradable implants is that they eliminate the secondary surgical procedure of implant removal. The implants degrade within the human body in the form of biocompatible products which automatically are liberated out of the human body.

8.6. Hydrogen Storage applications

Presently, the energy system is primarily dependent on fossil fuels. Therefore, its future requires alternative sources. Hydrogen has been identified as one of the most encouraging sources of energy. One of the primary aspects of energy utilization from hydrogen lies in storage and conversion of H₂ [402]. The conventional techniques of storing hydrogen (in cylinders) have shortcomings such as low efficiency, leakages and hampered by high pressures. To overcome them, development of energy storage materials has taken place. These

Table 6
Applications of Mg composites in automobiles [179].

Reinforcement for Mg Matrix	Desired Property	Applications
Al ₂ O ₃ , SiC and/or graphite	Resistance against Wear	Bearing surfaces, cylinder liners, pistons and braking parts
Lesser dense ceramics	Light in weight and absorbing energy	Crumple areas, frames, reinforcements, batteries
Hydrophobic reinforcements, biomimetic coatings	Self-Cleansing	Exposed metal parts, coolant pumps and water jackets
Graphite, MoS ₂ , HBN, and various solid lubricants	Self-Lubricating	Bearing journals, cylinder liners, pistons and gear surfaces
High conducting carbon, or CBN powder	High thermal stability	Brake parts, turbo/supercharger parts and electronic packaging
Particles of Al ₂ O ₃ / SiC, CNTs and carbon ceramics	High Strength	Brake rotors, connecting rods and brake callipers
Fly ash/unwanted sand for filling	Cost Effective	Inlet manifolds, accessory brackets, valve and alternator covers, coolant pumps

energy storage materials play a significant role in the area of secondary energy, fuel cells as well as batteries. These can be correlated to the applications pertaining to spacecraft, electric vehicles and submarines.

Research on Mg as a hydrogen storage medium started five decades ago due to its high availability, low density and its nontoxic nature. The abundant availability of Mg reduces the raw material cost. The magnesium hydride (MgH₂) possesses high gravimetric (7.6 wt.% H₂) and volumetric capacities (110 g of H₂ per liter) which makes it an ideal material for storing hydrogen [403]. Moreover, the hydrides of Mg have the ability to oxidize rapidly and exothermically in air. From an industrial perspective, this makes Mg a feasible prospect for large scale applications. The Mg materials for H₂ storage are classified as pure Mg, Mg composites and Mg alloys. For pure Mg, the capacity for H₂ storage is relatively higher but practically pure Mg has high H₂ desorption temperature and slow kinetics at the time of H₂ release or uptake. This limits its practical applications. The unwarranted thermodynamic stability of MgH₂ and lower kinetics have paved way to a numerous techniques such as alloying, nanosizing as well as doping to obtain the desired kinetics and thermodynamics of Mg for H₂ storage [404].

The idea behind alloying is to form Mg alloys with lower thermodynamic stability. Nanosizing has a significant effect on H₂ release and absorption kinetics of Mg alloys. This is because the dependency of kinetics on particle size. Previous research signifies that reduced particle size enhances the surface area/volume ratio promoting quick H₂ diffusion [405]. This H₂ diffusion takes place at the Mg/ Mg hydride interface or internal boundaries which provides a reduced pathway. The doping catalytics lower the reaction energy barrier to promote H₂ uptake or release process in Mg based systems. The catalysts can be metals or oxides of metal. Therefore, a large research progress has been observed in the recent past, for Mg based hydrogen energy storage systems.

Apart from MgH₂, LiBH₄ was also proved to have a high gravimetric capacity of 18.5 wt.% as well as volumetric H₂ density of 121 kg H₂ per cubic meter. But its poor thermodynamics and slow dehydrogenation kinetics restricted its appli-

cation for fuel cells. LiBH₄ requires a temperature (500 °C) greater than its melting point (approx. 275 °C) for the process of de-hydrogenation or re-hydrogenation to take place. Both MgH₂ and LiBH₄ have limitations in terms of their thermodynamics and kinetics. Tuning these is a major concern for hydrogen storage. In this aspect, previous studies have suggested that the system of LiBH₄ + MgH₂ has 11.6 wt.% H₂, theoretical gravimetric capacity, with the ability to store and release H₂ at relatively lower temperature. But irrespective of exceptional theoretical hydrogen storage capacity, the LiBH₄ + MgH₂ has restricted applications due to slow kinetics [406]. Based on this literature, Ding, Zhao, et al. devised a new technique called BMAS (Ball milling with aerosol spraying) to enable a reaction between MgH₂ and LiBH₄, close to the room temperature. In BMAS, thorough mixing of nano sized LiBH₄ and MgH₂ particles was accomplished, by high energy ball milling of MgH₂ (micro sized) particles, with simultaneous aerosol spraying of nano-LiBH₄/THF droplets. The LiBH₄ + MgH₂ mixture, formed at nano level, was capable of absorbing as well as releasing approximately 5 wt.% of hydrogen at 265 °C in a reversible manner. This is the highest ever reversible hydrogen storage and release recorded at temperature less than or equal to 265 °C [407]. This excessive reversible storage of H₂ was possible through two different reaction paths. In the first path of reaction, decomposition of nano-LiBH₄ into Li₂B₁₂H₁₂ takes place and this Li₂B₁₂H₁₂ further combines with MgH₂ forming MgB₂, LiH and H₂. In the second reaction path, the decomposition of nano-MgH₂ into Mg and H₂ take place and there is a possibility of Mg to react with LiBH₄ giving rise to MgB₂, LiH and H₂. Their study established that nano engineering can overcome the issues of kinetics as well as improve hydrogen release at lower temperatures through thermodynamically favorable systems like LiBH₄ + MgH₂. The study was further done for analyzing dehydrogenation kinetics of solid BMAS powder having 25% and 50% LiBH₄ at temperature of 265 °C. For 25% LiBH₄, it was observed that the rate-limiting step is nucleation and growth of MgB₂ and LiH at the interface of the nano sized LiBH₄ and MgH₂ particles [408]. Investigations in the lines of thermodynamics as

well as dehydrogenation kinetics on 50% LiBH_4 proved that solid state BMAS powder has dissociation pressures of about 1910% and 700% greater than commercial MgH_2 and LiBH_4 respectively. This indicates greater thermodynamic force for H_2 release. Moreover, the thermal analysis depicted reduced activation energy in BMAS powder by a margin of 30.6 and 23.3 kJ per mol in comparison to ball milled MgH_2 + carbon mixture and bulk LiBH_4 respectively [409]. Therefore, the BMAS technique proved to be effective for promoting H_2 release from solid state LiBH_4 + MgH_2 mixture. Further investigations on solid state hydrogen storage, 4.11 wt.% of H_2 release was achieved from solid state LiBH_4 + MgH_2 mixture which is the highest recorded till date [410]. With such advancements in the field of magnesium based hydrogen storage materials, the future looks extremely bright.

9. Conclusions

Many aspects have been covered in the comprehensive review of magnesium and its alloys. It is of fundamental importance to understand the value of magnesium as an element. Elements with exceptional qualities like good strength to weight ratio, low density, biocompatible, favors osteogenesis and less cytotoxic is very rare to find. These mechanical properties favor the use of magnesium in various structural applications, automobiles and biomedical applications. With the trend shifting towards light weight components, it gives large scope for magnesium with lower density to explore different engineering fields especially the automotive sector. Mg can definitely be termed as the one-off metal considering its mechanical properties and the broad range of applications it can be utilized.

There is no element which is perfect. Likewise, magnesium also has its drawbacks and its extremely low resistance to corrosion being the most important of them. Magnesium has the tendency to oxidize rapidly when exposed to aqueous or atmospheric conditions and hence the poor corrosion resistance properties. In order to enhance the material properties of magnesium, it has to be alloyed with other elements. A detailed discussion has been done highlighting the advantages and disadvantages of various alloying elements. The influence of some of the important alloying elements on the mechanical characteristics has been tabulated. It is to be noted that very few elements are compatible with magnesium and therefore meticulous study of various elements is to be carried out before alloying them with magnesium.

Magnesium has the tendency to form alloys with various elements. The broad classification of various alloys has been discussed. Mg forms binary, ternary, quaternary alloys depending on the number of alloying elements added to it. Some of the important alloys are Mg-Ca, Mg-Al, Mg-Zn, Mg-RE, Mg-Li etc. Depending on the manufacturing techniques, the alloys are either cast alloys or when some secondary operations like extrusion are carried out, the alloys are extruded alloys. Literature related to different types of magnesium alloys and their behavioral characteristic has been compiled and discussed in detail. It is to be noted that in comparison to the

cast Mg alloys, mechanical properties like yield strength, ultimate tensile strength or elongation are higher in the extruded alloys. This is due to the refined grains and a homogeneous microstructure obtained post the secondary operation done on the alloys. For superior properties, the focus has shift in the development of Mg-RE alloys and Mg-Li alloys for biomedical applications. Due to the exceptional bio-functionality and biocompatibility the applications of Mg-RE alloys have significantly grown in bioimplants.

Production of composite materials to attain exceptional material properties is a known aspect. The combined mechanical properties of two materials are achieved through composite materials in which one is the metal matrix and the other is reinforcement. The metal matrix composites (MMC) of Mg have been elaborated. The different types of reinforcements and the factors influencing reinforcement selection are discussed. In order to obtain Mg MMC with desired properties, it is essential that the metal matrix and the selected reinforcement are compatible. If not, there would be adverse effects leading to poor performance of the material composite.

One of the major issues in the casting of Mg alloys is the inclusions or the impurities present in the Mg melt. The inclusions originate at the time of metal casting in the form of iron and some other compounds. They result in oxidation of the casting and result in poor castings. The theory related to melt inclusions has been discussed in detailed elaborating on the reason for inclusions, the harmful effects of the inclusions at the time of casting and how they can be controlled in the alloys have been broadly discussed.

One of the primary factors determining the quality of the products is the manufacturing process. It is important that the right technique is selected in obtaining the product of desired quality with desired characteristics and dimensions. An entire chapter has been dedicated to the various manufacturing, especially casting techniques of the magnesium alloys. The techniques of severe plastic deformation are also reviewed which are used for producing high strength alloys.

Magnesium and corrosion are synonymous. For wide use of Mg alloys, it is essential to understand and control the corrosion process. Therefore, the corrosion mechanism, modes of aqueous corrosion, influence of corrosion on Mg and how it can be curbed has been elaborated in an exclusive chapter. The solubility of metals in Mg and their tolerance limits are extremely critical for alloying as they have a negative influence on corrosion. It is necessary to gain knowledge of it. These topics have also been discussed.

One of the wide applications of Mg is in the field of Biomedicine where by making use of its corrosive nature, it is used as biodegradable implants, stents etc. For this, the behavior of Mg within the human body or within the simulated body environment is to be studied. A complete section has been devoted to the biodegradable nature of Mg. The cause and remedy for biocorrosion has been discussed along with machining techniques for the production of implants. The use of Mg for hydrogen energy storage has been discussed in brief. This is one of the most important applications of Mg.

This provides a basic idea on how Mg plays a significant role in this area is discussed.

Lastly, the various structural applications of magnesium alloy in the aerospace and automobile sectors along with their growth prospects and limitations have been discussed. With these topics covered to a greater extent, the authors believe this entire review on magnesium and its alloys helps the future researchers and paves way for advancements in this field.

Glossary

AMMCs:	Aluminium Metal Matrix Composites
APE:	Aging Prior to Extrusion
ASE:	Asymmetric Extrusion
CST:	As Cast
CPCs:	Calcium Phosphate Ceramics
CNTs:	Carbon Nano Tubes
CTE:	Coefficient of Thermal Expansion
CVD:	Chemical Vapor Deposition
DMD:	Disintegration Melt Deposition
DMEM:	Dulbecco's Modified Eagle Medium
DRX:	Dynamic Recrystallization
DRXed:	Dynamically Recrystallized
DSR:	Differential Speed Rolling
EEM:	Enthalpy Exchange Material
ECAE:	Equal Channel Angular Extrusion
ECAP:	Equal Channel Angular Pressing
EDM:	Electric Discharge Machining
EPD:	Electrophoretic Deposition
Ext:	As Extruded
FA:	Flurapatite
FSP:	Friction Stir Processing
HA:	Hydroxyapatite
HAP:	Hydroxyapatite Particulates
HCP:	Hexagonal Close Packed
HE:	Hydrogen Evolution
HER:	Hydrogen Evolution Reaction
HP:	Hall-Petch
HPT:	High Pressure Torsion
HRDSR:	High Ratio Differential Speed Rolling
HSRR:	High Strain Rate Rolling
ICP:	Inductively Coupled Plasma Optical Emission Spectrometry
LBM:	Laser Beam Machining
LPSO:	Long Period Stacking Ordered
MAO:	Micro Arc Oxidation
MMCs:	Metal Matrix Composites
MS:	Mass Spectrometry
m-SBF:	Modified Simulated Body Fluid
OCP:	Open Circuit Potential
ORR:	Oxygen Reduction Reaction
PBS:	Phosphate-Buffered Saline
PGA:	Polyglycolic Acid
PLA:	Polylactic Acid
PM:	Powder Metallurgy
PP:	Pearl Powder

PSN:	Particle Simulated Nucleation
PVD:	Physical Vapor Deposition
R&D:	Research and Development
RE:	Rare Earths
REE:	Rare Earth Elements
Roll:	As Rolled
SASE:	Severe Strain Asymmetric Extrusion
SBF:	Simulated Body Fluid
SHS:	Self-Propagating High-Temperature Synthesis
SMAs:	Single and Multi-Layered Self-Assembled Coatings
SPD:	Severe Plastic Deformation
SS:	Stainless Steels
STEM:	Scanning Transmission Electron Microscopy
UTS:	Ultimate Tensile Strength
VMSC:	Vertebral Mesenchymal Stem Cells
YS:	Yield Strength
YTS:	Yield Tensile Strength

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The role and significance of Magnesium in modern day research-A review

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2021-06-24

Elsevier

<https://doi.org/10.1016/j.jma.2021.05.012>

Satya Prasad SV, Prasad SB, Verma K, et al., (2022) The role and significance of magnesium in modern day research - a review, Journal of Magnesium and Alloys, Volume 10, Issue 1, January 2022, pp. 1-61