CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

The present chapter is an overview of composite materials, types of composites and their processing techniques. Importance of Fe, Ni and their alloys as matrix phase for synthesizing metal matrix composites (MMCs) is given in this chapter. It also includes the previous studies reported on ceramic reinforced MMCs for high strength applications. For this, related references have also been provided with each section for the literature support.

1.1 Composite

A composite is a material made up of two or more physically and chemically distinct materials known as matrix and reinforcement. The combination of two or more materials produces a set of unique characteristics, which may or may not be there with the parent materials. Here, a matrix is a continuous phase which holds the reinforcement in composite, whereas, reinforcement is a well-distributed phase in the matrix having higher strength than the matrix phase. The purpose of embedding reinforcement in the matrix is to improve the mechanical, electrical or electrochemical behavior of the composite. The composite properties comprise the combined properties of each phase. It depends upon the individual properties of matrix and reinforcement, their interface and the mechanical/chemical bonding between them [1]. Conventional monolithic materials have limitations in achieving the good combination of strength, stiffness, toughness, and density. To overcome these shortcomings and to meet the ever-increasing demand of modern day technology, composites are promising materials of recent interest. There are numerous other factors which influence the final properties of any composite material. These are [2, 3]:

- The nature of matrix as well as reinforcement phase
- Amount and type of reinforcement
- Compatibility between both the phases
- Processing conditions and techniques
- Morphology of the reinforced particles

Fig. 1.1 shows the classification of composites based on their reinforcement phase. On the basis of reinforcement phase, these may be particles reinforced composites; fibers reinforced composites (continuous or discontinuous) and structural reinforced composites etc. Particles reinforced composites may have the particles of ceramic, metal, glass or glass ceramic. Composites have higher compressive, shear and tensile strength as compared to others. In the fiber-reinforced composites, strong interfacial bond along the fiber length increases the modulus of a composite. The properties of these composites depend on the length and orientation of fibers. The reinforcement material may be metal, ceramic or polymer whereas the matrix phase may be some metal, metal alloy, polymer, glass, glass ceramic or any ceramic material [4]. Fig. 1.2 shows the types of composites based

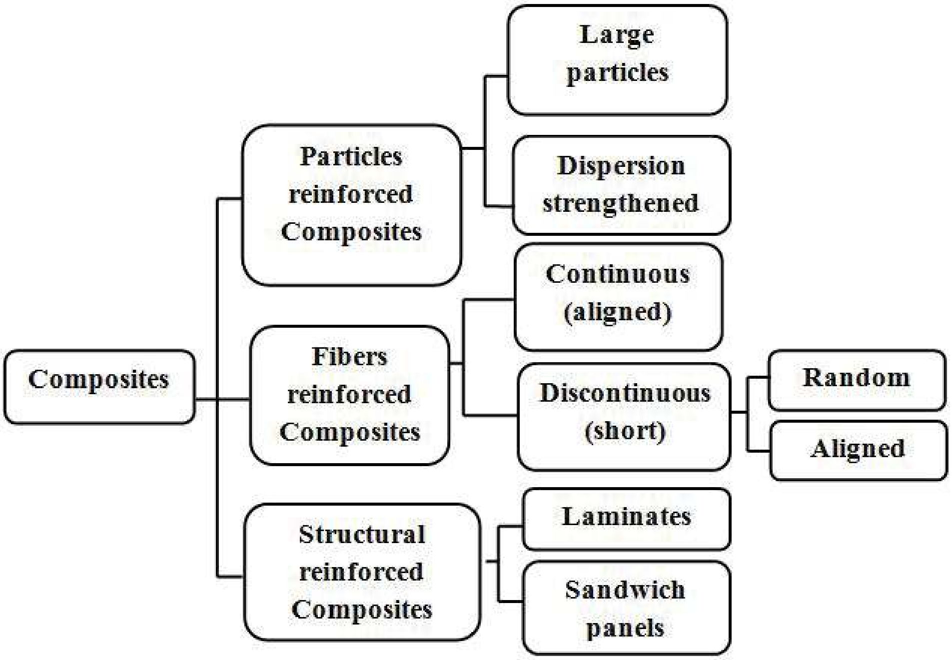

FIGURE 1.1: Classification of composites based on the reinforcement phase [4]

on the matrix phase. Depending upon the type of matrix phase, composites are classified into three major groups:

- Polymer Matrix Composites
- Ceramic Matrix Composites
- Metal Matrix Composites

Polymer matrix composites may contain either thermoplastic or thermoset polymers as a matrix phase. Generally, epoxy, polyester, phenolic, etc. are used as thermoset polymers, whereas, polyethylene, nylon, poly vinyl chloride, etc. are used as thermoplastic matrix. To improve the strength and stiffness of polymer composites, these matrices are generally reinforced with glass fibers [6].

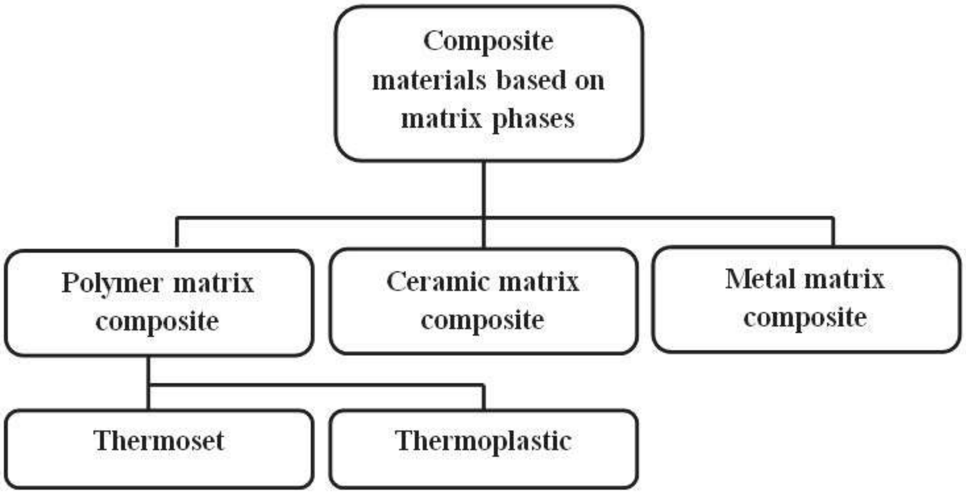

FIGURE 1.2: Classification of composites based on matrix phase [5]

Ceramic matrix composites are made by using ceramic as a matrix phase. These composites may have metal, polymer, glass or another ceramic material as reinforcement phase. Ceramic materials can be used both as a matrix and reinforcement in ceramic matrix composites. For example, SiC is used both as a matrix as well as reinforcement phases in multiple forms to attain the desired properties.

Metal matrix composites contain metal as matrix phase, whereas, reinforcement phase may be made up of any other metal, ceramic or glass-ceramic. Lightweight metal matrix composites use Al, Ti, Mg, etc. as matrix phase. These have been used in aerospace, packaging, transportation and defense areas. For the tribological, heavy duty and high strength applications, Fe, Ni, and their alloys are used. To calculate the final properties of any composite, rule of mixture is generally used for matrix and reinforcement phases. However, it is not always followed and usually valid for only continuous fibers reinforced composites [7].

1.2 Metal Matrix Composites

Metal Matrix Composites become interesting for use as constructional and functional materials if the property profile of conventional materials does not reach the increased standards of specific demands [8]. Metal matrix composites (MMCs) possess significantly improved properties including high mechanical strength, good damping capacity, better wear resistance and good corrosion resistance. A metal matrix composite (MMC) is a composite material containing at least two constituents, one being metal. The other material may be another metal or a ceramic or an organic compound. A hybrid composite is known to be composed of at least three materials. Typical reinforcements include carbon, silicon carbide or any ceramic oxide such as alumina, titania etc. Up to a certain reinforcement content, composites show indirect strengthening due to the stess generation at the phase boundaries, resulting from less thermal mismatch of phases but when this mismatch increases beyond a certain limit, then the degradation in properties occur. Therefore, the uniformity of phases and processing parameters during manufacturing is an important aspect which makes the processing complex.

Bolzoni et al. [9] have studied the properties of titanium alloys with the addition of 430 stainless steel synthesized by powder metallurgical route. Production of titanium alloys becomes costly as compared to steel and aluminium like metals at the industrial level. That is why the combination of powder metallurgy route and addition of low cast alloying element has made the process comparatively cheaper as compared to other industrial processes. In this process, titanium and stainless steel were blended and sintered.

The final sintered product was found to have properties comparable with other well developed Ti_6Al_4V titanium alloys due to its very good relative density as well as mechanical strength. Addition of spherical stainless steel powder did not affect the compressibility of original composition but prevented the formation of inter-metallic Ti-Fe. The produced low-cost titanium alloys can be utilized for structural applications.

Soyama et al. [10] have worked on the effect of zirconium addition on sintering behavior, microstructure and creep resistance of alloy Ti–45Al–5Nb–0.2B–0.2C produced by powder metallurgy route. The presence of β phase may be detrimental for creep properties mainly for titanium aluminides, Nb and Mo. Therefore, a neutral element Zr has been added in to Ti–45Al–5Nb–0.2B–0.2C alloy by using powder metallurgy route. Variation in Zr content has been done from 1-5 atom%. With increasing Zr content, the melting point of the whole composition decreased which resulted in a decrease in the sintering temperature. γ-phase formation with increased creep resistance and hardness was also found with the addition of Zr content by using powder metallurgy route.

Liu et al. [11] have worked on a comparative study of two different titanium-based alloys named Ti-Ni and Ti-Sn by using powder metallurgy route. Titanium is a light weight material, but it has a drawback of residual porosity which makes its application limited. Therefore, the addition of Ni and Sn was done to make Ti-Ni and Ti-Sn alloys, respectively up to maximum alloying of 10%. A better sinterability with reduced sintering temperature and better density was found for the above alloys as compared to pure titanium. Nickel addition increased the alloy density up to 99.5% whereas Sn has made it up to 98.5%. The microstructural study has revealed a new phase Ti_2Ni with more angular shaped grains for Ti-Ni alloy. Whereas there were not many microstructural changes in Ti-Sn alloys and therefore, other mechanical properties also remained approximately same. This report concluded with promising characteristics for Ti-Ni alloy synthesized by powder metallurgy route as compared to pure titanium.

Asgharzadeh et al. [12] have studied the mechanical and microstructural properties of alloy Mg-Zn-Y prepared by powder metallurgy. A powder having composition $MgZn_{4.3}Y_{0.7}$ was prepared by using an inert gas atomizer which was then extruded at 380°C with different extrusion ratios. Addition of fine Mg grains enhanced the hardness and mechanical properties of the prepared samples. Extrusion ratio has proved to have a significant impact on the structural and mechanical properties. The microstructural study has proved the presence of icosahedral phase nanoparticles and this resulted in high-temperature strength of prepared samples. The smaller dislocation mean free path was observed due to the finer Mg alloy particles and resulted in higher strength. In the $MgZn_{4.3}Y_{0.7}$ extruded alloy, ultimate tensile strength was reported $\sim$240 MPa when the initial particle size of used powder was $\sim 120\mu$m which increased up to $\sim$275 MPa for the alloy where particle size $\sim 20\mu$m was used.

Fu et al. [13] have studied the effect of cobalt addition as well as sintering route on the microstructure and mechanical nature of high entropy alloy (HEA) $Al_{0.6}NiFeCrCo$ synthesized by powder metallurgy route. Spark plasma sintering (SPS) and hot pressing (HP) routes were utilized for the consolidation of initial powder. The microstructural study revealed a significant effect of cobalt doping on the phase structure of mechanically alloyed powder as well as consolidated bodies. The powder was found to have 61 vol.% of BCC and around 39 vol.% FCC solid solution phases for the alloy $Al_{0.6}NiFeCrCo$. When Co doping was not done, BCC and FCC phases were found in 85 vol.% and 15 vol.% respectively for the composition $Al_{0.6}NiFeCr$. It shows that FCC phase amount increased by Co doping. The same effect was evident for the bodies consolidated by SPS and HP routes. A higher strength and hardness value with reduced plasticity was found by using SPS route as compared to HP route for $Al_{0.6}NiFeCr$. Doping of cobalt has also increased the strength and Vicker's hardness, whereas, plasticity has been reduced for the bulk $Al_{0.6}NiFeCrCo$.

For heavy-duty applications such as power plants, automobiles, cutting tools and aviation, heavy metals such as Fe, Ni and W are used. These provide high strength, large load bearing capacity and high abrasion resistance. Iron, iron-nickel alloys, cobalt-nickel alloys are commonly used as matrix phase for high temperature and high strength applications. Conventional wrought and cast alloys are common alloys used as matrix materials. Special alloys are also used due to the advantage of fast solidification during the powder production. [14].

1.3 Processing Routes for Metal Matrix Composites

Fig. 1.3 shows different routes used for synthesizing metal matrix composites. Classification of metal matrix composites processing is done in three ways [15]:

1. In-situ processing

2. Liquid phase processing

3. Solid state processing

1.3.1 In situ synthesis

It involves the chemical reaction within the matrix for the formation of a reinforcement phase. Thermodynamic compatibility at the matrix-reinforcement interface can be achieved using this synthesis route. The other advantages of this route are the high purity reinforcement phase, a strong bond between matrix and reinforcement phase [16].

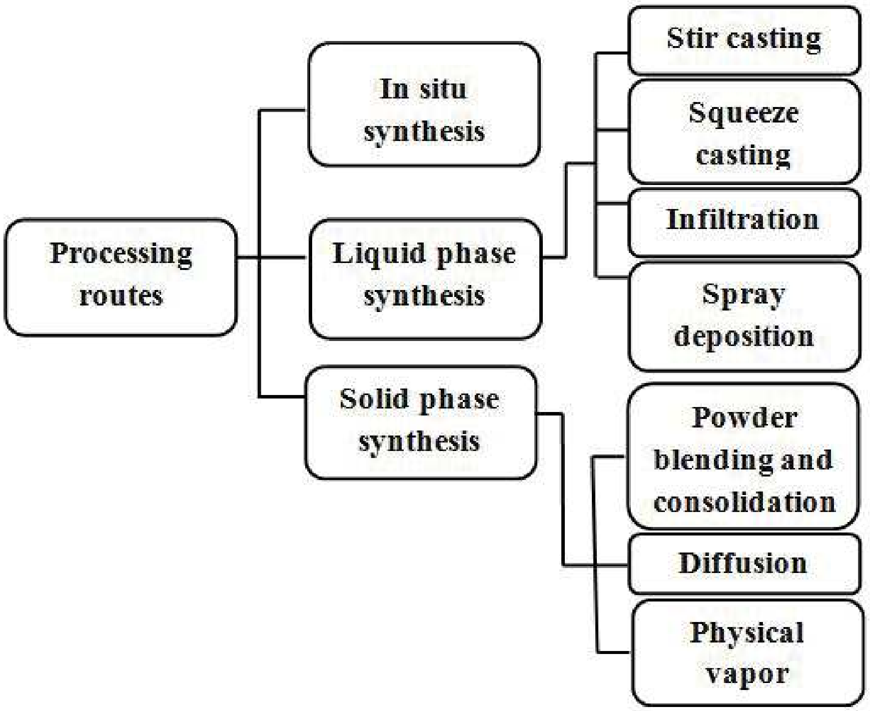

FIGURE 1.3: Different synthesis routes for metal matrix composites [15]

1.3.2 Liquid phase synthesis

It involves some synthesis routes such as stir casting, squeeze casting, infiltration, etc. [17]

(a) **Squeeze casting** : In squeeze casting, molten metal is solidified under pressure within a die. Molten metal is poured into an open die, due to which heat rapidly transfers from the melt to die under high pressure. It results in a pore-free and fine-grained body. Heat treatment is given to the fabricated parts as per the requirement. Squeeze casting is classified in two forms. First is direct and second is the indirect squeeze casting. In the direct method, die is the part of the mold itself and pressure is directly applied to the melt, whereas, indirect squeeze casting is a two-step process, where pressing is done at low pressure to prepare the preform followed by solidification at higher pressure.

(b) **Stir casting** : This route involves the addition of reinforcement particulates in molten metal followed by solidification. Pre-treated particulates are specifically used for better bonding and strengthening with matrix phases. But the problem is the sedimentation of particulates, which, occurs during synthesis which results in the non-uniformity of reinforcement phase. 5-100 μm size particles up to 30% content can be added in metal alloy using this route. For example, Al-B_4C composite, where the B_4C content is 10-15%. In a few studies, the reinforcement particles are added in the semi-solid metal alloy phase to overcome this problem [18].

(c) **Spray deposition** : A 5-10% porous layer of reinforcement is deposited on a metal surface. Further consolidation is done to achieve full densification. In case of fiber reinforcement, metal matrix is sprayed on the fibers and then densified. The volume fraction and their distribution are affected by fiber spacing and layer formation [19].

(d) **Infiltration** : It is a process to infiltrate the molten metal in the porous reinforcement (whiskers/ fibers) form. To retain the shape of fiber/ whiskers, metal mixture or silica is added to the melt. 10-70% volume fraction of reinforcement can be added to this route, depending upon the porosity level [20].

1.3.3 Solid state synthesis

Solid state synthesis includes different processing techniques such as powder blending followed by consolidation and physical vapor deposition [19].

(a) **Powder blending followed by consolidation** : In this method, metal powder and reinforcement phase is homogeneously mixed either in a dry or wet medium. This mixture is then compacted and consolidated at a high temperature. Compaction is done at room temperature at an optimized load to achieve high green density. Sintering is generally done at a temperature, below the melting point of the matrix phase. It includes the neck growth and elemental diffusion at a higher temperature which, results in pore removal and densification. An optional secondary process such as extrusion can also be used for better results [21].

(b) **Diffusion bonding** : Diffusion bonding occurs between the metal surface and continuous/discontinuous fibers under pressure. Continuous or discontinuous fiber reinforced Al or Mg-based metal matrix composites are generally fabricated using this route [16].

(c) **Physical vapor diffusion** : In this method, metal vapor is deposited on the surface of the fibers. Fibers are passed through a high partial pressure chamber of metals. The fiber coating occurs after condensation of deposit. Usually, the deposition rate varies from 5 to 10 μm /min. These coated fibers finally are compacted using cold isostatic or hot pressing technique [16].

1.4 Mechanical and Corrosion Behavior of Metal Matrix Composites

In case of metal matrix composites, reinforcement phase is incorporated in a metal matrix for altering different properties such as hardness, thermal conductivity, wear resistance, etc. These reinforcement phases may be either continuous or discontinuous. Al_2O_3, SiC, TiC, WC are the commonly used discontinuous reinforcements used for metal matrix composites [22].

The demand profile of reinforcements for metal matrix composites is determined by processing conditions along with the type and amount of the matrix phase. The following demands are generally applicable [14]:

- Mechanical and chemical compatibility,
- High young’s modulus,
- Low density
- High compressive and tensile strength,

- Economic efficiency and
- Thermal stability

The above requirements can be fulfilled by using non-metal inorganic reinforcement components. The combination of two or more reinforcements can also be done for metal matrix synthesis. These composites with multiple reinforcements are known as hybrid composites. Various kinds of metals are used for producing different types of machinery. Iron and its alloys are known for their high strength and high melting temperature and are widely used for tribological and load-bearing applications [23]. Metal matrix composites (MMC's) have been found as special candidates serving the above purpose. These composites consist of at least two constituents, which are physically and chemically distinct. One phase is suitably distributed into another to achieve the combined properties of both the phases in the final composite. The addition of reinforcement phase strengthens the matrix by providing it support. Fiber reinforcement to develop MMCs has been focused so far. But fibers as reinforcement phase are costly, and they also improve the properties in a particular direction. Particles as a dispersion or reinforcement phase are less expensive, and they can be easily added and distributed throughout the matrix by selecting the appropriate route [24]. Ceramic particles reinforced metal matrix composites are potential candidates for structural, automobile, aviation, and transportation applications. The properties and applications of these composites can easily be altered by varying the process parameters such as type and amount of reinforcement as well as the matrix phase, synthesis route, and processing temperature [24]. Ceramic particles (ex. TiC, SiC, Al_2O_3, ZrO_2, etc.) are hard and they improve the structural, mechanical and electrochemical behavior of these composites when added in some metal matrix [25].

The use of different ceramic reinforcements in metal matrix composites has been done and reported in various literature. A few of them are as follows:

Corrochano et al. [26] have firstly used 10 vol.% Al_2O_3 whiskers as a reinforcement phase in Al–Mg–Si alloy matrix. This single crystal α-Al_2O_3 reinforcement phase was developed by vapor liquid solid deposition. The high-quality mechanical properties were evident at both room temperature, and high temperature for Al_2O_3 whiskers reinforced Al-based composite as compared to pure alloy phase. Use of 20% whiskers phase has shown inferior properties than 10% reinforced composite. The improved mechanical behavior was attributed to the high-quality reinforcement phase and also the strong bonding between matrix and reinforcement phase.

Kumar et al. [27] investigated the effect of different reinforcements Si_3N_4, AlN and ZrB_2 on the mechanical and corrosion behavior of Al2618 alloy matrix composites. The concentration of reinforcement was done from 2 to 8% at an interval of 2. The improvement in ultimate tensile strength, compression strength, and microhardness was observed with increasing the reinforcement content due to their uniform distribution. Along with the mechanical behavior, corrosion study in 3.5% NaCl solution has also shown the increase in corrosion resistance which increases with reinforcement content. It is reported to be dependent on the secondary phase, microstructure, density and interaction products.

Almomani et al. [28] reported the effect of SiC (2, 10 and 15%) addition on the corrosion behavior of Cu-30Zn brass prepared by powder metallurgy in a 3.5% NaCl solution. Weak micro-galvanic coupling between the matrix and SiC particles resulted in a decrease in corrosion rate. SiC particles retarded the pits propagation in the matrix by anodic dissolution around SiC particles. Still higher SiC content (15%), the corrosion resistance again decreased due to the increase in local galvanic couple between covered and uncovered surfaces.

Yang et al. [29] reported the multiple reinforcement of TiB+TiC+La_2O_2 in Ti matrix by reacting Ti, B_4C, LaB_6 and oxygen.The reaction was done with the help of homogeneous melting in a vacuum furnace. The better strength and plasticity was observed in multiple reinforced composites (TiB+TiC+La_2O_3) as compared to (TiB+TiC) reinforced composite.

Lu et al. [30] reported the synthesis of multiple ceramic particles reinforcement (TiB+TiC+ Nd_2O_3) in Ti matrix composite using powder metallurgy route. Reinforcement was done with the help of chemically reacting Ti, B_4C, NdB_6 and oxygen together. Microscopic examination revealed the uniform distribution and different shapes of reinforcement phases. The addition of NdB_6 resulted in reduced grain size and improved densification behavior.

Singh et al. [24] studied the effect of SiC particles reinforcement on the corrosion behavior of Al-Cu alloy. The corrosion test was conducted in 3.5% NaCl solution at 30°C. Reinforcement percentage influenced the microstructure and corrosion behavior of the composite. Up to 10% SiC content, the increase in corrosion resistance was observed which again decreased beyond this SiC concentration. Agglomeration between SiC particles resulted in high SiC content. The localized corrosion in composites resulted due to the adsorption/diffusion at the interface.

The self-lubricating hexagonal boride reinforced Cu composite has been synthesized using powder metallurgy route [31]. Study of consolidation pressure (300-1200 MPa) and sintering temperature (900-1000°C) on the mechanical, tribological and electrical behavior was investigated. Maximum green and sintered density were achieved in samples compacted at 700 MPa and sintered at 950°C/2h. An increase in h-BN resulted in a decrease in wear rate up to a certain BN concentration. The failure in the composite was observed with 10% BN examined at 30N normal load. The decrease in compression strength and electrical resistivity was evident with the addition of h-BN.

Furlan et al. [32] have developed the MoS_2 reinforced Fe based composites for use in extreme operating conditions. MoS_2 is mostly used solid lubricant and reacts with iron at usual processing temperature. The effect of alloying elements as well as concentration and size of MoS_2 on the thermodynamics, microstructure and tribological behavior of composite has been investigated. The reaction between Fe and MoS_2 occurred at 850°C which is less than the expected temperature from Gibb's energy curve. But, the content and size of MoS_2 have not shown any effect on the reaction temperature. The diffusion of Mo and S from MoS_2 particles into the iron matrix formed iron sulfide and iron-molybdenum mixed sulfides. The tribological behavior has shown the decrease in friction coefficient due to the presence of self-lubricating MoS_2.

Chang et al. [33] reported Co and Ni-Fe added WC based composites sintered from 1250 to 1400°C. Increasing the sintering temperature resulted in improved mechanical and corrosion properties. The liquid phase sintering occurred in superior mechanical properties of the composites. The relative density and hardness for WC-CO system reached 99.76% and 84.4+0.5 HRA respectively whereas for WC-Fe-Ni system, hardness 85.3+0.5 HRA was observed for 99.68% dense composite. The minimum corrosion resistance and highest polarization resistance was found in WC-Ni-Fe composite sintered at 1400°C when tested in 0.15 M HCl solution.

Baghani et al. [34] synthesized Al_2O_3 nano particles reinforced (0 to 20% at an interval of 10), Fe based metal matrix composite using microwave sintering. The effect of ceramic nano particles on the microstructure, mechanical and corrosion behavior was investigated. Increasing hard ceramic particles in soft Fe matrix resulted in improved wear resistance due to the hindered dislocation moment but was not found useful in improving the corrosion resistance as they reduced the polarization resistance in 3.5% NaCl solution.

Akhtar et al. [35] reported the microstructure and wear properties of 30 to 70 wt.% TiB_2 and TiC reinforced steel matrix composites by powder metallurgy. Prismatic TiB_2 and spherical TiC grown phases were evident from microscopic examination resulting from reaction among Ti, C, and FeB in the matrix. An increase in the wear resistance was observed when the reinforcement increased from 30 to 70%. On increasing the normal applied load and sliding distance resulted in more wear loss. High wear loss of composites was observed when the applied load was increased to 200N. The microploughing mechanism was evident on the worn surface of high reinforced composite whereas grooves along with micro ploughs were present in low reinforced composites.

Babakhani et al. [36] have used combustion synthesis and spark plasma sintering for the synthesis of Fe-Al_2O_3 composites. The formation of Al_2O_3 occurred as a result of an exothermic reaction between Al and Fe_2O_3 after spark plasma sintering of 5-20% ($Al+Fe_2O_3$) along with balanced Fe powder. An increase in Fe content resulted in an increase of time to obtain maximum combustion temperature. Rise in Fe content was also found responsible for porosity enhancement. Maximum porosity measured around 60% for the composite containing 95% Fe.

Zhong et al. [37] reported the in-situ fabrication of TiC reinforced Fe based composites using in-situ reaction between gray cast iron and titanium wires. Infiltration casting followed by heat treatment at different temperatures was used for the composite synthesis. Heat treatment was done at 1138°C for different time duration, i.e., 0, 1, 6 and 11 h. Increasing the heat treatment duration up to 6h resulted in increased microhardness of composite region. Beyond this duration, no significant increase was evident. High wear resistance was also observed in the TiC reinforced composites as compared to monolithic gray cast iron due to hard TiC region.

Gupta et al.[38–40] have studied the mechanical and corrosion behavior of $Fe\text{-}Al_2O_3$ (Al_2O_3=5-30 wt.%) metal matrix composites prepared by powder metallurgy route. Authors have confirmed the formation of $FeAl_2O_4$ in sintered composites from the XRD and SEM analysis. They have also reported the effect of CoO and CeO_2 on the wear and corrosion properties of $Fe\text{-}Al_2O_3$ composites. The addition of dopants have been found trapped between the Fe and Al_2O_3 grains which retarded the formation of $FeAl_2O_4$ phase in composite. It resulted in enhanced densification. Doping of CeO_2 was reported to be helpful in enhancing the hardness, wear resistance and corrosion resistance of composites.

1.5 Fe-Ni phase diagram

The Fe-Ni phase diagram is shown in Fig. 1.4. From this Fe-Ni phase diagram [41], complete solid solubility region occurs above 910°C at all the whole composition range. Below this temperature range, α-BCC (kamacite) is stable in pure iron. Addition of Ni is done to stabilize γ-FCC (taenite) phase. If cooling is done from 910°C to lower temperature, dual microstructure containing α-BCC + γ-FCC phases co-exist. At around 50 mole% Ni content, (Fe,Ni) phase formation occurs during cooling below 345°C.

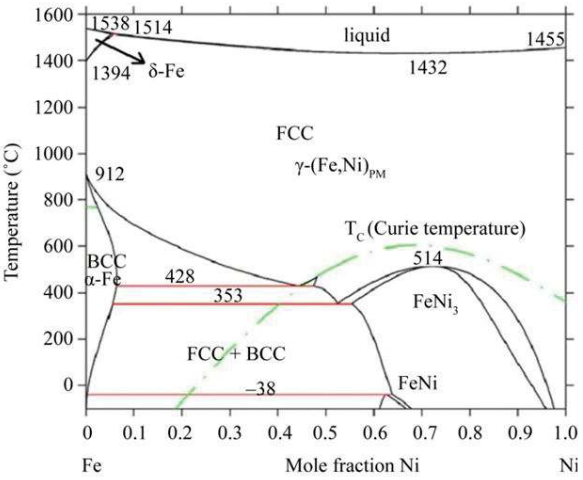

Figure 1.4: Fe-Ni phase diagram [41]

From Fig. 1.5, it can be seen that the transformation from γ to γ+α occurs at a much lower temperature on cooling than on heating [41]. Alloys containing less than 6 wt.% Ni change completely to the BCC structure during cooling. With more Ni content, it becomes difficult to complete the transformation. Therefore, slow cooling helps in forming BCC+FCC patterns in the resulting microstructure.

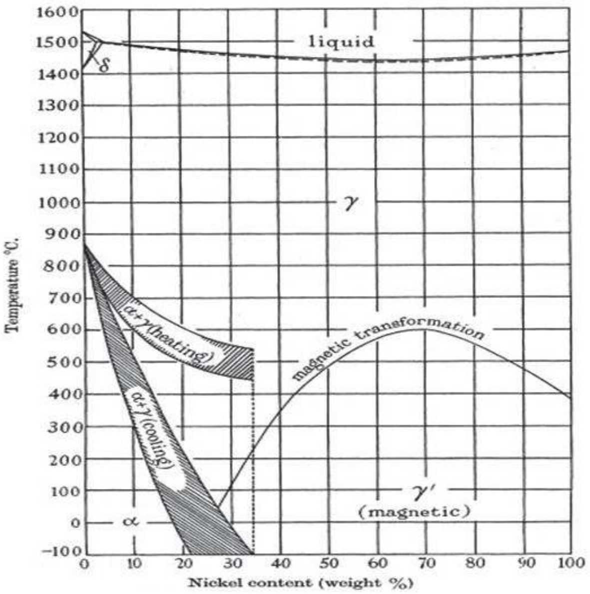

FIGURE 1.5: Fe-Ni phase diagram [41]

1.6 Fe and Ni-based alloys synthesis via different routes and their properties

Alloys and intermetallics are known as potential candidates for structural applications at high temperature due to their high strength, high modulus and oxidation resistance as compared to the conventional metals [8,42]. Their formation occurs due to the chemical reaction between two or more metallic elements which results in good interfacial bonding during sintering [43]. Many fabrication routes such as hot pressing [44–46], plasma synthesis [47], powder metallurgy [48], stir casting etc. [49–51] have been reported previously for the formation of these compounds. The above fabrication routes provide several advantages such as (a) thermodynamic stability between formed compounds and matrix (b) homogenous phase distribution (c) strong interfacial bonding and (d) better mechanical properties [15]. Despite the development and popularity of lightweight materials, iron-based alloys are widely used in manufacturing equipment, mining industries, and other heavy-duty applications due to their high strength and wear resistance [52, 53]. Alloying of different elements such as Cr, Si, Ni, Ti, etc. in iron matrix results in the evolution of desired properties for relevant applications. Among all the known alloying elements, Ni has gained the attention of many researchers due to their versatile behavior. It improves the chemical inertness, mechanical response, phase formation and toughness of iron-based materials [54–56].

For the last several years, a lot of attention has been paid to develop Fe-Ni alloys due to their versatile behavior for many applications. For example, Fe-2%Ni alloy has been reported to exhibit high wear resistance and mechanical strength [57]. Fe-36%Ni and Fe-42%Ni are known for low thermal expansion and high strength [58].

Valderruten et al. [59] have used mechanical milling (10, 24, 48 and 72h) followed by sintering at 1000°C for synthesizing $Fe_{100-x}Ni_x$ (x= 22.5, 30 and 40 at%) alloys. Effect of phase composition on the structural and magnetic behavior of the prepared alloys was studied. Presence of two different BCC and FCC phases has been reported in all the milled samples, whereas no phase change is reported with increasing milling time. Also by fitting the Mösserbauer curve with hyperfine distribution model, the formation of BCC ferromagnetic and FCC paramagnetic grains was confirmed. The magnetic behavior of both mechanically alloyed and sintered samples was found to be similar. This study has reported the possibility that the mechanically milled Fe-Ni powders after compaction and sintering will preserve the magnetic and structural properties, which could be used for several applications.

Pavithra et al. [60] reported the electro-deposition of Fe-Ni alloy on a copper substrate using sulphanilic acid sulfate bath. The effect on current density, phase, and morphology on the magnetic and electrochemical behavior has been investigated. The conditions were optimized for better final properties. The variation in alloy composition from BCC to FCC has occurred with an increase in current density. The presence of intermetallic phase $FeNi_3$ is observed at higher current density. This resulted in higher micro-hardness. The improved magnetic and corrosion behavior was correlated with the crystallite size and surface morphology.

An et al. [61] reported the formation of refined Fe/Ni surface formation using ‘surface mechanical attrition alloy treatment (SMAAT)’ followed by low-temperature annealing on a pure iron base. During this process, plastic deformation occurs when Cr balls hit the iron surface. This plastic deformation results in the enhanced concentration of defects which increases the diffusion of Ni in the iron surface. This results in more alloy formation. This alloy formation is enhanced with the help of surface annealing at 450°C due to enhanced diffusion rate. The wear resistance of the treated surface has been found to be improved in the load range 15-55N due to the formation of nanocrystalline Fe/Ni alloy resulting from the combined effect of diffusion and grain refinement at the interface.

Ni et al. [62] investigated the effect of Fe content on the hardness and microstructure of nanocrystalline Ni, Ni-20Fe, and Ni-30Fe during room temperature rolling. Softening and strain hardening was evident with the addition of iron from the microstructure associated with staking faults energy. Increasing the Fe concentration was found responsible for enhanced crystal defects and grain size which improved mechanical behavior.

Li et al. [63] have reported the effect of Ni/Fe ratio and grain size on the hardness behavior of electro-deposited Ni-Fe nano-crystalline alloys. Electro-deposition was done followed by annealing on a cold worked substrate of copper. Increase in Fe concentration resulted in grain refinement and hardness in the FCC structure. A significant grain refinement was observed from 4 to 21% Fe. Beyond this limit, there was no further refinement. BCC structure resulted in 4 nm crystallite size above 21% Fe. Maximum strength was observed in Ni-Fe nanocrystalline alloy containing 20% Fe. Above 35% Fe content, cracking in the deposition occurred due to internal stress generation.

Taghvaei et al. [64] reported the synthesis of phenolic resin coated nanocrystalline Fe-5% Ni alloy powder using the mechanical alloying method. The formation of solid solution BCC-Fe(Ni) was evident after 24 h milling duration. Increasing the milling time to 96 h resulted in steady-state nanocrystalline powder up to 10 nm particle size with superior magnetic and electrical properties as compared with pure iron powder. The change in relaxation frequency from 800 kHz to more than 1 MHz with reduced eddy current loss was also observed in this Fe-Ni based composite powder.

Gheisari et al. [65] synthesized soft magnetic Fe-45%Ni alloy powder by using mechanical alloying and optimized the effect of rotation speed and duration on the obtained powder characteristics. An increase in the milling time resulted in small grain size and increased lattice parameter. Lattice strain was first found to increase with increasing milling time and was maximum at a rotation speed of 250 rpm due to increased dislocation density. Above this speed, strain started decreasing up to 350 rpm and then became constant beyond this speed. Complete FCC γ-Fe-Ni phase formation occurred after milling for 24 h at 350 rpm.

Koohkan et al. [66] focused on the synthesis of Fe-10%Ni and Fe-20%Ni nanocrystalline powders by mechanical alloying. The increase in intrinsic flux density was observed for powders milled for 70 h beyond which it started decreasing. Increase in coercivity was observed with increased milling time up to 100 h. With this, the reduction in crystallite size and increase in microstrain was also observed. The crystallite size of obtained powders was found to be in the range 65-70 nm. A very long milling time resulted in a slight increase of Hc due to temperature rise occurring during milling.

Czerwinski et al. [67] have reported the electrodeposition of additive free 400 μm thick nanocrystalline Fe-Ni alloy (Ni$\sim$12-15%) using chloride electrolyte. The deposited layer of alloy composition was found to have 5.5-7 nm grain size. The increase in current density during deposition resulted in reduced grain size and increased hardness values in the range 647-711 H_V. The deposited layer showed the network of microcracks perpendicular to the substrate surface. The tensile stress of $\sim$1400 MPa was generated initially during deposition. The fast decrease in stress (70-90 MPa) was observed at higher current resulting in cracking.

1.7 Chemical routes for Fe-Ni alloy synthesis

A broad composition range of Fe-Ni alloys also exhibits soft magnetic behavior besides low thermal expansion and high mechanical strength. Therefore, there is an appreciable demand of iron-nickel based nanocrystalline alloys due to their high saturation magnetization and low coercivity. These are used for magnetic applications such as sensors, electromagnetic wave absorbers, and inductive devices [68, 69]. These alloys also show better cooling power than rare earth-based magneto-caloric materials and are in demand for waste heat recovery system and magnetic cooling systems [70, 71]. Fe-50%Ni alloy is known for its superior magnetic properties such as high permeability, high saturation magnetization, and less coercivity.

Mechanical, thermal and magnetic properties of the alloy powders solely depend on the phase formation, morphology, and density. For example, the soft magnetic behavior is directly affected by domain wall barriers which are created by pores in the microstructure. The Fe-Ni phase diagram shows that Curie temperature and magnetic behavior of γ phase depends on the composition [72,73]. Coercivity, saturation magnetization, and permeability are also sensitive to the crystallite size of the prepared powder. Synthesis and magnetic behavior of various Fe-Ni alloys compositions have been investigated extensively. Various conventional synthesis routes have been adopted by researchers for the development of different Fe-Ni alloys. But all these are either more time or high energy consuming for alloy formation [74, 75]. Alloy powders obtained by chemical route are more homogenous and have nano size. Auto-combustion synthesis is one of the chemical routes which is used for producing nanocrystalline oxide powders [76, 77]. This process uses inexpensive raw materials, and the mixing is achieved at the molecular level. It provides the uniformly distributed mixture. Also, it is less time and energy consuming process. This also produces very fine powder as compared to other conventional routes. Producing Fe-Ni alloy using auto-combustion route is a novel route for achieving nanocrystalline powders. Various chemical routes have been studied for achieving Fe-Ni nanocrystalline alloy powders. Some literature based on the synthesis and study of Fe and Ni-based alloys using chemical routes are given below:

Lu et al. [78] have worked on CTAB (cetyl-trimethyl ammonium bromide)-mediated synthesis of Fe-Ni alloy nanochains and their magnetic properties. They successfully synthesized iron-nickel nanoparticles assembled in one-dimensional nano chains using simple CTAB mediated assembly method. The synthesized product consisted nanochains with 90-110 nm dia and several μm length. It was found that CTAB helps in the formation of iron-nickel nano chains. It is due to the dipole interaction between neighboring particles resulting in linear particle organization. Enhanced magnetic coercivity was reported in the material containing nano chains as compared to nanospheres. The excellent stability and the magnetic properties of synthesized iron-nickel nano chains established a model for fundamental investigations and promising applications in various fields of nanotechnology.

Santos et al. [79] have synthesized Fe-Ni alloy powder using a Proteic sol-gel route using different temperature and flow reduction conditions. Formation of pure FeNi alloy was observed after reducing the obtained powder in the hydrogen atmosphere at 600 and 700°C. The obtained powders were found stable against oxidation up to 250°C. The magnetic characterization supported the formation of FeNi alloys with soft magnetic behavior.

Pandey et al. [80] reported the polyol reduction of mixed cobalt nickel hydroxides (prepared by co-precipitation) for the synthesis of nanocrystalline Co-Ni alloys with varying Ni concentration. FCC Co-Ni alloy powders having spherical particles were obtained having 17-25 nm crystallites. The resulting alloy powders showed super paramagnetism with negligible coercivity. The magnetic behavior was reported to be influenced by Co% viz an increase in Ms was observed with increasing Co content.

Liu et al. [81] reported the synthesis of Fe-50%Ni alloy powder using solution combustion synthesis route. Glycine was used as a fuel during combustion. The effect of glycine to nitrate on the powder morphology was examined, and G/Fe=1.5 was found to be optimum for obtaining the fine powder. The obtained powders were reduced in a hydrogen atmosphere at different temperatures and their magnetic behavior was investigated.γ-Fe,Ni phase was achieved in reduced powders having crystallite size below 100 nm. The soft ferromagnetic behavior was observed in the prepared powders. The maximum soft magnetic behavior with highest saturation magnetization and least coercivity was observed in the powder obtained by reducing at 700°C.

Lu et al. [82] have synthesized $FeNi_3$ nanoparticles resulting from the reduction of Fe^{+2} and Ni^{+2} together, taking the molar ratio of Fe and Ni as 1/3. Iron chloride and Nickel chloride were taken as initial materials which were reduced with the help of hydrazine hydrate. Nearly spherical $FeNi_3$ particles of ferromagnetic nature were obtained having the particle size 50-200 nm. The magnetic measurements have shown the saturation magnetization 110 emu/g and coercivity 100 Oe in the resulting powder. It is reported that this could be helpful in producing $FeNi_3$ nanoparticles in mass.

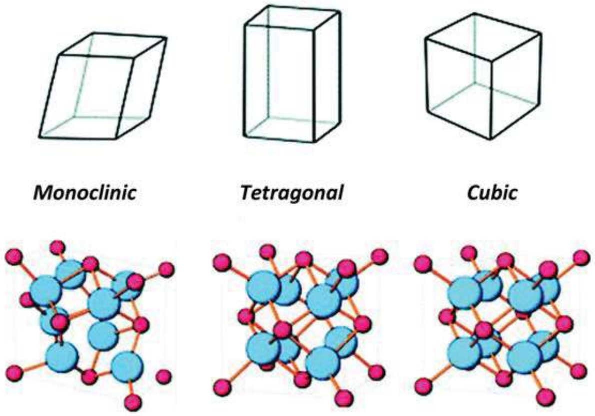

FIGURE 1.6: Different ZrO_2 Polymorphs [83]

1.8 ZrO_2 dispersed Metal Matrix Composites

Zirconia (ZrO_2) is one of the most important oxide ceramics. Fig. 1.6 shows different phases of ZrO_2 along with their crystal structure which are stable at different temperatures. ZrO_2 has three stable polymorph modifications. One is monoclinic phase (m- ZrO_2) which is stable from room temperature up to 1170°C, second is tetragonal (t-ZrO_2), stable between 1170°C and 2370°C, and third is cubic (c-ZrO_2) which is stable above 2370°C. As is known, doping suitable metal cations is an effective way to stabilize the high temperature tetragonal t-ZrO_2 and cubic-ZrO_2 phases at room temperature (RT). In particles the tetragonal t-ZrO_2 phase may also be stable in pure ZrO_2 if the particle size is below a critical size [84–86]. Many physicochemical properties of ZrO_2-based materials are determined by the relationship between these modifications, which strongly depend on the preparation conditions. Many researchers have worked on the ZrO_2 particles reinforcement for MMCs fabrication.

Abdizadeh et al. [87] have studied the effect of ZrO_2 particles reinforcement on the mechanical behavior of A356 Al/ZrO_2 composites synthesized via stir casting route. The reinforcement content was varied from 0 to 15 vol.% at an interval of 5 and cast in a temperature range 750 to 950°C at an interval of 100°. In composite cast at 750°C, the increase in reinforcement content resulted in enhanced hardness and ultimate tensile strength (UTS) as compared to the unreinforced alloy. Maximum hardness $\sim$70 BHN and UTS$\sim$232 MPa were reported for composite with 15 vol.% ZrO_2 content.

Myagkov et al. [88] reported the synthesis of Fe-ZrO_2 nanocomposite thin films produced via a thermite reaction between Fe_2O_3 and Zr layers. The formation of α-Fe and ZrO_2 resulted from the reaction between Zr and Fe_2O_3 layers above $\sim$250°C. Annealing above 500°C resulted in the formation of α-Fe nanocrystals ($\sim$34 nm) embedded in the cubic or tetragonal ZrO_2 matrix. Produced nanocomposite films were found to have good chemical stability and soft magnetic behavior with high Ms.

Fangnao Xiao et al. [83] synthesized W-ZrO_2 composite via combined azeotropic distillation and powder metallurgy route. $Zr(NO_3)_4$ was decomposed to ZrO_2 particles after incorporating the aqueous solution of $(NH_4)6H_2W_{12}O_{40}$ and $Zr(NO_3)_4$. The density and hardness of the composite were found to decrease with increasing reinforcement content. The maximum wear resistance was found in W-3% ZrO_2 composite, above which it again decreased.

Jha et al. [89] reported the fabrication of Fe-ZrO_2 composites via a simple powder metallurgy route. The variation in reinforcement content was done from 5 to 30 wt.%, and sintering was done in a temperature range from 900 to 1000°C. Both solid-state sintering and reactive sintering in the composite resulted from $Zr_6Fe_3O_4$ phase formation and densification. Final properties such as density and hardness of the composite were reported dependent on the sintering schedule and phase formation in a composite. In the composites, most of the load is carried by the high modulus, high strength reinforcement, so for a given stress, the composite undergoes a lower average strain than the unreinforced alloy [3]. These composites show good mechanical behavior up to an optimum content of reinforcement and provide initial strength to the composite. Previously, not much work has been done on the effect of ZrO_2 reinforcement in metal matrix instead of the high melting temperature and strong bonding of ZrO_2 among most of the ceramic reinforcements. Therefore, our work is focused towards synthesis and studying the effect of ZrO_2 content on the mechanical and electrochemical behavior of (Fe-Ni)-ZrO_2 metal matrix composites.

1.9 Applications of Metal Matrix Composites

There are a large number of applications of metal matrix composites. A few of these are as follows:

1. Aluminium matrix composites are known for their light weight and are highly used in automobile industries. They have their uses in pistons used in diesel engines, cylinder bores in engine blocks, propeller shafts, intake and exhaust valves, drive shafts and different brake components.
2. MMC's have their uses in the aircraft coverings, rotor blades and ventral fins. These components are generally fabricated by powder metallurgy route.

3. Various other aeronautical components such as fan exit guide vanes used in the engines are made of SiC reinforced Ti matrix composites [90].

4. Iron matrix composites have been developed to satisfy the requirements for structural parts working at high temperature, high speed and high wear resistance conditions, such as the roll collars and guide wheel of a high-speed wire rod mill.

FIGURE 1.7: Ultra-hard and wear-resistant components manufactured from Fe/TiC MMCs [91]

The industrial and infrastructural demand of metal matrix composites covers about 6% of the total market of MMCs. Cermets, different cemented carbide composites, electroplated diamond tools, Cu and Ag-based MMCs in an electrical field, TiC reinforced Fe, Ni-based MMCs and Cu infiltrated steel components are in demand for industrial applications. TiC reinforced Fe,Ni metal matrix composites are used in cutting, piercing, metal working, punching, drawing and rolling. These composites are in demand due to very high wear resistance and hardness. Extruder nozzle, extrusion dies, hammers, crimp rollers, etc. components are made by these composites. Fig. 1.7 shows some of the wear resistant components made from Fe/TiC metal matrix composites. The prepared composite is expected to have possible applications in structural applications and in high speed and wear resistance conditions such as roll collars and guide wheels of roll mill.

It is expected that the present chapter will be helpful in understanding the composite materials and their types. Different processing parameters such as synthesis routes, type, and content of reinforcement phase affect the properties and applications of metal matrix composites. This chapter is an effort to cover the related change in the behavior of MMCs which are reported in previous literature. The use of different MMCs in industrial and non-industrial areas are also mentioned in this chapter.