CHAPTER-2

LITERATURE REVIEW

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This chapter provides information about magnesium alloy as lightweight material and its application in the different field of engineering and technology. The effect of various alloying elements and its temper designation are discussed as per ASTM standard. Various techniques used for protecting molten magnesium alloy along with different methods of fabrication are mentioned. Theoretical prediction of composites properties, strengthening factors and wear behavior along with the contributions of other researchers are discussed. The motivation of the current work is discussed in the last section of this chapter.

2.1. Introduction

Magnesium is an energy efficient material, and it can replace steels, aluminum alloys, and some plastic-based materials due to its light weight and excellent heat transfer capability in various application. Magnesium and their alloy are lightest structural metals, as stiffness and specific strength of magnesium exceed most of the structural metals and some plastic-based materials.

The lavishness and safety feature of recent cars increases the average weight of the vehicles by 20% since last three decades [14], [15], which enhances the fuel consumption and greenhouse gas emission. The scientists and engineers are using lightweight materials such as titanium, aluminum, and magnesium alloy for the last three decades. The consumptions rates of lightweight material are also increasing day by day because of weight reduction as one of the crucial tasks for automobile manufacturers. This leads to saving of fuel and a decrease in the emission of CO_2 [14],

[16]. Magnesium is one of the most promising lightweight materials. Currently, it is underutilized for most of the engineering applications. Magnesium is the 6th most abundant element representing 2.7% by weight of the earth crust [17]. The most common ores of magnesium are magnesite ($MgCO_3$), dolomite ($MgCO_3.CaCO_3$), carnallite ($KCl.MgCl_2.6H_2O$), and also seawater [18] (3rd most abundant dissolved mineral in the sea water).

Magnesium is the lightest of all structural metals due to its low density which is around 1.74 g/cm^3; therefore, it is approximately 35% lighter than aluminum, 60% lighter than titanium, and 75% lighter than zinc and 80% lighter than steels [19], [20]. Low density and high specific mechanical properties of magnesium alloy based materials are mentioned in Figure 2.1 and Figure 2.2 compared to other lightweight materials. Magnesium also actively participates in low and critical weight applications.

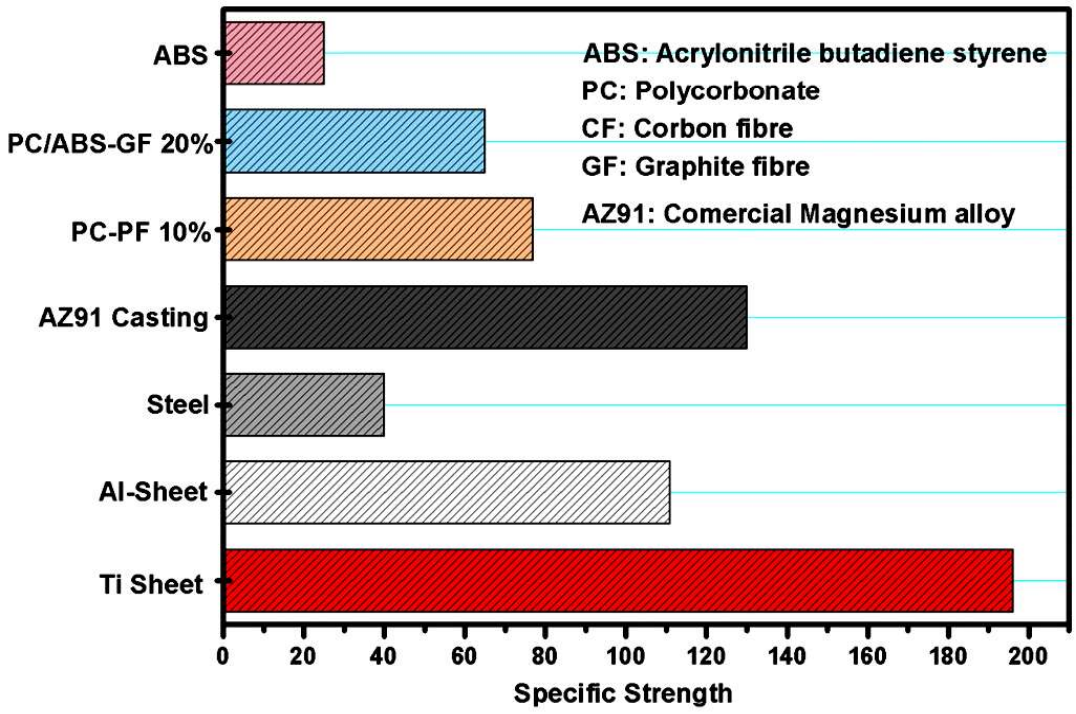

Figure 2. 1: Specific Strength of different materials [20]

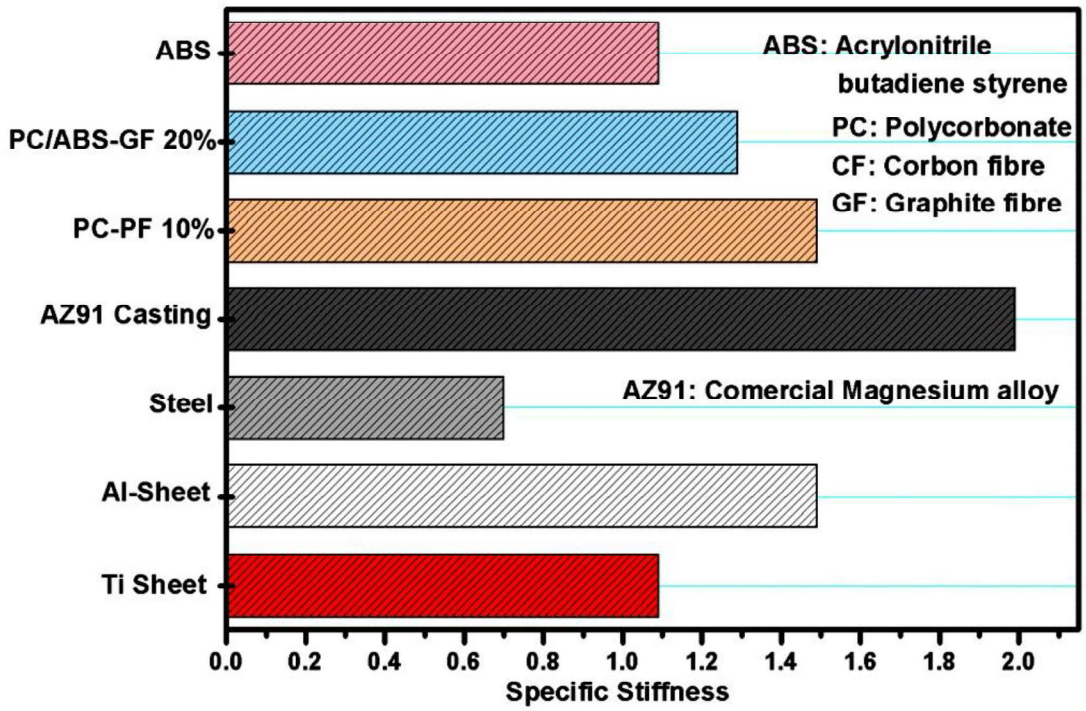

Figure 2. 2: Specific stiffness of different materials [20]

2.2. Applications and limitations of magnesium and its alloy

Many outstanding properties of magnesium and its alloys are high strength, low density, excellent damping capacity, good elastic shielding effect and excellent fluidity for casting. It also exhibits nonmagnetic, low heat capacity, satisfactory heat conduction, negative electrochemical potential, recyclability and non-toxicity relative to other engineering materials. The properties mentioned above makes magnesium alloy very attractive in numerous industries especially in automobile aerospace and electronics industries, where the strength to weight ratio is a crucial concern in the selection of lightweight materials. It is anticipated that a much broader application of magnesium will be made in the coming days of the twenty-first century such as 3C (computer, consumer product, and communication) industries. Despite many attractive applications magnesium alloys also face some limitation in term of its usability. The classifications of magnesium alloy based on its applications are presented in Figure 2.3.

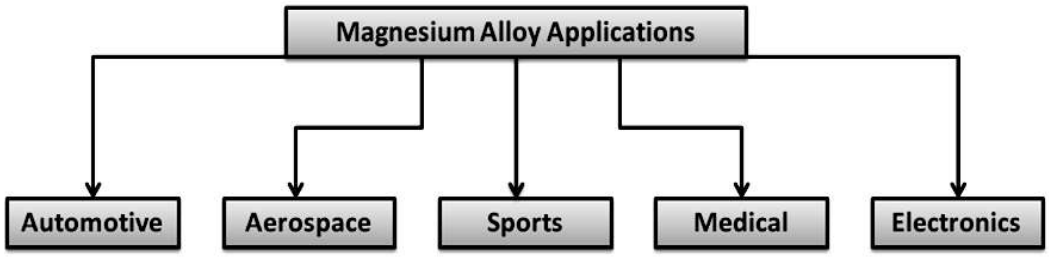

Figure 2. 3: General classification of applications magnesium alloys

2.2.1. Automotive applications of magnesium and its alloys

The increasing environmental and legislative concerns over the automotive industry to produce fuel-efficient, lighter and high-performance vehicle has resulted in the use of magnesium and its alloys. Magnesium alloy castings are widely used by most of the well-established automobile manufacturers including GM, Ford, Audi, Volkswagen, Daimler Chrysler (Mercedes-Benz), BMW, Toyota, Jaguar, Hyundai, Fiat, and Kia Motors corporations [1], [16], [21]–[25]. Magnesium is used as a piston in a racing car for 'Indy 500' in 1921 by Dow Chemical [26] in the united state. The use of magnesium in the interior parts such as the steering column housing, steering wheel, seat frame, driver airbag housing, and lock body of Hyundai Azera and Kia Amanti. According to Hyundai and Kia motors, there is 6 kg reduction in weight per car by using magnesium in the seat frame [27]. Magnesium piston is first time used in Germany by Elektronmetall Bad Cannstatt in 1924, and there were more than 4 million in operation by 1937 [28]. Magnesium crankcase developed by sand casting was other early applications of magnesium as an automotive material of Chevrolet by GM in 1931's [29]. Commercial forms of sand-casted magnesium have also been reported in England including lower crankcases for city buses and transmission housing for tractors in the 1930's [30]. Crankcases along with its housing are also developed by high pressure die casting in Germany. In the Audi A4, and VW Passat magnesium parts are widely used in the gearbox housing [31]. In the Toyota Lexus Carina, Corolla, and Celica, the

magnesium alloys are used for making steering wheels [32]**.** The major magnesium automobile components such as instrument panel beam, steering component, transfer case, seat support, cam cover, lock body, airbag housing and radiator support [27] are shown in Figure 2.4.

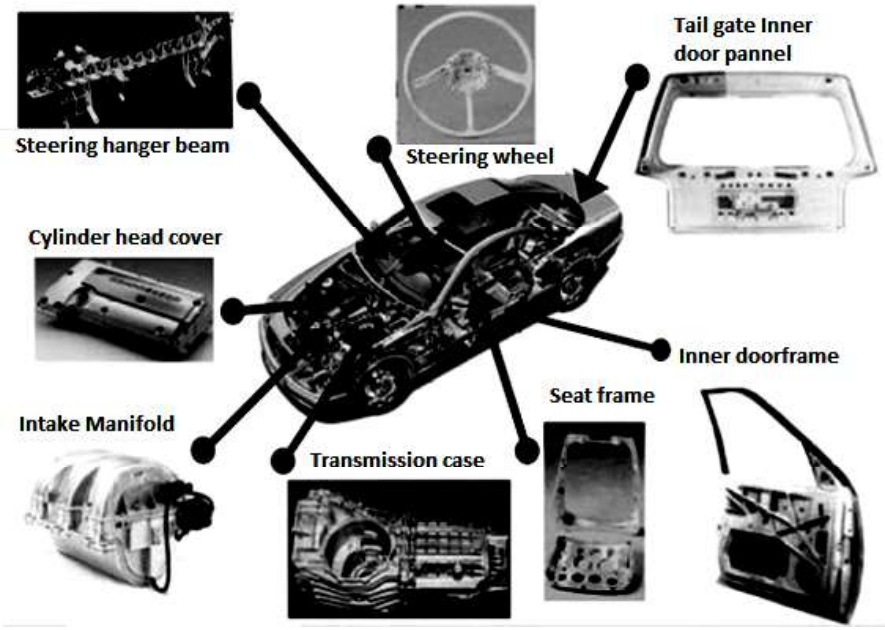

Figure 2. 4: Applications of magnesium alloys parts in an automobile [33]

2.2.2. Aerospace Applications

Magnesium as the structural metal was used by German military aircraft in **World War-I** and broadly in **World War-II**. The United States air force also used a large amount of Mg in many long-range bombers such as B-36 and B-52[26]. Boeing 727 made during 1962-1984 had around 1200 magnesium parts including leading & trailing edge flaps, actuators, control surfaces, wheels, door frames, engine gearboxes, power generation components, and other structural items. Soviet aircraft industry had also used magnesium in TU-95 MS plane by 1550 Kg and TU-134 plane by 780 Kg of magnesium component at a different location of the aeroplane [34]. The potential use of

magnesium alloy in modern aviation has been drastically reduced due to perceived hazards with magnesium parts in the event of a fire.

The International Air Transport Association (IATA) legislation limited uses of magnesium alloy to non-structural parts only, because of corrosion problem reported in the 1950's and 1960's [35] Nowadays with the use of the proper alloying element in magnesium alloy, the mechanical and corrosion resistant of magnesium has enhanced surprisingly [36]. Magnesium is not used in a structural application by major aircraft manufacturers such as Airbus, and Embraer [34], but it is mostly used in cast gearboxes and some other non-structural components of the helicopter industry. Now the aerospace industry around the world is taking an interest in resolving the regulatory barriers and technological challenge for magnesium applications. Many research programs of European country are using magnesium and its alloy for aerospace applications and manufacturing process for aerospace applications. People are expecting that magnesium will become a significant structural material for the future aerospace industry. Figure 2.5 shows the different parts made of magnesium alloy for aerospace applications. Spacecraft and missiles are also using magnesium and its alloys. Lift-off weight reduction is essential in their design, and material can withstand the extreme conditions faced during their operation. Magnesium and its alloys are capable of withstanding the extremely elevated temperatures, the impact of high energy particles and matter, and exposure to ozone. Magnesium is also used in massive quantity in intercontinental ballistic missiles such as Atlas, Titan, and Agena [37]. The magnesium alloys are also used in different parts of the helicopter as shown in Figure 2.6.

Figure 2. 5: (a) AZ80 compressor wheel produced by closed-die forging; (b) WE43 impeller with twisted blades; (c) WE43 compressor upper case for air conditioning system produced by closed- die forging; (d) AZ31B euro copter antenna support produced by deep drawing; (e) AZ80- forged airbus window frame; (f) AZ80- forged door stop fitting [38]

Figure 2. 6: Different parts of the helicopter where magnesium alloy is used [39]

2.2.3. Sports applications

The excellent specific strength and ability of magnesium alloy and it's composites to form complex shapes resulted in their applications in the sports-related product. The magnesium-based material is used in many sports-related parts such as the handle of archery bows, golf clubs and, tennis rackets, bicycle frame and chassis for in-line skates. Bicycle frame made from magnesium alloys or composite is capable of absorbing shocks and vibrations [40]. Therefore the rider feels more comfortable ride by exerting less energy [37].

During recent years, magnesium alloy has become primary functional materials in the leisure and sports industry. The productions of the front fork, post, frame, pedals, wheel, gear plate or breaking equipment, are just beginning the process of use magnesium alloy. The recent applications of magnesium-made sports equipment include the bottom of roller skates, hockey stick, baseball bat, golf ball, arrow handle, snowboard, snowboard bottom, snow boots bindings, belt hooks of ski boots, automatic board frame, row paddle stick, and wheel, etc., as shown in Figure 2.7. Even though magnesium alloy made materials have lightweight property, it has inferior corrosion resistance.

The manufacturers of magnesium product are actively improving the technology to make the better and attractive surfaces, so that among current fishing equipment, rotary turner, magnesium fly reel, and handles and many other fishing parts has been started to be produced using magnesium alloy [41].

Figure 2. 7: Application of Magnesium alloy in sports and leisure equipment [41]

2.2.4. Medical applications

In the first half of the 20th century, magnesium was first presented as an orthopedic biomaterial in the medical industry [42]. Numerous qualities and properties make magnesium an extremely alluring alternative for use in implants and similar applications. In general, the densities of implant materials is having in the range from 3.1-9.2g/cm^3, but the natural bone densities are having in the range of 1.8-2.1g/ cm^3. The densities of magnesium alloy are in the range of 1.74-2.0g/cm^3 which is comparable to human bone density. The fracture toughness, compressive yield strength,

and elastic modulus of magnesium alloy are similar to the natural bone [37]. The applications of Magnesium alloy as a human body implant are shown in Figure 2.8.

Magnesium is already present in the human body around one mole in a 70 kg man generally as ions; half of this is found inside the bone tissue [43]. The magnesium inside the human body support metabolic responses, and it has excellent biocompatibility and nontoxic behaviors. Therefore, uncoated implants of magnesium can be consumed in body fluid through corrosion because of its biodegradable properties, which eliminates the requirement of further surgery to remove implants [41], [42] [43], [44].

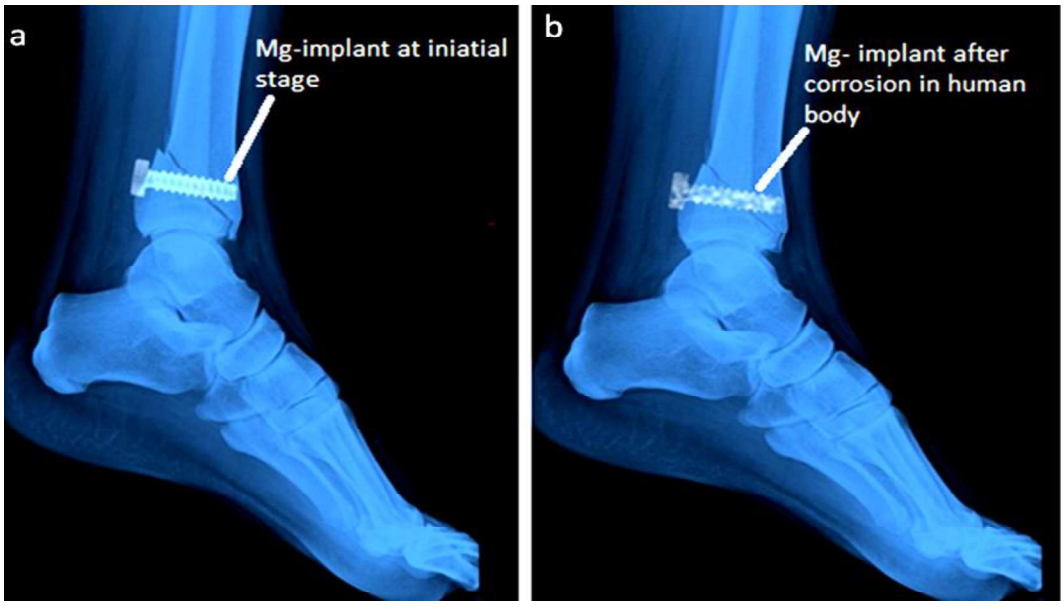

Figure 2. 8: Application of magnesium alloy as an orthopedic implant [45]

2.2.5. Electronics Applications

The demand for portable electronic equipment increased tremendously, and its components should be stylish, rugged, and lightweight. The trend in the electronic equipment industry has also been changed; people are looking for products which are more personal and portable. Hence the components which are used for making equipment should be lightweight and durable. The component made by magnesium and

its alloys is exhibiting massive improvement in strength, heat transfer, and the ability to shield electromagnetic radiation and radiofrequency interference in comparison to plastic counterparts [37]. The magnesium alloy is used in many electronic equipment housings such as mobile phones, cameras, laptops and portable media players [40], [46]–[48]. The applications of die-cast magnesium alloy for laptop case are shown in Figure 2.9, whereas for digital camera and handy cam housing is shown in Figure 2.10.

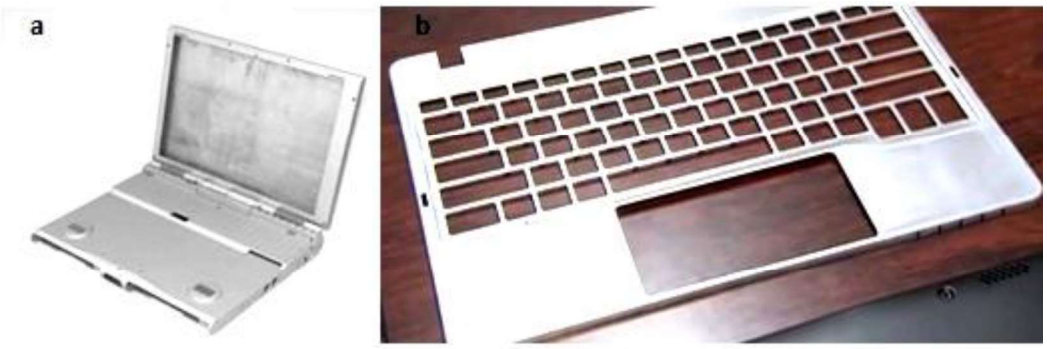

Figure 2. 9: Die-cast magnesium alloy laptop computer case (Image courtesy of Stihl and spotlight metal) [49], [50]

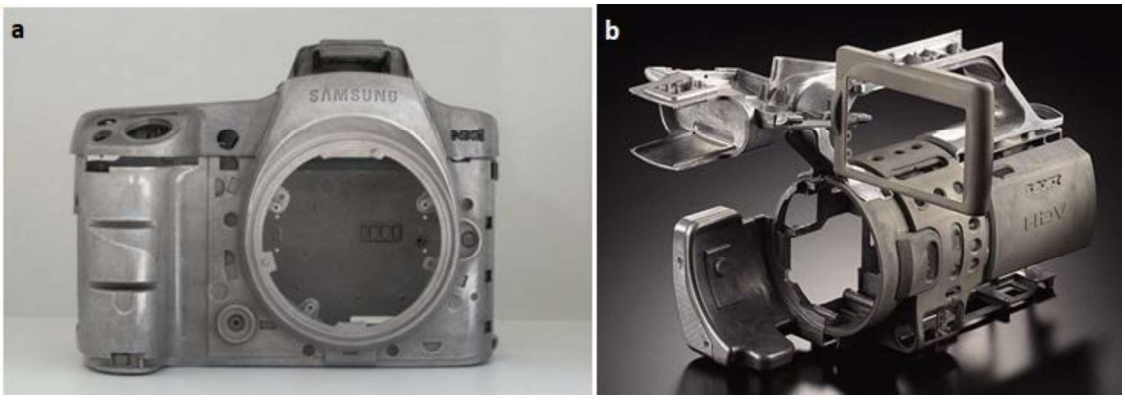

Figure 2. 10: Use of magnesium alloy in the housing a) digital camera and b) handy cam [51]

2.2.6. Other applications

Magnesium dies castings, and semi-strong moldings are utilized in the number of the optical product. Cameras for both film and digital picture catching required intricate, durable, and alluring housing for these systems [52]. Figure 2.11 shows the magnesium alloy based edge eyewear.

Figure 2. 11: Thixomolded magnesium compound edge eyewear [53]

Power hand instruments, enhance workers effectiveness, but the mechanization, which permits this change, adds to the unwanted weight on the equipment. The lightweight magnesium offers a significant market in the power tool industry to decrease the weight of the hand tool. The capacity to form thin-walled, complex die castings and moldings from magnesium alloy fulfill the requirements of this industry [37]. Hand-held work instruments and devices, for example, cutting tools, hand drills, hand shears, pneumatic nail gun, and weed whackers are ideal components for magnesium applications. The magnesium alloy with comparative strength, low density, and vibration damping abilities are for the most attractive attributes in the formation of handheld instruments [52]. Figure 2.12 shows the circular power saw made by die-cast magnesium.

Figure 2. 12: Circular power saw made by die-cast magnesium bases and blade guard [49]

2.2.7. Limitation of Magnesium

Despite various excellent and exciting properties of magnesium alloy, there are still some limitations which restrict the broad application of magnesium and its alloys. The various challenges related to the usability of magnesium and their alloys are:

1. Poor corrosion resistance.
2. The requirement of unique protection during melting and casting.
3. Difficult to deform as per requirements.
4. Low properties at elevated temperature.
5. Lower stiffness
6. Recycling cost is high.
7. Difficult to join
8. The high cost of material

2.3. Magnesium alloys and its temper designation

Pure magnesium is rarely used in engineering application without the addition of proper alloying elements. The addition of alloying elements in magnesium is used to improve the formability, strength and corrosion resistant. Magnesium is highly active and can react with another metallic element to form inter-metallic compounds. In most of the magnesium alloy, the presence of inter-metallic phase can be observed. These phases aid to influence the microstructure, and hence affect the mechanical behaviors of the magnesium alloys. Solid solution hardening and precipitation hardening are the key mechanisms to enhance the mechanical performance of the magnesium-based materials. The most common alloying elements are aluminum and Zinc. Zirconium, Manganese, Silicon and rare earth metal are used as alloying elements that have a noteworthy outcome on the behaviors of the resultant alloy.[18], [54]**.** Iron, Nickel, and Copper are

considered to be harmful impurities that need to be properly controlled to ensure the quality of the magnesium alloys. [18], [55], [56].

2.3.1. Effect of addition of alloying elements in magnesium

Magnesium is mostly used in alloy form because of inferior mechanical properties and low corrosion resistance. A huge number of magnesium alloys are currently being produced commercially by adding Al, Mn, Zn, Zr, Rare earth and Ag as an alloying element. On addition of alloying element, magnesium alloy becomes strong and lightweight [57]–[59]. The magnesium alloys based materials can be grouped into following alloys system.

i) Mg-Al alloy

ii) Mg-Al-Zn Alloy

iii) Mg-Al-Zn-Mn alloy

iv) Mg-Zr alloy

v) Mg-Zn-Zr alloy

vi) Mg-Zr-RE alloy

vii) Mg-Zr-RE-Ag alloy

viii) Mg-Zr-RE-Yttrium alloy

ix) Mg-Zr-Th alloy

x) Mg-Zr-Th-Zn alloy

xi) Mg-Zr-Th-RE-Ag alloy

Most of the magnesium alloys have an excellent combination of die castability, corrosion resistance, and mechanical properties, but they exhibit poor creep resistance at a temperature exceeding 125°C [60]. To increase the use of magnesium for reducing the weight of an automobile, another growing application area of the magnesium alloy is in

the powertrain system (where engine pistons can operate up to 300℃, engine block up to 200℃ and automatic transmission cases up to 175℃). These applications are also subjected to cyclic thermal and mechanical loadings and require materials with the ability to resist permanent plastic deformation due to creep. Presently the automatic powertrain components are made of cast iron or aluminum alloy (A380). Many efforts have been put since last two decades into the development of creep resistant magnesium alloy for die casting application [59], [61]–[63]. The new creep resistance alloys can be categorized as follows.

i) Mg-Al-RE alloy

ii) Mg-Al-Ca alloy

iii) Mg-Al-Ca-RE alloy

iv) Mg-Zn-Al-Ca alloy

v) Mg-Al-Sr alloy

vi) Mg-Al-Si alloy

vii) Mg-RE-Zn alloy

The primary purpose of adding of alloying element is to improve corrosion behavior, physical properties, mechanical properties, welding ability and machinability as described below [64].

Aluminum: Addition of aluminum in magnesium results in the enhancement of castability, hardness, and strength. The alloy more than 6wt% of the aluminum can be heat treated [18]**. Calcium:** The addition of calcium can improve grain refinement and creep resistance. Addition of Ca in magnesium improves corrosion resistance, thermal and mechanical properties of magnesium. **Copper:** Copper has limited solid solubility in magnesium [17]. The study has shown that the addition of copper in magnesium improve room temperature [5], [65], [66] and high-temperature strength [18]**. Iron:**

Iron is very much harmful to magnesium alloy, and even a small amount of it is detrimental to the corrosion resistance. **Lithium:** Lithium has a comparatively high solid solubility in magnesium. The addition of lithium can decrease the density of magnesium alloy below to that of pure magnesium. Addition of lithium leads to reduce in strength and increase in ductility [18],[67]**. Manganese:** The addition of manganese enhances the corrosion resistance of Mg-Al and Mg-Al-Zn alloys in the saltwater.

Nickel: Nickel has limited solid solubility in magnesium [17]. Hasan et al**.** [68] have reported that the addition of Nickel in magnesium leads to the formation of Mg_2Ni inter metallic's which resulted in an increase in strength at room temperature. **Rare earth metals:** Rare earth metals are added to increase high-temperature strength, corrosion resistance, and creep resistance. **Silicon:** Silicon can improve the fluidity of the molten alloys. **Silver:** Silver is used in combination with the rare earth metal to enhance the high-temperature strength and the creep resistance**. Strontium:** Addition of strontium enhance the creep performance but no significant improvement in yield strength and ultimate tensile strength [61]. **Thorium:** The addition of the thorium leads to an improvement in creep strength up to 370^0C. The weldability of magnesium alloys is improved by adding it. **Tin:** Tin addition with aluminum in magnesium improves ductility. It also assists in reducing the cracking tendency during forging. **Yttrium:** It incorporated with other rare earth metal to enhance the high-temperature strength and creep performance**. Zinc:** Zinc is one of the major and effective alloying elements in magnesium. It is generally used in combination with aluminum to increase the strength without losing ductility. **Zirconium:** Zirconium can work as an excellent grain refiner when incorporated into alloys contains zinc, thorium, rare earth metals or a combination of these elements[18].

2.3.2. Magnesium alloy designations

The American Society develops the method of designation used for magnesium alloys for Testing of Materials (ASTM B-275**)** [69]**.** It gives an approximate and immediate idea about the chemical composition of the two most significant alloying elements. The two most significant alloying elements are represented by abbreviation letter of the element and followed by figure represents the approximate percentage of these significant constituents. The designation of a typical magnesium alloy consists of a standard three-part ASTM system [69]

Part 1: - Indicate the two largest alloying elements with their code (refer to Table 2.1). The code letters corresponding to main alloying elements arrange in decreeing order of their percentage or alphabetically if the percentage is the same.

Table 2. 1: ASTM designation system of magnesium alloy [18], [70]

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

Table 2. 2 Temper designation for magnesium alloy [18]

General Divisions	
F	As fabricated
O	Recrystallized Annealed, (wrought product only)
H	Strain Hardened
T	Thermally treated
W	Solution heat treated
Subdivisions of "H"	
H1	Strain hardened only
H2	Strain hardened then partially annealed
H3	Strain hardened then stabilized
Subdivisions of "T"	
T1	Cooled from an elevated temperature shaping process and naturally aged
T2	Annealed (cast products only)
T3	Solution heat treated and cold work
T4	Solution heat treated and naturally aged to a substantially stable condition
T5	Cooled from an elevated temperature shaping process and artificially aged
T6	Solution heat treated and artificially aged
T7	Solution heat treated and stabilized
T8	Solution heat treated, cold worked and artificially aged
T9	Solution heat treated, artificially aged, and cold worked
T10	Cooled from an elevated temperature shaping process, artificially aged, and cold worked

Part 2:-Indicate the amount of the two largest alloying elements in weight percentage by round off percentage.

Part 3:- It differentiates two alloys with the same percentage of the two main alloying elements.

2.3.3. Temper designation of magnesium alloy

The ASTM method also extended to develop a code system for the temper designation of magnesium alloy by ASTM B296-03 [71]. The temper designation is motioned just after alloy designation, and a hyphen separates it. The example of temper designation is given as AZ91C-T_4, where T_4 is the temper designation. Table 2.2 represents some temper designation as per ASTM standard.

2.4. Melting and melt protection of magnesium alloy

The melting of magnesium and its alloy can be done in a ceramics crucible as well as in a metallic crucible (Fe-base) because molten magnesium does not react with Fe-metal, but if aluminum is present as an alloying element in magnesium, then there is a chance of reaction between Al-atoms and Fe-atoms. The behavior of the molten magnesium alloy is different from aluminum alloy. The aluminum alloy forms a continuous impervious oxide over the molten metal, which restricts further oxidation. On the other hand magnesium alloy, form a loose, porous oxide layer on the molten metal surface, which passes oxygen through this layer and support burning [72], [73]. Therefore protection of molten magnesium is necessary to avoid oxidation. Figure 2.13 shows the effect of melt protection on magnesium alloy. There are various techniques for protecting magnesium and magnesium alloy, some of which given below:

- Flux Protection Process.
- Reactive Elements Effect (REE).
- Protection Using SF_6.
- Vacuum Assisted Inert Atmosphere.
- Some other gaseous mixture protection

a) Molten magnesium without melt protection b) Molten magnesium with melt protection

Figure 2. 13: Showing the effect of magnesium melt protection [74]

2.4.1. Flux protection process

Flux protection process was used before the gaseous protection process was developed. The salt fluxes are a mixture of sodium and potassium (KCl and NaCl) with magnesium chloride ($MgCl_{2)}$ or calcium fluoride (CaF_2). $MgCl_2$ is generally used in magnesium alloys, which contains Al, Zn, and Mn as an alloying element, for examples AZ91D, AM60, AM50, and AZ31 commercial magnesium alloys [75]. A small quantity of flux (about 1% of charge weight) is placed in the bottom of the crucible, and it is preheated up to dull red hot [18]. Additional flux is sprinkled into the surface of the molten metals during melting and casting operations [76].

2.4.2. Reactive elements effect

Addition of small quantities of rare earth elements into high-temperature alloys containing chromium or aluminum produce some beneficial effects [77], [78]. It is called the "reactive element effect" (REE). The original concept of rare earth element effect has been adapted to increase the corrosion resistance of refractory alloys without impairing their creep resistance, and it was extended to other highly reactive elements (which have a very high affinity toward oxygen). The ‘active elements’ suggested by

Pfeil's patent were Sc, Y, La, Ti, Zr, Hf, Nb, Ta, Al, Si, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th [79]. The effect of the REE on high-temperature oxidation of magnesium was recently published by Czerwinski [78], including Be, Ca, Sr and Ti, which readily oxidize when exposed to oxygen, and prevent the oxidation of magnesium alloy during melting. The effect of Ca, Be, Sr and Ti additions into molten magnesium are given below.

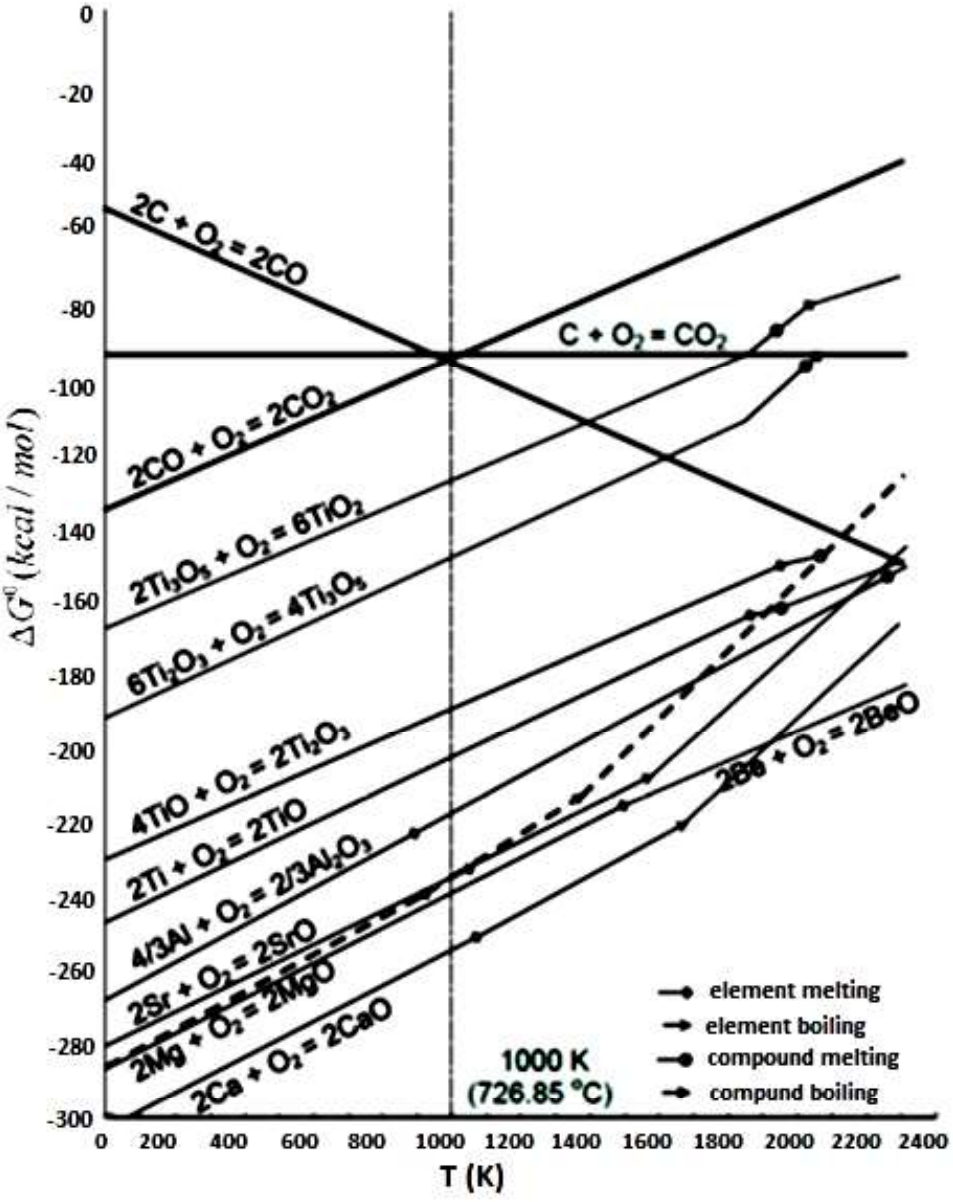

Figure 2. 14: Schematic of the Ellingham diagram for selected oxides, the magnesium oxidation is marked with a dashed line [80]

Figure 2.4 represents an Ellingham diagram [80] for the formation of some oxides including Al and Mg oxides. It can be seen that affinity to oxygen until ~1000 K (726.85 ″C) for the elements decreases in the following order Ca > Be > Mg > Sr > Al > Ti. Sakamoto et al. [81] reported that the thin oxide layer is formed on the surface of molten Mg-1.5Ca. The formation of CaO on the outer layer of the molten magnesium protects it from being oxidized.

2.4.3. Protection using SF_6

The protection of molten magnesium using air/SF_6 as a protective gas mixture was developed in the 1970's. A significant breakthrough in the processing of magnesium alloy has been received after the discovery of SF_6. SF_6 is an exceptionally valuable oxidation inhibitor for magnesium alloys. The exact mechanism of protection has been reported by Alan A. Luo [76]. However, SF_6 has a very high global warming potential approximately 24,000 times that of CO_2, because of very long retention in the atmosphere (3200 years). Which means that emission of 1 kg SF_6 is equivalent to that of 26.5 MT CO_2 [82]. Many national governments and company around the world are willing to eliminate the use of SF6 in the melting and casting of magnesium. Many end users of the magnesium worldwide will continue to demand consistently for high-quality magnesium products and developing magnesium casting technique with improved environmental conditions that will be alternative to flux less melt protection and other than SF_6 [74]. Figure 2.15 shows the effect of SF_6 hazardousness on the environment in comparison with emission and absorbent. One standard cylinder 52 kg cylinder of SF_6 is equivalent to 1,243 tonnes of CO_2. Therefore, the elimination of 1 cylinder of SF_6 is similar to eliminating 240 U.S. passenger cars for one year or planting approximately 210 acres of trees on the land.

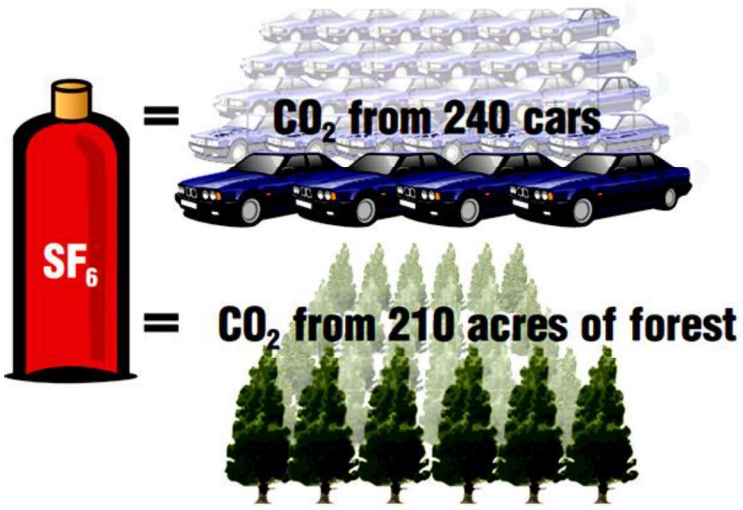

Figure 2. 15: The hazardless of one standard cylinder 52 kg of SF_6 equivalent to CO_2 emission by 240 U.S. passenger for one year or absorption of it by planting 210 acres of trees [74]

2.4.4. Vacuum-assisted the inert atmosphere

Protecting the molten magnesium metal in open environment under the blanket of an inert gas such as argon or helium is dangerous because no protective layer is present over the melt surface and magnesium metal may evaporate in the environment, resulting in safety hazards. The vacuum assisted inert atmosphere one of the most suitable processing technique for magnesium alloy (a detail discussion about this process has been discussed in chapter-4 of this thesis).

2.4.5. Some other gaseous mixtures protection

Gaseous mixtures containing HFC-134a, NOVEC 612, BF_3 (Magshield System) and solid CO_2 have been successfully employed in protecting molten magnesium [83]. The Cooperative Research Centre developed the HFC-134a protection method for Cast Metals Manufacturing (CAST) (Australia) for safeguarding the molten magnesium [84]. Use of NOVEC as a protective gas for protecting molten magnesium was started at the end of the year 2000 [85]. Liquid NOVEC^{TM} 612 preparation changes into a stream of

concentrated gas, which is later diluted by the carrier gas into the required concentration [83]. BF_3 as the protective gas is formed in this system as the result of the decomposition of solid fluoroborides directly inside the furnace, according to the reaction [83]:

$$KBF_4(s) \rightarrow BF_3(gas) + KF(s) \quad (2.1)$$

or

$$NaBF_4(s) \rightarrow BF_3(gas) + NaF(s) \quad (2.2)$$

2.5. Synthesis techniques for magnesium-based materials

The various synthesis techniques have been developed over the years to synthesize magnesium-based materials. The selection of proper synthesis techniques is not a very easy task, as the microstructure of the materials is highly dependent on processing parameters. The materials with the same constituent if processed with different synthesis techniques then the properties of materials will be different. The synthesis techniques or processing methods of magnesium alloy broadly classified into the following two categories [2], [18], [40], [86].

i. **Solid-phase method**

ii. **Liquid phase method**

Liquid phase processing techniques are more beneficial and economical in comparison to solid phase processing. Solid phase processed materials exhibit the following advantages and disadvantages of comparing with the liquid phase processing.[87]

Advantages:

a) Refined micro-structural features.

b) The capability of producing meta-stable phases in the microstructure.

c) Superior Strength levels.

Disadvantages:

a) High processing cost

b) Tedious handling of fine powders

c) Thickness Limitations

d) Lower fracture Toughness and ductility

2.5.1. Liquid-Phase Processes

The different liquid phase processing methods can be grouped into the following categories [2], [18], [40], [86].

i) Sand casting

ii) Die casting

iii) Squeeze casting

iv) Semi-Solid metal(SSM) casting

v) Stir casting (most appropriate for composite)

vi) Spray Forming

vii) Melt infiltration techniques

viii) In situ synthesis

2.5.2. Stir casting

Stir casting is used for processing both magnesium alloys and its composites. Different proprietary methods are generally used to perform the additions of reinforcements into metal matrix composites**.** After adding reinforcement, it was mixed fairly by a suitable method and eventually cast either in the form of a billet or some shaped parts [2], [12]. A schematic diagram of the stir casting process is represented in Figure 2.16. Besides the various advantage of the stir casting process, some difficulties are encountered during the stir casting process of MMCs, which include the following issues:

(i) Agglomeration of reinforcement particle.

(ii) Settling or floating of reinforcement particle (due to density difference)

(iii) Fracture of reinforcing phase during agitation.

(iv) The interfacial reaction between the reinforcement and matrix materials.

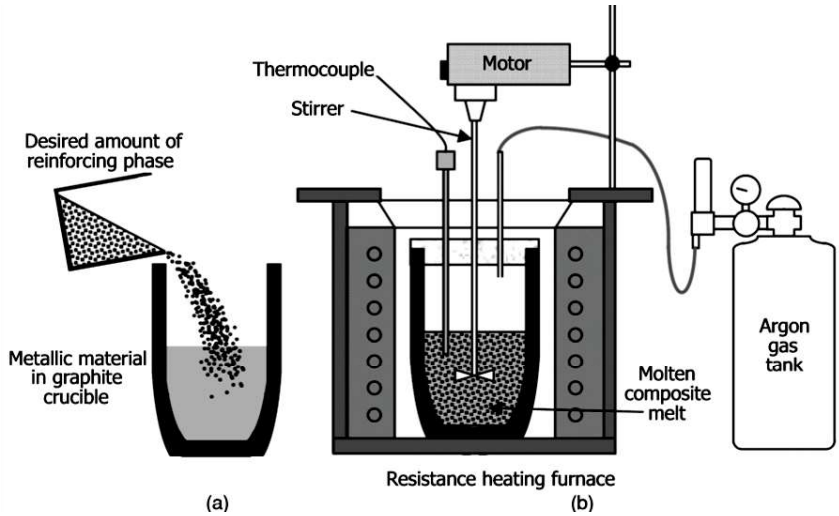

Figure 2. 16: Schematic of stir casting set-up for magnesium casting [87]

2.6. Metal matrix composites

Metal matrix composite is increasingly sought for a wide range of application in the automotive, aerospace, electronics and sports industry because of several good mechanical and physical attributes. The MMC consist of a matrix material that is either metal or metallic alloy and the reinforcing material that can be ceramic, metallic, refractories, inter-metallic or semiconductor. Higher ductility and recyclability of the MMC will increase its application in automobile and aerospace industries. The MMC offered the following advantages over monolithic metallic materials:

i) Higher strength to weight ratio

ii) Higher specific modulus

iii) Enhanced elevated temperature stability regarding better creep resistance

iv) Improved fatigue characteristics

v) Enhanced damping characteristics

vi) Enhanced abrasions and wear resistance.

The properties of metal matrix composite can be tailored as per the requirement of the end applications. The end properties of the MMC will depend on various factors, and their optimization is a must to realize the desired combination of properties. Some key factors are listed below:

i) Properties of the matrix materials

ii) Types of the reinforcement

iii) The volume fraction of the reinforcement

iv) Size of the reinforcement

v) The orientation of the reinforcement

vi) Distribution of the reinforcement

vii) Compatibility of reinforcement with matrix

viii) Processing techniques

Based on reinforcement, the MMC can be grouped into the following types as presented in Figure 2.17.

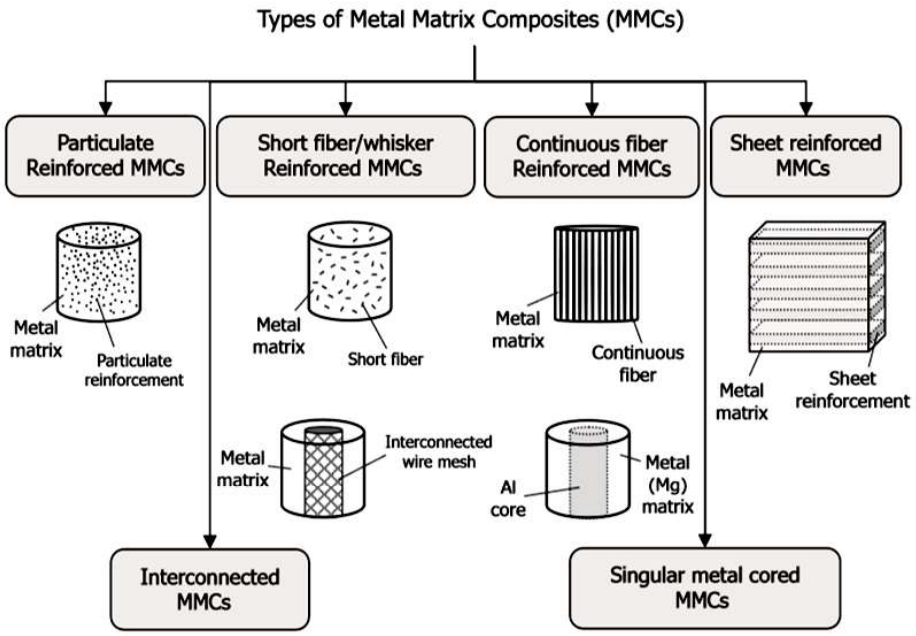

Figure 2. 17: Metal matrix composites types [87]

2.6.1. Matrix materials

Matrix phase is a continuous phase in the composite that surrounds and binds the reinforcement. The applied external load is taken up by the matrix phase, and then it is transferred to the reinforcing phase. Table 2.3 shows the list of some typical metallic matrix materials. Aluminum, Titanium, and Magnesium alloy are the most common matrix materials due to the high demand for lightweight and high strength materials. Some other lightweight materials such as bronze, cobalt, lead, niobium, lead, silver supper alloy (Ni-based and Fe based) [86] and Sn-based solders [88]–[90].

Table 2. 3: List of some typical matrix materials [86], [88]–[90]

Metallic Matrices
Aluminum and its Alloy
Bronze
Copper
Cobalt
Lead
Magnesium and Its Alloy
Nickel
Niobium
Silver
Sn-Based Solder
Superalloy (Ni-based and Fe-based)
Titanium alloys
Inter metallic (Nickel aluminides, Titanium aluminides

2.6.2. Reinforcements

For the fabrication of metal matrix composites, the reinforcements are purposely introduced into the metal matrix. The reinforcements are judiciously used in different types, shapes, amounts, and length scale (micron, submicron and man-size) depending on the required end properties of the composites materials. In general, the reinforcements can be grouped into the following: a) Ceramic, b) Metallic and c) Inter-metallic.

2.6.3. Selection reinforcements for matrix

Various reinforcement has been successfully incorporated into different matrix materials to make composites. To ensure appropriate selection of reinforcement to be added in the matrix, the following point should be taken into consideration [2], [12], [66], [91]

i) Size of the reinforcement

ii) Physical properties of the reinforcement

- Density should be low for weight critical applications
- The melting point should be high to avoid chemical reaction[66], [68]
- The coefficient of thermal expansion
- Thermal conductivity as per requirements
- Electrical Conductivity as per requirements
- Wettability with matrix phase should be high

iii) Mechanical Properties

- Elastic Modulus should be high
- Strength should be high
- Hardness should be high

iv) Cost of reinforcement [2]

v) Corrosion resistant should be high

vi) The price should be low

In the case of powder metallurgy routes of the composite preparation, the selection of the size of the matrix and reinforcement powder is one of the significant tasks. However, in the case of liquid metallurgy routes of the composite processing, the thermal stability, reactivity with matrix and wettability of the reinforcement will decide the selection of proper reinforcements [2]. It is more comfortable to incorporate the larger size reinforced particle into molten metal than its nano-sized counterparts. The agglomeration of a particle in the molten metal directly depends on the size of the particle [92]. In general, the increase in reinforcement will enhance the properties of the composites, but there is some threshold value beyond which the properties will degrade. The threshold value of the reinforcement will also depend on the size of the reinforcements [93]. Therefore the proper selection of reinforcement and its factors will play an essential role in the fabrication of the composites. A considerable number of the reinforcements have been successfully incorporated into metal matrix composites. The list of some essential and commonly used reinforcements properties are listed in Table 2.4.

2.6.4. The interface between matrix and reinforcement

The interface between matrix and reinforcement plays an essential role in the processing of metal matrix composites (MMCs). Generally, the matrix materials and the reinforcement are not in thermodynamic equilibrium, and there may exist the thermodynamic driving force for the interfacial reaction to lower the overall system energy. The interface characteristics of the composite influence the crack resistance and load transfer during deformation.

Table 2. 4: Some common reinforcements and their properties

Reinforcement	**Density** ($\times 10^{-3}$ kgm^{-3})	**CTE** ($\times 10^{-6}$ $^{0}C^{-1}$)	**Elastic Modulus** (GPa)	**Strength** (MPa)	**References**
Al_2O_3	3.98	7.92	379	221	[12]
AlN	3.26	4.84	310	2069	[12]
B_4C	2.52	6.08	448	2759	[12]
C	2.18	-1.44	690	---	[12]
CNT	1.33-1.40	---	~1000	~30,000	[94]
Cu	8.94	18.3	129.8	----	[95]
MgO	3.58	11.61	317	41	[12]
SiC	3.21	5.40	324	---	[12]
SiO_2	2.66	<1.08	73	---	[12]
SnO_2	6.95	3.76	233	---	[88], [96]
TiC	4.93	7.60	269	55	[12]
WC	15.63	5.09	669	---	[12]
ZrO_2	5.89	12.01	132	---	[12]

If the interfacial bond is weak, the interface will fail before any effective stress transfer occurs, and no strengthening will be achieved. To improve the bond strength of the interface, it is essential that

i) Wetting should be high

ii) Formation of oxide is minimized

iii) Chemical interaction should be controlled

The interfacial bonding between the reinforcement and the matrix in metal matrix composite can be broadly classified into

i) Mechanical Bonding (Interlocking)

ii) Chemical Bonding.

The wettability of a solid by a liquid is determined by the angle of contact, which liquid makes on the solid. This contact angle (□) (as shown in Figure 2.18) is defined from the

following Young's equations [97].

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} Cos\theta \qquad (2.5)$$

$$\theta = Cos^{-1}\left(\frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}\right) \qquad (2.4)$$

Where γ_{sg}, γ_{sl} and γ_{lg} are the interfacial energies between solid-gas, liquid-solid and liquid -gas phases respectively.

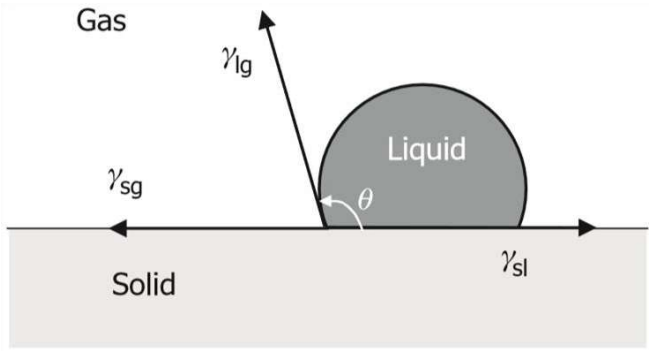

Figure 2. 18: Contact angle (θ) between solid-liquid, solid-gas, and liquid –gas [87]

Wetting will take place when $\theta < 90^0$ (i.e., $\gamma_{sg} > \gamma_{sl}$), In the case of perfect wetting, the contact angle should be 0^0. If $\theta > 90^0$ the wettability will be low. There is no wetting action at $\theta = 180^0$. Mortensen et al.[98] reported that wetting of ceramics particle (C, SiC, Al_2O_3, and B_4C) is poor with aluminum and its alloys at a temperature below 950°C. In order to improve wetting, the contact angle should be reduced. The contact angle depends on the following :

i) Solid-liquid interfacial energy (γ_{sl})

ii) Liquid metal surface tension

iii) Solid Surface energy

These can be achieved by:

i) Ceramics particle heat treatment

ii) Metallic coating of the ceramic particle

iii) Metallic matrix alloyed with reactive materials

The strong interface in composites is generally associated with the formation of a strong chemical bond between reinforcement and metallic matrix [99]–[102]. To improve the interfacial bond and resulting performance of the metal matrix composite, the following methods are used [103], [104].

i) Alloying of matrix materials

ii) Modifying the reinforcement

iii) Modifying the temperature cycle of the composite synthesis process.

iv) Heat treatment of the processed composite.

The increased interfacial reactivity, which improves the wetting of the reinforcement is one of the conflicting requirements, and it should be taken into account during the processing of the MMCs [2], [12]. Generally, high chemical affinity is desired between the metallic matrix and the reinforcement. On the other hand, to avoid unwanted interfacial chemical reactions, low chemical affinity is preferred [103]. Imperfections at the interface between the matrix and the reinforcement can facilitate the nucleation of cavities and cracks during loading of the composite [105]. When bonding at the interface is incomplete, the tensile loads placed on the matrix cannot be effectively transferred to the reinforcement. This leads to a decrease in the load carrying capacity of the composite and results in premature failure of the composite [105]. The interfacial imperfections may occur in composite due to the following reason:

- ✓ Precipitation reactions
- ✓ Interfacial reactions
- ✓ Reinforcement segregation
- ✓ Reinforcements Clustering

The imperfections geometry of the reinforcement also plays an essential role in the interfacial failure. Nutt et al. [106], [107] have reported that void nucleation through interfacial de-cohesion at the fiber ends resulted in premature failure of Al-SiC whisker composites.

2.7. Theoretical prediction of composite properties

The various theoretical properties such as density, electrical conductivity, coefficient of thermal expansion, elastic modulus and yield strength of the composites materials may be predicted using various models. The representative volume fraction is one of the essential criteria which are used in the prediction of composite properties. The various models which are being used to predict the different theoretical properties of the composites are given below. Out of these models, one or more than one models may be used to predict the theoretical properties.

- Rule of Mixture
- Rayleigh- Maxwell Equation[108], [109]
- Kerner's Model [110]
- Turner's model [111]
- Halpin- Tsai Model [111]
- Shear Lag theories[112]
- Strengthening factor's[113], [114]

2.7.1. Density

The theoretical density value of the composite material can be predicted using the simple rule of mixture (ROM) model. The ROM model is a function of the volume fraction and density of the respective matrix and reinforcing phases. The density of the composite ρ_{comp} can be determined by [108].

$$\rho_{comp} = \rho_m V_m + \rho_r V_r \theta = Cos^{-1}\left(\frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}\right) \quad (2.5)$$

and

$$V_m + V_r = 1 \quad (2.6)$$

Where ρ_m and ρ_r represent the density of the metal matrix and reinforcement, respectively, whereas V_m and V_r represent the volume fraction of the matrix and reinforcement, respectively incorporated in the matrix material.

2.7.2. Coefficient of thermal expansion

a) Rule of Mixture (Upper bound)

The rule of mixture model can be used to predict the upper bound of the coefficient of thermal expansion of the composite, α_{comp} [111]

$$\alpha_{comp} = \alpha_m V_m + \alpha_r V_r \quad (2.7)$$

Where α_m and α_r represent the coefficient of thermal expansion of the matrix material and reinforcement, respectively.

b) Turner's model (lower bound)

The model by Turner predicts the lower bound of the coefficient of thermal expansion of the composite, α_{comp} [111]

$$\alpha_{comp} = \frac{\alpha_m V_m K_m + \alpha_r V_r K_r}{V_m K_m + V_r K_r} \quad (2.8)$$

Where K_m and K_r represent the bulk modulus of the matrix material and reinforcement, respectively.

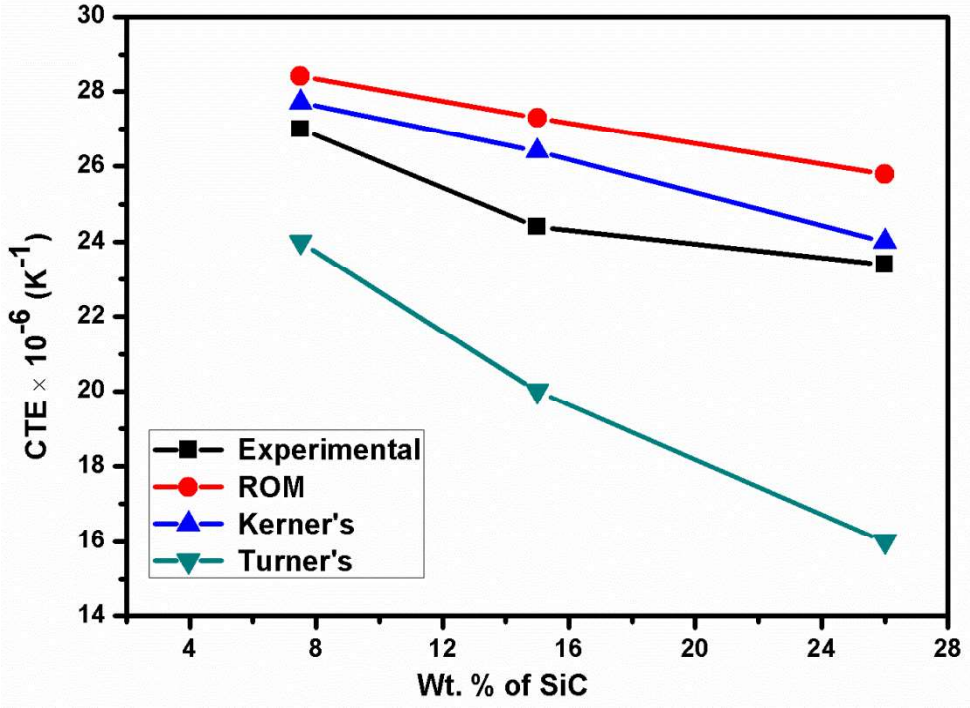

Figure 2. 19: Experimental and theoretical CTE values predicted from the various models as a function of weight percentage of SiC reinforcement particulate (25 μm) in Mg matrix [115]

c) *Kerners Model*

According to Kerner [110], the prediction of the coefficient of thermal expression is given below:

$$\alpha_{comp} = \alpha_m - V_r(\alpha_m - \alpha_r)\left[\frac{K_m(3K_r + 4G_m)^2 + (K_r - K_m)(16G_m^2 + 12G_mK_r)}{(4G_m + 3K_r)\left[4V_rG_m(K_r - K_m) + 3K_rK_m + 4G_mK_m\right]}\right] \quad (2.9)$$

Where G_m is the shear modulus of the matrix and the Figure 2.19 showing the graphical representation of experimental along with the predicted value of CTE derived through different models as a function of weight percentage of SiC reinforcement particulate (25 μm) in Mg matrix.

2.7.3. Elastic Modulus

a) Rule of mixtures

The rule of mixtures for the elastic modulus enables the computation of the linear upper bound composites elastic modulus. The elastic modulus E_{comp} [111] is given as:

$$E_{comp} = \frac{E_m V_m + E_r V_r}{V_m + V_r} \tag{2.10}$$

Where E_{comp}, E_r and E_m represent the elastic modulus of the composite, the reinforcement, and the metallic matrix respectively, whereas V_m and V_r represent the volume fraction of the matrix and the reinforcement, respectively. The nonlinear lower bound elastic modulus of the composites can be computed by [111]

$$E_{comp} = E_m \left[\frac{E_m V_m + E_r (V_r + 1)}{E_r V_m + E_m (V_r + 1)} \right] \tag{2.11}$$

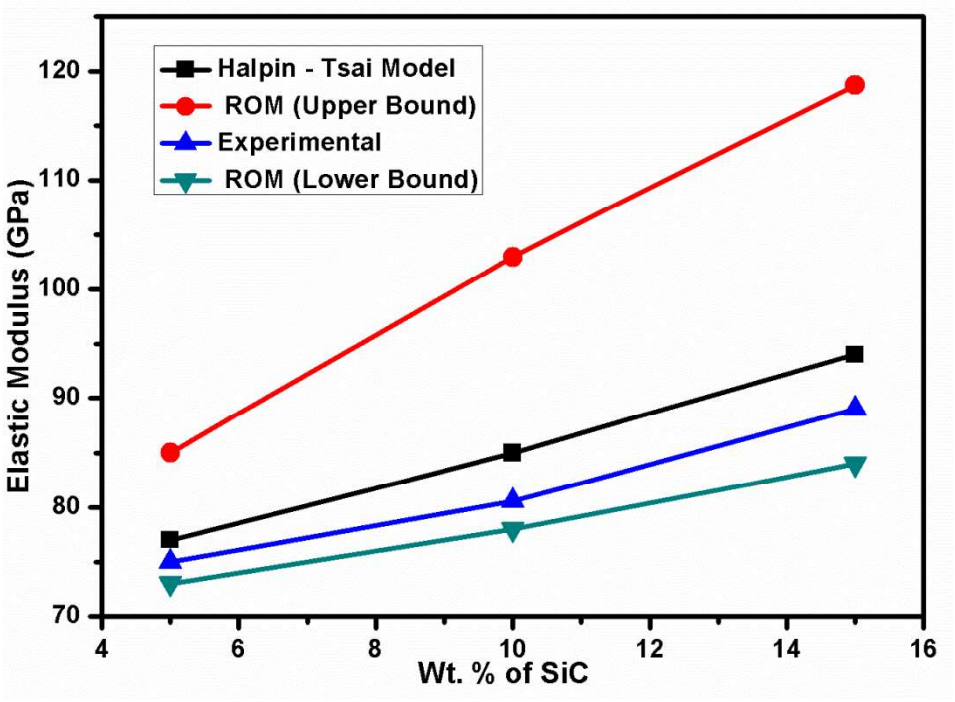

Figure 2. 20: The Experimental and theoretical elastic modulus values predicted through different models, as a function of the amount of SiC in the aluminum matrix [87]

b) Halpin- Tsai Model

The elastic modulus of the composites can also be predicted by the Halpin- Tsai model [111], which gives quite a reasonable accuracy. The elastic modulus E_{comp} is given as:

$$E_{comp} = \frac{E_m(1+2sqV_r)}{1-qV_r} \tag{2.12}$$

Where q is represented as

$$q = \frac{E_r/E_m - 1}{E_r/E_m + 2s} \tag{2.13}$$

Where s represents the aspect ratio of the reinforcement. Figure 2.20 shows the experimental results of the elastic modulus along with predicted values through different models.

c) Effect of Porosity on Elastic Modulus

The relation between elastic modulus of the porous material € with the elastic modulus of the fully dense material (E_0) and the pores volume fraction (p) is expressed by a model [116] as follows:

$$E = E_0\left(1-p^{2/3}\right)^{1.21s} \tag{2.14}$$

Where the power factor s is

$$s = (z/x)^{1/3}\left\{1+\left[(z/x)^{-2}-1\right]\cos^2\alpha_d\right\}^{1/2} \tag{2.15}$$

Where z/x represent the aspect ratio of the pore and α_d is the relative orientation of the pores concerning the stress axis. The value of α_d =56^0 [117] for material with random orientation of pore and then orientation factor $\cos^2\alpha_d$ is equal to 0.31.

2.7.4. Yield strength

The yield strength of the metal matrix composite can be calculated with the help of shear lag theories and different strengthening mechanism.

a) Shear Lag Theories

To estimate the yield strength of the discontinuously reinforced composites, the modified shear lag theory [112] may be used to take in to account the tensile transfer load from the matrix to discontinuous reinforcement.

In case of the SiC platelets, the assumed shape is the rectangular plate given in Figure 2.21, and the yield strength of the composites $\sigma_{comp,y}$ is predicted using Nardone and Prewo [112] model

$$\sigma_{comp,y} = \sigma_m (V_p \, S/4 + V_m) \qquad (2.16)$$

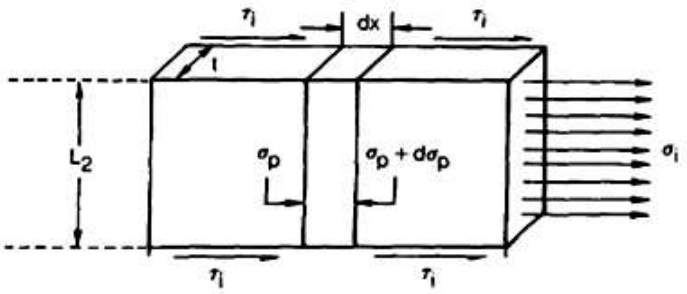

Figure 2. 21: Schematic illustrations of the stresses of a rectangular platelet [112]

Where V_p and V_m represent the volume fraction of the platelets type of reinforcement and matrix material, respectively, whereas σ_m and shows the yield strength of the matrix materials and the aspect ratio of the reinforcements.

b) Strengthening factors

Yield strength of the composite is observed to be increasing with the increase in the volume fraction of SiC particle in magnesium alloy (AZ91) composite. The various strengthening mechanism which contributes to increase Yield strength of the metal

matrix composite i.e. (a) Generation of geometrically necessary dislocation to accommodate thermal and elastic modulus mismatch between the matrix and reinforcement (b) Load- bearing effects due to the presence of reinforcement (c) Orowan strengthening (d) Hall- Petch effect due to grain size refinement

The Yield strength of the composite $\sigma_{comp,y}$ can be given by Dai et al. [113]

$$\sigma_{comp,y} = \sigma_{mo} + \Delta\sigma \tag{2.17}$$

Where σ_{mo} = Yield strength of the unreinforced matrix

$\Delta\sigma$ = Total improvement in Yield strength

The total value of $\Delta\sigma$ is estimated by equation (2.17) [91], [118]

$$\Delta\sigma = \sqrt{\left(\Delta\sigma_{CTE}\right)^2 + \left(\Delta\sigma_{EM}\right)^2 + \left(\Delta\sigma_{load}\right)^2 + \left(\Delta\sigma_{Orowan}\right)^2 + \left(\Delta\sigma_{Hall-Petch}\right)^2} \tag{2.18}$$

$\Delta\sigma_{CTE}$ and $\Delta\sigma_{EM}$ are the stress increment due to the coefficient of thermal expansion and elastic modulus mismatch between the reinforcements and the metallic matrix respectively. These two value can be calculated by the Taylor dislocation strengthening relation [91], [113], [119]

$$\Delta\sigma_{CTE} = \sqrt{3}\beta G_m b\sqrt{\rho_{CTE}} \tag{2.19}$$

and $$\Delta\sigma_{EM} = \sqrt{3}\alpha G_m b\sqrt{\rho_{EM}} \tag{2.20}$$

Where α and β are the strengthening coefficient, G_m is the shear modulus of the matrix, b is the Burger vector. ρ_{CTE} and ρ_{EM} represent the dislocation density because of the coefficient of thermal expansion and elastic modulus mismatch respectively. The geometrically necessary dislocation density due to elastic modulus mismatch ρ_{EM} can be given as [120]

$$\rho_{EM} = \frac{\lambda^m}{b\lambda} \qquad (2.21)$$

Where λ^m is the shear strain and λ is the local strength scale of the deformation field and λ can be defined as[121]

$$\lambda = d_r \left[\left(\frac{1}{2V_r} \right)^{1/3} - 1 \right] \qquad (2.22)$$

Where d_r is the smallest dimension of the reinforcement and V_r is the volume fraction of the reinforcement. The geometrically necessary dislocation density due to CTE mismatch ρ_{CTE} can be given as [122]

$$\rho_{CTE} = \frac{BV_r\varepsilon_{CTE}}{b(1-V_r)d_r} \qquad (2.23)$$

Where B is a geometric constant and ε_{CTE} is the misfit strain due to the different CTE mismatch value of the metallic matrix and reinforcements. ε_{CTE} can be given as

$$\varepsilon_{CTE} = (C_m - C_r)\Delta T = \Delta C.\Delta T \qquad (2.24)$$

Where C_m and C_r represent the CTE of the metallic matrix and reinforcements, respectively. ΔT is the temperature change. Effective load bearing capacity is highly dependent upon the interfacial bonding between the matrix and the reinforcement. According to a modified shear log model, the improvement in Yield strength due to load- bearing effect ($\Delta\sigma_{load}$) can be expressed by[113]

$$\Delta\sigma_{load} = \frac{V_r\sigma_{mo}}{2} S_r \qquad (2.25)$$

Where S_r is the aspect ratio of the reinforcements. For particulate reinforcement $S_r = 1$ [123] Orowan strengthening plays a very important role in the improvement of the yield strength in case of Nano- Composite. Improvement in yield strength due to Orowan-Ashby equation [121]

$$\Delta\sigma_{Orowan} = \left(\frac{0.13 G_m b}{\lambda}\right) \ln\frac{d_r}{2b} \qquad (2.26)$$

Improvement in Yield strength due to grain size strengthening can be described by the Hall-Petch equation [124]

$$\Delta\sigma_{Hall-Petch} = KD^{-1/2} \qquad (2.27)$$

Where K is the constant and D is the grain size of the metallic matrix.

2.8. Mechanical properties based contributions

Many researchers have studies microstructural and mechanical properties of magnesium alloy, and it's composite, some contributor's works are mentioned below:

Chua et al. [125] fabricated and studied mechanical properties of AZ91 magnesium alloy based composite reinforced with different size of SiC particulates by powder metallurgy route. Authors also observed that the mechanical properties are decreased with increase in the size of the reinforcement. Jinhai Gu et al. [126] have studied mechanical properties and damping capacity of hybrid metal matrix composite reinforced with SiC particulate and mullite (Al_2O_3. SiO_2). It was concluded that the strength had improved strongly at the expense of its damping capacity. Y.L.Xi et al. [127] investigated the tensile strength of ZK51 magnesium alloy composite reinforced

with Ti-6Al-4V particulate. The remarkable improvement of tensile strength was observed in comparison with unreinforced magnesium alloy. Chang et al. [128] fabricated magnesium amorphous ($Mg_{65}Cu_{20}Y_{10}Ag_5$) alloy based composites reinforced with 1-5 vol % of spherical nano-sized ZrO_2 particles through mechanical alloying. Szaraz et al. [129] studied the microstructure and mechanical properties of the WE54 magnesium alloy composites reinforced with 13 vol. % of SiC particulates fabricated through powder metallurgy technique. In this process, grains are refined, and yield strength enhancement was observed. Poddar et al. [130] fabricated Mg and Mg alloy (AZ91) based composites reinforced with 15 Vol. % of SiC particulate of average particle size 15 μm and 150 μm through stir casting technique. The enhancement in hardness and elastic modulus on the addition of SiC particulates was observed. Cao et al.[131] studied high-temperature mechanical properties of AZ91 by adding 1.0 wt% AlN nano-particles. Enhancement in tensile strength, yield strength and ductility were obtained at a temperature more than $200\,^{0}C$. Honma et al. [132] reported that extruded magnesium alloy (AZ91D) based composites reinforced with Si-coated carbon nanofibres show maximum tensile stress of 470MPa. The coating of nanofibre improves the wettability, resulting in homogeneous distribution reinforcement. Dudina et al. [133] studied the effect of metallic glass reinforcement in magnesium alloy composite. Mechanical and fracture behaviors of AZ91 alloy reinforced with Si and SiC particulates were examined by Trojanova et al. [134]. Rohatgi et al.[135] incorporated a varied percentage of (5, 10 and 15 %) fly-ash in magnesium alloy AZ91 using die casting techniques. The enhancement in mechanical properties and decrease in density on the addition of fly-ash in AZ91 alloy were observed. Umeda et al. [136] fabricated pure magnesium composites reinforced with pure Ti particulates through powder metallurgy route. Improved tensile strength and good elongation were observed in

composite compared monolithic magnesium. Francis et al**.** [137] synthesized magnesium alloy based nanocomposite reinforced with different percentage of Al_2O_3. Based on mechanical characterization, it was concluded that (out of 3.5, 7 and 14%) 7 vol. % was the most suitable combination of reinforcement. Wang et al. [138] fabricated Mg-Zn-Ca composites reinforced with three different volume fraction of (5, 10 and 15%) through stir casting techniques. A significant influence in mechanical properties and secondary phases are observed in the composite. Deng et al. [139] incorporated three different sizes (0.2, 5 and 10 μm) of reinforcement in different percentage (2, 5 and 10 %) in AZ91 alloy by stir casting technique. Grain refinement and strengthening effect lead to enhancement in mechanical were observed. Bedolla et al**.** [140] synthesized AZ91E magnesium alloy based composite reinforced with 49 vol. % of AlN through pressureless infiltration technique. The average value of the elastic modulus of 122 GPa, hardness of 260 HV and coefficient of thermal expansion of 9.53×10^{-3} (in the temperature range of 27-227 ^{0}C) were observed. Alam et al. [141] developed two new nano composite of magnesium alloy by incorporating Al (1 and 2 % by wt.), Ca (1 and 2 % by wt.) and 1.5 % nano-sized Al_2O_3 particulates into AZ31 alloy by the disintegrated melt deposition technique. Superior combination of tensile strength, yield strength, and ductility along with the enhanced hardness of the composite were observed in comparison to developed composites. Matin et al. [142] performed the casting of pure magnesium and AZ80 alloy based composite reinforced with different wt % (1.5, 2.5 and 3.5) percentage of SiC nanoparticles. They have observed that the hardness value along with tensile and ductility is increased by increasing the SiC content.

2.9. Friction and wear properties

2.9.1. Dry Friction and its Origin

Dry friction is the resisting tangential force act at the common boundary surfaces of the two mating bodies which are in relative motion concerning each other under the action of an external applied and tangential force. Dry friction is further divided into static (for non-moving surfaces) and kinetic friction (for moving surfaces). The asperities on the mating surfaces produce dry friction when the mating surface is in motion or about to move relative to each other [143], [144].

The Frictional behavior is essential tribological properties of materials not only because of interest in the frictional force among sliding surfaces but moreover since it generally affects the wear behavior [145], [146]. Frictional force in metals was generated as an outcome of three basic mechanisms of asperities deformation, plowing, and adhesion. The asperity deformation evaluates the static coefficient of friction as well as the dynamic coefficient of friction because the asperities are constantly generated due to de-lamination of the sliding surface [143], [144]. On the other hand, the contribution of asperities deformation to the dynamic coefficient of friction is limited in comparison to the contribution by adhesion and plowing [146]. In a compelling circumstance where the surfaces become smooth, then the majority of the applied normal load is carried by the flat contacts and the entrapped wear particles.

Consequently, the role of the asperity deformation on the frictional force is likely to be a small fraction of the approximate value in a dynamic situation. A frictional force can emerge additionally because of the adhesion of two nearly smooth surfaces. The adhesion force arises due to the interlocking of two almost flat portions of the surface or the inter-atomic interactions of particles nearby. The plowing feature of the frictional force can be developed due to the penetration of wear particles or due to the

penetration of hard asperities. When both surfaces are of the same hardness, then the wear particle can penetrate both the surfaces. The movement of mating surfaces concerning each other generates grooves in one or both of the surfaces. However, sometimes wear particles can fasten in the very rough hard surface and plow the soft surface. The concept of friction due to plowing was developed by Sin et al. [147].

To clarify the time-dependent friction behavior of the tested materials, a plot of friction versus slid distance may be subdivided into the six stages as shown in Figure 2.22, and each stage is discussed below qualitatively [1 4 4]

Stage I: In this early stage, the frictional force is mainly the result of plowing of the surface by asperities. The asperities deformation will take place at the beginning of sliding which affects the static coefficient of friction. The coefficient of friction (μ) is mostly independent of material properties, the surface and the environmental conditions [146].

Stage II: The friction force begins to grow slowly due to enhancement in adhesion. Due to the presence of lubrication in the interface, stage I persists for a longer time. The rise in slope in stage II is primarily due to the generation of wear particles by the fracture and asperity deformation are entrapped between the sliding surfaces and contribute to the plowing of the surfaces.

Stage III The rapid increase in some wear particle will entrap between the sliding surface results in higher wear rate. The adhesion also increases the due formation of clean interfacial areas. The force required for asperities deformation will also contribute to the frictional force in this stage. The wear particles are generated by subsurface deformation, crack nucleation and crack propagation postulated by the de-lamination theory of wear [144]. The plowing is caused by

when wear particles entrapped between the sliding surfaces. The plowing will be the maximum, if wear particles entrapped between the surface of the same hardness, because of penetration into both surfaces by avoiding slippage between the particle and the surface [146].

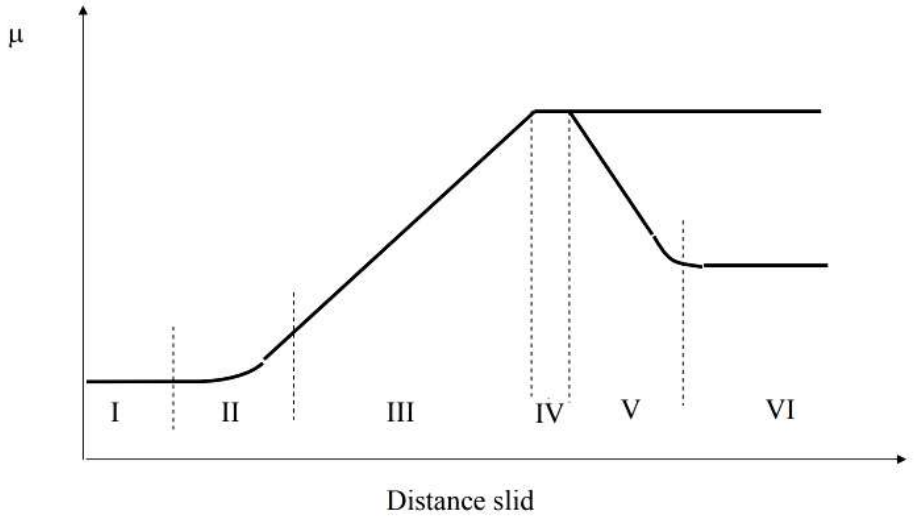

Figure 2. 22: The six stages in the coefficient of friction versus distance slid relationship [144]

Stage IV: In this stage, the friction force is constant because the number of wear particles entrapped between the interfaces remains constant and the contribution of adhesion also steady. It will happen only when the number of entrapped particles leaving the interface and the numbers of the newly entrapped particles are equal.

Stage V: In this stage, the friction value decreases because of the asperities of the hard surface are gradually removed, creating a mirror finish which results in a decrease in plowing and asperity deformation.

Stage VI: Eventually, when both the surfaces become mirror smooth to a maximum extent, then frictional force levels will be zero. However, the surfaces are never entirely smooth because there are forever "potholes" due to de-

lamination wear particles. Therefore the decreased and constant value of frictional force was found in this stage.

Madakson [148] reported that the friction at the initial stage rises and then settle to an almost constant value. Madakson suggested that the friction force depends on the environment, material properties, the area of real contact, surface roughness, deformation, rubbing velocity and surface energy. A model of friction is presented which suggests that the friction force results from adhesion interlocking of asperities, where he introduced most of the variables that affected the friction force like, the environment, temperature, normal load, and so on. Liu et al. [149] described the source of the friction force between two mutually contacting solid surfaces arises due to the interaction between the asperities where actual contact occurs. The main processes concerned in these interactions are (i) contacting points adhesion and (ii) deformation either plastic or elastic of the asperities by load [150].

The F_a is the force required to shear the adhesion bond, and the F_d is the force needed to produce elastic or plastic deformation of the obstructing asperities. If N is the applied normal load on the contacting surface, the coefficient of friction μ is given by Bowden et al. [151], [152].

$$\mu = \frac{F_a + F_b}{N} = \frac{F_a}{N} + \frac{F_b}{N} = \mu_a + \mu_b \qquad (2.27)$$

Where μ_a and μ_b are, the coefficients of friction due to adhesion and deformation respectively.

2.9.2. Dry sliding wear

Dry sliding wears behaviors of materials to determine the application of their parts, where relative motion gradually damages the functionality of the materials. The progressive loss or damage of substance from the operating surface of a body occurring as a consequence of the constant interfacial relative rubbing process is called wear. Depending on the nature of movement or the media involved in interaction under different load and sliding velocity, different types of wear have been classified as follows: (1) Adhesive wear, (2) Abrasive wear, (3) De-lamination wear (4) Oxidation wear (5) Thermal softening and melt wear

Adhesion is the phenomenon resulting in an attractive force between two surfaces in close contact. The adhesive wear in the metals and alloys occurs during the growth and destruction of adhesive junctions followed by transfer, oxidation, and diffusion between sliding surfaces. Adhesive wear is associated with low sliding velocity, small load, and smooth surfaces.

Abrasive wear occurs when two surfaces, one of which is harder and rougher than the other, are in sliding contact. This type of wear is dangerous because it can occur suddenly with the introduction of a contaminant and leads to high wear rates and extensive damage to the surfaces.

When a detachment of the worn surface materials in sheet form is produced, then wear mechanism de-lamination. It is due to the formation of cracks during the wear process that is perpendicular to the sliding direction and growth of surface crack that causes the ultimate detachment[153].

Oxidation wear is present in almost all tested condition and was the primary mechanism for the sample worn at the lesser load. The oxidation of surfaces occurs due to frictional heating during sliding. Therefore the wear happened due to the removal of the oxide fragments. There is a critical combination of speed and load, beyond that, the rate of elimination of the oxide film during sliding becomes higher than its rate of formation, and a transition to metallic wear occurs [154].

When sliding speed and applied normal load increases beyond specific critical value, the temperature at the contacting asperities might go beyond the melting point of the matrix materials, thus increase in the bulk temperature causing continuing softening of the matrix. Further, an increase in sliding speed and applied normal load raises the heat leading to melting wear[154].

Wear particles in elastic-plastic solids are generated during sliding by one or more of the following three mechanisms: (i) asperity deformation and fracture, (ii) plowing, (iii) de-lamination, which results in large wear particles by the process of plastic deformation of the surface layer,

The wear particles produced by these processes can either transfer to the counter face by mechanical interlocking and by adhesion. They may also leave the interface in the form of loose wear particles called wear debris as seen in the most sliding situation.

2.9.3. Friction and dry sliding wear in hard particulates reinforced composites

The friction coefficient of various composites containing hard particles shows the higher coefficient of friction which may be attributed to higher deformation during asperity-asperity interaction [149] despite the reduced contribution of adhesion wear. Rana and stefanescu [155] have observed a substantial decrease in coefficient of friction with an increasing volume fraction of SiC particles. However,

they found that increasing the size of SiC particles for a given volume fraction has hardly much effect on the coefficient of friction. Similarly, M.Roy et al. [156] have observed a lowering of the coefficient of friction in the composite reinforced by hard particles, but the particle size does not affect the coefficient of friction. Sato and Mehrabian [157] have observed that by reinforcing Al-4Cu-O. 75Mg alloy reinforced by a wide range of particles like alumina, TiC, SiC, silica and silicon carbide, results in a higher coefficient of friction and lower wear rate in the composites. Surappa et al. [158] have observed that when reinforced with five wt% alumina, both Al and Al-Si alloy show improved wear resistance. Anand and Kishore [159] have also noted a similar effect of a continuous decrease in wear rate with increasing corundum content in Al-Zn alloy up to 30 wt% of corundum. Iwai et al. [160] have observed that the wear rate in SiC whisker-reinforced composite decreases with an increasing volume fraction of reinforcement under mild wear. It has been attributed to smaller wear particles owing to the increase in hardness.

From the results on the wear rate and coefficient of friction summarised above, it is apparent that there is divergence. It may be due to processing which may decide the state of interfacial bonding. If the hard particles are not well bonded, there might be easy deboning of the particles resulting in increased contribution to wear rate more than compensating the decrease in the real area of contact due to increased hardness.

The results of wear should be rationalized by its variation proposed by Archard [161]. It was assumed that all the engineering surfaces are rough and the asperities of the relatively hard material are indented in the soft material during contact. Thus, the contact between two surfaces is limited to local contacts at the asperities, and the actual area of contact may be significantly lower than the apparent area of contact.

These relatively small local contacting areas thus share the entire load at the contact and the resulting stress there may be very high. Under this high stress, there may be adhesive welding in the contact region, and relative motions between the contacting surfaces break these contacts.

2.10. Contributions by researchers in wear behaviors

Many researchers have studies wear behavior of magnesium alloy and its composites. Idris Janaliah et al. [25] performed pin on disk dry sliding wear and corrosion tests AZ91 alloy based composites reinforced with 0, 5, 10, 15 and 20 wt% of SiC particulates. Lim et al. [162] investigated dry sliding wear behaviors of the 8 Vol % SiC_p reinforced magnesium matrix composite under the load of 10 N and 30 N and sliding velocity range of 0.2-5.0 m/s. He concluded that the wear mechanism is a function of load and velocity. Jiang et al. [163] developed a magnesium matrix composite with varying percentage of B_4C particulates through powder metallurgy route. Based on experimental result, he concluded that hardness and wear resistant of the composites were higher than as cast magnesium and increased with increasing vol.% of B_4C from 10% to 20%. Zhang et al. [164], [165] studies the combined effect of graphite particle and short fiber Al_2O_3 reinforced AZ91-0.8% Ce composites developed thorough squeeze-infiltration techniques. The wear resistance improved because of the lubricating action of graphite and wear resistant further enhanced as the particle size of graphite increases. Semenov et al.[166] investigated that severe plastic deformation will increase the coefficient of friction and reduces the wear rate in case of SiC powder hardened AZ91 magnesium alloy. Mondal and Kumar [167] examined the wear behavior of AE42 magnesium alloy, and it composites reinforced with Saffil short fibers and SiC_p in various combination. The wear rate of hybrid composite is observed to be lower than saffil short fibers composite and magnesium alloy. Franco et al. [168]

fabricated TiC reinforced AZ91 alloy based metal matrix composite by pressureless infiltration technique. Dry sliding wear test of the composite was performed at different load and different disk materials (i.e., AISI 4140, AiSI 1045 and H13 steels). Abrasion and adhesion type wear mechanism of the composite were examined. Srinivasan et al. [169] estimated dry sliding wear behavior of the cast and extruded nano-composite under the normal load of 10 N at different sliding speeds for a distance up to 2000 m. Lower wear rate was observed in nanocomposites due to higher hardness on the addition of reinforcement.

2.11. The motivation of the work

The common motivation to choose magnesium and it alloy based composites as an area of research are: **a)** Lightest in all structural metal, **b)** Good conductor of heat and electricity, **c)** reduction in weight of automobile and aircraft result in to decreased CO_2 emission, **d)** Ease of recycling, **e)** To check the feasibly of processing magnesium and it alloy in different environmental condition.

Based on the literature survey, it is found that pure magnesium and magnesium alloy based nano and micro-composite containing ceramics and metallic reinforcement have been developed using different processing techniques. At the time when present Ph.D. work started limited work was available on liquid processing methods of magnesium alloy.

The main objective of current research is to design and develop an experimental set-up for processing of magnesium alloy, and it's composited through stir casting techniques. The other objective is to study the effect of a small variation of different size of reinforcement in AZ91 alloys based metal matrix composite. In the current work initially, an unsuccessful attempt is made to cast magnesium alloy by using small

amount NaCl flux. About 30 % of the magnesium was oxidized in the melting process. Further, a new concept and design are developed to process magnesium alloy and composites. In the new stir casting, set-up vacuum assisted inert atmosphere is used during melting and casting.

The cast product is further investigated to know the effect of variation of reinforcements in magnesium alloy based composites. It may be noted that the composites developed during the current study based on the elemental composition of magnesium alloy and variation wt % of reinforcement are new and have not been investigated in the past by using the methodology described in this thesis.