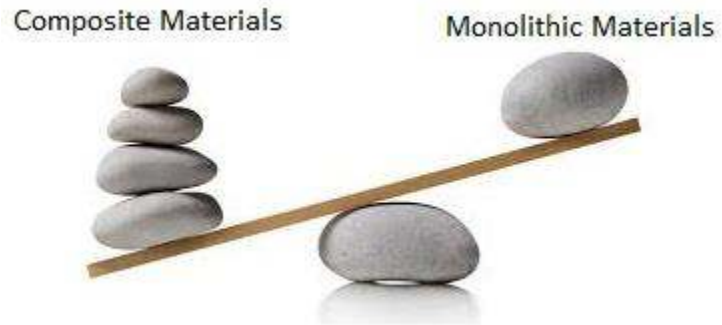


# Chapter 1



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## INTRODUCTION

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### 1.1 Introduction

High strength and light weight material is an essential requirement in space, aerospace, ground vehicles, aerodynamics, propelling systems and structural applications. Stringent guidelines on emission and depleting petroleum resources make the task of designing a material difficult for such applications. The global need is to have better fuel-efficient vehicles for energy conservation. This will require engines with reduced friction and wear.

There is wide range of components such as cylinder blocks, cylinder liners, drive shafts, brake drums, connecting rods, pistons, gears, suspension systems etc. where we need to optimize wear and friction. Innovation in such areas depends directly or indirectly on materials used. High performance in sectors such as automobile, aerospace, marine etc. is directly related to high speed, fuel efficiency, high temperature strength & stiffness, etc.; hence, we require materials which are suitable for rigorous working conditions. But conventional materials do not fulfil such requirements, while composites can be tailored

to provide combination of required properties with suitable choice of matrix and reinforcement.

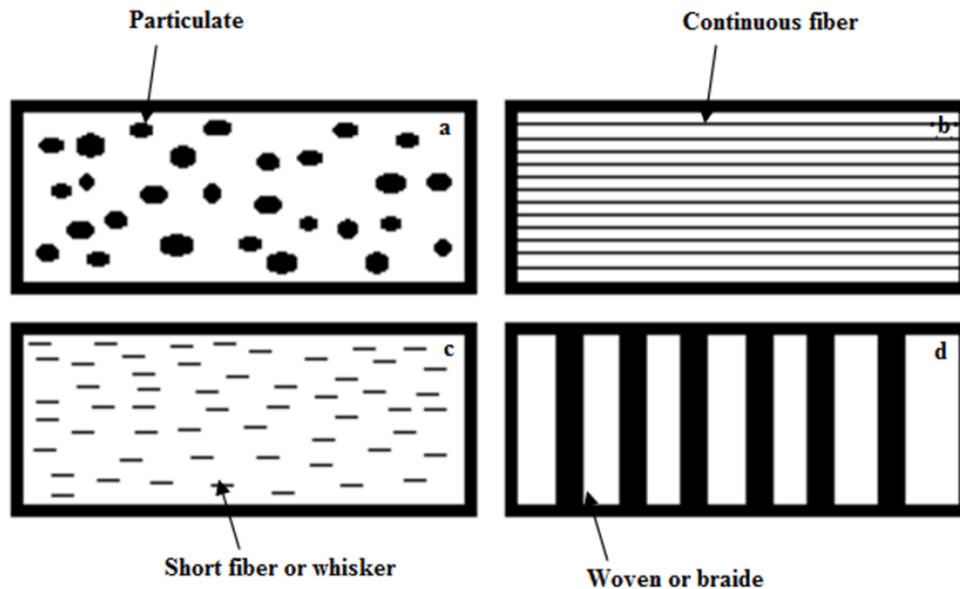
## **1.2 Metal – Matrix Composites (MMCs)**

Materials consisting of phases at macroscopic level are referred as composites. The larger phase of the composite is called matrix phase and the phase in smaller fraction is termed as reinforcement phase, however, in some typical cases reinforcement in the form of fiber can be as high as 70% but matrix still remains the continuous phase. Examples of composite materials are available in our nature itself such as wood (composite of cellulose fibers and lignin), bone (soft collagen fibers in mineral matrix) etc. Metal – matrix composite is one of the categories of composites in which matrix is an alloy or metal [Handbook ASM Vol. 21, 2001; Chawla, 2012].

In composites, matrix phase holds the reinforcement in particular orientation and position and reinforcement phase improves the strength and stiffness with load transfer [Handbook ASM Vol. 21, 2001]. On the basis of matrix, composites can be classified as organic-matrix composites (OMCs), ceramic-matrix composites (CMCs) and metal-matrix composites (MMCs) [Surappa, 2003]. The composites can also be divided on the basis of reinforcement. Broadly, reinforcement could be in the form of fiber or particulate, though they can again be classified into sub categories: short fibers, filament, whiskers, woven or braided fibers etc. [Handbook ASM Vol. 21, 2001]. Schematic diagram of composite with different reinforcements is shown in Fig.1.1a-d.

As compared to constituent counterparts, metal-matrix composites provide high temperature operating limits, and can be tailored to give improved strength, stiffness,

thermal conductivity, abrasion resistance, creep resistance and thermal stability etc. Unlike polymer – matrix composites (PMCs), MMCs are nonflammable, do not outgas in vacuum and suffer minimal attack by organic fluids such as fuels and solvents. While comparing with ceramic – matrix composites (CMCs), metal-matrix composites have much better ductility. In MMCs reinforcement are either continuous or discontinuous and their amount ranges from 10 to 70 vol.%. These reinforcements could be in the form of fiber, filament, whiskers or particulate of  $Al_2O_3$ , SiC,  $TiB_2$ , graphite etc.



**Figure 1.1** – Schematic diagram of (a) particulate reinforced composite, (b) continuous fiber reinforced composite, (c) short fiber or whisker reinforced composite, and (d) woven or braided composite [Zweben, 1998].

Among metal-matrix composites, AMCs are most widely used due to abundant availability of aluminium, its low cost, low density and easier fabrication routes. In AMCs pure aluminium or aluminium alloys are used as a matrix phase and non-metallic phases generally ceramics are used as a reinforcement phase. The properties of AMCs can be altered either by changing morphology of matrix/reinforcement or by varying volume fraction of reinforcement. AMCs have several advantages over unreinforced aluminium/aluminium alloys as mentioned below [Surappa, 2003]:

- High specific strength
- High stiffness
- Low density
- High wear and abrasion resistance
- Good high temperature properties
- Good damping capabilities

These properties work as a driving force for AMCs in automobile, aerospace and marine related applications.

### **1.2.1 Preparation of AMCs**

AMCs can be produced by two methods namely *exsitu* and *insitu* processes. In *exsitu* process second phase to be reinforced is already available and is added to solid or liquid state matrix. While in *insitu* process second phase to be reinforced is generated by chemical reaction between suitable inorganic salts and matrix material [Zhang et al., 2007]. AMCs prepared by *insitu* process show better properties as compared to materials synthesized by *exsitu* process [Zhao et al., 2010].

#### **1.2.1.1 Exsitu processes**

- **Liquid ingot casting**

In this process, the second phase reinforcement particles are mixed in the melt by mechanical stirring. Vortex formation helps in uniform distribution of reinforcement particles. Throughout the processing the inert atmosphere is maintained. Melt is poured into the mould and allowed to solidify. SiC reinforced Al alloy composite has been fabricated by this technique. AA6061 alloy was brought to melt condition in graphite crucible kept in electric resistance furnace. Melt was superheated to 750°C and SiC

powder was added while stirring mechanically. After 30 minutes of mixing melt was poured into the preheated mould [Moses et al., 2014; Zhang et al., 2007].

- **Powder metallurgy**

Mechanical mixture of matrix and reinforcement powders are compacted and sintered in this technique. AMC with Al<sub>2</sub>O<sub>3</sub> particles (mean particle size 50 nm) reinforced in aluminium (mean particle size 28 μm) have been prepared by this technique. The aluminium and alumina are mixed in the ethanol and dried at 150°C followed by cold isotropic pressing and sintering [Kang and Chanb, 2004; Zhang et al., 2007].

#### 1.2.1.2 *In situ* processes

- **Self-propagating high-temperature synthesis (SHS)**

In this process, reactant powders are preheated in an electric oven followed by ignition. During ignition the powders react exothermically to give final product. By this process AMCs reinforced with fine fibrous titanium carbide (TiC) and multi reinforcements (TiC+TiB<sub>2</sub>) have been fabricated [Coi et al., 1992; Gotman and Koczak, 1994].

- **Rapid solidification processing (RSP)**

In RSP process, the molten material is rapidly solidified after reinforcement of particles in the matrix at high temperature. This process is combination of traditional ingot metallurgy with rapid solidification [Tong, 1998]. This process results in refined microstructure with minimum particle segregation, fine particle size and homogeneous distribution of particles. The composites prepared by this method show improvement in the physical and mechanical properties [Srivatsan and Sudarshan, 1993]. Al-TiC composites with different compositions and uniform distribution of TiC particles have

been produced by this process. These composites exhibit improved mechanical properties [Tong, 1998; Tong and Fang, 1998a, 1998b].

- **Reactive hot pressing (RHP)**

The process was started to prepare TiB<sub>2</sub> reinforced aluminium/aluminium alloy composites. In this process second phase reinforcement particles are generated in the matrix by exothermic reaction of reactant powders. Powders of aluminium, titanium and boron are blended to prepare the compacts. These compacts are heated at high temperature in vacuum for few minutes. During this period titanium reacts with boron to form TiB<sub>2</sub>, then compacts are cooled to a specific temperature and hot-pressed. The *insitu* reaction generates submicron size TiB<sub>2</sub> particles in the matrix. Hybrid composites with Al<sub>2</sub>O<sub>3</sub> and TiB<sub>2</sub> reinforcement in the aluminium matrix have also been produced by this technique [Ma et al., 1993; Ma and Tjong, 1997; Tjong et al., 2005].

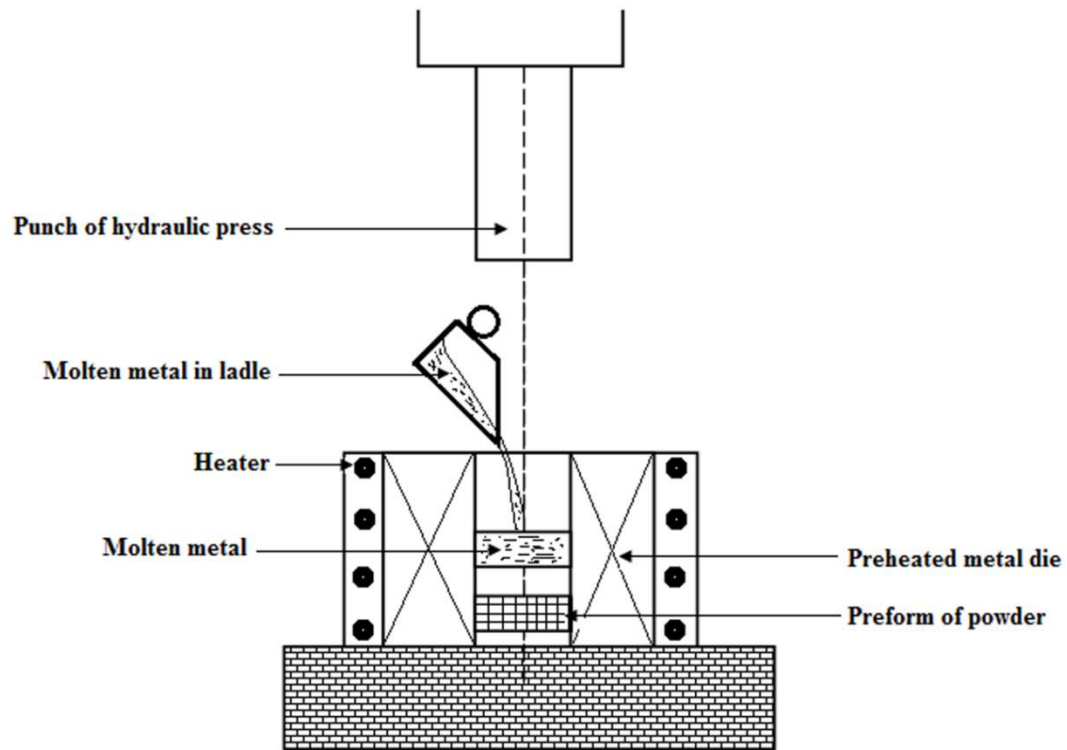
- **Reactive spontaneous infiltration (RSI)**

In the RSI process, the molten matrix material is infiltrated through porous preform. The reaction between matrix melt and preform generates second phase ceramic reinforcement particles which are in thermodynamic equilibrium with matrix phase [Dunand et al., 1993]. Micron size Al<sub>2</sub>O<sub>3</sub> particles have been generated in the aluminium matrix by infiltrating aluminium melt into preform of SiO<sub>2</sub> or Mg and SiO<sub>2</sub> mixture [Nanabe and Aswath, 1996, 1997].

- **Reactive squeeze casting (RSC)**

In this process molten matrix material is poured on preform of the inorganic powder kept in pre-heated die followed by squeezing. The reinforcement particles are generated

by the reaction of molten matrix materials with preform inorganic salt powder. This process has also been used to prepare hybrid composites with  $\text{Al}_2\text{O}_3$  and  $\text{Al}_3\text{Ti}$  reinforcement. The schematic diagram of experimental setup is shown in Fig. 1.2 [Fukunaga et al., 1991; Pan et al., 1997].



**Figure 1.2**– Schematic diagram of experimental set-up for composite fabrication by RSC process [Fukunaga et al., 1991].

- **Exothermic dispersion (XD)**

In this process, the chemical elements (namely, R1 and R2) in required amount are heated at high temperature in the presence of matrix material (M). These chemical elements react exothermically and form submicron size ceramic particles (R1R2) in the matrix. Figure 1.3 shows schematic diagram of the fabrication process of composite materials.  $\text{TiB}_2$  reinforced AMC have been fabricated by this process.  $\text{TiB}_2$  particles are generated by the chemical reaction between Ti and B powders at high temperature in

the presence of aluminium powder under argon atmosphere. AMCs with other reinforcements have also been produced by this technique [Kuruvilla et al., 1990; Vyletel et al., 1991; Vyletel et al., 1993].

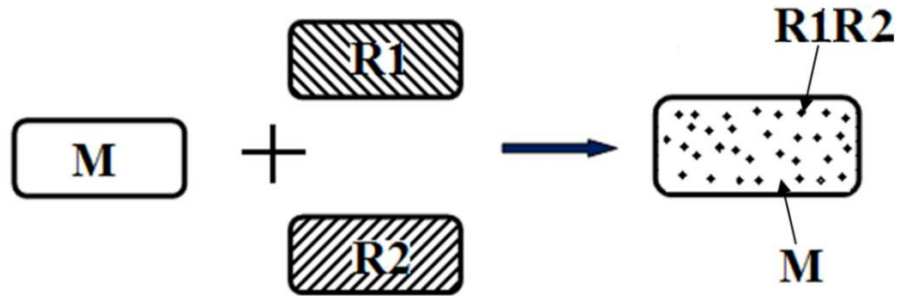


Figure 1.3– Schematic diagram of the composite fabrication by XD process.

- **Vapour-liquid-solid (VLS) reaction technique**

In this process, the matrix alloy consisting of reinforcement forming element is brought to melt condition and a suitable gas is injected into the melt. This gas reacts with reinforcement forming element and the reinforcement is generated within the matrix alloy [Koczak and Kumar, 1989]. This procedure has been used to prepare TiC particulates reinforced aluminium matrix composites [Premkumar and Chu, 1993, 1995].

- **Mechanical alloying**

In mechanical alloying technique the composite materials are fabricated by the repeated cold welding, fracturing, and re-welding of reactant powders in a high-energy ball mill [Suryanarayana, 2004]. Al-Zr nanocomposites with  $Al_3Zr$  reinforcement have been fabricated by this process which exhibit better mechanical properties [Srinivasarao et al., 2009].

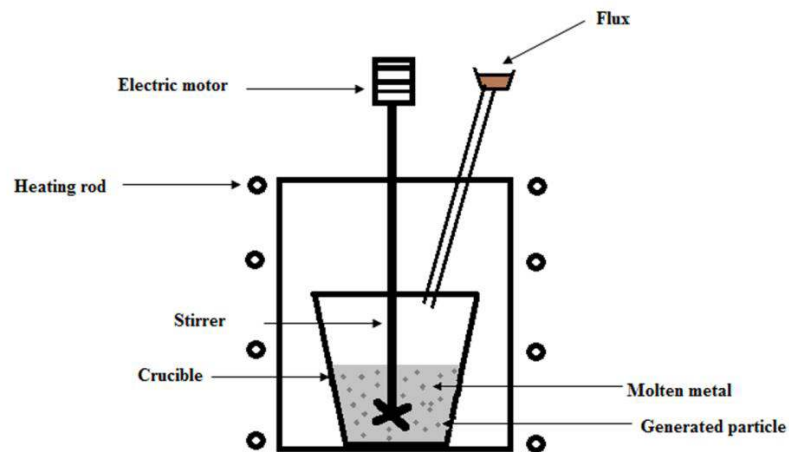


- **Isothermal heat treatment (IHT)**

In this process, the composite materials are exposed to high temperature which create new second phase particles. These particles act as reinforcement and improved mechanical properties are achieved. Hot rolled rods of Al/TiC have been used to create new reinforcement. These rods were exposed to 600°C temperature for different time periods. This resulted in the formation of Al<sub>3</sub>Ti and Al<sub>4</sub>C<sub>3</sub> phases by the chemical reaction between aluminium and TiC, resulting in improved mechanical properties [Satyaprasad et al., 1992].

- **Direct melt reaction (DMR)**

In this process, the matrix material is heated above the melting point and inorganic salts (flux) are introduced. These salts are thoroughly mixed in the molten matrix by continuous stirring. These salts react with the molten material to form reinforcement particles and continuous stirring helps in uniform distribution of reinforcement particles. The molten composite is poured into the mould to solidify. Figure 1.4 shows schematic diagram of the apparatus used to fabricate composite material by this technique [Zhao and Sun, 2001; Zhao et al., 2003].



**Figure 1.4**– Schematic diagram of apparatus used in DMR technique.

## 1.2.2 Applications of AMCs

AMCs are being used in different sectors but have gained special attention in components related to automobile, space, aerospace, marine etc. Table 1.1 provides an overview of the properties requirement for automotive components. Table 1.2 lists important mechanical properties of AMCs along with manufacturers, and Table 1.3 provides information regarding applications of AMCs in automobile industry with their properties and benefits. Detailed information on AMCs with different reinforcement has been provided [Rohatgi, 1991].

**Table 1.1** - Properties requirements for automotive components [Rohatgi, 1991].

System	Component	Justification
Engine	Piston Crown	High temperature, fatigue, creep, wear
	Piston Ring Groove	Wear resistance, weight reduction
	Rocker Arm	Weight, stiffness, wear
	Valve	High temperature, fatigue, creep, wear
	Wrist Pin	Specific stiffness, wear, creep
	Cylinder Block (liner)	Wear and seizure resistance, low friction, weight
	Connecting Rod	Specific stiffness, weight
	Bearings	Weight, reduced friction
Suspension	Struts	Damping, stiffness
Driveline	Shift Forks	Wear, weight
	Drive Shaft	Specific stiffness, fatigue
	Gears	Wear, weight
	Wheels	Weight
Housings	Gearbox Bearing	Wear, weight
	Differential Bearing Pumps	Wear, weight
Brakes	Disk Rotors Calipers	Wear, weight

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AMCs are also used in several components related to space and aerospace applications. Gr/Al composites are used in high-gain antenna boom for Hubble Space Telescope and B/Al composites in mid-fuselage section of space shuttle orbiter. SiC<sub>p</sub>/Al and SiC<sub>w</sub>/Al

are used to make the joints and attachment fittings for truss structures (structural components), electronic packages, thermal planes, housings, bushings etc. [Rawal, 2001]. Fan exit guide vanes of gas turbine engines, rotating blade sleeves of helicopters, flight control hydraulic manifolds etc are made of AMCs [Surappa, 2003]. The spars, tumbuckles, propellers and portholes are also made by AMCs for marine applications [Carden, 1999].

**Table 1.2** –Mechanical properties of AMCs with different matrices and reinforcement [Rohatgi, 1991].

Manufacturer	Matrix	Reinforcement*	Modulus <sup>†</sup> (GPa)	UTS (MPa)
Martin Marietta and Amax	Al base Al 2219	None TiC, 15 vol.%	74 69-117	221 400
Lanxide	Al base	None SiC, 45-55 vol. % Al <sub>2</sub> O <sub>3</sub> , 50-70 vol. %	69 152-179 193-262	124-172 400-448 200-276
Dural	Al base Al 2014 Al 6061 Al A356	None Al <sub>2</sub> O <sub>3</sub> , 10-20 vol. % Al <sub>2</sub> O <sub>3</sub> , 10-20 vol. % SiC, 10-20 vol. %	72 83-103 83-103 83-97	186-262 414-483 241-345 276-345
Comalco	Al base Al 6061	None Al <sub>2</sub> O <sub>3</sub> , 20 vol. %	69 85	310 330
Honda	Al base ADC12	None Al <sub>2</sub> O <sub>3</sub> (f), 10 vol. % Carbon(f), 10 vol. % Carbon(f), 5 vol. %	69 80 70 80	193 250 200 230
* All reinforcements are particles, with the exception of those used in Honda, which are short fibers. Wrought alloy properties are for extruded material. † Modulus values were measured at room temperature.				

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Automotive, aerospace or space vehicles applications of AMCs frequently face problems related to wear and friction. Hence, it becomes imperative to have detailed and relevant knowledge of wear and friction. Detailed discussion on wear and friction has been presented in following sections.

**Table 1.3** - Automotive demonstrator components of aluminium-matrix composites [Rohatgi, 1991].

Reinforcement	Component	Property	Benefits	Manufacturer
SiC(P)	Piston	Wear resistance, high strength	Reduced weight	Dural, Martin Marietta, Lanxide
Al <sub>2</sub> O <sub>3</sub> (f)*	Piston Ring Groove	Wear resistance	Higher running temperature	Toyota
Al <sub>2</sub> O <sub>3</sub> (f)*	Piston Crown (combustion bowl)	Fatigue resistance, creep	Opportunity to use Al, reduced reciprocating mass	T&N, JPL, Mahle and others
SiC(P)	Brake Rotor, Caliper, Liner	Wear resistance	Reduced weight	Dural, Lanxide
Fiber frax	Piston	Wear resistance, high strength	Reduced weight	Zollner
SiC(P)	Drive Shaft	Specific stiffness	Reduction of parts and weight	GKN, Dural
SiC(w)	Connecting Rod	Specific stiffness and strength; thermal expansion	Reduced reciprocating mass	Nissan
Al <sub>2</sub> O <sub>3</sub> (f) <sup>†</sup>	Connecting Rod	Specific stiffness and strength; thermal expansion	Reduced reciprocating mass	DuPont, Chrysler
Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub> - C	Cylinder Liner	Wear resistance, expansion	Increased life, reduced size	Honda
Gr(P)	Cylinder Liner, Pistons, Bearings	Gall resistance, reduced wear and friction	Increased power output	Assoc. Eng., CSIR, IISc. <sup>‡</sup>
TiC(P)	Piston, Connecting Rod	Wear, fatigue	Reduced weight and wear	Martin Marietta
Al <sub>2</sub> O <sub>3</sub>	Valve Spring, Retainer Cam, Lifter Body	Wear strength	Reduced weight, increased life	Lanxide

\* Short fibers. <sup>†</sup> Long fibers. <sup>‡</sup> CSIR; IISc.

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### 1.3 Wear

Wear is the process in which removal of material takes place from one or both the solid surfaces in contact. This phenomenon is observed when solid surfaces are in relative motion whether it is sliding, rolling or impact. Though this phenomenon is observed on the contacting surface but it depends on surface as well as bulk properties of the materials in contact. In most of the situations this process is undesirable, however, in some situations it is desirable [Bhushan, 1999].

On the basis of surface contact either mechanical or chemical, the wear process can be divided into six categories namely adhesive, abrasive, chemical, fatigue, impact and electrical-arc-induced wear. But during sliding motion mainly adhesive, abrasive and chemical (corrosive) wear are encountered and have been discussed below –

In **adhesive wear**, as name suggests adhesive bonds between the contacting surfaces are responsible for transfer/removal of material during sliding motion. This type of wear is very common and clearly observed when surfaces of similar materials interact with each other. The effect of adhesion decreases as the surface is contaminated by the absorbed gases or oils [Ludema, 1998]. In this wear, the contact between both solid surfaces occurs at the interface through asperities interaction which get deformed or detached during the sliding motion and generate the fragments. These fragments could be transferred from one surface to other surface or may be removed as wear particles [Bhushan, 1999].

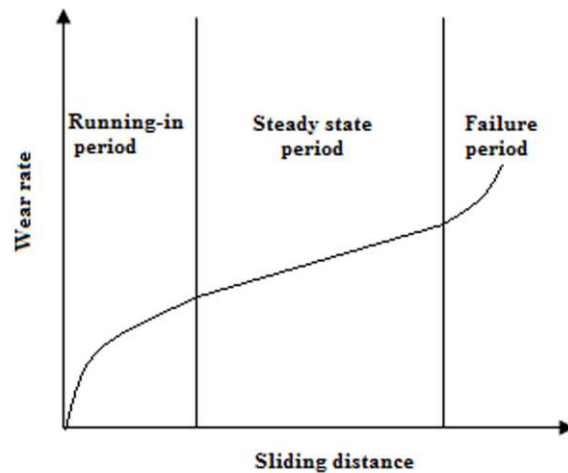
**Abrasive wear** takes place between two surfaces when the hard asperities of one surface or hard particles in the surface or from external source interact with soft counter surface. These hard asperities or particles cause plastic deformation, cracks, and grooves in the soft surface during sliding motion. The removal of material due to plastic deformation may occur in different modes such as plowing, cutting or wedge formation [Bhushan et al., 1985; Tylczak, 1998; Bhushan, 1999; ASTM standards G40, 2015].

**Chemical (corrosive) wear** may occur when contacting surfaces are in sliding motion in the presence of corrosive environment. Such situation may arise in the presence of lubricants. The favorable condition for this wear are corrosive environment imposed by

chemicals, high temperature, and high humidity. If the test is carried out in the presence of air than it is called oxidative wear due the presence of oxygen which acts as a corrosive medium in air [Bhushan, 1999; Dwivedi, 2010].

### 1.3.1 Stages of Wear

Wear of materials is expressed as wear rate which is volume loss from unit area in unit time or in sliding unit distance. Figure 1.5 shows the variation in wear rate with sliding distance with three distinct regions. In the initial period, wear rate is high and is known as the running-in period. In this period wear rate continuously changes from high to low wear rate. After certain period, wear rate becomes almost steady and not much change is observed which is shown as second stage. Finally, in third stage, wear rate increases sharply and failure of the material takes place [Handbook ASM Vol. 18, 1992; Bhushan, 1999; Mohan and Mohan, 2015].



**Figure 1.5** – Variation in wear rate with sliding distance [Handbook ASM Vol. 18, 1992].

### 1.3.2 Effect of Operating Parameters

The operating parameters which affect the wear rate of materials are sliding distance, sliding velocity, applied load, working temperature, humidity etc. The wear rate shows

an increasing trend with applied load in aluminium, aluminum alloys and AMCs due to the delamination of the surface, third-body wear, formation of grooves, etc. At low loads mode of wear is mostly mild and the nature of debris is dominated by oxides, however at high loads nature of wear changes to severe and the oxidative-metallic debris with dominance of metallic fragments is observed. But with the sliding velocity wear behaves in a different manner. Sliding velocity increases the surface temperature which enhances the oxidation process several folds. This oxide layer reduces the metal to metal contact and wear rate decreases initially with increasing sliding velocity and reaches a minimum value. But with further increase in sliding velocity oxide layer breaks leading to the gross material transfer and a sharp increase in wear rate is observed [Mohan and Srivastava, 2006]. Another mechanism responsible for decrease in wear rate is termed as a glaze layer. This layer is the sintered wear debris which comes out due to the tearing of oxide layer under high temperature and pressure [Rajaram et al., 2010]. If the same experiment is conducted under vacuum, it exhibits higher wear rate because any type of contamination including oxygen is unavailable that could have restricted metal to metal contact resulting in low wear [Bhushan, 1999].

#### **1.4 Friction and Laws of Friction**

Friction is the force which resists or opposes the relative sliding or rolling motion between two surfaces. There are several factors which affect the basic mechanism of friction such as physical, chemical and mechanical properties of the materials. At the microscopic level, the mechanism includes the adhesive forces between contacting surfaces, interaction of asperities, ploughing of one surface by the other harder surface, debris due to the fragmentation of the surface or by the fracture of oxide film and

environment [Bhushan, 1999; Mohan et al., 2015]. The basic laws of friction are as follows [Stachowiak and Batchelaor, 2005]:

- In static condition, maximum tangential force is directly proportional to normal load.
- During sliding motion, tangential friction force is proportional to the normal load.
- Friction force does not depend on the sliding speed and apparent area of contact.

According to Bowden and Tabor [1964] friction is caused by two main factors, namely adhesion and plastic deformation of asperities of contacting surfaces. They assumed that asperities are deformed plastically and attain a pressure which is equal to indentation hardness of the material. Therefore, the real area of contact can be calculated as:

$$A_r = \frac{P}{H} \quad (1.1)$$

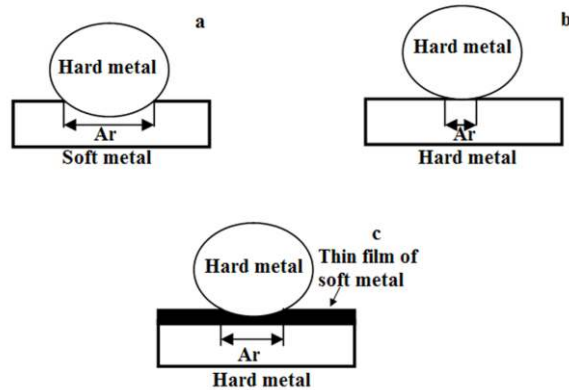
In addition, they also assumed that shearing of bonds during sliding also contributes to the friction. Therefore, coefficient of friction ( $\mu$ ) can be defined as follows:

$$\mu = \frac{P}{N} = \frac{A_r \tau}{A_r H} = \frac{\tau}{H} \quad (1.2)$$

Where, P is the normal load in newton, H is flow hardness in  $N/M^2$ , F is force in newton and  $\tau$  is shear stress. The above expression satisfies the Amontons law. There are two factors, namely real area of the contact ( $A_r$ ) and the shear strength of the junction ( $\tau$ ) under the sliding motion of two solid surfaces which affect the coefficient of friction. Schematic representation of different values of area of contact with shear strength is shown in Fig. 1.6a-c. When hard metal slides over the soft metal then real area of contact is large, whereas, shear strength is small leading to high coefficient of friction (Fig. 1.6a). But when hard metal slides over the hard metal, then real area of contact is



small and shear strength is large resulting in high coefficient of friction (Fig. 1.6b). In a case when hard metal is covered with the thin layer of soft metal and slides against hard metal then area of contact is small and shear strength is also small, that leads to low coefficient of friction (Fig. 1.6c) [Buckley, 1981].

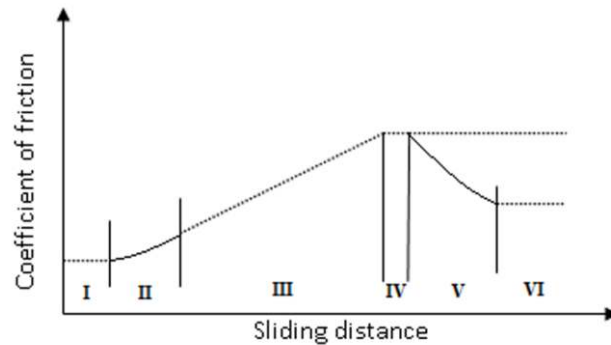


**Figure 1.6** – Schematic diagram of the two metallic surfaces in contact (a) hard on soft, (b) hard on hard and (c) hard on hard with thin film of soft metal [Mohan, 1989].

#### 1.4.1 Stages of Friction

The coefficient of friction (COF) depends on various factors such as adhesion, ploughing, deformation and third body particle during sliding motion. Six stages of COF with distance are shown in Figure 1.7. In the first stage, the friction force does not show more variation and remains almost steady. The ploughing component of the friction ( $\mu_{plow}$ ) dominates in this region. Adhesive component doesn't have much significance due to surface contamination. In the second stage, friction force increases because adhesive forces become prominent with time, however, there is sharp increase in friction force in third stage. The increased COF is due to the increase in number of wear particles and also due to increased adhesion as a result of oxide removal from the contacting surface. In addition, asperities on the surface may also contribute to friction force. In the fourth stage, the friction force does not show any change because the number of wear particles and the adhesion remain almost constant. In fifth stage,

friction force decreases due to the reduction in ploughing and asperity deformation. This kind of condition is achieved due to mirror smooth surface as a result of asperity removal. Finally, in the sixth stage, the friction force remains constant due to the same surface finish of both the surfaces. However, in reality, mirror smooth surfaces cannot be achieved as wear particles are always present. During sliding motion between the hard and soft surfaces, the wear particles are entrapped at the interface and there is hardly any change after fourth stage and the friction force remains constant [Suh and Sin, 1981; Mohan, 1989].



**Figure 1.7** – Variation in coefficient of friction with sliding distance [Mohan, 1989].

### 1.4.2 Friction of Materials

According to earlier understanding continuous welding and fracture of the surface was the responsible mechanism for sliding friction, but later studies suggested that plastic deformation is the main mechanism which occurs due to adhesion of surface asperities [Bowden and Tabor, 1950, 1964]. However, further studies added knowledge in this area and suggested other contributory factors to friction.

**Adhesion** takes place due to the inter-atomic attraction of contacting surfaces. Atomic bonds are formed due to force of attraction resulting in adhesion. During sliding motion

old adhesive bonds break and new bonds are formed. The contribution of adhesive forces to COF is denoted as  $\mu_{ad}$ . If the surfaces are not contaminated, then force due to adhesion is more which contributes to COF in a larger way. Contaminated surfaces exhibit low adhesive force and its contribution to overall COF is nominal. There are several factors such as crystal structure, surface conditions, applied load, contact duration, temperature at contact point etc. which affect the adhesion between surfaces [Bowden and Tabor, 1950; Bhushan, 1999;]. **Ploughing** of the softer surface takes place when it comes in contact with hard asperities/particles of the other surface. During sliding contact asperities of the hard surface interact with the asperities of the soft surface and plough them away contributing to COF. The contribution of ploughing to friction is denoted as  $\mu_{plow}$ . Studies have shown that ploughing component depends on slope of ploughing asperity, asperity geometry and also on presence of loose particles [Rabinowicz, 1965; Sin et al., 1979; Bhushan and Gupta, 1991].

During sliding if asperities are not ploughed away but deformed then they contribute as elastic ( $\mu_e$ ) and plastic ( $\mu_p$ ) components of **asperity deformation** ( $\mu_{asp}$ ) and finally to overall COF [Bhushan and Gupta, 1991]. During sliding sometimes particles from internal or external source are entrapped between surfaces as **third body** and contribute to overall COF. The contribution of third body in COF is denoted as  $\mu_{part}$  [Suh, 1986].

Hence, final equation of COF can be written as –

$$\mu = \mu_{asp} (\mu_e + \mu_p) + \mu_{ad} + \mu_{plow} + \mu_{part} \quad (1.3)$$

$$\text{where } \mu_{asp} = \mu_e + \mu_p \quad (1.4)$$

Friction is affected by properties of contacting materials and operating parameters such as sliding velocity, applied load, temperature and environmental conditions. If sliding surfaces are under normal environment then the friction is lower due to contamination,

but under vacuum surfaces remain clean causing higher coefficient of friction. In normal atmospheric conditions surfaces get oxidized as they are exposed to oxygen present in the air, but with increase in normal load oxide layer breaks and the friction increases. Variation in friction with sliding velocity is also observed. At the lower sliding velocity, the friction is low due to the oxide layer formed on the surface, but this layer gets damaged with increase in sliding velocity and coefficient of friction increases. Test temperature may also effect coefficient of friction. In case of material having low melting point melts due to localized heating may form a layer of low shear strength causing COF to decrease [Whitehead, 1950; Bhushan 1999; Mohan and Mohan, 2015].

## **1.5 Particulate Aluminium Matrix Composites (PAMCs)**

Reinforcements are used as fibres or particulates in aluminium/aluminium alloy matrix. Fibres can further be classified as whiskers, monofilaments, multi - filaments etc. but directional properties of fibres restrict their use in many applications, therefore, particulate reinforcement is preferred. Reinforcements which have been widely explored in particulate aluminium matrix composites include ceramics and intermetallics.

### **1.5.1 Intermetallic Reinforcement**

Varin [2002] summarized the data related to crystal structure, elastic modulus, density and melting point of tri-aluminide intermetallics of transition-metals ( $\text{Al}_3\text{Zr}$ ,  $\text{Al}_3\text{Ti}$ ,  $\text{Al}_3\text{Fe}$  and  $\text{Al}_3\text{Ni}$ ). He observed that  $\text{Al}_3\text{Zr}$  could be a good candidate as reinforcement in aluminium/aluminium alloy matrix. He fabricated  $\text{Al}_3\text{Zr}$  intermetallic in Al by conventional casting and consistently varied Mg in aluminium. He concluded that morphology of  $\text{Al}_3\text{Zr}$  changes from needle to feather as amount of Zr is increased. Morphology of  $\text{Al}_3\text{Zr}$  can also be altered by secondary process [Kumar et al., 2013].

Varin [2002] observed improvement in mechanical properties with generation and increasing volume fraction of  $\text{Al}_3\text{Zr}$  particles. He further added that the increased density of AMCs due to the incorporation of  $\text{Al}_3\text{Zr}$  is compensated by the addition of magnesium. Kumar et al. [2013] developed  $\text{Al}_3\text{Zr}$  particles in the AA6061 alloy by *insitu* technique and used friction stir process (FSP) which changed the  $\text{Al}_3\text{Zr}$  morphology from needle to spherical shape with improved hardness. They also reported that the improvement in hardness is due to increase in dislocation density.

Further, Dinaharan et al. [2014] prepared *insitu* composites with  $\text{Al}_3\text{Zr}$  and  $\text{Al}_3\text{Ti}$  reinforcement with same matrix (AA6061 alloy), and observed that  $\text{Al}_3\text{Zr}$  reinforced composite showed better wear resistance as compared to  $\text{Al}_3\text{Ti}$  reinforced composite in as cast condition. Agarwal et al. [2014] studied the physical, mechanical and tribological properties of Al/ $\text{Al}_3\text{Fe}$  composites fabricated by powder metallurgy route. They observed continuous improvement in strength parameters with increase in  $\text{Al}_3\text{Fe}$  amount. They also observed that with increase in wt.% of  $\text{Al}_3\text{Fe}$  wear rate decreased due to the formation of mechanically mixed layer (MML), whereas coefficient of friction showed increasing trend due to higher adhesion caused by the presence of iron in intermetallic. They also observed that with sliding velocity wear rate initially decreased and attained a minimum value and later it increased sharply. The initial reduction in wear rate is due to the formation of oxide layer, while after a certain sliding velocity the oxide layer breaks and third body phenomenon causes sharp increase in wear rate. Other workers have also observed similar tribological behaviour in composites prepared by liquid metallurgy [Srivastava and Mohan, 2006, 2011].

Ferreira et al. [2011] studied the tribo-corrosion behavior of centrifugally cast Al/Al<sub>3</sub>Ti and Al/Al<sub>3</sub>Zr functionally graded materials (FGMs). They observed that higher applied forces during fabrication increased the particle volume fraction and their orientation in the outer regions which leads to better tribo-corrosion. They also reported that Al/Al<sub>3</sub>Ti FGM exhibit better tribo-corrosion behavior as compared to Al/Al<sub>3</sub>Zr FGM. They further concluded that mechanism of tribo-corrosion depends on the mechanical properties of the reinforcement particles. Other workers have also used same fabrication technique to fabricate the Al base FGM materials [Hadad et al., 2010; Ferreira et al., 2011].

The aluminium alloy composites reinforced with Al<sub>3</sub>Ni intermetallic particles have also been fabricated by friction stir processing (FSP) to study the effect of multiple passes on Al<sub>3</sub>Ni particles, microstructure and mechanical properties. With increase in number of passes the reaction between Ni particles and the Al matrix increased and distribution of Al<sub>3</sub>Ni particles also improved, which enhanced the hardness and strength parameters [Qian et al., 2012]. Matsumuro and Kitsudo [2006] also prepared Al<sub>3</sub>Ni reinforced aluminium matrix composite by *insitu* process and studied the effect of processing temperature, stirring time etc. on morphology. They observed that the size of Al<sub>3</sub>Ni particles decreased with increase in temperature of molten metal and stirring time.

### **1.5.2 Ceramic Reinforcement**

Aluminium matrix composites have been produced with variety of ceramic reinforcements [Handbook ASM Vol. 21, 2001; Chawla, 2012]. Among ceramic reinforcements ZrB<sub>2</sub> has excellent high temperature properties, hence, present subsection has been focussed only on ZrB<sub>2</sub> reinforcement in different aluminium matrices.

Nano-size  $ZrB_2$  particle reinforced 2024 aluminium matrix composites were fabricated by melt *insitu* reaction and their microstructural features and mechanical behaviour were studied by Tian et al. [2014]. They found  $ZrB_2$  particles in rectangular and hexagonal shapes within a size range of 30 to 100 nm. These particles were uniformly distributed in the matrix and refined the aluminium-rich grains due to the pinning effect of  $ZrB_2$  particles which suppressed the grain growth. The refinement of Al-rich grains increased with increasing amount of  $ZrB_2$  particles. Strength parameters also improved due to good interfacial bonding between particles and matrix as well as due to grain refinement. Percentage elongation decreased after an initial improvement. The initial improvement could have resulted due to grain refinement with addition of  $ZrB_2$  particles, but segregation of these particles with increasing amount may result early failure and poor ductility.

Dinakaran et al. [2011] developed  $ZrB_2$  particles in AA6061 alloy matrix by *insitu* reaction technique. They observed spherical and elliptical morphology of  $ZrB_2$  particles and refinement of aluminium grains. They concluded that  $ZrB_2$  particles provided resistance to growth of aluminium-rich grains during solidification and these particles also act as nuclei for new Al-rich grains. They also observed that hardness, and ultimate tensile strength continuously improved with increase in amount of  $ZrB_2$  particles. The improvement in hardness is caused mainly due to the presence of harder  $ZrB_2$  particles, however dislocations generated in the matrix with the presence of these particles also contribute to hardness. While improvement in strength could be due to the interaction between generated dislocations and  $ZrB_2$  particles, clear interface between particles and matrix, absence of sharp edges and flaws in the particles.

The wear properties were also observed to improve with addition of ZrB<sub>2</sub> particles due to the higher hardness of the composites, grain refinement of matrix, strong bonding between particles and matrix and spherical shape of particles. Further, Dinaharan and Murugan [2012] studied the ZrB<sub>2</sub> reinforced AA6061 alloy matrix composites in context of wear and made several observations. They observed and concluded that increased number of ZrB<sub>2</sub> particles, increase in dislocations, and clear interface contribute to increase in strength and hardness. They also added that spherical particles delay the crack initiation and decrease the wear rate. But the increasing trend in wear rate with sliding velocity can be attributed to frictional heat and interfacial stress. Increase in sliding velocity generates more frictional heat and increase the penetration of hard asperities of counter surface into the soft surface that increases the weight loss. Wear rate also increases with load due to the fragmentation of asperities and generation of subsurface micro cracks.

Kumar et al. [2010] also prepared PAMC using AA6351 alloy as matrix with ZrB<sub>2</sub> particles as reinforcement by *insitu* reaction technique and compared the properties of as cast and heat treated (solutionized and solutionized & aged) composites. They observed that hardness increased with increasing amount of ZrB<sub>2</sub> particles, but maximum hardness was observed in the solutionized & aged composite due to the precipitation of  $\beta'$ - Mg<sub>2</sub>Si particles and finer particles of ZrB<sub>2</sub>. Wear test results show that the wear rate decreased with increasing amount of ZrB<sub>2</sub> particles due to high hardness of composites and good interfacial bonding between particles and matrix. Minimum wear rate was also observed in solutionized & aged composite due to the presence of ZrB<sub>2</sub> particles and  $\beta'$  precipitates.



### 1.5.3 Multiple Reinforcement

The aluminium matrix composite reinforced with  $\text{Al}_3\text{Zr}$  and  $\text{Al}_2\text{O}_3$  particles was fabricated by *insitu* reaction between aluminium and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  powder. Morphology and mechanical properties of composite were studied by Zhao and Sun [2001]. They reported  $\text{Al}_3\text{Zr}$  particles in polyhedron and rectangular shapes in a size range of 0.5 to 4  $\mu\text{m}$ , and equiaxed  $\text{Al}_2\text{O}_3$  particles in a size range of 0.2 to 1.0  $\mu\text{m}$ . They also observed that the interface between the  $\text{Al}_3\text{Zr}$  particles and aluminium matrix was clean with no reaction product. Larger number of dislocations appeared near polyhedral  $\text{Al}_3\text{Zr}$  particles as compared to rectangular  $\text{Al}_3\text{Zr}$  particles. The tensile strength improved with incorporation of  $\text{Al}_3\text{Zr}$  and  $\text{Al}_2\text{O}_3$  particles which could be due to the Orowan, grain-refining, and solid-solution strengthening. In another study on same type of composite Zhao et al. [2003, 2003] observed that twinning was the responsible mechanism for change in morphology of  $\text{Al}_3\text{Zr}$  particles. However, Li et al. [2009] found that tensile, wear, and corrosion properties of aluminium matrix composites with same reinforcements could be improved if material was prepared by squeeze casting instead of permanent mould casting because squeeze casting process reduces the casting defect and refines the grains of aluminium.

Aluminium matrix composites have also been prepared with  $\text{Al}_3\text{Zr}$  and  $\text{Al}_2\text{O}_3$  reinforcement by magneto chemistry *insitu* reaction technique using aluminium ingot and  $\text{Zr}(\text{CO}_3)_2$  powder [Zhang et al., 2007]. They observed uniform distribution of particles in a size range of 0.08–0.12  $\mu\text{m}$ . Tensile strength was observed to increase with increasing amount of flux up to a certain wt.% due to Orowan strengthening, whereas, elongation decreased continuously due to increased stress concentration sites.

Zhao et al. [2008] also produced AMC with same reinforcement by magneto-chemical melt reaction technique and studied the microstructure and strengthening mechanism. They could develop nanosize reinforcement particles with uniform distribution in aluminium matrix and observed improvement in strength and hardness. They found that Orowan, grain-refining, solid-solution and dislocation strengthening contribute to yield strength of the composite. Other workers also found the similar results while working on such composites [Zhao et al., 2008; Zhang et al., 2009a, 2009b; Zhao et al., 2010; Zhu et al., 2010; Zhu et al., 2012; Kaveendran et al., 2013a, 2013b].

Zhao et al. [2007] produced  $\text{Al}_3\text{Zr}$  and  $\text{ZrB}_2$  particles reinforced aluminium matrix composites by magneto chemistry *insitu* reaction technique and studied the effect of melt temperature on wear behaviour and morphology of reinforced particles. Morphology of  $\text{Al}_3\text{Zr}$  particles changed from spherical to tetragonal to rod-like and finally to fibers with increase in melt temperature, whereas,  $\text{ZrB}_2$  particles did not show any change in morphology. They observed minimum weight loss under dry sliding conditions for composite with spherical  $\text{Al}_3\text{Zr}$  particles. With similar reinforcement in the aluminium matrix, Zhang et al. [2007] and Zhang et al. [2008] studied the microstructural and wear behaviour. They found hexagonal and tetragonal particles of  $\text{Al}_3\text{Zr}$  and  $\text{ZrB}_2$  in a size range of 0.3 to 0.5  $\mu\text{m}$ . They also observed improvement in wear properties with increase in hard particles.

Yang et al. [2012] prepared aluminium matrix composites consisting of  $\text{ZrB}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Al}_3\text{Zr}$  particles by the direct melt reaction technique. They observed hexagonal  $\text{ZrB}_2$  particles of nanosize (50 nm), rod shape  $\text{Al}_3\text{Zr}$  particles with the length-diameter ratio of 20, while  $\text{Al}_2\text{O}_3$  particles had rectangular as well as ellipsoidal morphology.

Zhao et al. [2008] also prepared AMC with same reinforcement by magneto-chemical melt reaction technique and reported improvement in tensile and wear properties.

#### **1.5.4 Al-Mg Alloy Matrix**

Mandal et al. [2006] fabricated the Al-Mg alloy matrix composites with short steel fibers reinforcement by vortex method. They used uncoated, copper coated, and nickel coated steel wires and observed that the copper coated steel fibre reinforced composite showed maximum tensile strength and hardness. They concluded that copper coating on steel fibers restricted the formation of brittle nature intermetallic compound at the interface. In another study, Mandal et al. [2008] analysed physical and mechanical properties of copper coated steel fibers reinforced Al-Mg alloy matrix composites and observed improvement in strength parameters with increase in amount of steel fibers up to a certain wt.%. But beyond that the crack nucleation sites increased and strength decreased. Other workers also used Al-Mg alloys as matrix and reinforced it with SiC or B<sub>4</sub>C to study microstructural, physical, mechanical and wear behaviour [Lee et al., 2001; Zulfia and Hand, 2002; Dolatkhah et al., 2012].

### **1.6 Origin of the Problem**

Aluminium matrix composites (AMCs) have gained large attention due to their low density, high wear resistance and specific strength [Lloyd, 1994; Hassan et al., 2009; Rao and Das, 2011; Rohatgi, 2013]. The properties of AMCs can be tailored by altering the morphology of matrix, reinforcement phase and their volume fraction. But, particulate reinforced aluminium matrix composites (PAMCs) are attractive because they exhibit isotropic properties as compared to fibre reinforced composites [Surappa, 2003].

Liquid metallurgy route is the cheapest route for PAMCs production. This route has been widely explored using *exsitu* methods. In *exsitu* process reinforcement phase is directly mixed into the melt, but some problems are encountered like segregation of reinforcing phase and reactions at interfaces due to high temperature. These problems restrict their role in industrial production. Whereas, in *insitu* process reinforcing phase is generated within the melt by chemical reaction of inorganic salts and molten metal/alloy. In these composites clear interface between reinforcement and matrix, more uniform distribution of particles and better bonding between reinforcement and matrix are achieved which result in better mechanical and tribological properties [Zhang et al., 2007; Zhao et al., 2010]. Therefore, *insitu* process is gaining importance in PAMCs and it is preferred over *exsitu*. Direct melt reaction (DMR) *insitu* technique has become quite popular because, it is cheaper, simple and also have near net shape forming capability [Wang et al., 2011].

Several aluminium alloys such as Al-Si, Al-Cu, Al-Si-Mg etc. have been widely explored as matrices for PAMCs. Depending on property requirement for a particular application matrix and reinforcement have to be chosen carefully. Al-Mg alloy exhibits moderate-to high-strength, good work-hardenability, good welding characteristics and resistance to corrosion in marine environment. In addition, magnesium also reduces the problem related to wetting between matrix alloy and reinforcement particles by increasing the surface energies of the solids and decreasing the surface tension of the liquid matrix alloy [Saklakoglu et al., 2004; Pai et al., 1995]. Hence, it could be suitable PAMC matrix for many applications. Limited work is available on these alloys as PAMC's matrix. AMCs using Al-Mg alloy as matrix have been produced by *exsitu*

techniques and effect of reinforcement phase on microstructure and mechanical properties has been studied [Lee et al., 2001; Zulfia et al., 2002; Mandal et al., 2006; Mandal et al., 2008; Dolatkhah et al., 2012].

In general, non-metallics have been used as reinforcements in AMCs and large share of these non-metallics belongs to ceramics due to their high hardness and high temperature capabilities. Tri-aluminide intermetallics have low density, high melting point, high elastic modulus, excellent resistance to oxidation & corrosion. They remain in thermodynamic equilibrium with aluminium matrix and do not have intermediate reaction zone with matrix. Hence, tri-aluminides could be potential replacement of ceramics and PAMCs with improved mechanical and tribological properties can be produced [Zedalis and Ghate, 1985; Miao et al., 2000; Li et al., 2011]. Detailed study conducted on  $\text{Al}_3\text{Ni}$ ,  $\text{Al}_3\text{Ti}$ ,  $\text{Al}_3\text{Fe}$ , and  $\text{Al}_3\text{Zr}$  tri-aluminides shows that  $\text{Al}_3\text{Zr}$  has highest melting point and elastic modulus among all tri-aluminides.  $\text{Al}_3\text{Zr}$  reinforced PAMCs have been produced by conventional casting and their microstructure, density, hardness and compressive strength are studied in detail [Varin, 2002], however, a very limited work is available on tribological aspect.

Hence, In the present study, Al-Mg (AA5052) alloy has been chosen as matrix and  $\text{Al}_3\text{Zr}$  as reinforcement to prepare *insitu* composite by direct melt reaction (DMR) technique and the effect of vol.% of  $\text{Al}_3\text{Zr}$  particles on microstructure, mechanical and tribological properties has been studied. However, properties of PAMCs can further be improved by multiple reinforcement [Suresha and Sridhara, 2010; Devaraju et al., 2013; Baradeswaran et al., 2014; Rajmohan et al., 2014].  $\text{ZrB}_2$  with high melting point, high strength & hardness, high elastic modulus, excellent wear resistance, high thermal &

electrical properties, high corrosion resistance, high resistance to oxidation even at elevated temperatures, and excellent chemical resistance has been chosen for multiple reinforcement [Setoudeh and Welham, 2006; Zhang et al., 2008; Liu et al., 2009; Kumar et al., 2010; Sun et al., 2010; She et al., 2011]. In the present work  $(\text{Al}_3\text{Zr}+\text{ZrB}_2)/\text{Al-Mg}$  composites have also been prepared by DMR technique to study the effect of vol.% of  $\text{ZrB}_2$  particles on microstructure, mechanical and tribological properties of  $\text{Al}_3\text{Zr}/\text{Al-Mg}$  composite.

### **1.7 Objective of the Present Work**

On the basis of literature review it can be concluded that work on ambient and elevated temperature mechanical and tribological properties of Al-Mg alloy matrix composites with  $\text{Al}_3\text{Zr}$  and  $(\text{Al}_3\text{Zr}+\text{ZrB}_2)$  is limited. Therefore, the objective of the present work is to fabricate the composites namely  $\text{Al}_3\text{Zr}/\text{Al-Mg}$  and  $(\text{Al}_3\text{Zr}+\text{ZrB}_2)/\text{Al-Mg}$  and to study their morphology, mechanical and tribological behaviour at ambient as well as at elevated temperature. The experimental part has been presented in chapter 2. Chapter 3 and 4 deal with the characterization of  $\text{Al}_3\text{Zr}/\text{Al-Mg}$  and  $(\text{Al}_3\text{Zr}+\text{ZrB}_2)/\text{Al-Mg}$  composites. Chapter 5 presents the high temperature tensile and tribological properties of hybrid composite, and main conclusion and scope of the work is given in chapter 6. This study will help to explore the applications of composites in the field of tribology and may widen the scope of composites in related applications.