Chapter 2

LITERATURE REVIEW

2.1 Composite Material

Composite are different materials as compared to the conventional materials. Nature has varieties of composite materials. Common examples of composite materials are wood and bones. Wood is a composite material which consists of cellulose fibers reinforcement and lignin as matrix whereas a bone consists of collagen as reinforcement and apatite as matrix material. Composites mainly comprise of two parts as matrix and reinforcement. Normally, matrix is soft part whereas the reinforcements are hard part of the composite materials. In between matrix and reinforcement, there is an interface. The role of an interface is to share load across it and provide sufficient binding between matrix and reinforcement. Hence composite making is nothing but making of good interface.

It is known fact that the history of the composite materials is very old. In 3400 BC, the Mesopotamians (ancient people) used to glue various wood stick together to make first plywood. Since then, composite materials have used in different forms for various applications. In 2000 to 2100 BC, Egyptians used composite plasters to make death masks. In 1400 to 1500 BC, both Egyptians and Mesopotamians used different straws to reinforce mud items such as various house parts, wall mud plaster, pots, boats, etc. In around 1200's, Mongolian people have designed bows made of different wood, bamboos, natural resins, etc. In 1800's and 1900's people have started working on artificial synthesis of polymers such as bakelite, celluloid, polyester, polystyrene, etc. by polymerization methods.

In 1930's, most important decade for composite industries, advance resins have developed which is use even today. Also development in fiber reinforced polymer (FRP) was taken into place. In 1947, people have started working on construction of various automobile parts using composites. Designing of Corvette in 1953 is well known. In 1960's first carbon fiber was patented. This development has boost industries manufacturing of sports equipments. Since 1970's to even today, there are various approaches have taken place to develop cost effective materials which can replace traditional materials. Making ultra light weight and high strength components which can withstand extreme environments is the future of the composite materials where there are lot of researches going on worldwide.

Composite materials are highly demanding because of their flexibility in properties. One can design composites in such a way that custom (tailor made) properties can be achieved as per specifications and design. This opens up the market of new materials to the world. Combine action of matrix as well as the reinforcing constituents play vital role to achieve this stage. Depending on the applications, researcher can design composite materials in such a way that required properties can be obtained. General flow for the material synthesis is shown below:

Material Processing ⟺ **Material Structure** ⟺ **Material Properties** ⟺ **Material Application**

This means, depending on application, properties can be developed by making appropriate structure in the composite materials by adopting suitable processing route. Reverse approach is also famous from processing to application.

Engineering composite materials are artificially made materials which have different properties than that of original materials. Combining two traditional materials give rise to another level of properties which are different than identical properties of added constituents such as metal and ceramics. Researchers have tried to combine different varieties of materials to fabricate composites. Focus properties in composites are specific strength, stiffness, toughness and elevated temperature stability. The properties of final composites depend on various parameters of the reinforcement such as type, amount, size, shape, distribution and alignment [34].

2.2 Classification of composite materials

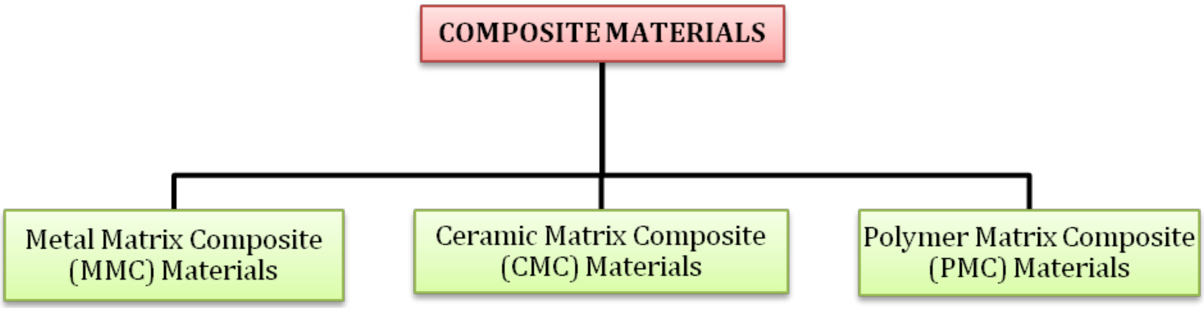


Figure 2.1: A classification of composite materials based on matrix materials.

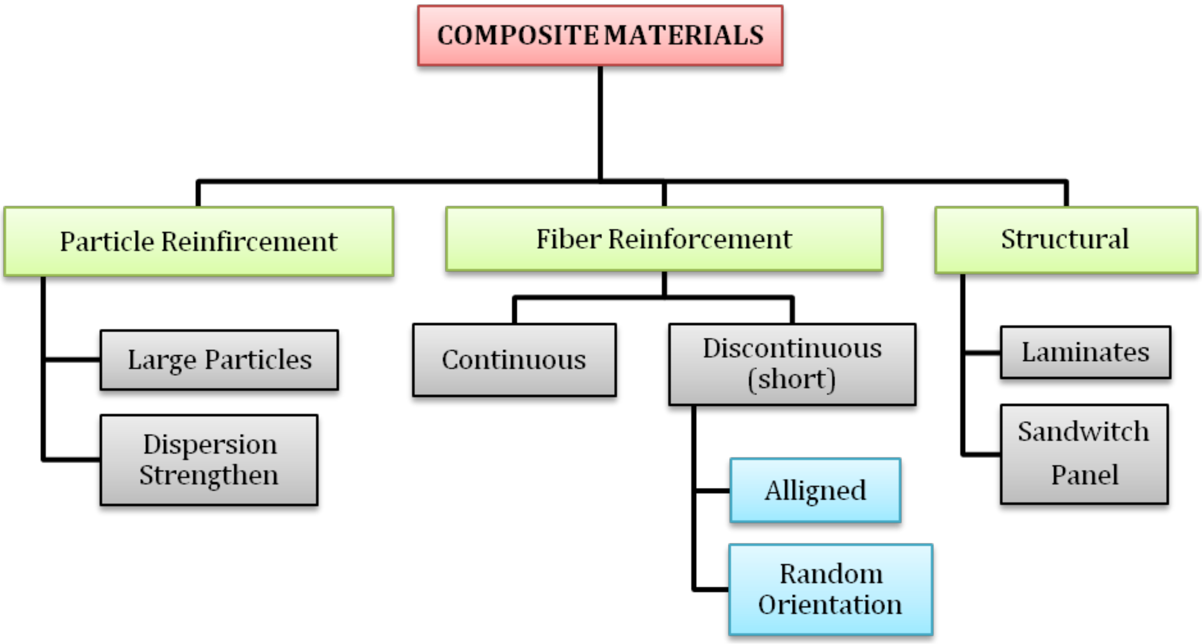


Figure 2.2: A classification of composite materials based on reinforcement materials.

Composite materials can be classified in two different ways as shown in figure 2.1 and 2.2. One based on matrix materials: (1) metals (MMC), (2) ceramics (CMC) and (3) polymers (PMC). And second is based on reinforcement: (1) particles, (2) fibers and (3) structural. Further divisions in these classifications can be seen in above figures.

2.2.1 Based on matrix

General *functions* of the matrix materials are:

- Provide enough bonding to the reinforcement,
- Provide suitable path for load sharing across the interface,
- Protect the reinforcement against any chemical reactions and mechanical abrasions,
- Keeping reinforcing constituents in proper positions and orientations,
- Prevent crack propagation and inter laminar shear, etc.

Matrix phase may be metallic, ceramic or polymeric materials based on which there are THREE sub classifications of composites as discussed below.

1. **Metal Matrix Composites (MMCs):**

   The composite in which matrix is a ductile metal or metal alloy are termed as metal matrix composites (MMCs). General matrix materials are Al, Mg, Ti and Cu. Examples of reinforcements used in MMCs are:

   (a) Powder particles: Al_2O_3, SiC, SiO_2, MnO_2, PbO, CdO, ThO_2, etc.

   (b) Fibers:

      i. *Continuous fibers:* C, SiC, Al_2O_3, B and other refractory metals and

      ii. *Short or chopped fibers:* Al_2O_3, C, SiC, etc.

   Volume fraction of the reinforcement should be limited to 10 to 60 volume %. Using various mentioned reinforcements, following *properties* can be raised:

   - Specific strength,
   - Stiffness,
   - Abrasion resistance,
   - Creep resistance,
   - Thermal conductivity,
   - Impact strength,
   - Dimensional stability,
   - Elevated temperature properties, etc.

   MMCs are used in following critical *applications*:

   - Automobile sector – engine parts,
   - Aerospace sector – space shuttle components, Hubble telescope parts, other satellite parts, rocket components, etc.
   - Turbine engine components, etc

   Advantages of MMCs are:

   - High ductility,
   - High modulus of elasticity,
   - Improved thermal shock resistance,
   - Easy to manufacture, etc.

   Disadvantages of MMCs are:

   - High density (in some cases),
   - High cost of materials and fabrication.

2. **Ceramic Matrix Composites (CMCs):**

   The composites in which both the reinforcements and matrix materials are ceramics materials are known as ceramic matrix composite (CMCs). CMCs are generally fabricated for,

- Improving fracture toughness,
- Improving creep behaviour,
- Improving failure resistance due to sudden changes in temperature, etc.

Example of CMCs is SiC whiskers in Al_2O_3 matrix which used in cutting tool mainly.

Advantages of CMCs are:

- High thermal stability,
- High load bearing capacity,
- High stiffness, etc.

Disadvantages of CMCs are:

- High brittleness,
- Costly manufacturing and material procurement,
- Not suitable against mechanical shock loading, etc.

3. **Polymer Matrix Composites (PMCs):**

In PMCs, both thermoplastics and thermosetting resins can be used. *Advantages* of thermoplastic resins against thermosetting resins are:

- They are tougher and have high strain to failure,
- They offer the potential of improved hot or wet resistance and
- No chemical reactions are involved.

Example of matrix and reinforcements are epoxy, polyetherether, ketone, polyimide, polysulfone and phenolics.

Advantages of PMCs are:

- Low cost,
- Light weight,
- High corrosion resistance,
- High toughness,
- Low density,
- Easy processing, etc.

Disadvantages of PMCs are:

- Low strength and stiffness,
- Low thermal stability,
- Low load bearing capacity, etc.

2.2.2 Based on reinforcement

As sown in figure 2.3, there are three sub classifications and then further divisions into that.

1. **Particle Reinforced Composites (PRCs):**

   Ceramic particle are usually lighter than the matrix and they are added into the matrix using suitable technological process. Matrix does not react with the reinforcement except at an interface area. Based on size, there are two sub divisions of this type of composite which usually known as particulate reinforced composite (PRCs).

   (a) Large particles (Approx. 1 micron) and
   (b) Fine particles (0.01 to 0.1 micron)

   Large particles generally added into the matrix in 20 to 40 volume %. This builds strength, toughness and wear resistance. Common examples of large size particle composite are vulcanized rubber reinforced with carbon black powder (20 to 50 micron size). Another example is CERMETS.

   Fine size particles improve the strength of the composite by dispersion strengthening mechanism. Common examples of fine size particles are Al_2O_3, PbO, BeO, ThO_2, MnO_2, etc. which can be added upto 15% volume fraction. These fine size particles generally do not react chemically with the matrix but certainly improve hardness and load bearing capacity of the overall composite system. Common examples of fine size particle reinforced composite are TD (Thoria – Dispersed) Nickel and SAP (Sintered Alumina Powder).

   Following *properties* can be increased using particles as reinforcement:

   - Wear and abrasion resistance,
   - Hardness,
   - Thermal and electrical conductivity,
   - Elevated temperature properties,
   - Low cost, low shrinkage while solidification and low friction, etc.

   The behaviour of particulate reinforced composites mainly governs by:

   - Distribution of the particles throughout matrix,
   - Relative volume fraction of constituents and
   - Interfacial bond strength.

2. **Fiber Reinforcement Composites (FRCs):**

   Fibers are generally very fine size wires with high length to diameter ratio (aspect ratio). Fibers can be added into the matrix in various sizes with various orientations by different technological processes. There are mainly TWO types of FRCs:

   (a) Long fibers, which are always aligned to one directions (figure 2.3a) and

   (b) Short fibers, which may be aligned or randomly oriented (figure 2.3b and 2.3c).

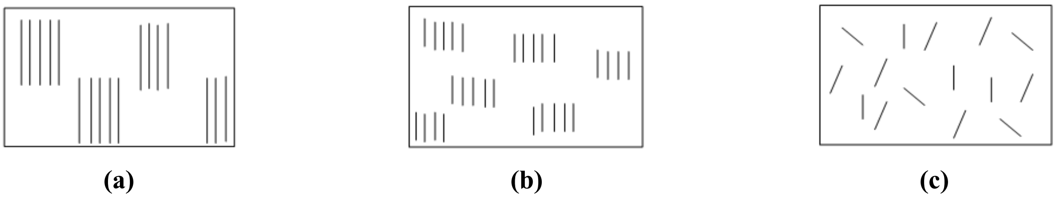


Figure 2.3: Different types of fiber reinforced composites.

Strength of such composite is highest in the direction of fiber alignment but lowest in transverse direction. Fibers are made of either metals, ceramics or polymeric materials. The important *characteristics* of FRCs are:

- Improved specific strength (ratio of tensile strength to specific gravity) and
- Improved specific modulus (ratio of modulus of elasticity to specific gravity).

The *properties* of FRCs depends on,

- The identical nature and properties of fiber and matrix materials,
- Their relative volume fraction,
- Orientation and distribution of fiber in the matrix,
- Interfacial bonding strength and
- Length of fibers or aspect ratio.

Very important parameter in the fiber is its critical length (L_c) which is define as the minimum length of the fiber which is required to attain ultimate fiber strength (σ_f) for given diameter of fiber when their interfacial bond strength is T_c.

$$\mathrm{L}_c = \frac{\sigma_f \mathrm{d}}{T_c} \tag{2.1}$$

Where,
σ_f = Ultimate fiber strength, d = diameter of fiber and T_c =interfacial bond strength.

Long fiber FRCs have fiber length more than L_c compared to short fiber FRCs. Hence long fiber FRCs have higher reinforcement efficiency than short fiber FRCs. Those fibers having length more than 20 to 100 times of critical length (L_c), are only termed as long fibers, otherwise short fibers.

Typical *examples* popular of FRCs are

- Glass fiber reinforced composites (GFRCs),
- Carbon fiber reinforced composites (CFRCs),
- Aramid fiber reinforced composites (AFRCs), etc.

Failure of FRCs occurs due to following reasons,

- Breaking of fibers,
- Micro-cracking of the matrix,
- Debonding of the fiber from the matrix at the interface,
- Delamination of laminated composites.

3. **Structural Composites:**

   This type of composites normally composed of different lamina or panels of different materials which are glued together in different angles. There are TWO sub divisions of these types of composite as

   (a) Laminar composites and
   (b) Sandwich panels

   Laminar composites (figure 2.4) are consisting of 2D sheet having unidirectional strength. Such sheets are stacked one over another in different directions and paste them tighter by chemical glue as binding materials. Common example is plywood.

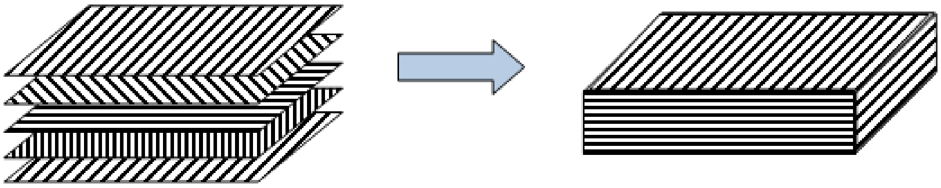


Figure 2.4: Laminar composite.

Sandwich panel (figure 2.5) is type of composite in which layers of low density materials is sandwiched between two layers of hard and strong sheets of other materials on both the sides. The inner material (core) is generally having honeycomb or hexagonal structure made of metallic foils whose axis are perpendicular to the face planes. Core should be light in weight and able to transfer load to the other end. It should have good corrosion resistance with enough stiffness which increase with core thickness.

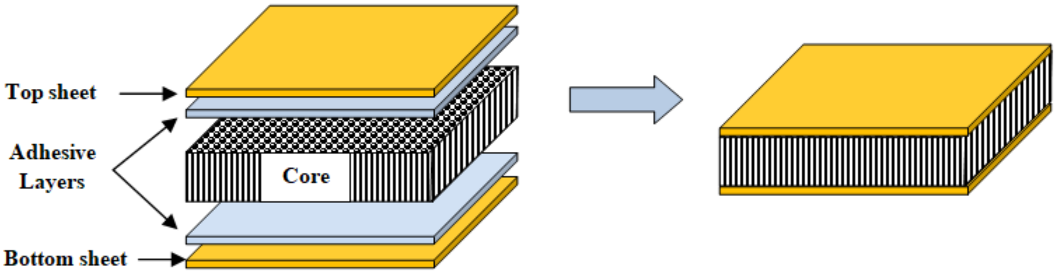


Figure 2.5: Sandwich panel.

Popular *applications* of sandwich panels are:

- Fabrication of aircraft wings,
- Fabrication of roof, wall and floor of the buildings,
- Design of ship, boat hulls, etc. [35]

2.2.3 The rule of mixture

The properties of composites depend on the principle of combine action of the matrix and the reinforcement. Determination of mass density of the composite (ρ_c), matrix density (ρ_m) and reinforcement density (ρ_r) can be done by [35],

$$M_c = M_m + M_r \tag{2.2}$$

$$\rho_c V_c = \rho_m V_m + \rho_r V_r$$

$$\rho_c = \rho_m \frac{V_m}{V_c} + \rho_r \frac{V_r}{V_c}$$

$$\rho_c = \rho_m f_m + \rho_r f_r \tag{2.3}$$

(where, f = volume fraction)

For hybrid composite,

$$\rho_c = \sum_{i=1}^{n} \rho_i f_i$$

For continuous and aligned fibers as well as for particulate reinforced composites, thermal conductivity and electrical conductivity can be found by,

$$K_c = K_m f_m + K_r f_r \tag{2.4}$$

$$\sigma_c = \sigma_m f_m + \sigma_r f_r \tag{2.5}$$

For thermal and electrical conductivity in perpendicular direction of alignment of the fibers,

$$\frac{1}{K_c} = \frac{f_m}{K_m} + \frac{f_r}{K_r} \tag{2.6}$$

$$\frac{1}{\sigma_c} = \frac{f_m}{\sigma_m} + \frac{f_r}{\sigma_r} \tag{2.7}$$

For modulus of elasticity, in case of continuous and unidirectional fibers,

$$E_c = E_m f_m + E_r f_r \tag{2.8}$$

This equation (1.9) is only valid for applied load is in the direction of the fiber alignment and it is within linear region of the stress-strain curve (i.e., in elastic zone). But for plastic zone, first matrix starts to deform and then entire load will transmit to the reinforcement materials. So,

$$E_c = E_r f_r \tag{2.9}$$

If the load is perpendicular to the fiber orientation, then every constituents behave differently. Hence in that case, modulus of elasticity can be given by,

$$\frac{1}{E_c} = \frac{f_m}{E_m} + \frac{f_r}{E_r} \tag{2.10}$$

2.2.4 Other types of composite materials

1. **Carbon – Carbon Composites (CCCs):**

   In this composite material, carbon fiber is reinforcement part and carbon is matrix part. Such composite has following *properties*, [36]

   - High tensile strength,
   - High resistance to creep,
   - High fracture toughness,
   - Low coefficient of thermal expansion,
   - High thermal conductivity,
   - Low susceptibility of thermal shock,

- Good elevated temperature properties, etc.

But at the same time, this composite material is having *limitations* like, high temperature oxidation (carbon burning problem), and high cost of fabrication. Such composites can be *used* as following:

- Rocket motor parts,
- Advanced turbine engine parts,
- Friction and anti-friction components in aircraft,
- High performance automobile parts such as in racing cars,
- Hot pressing molds, etc.

2. **Hybrid Composites:**

   In such composite materials, two or more types of reinforcements are added into the single matrix materials. Example is use of glass fibers and carbon fibers in MMCs. Glass – Carbon fiber PMCs possesses high strength, stiffness, impact resistance and low density. It is economical and possesses anisotropic properties. *Applications* of hybrid composite are as listed below:

   - Structural components,
   - Sports goods,
   - Medical components (orthopaedic), etc.

2.3 Manufacturing of the composite materials

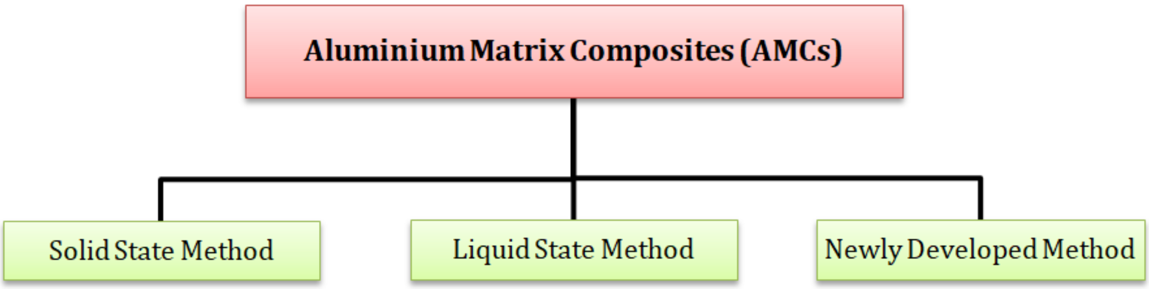


Figure 2.6: Different composite manufacturing techniques.

Following three methods are mainly use for preparation of composites;

In solid state process, following methods are included:

1. Powder metallurgy and sintering
    - Conventional sintering
    - Microwave sintering
    - Spark plasma sintering
    - Hot compaction
    - DC assisted sintering
2. Foil diffusion bonding
3. LASER deposition method
4. Deformation processing
5. Powder thixo-forming
6. Equi-channel angular pressing

In liquid state process, following methods are included:

1. Pressureless methods
    - In-situ dispersoids
    - Spray process
        - Osprey process
        - Rapid solidification process
    - Dispersion process
        - Stir casting (developed by S. Ray in 1969 [37])
        - Compocasting (developed by Flemings and Mehrabian [38])
    - Centrifugal casting
    - Gravity die casting
    - Ultrasonic assisted casting
2. Pressure impregnation methods
    - Melt infiltration
    - Lanxide process
    - Squeeze casting
    - Screw extrusion

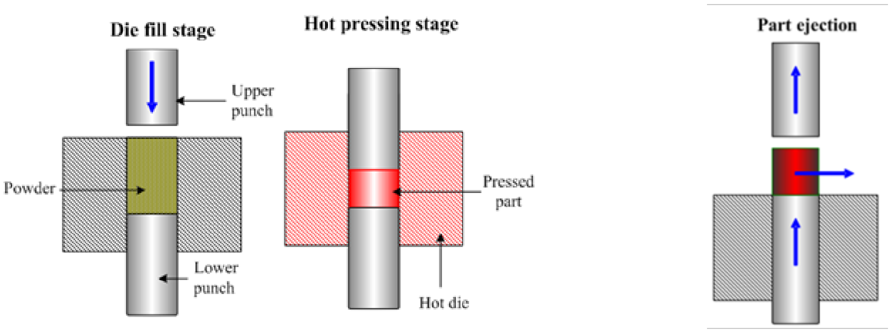
In newly developed process, following methods are included:

1. Vapour deposition process
2. Sandwich processing
3. Disintegrate melt deposition
4. Friction stir processing
5. Metal suttering
6. Microwave assisted hot pressing
7. Molecular level mixing

2.3.1 Solid state process (Powder metallurgy route)

The composite powder initially shaped into desired component shape by following any powder consolidation techniques such as

- Single or double action compaction (figure 2.7)
- Powder extrusion,
- Powder rolling,
- Powder forging, etc.



(a) **(b)**

Figure 2.7: Single action compaction of powder mix.

After manufacturing of green compact, sintering is carried out. Sintering can be of two types:

(1) Solid state sintering and (2) Liquid phase sintering (LPS)

1. **Solid phase sintering:**

   Sintering is diffusion controlled method in which consolidation of powder particles is carried out by means of heating the green compact to a temperature just below the melting point of low melting point constituent. Temperature of the sintering is depends on type of metals. Driving force of this diffusion is the change in surface free energy at different locations on particle surfaces. By doing so, pore volume continuously decreasing which leads to densification of the parts. The moment when the surface free energy change becomes zero, sintering will stop.

   In sintering, green composite compact is subjected to control heating, holding and cooling in sintering furnace. Strengthening of powder component is attributed to atomic diffusion. Following is the list of diffusion mechanism observed during sintering.

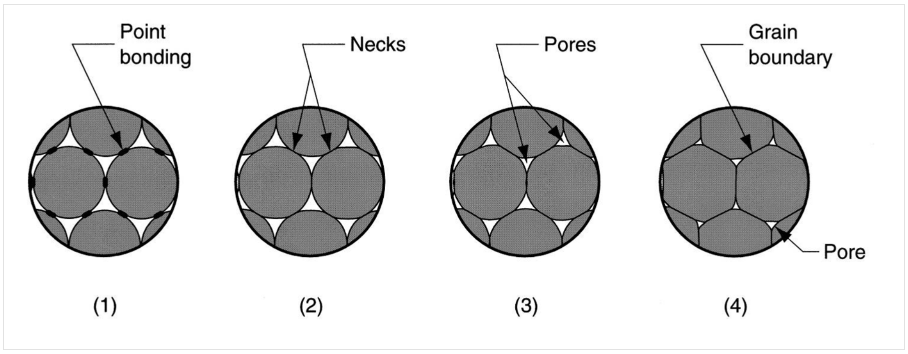


Figure 2.8: Sintering stages: (1) initiation of bonding at contact points; (2) formation of the necks; (3) reduction of pore size; and (4) development of the grain boundaries.

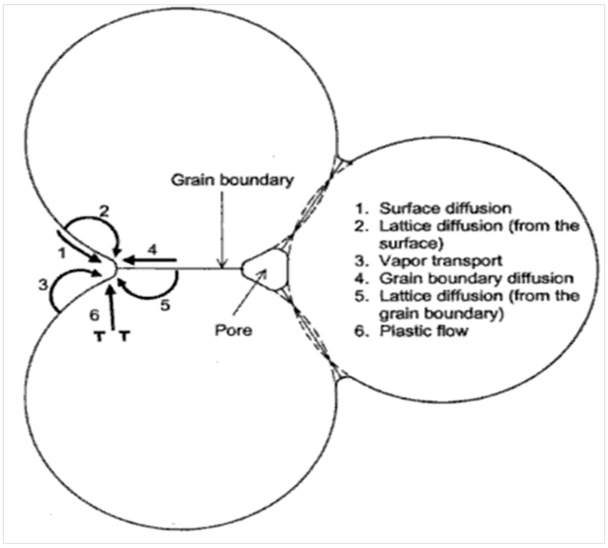


Figure 2.9: Three particle model showing various diffusion mechanisms.

As shown in figure 2.9, a densification during sintering may take place by one of several sintering mechanism as,

- Surface diffusion,
- Lattice diffusion from the surface Volume,
- Vapour transport (Evaporation and condensation),
- Grain boundary diffusion,
- Lattice diffusion from the grain boundary (Recovery and recrystallization) and
- Plastic flow (or) viscous flow

Diffusion is a mass transport mechanism which is based on the concentration gradient of vacancies. Both temperature and chemistry affect the level of vacancy amount. Vacancy gradient exist between two particle surfaces. According to Gibbs-Thomson equation, the driving force for mass transport during sintering can be expressed as,

$$\mu - \mu_o = RTln\left(\frac{p}{p_o}\right) \tag{2.11}$$

Where, μ is initial surface chemical potential and μ_o is final surface chemical potential, R is the universal gas constant , T is the temperature in K and p and p_o are partial pressure over the curved (stressed) and flat (stress free) surfaces. Mass transport occurs from stress free flat surfaces to stressed (curved) surfaces i.e, from convex surface to concave surface of particle joint (called *neck*). Values of p and p_o decide the rate of sintering and mass transport. If the vacancy concentration is considered, then above equation changes to,

$$\mu - \mu_o = RTln\left(\frac{C}{C_o}\right) \tag{2.12}$$

Where, C and C_o are the vacancy gradients around the curved and flat regions. Different variables affecting on all six variables are listed below:

(a) *Surface diffusion mechanism*

$$R_1 = 2D_s\delta_s FK_1^3 \tag{2.13}$$

$$F = \frac{\gamma_s\Omega}{kT} \tag{2.14}$$

Where, R_1 is the neck growth rate for surface diffusion, D_s is surface diffusion, K_1 is curvature difference, γ_s is surface free energy, Ω is atomic or molecular weigh and k is the Boltzmann constant.

(b) *Lattice diffusion mechanism*

$$R_2 = 2D_v FK_1^2 \tag{2.15}$$

Where, R_2 is the neck growth rate for lattice diffusion and D_v is lattice diffusion coefficient.

(c) Vapour transport mechanism

$$R_3 = P_v F K_1 \left(\frac{\Omega}{2\pi \rho_o k T} \right)^{\frac{1}{2}} \tag{2.16}$$

Where, R_3 is neck growth rate for vapour transport mechanism, P_v is vapour pressure and ρ_o is theoretical density.

(d) Grain boundary diffusion mechanism

$$R_4 = \frac{4 D_B \delta_B F K_1^2}{x} \tag{2.17}$$

Where, R_4 is neck growth rate for grain boundary diffusion mechanism, D_B is grain boundary diffusion coefficient and δ_B is effective grain boundary thickness.

(e) Lattice diffusion from the grain boundary mechanism

$$R_5 = 4 D_v F K_1^2 \tag{2.18}$$

Where, R_5 is neck growth rate for lattice diffusion from grain boundaries.

(f) Plastic flow mechanism

$$R_6 = \frac{4}{9} K_1 N_x^2 D_v F \left(K_1 - \frac{3 \epsilon x}{2 \gamma_s a} \right) \tag{2.19}$$

Where, R_6 is neck growth for plastic flow mechanism, N is the dislocation density and ϵ is shear modulus.

Both the shrinkage which occurs due to viscous flow, plastic flow, volume diffusion and grain boundary diffusion as well as shape change of neck which occurs due to surface diffusion and vapour transport (evaporation and condensation) mechanism can be explain by above three particle model [39].

2. **Liquid phase sintering (LPS):**

   In liquid phase sintering (LPS) in binary or ternary system, heating of the compact done in such a way that atleast one liquid phase form in the green compact. During the process, liquid phase spreads around the solid particles leading to the re-arrangements of unmelted particles. Liquid metals also flows in the pores and channels connecting pores. This will give highly dense product. To improve the quality of the product, wettability of the solid surface should be adequate. Figure 2.10 represents the surface tension vectors.

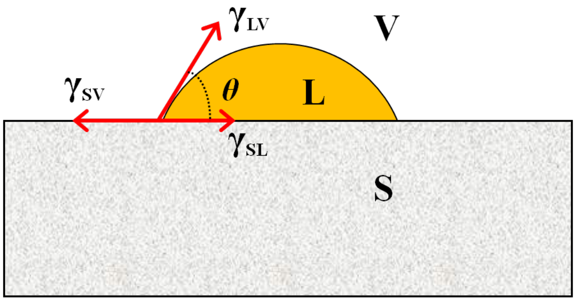
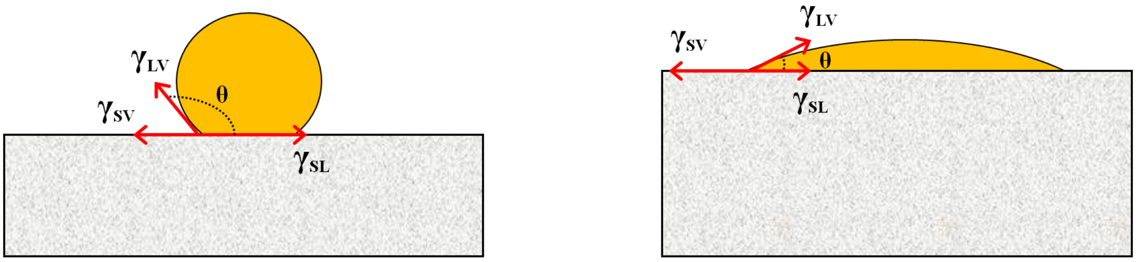


Figure 2.10: Wettability phenomena.



(a) **(b)**

Figure 2.11: (a) Large θ gives non-wetting condition and (b) small θ gives wetting condition.

Various surface energies mentioned in figure are as
γ_{SL} = solid-liquid interface energy
γ_{SV} = solid-vapor interface energy
γ_{LV} = liquid-vapor interface energy

At the triple junction of three phase, surface energies of different interfaces must be balanced. Following equation shows the equilibrium at the triple junction. This equation is known as *"Youngs' equation"*;

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos(\theta) \tag{2.20}$$

$$\gamma_{AB} = \gamma_{BL} cos(\theta_B) + \gamma_{AL} cos(\theta_A) \tag{2.21}$$

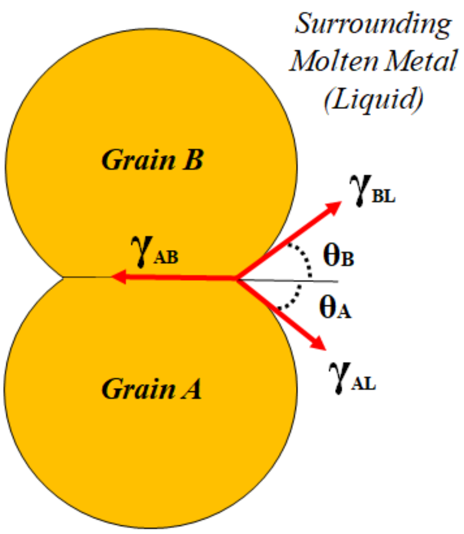


Figure 2.12: Wetting phenomena between two different grains during liquid phase sintering occurs when θ_A and θ_B approach zero.

Requirements in LPS

(a) Initial particle size must be small for larger driving force as it has higher surface energy

(b) Temperature control is necessary as diffusion coefficient not vary much in liquid phase with temperature

(c) Amount of liquid phase must be kept as minimum as possible.

Advantages of LPS

- Very fast rate of sintering due to enhanced kinetics
- Reduced inter-particle friction due to liquid phase presence
- More efficient packing
- Controlled grain size
- Low temperature sintering possible
- Difficult to sintered materials can also be processed easily like silicon nitride

Disadvantages of LPS

- Deshaping or distortion may occur due to excessive liquid phase formation during sintering,
- The final properties depend on the sintered microstructure,
- Product temperature should be kept limited due to the presence of low melting point material.

Examples of LPS

- Cutting and machining tools $(WC - Co)$
- Self lubrication bush bearing $(Cu - Sn)$
- Wear and bearing surfaces $(Al - Pb)$
- Radiation shields $(W - Ni - Fe)$
- Refractories for steel making $(Al_2O_3 - SiO_2)$
- Electrical contact materials $(W - AgorW - Cu)$
- Structural parts $(Fe - Cu - C)$
- Dental amalgam for tooth filling $(Ag - Hg)$
- Soldering alloy $(Pb - Sn)$
- Soft magnetic components $(Fe - P)$
- High temperature turbines $(Si_3N_4 - Y_2O_3)$
- Electrical capacitors $(BaTiO_3 - LiF)$, etc.

By adopting newly developed technology for composite manufacturing by powder metallurgy route; higher densification rate, improved microstructure, improved dispersion, better interface quality, higher stability in different environments, etc. can be achieved. It also offers better efficiency and performance level with minimum scrap. But at the same time, these technological advancements seek higher investment cost. Different reinforcement can be mixed using powder metallurgy method are industrial waste and agriculture waste.

Industrial waste includes:
Fly ash, industrial sludge, wast glass, red mud, slag, mines waste, furnace dusts, etc.
Agricultural and natural waste includes:
Coil fibers, wood ceramics, egg shells, rice hulks, bamboo, etc. [40,41]

N. Raghunathan et al. [42] have fabricated composite using rapidly solidified aluminium powder and alumina powder as mentioned in literature review section. A Olszowka-Myalska et al. [43] have utilized aluminium and titanium powders to synthesis Al_3Ti reinforced in-situ aluminium matrix composite. Aluminium and 9.6 mass % of Ti powders were ball milled. Mixture was then hot pressed in two stage process. In first stage, 1.5 MPa pressure was given at 400 ^oC for 20 minutes. In second stage, 15 MPa pressure was given at 630 ^oC for 20 minutes. Compact was annealed in vacuum at 650 ^oC for 1 hour. SEM-EDS analysis, TEM analysis and XRD analysis was carried out which showed the presence of Al_3Ti in-situ phase. No mechanical property evaluation was performed.

Dispersion reinforced composite and particle reinforced composites are composed of two (or) more elemental materials which may (or) may not alloy during sintering. If the material is not an alloy, several press-sintering cycles require obtaining full density by the solid-state sintering. Since the shrinkage of compact is quite predictable, extremely complex shape of variety of materials can be made by solid-state sintering, eliminating the need for final machining process.

Other classical *examples* of composite materials made by this technique are;

- Tungsten – Copper,
- Silver – Graphite,
- Iron – Copper,
- Nickel – Silver, etc.

The uses of these composites are;

- As a small powder metallurgical structural parts,
- Magnates,
- Gear bushing,
- Electrical compact materials, etc.

2.3.2 Liquid state process

During this process, the reinforcement particles are dispersed into the liquid matrix. Major challenge in this method is to achieve best interfacial bonding between matrix and reinforcements. Use of coated reinforcement particles may be added to deal with this problem sand to enhance the wettability. Such coated reinforcement are not only helps to improve wettability but also enhance interfacial chemical reactions. But this technique of coating the refractory particles may not desirable always as it may change melt chemistry and alter the mechanical properties at the end [44]. In some work, researcher have coated reinforcement particles and seen the effect of it on overall properties [45].

There are two categories in liquid state method such as:

1. Pressureless techniques and
2. Pressure techniques.

1. **Pressureless methods**

   (a) *In-situ dispersoids technique:*
   This method is famous among the other techniques. As mentioned earlier in detail, various ceramics powder particles, nano particles and organic particles are directly added to molten metal as reinforcements. In-situ phases are formed within the matrix having several advantages. Mainly aluminium, copper and their alloys are use as matrix materials. Reinforcements may have one or different types and added in one or more combinations to produce composites. As mentioned by Neeraj et al. [46], types of dispersoid are as follows:

   - Nano particles (10 to 1000 nm),
   - Nano rod (1 to 100 nm with aspect ration 3 to 5),
   - Micro particles (0.1 to 100 μm),
   - Short fiber ($\leq$ 1 μm),
   - Long fiber or multifilament (5 to 30 μm) and
   - Monofilament (100 to 150 μm)

   Main focus to synthesise in-situ MMCs is given in the improvement in conventional mechanical properties such as hardness, toughness, stiffness, chemical properties such as corrosive and chemical resistance. Various strengthening mechanism studied by different researchers are [46],

   - Orowon strengthening,
   - Grain refinement (Hall-Petch effect),
   - Solid solution strengthening and
   - Dislocation strengthening.

   In *Orowon strengthening* or the *dispersion strengthening* mechanism small micron level hard particles are distributed in soft and ductile metal. In MMCs, hard in-situ particles are well dispersed into the ductile matrix in such a way that they become an obstacle in the passage of the dislocation motion. In doing so, finely dispersed phases improved overall strength of the system. To generate such fine particles and to distribute uniformly into the matrix of ductile metals, either stir casting method or powder metallurgy methods can be employed. In this system, small in-situ generated particles (oxides, carbides, nitrides, borides, etc) should have very minimum solubility into the matrix.

   The resistance offered by finely distributed in-situ phases (harden than the matrix) to the motion of dislocations helps to increase strength of overall system. Interaction between the dislocations (line defects) and stress field around the in-situ particles improve tensile strength and hardness properties. Depending upon the amount of generated in-situ particles and their distribution, the extent of strengthening can be observed. Also it is depends on particle size, shape and properties.

In either dispersion strengthening or precipitation strengthening, when dislocations move in the matrix, there are only two possibilities. One in which dislocation is bent and makes a loop around the hard in-situ particles often called an *elastic interaction*. Such looping behaviour of the dislocation lie is described by Orowan and hence it is known as Orowan looping. While in another way, the dislocation has sufficient energy to intersect the hard particles by cutting it into two parts. The later possibility is often known as *plastic interaction*. In former case, the stress required by the dislocation to bent around the hard phase is inversely proportional to the distance between two hard in-situ particles (d). It is obvious that d will increases as the fineness of the generated hard phases increases which will leads to more strengthening effect. Neither too less nor too more interparticle spacing is good for strengthening. In fact, best strengthening can be observed in some intermediate spacing. It is seen that in various particles shapes such as round, disc and needle, needle shaped particles show maximum hardening and strengthening.

$$\tau = \frac{Gb}{d} \tag{2.22}$$

Where, G is the shear modulus, b is the Burgers' vector and d is the mean spacing between the particles. As per above equation, we can calculate the stress necessary to move the dislocation line of length d pinned at both the ends with Burgers' vector of b and shear modulus G.

Average particle distributions of in-situ particles are directly affects the strengthening of the composites. Volume fraction of the added particles along with its radius can give the mean interspacing of in-situ particles as shown below:

$$d = \frac{4(1-f)r}{3f} \tag{2.23}$$

Where f is the volume fraction of spherical particles of radius r.

Depending the value of interparticle spacing, strengthening levels can be different. To get optimized strength, one has to focus on correct spacing. Small and well distributed particles give high level of strengthening compare to coarse and unevenly distributes in-situ particles. Small in-situ particles can arrest dislocation and restrict its motion. This will give more strength [47–50].

(b) *Spray technique*

There are two techniques in this method that are the Osprey process and rapid solidification processing. In the Osprey method, molten metal stream is atomized by atomizing gas. At the same time, dispersoids are injected into the molten metal stream. After atomization, molten metal and fine dispersoids composite particles are forced to the substrate. Once the semi solid particles are deposited, they allow to cool. By doing so, we are getting composite materials shape by spraying method. Also such atomized composite particles can be collected which are later processed by hot forming to give net shape. Temperature of the alloy, speed of the gas jet and temperature of the substrate decide final properties of the composite.

In rapid solidification process, liquid composite slurry is impinges with pressure on rotating water cooled copper wheel. Immediate solidification of the slurry results into flake type composite particles. These particles are then subjected to hot forming where powder mix is shaped into net or near net shape. The final properties of the composite is mainly attributed to the speed of rotating water cooled copper wheel and amount of slurry impinged [37].

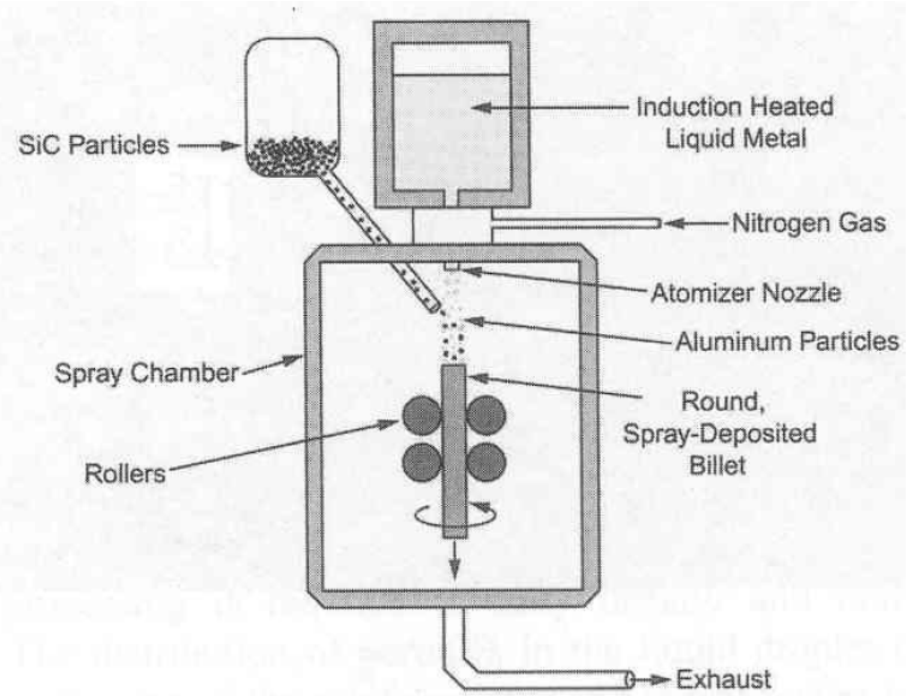


Figure 2.13: Schematic diagram of spray deposition method. [51]

(c) *Dispersion technique*

In dispersion method, there are two techniques such as stir casting and compocasting. Stir casting process was developed by S. Ray in 1968 while making $Al - Al_2O_3$ system [37]. In stir casting method, reinforcement particles are fully disperse into the molten bath by means of stirring action.

Stirring can be achieved by either of the following *four* technique:

i. Mechanical Stirring by impeller (figure 2.15)
ii. Electromagnetic Stirring [52]
iii. Magneto-hydrodynamic Stirring
iv. Ultrasonic Stirring [53]

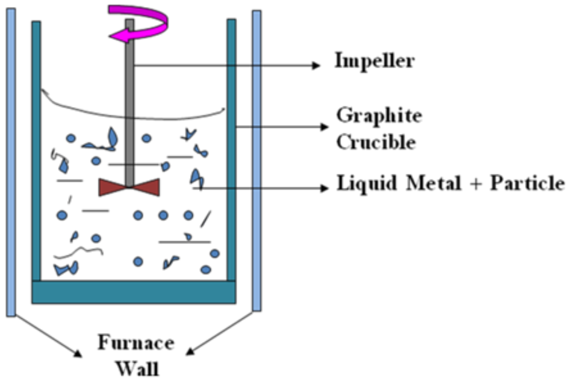


Figure 2.14: Line diagram of stir casting.

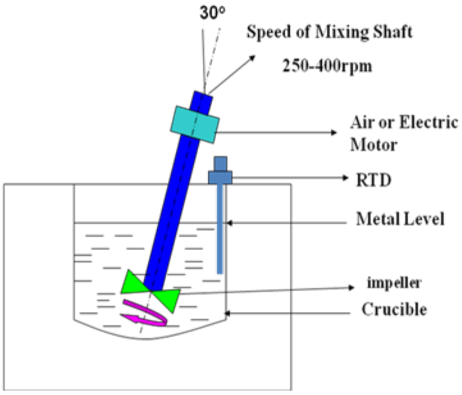


Figure 2.15: Mechanical Stirring by impeller.

There are chances of air bubble entrapment if the stirring speed is high (more than 300 rpm). The inert gas purging may be done for removing the entrapped gas bubbles. Wettability is general issue in this method. Hence to improve wettability of non metallic particles, wetting agent (generally alkali earth element as magnesium) can be added. This is very common method to make MMCs. There are few major concerns in this method are listed below:

- Making a quality interface,
- Dispersion of non metallic particles more than 30 vol. % [54, 55] and
- Segregation and flotation of added reinforcements,

The dispersion of the reinforcement particles is mainly depends upon the followings:

- Geometry of the stirrer,
- Stirring speed and time,
- Position of the stirrer into the melt,
- Size, shape, morphology and properties of the reinforcement and
- Processing temperature.

There is recent development in stir casting called two step mixing. In this process, reinforcements are added in two stages. Initially the melt is melted completely and then brought to the temperature between liquidus and solidus temperature (i.e. semi solid stage) followed by the addition of preheated reinforcements and mixed. After achieving proper mixing, bath is again heated above the liquidus temperature and again mix thoroughly. This two step mixing helps to make good quality interface [56].

Stir casting is the low cost fabrication method having cost of the composite almost one third to one tenth as compared the composites fabricated using other method. The stir casting can produce composite in large quantities (mass production) [57, 58].

2. **Pressure impregnation methods**

   (a) *Melt infiltration technique*

   Perhaps the simplest method of preparing the dispersed phase of continuous-skeleton composite materials is by melt infiltration which is often known as impregnation technique. In this method a green compact is prepared by cold (or) hot pressing of metals (or) oxides powder in a shaped die. The principle of infiltration process is shown in figure 2.16.

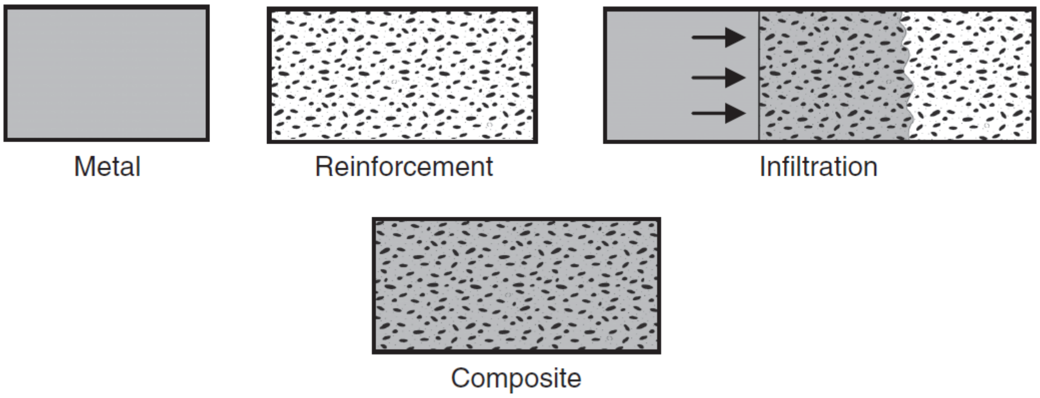


Figure 2.16: Schematic illustration of infiltration process. [59]

There are *four* different approaches to infiltrate preform (figure 2.17) such as:

i. spontaneous infiltration,
ii. squeeze casting
iii. gas pressure infiltration and
iv. centrifugal infiltration.

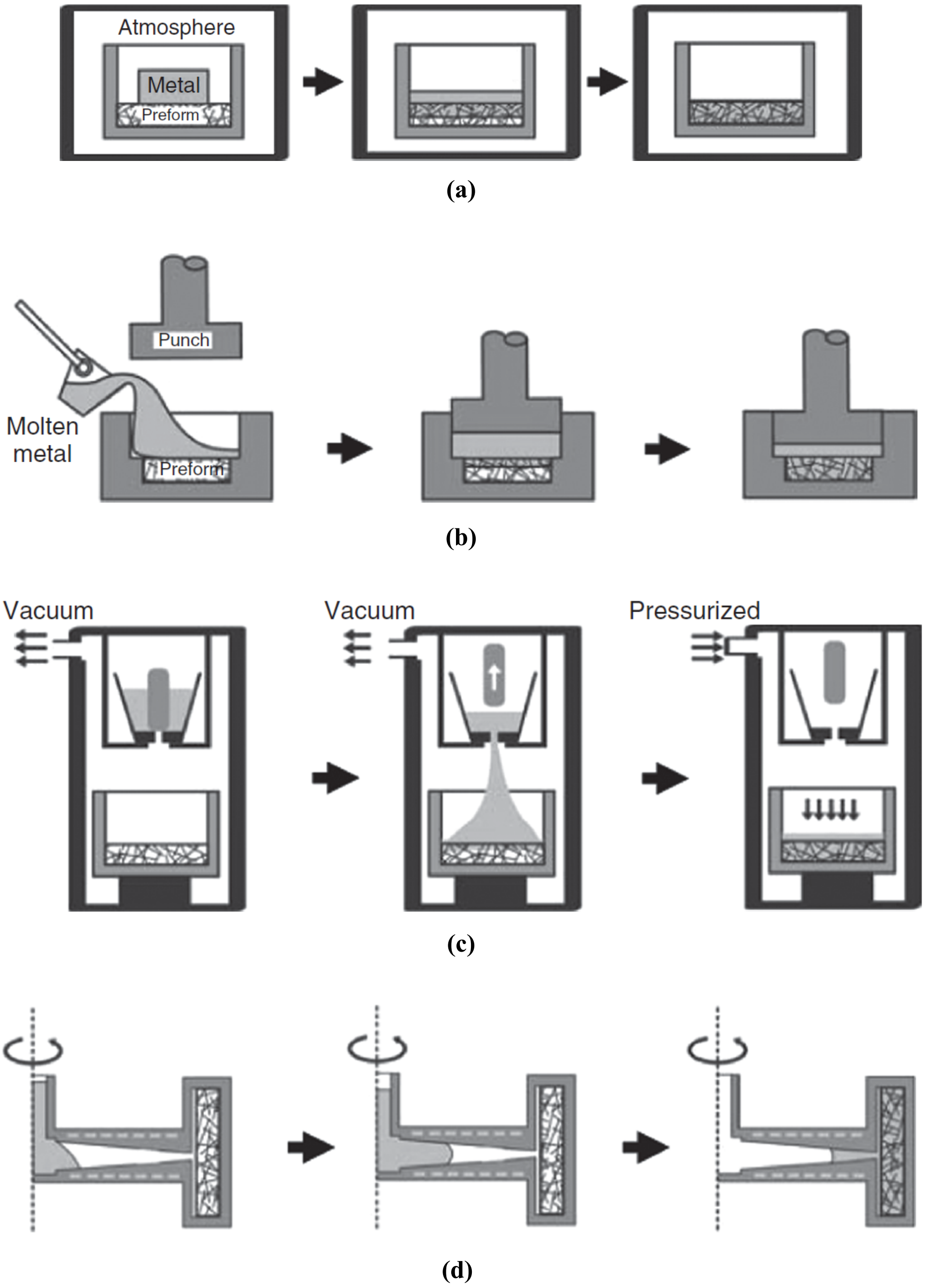


Figure 2.17: Schematic illustrations of major infiltration processes: (a) spontaneous infiltration, (b) squeeze casting, (c) gas pressure infiltration, and (d) centrifugal infiltration.
[59]

In all methods, liquid metal is pressurised by some media or by mechanical plunger so that it can penetrate to long distance pores and uniform density distribution can be achieved. More compact parts can be produced using this technique. Split die is used which opens in two parts after solidification of the casting. Classical example of ideal infiltration couple is Tungsten – Copper.

The prepared powder skeleton is sufficiently strong to handle but has the limited mechanical strength. It consists of 30 to 50% voids, the particles being connected to one another by mechanical interlocking (or) cold welding.

The porous compact is then placed in the furnace with the contact of impregnate and heated above the melting point of impregnate (which must have melting point below the melting point of the skeleton material). To obtain optimum and complete impregnation, the liquid infiltrate and the solid skeleton should be mutually insoluble, and the surface energy should be such that ideal wetting (zero contact angle) occur. If the liquid infiltrate dissolve the skeleton (or) it is soluble in it, impregnation will be incomplete due to skeleton erosion (or) early impregnation freezing.

Capillary flow of liquid metal occurs via channels of porous preform. Net force to rise liquid metal in skeleton depend on balance of capillary force and gravity force. If capillary force is sufficient enough, then liquid metal will rise into the porous preform through all connected pours. But if, gravity force is more then capillary force, additional pressure difference should be given to facilitate metal rise. The direction of the net force is depend upon the configuration of the preform with respect to liquid metal bath. Surface tension force and viscous drag of the molten metal also play vital roles. In either case the resulting composite will be porous and of lower strength than fully dense composite. If the wetting of the molten infiltrate on the skeleton is greater than about 30^o, incomplete impregnation will likewise occur and result in the porous structure.

Infiltration length or height is mainly depends on time of exposure,

$$h^2 = kt \tag{2.24}$$

Where, h is the length or height liquid metal infiltration, k is constant parameter often depend on available effective pressure to overcome net force and t is the time. Constant k should not be negative otherwise, infiltration will not occur. The infiltration index (I) can be given as follows,

$$I = p^2 \gamma_{LV} \left[\left(\frac{1}{\phi} - 1 \right) (cos\theta + 1) \right] \tag{2.25}$$

Where, ϕ is the porosity volume fraction in the preform, γ_{LV} is the surface tension at the interface (liquid-vapour), θ is the contact angle and p is the capillary radius of the channel. Thus better infiltration can be achieved by lowering the contact angle and porosity in the preform [37].

(b) *Lanxide technique*

Lanxide process is similar to melt infiltration. In this process, ceramic preform is kept on the matrix metal or alloy ingot. This assembly is then heated in the furnace to the temperature above the melting point of the matrix metal. Suitable environment is generally used to avoid unnecessary contamination. As the matrix metal melts, it penetrates to ceramic preform by capillary motion. Size of pores, size of ceramic particles, wettability index and infiltration temperature are most important parameters which decide final properties of the composite.

(c) *Squeeze casting technique*

Squeeze casting which is also refer as extrusion casting, liquid pressing, pressure crystallization and squeeze forming is technique of pressing liquid metal or alloy to form sound composite casting. Generally applied pressure is in the range of 31 to 108 MPa. Initially idea was given by Chernov in 1878. But in recent years, industrialization is possible due to advancement of the technology. Main objective of squeeze casting is to force liquid metal to penetrate all pores of the ceramic preform. It has suggested that there were improvements in various properties like the yield strength by 10 - 15%, fatigue strength upto 80% with equal dimensional accuracy as compared to die cast products [60]. In squeeze casting following steps are followed:

i. Pouring liquid metal into the die cavity containing the preform,
ii. Application of pressure through plunger which is connected with the hydraulic press system,
iii. Maintaining the pressure till complete solidification is achieved and
iv. Removal of the casting from the cavity with the help of ejector pins.

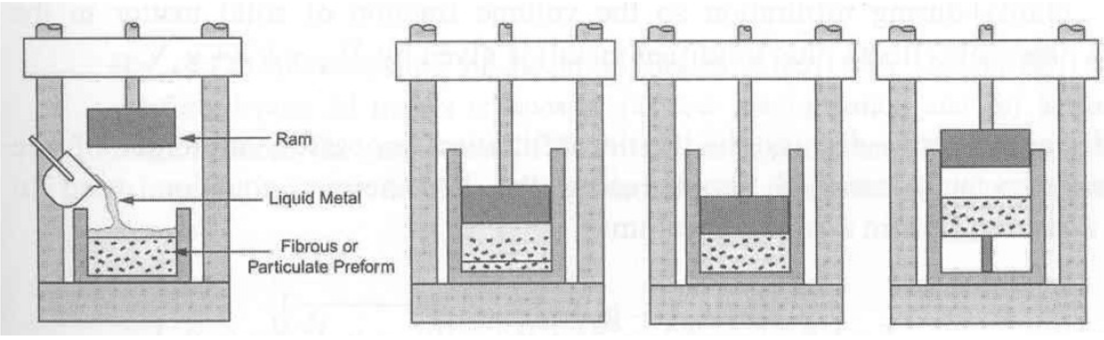


Figure 2.18: Schematic diagram of squeeze casting method.
[51]

Classification of the squeeze casting is shown in figure 2.19. The squeeze casting process was developed to have pore free, fine grained aluminium alloy component with superior properties than conventional permanent mold casting. There are two basic variants of this technique namely, (a) direct squeeze casting and, (b) indirect squeeze casting, as shown in figure 2.20.

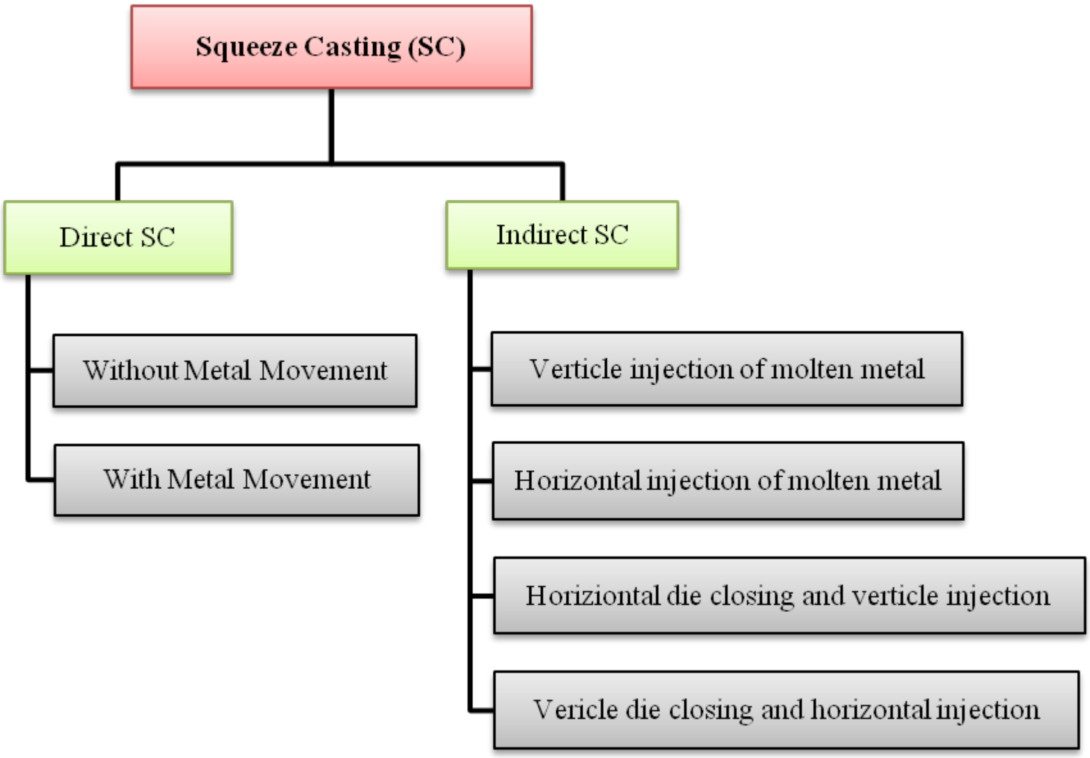


Figure 2.19: Classifications of the Squeeze Casting process [60]

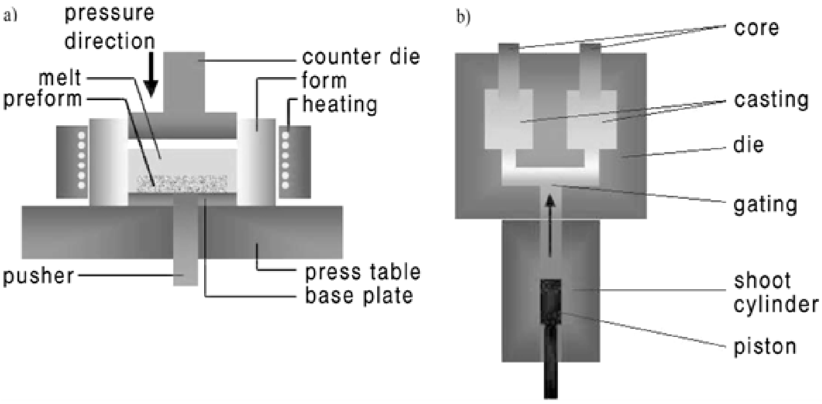


Figure 2.20: Direct and indirect squeeze casting: (a) Direct Squeeze Casting and (b) Indirect Squeeze Casting.

[61]

More precisely, this process basically employed for those aluminium alloy which are difficult to cast by conventional methods, e.g., silicon-free alloy used in diesel engine piston where high temperature strength is needed. The squeeze cast products generally have superior properties than the die cast products due to more density, porosity free structure and better microstructure.

Advance composite materials can be manufactured using squeeze casting process. Using this technique, other metal casting can also be manufactured such as steel and cast iron products, Cu alloys, Mg alloys, Al alloys, etc.

Classical examples of composite materials made by this technique are;

- Tungsten-Nickel-Copper,
- Tungsten-Nickel-Iron,
- Iron-Copper,
- Tungsten-Carbide-Cobalt,
- Titanium-Carbide-Nickel,
- Magnetite (Fe_3O_4)- Wustite (FeO), etc.

These materials can be used for;

- Weights,
- Radiation shields,
- Powder metallurgy structural parts,
- Rock killing bits,
- Refractory bricks, etc. [35]

3. **Newly developed method**

   (a) *Vapour deposition technique*

   Various deposition techniques are developed such as plating, electro-deposition, CVD, PVD, etc. where metal or alloy gets vaporised and deposited to the substrate. In CVD method, vapours of one components is mixed with another component vapour on the substrate at high temperature. In the electro-deposition technique, the electrolyte solution containing matrix metal ions and suspended dispersoids particles are used. Substrate is made cathode on which decomposition reaction takes place and dispersoids particles get entrapped. Example of electro-deposition methods is making nickel matrix composite using nickel sulfamate solution. Another example is making aluminium matrix composite reinforced by silica using $AlCl_3$ - dimethylsulphone electrolyte. This technique has advantages like easy control and rapid solidification. The limitations are void formation and poor interfacial bonding.

2.4 Aluminium Matrix Composites (AMCs)

Aluminium alloy castings are the most versatile of all foundry alloys, because of their unique combination of properties with different alloying addition. Al alloys are characterized by their low specific gravity, low melting temperature, excellent castability, good machinability, better corrosion resistance, good electric and thermal conductivity.

At present the cast aluminium alloy based particulate reinforced composites have promising materials for a number of engineering applications. The application of these materials involves pump bodies, automobile and aerospace. The aluminium series 1XXX, 2XXX, 5XXX, 6XXX and 7XXX are generally employed as matrix metal in advanced composite materials. Particle reinforced MMCs have now become important structural materials. Cast particulate reinforced composite highly recommended particularly for the automobile sector due to ease in fabrication.

2.4.1 About Aluminium

Aluminium is 3^{rd} most available chemical element in the earth crust (see table 2.1). Aluminium is as element of group III of Mendeleev's periodic table. On the outer shell, there are three electrons which are called its valency. There are also monovalent and divalent aluminium compounds, but they are not stable. Activity point of view, aluminium is less active compared to sodium and magnesium. Table 2.3 showing solid solubility of various elements in aluminium. Purity of aluminium is ranging from 99% to 99.999%. There are three different types of aluminium production such as:

1. commercially pure aluminium,
2. refined aluminium and
3. zone refined aluminum.

Table 2.1: Availability of various elements from the earth crust.

Element	weight %	Element	weight %
O	45.2	Na	2.32
Si	27.2	K	1.68
Al	8	Ti	0.86
Fe	5.8	H	0.14
Ca	5.06	Mn	0.1
Mg	2.77	P	0.1

Table 2.2: Generally adopted nomenclature for various degree of aluminium purity.

Aluminium, %	**Designation**
99.50-99.79	Commercially Pure
99.80-99.949	High Purity
99.950-99.9959	Super Purity
99.9960-99.9990	Extreme Purity
Over 99.9990	Ultra Purity

Table 2.3: Solid solubility of various elements in aluminium.

Element	**Temperature** (^oC)	**Max. solid solubility** (wt %)	**Element**	**Temperature** (^oC)	**Max. solid solubility** (wt %)
Cd	649	0.4	Ni	640	0.04
Co	657	<0.02	Si	577	1.65
Cu	548	5.65	Ag	566	55.6
Cr	661	0.77	Sn	228	~0.06
Ge	424	7.2	Ti	665	~1.3
Fe	655	0.05	V	661	~0.4
Li	600	4.2	Zn	443	70
Mg	450	17.4	Zr	660.5	0.28
Mn	658	1.82			

Table 2.4: The density of molten 99.996% aluminium.

Temperature, ^oC	**Density**, gm/cm^3
660	2.368
700	2.357
750	2.345
800	2.332
850	2.319
900	2.304

Aluminium has FCC crystal structure with coordination number 12. It has 4 atoms per unit cell. The value of lattice parameter of aluminum is 4.05 x 10^{-10} m at 298 K based on which the atomic diameter of aluminium can be calculated as 2.86 x 10^{-10} m. From the lattice parameter, aluminium density can be found as 2.72 gm/cm^3 which is almost one third to the steel (7.8 gm/cm^3). The density of cold worked aluminum (polycrystalline form) decreases upto 0.1% to 0.3% at 99% deformation. Different elements affect the density of aluminium in different ways which depends upon the density of added elements. Mainly, the density of aluminium is affected by Fe/ Si ratio as Fe increases the density of the aluminium increases and decreases with Si. Because of its low density, aluminium is more used in transportation and aerospace industries. Strength to weight ratio of aluminium Matrix composite have also been very important consideration as far as engineering design is considered in which properties like stiffness or resistance to buckling are of prime importance. For example iron or steel beam of 10 kg weight will have same stiffness as beam of equal dimensions made up of titanium 7 kg, aluminium 4.9 kg, magnesium 3.8 kg and beryllium 2.2 kg only.

Aluminium has high oxidation resistance due to the formation of thin oxide film which is transparent and highly coherent in nature. The oxide film spontaneously forms upon scratching on the surface of aluminium. Aluminium can resist corrosion in wide variety of mediums like water, salt, chemical and physical agents. Aluminium has highly reflective surface (when it is unanodized) to almost all types of radiation such as visible light, radiant heat and electromagnetic waves. Due to reflective in nature to wide range of wavelengths, aluminium metal can be used in decorative and architectural point of you also.

Aluminium possesses good electrical conductivity as well as thermal conductivity. Some alloys shows high electrical resistivity also. By certain modification by alloying, aluminium can be used in high voltage application such as transmission cables.

Thermal conductivity of aluminium is almost 50% to 60% of the copper which opens up many applications of aluminium in electrical heater, heat exchangers, evaporators, automotive engine cylinder heads and even radiators.

Non ferromagnetic nature of aluminium is very important property due to which it can be used in electrical and electronics applications as well.

Aluminium is also non pyrophoric in nature due to which it can be used in flammable and explosive material handling purpose or in that environment. Non toxic nature of Aluminium is main reason why it can be used in food and beverages industries. Appearance of Aluminium is very attractive upon light polishing and finishing. It’s also possible to give wide variety of colours to aluminium surface by anodizing treatment.

Aluminium also has good workability and the castability. Hence it can be cast by any known method of casting as well as it can be easily rolled to thin foil, forged, drawn to fine wires, spun, stamped to almost any profiles and shapes [62–65].

Types of aluminium and its alloys

There are two major categories of aluminium alloys (1) wrought product and (2) cast products. There are further divisions into above categories depending upon response to thermal energy. That means (1) heat treatable alloys and (2) non heat treatable alloys. Aluminium association system is most widely recognised system to categorise aluminium alloys as per the table given below.

1. Wrought Aluminium alloy designation:

Table 2.5: Designation of wrought aluminium alloys.

Alloy Series	Principle Alloying Elements
1XXX	99.00% Pure Aluminium
2XXX	Cu
3XXX	Mn
4XXX	Si
5XXX	Mg
6XXX	Mg, Si
7XXX	Zn
8XXX	Other elements

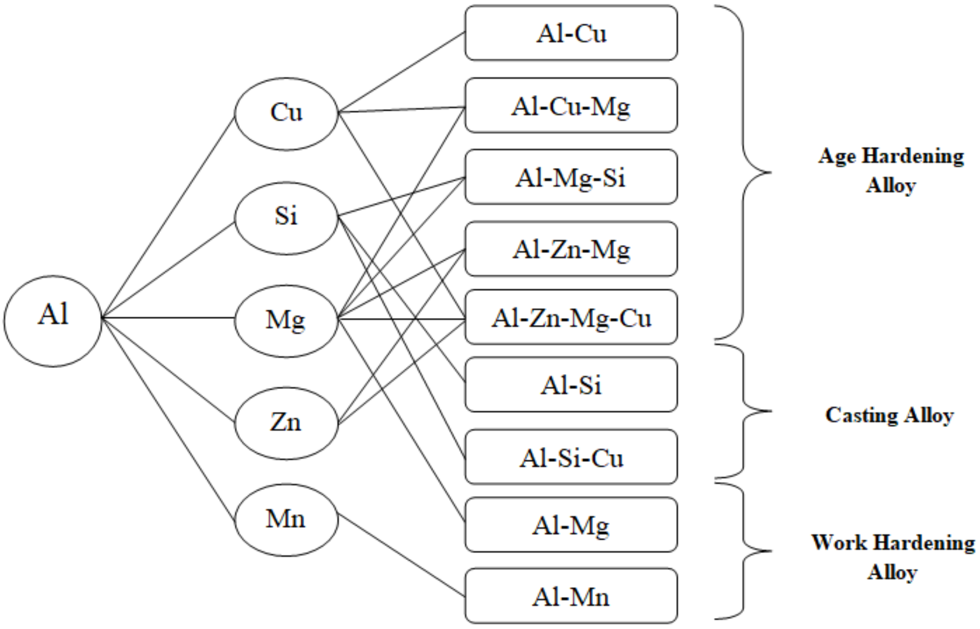


Figure 2.21: The principle aluminium alloys.

1XXX:
It is also known as commercially pure aluminium. All impurity elements like silicon, iron, etc. are very low in amount. All impurities present are in equilibrium state with aluminium forming various stable phases as $FeAl_3$, Fe_3SiAl_{12}, $Fe_2Si_2Al_9$, etc. In addition to this, metastable phase such as $FeAl_6$ may form which has the same crystal structure as $MnAl_6$. 1100 alloy has resistance to corrosion attack due to chemicals or bad weathering.

This alloy is low cost, ductile and easy to weld. This alloy has applications in the electrical and chemical fields. It has high thermal and electrical conductivity, excellent workability, moderate strength. Example of these alloys are 1100, 1350 etc.

2XXX:
This series is also known as Al-Cu alloy. Copper, magnesium, manganese, silicon and iron are present is minor elements. This alloy has various phases in the microstructures like $(Mn, Fe)Al_3$, $(Mn, Fe)Al_6$, Mg_2Si, $CuAl_2$, $(Mn, Fe)_3SiAl_{12}$ and Al_2CuMg. Example of these alloys are 2011, 2014, 2017, 2024, 2219, etc. 2014 is different from 2024 as magnesium content is less and silicon content is high. Alloy 2011 consists of mixture of aluminium, copper, iron and silicon. Normally solution treatment is given to obtain good properties.

In this alloy, mechanical properties are equal or sometimes even better than low carbon steel. When precipitation hardening or age hardening is given to this alloy, further increase in the yield strength can be observed at the cost of strength and ductility. This alloy has low corrosion resistance compared to that of the other aluminium alloys and may subject to the intergranular corrosion in some instances. Hence galvanic protection must be given by appropriate aluminium alloy to protect it from corrosion when it is used. This alloy is commonly used to make truck frames, aircraft structures, automotive parts as cylinder and piston, machine parts, fasteners, high strength structural application, etc.

3XXX:
This series is also known as Al-Mn alloy. This alloy can be compared with 1XXX alloy. In this alloy manganese content little more than 1XXX and hence properties like strength 20% more than 1XXX. Mn up to 1.5 wt % can be added into aluminium effectively. 3003 is a popular alloy in this class of aluminium alloy series. In this alloy, various phases are formed during manufacturing such as $(Mn, Fe)Al_6$ and $(Fe, Mn)_3SiAl_{12}$.

Applications of these alloys are in manufacturing of fuel tanks, chemical equipments, cabinets, pressure vessels, agricultural applications, architectural applications, building products, hospital and medical equipments, etc.

This alloy has slightly improved formability and weldability then 1XXX alloy. Examples of these alloys are 3003, 3004, 3105, etc.

4XXX:

It is also known as aluminium silicon alloy. The addition of silicon up to 12 wt % in this aluminium can decrease the melting range. Even though being non heat treatable alloy, this series alloy is used to make consumables in welding and brazing due to its good joining characteristics. Example of these alloys is 4343.

5XXX:

Magnesium is a major alloying element in the series of alloys. Depending upon the level of magnesium, different phases are formed such as Mg_2Al_3, Mg_3Al_2 (metastable phase), etc. which precipitate at grain boundary or within grain. Sometimes along with magnesium chromium may also be added forming $Cr_2Mg_3Al_{18}$ or when Mn is present, it may form $MnAl_6$ as dispersoids. Magnesium is considered to be more effective than manganese as a hardening agent. For example, 0.8 wt % magnesium is equivalent to 1.25 wt % manganese. Good weldability and good corrosion resistance to marine environment are unique characteristics of these alloys.

This series alloys are used to fabricate pressure vessels, fan blades, tanks, electronic panels, electronic chassis, hydraulic tube, agricultural equipments, architectural parts, automotive parts, building products, chemical equipments, containers, cooking utensils, fasteners, hospital and medical equipments, kitchen equipments, marine applications, railroad cars, trucks and trailers, cable sheathing, rivets, zippers, fence wire, cryogenic equipment parts, freight cars, TV towers, drilling rings, transportation equipment parts, missile components, dump truck bodies, etc. Example of alloys in this series are 5005, 5050, 5052, 5056, 5083, 5086, 5182, 5183, 5154, 5252, 5254, 5356, 5456, 5457, 5554, 5556, 5652, 5654, etc.

6XXX:

In these alloys series, magnesium and silicon are the main alloying elements in aluminium. This series alloys are not as strong as 2XXX alloys but 6XXX is good for formability, weldability, machinability and corrosion resistance. The precipitation hardening effect due to formation of stable Mg_2Si phase is common in this series. Mg_2Si can dissolve into the matrix upon solutionizing treatment. Common alloys in this series are 6003, 6009, 6010, 6013, 6053, 6061, 6063, 6066, 6070, 6101, 6151, 6201, 6205, 6253, 6262, 6351, 6463, etc.

Application of these alloys are in manufacturing of truck components, railroad cars, pipelines, marine equipment parts, agricultural equipment parts, aircraft parts, building products, automotive parts, architectural parts, chemical equipment, dump bodies, fence wires, fasteners, electrical and electronic components, fan blades, general sheet metal products, highway sign boards, hospital and medical equipments, kitchen utensils, storage tanks, etc.

7XXX:
Zinc is added upto 8 wt % to fabricate 7XXX alloys as a major alloying element. Other elements such as magnesium, copper and chromium may also be added to enhance certain properties. Additions of Mn, Zr and Zn elements are also seen to fabricate these alloys. Microstructures normally contain Mg_2Si, $(Fe, Cr)_3SiAl_{12}$, $MgZn_2$, etc. If iron is found in chemical analysis then there are strong chances of formation of Al_7Cu_2Fe along with above mentioned phases or dispersoids. The quantity and size of dispersoids depends on the individual composition and prior thermal history. Strength of such alloys is normally higher as compared to previous alloys at the same time they are costly too. These alloys can be used in aircraft and other structural components mainly. Examples of alloys in this series are 7001, 7005, 7008, 7010, 7049, 7050, 7072, 7075, 7079, 7108, 7115, 7149, 7150, 7178, etc.

8XXX:
In this alloy series, other elements are added such as Ce, Li, V, etc. This has high elevated temperature properties plus strength due to dispersion strengthening mechanisms by various dispersoids. When they contain Li, it possesses low density and higher stiffness. Examples of these alloys are 8009, 8019, 8090, etc. Commonly these alloys are used in some aircraft and aerospace applications like helicopter parts [36, 65, 66].

2. Cast Aluminium alloy designation:
   Cast alloy designation system is similar to the wrought designation system except this designation system has three digits plus some value in decimal like XXX.X. Silicon in cast aluminium alloys is higher compared to wrought alloys. In cast alloys silicon ranges from 4 to 12 wt% of aluminium. Silicon is responsible for increasing casting properties of aluminium. Alloys containing less than 12 wt % silicon are termed as hypoeutectic, at 12 wt % silicon is eutectic whereas at more than 12 wt % silicon they are known as hypereutectic alloys. Strengthening mechanisms and response to thermal treatment are same as wrought aluminium alloys.

   1XX.X:
   This alloy has 99% aluminium minimum which is known as commercially pure aluminium.

Table 2.6: Designation of cast aluminium alloys.

Alloy Series	Principle Alloying Elements
1XX.X	99.00% Pure Aluminium
2XX.X	Cu
3XX.X	Si, Cu, Mg
4XX.X	Si
5XX.X	Mg
6XX.X	Unused series
7XX.X	Zn
8XX.X	Sn
9XX.X	Other elements

2XX.X:
This aluminium copper group contains 4% to 6% Cu and 0.25 to 0.35% Mg. This alloy shows the highest strength as well as hardness and they are used almost everywhere. In this alloy minor amounts of Mn, Cu, Cr, Ni, V, etc. are also added to improve other related properties. These alloys show the highest hardness and strength among other cast alloys. Using appropriate heat treatment these properties can be further improved. Examples of cast alloys in this series are A201.0, 202.0, 204.0, A206.0, 222.0, 224.0, 238.0, 240.0, 242.0, 243.0, etc.

3XX.X:
In this series aluminium contains magnesium and copper both along with silicon into it. Also Ni and Be can be added in some cases. Silicon contains in the range of 5 to 22% where copper can be added upto 4.5% and 0.3% to 0.6% magnesium. Both Copper and magnesium increase strength and hardness in as cast condition of the alloys which can further increase by artificial ageing or by combination of solution treatment and artificial ageing. Various precipitates like Mg_2Si, Al_2Cu, Al_2CuMg, etc. can be seen in microstructure. This alloy also has improved high temperature properties and low thermal expansion coefficient due to silicon and nickel which can be helpful in the application like engine parts. Examples of the alloy in this series are 332.0, 336.0, 356.0, 361.0, 380.0, 384.0, 393.0, etc.

4XX.X:
This cast aluminium alloy group also known as binary Al-Si alloy because Si is a major

alloying element. 5% to 12% Si is commonly added in 4XX.X alloys to obtain properties like high ductility, impact resistance with moderate strength and hardness. See figure 2.22 for phase diagram of Al-Si alloy.

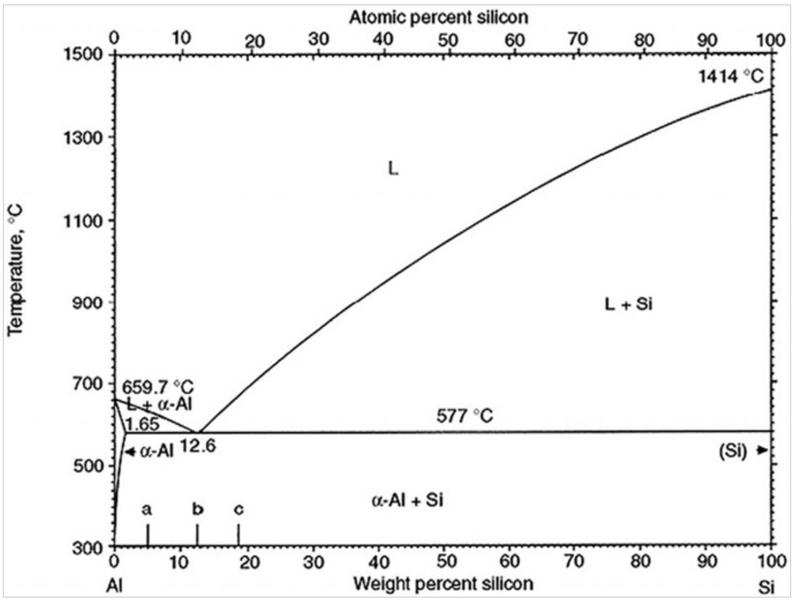


Figure 2.22: Phase diagram of aluminium silicon alloy.

5XX.X:

Magnesium is the primary element in this series of alloys. These alloys possess moderate to high strength along with improved toughness properties, high corrosion resistance, machinability and appearance properties. These alloys can be used in marine applications, decorative items, building parts etc.

6XX.X:

This series is an unused series and hence not considered here.

7XX.X:

Zinc is the primary alloying element here in aluminium. Magnesium can be added along with zinc as a secondary alloying element. In combination, both elements help to improve properties like corrosion resistance, strength, finishing characteristics, etc.

8XX.X:

This alloy series is also known as Al-Sn alloys because of addition of tin as primary alloying element upto 6% along with copper and nickel as secondary alloying elements. Due to tin, lubricity can be improved and hence these alloys are used to manufacture bearings and bushes.

Aluminium temper designation system:

- **F** - As fabricated
- **O** - Annealed,
- **B** - Strain hardening,
- **W** - Solution heat treated,
- **T** - Thermally treated

Subdivisions of HR designation:

- **H1** - Strain hardening only,
- **H2** - Strain hardening and partially enabled,
- **H3** - Strain hardening and stabilised,
- **H4** - Strain hardening and painted

HX2 - Quarter hard, **HX4** - Half hard, **HX6** - Three quarter hard, **HX8** - Full hard, **HX9** - Extra hard.

Subdivisions of T designations:

- **T1** - Naturally aged after cooling,
- **T2** - Cold worked and naturally aged,
- **T3** - Solution heat treated, cold worked and naturally aged,
- **T4** - Solution heat treated and naturally aged,
- **T5** - Artificially aged,
- **T6** - Solution heat treated and artificially aged,
- **T7** - Solution heat treated and stabilised or over aged,
- **T8** - Solution heat treated, cold worked and artificially aged,
- **T9** - Solution heat treated, artificially aged and cold worked,
- **T10** - Cold worked and artificially aged,
- **T-51** - Stress relieved by stretching,
- **T-52** - Stress relieved by compressing,
- **T-54** - Stress relieved by both stretching and compression.

Effect of alloying elements:

The alloying elements affects various properties of aluminium and its alloys in terms of physical properties, mechanical properties, chemical properties, microstructural properties, technological properties, etc. Different elements that are added in aluminium are Cu, Mn, Mg, Si, Zn, Cr, Co, Sb, As , Be, Bi, B, Cd, Ca, Ce, Ga, Zn, Fe, Pb, Li, Mo, Ni, etc. and even mixture of these elements. Below only few elements and their effects are listed:

Magnesium:
It can be soluble in aluminium up to 17.4%. Magnesium precipitates at the grain boundaries as high anodic phases like Mg_5Al_3 or Mg_5Al_8 which makes alloys suitable to stress corrosion cracking. Magnesium generally increases strength of the alloy at the cost of ductility. It also improves difficulties in forming and generally forms cracking during hot rolling. There are also chances of formation of FCC Al_3Mg_2 or Al_2Mg_3 depending upon the amount of magnesium in aluminium. If S is present, magnesium tends to form Mg_2Si precipitates to increase strength. But if iron is present, then it affects strength inversely.

Manganese:
It is considered as an impurity in aluminium when it is present upto 50 ppm. It has very limited solubility in aluminium. Mn increases strength, grain refinement, formability and corrosion resistance. Mn precipitates in the form of $(Mn, Fe)Al_6$, $(Fe, Mn)Al_{12}Si$, $Al_{20}Cu_2Mn_3$, etc. depending on the presence of other impurities like iron and silicon in aluminium. Manganese reduces the solubility of iron and silicon in aluminium. It also improves elevated temperature properties in Al-Si alloy. See figure 2.23.

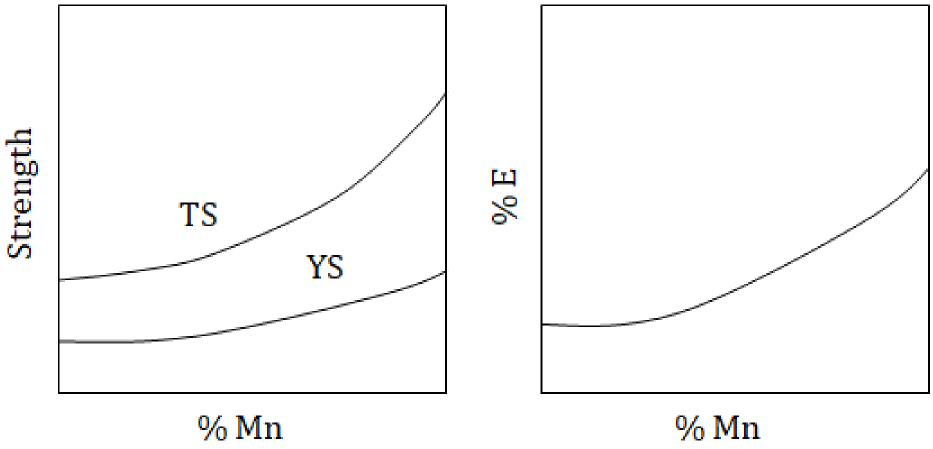


Figure 2.23: Variation of properties with manganese amount.

Silicon:
After iron, silicon is considered as another impurity in commercial pure aluminium which

present in the range of 0.01 to 0.15 wt % to as high as 1.5 wt % in wrought alloys. Adding silicon into aluminium reduces its tendency towards cracking and brittleness. Silicon improves castability and fluidity of molten aluminium.

Iron:

Iron is the most common impurity found in aluminium. Iron is generally present in aluminium as intermetallic due to its limited solubility up to 0.05 wt % in solid state of aluminium. It improves strength slightly but at high temperature better creep resistance can be obtained. Iron helps in grain refinement also. Iron forms different phases with aluminium like Al_3Fe, Al_6Fe, etc. depending upon the amount of iron in aluminium and solidification rate. When silicon is present, it can form alpha and beta phases. Alpha phase has cubic crystal structure which generally appears as “Chinese script” eutectic whereas beta-phase appears as needles or platelets. Sometimes, it is observed that when iron is present, it reduces stickiness between mould and the casting.

Carbon:

Carbon is also considered as an impurity in aluminium. It forms carbide of aluminium such as Al_4C_3. If other elements are present such as manganese and silicon then carbon can form complex carbides in the microstructure during solidification such as Mn_3AlC. Mn_3AlC is known as the Mn rich kappa phase which is responsible for age hardening. It has magnetic properties and can improve strength and hardness of the overall system.

See the figure 2.24 showing effect of various major elements on yield strength of aluminium in annealed state.

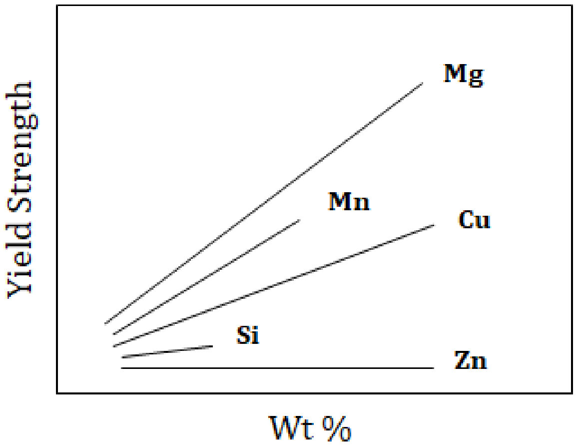


Figure 2.24: Variation of yield strength with different elements.

Apart from alloying elements and impurities, various microstructural constituents also change Mechanical properties such as

1. *Coarse intermetallic compounds:* Compounds such as $(Fe, Mn)Al_6$, Al_3Fe, Al_7Cu_2Fe, α-(Fe,Mn,Si)Al, etc. are often known as insoluble compounds which are generated due to impurities such as iron, manganese and silicon in aluminium. Other types of compounds which are having soluble constituents consist of equilibrium intermetallic compounds such as Al_2Cu, Al_2CuMg and Mg_2Si.

2. *Smaller submicron particles or dispersoids:* These particles are generally of 0.05 to 0.5 micron in size. Examples of such compounds are $Al_{20}Mn_3Cu_2$, $Al_{12}Mg_2Cr$ and Al_3Zr. These particles reduce recrystallization and grain growth while processing as well as during heat treatment.

3. *Fine precipitates:* Size of these particles is generally up to 0.1 micron. These particles give more effect on strengthening during age hardening.

4. *Grain size and shapes:* Major effect on mechanical properties is due to the shape of grains and their sizes. During solidification, more nucleation led to fine grain size structures. In aluminium response to grain growth is very high upon heating. During hot working of wrought products, aluminium experiences dynamic property variations depending on size and shapes of the grains.

5. *Dislocation substructure:* During cold working, dislocation substructure and formation of sub-grains normally observed which can further improve the mechanical properties.

6. *Crystallographic texture.*

Melting point of aluminium is very sensitive to purity. Specific heat of aluminium increases very sharply initially with respect to the temperature raise upto 300 K. After 300 K, growth in specific heat is slow.

Thermal conductivity of pure aluminium rises steeply to a maximum at approximately 20-30 K, drops rapidly first and then slowly reach minimum value at room temperature. Again, purity plays vital role in all these values. Both elastic and plastic deformation changes the thermal conductivity upto 2-3% at the most.

As shown in the table 2.7, the temperature increases, lattice expansion is observed which leads to overall metal thermal expansion. Thermal expansion [$L_T = L_0(1 + \alpha T + \beta T^2 + \gamma T^3)$], where α, β and γ as the coefficient value given in literatures] of aluminium is generally found on (1 1 5), (0 2 4) and (2 2 2) planes upto 493 K. Only metals having expansion coefficient larger that aluminium are Mg, Zn, Li, etc. increase it, all the others ones reducing it.

Various mechanical properties of aluminium is shown in table 2.8. Hardness of aluminium alloys is ranges from 180 MPa for commercial metal dead soft to 2000 MPa on Vickers scale for solid solution heat treated condition. Strength as well as hardness both decreases as purity level of aluminium increases. Percentage elongation of 99.99% pure aluminium metal is 25% to 65%. Low Fe/ Si ratio produces slightly higher strength. Cu is only one metal that produces measurable increase in strength.

Table 2.7: Thermal expansion of aluminium.

Temperature, K	**Thermal Expansion,**α (X $10^{-6}K^{-1}$)	**Temperature,** K	**Thermal Expansion,** α (X $10^{-6}K^{-1}$)
25	0.5	350	24.1
50	3.5	400	24.9
75	8.1	500	26.5
100	12.0	600	28.2
150	17.1	700	30.4
200	20.2	800	33.5
250	22	900	37.3

Table 2.8: Mechanical properties of aluminium.

	Amount of cold work	*UTS (MPa)*	*YS (MPa)*	*%E*	*Hv (MPa)*
High Purity (99.999%)+	Annealed	40-50	15-20	50-70	120-140
	40%	80-90	50-60	15-20	220-240
	70%	90-100	65-75	10-15	260-280
	90%	120-140	100-120	8-12	320-350
Commercially Pure (99% to 99.7%)	Annealed	80-120	30-60	25-50	180-250
	40%	120-180	100-150	5-10	300-350
	70%	170-250	120-200	2-6	400-500
	90%	250-300	220-280	1-4	450-500

Most mechanical properties increase with decreasing temperatures. Above room temperature, hardness, strength and impact resistance decreases whereas plasticity increases. The strength at high temperature can be increased by Si and more by Fe. Elongation of 99.99% pure aluminium increases with decreasing temperature to 65-70% at 70 K but then increase afterwards above

400 K. Rapid increase in strength found below 70 K. Level of cold work increases the strength but decreases the ductility. Strength shows a maximum when [1 1 1] direction is parallel to stress direction while maximum elongation corresponds to the stress at 45^o to the [1 1 1]. Fine grains give high strength and hardness and it decrease the elongation [36, 63, 65–69].

2.4.2 Reinforcement used to make AMCs

Each alloying element imparts distinct properties of aluminium. The most widely and best developed aluminium matrix composite (AMC) systems are those made using reinforcement with SiC, alumina (Al_2O_3) and graphite. The most widely used matrix system for AMC is generally commercial pure aluminium (LM 0) and 6XXX which has 10 to 13 % Si (LM 25).

The SiC dispersed composites exhibited good wear resistance and mechanical properties for various engineering applications including automotive. The composite systems investigated in the laboratory and some specific observations are explained below in brief;

1. Coconut shell char: Up to 30 vol. % of coconut shell char could be incorporated in Al-alloy matrix. About 5 vol.% of the shell char in the matrix could impart adhesive wear resistance to the matrix. The presence of particles in the matrix reduces the tensile property. The composite made with this system can be used for mild wear resistance applications under low loads and pressure.
2. Zircon ($ZrSiO_4$): Up to 30 wt. % zircon can be introduce in Al-matrix. This will improve hardness as well as wear resistance of the composite.
3. Zirconia (ZrO_2): About 5 vol. % of ZrO_2 particles (2-10 mm size rang) can be introduced in the Al-alloy matrix. Hardness, tensile properties (UTS, YS and % Elongation) as well as high temperature strength can be improved.
4. Titania (TiO_2): In wrought alloy (7020) matrix with 5 wt.% TiO_2 (0.01 to 10 mm) get superior UTS and % Elongation at room temperature as well as up to 523 K.
5. Fly ash: About 30 vol. % of fly ash can be introduced in Al-alloy matrix. With increasing amount of fly ash, UTS, % Elongation and density of the composite is decrease.
6. Glass powder: The ground borosilicate glass particulates incorporated in AMC where it got fibrised during extrusion in the direction of the extrusion. The tensile properties of this extruded AMC are much superior to the base metal.
7. Graphite powder: About 50 vol. % graphite can be prepared which can be diluted to the require level by dissolving it in the base alloy.

8. Short carbon fiber: Short or chopped carbon fiber of the length 1, 3 and 6 mm introduced in Al-alloy matrix. About 8 % carbon fibers improve the UTS by about 10% and modulus by about 15%. Marginal improvement in the properties be seen when short carbon fibers having length less than critical one.

The AMCs are generally have 2XXX and 6XXX series as the matrix materials whereas the reinforement materials could be Alumina (Al_2O_3) and silicon carbide (SiC) particles. Other reinforement phases are continuoes fibers like alumina, silicon carbide, graphite, etc.

The AMCs are manufactured using any of the fabrication methods such as powder metallurgy (sintering), stir casting or infiltration.

The common *properties* found in AMCs are elevated temperature strength, stiffness, low density, improved thermal conductivity, high abrasion resistance, etc.

The AMCs are used for manufacturing automotive parts (pistons, push rods, brake components), brake rotors for high speed trains, bicycles, golf clubs, electronic substrates, cores for high voltage electrical cables [36, 66, 70].

It has been seen that there are TWO different approached of making metal matrix composite materials namely, (1) Ex-situ method and (2) In-situ method.

2.4.3 Ex-situ method:

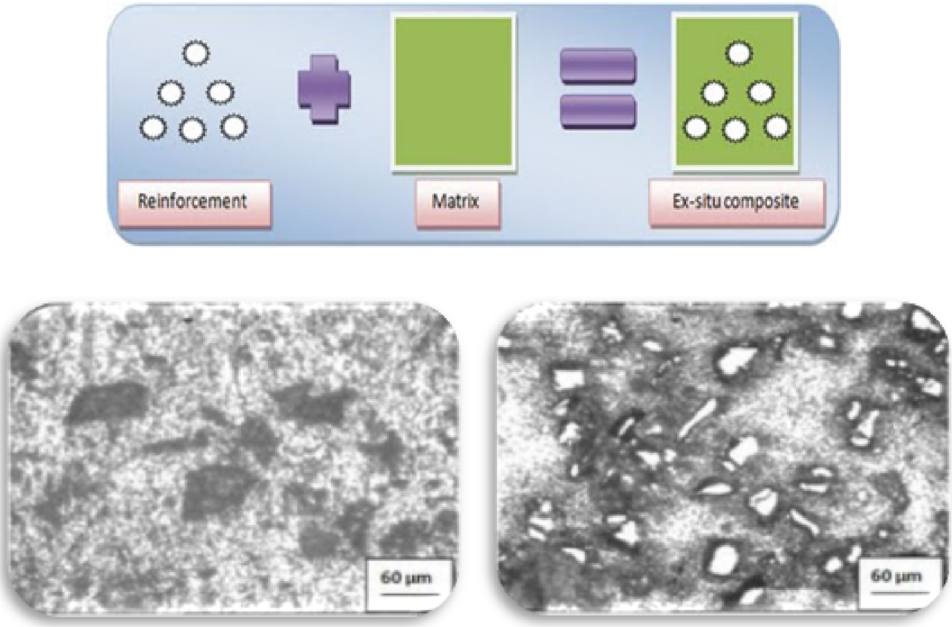


Figure 2.25: Ex-situ composite and microstructures showing various phases in (a) $AA7075Al - SiC$ and (b) $AA7075Al - Al_2O_3$

In ex-situ method, reinforcements are synthesised and modified externally before adding them into the liquid metal. The composites manufactured by ex-situ method always having poor thermodynamic stability between matrix and reinforcement. They are also having poor high temperature properties. Several defects such as agglomeration and uneven microstructure can be seen in ex-situ composites [71].

2.4.4 In-situ method:

In in-situ method, reinforcements are synthesised and modified internally in the molten matrix metal where they transform to another thermodynamically stable phase. Such induced phases are more coherent to the matrix which improve the properties of the composite by principle of combined action. In-situ generated particles also have fine size, uniform distribution and improved interfacial bonding [31, 71].

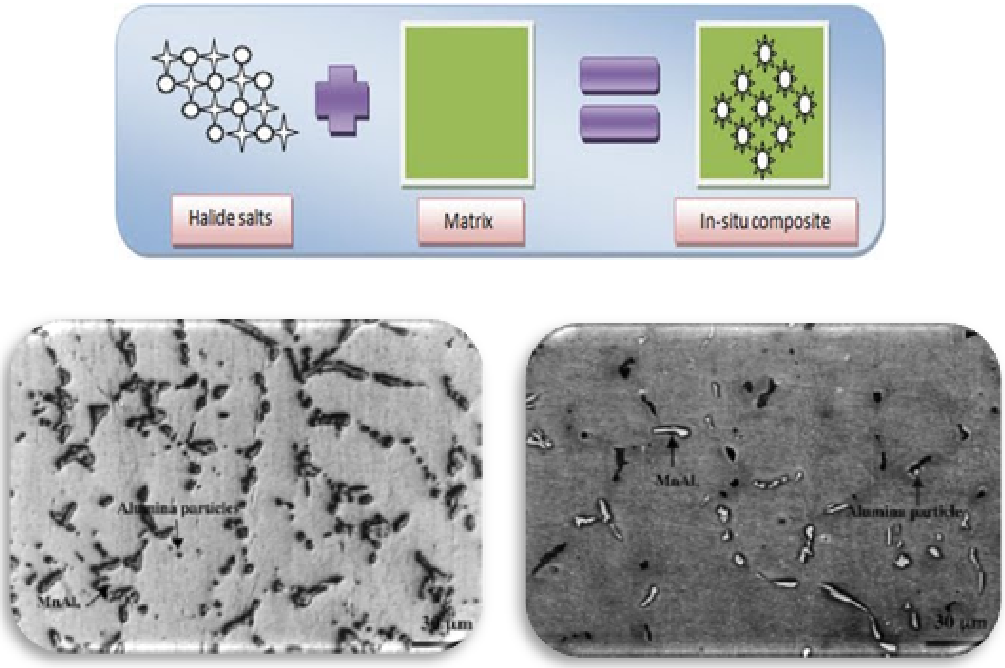
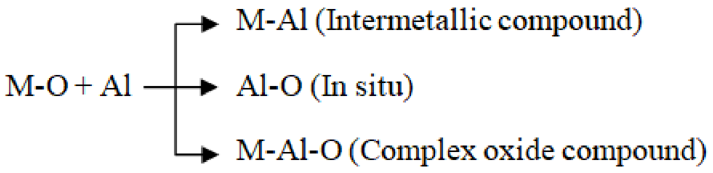


Figure 2.26: In-situ composite and microstructures showing various generated phases.

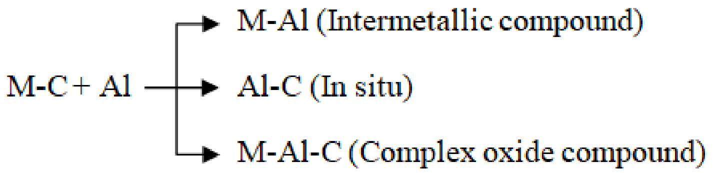
As per the comparative study between ex-situ and in-situ $AlSi_5Cu_3$ - 3% TiB_2 metal matrix composite system by Ayar and Sutaria [72], more stable TiB_2 intermetallic particles along with distinct and reaction free interface have been developed in in-situ method. Compared to the ex-situ system, in-situ composite showed homogeneous distribution of generated TiB_2 in-situ particles in the matrix which leads to the improved average values of hardness and ultimate tensile strength.

Variety of in-situ phases are as shown in following different cases:



Other MO = Cr_2O_3, Fe_2O_3, TiO_2, SiO_2, B_2O_3, MoO_3, etc.

Figure 2.27: Case I: Addition of MO in molten aluminium



E.g., For MC = TiC

$$13\,\mathrm{Al} + 3\,\mathrm{TiC} \longrightarrow 3\,\mathrm{Al_3Ti}\,(\mathrm{Intermetallic}) + \mathrm{Al_4C_3}\,(\mathrm{In\,situ}) \tag{2.26}$$

Other MC = SiC, B_4C, etc.

Figure 2.28: Case II: Addition of MC in molten aluminium.

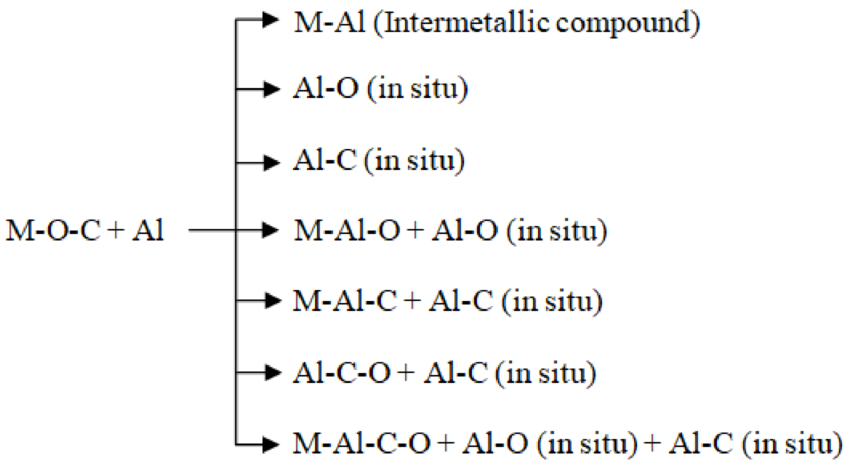


Figure 2.29: Case III: Addition of MOC in molten aluminium

As stated earlier, in-situ composites can serve many useful properties that normal composites cannot fulfil. In-situ composites consist of in-situ phases that are thermodynamically stable, highly coherent with the matrix, tiny in size and high temperature stable with clean interface. This in-situ phase possesses strong interfacial bonding. Through the interface, load can be shared from the matrix to the reinforcements which are generally stronger than the matrix. Optimum interface thickness is required for effective load sharing and improving overall strength of the composite by the principle of combined action. To enhance interfacial bonding and to achieve clean as well as uniform thickness of an interface around the reinforcing particles, it is important to have good wettability of the reinforcement particles with the matrix metal. For effective strengthening, the reactions at the interface (interfacial reactions) should be controlled by balancing reaction zone (processing time and processing temperature of fabrication) so that proper bond can be formed.

Since reinforcement particles are ceramic and matrix is the metal, the wettability always lacking between the matrix and the reinforcement. To enhance interfacial characteristics and wettability, alkali earth metal is added such as magnesium. Main role of alkali earth metal is to decrease surface tension of the liquid matrix metal so that it can wet ceramic particles effectively. Addition of 3 wt % magnesium metal into liquid aluminium can decrease surface tension from 7.6 dNm^{-1} to 6.2 dNm^{-1} at 720 ^{o}C [6]. Also increasing Mg content, can reduce contact ange and improve wetting as observed by Ali Sangghaleh et al. [73] in his paper on effect on magnesium addition on the wettability of alumina by aluminium. In this paper, researchers have compared $Al - Al_2O_3$ system with $Al - Mg - Al_2O_3$ system and found improved interface quality at lower temperature when Mg is added. There are three ways of getting in-situ dispersion:

1. Metal – oxide reaction [often called direct metal oxidation (DIMOX)],
2. Metal – halide salt reaction and
3. Metal – gas reaction.

Both solid solution strengthening and particulate (dispersion) strengthening have been observed in in-situ composites. As stated by A. Sato and R. Mehrabian [74], there could be one of the *five* types of bond formed between liquid matrix and particles added:

1. The dissolution and wetting bond,
2. The reaction bond,
3. The exchange reaction bond,
4. The oxide bond and

5. The mixed bond.

Reinforcement selection depends on following list [75]:

- low density,
- mechanical compatibility,
- chemical compatibility,
- thermal stability,
- high Young's modulus,
- high tensile strength,
- high compression,
- good processability,
- economic efficiency.

Most of the above demands can be fulfilled by non metallic inorganic compounds.

The *advantages* of in–situ MMC's over ex-situ MMC's:

- Using in–situ synthesis method, fine size particles (phases) can be generated as compared to particles in ex-situ methods of fabricating MMCs. More fine particles, give better strengthening effect.
- Cohesion and bonding strength of in-situ generated particles are always better than that of ex-situ methods.
- Homogeneous dispersion is possible in case of in–situ synthesis as compared to that in ex-situ synthesis.
- In-situ MMC fabrication is comparatively economical.

The *problems* with in–situ MMC's:

- Reinforcement particles which are added while making in-situ MMCs should be carefully selected as far as thermodynamic stability with matrix system is concerned.
- The size of system generated in-situ phases is not fixed [70, 76].

The various techniques for in-situ composite fabrication is listed below [77]:

1. Solid-liquid reaction method
    - Self-propagating High-temperature Synthesis (SHS),
    - Exothermic Dispersion (XD^{TM} process)
      It is developed by Martin Marietta Laboratory in 1980s,
    - Reactive Hot Pressing (RHP),
    - Combustion Assisted Cast (CAC),
    - Direct Reaction Synthesis (DRS),
    - Flux Assisted Synthesis (FAS),
    - Reactive Spontaneous Infiltration (RSI),
    - Direct Melt/ Metal Oxidation (DIMOX),
    - Rapid Solidification Processing (RSP),
    - Reactive Squeeze Casting (RSC).
2. Vapour-liquid-solid (VLS) reaction
3. Solid-solid reaction process
    - Mechanical Alloying (MA),
    - Reactive Hot Pressing (RHP),
    - Isothermal Heat Treatment (IHT)
4. Liquid-liquid reaction process

In this research work, processing of in-situ aluminium matrix composite was done by using commercially pure aluminium and MnO_2 particles. Sequence of addition of MnO_2 also varies along with variation of weight percentage of MnO_2 particles. Resultant composite materials have been characterized using various testing methods to evaluate its properties.

2.5 Application of composites

The range of applications is very large. A few examples are shown below;

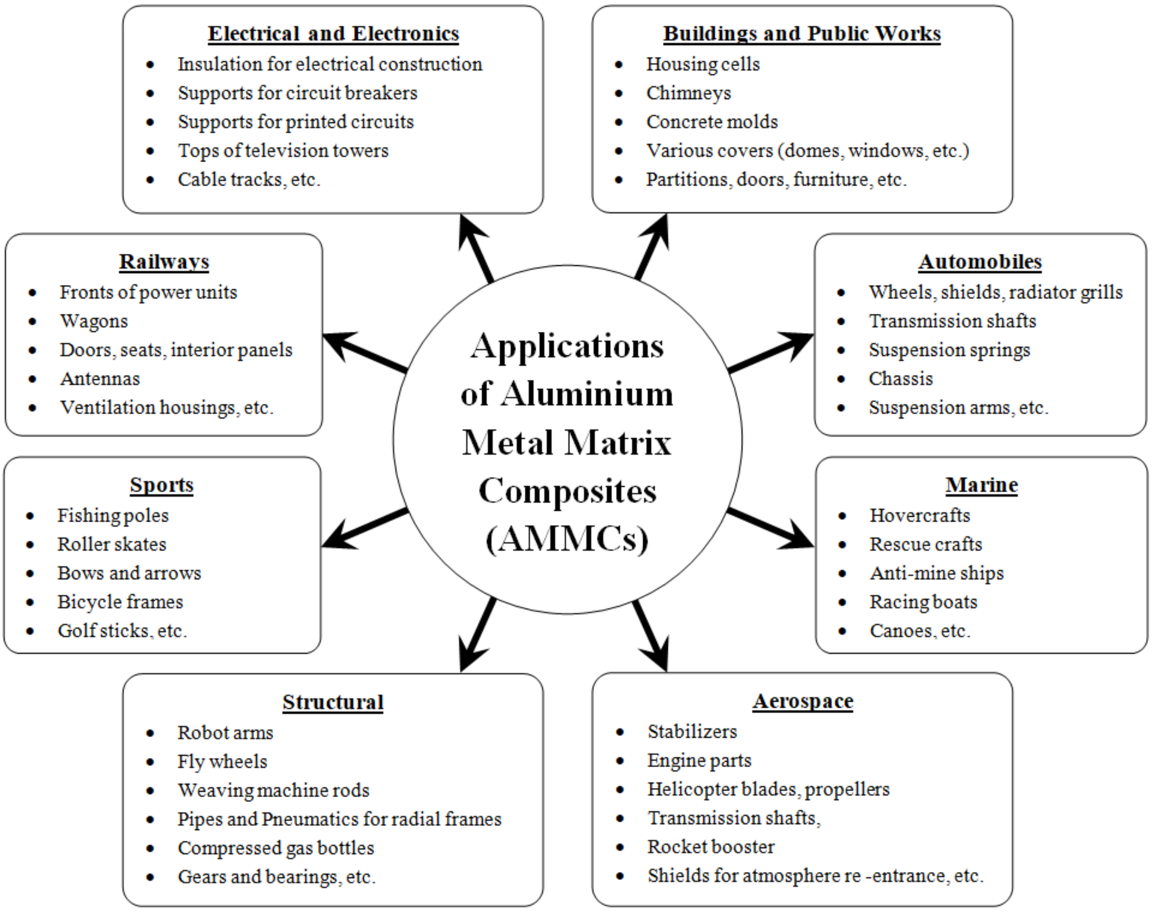


Figure 2.30: Applications of the Aluminium Metal Matrix Composites (AMMCs) in various fields. [34, 78]

2.6 Literature review of technical papers

S. V. Kamat et al. [1] have used Al_2O_3 (5 to 50 micron) as reinforcement constituents of 2 to 20 wt % of the matrix metal. Two types of the matrix metals were used such as 2014-O and 2024-O. Slurry casting method was employed to fabricate these composite materials. Tensile property and fracture toughness were evaluated. $MgAl_2O_4$ and $CuAl_2O_4$ spinel structures formed at the interface between the matrix and reinforcement. Results showed increase of yield strength and UTS. Where strain to failure decreased as the volume fraction of Al_2O_3 increased for constant particulate size. Fracture toughness decreased as volume fraction increased for constant Al_2O_3 particulate size. 2024-O matrix composite had less fracture toughness than 2024-O matrix composites.

P. C. Maity et al. [2] in their research work used Al-2Mg alloy as matrix metal and MnO_2 as reinforcement constituents of 2 wt % and 5 wt % variations. To synthesise the composite materials, vortex method was employed. Graphite impeller was used to stir the molten bath at 1250 rpm and 973 K. MnO_2 particles were introduced into the vortex formed while stirring. Composite bath was allowed to air cooled in the crucible. Microstructure study on JEOL microscope and EPMA analysis were carried out. For XRD study, $Al - 2Mg - 5MnO_2$ sample was remelted at 973 K and it was treated with C_2Cl_6 to extract the particles from it. These extracted particles were subjected to X-Ray analysis in Siemens D500 diffractometer with MoK_α radiation in 2θ range 10^o to 42^o. For mechanical property evaluation, composite ingot was remelted at 973 K again and cast into graphite mould containing tensile sample shapes. Microhardness testing was performed on LECO microhardness tester, hardness was measured using Vicker's hardness tester and tensile testing was performed on Instron machine. Both microhardness and hardness values were improved. Researchers claimed that there were MgO and $MgAl_2O_4$ formations as in-situ phases in the microstructures. UTS values were found much higher than the base alloy due to solid solution strengthening. It was determined that strength of $Al - 2Mg - 5MnO_2$ was lower than $Al - 2Mg - 2MnO_2$ system whereas the percentage elongation (ductility) of the composites was higher than the base alloy.

P. K. Rohatgi et al. [5], has studied with SiO_2 particles to fabricate MMC. Average size of SiO_2 particles are 53 micrometer. In this study, commercially pure aluminium was melted in oil fired furnace or an electric resistance heating furnace at 800 ^oC to 920 ^oC. Melt was transferred to holding furnace were temperature of 760 ^oC to 780 ^oC was maintained. Melt was stirred using steel impeller (coated with chia clay) at 450 rpm. Preheated SiO_2 particles at 500 ^oC were added into the bath. Authors used two approaches of using base metal. In the first approach, Al-Mg alloy was made and cast into the mould. This alloy was remelted and then addition of SiO_2 particles was carried out. In the second approach, commercially pure aluminium was melted and then addition of Mg and SiO_2 was carried out. In some cases, the melt was prepared in 10 KW induction furnace at 1200 ^oC followed by SiO_2 addition. In both approaches, it was found that the recovery of Si was increasing. EPMA analysis was carried out to check the presence of different elements at the interface. Centrifugal casting at 720 ^oC melt temperature was done in rotating mould at 800 rpm. It was proved that the hardness increased upto four times whereas weight loss reduced upto three times in abrasion test compared to the base metal without dispersion.

According to Banerji et al. [6], two base alloy systems were used as commercial pure aluminium and $Al - 11.8Si$ eutectic. ZrO_2 sand particles were added into the molten matrix. After thorough mixing, the melt bath was subjected to gravity and pressure die casting (for high ZrO_2). ZrO_2 sand particles having 40 to 200 micron size. A bottom pouring furnace was used. 800 ^oC was the processing temperature where degassing was done using dry nitrogen having

99.9% purity. Speed of the stirrer was maintained at 400 rpm. ZrO_2 sand particles were added at 100 grams/ minute. Up to 5 wt % magnesium was employed to deal with wettability issues. 3 wt % ZrO_2 was dispersed in the commercially pure aluminium matrix whereas up to 5 wt % ZrO_2 particles were dispersed in the $Al - 11.8Si$ system. In this paper, the roles of magnesium were nicely discussed. Weight percent Zr recovery was established. XRD analysis and EPMA analysis were carried out. Scanning electron micrographs of fracture and abraded composite were shown for different systems in the paper indicating good bonding between particle and matrix. Hardness data and 0.2% proof stress analysis were also carried out. It was proved that with increasing magnesium addition up to 3 wt %, ZrO_2 particles can be increased up to 30 wt %. Also 142% hardness, 72% abrasive wear resistance, 43% elastic modulus, 11% in 0.2% proof stress and 10% UTS were improved. However the ductility was decreased.

M. K. Surappa et al. [7] have used three different matrix alloy systems such as Al, $Al - 3Cu - 4Si$, $Al - 11.8Si$ and $Al - 16Si$. Three reinforcement materials such as $\gamma - Al_2O_3$, $\alpha - SiC$ and illite clay were dispersed in above matrix materials. Centrifugal casting method was used. Al_2O_3 particles were heat treated prior to addition. Liquid composite bath was poured in rotating mould at 720 ^oC and 800 rpm which was increased to 1000 rpm while pouring. Microstructural analysis, wear testing, tensile testing and hardness testing were carried out. Pin on disc method was used to evaluate wear resistance of the composites. Heat treatment of Al_2O_3 particles was performed by heating powder to 900 ^oC which changed particle surface chemistry and lead to dehydroxylation. Dehydroxylation helps to increase surface energy of the powder particles. Heat treatment of the ceramic particles decreases contact angle and increases wetting angle on particle surface. It was claimed by the authors that wetting angle on reinforcement particles was more than 90^o. It was also notes that as the temperature of SiC particles increases, from melting point of Al to 1100^o, wetting angle was dropped from 154^o to just 40^o which lead to rejection of SiC particles at high temperature. The process variables affecting the dispersion of Al_2O_3, SiC and illite clay particles in matrix alloy are: (1) temperature and time of heat treatment, (2) particle size and shape, (3) temperature of melt during introduction of ceramic particles, (4) addition rate of ceramic particles, (5) percentage of dispersoids and (6) melt degassing. Influence of heat treatment temperature and time on the dispensability of Al_2O_3, SiC and illite clay particles was well justified in this research work. It was also observed that as the size of the reinforcement constituents dropped, the recovery of all three reinforcements decreased. The results showed improvements in the hardness, UTS whereas percentage elongation was reduced as volume fraction of the reinforcement increased. The abrasive wear of aluminium decreased in the system at 3 wt % Al_2O_3 particles.

Akira Sato et al. [12] in their research, three different matrix alloys were utilized as $Al - 4Cu$, $Al - 4Cu - 0.75Mg$ and 6061 aluminium alloy. Alloy was melted in gas fired furnace and cast into two cylindrical graphite moulds. One casting was hot extruded and second was used for friction and wear test. Various reinforcement materials were used such as Al_2O_3, SiC, MgO, glass beads, crushed glass, slag, Si_3N_4, TiC, silica sand, boron nitride, natural mica and synthetic mica. Morphologies of reinforcement used were wedge shape, irregular shape, spherical shape and flakes. Composite samples were subjected to wear testing on pin and dish machine where coefficient of friction was calculated. Microstructural analysis was carried out to check the distribution of non metallic particles into the matrix. Using friction and wear study, authors have reported the thirotropic behaviour of the composite which establish the relation between viscosity and rate of shear. The weight loss in the samples containing glass, sand and mixture of irregular particles and SiC whiskers increased as the sliding velocity increased. Whereas in hard particles reinforced composites, the weight loss was not significantly affected by sliding velocity. The composite samples containing spherical MgO and wedge shape particles of boron nitride has wear out 4 to 5 times as much as the matrix alloy. Composites containing carbon, natural mica and 7 wt % Al_2O_3 were not changed in their wear behaviour. It was seen that fine non metallic particles, fibers and small flakes of mica improved the strength of the composites.

P. C. Maity et al. [24], have synthesised the aluminium matrix composite using commercially pure aluminium as matrix metal and TiO_2 particles as reinformcements. After melting of commercially pure aluminium, TiO_2 particles were added into the vortex formed while stirring. Stirring of molten bath was carried out using graphite impeller. It was said that TiO_2 particles reduced to Ti and O which further react to form Al_3Ti, $AlTi$ and Al_2O_3 as in-situ phases into the matrix. XRD analysis was carried out by PW 1840 X-Ray diffractoometer in the 2θ range 15^o to 80^o using CuK_α radiations. Micro hardness on LECO tester was performed. It was concluded that he hardness of these composites were higher than the composites produced by incorporating Al_2O_3 directly in the aluminium matrix.

$Al(Mg, Mn) - Al_2O_3(MnO_2)$ composites were fabricated by A. Hamid, et al. [31] and studied various properties like ductility, strength, porosity, etc. Stir casting method was used to make MMCs. In microstructural analysis, authors have claimed the presence of $MnAl_6$ and Al_2O_3 as in-situ phases having fine size or blocky appearance. In this research MnO_2 powder was used as reinforcement in commercially pure aluminium matrix. Bottom pouring furnace was utilized for casting in metallic mould. Synthesis of the composite was done at 670 ^oC, 730 ^oC and 780 ^oC with 1 wt %, 3 wt % and 5 wt % variation of reinforcement. Processing time was 3, 7, 10 and 15 minutes. Magnesium metal was added as wetting agent in two sequences. Authors have reported variation of the porosity with respect to the processing temperature and reinforcement amount. Tensile strength was reported with variation in processing time, temperature, Mn content and the particles extracted were discussed in detail. As the processing temperature and time increased, reduction of MnO_2 enhanced which lead to more formation of in-situ phases such as $MnAl_6$ and Al_2O_3. Subsequently, these in-situ phases have increased overall properties of the composite system.

Sahoo, et al. [79] in his research paper analysis of in-situ formation of titanium carbide in aluminium alloy, has used $Al - Cu - Ti$ system with $Ar - CH_4$ gas to generate in-situ phases. Two variations of the base system $Al - 4.4Cu$ and $Al - 4.5Cu$ were used. After melting, CH_4 gas was introduced via gas diffuser system at processing temperature 1473 K to 1573 K for 20 minutes to 2 hours. In this paper, authors have claimed the formation of in-situ phases by vapour-liquid-solid (VLS) reaction by gas-liquid reaction. The emphasis was given on the thermodynamic aspects of titanium carbide production. In-situ phases such as Al_4C_3 or TiC depending on alloy chemistry were formed. Carbon supplied via CH_4 gas was important to justify reaction efficiency which was claimed as rate limiting parameter at terminal solubility. Also the depletion of Ti from the melt to generate its carbide in the melt by diffusion was another rate limiting step. This phenomenon was nicely explained by bubble model in this paper. Effects of such in-situ phases on mechanical properties were not discussed.

N. Raghunathan, et al. [42] have used powder metallurgical approach to process in-situ composite. $Al - 4Cr - Fe$ system was utilized containing 35 micron (8 to 110 micron range) powder size of the base alloy and 5 micron size Al_2O_3 reinforcement powder was used. Experiments were performed in two batches of 600 gm each. In first batch, base alloy powder was subjected to double action cold compaction at 500 MPa load. 5 MN vertical press having flat face die and 20:1 reduction ratio was used for hot extrusion at 400 to 550 ^oC followed by quenching. Second batch of 600 gm powder was further divided into three batches of 200 gm each. In these three segments, dried Al_2O_3 powder of 5 wt %, 10 wt % and 15 wt % was added respectively. After thorough mixing, the powder mix was subjected to double action cold compaction at 500 MPa load followed by hot extrusion at 400 to 550 ^oC. Reduction in interfacial energy was the main reason for the particles coarsening and interfacial area growth. Various microstructures and mechanical properties were evaluated such as tensile strength and ductility. Authors have successfully proved the increasing of these properties as the reinforcement amount increased. As Al_2O_3 amount increased, porosity increased at the cost of strength and modulus.

V. Narain et al. [80] used $Al - 3Mg$ system as matrix material and reinforcement MnO_2 of 3 wt %, 5 wt % and 8 wt % variations. MnO_2 was of 8.7 micron in size. Stir casting method was used to process MMCs. Resistance heating furnace was employed to melt the composite bath at 800 ^oC. Stirring was done at 700 rpm during addition of preheated MnO_2 particles. Slurry was cast into water cooled copper mould. Resultant composites were characterized in as cast and as forged conditions. It was noted that the hardness values of composite having $Al - 8Mg - MnO_2$ system increased as MnO_2 content was increased both in cast and forged samples. Whereas in Al-3Mg-MnO2 system, hardness was increased in as forged samples but in as cast samples hardness was dropped after the addition of 5 wt % MnO_2. The tensile strength of resultant composite materials was found maximum at 5 wt % MnO_2 in both as cast and as forged samples. Yield strength was found increasing more rapidly in $Al - 3Mg - MnO_2$ samples compared to $Al-8Mg-MnO_2$ samples as the MoO_2 variation increased. Ductility of both systems was decreased which was attributed to increasing the hardness. Increasing MnO_2 content leads to fine grain structure as the nucleation sites increases. This phenomena gave improved hardness at the cost of ductility. As the strain hardening value reaches the saturation, stress transferred to the reinforcing particles and than the next particles like a cascading motion. The ductility of $Al-8Mg-MnO_2$ system was decrease as MnO_2 content was increased. After forging, these value of the ductility was further reduced.

Lawrance C. A. et al. [56] have fabricated $Al6061 - TiB_2$ metal matrix composite using stir casting method. In this research work, Al6061 alloy was melted at 850 ^oC in resistance heating furnace. Halide salts viz. potassium hexaflurotitanate (K_2TiF_6) and potassium tetraflurobrate (KBF_4) were introduced into the molten alloy. Using mild steel stirrer coated with zirconia, melt was stirred at 600 rpm followed by holding for 15 minutes upto 45 minutes. This was done to investigate the degree of reaction and growth behaviour of TiB_2. Microstructural analysis was carried out showing formation of TiB_2. Tensile specimens were prepared and tested as per ASTM E8 procedure at room temperature using Hounsfield tensometer. As the reaction holding time (RHT) was increased from 15 minutes to 45 minutes, yield strength and UTS were increased upto 30 minutes holding time whereas percentage elongation was found minimum at 30 minutes of holding time. Hardness was found maximum at 30 minutes of RHT.

V. Narain et al. [81] have processed $Al - 8Mg - MnO_2$ composite using stir casting method. Commercially pure aluminum of 99.6 wt % purity was taken as the matrix material and MnO_2 particles of 1 to 20 micron size were added in different amounts (3, 5 and 8 wt %). Matrix metal was melted at 800 ^oC using resistance heating furnace with bottom pouring facility. Stirrer and MnO_2 powder were preheated at 400 ^oC before introduction into the molten melt. Fixed amount of 8 wt % Mg was added after wrapping in aluminium foil into liquid bath after addition of the reinforcement. After stirring for 5 minutes at 800 ^oC, liquid composite bath was cast into water cooled copper mould. One section of cast composite was utilized to determine various properties in cast condition while second section was subjected to the hot forging at 400 ^oC for 22% reduction. Chemical analysis was performed using GBC AVANTA-M atomic absorption spectrometer (AAS). 10 gm of composite sample was dissolved in HCl to extract oxide particles by selective leaching process. Sodium sulphate (Na_2SO_4) was utilized to settle down suspended particles. These particles were extracted using ashless paper which was later burned at 700^o in pre weighed silica crucible. XRD analysis of residual particles was performed in 2θ range of 5^o to 110^o using $CuK\alpha$ radiations and Ni filter (20 μA current and 35 KW voltage was used). Porosity and density were measured by water immersion method using ASTM C135-96 standard. Similar technique was used to measured density of extracted particles. Fracture toughness was measured using servo hydraulic model 8800 Instron universal testing machine as per ASTM E813-81 specification. Authors claimed Al_2O_3 and $MnAl_6$ were generated as in-situ phases in the microstructure. Amount of these in-situ phases were increased as addition of MnO_2 increased. However, in XRD pattern $MnAl_6$ was not present. According to the authors, this was due to dissolution of $MnAl_6$ while acid leaching. Mn recoveries were found increasing from 1.134 wt % to 3.128 wt % as the amount of MnO_2 was increased from 3 wt % to 8 wt %. It was noted that there were no consistent trend in density data whereas porosity increased with respect to MnO_2. Significant rise in hardness was observed after forging due to work hardening of matrix as well as healing of porosity. In cast composites, yield strength was increased and ductility was decreased. Tensile strength was found maximum at 5 wt % MnO_2. In as forges composites, yield strength and tensile strength both were increased significantly but the ductility was decreased. Fracture toughness values were decreased as MnO_2 content increased. Similarly, T/E ratio (it is the ratio of slope of J-R curve and the square of the flow stress) was decreased throughout addition of MnO_2.

Coarser particles generally have poor bonding strength at the interface as in the case of ex-situ composites whereas in-situ composites have phases generated within the matrix having size less than micron. Hence ductility and tensile strength of in-situ composites are higher than that of the ex-situ composites. S. Ghanaraja et al. [82] have synthesized aluminium matrix composites using commercial pure aluminium as matrix and nano sized Al_2O_3 powder as reinforcement. MnO_2 and Al powder were first milled to generate nano sized Al_2O_3 particles. In this mixture, 1:7 proportions of Al and MnO_2 powder was maintained. Addition of nano sized particles enhanced strengthening effect as well as the ductility. Addition of just 1 wt % multi walled carbon nano tube (MWCNT) in 2024 aluminium alloy could increased yield strength and tensile strength at the cost of ductility (Deng et al. [83]). About 750 gm of commercially pure aluminium was melted in muffle furnace upto 760 ^oC followed by addition of pre-milled particles. The composite bath was stirred using coated stirrer having pitch blade design. Particles were added with very slow rate of 6 to 8 gm per minute. Block of 5 wt % Mg was immersed into the molten bath to enhance wettability. Molten metal was cast in graphite coated and preheated split type permanent steel mould. There were two sizes of reinforcement particles studied in this work. One was added nano sized particles and another was coarse sized particles generated during synthesis of composite due to internal oxidation. Chemical analysis was carried out by spectroscopy and XRD analysis by CuK_α radiation in 2θ range of 10^o to 110^o and Ni filter. SEM and TEM study were also carried out for microstructural analysis. Brinell hardness testing was performed as per ASTM E10 and tensile testing was performed as per ASTM E8M specification at room temperature and strain rate of 6.67 x $10^{-4}s^{-1}$. Results showed that both tensile strength and yield strength were increased upto 3 wt % of powder mix and then decreased. Ductility was decreased slightly upto 3 wt % powder mix and later significant drop was observed. This was due to increasing porosity in the composite. The Brinell hardness was measured across the height of an ingot. Hardness value was lowered towards the top of the ingot and maximum at the bottom location in all combinations.

To generate Al_2O_3 in-situ particles in aluminium melt, Fe_2O_3 (5 to 19 micron size) was added by P. C. Maity et al. [84]. Fe_2O_3 particles were reacted with molten aluminum at 700 ^oC to promote Al_2O_3 in-situ dispersoids. 2 wt % Fe_2O_3 particles were incorporated in aluminium matrix followed by XRD and EPMA analysis. Stir casting method was used to disperse generated dispersoids uniformly into the bath. 400 gm of aluminium was melted in resistance heating furnace. 1200 rpm of stirring speed was maintained while addition of reinforcement particles by the graphite impeller for 2 minutes. Molten composite bath was allowed to cool in air within graphite crucible itself. To identify various phases formed, top of the cast ingot was remelted at 700 ^oC and treated with 0.3 wt % hexachloroethene. Rejected particles from melt were extracted and analysed under XRD machine with CuK_α radiation in 2θ range of 15^o to 80^o. EPMA of cast ingot was carried out by JEOL JCXA 733 analyser. In extracted particles, $\alpha - Al_2O_3$ (0.5 to 1.0 micron size) and Fe were confirmed by XRD method. No mechanical properties have been evaluated in this work.

Commercially pure aluminium of 750 gm was melted along with 5 wt % TiO_2 and 5 wt % Mg in muffle furnace by A. A. Hamid et. al. [85] to study $Al(Mg, Ti) - Al_2O_3(TiO_2)$ system. Stir casting method was used to cast composite samples in the steel mould. Stirring was carried out with pitch blade design stirrer for 180 seconds initially at 500 rpm and later at 300 rpm. No degassing was carried out during casting. For the purpose of comparative study, $Al - Mg - Ti$ alloy was fabricated without addition of any reinforcement and maintaining similar processing conditions. Processing temperature was varied from 670 ^oC, 730 ^oC, 780 ^oC and 850 ^oC to study various levels of in-situ phase formation. TiO_2 was preheated at 300 ^oC and added to the melt with 0.1 to 0.3 gm per second rate. For chemical analysis and XRD, particles were extracted from the composite sample in 2M HCl for selective dissolution of aluminium matrix. Suspended particles were settled using 0.1M sodium sulphate (Na_2SO_4). Extracted particles were filtered out using ashless paper and burned at 700 ^oC for 60 minutes. CuK_α radiation in 2θ range of 20^o to 100^o utilized for XRD study. Atomic absorption spectroscopy (AAS) was carried out for further chemical analysis. For in-situ particle size analysis, 25 gm of composite sample sectioned from the middle of the cast ingot was dissolved in 2M HCl. The extracted particles were filtered out using distilled water and dried. MALVERN particle size analyser was used for particles size analysis. Microstructures revealed the presence of Ti(Al,Fe) intermetallic and reinforcement particles. XRD peaks showed the presence of α–Al_2O_3, $Mg–Al_2O_4$, $MgTi_2O_4$, $Mg_2Al_6Ti_7O_{25}$, etc. in-situ phases. Hardness, tensile strength, yield strength and ductility were found highest in bottom location of the cast ingot. As the processing temperature increased, hardness and the amount of the porosities were increased but tensile strength, yield strength and ductility were decreased.

Trybological behaviour was analysed in $Al(Mg, Mo) - Al_2O_3(MoO_3)$ composite by A. A.

Hamid et al. [86]. To improve wettability of ceramic powder 5 wt % Mg was added. Stir casting method was employed for casting composite bath in steel mould. 1.24 micron size of MoO_3 preheated at 850 ^oC at the rate of 0.1 to 0.3 gm per second. Pitch blade stirrer was used to stir the composite bath vigorously for uniform mixing at 500 rpm initially for 5 minutes and after that speed was brought down to 300 rpm. Bottom pouring furnace was used having graphite stopper at the bottom of the furnace. After the pouring liquid metal the mould was immediately transferred for water cooling. Using similar processing parameters, Al-Mo alloy and commercially pure aluminium was fabricated for comparative study. XRD analysis, SEM analysis, hardness testing, tensile testing and dry sliding wear testing were performed. It was noted the generation of $Mo(Al, Fe)$ intermetallics having scriptlike, platelike and blocky appearance along with reinforcement particles and porosity in the microstructure. XRD analysis of the extracted particles showed the presence of $MgMoO_4$, $MgAl_2O_4$, $\alpha - Al_2O_3$, etc. Dry sliding wear test was carried out at 9.8 N, 14.7 N, 19.6 N, 24.5 N, 29.4 N, 34.3 N and 39.2 N loads.6 mm diameter and 20 mm length cylindrical pins with flat polished end were pressed against hardened EN 24 steel disc having 62 to 65 HRC. The track radius was kept constant at 50 mm and rotating speed of the disc was maintained at 200 rpm. Corresponding linear sliding speed of 1.05 m/s and total sliding distance of about 3142 meters were used. The densities of cast in-situ composites and unreinforced alloy were measured using pycnometer. It was observed that the cumulative volume loss increased linearly with increasing load and sliding distance. Hence wear rate was also increased linearly with increasing normal load values. Cast in-situ composite was having minimum volume loss as compared to cast Al-Mo alloy and cast commercial aluminium samples. Comparatively wear rate was found lower in cast in-situ samples. Coefficient of the friction (frictional force/ the normal load) of the in-situ composite samples was raised initially and then fluctuates about the mean value with further sliding [40, 87].

Following table 2.9 indicates year wise similar research work carried out by different authors with details of matrix and reinforcement:

Table 2.9: Similar work reported by different researchers

Author	Year	Matrix and Reinforcement
C.W. Reese et al. [88]	2020	$Al - TiC$
T. Wang et al. [89]	2019	$Ti - B_4C$
Metin Onal et al. [90]	2016	$Al - Al_2O3$
M. M. Tash et al. [91]	2016	$Al - Si - CuAl_2$
Biswajit Das et al. [92]	2015	$Al–Cu–TiC$
		$...cont.$

Author	Year	Matrix and Reinforcement
G.L. You et al. [93]	2013	Al–CuO
E. Georgatis et al. [94]	2013	$Al - Mg_2Si - Si$
Rai et al. [95]	2013	$Al - TiC$
Rana et al. [96]	2012	$LM6$ Al alloy
Dinaharan et al. [97]	2012	$AA6061 - ZrB_2$
Zhang et al. [98]	2012	Al–TiO_2
Ramesh et al. [99]	2011	$Al6061$–TiB_2
Dumitru-Valentin Drăgut et al. [100]	2011	$AA6060 - AlB_2$
Wang et al. [101]	2011	$Mg_2Si - AZ91D - Mg$
Hongming Wang et al. [102]	2011	$Al - (Al_2O_3)p$
H. Zhu et al. [103]	2010	$Al - ZrO_2$
Zhang Jing et al. [104]	2010	$Al - CuO$
Zhao et al. [105]	2010	$Al - Al_2O_3, Al_3Zr$
Christy et al. [106]	2010	$Al6061 - TiB_2$
Ramesh et al. [107]	2010	$Al6063$–TiB_2
Yanga et al. [108]	2010	$(Al, Cu) - Al_2O_3$
Hoseinia et al. [109]	2009	$Al - Al_2O_3$, Glass
Dyzia et al. [110]	2008	$Al - AlN$
Włodarczyk-Fligier et al. [111]	2008	$Al - Al_2O_3$
Xiuqinga et al. [112]	2006	$Mg - TiC$
Emamy et al. [113]	2006	Al–TiB_2
Shabestari et al. [114]	2004	$Cu - Al$ alloy
Wang et al. [115]	2004	$Al - Al_3Ti$
Peng Yu et al. [116]	2004	$Al - Al_2O_3$
Q.G. WANG [117]	2003	$A356 - A357$ Al-alloy
J. Zhang et al. [118]	2001	$Al - Mg_2Si$
X. C. TONG et al. [119]	2001	$Al - TiC$
J. Zhang et al. [120]	2000	$Al - Mg_2Si$
J. Zhang et al. [121]	2000	$Al - Mg_2Si$ mischmetal
		...cont.

Author	**Year**	**Matrix and Reinforcement**
H.X. Peng et al. [122]	2000	Al_3Ti–Al_2O_3
D. Mattissen et al. [123]	1999	$Cu - Ag - Nb$
Yoshikawa et al. [124]	1999	$Al - Al_2O_3, SiO_2$
Yue et al. [125]	1999	$Al - TiB_2$
Peng et al. [126]	1997	$Al_3Ti - Al_2O_3 - Al$
Maity et al. [127]	1997	$Al - CuO$
Yuyong Chen et al. [128]	1995	$Al - TiO_2$
C.H. Cáceres et al. [129]	1995	$Al - Si - Mg$
Maity et al. [130]	1993	$Al - Al_2O_3$
Henager et al. [131]	1992	$MoSi_2 - SiC$
Ghosh et al. [132]	1986	$Al - Al_2O_3$
Levi et al. [133]	1978	$Al - Al_2O_3$ fiber