CHAPTER 2
LITERATURE SURVEY

This chapter includes introduction of magnesium, its alloy development and effect of alloying element on properties of magnesium alloy. It also contains magnesium melting practices such as fluxless and fluxing technique. Detailed studies on Mg-Mn alloys, Mg-Cu alloys and Mg-Ni alloys have also been included. Furthermore, the research gap and the objectives of the study are explained based on the literature review.

2.1 Introduction

Mg was first discovered in 1808 by chemist and scientist Sir Humphrey Davy. In his work, he proved that magnesium oxide was an oxide of a new metal. This silvery-grey metal found in the compound form. It is the third most common element dissolved in seawater and the eighth most common element found in the earth's crust. Approximate 2.5 % of its composition available at earth's outer surface. [10, 16, 24] Pure magnesium is produced from its compounds such as dolomite ($MgCO_3.CaCO_3$), magnesite ($MgCO_3$), carnallite ($KCl.MgCl_2.6H_2O$), brucite ($Mg(OH)_2$), olivine ($(MgFe)_2SiO_4$), biscovite ($MgCl_2.6H_2O$) and sea water (Mg^{2+}(aq)). [25–27]

Magnesium is the lightest structural material of modern times and has a density of 1.74 g/cm³, which is much lower compared to industrial metals such as Fe, Cu, Ti, Al, etc. Due to its low density and high specific mechanical properties, it is being intensively pursued in many industries for weight-critical applications. Figure 2.1 shows the comparison of the density values of magnesium with other metals. [28, 29]

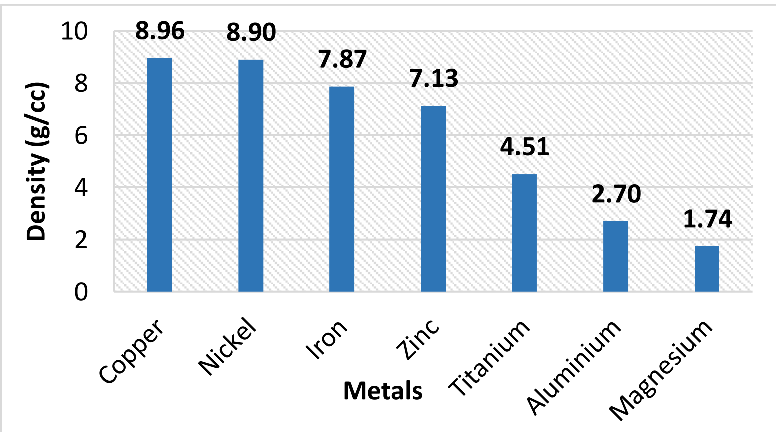


Figure 2.1 Density of different metals (g/cc) [29]

The early uses of magnesium included flash photography and ignition. It's interesting to note that 1878 marks the beginning of its use as a biomaterial. Then, observe the widespread military use of magnesium alloys in aviation both before and during World War II. [30, 31] Germany started producing electrolytic magnesium for commercial purposes in 1886 and remained the only nation doing so until 1916. Die cast magnesium alloys (AZ; 2,5−3,0% Al; 3,0−4,0% Zn) pistons made by Elektron Metall Bad Cannstatt, Berlin (Mahle group) was utilised for the first time in Germany in 1925, and by 1937, more than 4 million of them were in use worldwide. Mg was also used in the crankcase of the 1931 Chevrolair by General Motors. [32–34] By 1938, Germany's production had climbed to 20,000 tonnes, making up 60% of the world's output. By 1943, the US had built 15 new unit for magnesium production facilities, with a combined capacity of more than 265,000 tonnes. In the fields of defence and aerospace engineering, magnesium is regarded as a useful material to use for parts of aircraft and missiles, as well as for aircraft engine mounts, control hinges, fuel tanks, and wings. [13, 16]

Magnesium was one of the primary metals used in aerospace construction and was extensively employed in German military aircraft beginning in World War I and continuing through World War II. Magnesium sheet, castings, forgings, and extrusions were extensively used in the long-range bombers B-36 (Fig. 2.2) and B-52 of the US Air Force. [16]

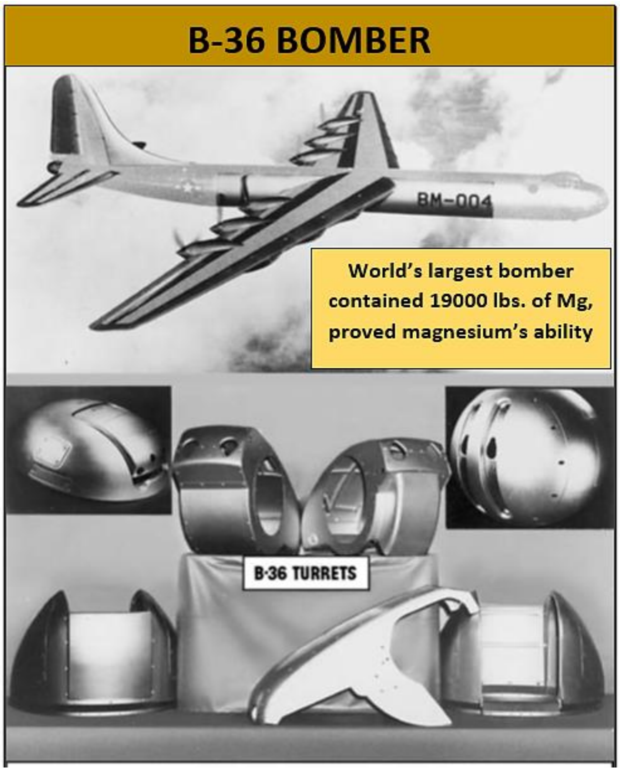


Figure 2.2 B-36 Bomber [34]

Magnesium sheet was used on several rockets, such as the Atlas Agena, Polaris, Vanguard, Jupiter, and Titan 1 (Fig. 2.3).[34] Mg was used extensively in the manufacturing of aircraft in the former Soviet Union. For instance, the TU-95MS plane contained 1550 kg of the element, and the TU-134 contained 780 kg of magnesium in various parts of the aircraft. Unfortunately, The International Air Transport Association (IATA) legislation restricting the use of Mg alloys to non-structural elements due to corrosion issues observed in the 1950s and 1960s. [35, 36]

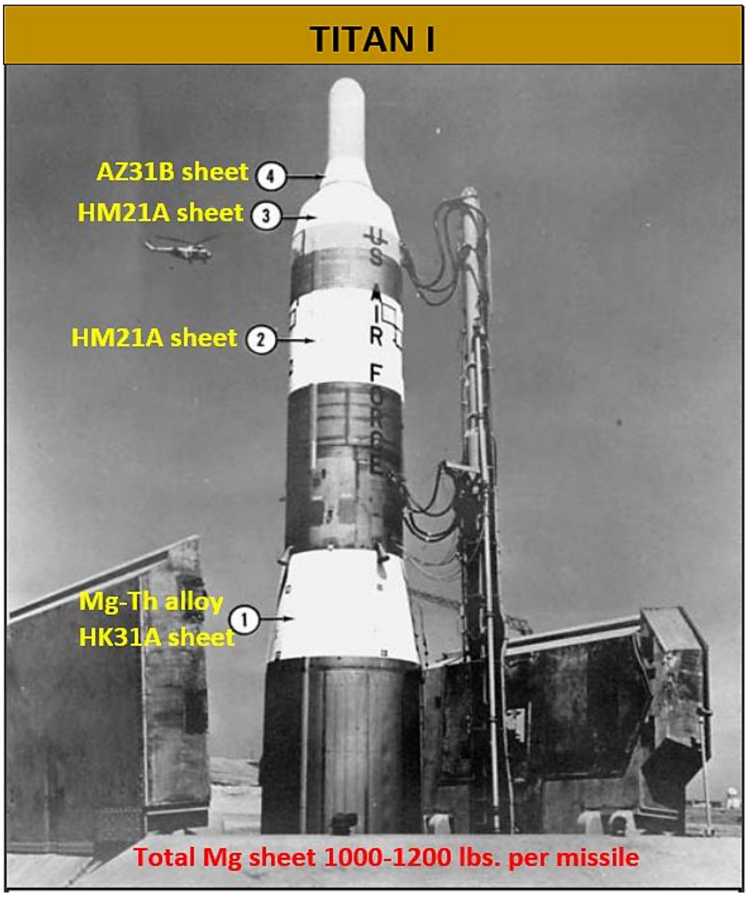


Figure 2.3 Titan I rocket [34]

2.1.1 Characteristics of Pure Magnesium

As an alkaline earth metal, magnesium is included in Group 2 of the periodic table of elements. Its lattice parameters at room temperature are a = 0.32092 nm and c = 0.52105 nm. It has a c/a ratio of 1.6236. Magnesium's atomic properties, some physical, electrical, and mechanical properties is shown in figure 2.4 & 2.5. [37]

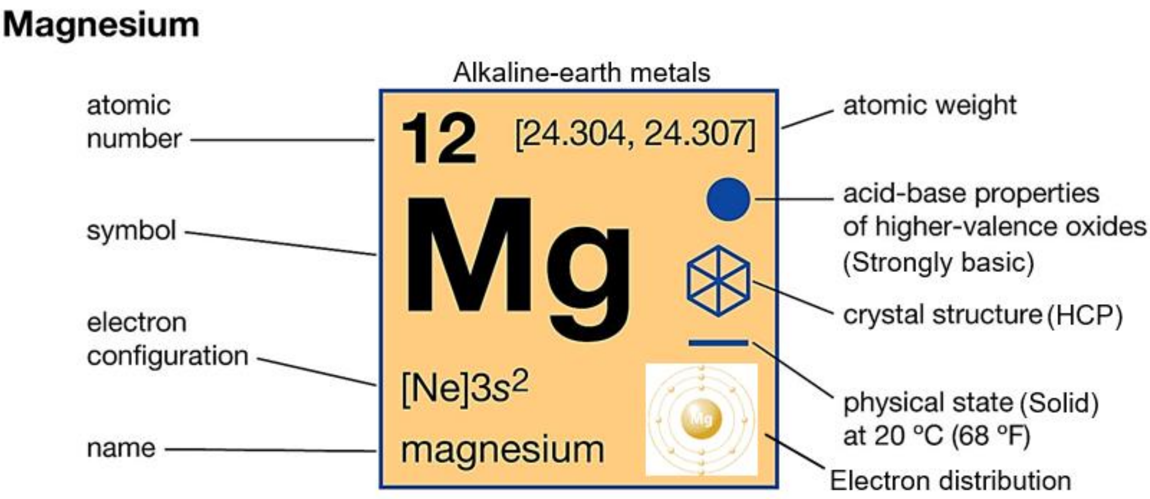


Figure 2.4 Atomic properties of magnesium [38]

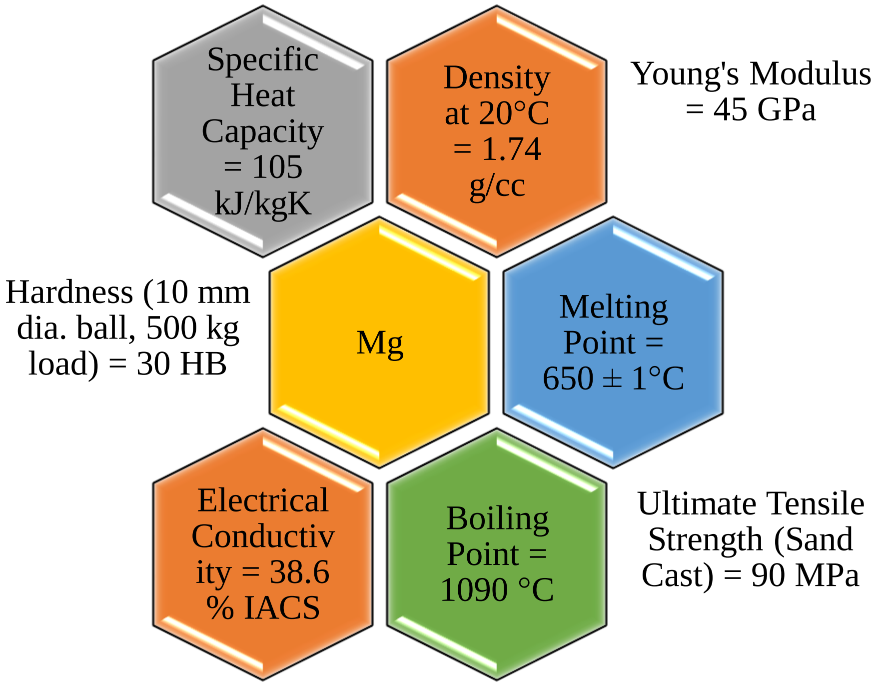


Figure 2.5 Some physical, electrical, and mechanical properties of magnesium [26, 28]

2.1.2 World Production and Consumption of Magnesium

Currently, North America holds the top position in the automotive industry for consumption of magnesium alloy, with a 30% annual growth rate. Shanghai Automotive Company in China is a pioneer in using magnesium alloys in the manufacturing of vehicle transmission cases, increasing the country's yearly usage of magnesium to more than 2000 tonnes. According to reports, China produced 912,600 tonnes of metallic magnesium in 2017 and 863,000 tonnes in 2018.

Data collected from 2014 to 2018 years (Fig. 2.6) show that domestic supply and demand for magnesium have reached equilibrium, with demand growing annually. [39] The global production of magnesium experienced fluctuations over the analyzed period. After reaching its peak in 2019 at 1,120 kilometric tonnes, magnesium production showed a decrease in subsequent years, with 2020 and 2022 both recording production levels of 1,000 kilometric tonnes. Despite these fluctuations, overall production remained relatively stable, with values ranging from 795 kilometric tonnes in 2012 to 1,070 kilometric tonnes in 2021. The production of magnesium on a global scale over the past decade is depicted in figure 2.7. [40]

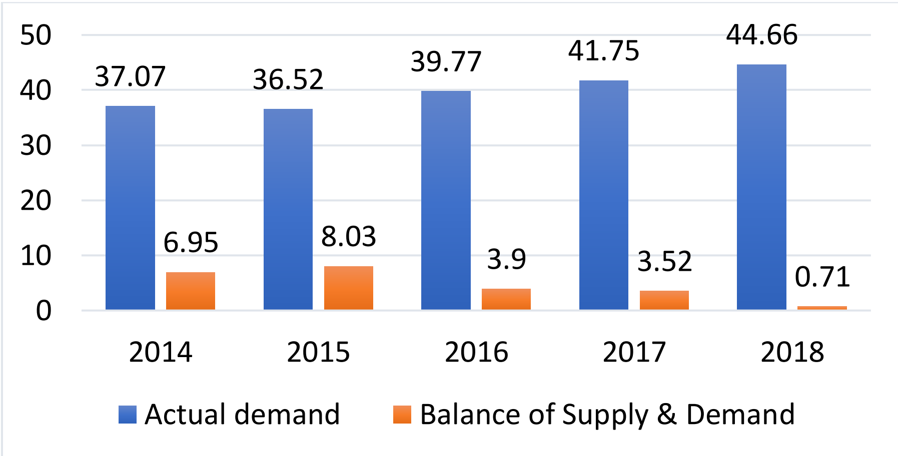


Figure 2.6 Actual Mg consumption and the supply-demand balance in China (in 10,000 tonnes) [39]

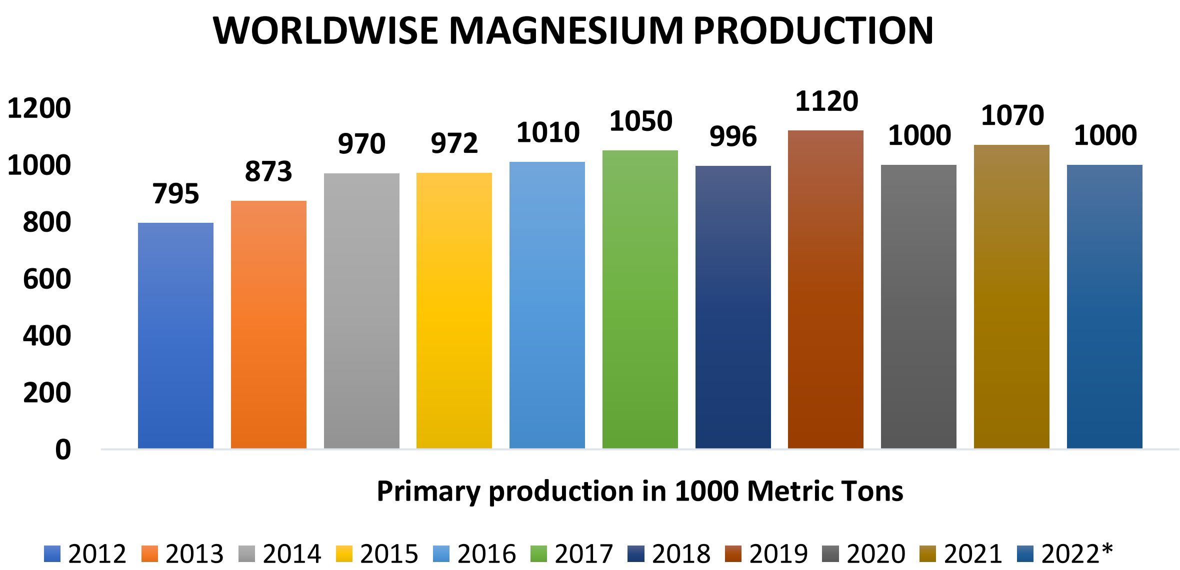


Figure 2.7 Worldwide Mg production (in kmetric tons) [40, 41]

According to data from Globe Newswire, Asia-Pacific is the region that consumes the most magnesium on the world market, with considerable demand coming from nations like China, India, and Japan, among others Asian countries.[19] Additionally, the automotive and aerospace industries are the primary consumers of magnesium alloys worldwide, as stated by Mordor Intelligence data for 2019. These industries have a substantial demand for magnesium alloys due to their desirable properties and lightweight characteristics. Graph of magnesium alloy market by End-user industry is shown in figure 2.8.[42]

In 2021, the global metal magnesium market size was valued at USD 4.39 billion, and it is projected to grow at a compound annual growth rate (CAGR) of 5.3% from 2022 to 2030, according to industry reports. This growth is expected to be driven by the increasing demand for magnesium alloys in various end-use industries, particularly in die casting and aluminum alloy applications. The market analysis report from Grand View Research highlights the growing product demand from these industries, which is anticipated to fuel the market's expansion. [43]

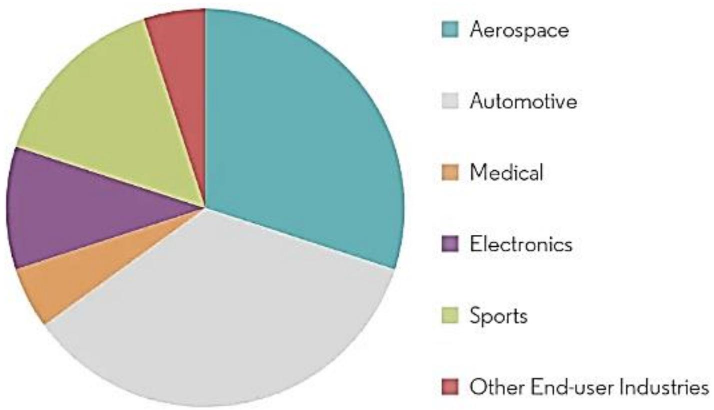


Figure 2.8 Mg Alloy Market, volume % by End-user Industry, Global 2019 [42]

2.2 Alloying Systems

The first step toward understanding magnesium alloys is to identify all kinds of alloys and to know the effect of each alloying element.

2.2.1 Designation of Magnesium Alloy

According to the American Society for Testing and Materials (ASTM B275), Table 2.1 displays the abbreviation letters for the alloying components that are frequently used to indicate magnesium alloys. Each alloy is identified by letters denoting the primary alloying components, followed by numbers denoting the proportions of these elements. [28, 44, 45]

Table 2.1 ASTM designation system of magnesium alloys[28]

Alloying Element	Letter	Alloying Element	Letter
Aluminum	A	Nickel	N
Bismuth	B	Lead	P
Copper	C	Silver	Q
Cadmium	D	Chromium	R
Rare earth metals	E	Silicon	S
Iron	F	Tin	T
Thorium	H	Yttrium	W
Zirconium	K	Antimony	Y
Lithium	L	Zinc	Z
Manganese	M		

3 components make up the designation of a standard magnesium alloy.

- **1st Component:** The two primary alloying elements are represented by two abbreviation letters in the original alphabet, which are placed in decreasing proportion order. The letters are placed alphabetically if the alloying element percentages are equal.
- **2nd Component:** The two primary alloying elements' quantities (in weight % terms) are listed. There are two whole numbers in it, which represent the two alphabets.
- **3rd Component:** It makes a distinction between various alloys that include the same amounts of the two primary alloying components. As compositions become more common, each letter in the alphabet is given a position, as in:

A	**First compositions, registered with ASTM**
B	Second compositions, registered with ASTM
C	Third compositions, registered with ASTM
D	High purity, registered with ASTM
E	High corrosion resistance, registered with ASTM
X	Experimental alloy, not registered with ASTM

For example, consider AZ91E magnesium alloy:

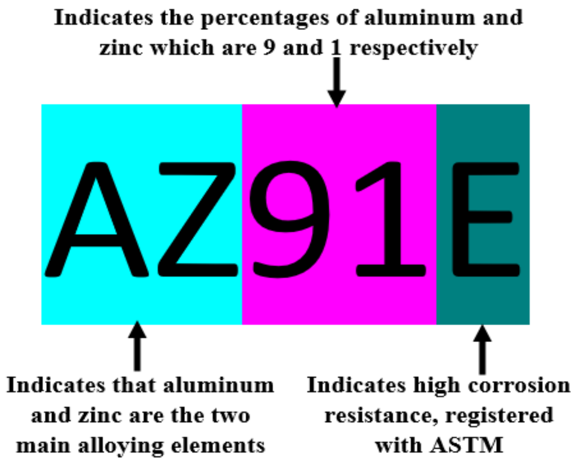


Figure 2.9 AZ91E magnesium alloy designation

2.2.2 Effect of Alloying Elements on Magnesium Alloys

Ultra-pure magnesium is known for its excellent corrosion resistance. However, to further enhance the material properties, appropriate alloying and processing techniques are employed. By introducing alloying elements, the mechanical properties of magnesium can be directly improved through various mechanisms such as precipitation hardening, grain refinement, and solid solution strengthening. These techniques aim to optimize the microstructure and enhance the overall strength and performance of magnesium alloys. [40, 46] Effect of various alloying elements on magnesium is discussed in table 2.2.

Table 2.2 Effect of different alloying elements on magnesium [28, 34, 40, 47]

Alloying Element	Influence on magnesium properties
Aluminium	▪ Improves hardness, strength and castability ▪ limited creep resistance because of $Mg_{17}Al_{12}$ phase ▪ An increase in aluminium content decreases the alloy's ductility ▪ Al concentrations exceeding 3 wt.% enhance corrosion rates by promoting cathodic reactions
Arsenic	▪ It reduces corrosion rate by preventing cathodic reactions from occurring (cathodic poison - stops the recombination of hydrogen)
Bismuth	▪ Enhances the processes at the cathode and anode, which increases corrosion ▪ Increases the creep and tensile properties
Beryllium	▪ Presence of less than 30 ppm coarsen the grains

	▪ lowers the oxidation of the surface melt ▪ Presence of more quantity decrease the corrosion resistance ▪ Some organizations are refusing to use it since it may be carcinogenic
Calcium	▪ Improves mechanical & thermal properties ▪ Minimizes the oxidation process during casting and heat treatment ▪ If the proportion is higher than 0.3 it improves the rollability of magnesium sheets ▪ The allowed amount for biocompatibility is 1 wt.%
Cerium	▪ Enhances plastic deformation ability, magnesium elongation, and work hardening rates ▪ Increases corrosion resistance and decreases yield strength
Copper	▪ Raises room temperature and high temperature strength ▪ Lowers ductility ▪ Decrease corrosion resistance
Iron	▪ Corrosion resistance is tolerable up to 0.005 %, above that, it is detrimental ▪ The solubility of iron in magnesium is extremely low, around 0.001 wt.%.
Lithium	▪ Lithium exhibits a low density of 0.54 g/cc and demonstrates high solubility in magnesium ▪ Alter the crystal structure to affect a material's ductility (Improves ductility) ▪ Reduces strength
Manganese	▪ Increase salt water corrosion resistance, refine grains ▪ Reduces harmful effect of iron ▪ Manganese has minimal influence on the tensile strength of magnesium alloys, but it slightly improves the yield strength.
Molybdenum	▪ Insoluble in magnesium ▪ Corrosion current density of the AZ91E alloy was improved by adding 0.1 wt.% ▪ enhances ductility, young's modulus, and hardness
Nickel	▪ Increases yield strength and ultimate tensile strength ▪ Decreases corrosion resistance

Cerium	▪ enhance magnesium's high temperature resistance, corrosion resistance, and creep resistance ▪ For a substantial elongation only 0.2% cerium is added
Gadolinium	▪ Highly soluble ▪ lower the cathode's rate of reaction
Holmium	▪ lowers the rate of corrosion when added to the AZ91D alloy in amounts of 0.24 and 0.44 weight percent
Lanthanum	▪ Above 3 to 5 wt.% limit increase corrosion rates
Neodymium	▪ Improve strength ▪ Increase corrosion rate
Silver	▪ Added with rare earth elements to age improve age hardening response
Strontium	▪ Refine grain ▪ Improves creep and corrosion resistance
Silicon	▪ Increase fluidity ▪ Increase creep resistance
Tin	▪ Used with aluminium leads to an increase in ductility ▪ Improved compressive strength and corrosion resistance
Thorium	▪ Creep is increased to 370 °C ▪ Improved weldability of alloys containing zinc
Titanium	▪ Improve ductility and YS
Yttrium	▪ Creep and high temp. resistance improve ▪ Accelerates the corrosion reaction
Zinc	▪ Increased yield stress and better corrosion resistance ▪ Decreases cracking when forging magnesium alloys ▪ Increases the fluidity of the alloys during casting
Zirconium	▪ Excellent grain refiner ▪ Improves tensile strength

2.2.3 Alloy Development

Magnesium in its purest form is soft and mechanically weak. [45] As a result, major efforts have been made to create Mg alloys for various uses, which is shown in figure 2.10. By the 1920s, aluminium had already emerged as the most significant alloying element for greatly improving tensile strength, particularly by forming the intermetallic $Mg_{17}Al_{12}$ phase. Similar results can be obtained with Zn and Mn, whereas the presence of silver improves high-temperature strength. Rare earth elements are becoming increasingly desirable because they provide a large increase in strength by precipitation hardening. [28] A list of commonly used magnesium alloys is given in table 2.3 and mechanical properties of various casting alloys are shown in figure 2.11. [48]

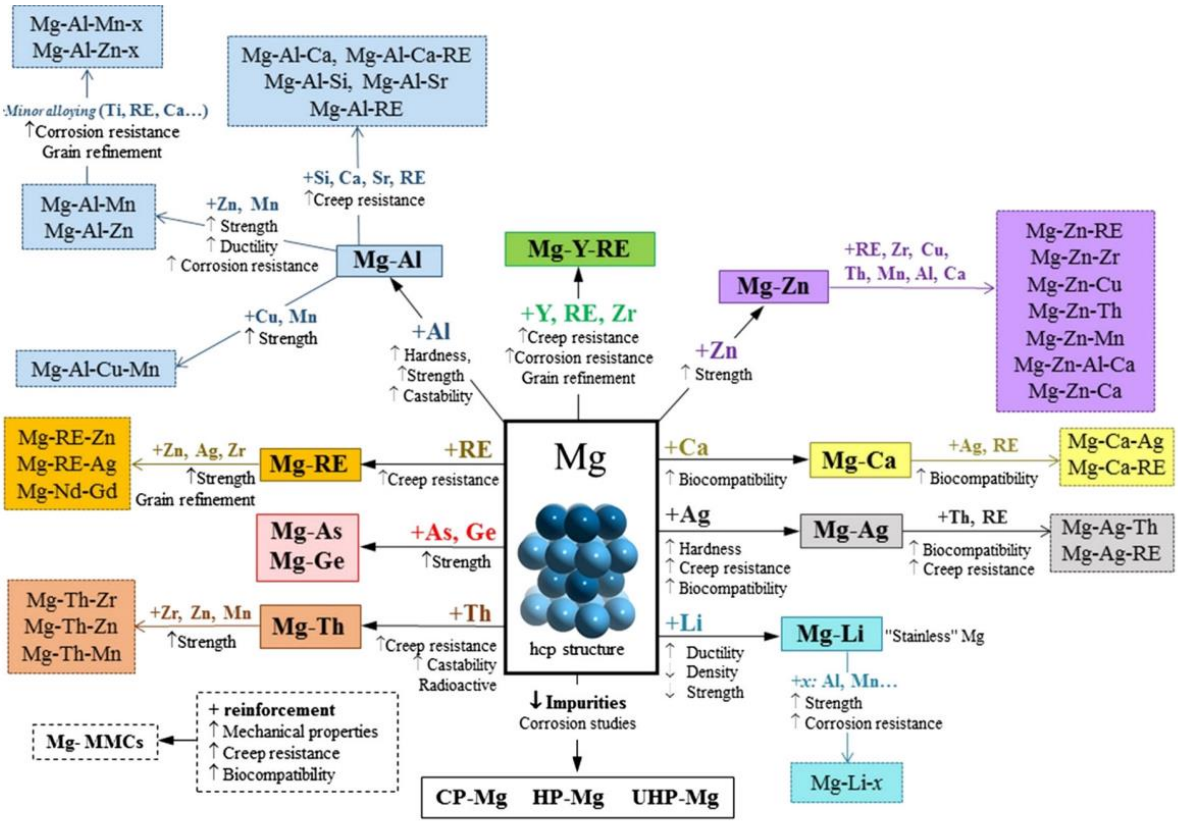


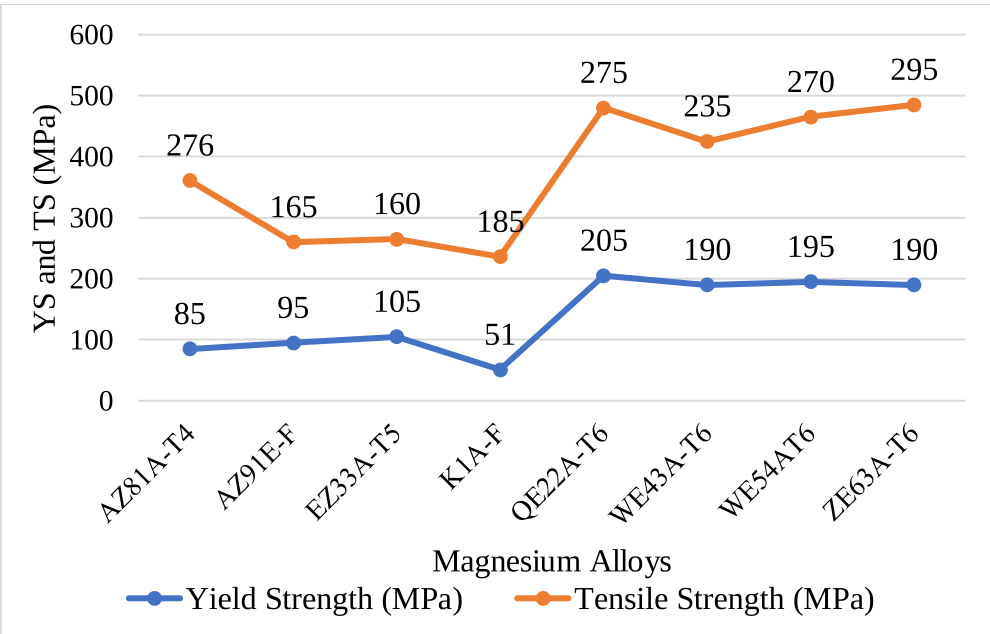
Figure 2.10 Overview of Magnesium Alloy Development [49]

Table 2.3 A list of common Mg alloys [48]

(a) Aluminum as Main Alloying Element								
Designation	**Al**	**Fe(max)**	**Mn**	**Ni(max)**	**RE**	**Si**	**Zn**	**Forms**
AJ52A	5	-	0.38	-	2.0 (Stronsium)	-	0.2	
AJ62A	6	-	0.38	-	2.5 (Stronsium)	-	0.2	
AM50A	4.9	0.004	0.32	0.002	-	-	0.22	
AM60B	6	0.005	0.42	0.002	-	-	0.22 (max)	DC
AS41B	4.2	0.0035	0.52	0.002	-	1	0.12	
AZ91D	9	0.005	0.33	0.002	-	-	0.7	
AZ31B	3	0.005	0.6	0.005	-	-	1	S, P, F, E

AZ61A	6.5	0.005	0.33	0.005	-	-	0.9	F, E
AZ80A	8.5	0.005	0.31	0.005	-	-	0.5	
AZ81A	7.6	-	0.24	-	-	-	0.7	SC, PM, IC
AZ91E	9	0.005	0.26	0.001	-	-	0.7	SC, PM
(b) Other Elements as Main Alloying Element								
Designation	**Ag**	**Fe(max)**	**Mn**	**Ni(max)**	**RE**	**Zn**	**Zr**	**Forms**
EZ33A	-	-	-	-	3.2	2.5	-	SC, PM
K1A	-	-	-	-	-	-	0.7	
M1A	-	-	1.6	-	-	-	0.7	E
QE22A	2.5				2.2	-	-	SC, PM, IC
WE43A	-	0.01	0.15	0.005	4 (Yttrium)	0.2	0.7	
WE54A	-	-	0.15	0.005	5.1 (Yttrium)	-	0.7	
ZE41A	-	-	1.5	-	1.2	4.2	0.7	
ZE63A	-	-	-	-	2.6	5.8	0.7	
ZK40A	-	-	-	-	-	4	0.7	E
ZK60A	-	-	-	-	-	5.5	0.7	F, E

DC: Die Casting, **SC:** Sand Casting, **IC:** Investment Casting, **PM:** Permanent Mold, **E:** Extrusion, **F:** Forging, **P:** Plate, S: Sheet



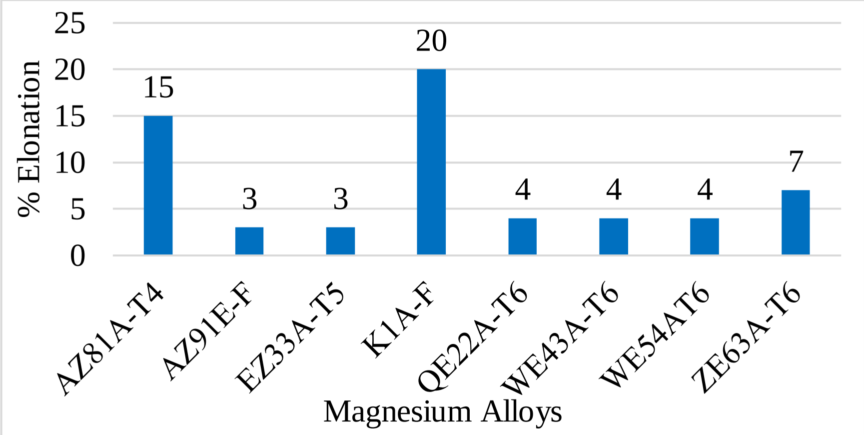


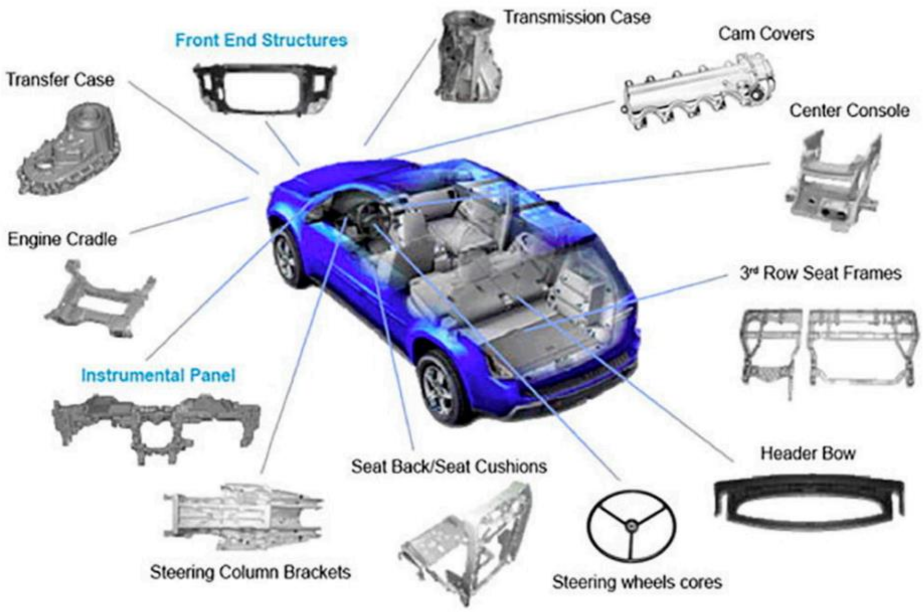
Figure 2.11 Mechanical properties of various Mg alloys [48]

2.3 Applications of Magnesium Alloys

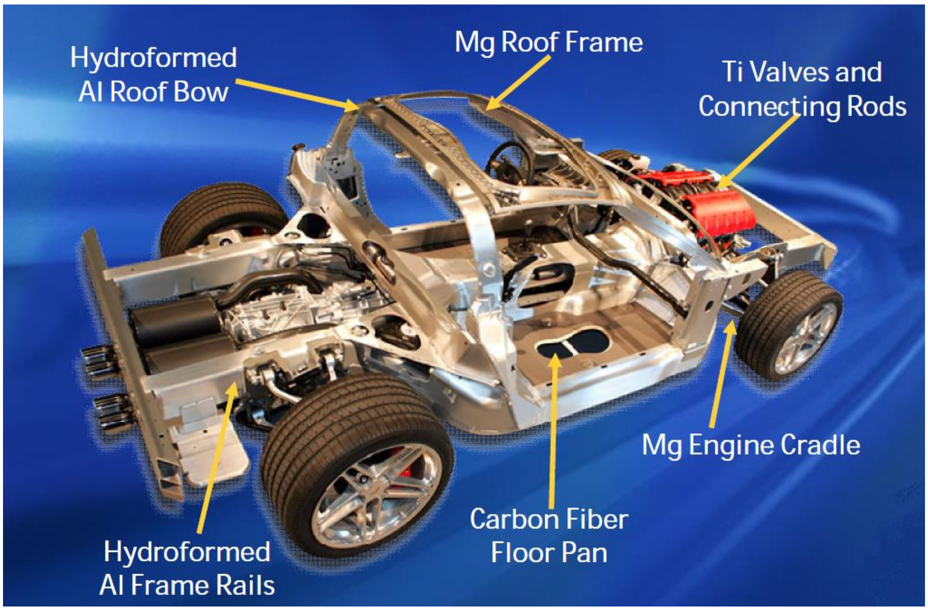
The significance of magnesium and its alloys is highlighted by research and development in the automotive sector. Because magnesium is the lightest structural material, it significantly lowers fuel consumption and CO_2 emissions. The low density of magnesium and its alloys further attracts car makers to study the use of it as alternative for steel and aluminium components. [50] The use of magnesium alloys in automotive parts significantly reduces vehicle weight, which reduces fuel consumption and exhaust emission. [39] A 100-kg weight reduction in the vehicle results in a fuel savings of up to 0.4 litres per 100 km. [51]

The engine cradle and top frame of the General Motors Chevrolet Corvette Z06 are made of magnesium. When compared to aluminium, the Z06 cradle weighs 35% less and delivers improved damping of engine vibrations and noise. The magnesium alloys parts which are used in automotive industries are shown in figure 2.12. [52, 53]

Engine blocks, gearboxes and clutch housings, oil pans, wheels, and engine cradles are some of the most typical magnesium uses, where stress may be distributed and excessive loads avoided. When compared to steel and aluminium, magnesium offers weight savings of 40-50 percent and 15-33 percent, respectively. [2, 51]



(a)



(b)

Figure 2.12 (a) Use of Mg alloys in various automobile parts (b) GM Chevrolet Corvette Z06 [52, 54]

Magnesium alloy parts are used extensively in the aviation industry, ranging from gearbox and engine components, gearbox casts, wings, fuselage skin, door, wheels, and undercarriage, through dashboard panels and seat components. For instance, the Boeing 727 aeroplane comprises over 1200 magnesium parts. Figure 2.13 & 2.14 shows the use of magnesium alloy in the aerospace industry. [51]

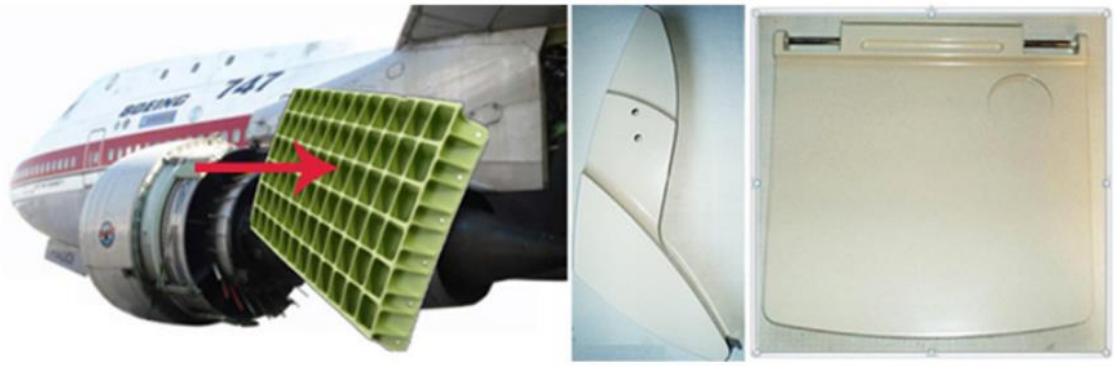


Figure 2.13 Boeing 747 (wing and seat) [51]

Figure 2.14 Various parts made by Mg alloys in aeroplane [51]

The outstanding specific strength and capability of magnesium alloys composites to produce complicated shapes resulted in several uses in sports-related equipment. The damping properties of the magnesium alloys make it a suitable choice for bicycle frames and in-line skate chassis, because magnesium can absorb shock and vibration. This absorption helps bikers to use less energy while enjoying a smoother, more comfortable ride. [55, 56] The applications of magnesium alloys in sports sector is shown in figure 2.15.

Figure 2.15 Use of magnesium in sports equipment [56]

The tendency in the electronic equipment sector is to make goods more personal and portable. Magnesium alloys meet the necessary standards because they are as light as plastic with better strength and heat transfer capacity. As a result, Mg alloys are used for mobile phone, computer, laptop, and portable media player housings (Fig. 2.16). [34] Over the last decade, magnesium has also found increased use in orthopaedic and cardiovascular applications, particularly for coronary stents and bone implants. The German-based Syntellix Company developed and launched MAGNEZIX® (Fig. 2.17), a really innovative material that, despite its metallic qualities and excellent stability, can be totally absorbed within the body and replaced at the same time by the body's own bone tissue. [57]

Figure 2.16 Use of Mg alloys in electronics [58–60]

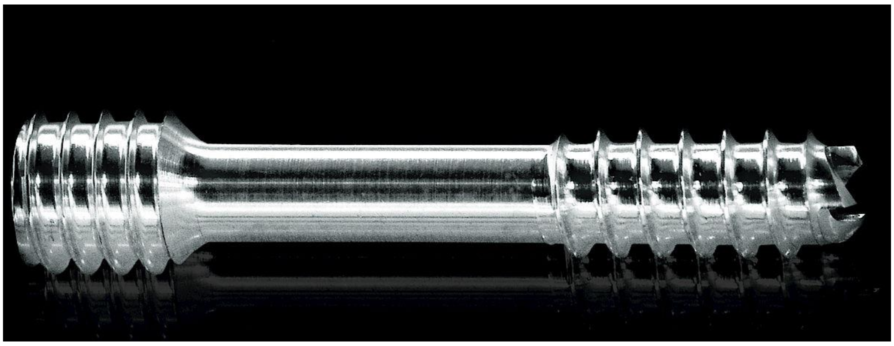


Figure 2.17 MAGNEZIX® magnesium bioabsorbable implant (developed by syntellix company, Germany) [57]

2.4 Effect of Manganese on Magnesium Alloys

Manganese is used in several magnesium alloys to enhance corrosion resistance and creep properties (with a rare earth addition). It is used in Mg-Al alloys, Mg-rare earth alloys, Mg-Zn alloys, and many other alloys to reduce the influence of the iron (Fe) impurity content on overall corrosion control.[18, 61–63] Manganese addition significantly reduces the solubility of iron in magnesium. As a result, iron precipitate settles at the bottom of the magnesium melt. Excess iron is removed through the precipitation and settling of intermetallic particles containing iron, manganese, and other alloying components. Furthermore, during the oxidation of magnesium, manganese creates a protective layer. For these reasons, small amounts of manganese are added to commercial Mg alloys. [64]

Manganese additionally assumes a significant job in the control of the microstructure. For instance, it controls the crystal grain size of magnesium while solidification and refines the grains. Manganese presence prevents unusual germination, which happens during heat treatment. [65] It is by and large added with around 0.34% to change the iron and other heavy metal elements by converting into moderately harmless inter-metallic compounds.[18]

Pure magnesium-manganese alloys such as Mg-1.5Mn and Mg-2Mn are counted as alloys for general use with medium strength values. The alloying content is limited to a maximum of 2.2% manganese. The influence of the manganese content on the mechanical properties is rather low (Fig. 2.18). In rolled condition alloys with more than approximately 1.5% manganese, offers higher strength. [34]

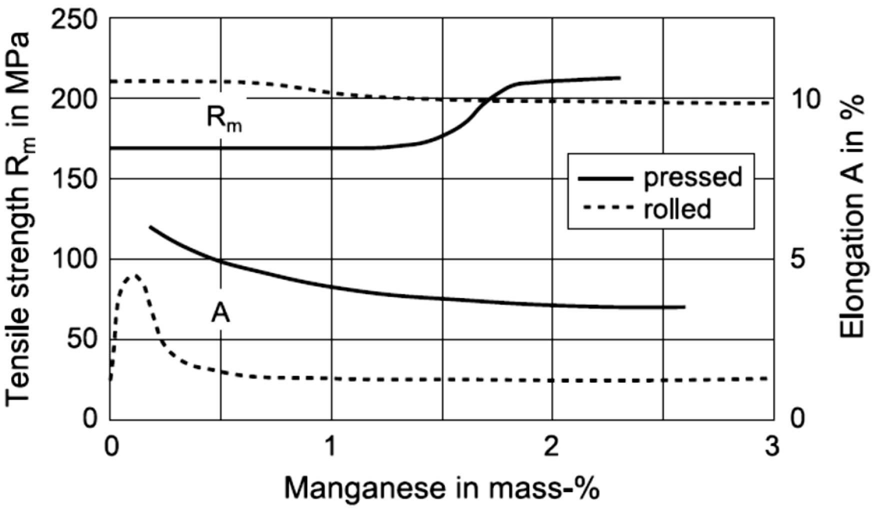


Figure 2.18 Effect of Mn on the mechanical properties of magnesium [34]

In the presence of other alloying elements, the level of manganese additions varies which depends on the mutual solubility of iron and manganese. [18, 62] Solubility of manganese decreases with decreasing temperature causing more precipitation of manganese. As shown in figure 2.19, the Mg-Mn system is described by a wide miscibility gap in the liquid state and very less experimental information is accessible on this system. This system has very limited experimental data, and the data that is accessible is contradictory with one another. The majority of the evidence provided is on the Mg-rich side, showing the limited solid solubility of manganese in Mg. Tiner determined that the maximum solid solubility of Mn in Mg is 2.0

at. % at 924 K. Using X-ray analysis, Petrov et al. observed a substantially lower solubility limit of 1.03 at. % Mn in Mg. [10]

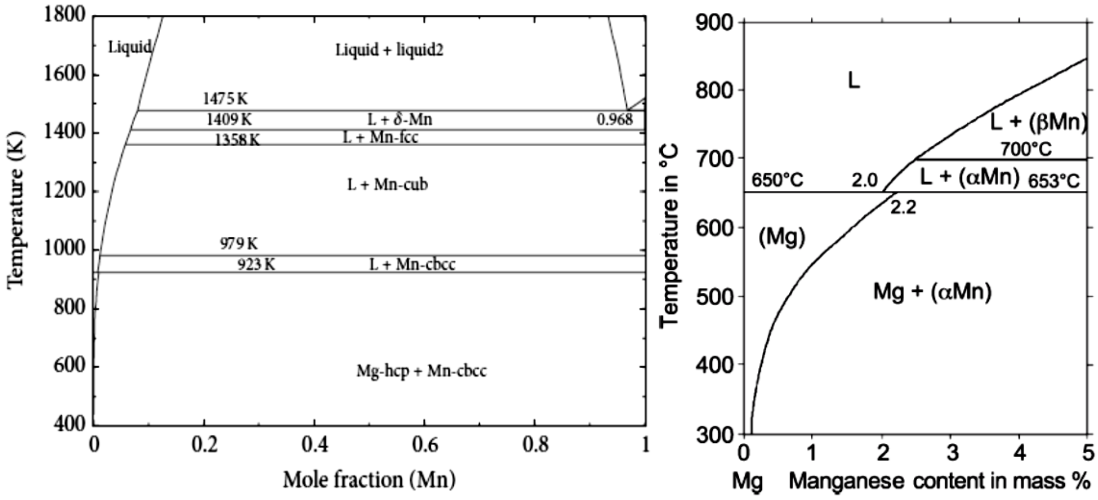


Figure 2.19 Mg-Mn binary phase diagram [10, 34, 66]

Nayeb-Hashemi and Clark examined the partial equilibrium phase diagram of the Mg-Mn system from 0 at. % to 3 at. % Mn. [37, 67] As a base, Nayeb-Hashemi and Clark had taken the results of thermal analysis, microscopic observation, and hardness measures of Petrov et.al. study [68]. They stated that the Mn solubility limit in Mg to be 0.996 at. % Mn. There were no intermediate compounds discovered between the Mg and Mn terminal sides, supporting the presence of a wide miscibility gap in the liquid phase and showing that Mg and Mn atoms preferred to be separate in the liquid and solid phases. Grobner et al. [69] used DTA and thermodynamic modelling to determine the full Mg-Mn phase diagram. Their predicted Mn solubility limit in Mg agreed well with Nayeb-Hashemi and Clark. [37]

2.4.1 Mg-Mn-O System (O- Other alloying element)

Manganese-containing Mg alloys can improve corrosion resistance as well as ductility and tensile characteristics. Manganese addition is often strategic, with the goal of reducing the effect of the iron (Fe) impurity content on the overall corrosion of Mg-Al alloys. Mn additions form an $Al_8(Mn,Fe)_5$ phase in the presence of Al and Fe, which can neutralise the Fe impurities. This is significant because any Fe present in Mg is insoluble and forms a pure-Fe (bcc) phase in the Mg matrix. This pure Fe has a considerable potential difference as compared to Mg and can sustain cathodic processes very efficiently, resulting in a strong local cathode. $Al_8(Mn,Fe)_5$ intermetallic lower the potential difference and cathodic potency. [70, 71] Table 2.4 shows the effect of Mn in magnesium systems.

Table 2.4 Effect of Mn in magnesium systems [70, 71]

Systems	Mn (%)	Purpose Mn addition
Mg-Al-Mn (AM series)	0.3-0.5	▪ Neutralise the Fe impurities by $Al_8(Mn,Fe)_5$ phase. ▪ Formation of Al_8Mn_5, $Al_{11}Mn_4$
Mg-RE-Mn (Mg-Gd-Mn, Mg-Nd-Mn, Mg-Y-Mn)	0.81-1.90	▪ Increase tensile yield strength but decrease plasticity.
Mg-Mn-Sc	1.0	▪ Improve creep resistance of the alloy due to formation of Mn_2Sc and other Mn_xSc_y phases (Better than WE43 alloy at 350ºC).
Mg-Al-Sn-Mn	0.01-0.34	▪ Improve corrosion resistance by formation of $Al_8(Mn,Fe)_5$ phases

2.4.2 Summary of Previous studies on Mg-Mn alloys

Dongdong Gu et.al. studied the influence of Mn on the microstructure and mechanical properties of a Gd (low content) on magnesium alloy. They found that the solid solubility of Gd could be adjusted by combining Mn addition with different processing phases to modify the morphology of the phase and enhance the alloy's properties. After hot extrusion, the strength of Mg-4Gd (-0.8Mn) alloy is greatly increased. The increase in yield strength and ductility of the as-extruded Mg-4Gd-0.8Mn alloy is mostly due to grain refining and texture intensity reduction. [72]

G.T. Parthiban et.al. worked on the effect of Mn addition on the sacrificial anode properties of electrolytic magnesium. They conclude that Mn addition control the iron impurity 0.006 % and other impurities 0.005 %. Due to this anode characteristics of the Mg-Mn alloy was improved. 0.18 % Mn containing alloy shows minimum corrosion rate and maximum anode efficiency so it could be use as a sacrificial anode. [73]

Sheng Yao et.al. studied the influence of Mn on Mg-3Al alloys. They studied microstructure and corrosion properties of Mg-3Al-xMn alloys. As per the results, they conclude that manganese presence didn’t refine the grains of Mg-3Al-xMn alloys. In all manganese containing systems, AL8Mn5 intermetallic compound was found. Furthermore, electrochemical and hydrogen evolution studies revealed that Mn addition gradually increased the corrosion resistance of Mg-Al alloys in NaCl solution. [74]

M. Celikin et.al. worked on creep behaviour of Mg-Mn alloys. As discussed in this paper, Mg-1.4Mn alloy shows significant creep strength at 15 MPa over a temperature range of 100-225 °C compared to pure Mg. The cast structure of Mg-1.4Mn alloy comprises Mn_3Si precipitates. Length of the precipitates is 0.3-3 μm in length that do not coarsen during creep, resulting in dislocation pile-up during low temperature compression creep experiments. [75]

D.S. Gandel et.al. studied the effect of Mn, Zr and Fe on the corrosion behaviour of magnesium. In this investigation, pure Mg samples and samples with various amounts of Mn or Zr were produced. Corrosion resistance was evaluated using both electrochemical and immersion testing. As shown in SEM-EDS results (Fig. 2.20) poor solubility components cause the formation of separate Mn and Fe particles in the Mg matrix. These particles are basically pure Mn and Fe, rather than intermetallic phases containing Mg. With a few wt.% of manganese addition, the Mn particles appear to expand up to 15 μm in size, whilst the iron particles only form up to 1 μm in size. From this result, conclude that in the absence of Al, manganese was found to be useful in minimising the effects of Fe contaminants. It was discovered that a Fe:Mn ratio of 0.02 was required for Mn to be most effective. [76]

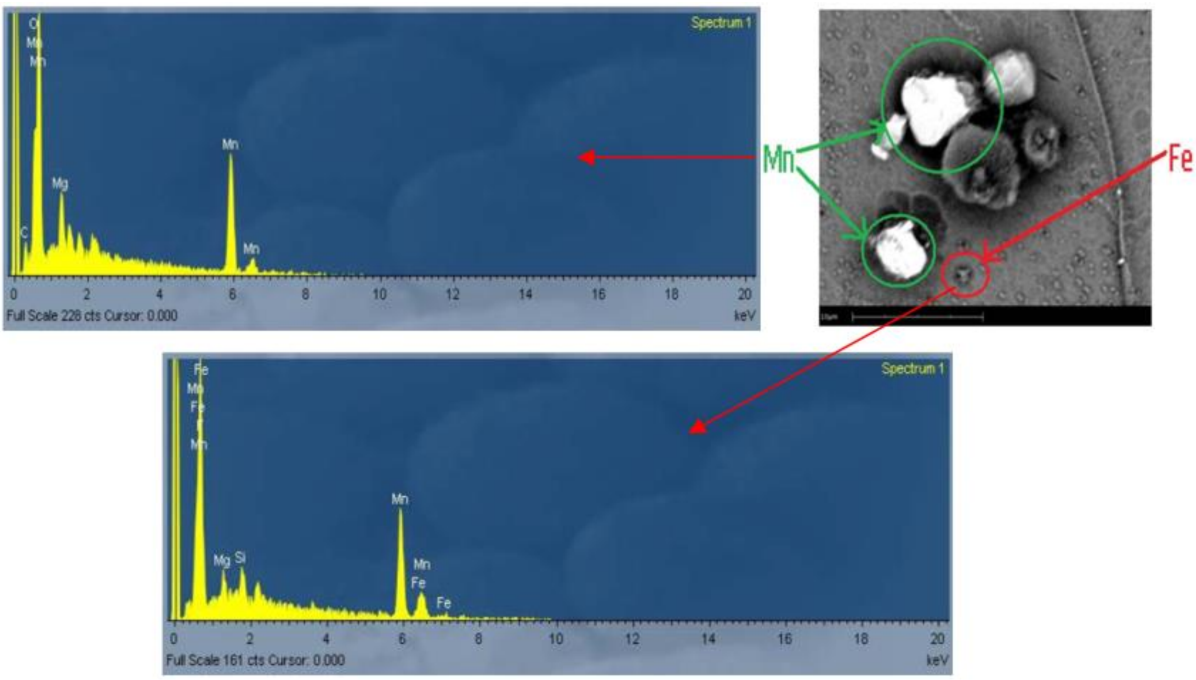


Figure 2.20 SEM-EDS analysis 4.07 wt. %Mn and 0.061wt. %Fe [76]

Marjan Razzaghi et.al. studied mechanical properties of AM20 and AM21 alloys in cast and wrought form. Results of XRD and EDS analysis shows that Al_8Mn_5 and Al_2Mn_3

compounds were form in this alloy. Compare to the cast form, it was found that presence of 0.5 wt.% Mn was favouring a finer grain size in the extruded form. [77]

Another research work on Mg-Mn-O alloy is shown in table 2.5.

Table 2.5 Research work on Mg-Mn-O System

Authors	Paper Name	Year	System	Mn (%)	Study
R.M. Wang et.al. [78]	An investigation on the microstructure of an AM50 magnesium alloy	2003	Mg-Al-Mn	0.57	TYS Microstructure
C. Tang et.al. [79]	Role of Manganese in the Soldering Reaction in Magnesium High Pressure Die Casting	2004	Mg-Al-Mn	0.178 0.362 0.520	Soldering formation
A. Kiełbus et.al. [80]	Microstructure of AM50 die casting magnesium alloy	2006	Mg-Al-Mn	0.45	Microstructure
Yosuke Tamura et.al. [65]	Liquid Solubility of Manganese and Its Influence on Grain Size of Mg-Al Alloys	2006	Mg-Al-Mn	0.02 0.08 0.13 1.27 1.64 2.27	Grain size Phases Microstructure
Faramarz Zarandi et.al. [81]	Effect of Al and Mn additions on rolling and deformation behavior of AZ series magnesium alloys	2008	Mg-Al-Zn-Mn	0.06-0.25	TYS UTS
Ning Liu et.al. [82]	Electrochemical corrosion behavior of cast Mg–Al–RE–Mn Alloys in NaCl solution	2008	Mg–Al–RE–Mn	0.4	Corrosion
Z. Zhao et.al. [83]	Microstructure & tensile properties of AM50A Mg alloy prepared by recrystallisation & partial melting process	2010	Mg-Al-Mn	0.3	YS UTS % Elongation .
D.S. Gandel et.al. [84]	The influence of Mn on the corrosion of Al-free Mg-alloys	2011	Mg-Mn	0.001-4.07	Corrosion
K. Illkova et.al. [85]	Acoustic emission study of the deformation behavior	2012	Mg-Mn-RE	1.0	TYS UTS

	of Mg-Mn alloys containing rare earth elements				Grain size
Faruk Mert et.al. [86]	Influence of Ce addition on microstructure and mechanical properties of high pressure die cast AM50 magnesium alloy	2013	Mg-Al-Mn-Ce	0.32 0.35 0.43	Hardness UTS % Elongation Grain size
A.V. Koltygin et.al. [87]	Development of a magnesium alloy with good casting characteristics on the basis of Mg- Al-Ca-Mn system, having Mg Al_2Ca structure	2013	Mg- Al-Ca-Mn	0.32 0.48	YS UTS % Elongation
Tianyu Zhu et.al. [88]	Effects of Mn addition on the microstructure & mechanical properties of cast Mg-9Al 2Sn (wt.%) alloy	2014	Mg-Al-Sn-Mn	0.01-0.34	Grain size UTS
Heon-Young Ha et.al. [89]	Improved corrosion resistance of extruded Mg–8Sn–1Zn–1Al alloy by microalloying with Mn	2015	Mg–8Sn–1Zn–1Al alloy	0.0089 0.12	Corrosion resistance
Dae Hyun Cho et.al. [90]	Effect of Mn addition on corrosion properties of biodegradable Mg-4Zn-0.5Ca-xMn alloys	2017	Mg-4Zn-0.5Ca-xMn	0.4 0.8	Corrosion resistance
Wenbo Du et.al. [91]	Effects of trace Ca/Sn addition on corrosion behaviors of biodegradable Mg–4Zn–0.2Mn alloy	2018	Mg–4Zn–0.2Mn	0.2	Corrosion resistance
Ahmad Bahman et.al. [92]	Corrosion behavior of Mg–Mn–Ca alloy: Influences of Al, Sn and Zn	2019	Mg-Mn-Ca	0.52	Corrosion behaviour
Xinming Di et.al. [93]	Competitive Effect of Grain Size and Second Phase on Corrosion Behavior of Biodegradable Mg-3Zn-1Mn-xSr Alloys	2021	Mg-3Zn-1Mn-xSr	1.0	Microstructure, Corrosion behaviour
Dae Hyun Cho et.al. [94]	In vitro and in vivo assessment of squeeze-cast Mg-Zn-Ca-Mn alloys for biomedical applications	2022	Mg-4Zn-0.5Ca-xMn	0.4 0.8	Microstructure, Mechanical Properties, Corrosion Performance

2.5 Effect of Copper on Magnesium Alloys

Nowadays there is an enormous need for the development of corrosion-resistant magnesium alloys. Therefore, the role of alloying elements and impurities must be thoroughly understood as a prerequisite. As per previous studies, the presence of copper, nickel, and iron elements in magnesium alloys intensively increases its corrosion rate. If copper presents greater than 0.05 wt. %, it reduces corrosion resistance and ductility both. [12, 34] It has a detrimental effect on corrosion in AZ and AM alloys, but comparatively, it is less harmful than nickel and iron. Copper precipitates Mg_2Cu has a lower potential compare to $FeAl_3$. Mg_2Cu functions as an efficient cathode, promoting hydrogen evolution.

Copper addition to Mg-Al-Zn alloys has also been demonstrated to have a negative effect on corrosion resistance. This could be due to copper inclusion in the eutectic phase as Mg (Cu, Zn). Copper has a tolerance limit of 300 ppm; however, it is known that larger amounts can be accepted if the zinc content exceeds the standard minimum of 0.4%. A minor quantity of copper improves the creep strength of magnesium die castings, but it greatly increases salt water corrosion. [95] In addition to this copper is also useful for improving, room temperature and high-temperature strength of magnesium alloy, hence it is added as an alloying element in Mg-Mn-Zn alloy.[18]

2.5.1 Summary of Previous Studies on Mg-Cu Alloys

Yu Zhang et.al. investigated effect of copper on microstructure and mechanical properties of Mg-6Zn alloy. The use of Mg-Zn binary alloys is limited due to their formed dendritic microstructure and low mechanical characteristics. So, in this study copper was added as a micro alloying addition to check its influence on Mg-6Zn alloy. The results show that adding Cu not only successfully refines the grains, but also modifies the eutectic morphology and enhances the mechanical properties of the alloys. The primary phases of the alloys investigated are Mg, MgZn2, Mg2Cu, and CuMgZn. Mg2Cu phase develops when the Cu content exceeds 0.8 wt.%. Meanwhile, the eutectic morphology changes to a dendritic or lamellar structure, which has a negative impact on the tensile characteristics. Furthermore, the alloy containing 0.8% Cu has the best UTS of 196 MPa, whereas the alloy having 1.5 wt.% Cu has an outstanding elongation of 7.22%. [96]

Shaozhen Zhu et.al. studied the effect of copper on microstructure and mechanical properties of Mg-6Zn-4Al alloy (as cast and heat treated). The results reveal that the grain sizes of the alloys reduce significantly as Cu addition increases, and the eutectics are refined by 0.5% Cu addition. The icosahedral quasi-crystalline phase is observed in Mg-6Zn-4Al and Cu-containing alloys, and the MgAlCu phase occurs due to Cu addition in the Cu-containing alloys. Cu-containing alloys exceed Mg-6Zn-4Al alloys in terms of age-hardening response during single-aging treatment. The combined impacts of fine grains and the evenly distributed high-density fine precipitates are responsible for 202 MPa yield strength, 312 MPa ultimate tensile strength, and 7% elongation. [97]

M. Lotfpour et.al. had worked on effect of different content of copper on structure, mechanical properties and corrosion behaviour of Mg-2Zn Alloy. Result shows that in 5 wt% Cu addition, the alloy's average grain size reduced from about 1000 μm to nearly 200 μm in as-cast state. Microstructural analyses showed that the predominant intermetallic in Mg-2ZnxCu alloys are α-Mg, MgZnCu, and $Mg(Zn,Cu)_2$, which are primarily found at the grain boundaries. The results of the mechanical testing proved that adding Cu considerably raised the hardness values. Although the addition of 0.5 weight percent of copper increased the alloy's ultimate tensile strength and elongation values, the addition of more amount of copper reduced the alloy's tensile strength by generating a semi-continuous network of brittle intermetallic phases. The results of the polarisation test indicate that Cu removes a protective layer from the surface of the Mg-2%Zn alloy. The Mg-2%Zn-x%Cu alloy with 0.1 weight percent of Cu has the best anti-corrosion property. However, more Cu addition increased the volume percentage of intermetallics, ultimately resulting in an increase in corrosion rate driven on by the galvanic couple effect. [98]

Hong-mei Zhu et.al. investigated influence of copper on ZK60 alloy. The results demonstrated that Cu can successfully remove intragranular solute segregations from the alloy, and that increasing the amount of Cu causes a significant reduction in the grain size of the alloy. In the Cu-containing alloys, a ternary eutectic phase MgZnCu with a FCC structure has been found. This phase is mostly distributed at the grain boundary and serves as the microcrack nucleation sites during the plastic deformation process. It is also discovered that the alloy's tensile characteristics first improve with a trace addition of 0.5%–1% Cu and then decline with an additional addition of up to 2.0%. [99]

Shiyu Zhong et.al. studied the copper effect on Mg-2Gd magnesium alloy. The result shows that as the Cu content increased, more Mg2Cu second phases precipitated and the grain size was refined. Although strain hardening rate and elongation reduced, hardness, tensile strength, compressive strength, and degradation rate increased. Overall, the inclusion of Cu can successfully balance the Mg-2Gd alloy's extensive mechanical properties and rate of degradation. [100]

Shuqun Chen et.al. investigated influence of copper on microstructure, mechanical and damping properties of Mg-1Mn alloy. The results indicate that the inclusion of Cu significantly reduces the grain size of the Mg-1%Mn alloy and reveals the existence of a new binary phase, Mg_2Cu, which segregates along grain boundaries in the form of separated eutectic and affects the tensile characteristics When the strain amplitude is low, the damping capabilities of Mg-Cu-Mn alloys change very slightly as the Cu increases. [101]

Junxiu Chen et.al had worked on corrosion and antibacterial properties of Mg-Cu alloys. The study showed that when Cu content increased, the galvanic corrosion between the Mg matrix and the Mg_2Cu intermetallic phase significantly enhanced the corrosion rate of Mg-Cu alloys. In a 0.9 wt% NaCl solution, Mg–0.3Cu alloy corroded roughly ten times more quickly than Mg–0.1 Cu alloy. Antibacterial tests revealed that the addition of Cu over 0.1 weight percent effectively decreased the viability of Candida albicans in Mg-Cu alloys. Due to its excellent corrosion resistance and antibacterial activity, Mg-0.1Cu offers good potential for usage as antibacterial implants. [102]

Zheng Ming-yi et.al. studied Mg-3Cu-1Mn alloy which is processed by equal channel angular pressing. They studied mechanical and damping properties. The result demonstrates that the yield strength and tensile strength of the as-extruded Mg-Cu-Mn alloy are decreased, but the ductility is increased, following ECAP processing. The grain of the alloy is greatly refined to about 4 m. The damping capacity of the Mg-Cu-Mn alloy changes after the ECAP processing, going from being much higher at low temperatures to significantly lower at high temperatures. The yield strength and tensile strength of the ECAPed alloy are further reduced after 1 hour of annealing at 300 °C, while the ductility is noticeably increased. At room temperature, the as-annealed alloy's damping ability increases; at higher temperatures, it decreases. [103]

2.6 Effect of Nickel on Magnesium Alloys

The solid solubility of nickel in magnesium is limited. [70] The cathode activity of nickel in Mg alloys is greater than that of iron in pure Mg and Mg alloys, because, as indicated in figure 2.21, nickel precipitates in magnesium alloys as Mg_2Ni, which is more cathodically active than $FeAl_3$ and Fe. [95] Hassan et al. [104] reported that the formation of Mg_2Ni intermetallic increases room temperature yield strength and ultimate tensile strength. On the other side, when nickel presents more than 0.004 wt.%, it drastically increases the corrosion rate. This detrimental effect of nickel limits its use in industrial fields. [105, 106] Due to this reason, the use of nickel is limited in magnesium alloys. [26]

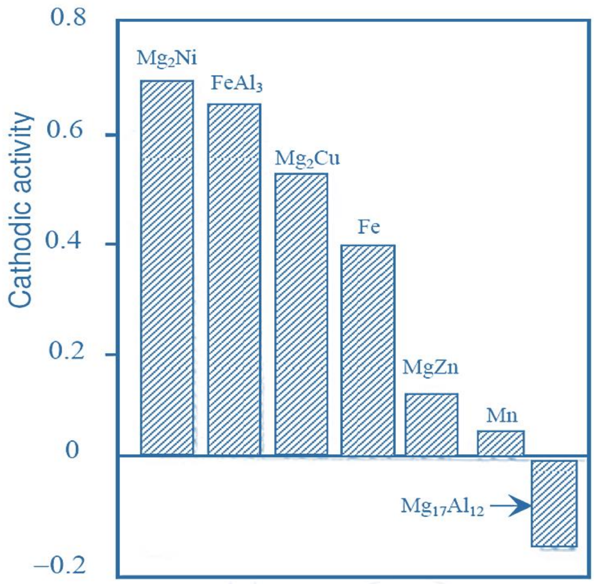


Figure 2.21 Compared to their alloy matrix, the cathodic activity of precipitated phases of Mg alloys in salt water [95]

2.6.1 Summary of Previous Studies on Mg-Ni Alloys

X. S. Hu et.al. studied damping characteristic of Mg and Mg-Ni alloys. The result shows that Pure Mg and hypoeutectic Mg-Ni alloys both exhibited excellent damping capabilities. At 100^{o}C and 230^{o}C, respectively, two damping peaks (P_1,P_2) were discovered. P_1 was a newly discovered damping peak that was thought to result from dislocation movement and has significant practical implications. They found that less than 12.1 wt.% Ni-containing Mg-Ni alloys possess high damping values. [107]

Hao-yi Niu et. al. developed Mg-4Zn-xNi alloys. According to their findings, the compressive strength and microhardness value increased with increasing nickel content. The presence of the Mg_2Ni phase in the Mg-Zn series alloy aggravates galvanic corrosion and increases the degradation rate. Result shows that the Mg-4Zn-2Ni alloy had a compressive strength and degradation rate of 512.6 ± 4.2 MPa and 619.35 mm/y, respectively, which were both greater than the values currently used for Mg alloys of fracturing balls. [108, 109]

J. H. Greenblatt studied corrosion behaviour of Fe and Ni containing magnesium alloys. according to tests of corrosion rates on coupled and uncoupled Mg alloys. Based on measurements of the corrosion rates on coupled and uncoupled magnesium alloys, it has been determined that the production of protective oxide layers is what causes the reduction in self-corrosion rates. [110]

P. Perez et.al. worked on Mg-Ni-Y-RE system. Microstructure and mechanical properties of as cast and hot extruded (400°C) samples were analysed. According to the results, A significant volume fraction of second phases, including coarse $Mg_{12}RE$, long period ordered stacking structure (LPS phase), and fine Mg_2Ni particles, are embedded in a fine-grained magnesium matrix. Up to 250°C, both alloys exhibit good strength values. The yield stress values for low- and high-alloyed magnesium alloys at room temperature are 295 and 405 MPa, respectively. The exceptional strength of these alloys at temperatures below 250°C is due to load transfer from coarse $Mg_{12}RE$ and LPS particles to the magnesium matrix. Both alloys showed a superplastic behaviour at high temperatures and modest stresses. [111]

Yongqin Wang et.al. studied on influence of small quantity of nickel (0.1, 0.2, 0.5 weight %) on microstructure and properties of Mg-2Gd alloy. As per result, with increasing nickel amount, the volume % of LPSO (long period stacking ordered) increase and average grain size of Mg decrease. The texture of the material changed from the rare earth texture to the basal fibre texture after the addition of Ni, and the strength, hardness, and corrosion rate were all increased while the elongation was reasonably decreased. Results prove that The Mg-2Gd alloy's strength and degradation rate were significantly increased by the addition of Ni, which was primarily the result of grain refinement, enhanced basal fibre texture, and the formation of LPSO phases. [105]

Chen Shuqun et.al. investigated microstructure, mechanical and damping properties of Mg-3Ni-xCu alloy (x=0.5%, 1.5%, 3%). The research indicates that the size of α-Mg dendrites can be reduced by the addition of Cu, and a new binary phase, Mg_2Cu, which mostly distributes among the inter-dendrites in the form of a characteristic lamellar-like eutectic microstructure and enhances the mechanical properties, can be discovered. As per the SEM-EDS result (Fig. 2.22) and binary diagram of Mg-Ni and Mg-Cu, they confirmed that two different types of eutectic phases, (α-Mg + Mg_2Ni) and (α-Mg + Mg_2Cu), respectively, make up the lamellar-shaped microstructures of Mg-Ni-Cu alloys.

The damping capacities of alloys containing Cu do not significantly vary with increased Cu addition in the low strain amplitude range, whereas internal friction values steadily decrease with grain refinement and increasing eutectic phase content in the high strain range. [112]

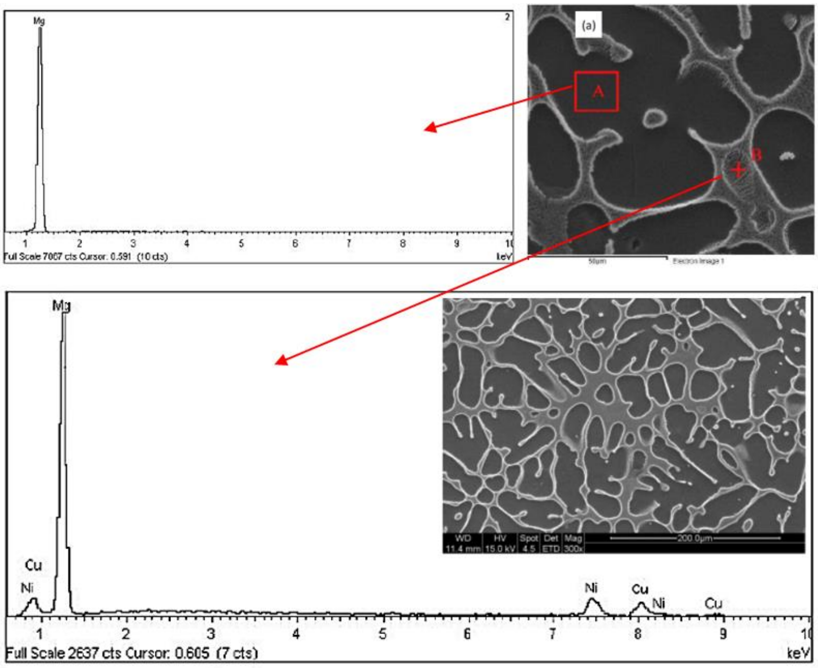


Figure 2.22 SEM-EDS analysis of Mg-3%Ni-3.0%Cu alloy [112]

2.7 Magnesium Melting Practice

Molten magnesium has a high tendency to oxidize. So, to protect it from oxidation and burning, surface care should be taken. If the oxidation of magnesium is not controlled, a porous, non-sticky MgO layer is formed on the surface of the molten metal. This layer cannot be prevented, so it creates a passage of oxygen into magnesium melt. As a result, the liquid metal burns and forms more oxide. In addition, magnesium and its alloys evaporate easily, so the extremely fine powder will form around the cold areas of the melt. This magnesium dust easily ignites due to the high surface-to-volume ratio. Therefore, to prevent the melt from oxidation and control magnesium from evaporation is very crucial. [113–116] Magnesium melting is done by two methods.

- Flux-less Method (in presence of gas or vacuum)
- Fluxing Method [117]

2.7.1 Flux-less Method

In the flux-less method, nonreactive gases such as nitrogen, argon, and oxide film modifiers such as sulphur hexafluoride (SF_6), and sulphur dioxide (SO_2) are used as a cover gas. Sulphur hexafluoride provides an effective barrier due to the formation of a dense magnesium oxide and magnesium fluoride film. This film protects magnesium from oxidation and evaporation. However, SF_6 has a warming potential, 23,900 times greater than carbon dioxide (CO_2) and is progressively expensive so it is banned in many countries. The gases used to cover the surface of molten magnesium must be continuous, fresh, and free of moisture. Because of the high cost and environmental pollution, the alternative fluxing method is also preferred by the magnesium casting industries.[118–121]

2.7.2 Fluxing Method

Each type of flux plays an important role in the magnesium melting and refining process. The main characteristics of the covering fluxes are to protect the magnesium melt against oxidation, melt before melting of magnesium, cover the surface properly, and form a dense strong film that is easily separable during pouring. As per individual characteristics, a combination of chlorides, fluorides, and oxides is used as a flux that is shown in table 2.6. [45, 122–127]

Table 2.6 Characteristics of various chemicals used for flux preparation

Chemicals	Characteristics
Chlorides	• The higher density of the chlorides causes the impurities to sink to the bottom of the melt as sludge. So, a combination of $MgCl_2$ and KCl was used to provide the low melting point eutectic. • $MgCl_2$ minimizes surface oxidation by creating a thin-film layer on the metal surface. • $MnCl_2$ is also used as an effective and economical additive in flux for the removal of iron in the production of magnesium alloys. • $BaCl_2$ was added to adjust the melting point. Due to its high density, encourage the flux and the flux-oxide particulates to settle at the bottom.
Fluorides	• Fluorides are added due to their better wet-ability and chemical reactivity with magnesium oxide. • The barium, strontium, and calcium fluorides provide the density required for the salt to effectively mix with the magnesium and then settle out at the bottom of the crucible by making high-density inclusions like MgF_2.

Oxides	• MgO absorbs the chlorides. • It also offers typical density to cover and refine the metal.

Fluxes and gases used for magnesium melting are shown in figure 2.23.

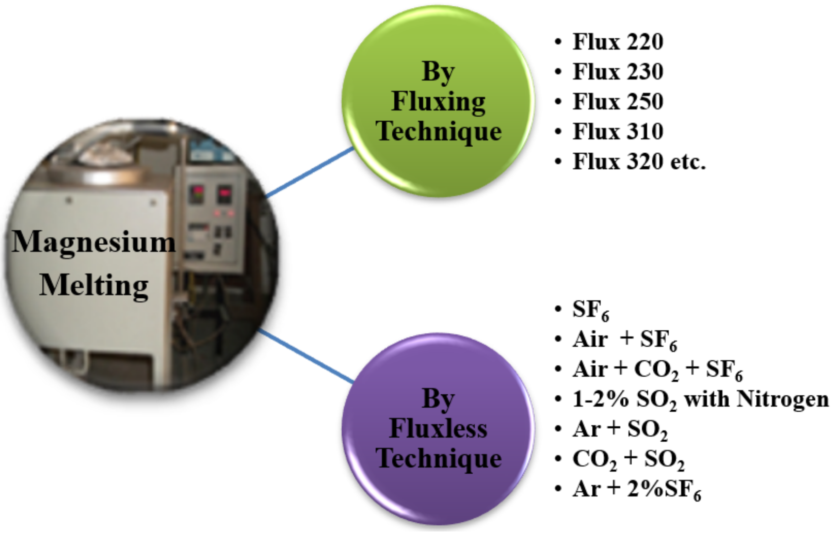


Figure 2.23 Fluxes/Gases used during magnesium melting

2.8 Research Gap

The following issue is addressed in the current research:

Research Gap 1

Due to the high oxidation susceptibility of molten magnesium, melt protection is required during melting and alloying. To overcome this problem, fluxless techniques are mainly used by industries. However, method is very costly and gases (SF_6) used in this method are very toxic, creates more pollution in environment. Thus, to protect the melt from the oxidation, development of cost-effective and environment friendly method (fluxing) is necessary.

Research Gap 2

In various magnesium alloys, manganese is added to improve corrosion resistance and creep property with other alloying element. But, as discussed in section 2.4, researcher has a different opinion regarding manganese solubility and recovery in magnesium. The literature on improving manganese recovery in magnesium and related alloys is insufficient. To understand the same different sources of manganese and temperature variations studies are included as a part of the present research work.

Research Gap 3

Copper and nickel addition to magnesium alloys was mostly discussed in past studies. Mostly, researcher had studied the influence of copper on the Mg-Zn, Mg-Zn-Al, ZK60 and Mg-Gd alloy. Few researchers studied damping properties and mechanical properties of Mg-Cu-Mn alloy and Mg-1Mn-Cu. But work on different amount of manganese and its effect on microstructure, mechanical properties and corrosion behaviour on Mg-xCu alloys (x=1,2,3) are still need more attention. Present research work included the same in details. In the case of nickel, mainly researcher had worked on Mg-Ni, Mg-Zn-Ni, Mg-Ni-Cu and Mg-Ni-RE systems. Almost negligible work was done on microstructure, mechanical properties and corrosion behaviour of Mg-Ni-Mn alloy. Present research included all necessary work for the same.

2.9 Objective of The Work

The present research work has been planned with the following objectives considering the research gap discussed above.

- Synthesis and characterization of magnesium melting fluxes.
- Increase the amount of manganese by addition of various sizes and forms of Mn sources like manganese coarse powder, manganese chloride, manganese oxide, manganese fine powder, and electrolytic manganese flakes and finally studied their behavior in magnesium in terms of microstructure, mechanical properties and corrosion behaviour.
- Develop Mg-Mn alloys by varying temperatures and study their effect on the solubility of manganese in magnesium. Also, study microstructure, mechanical properties and corrosion behaviour of developed alloys.
- Develop Mg-xCu and Mg-xCu-yMn alloy (where x=1,2,3 and y=1,2,2) and study the microstructure, mechanical property, and corrosion behavior of them
- Develop Mg-xNi and Mg-xNi-yMn alloy (where x=1,2 and y=2,2,3) and study the microstructure, mechanical property, and corrosion behavior of them.