CHAPTER – 1

INTRODUCTION AND LITERATURE REVIEW

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1.1 Aluminum and aluminum alloys

Aluminum is the second most plentiful metallic element on earth and an economic competitor in engineering applications. Aluminum is used extensively in the modern world, and the uses of the metal are extremely diverse due to its unusual combinations of properties. Structural components made from aluminum and its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials. Aluminum being a very light metal is the most widely used non-ferrous metal and has about a one-third the density and stiffness of steel. The yield strength of pure aluminum is 7-11 MPa, while aluminum alloys have yield strengths ranging from 200 MPa to 600 MPa [Kainer (2006)]. Aluminum crystallizes in a face-centered cubic (fcc) structure and has a stacking-fault energy of approximately 200 mJ/m^2 [Clyne *et al.* (1993)].

Aluminum alloys have a wide diversity of industrial applications because of their light weight, relatively high specific strength, high electric conductivity and corrosions resistance. Generally, they are used more often than any other metal, except steel [Miracle (2005)]. They have been widely used in automotive, aerospace, and construction engineering due to their good superior mechanical properties along with good machinablity, weldability, and relatively low cost [Heinz *et al*. (2000) and Lloyd (1994)]. The need to pursue new materials which are lighter and stronger is still ever present. The mechanical, physical and chemical properties of aluminum alloys depend on composition and microstructure. The addition of selected elements to pure aluminum greatly enhances its properties and usefulness. Because of this, most applications for aluminum utilize alloys having one or more elemental additions. The major alloying additions used with aluminum are copper, manganese, silicon, magnesium and zinc; other elements are also added in smaller amounts for grain refinement and to develop special properties. Aluminum alloys are divided into major categories namely wrought compositions and cast composition. Further differentiation for each category is made based on the primary mechanism of property development. A four digit numerical designation system is used to identify the wrought aluminum and aluminum alloys. Aluminum alloy series along with the alloy composition and strengthening method is given in Table. 1.1.

Table: 1.1: Aluminum alloy series designation [Avis (1994)]

Aluminum series	Alloy composition	Strengthening method
1xxx	Al	Cold work
2xxx	Al-Cu-Mg (1-2.5 %)	Heat treat
3xxx	Al-Mn-Mg	Cold work
4xxx	Al-Si	Cold work (some heat treat)
5xxx	Al-Mg (1-2.5%Mg)	Cold work
6xxx	Al-Mg-Si	Heat treat
7xxx	Al-Zn-Mg	Heat treat
8xxx	Al-Li-Cu-Mg	Heat treat

The other way of designating aluminum alloys proposed by aluminum association involves European numbering system is indicated as EN-AW. Of the aluminum alloy series, 6xxx/EN AW 6xxx series of Al-Mg-Si alloys is known as structural alloy. The major characteristics of this series include high corrosion resistance, excellent extrudibility, moderate strength and typical ultimate tensile strength ranging from 125 to 400 MPa (18-58 ksi). EN AW6082 has the highest strength of the 6xxx series alloy. As a relatively new alloy, the higher strength of EN AW6082 has seen it replace EN AW6061 in many applications. The addition of a large amount of manganese controls the grain structure which in turn results in a stronger alloy.

1.2 Composites

Composites are multifunctional material systems that provide characteristics not obtainable from any discrete material. They are cohesive structures made by physically combining two or more compatible materials, different in composition and characteristics and sometimes in form. Composites according to Kainer (2006) is as follows "the possibility of combining various material systems (metal-ceramic-non-metal) gives the opportunity of unlimited variation and the properties of these materials are basically determined by the properties of their single components". Composite materials are composed of at least two phases; a matrix phase and a reinforcement phase. Matrix and reinforcement phase work together to produce combination of material properties that cannot be met by conventional materials [Harris (1988)]. In general by definition, composites are a combination of two or more materials (reinforcing elements, fillers, and composite matrix binder), differing in (i) form or (ii) composition on macro scale. The constituents retain their identities, that is, they do not dissolve or merge completely into one another although they act in concert. In most of the composites, reinforcement is added to matrix- the bulk material to increase the strength and stiffness of the matrix. Composite materials are usually classified on the basis of the physical or chemical nature of the matrix phase [Kim *et al.* (1991)], e.g., polymer matrix, metal-matrix and ceramic composites. Carbon fibers are commonly used in aluminum matrix to synthesize composites showing low density and high strength. In general, the characteristics of composites are as follows:

(i) It is not an equilibrium mixture of phases/elements driven by thermodynamic equilibrium. Therefore phase relationship/phase diagrams for the combination do not exist.

(ii) The interface is incoherent. There is chemical or physical bonding between them but no coherent orientation relationship between matrix and reinforcements.

(iii) It can normally be processed by liquid/solid, solid/solid combination of matrix and reinforcements.

(iv) The property enhancement is mainly due to the 'Rule of mixture' (linear or inverse)

1.3 Metal Matrix composites

Metal matrix composites (MMCs) refer to a kind of material in which rigid ceramic reinforcements are embedded in a ductile metal or alloy matrix. MMCs combine metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus), leading to greater strength in shear and compression and to higher service temperature capabilities. The attractive physical and mechanical properties that can be obtained with MMCs, such as high specific modulus, strength, and thermal stability, have been documented extensively [Kainer (2006)]. Interest in MMCs for use in the aerospace and automotive industries, and other structural applications, has increased over the past 20 years as a result of the availability of relatively inexpensive reinforcements and the development of various processing routes which result in reproducible microstructure and properties. The family of discontinuously reinforced MMCs includes both particulates and whiskers or short fibres. More recently, this class of MMCs has attracted considerable attention as a result of

- Availability of various types of reinforcement at competitive costs,
- The successful development of manufacturing processes to produce MMCs with reproducible structure and properties, and
- The availability of standard or near-standard metal working methods which can be utilized to fabricate these MMCs.

Metal matrix composite reinforcements can be generally divided into five major categories namely particulates, whiskers, continuous fiber and discontinuous fiber.

The particulate-reinforced MMCs are of particular interest due to the availability of a spectrum of reinforcements at competitive costs and successful development of manufacturing processes to produce metal matrix composites with reproducible microstructure and properties. The most important factors influencing the mechanical properties of composites are the type, size, morphology and distribution of reinforcement. The reinforcement in MMCs could be in the form of continuous/discontinuous fibres, whisker or particulates, in volume fractions ranging from a few percent to 70 %. Properties of MMCs can be tailored to the demands of different industrial applications by suitable combinations of matrix, reinforcement and processing routes.

1.4 Aluminum based MMC's

Aluminium is the most popular matrix for the metal matrix composites (MMCs) and refers to the class of light weight high performance aluminium centric material systems. In the last few years, materials design and development has witnessed a considerable emphasis on strength to weight ratio, environmental friendliness and cost of materials along with their better properties and performance [Chawla (1997) and Clyne *et al.* (1993)]. Aluminium matrix composites (AMCs), which are considered to be one of such promising materials are on the forefront of research and have been widely investigated and are attracting unprecedented interest due to their possible applications in high performance structural and functional components [Torralba *et al.* (2003), Sobaczak *et al.* (2013), Miracle (2005) and Lloyd (1994)]. The properties of AMCs can be tailored by suitable combinations of the matrix alloy, type of reinforcement, volume fraction and processing routes to meet specific applications. This makes these composites unique in comparison to conventional unreinforced materials [Miracle (2005)]. AMCs have been utilised in high-tech structural and functional applications including aerospace, defence, automotive, and thermal management areas, as well as in sports and recreation [Mazahery *et al.* (2012), Bozic *et al.* (2010) and Xionga *et al.* (2011)]. It is interesting to note that research on particle-reinforced in India during the 70's attained industrial maturity in the developed world and is currently in the process of joining the mainstream of materials. AMCs are intended to substitute monolithic materials including aluminium alloys, ferrous alloys, titanium alloys and polymer based composites in several applications. AMCs offer a large variety of mechanical properties depending on the chemical composition of the Al-matrix. It is noted that the elastic modulus of pure aluminum can be enhanced from

70 GPa to 240 GPa by reinforcing with 60 vol.% continuous aluminum fibre. Similarly it is possible to process Al-9% Si-20vol% SiC_p composites having wear resistance equivalent or better than that of grey cast iron. Thus it is possible to alter several technological properties of aluminum/aluminum alloy by more than three orders of magnitude by incorporating appropriate reinforcement in suitable volume fraction.

The major advantages of AMCs compared to unreinforced materials are as follows [Surappa (2003)]:

- Greater strength
- Improved stiffness
- Reduced density (weight)
- Improved high temperature properties
- Controlled thermal expansion coefficient
- Thermal/heat management
- Enhanced and tailored electrical performance
- Improved abrasion and wear resistance
- Control of mass (especially in reciprocating applications)
- Improved damping capabilities

1.5 Processing of AMCs

Al based MMCs can be fabricated via various casting techniques such as reactive squeeze casting and rapid solidification processing, exothermic dispersion, reactive hot pressing, self-propagating high temperature synthesis (SHS) and mechanical alloying [Ibrahim *et al.* (1991), Sadeghian *et al.* (2009), Bartels *et al.* (1997) and Ma *et al.* (1997)]. Although casting techniques are quite inexpensive, problems such as incorporation of particles into the melt and agglomeration of particles during solidification limits the possibility of making homogenously dispersed particle reinforced MMCs [Suryanarayana *et al.* (2001)]. On the other hand, mechanical alloying (MA)/ mechanical milling (MM) is a versatile technique for the fabrication of novel materials such as nanocomposites. Solid-state powder processing technique involving repeated cold-welding, fracturing and rewelding of powder particles in a high-energy ball mill by means which homogenous particle distribution in the matrix can be achieved [Scudino *et al.* (2009)]. MA offers advantages of room temperature manufacturing including avoidance of the strong interfacial reactions and minimization of the undesired reactions between the matrix and the reinforcement. Furthermore, it enables a great degree of controlling the product microstructure (volume fraction, size, shape etc.) which is comparatively absent in the liquid phase or SHS routes [Yu *et al.* (2007) and Slipenyuk *et al.* (2006)]. Thus, the main advantage of powder metallurgy route employing MA over other techniques is the low process temperature and the economic feasibility of large-scale production allowing the commercial processing of MMCs [Erich (1986) and Harrigan (1986)].

1.6 Development of Al-based composites by mechanical alloying

Materials design and development has witnessed a considerable emphasis on strength to weight ratio, environment friendliness and cost of materials along with their better properties and performance [Chawla (1997) and Clyne *et al*. (1993)]. Aluminum matrix composites (AMCs), which are considered to be one of such promising materials, have been widely investigated and are attracting unprecedented interest due to their possible application in high performance structural and functional components [Miracle (2005), Heinz *et al*. (2000), Lloyd (1994), Torralba *et al*. (2003) and Sobczak *et al*. (2013)]. The properties of AMCs can be tailored by suitable combinations of the matrix alloy, type of reinforcement and processing routes to meet specific applications. This makes these composites unique in comparison to conventional unreinforced materials [Miracle (2005)]. However, powder metallurgy, employing mechanical alloying during high-energy ball milling, is considered as a promising route. This technique ensures a homogenous distribution of refined hard reinforcement particles and significant grain size refinement of matrix alloy by the repeated welding and fracturing [Lu *et al*. (1998)]. Various types of materials, ranging from typical ceramic hard reinforcements, such as SiC, Al_2O_3, B_4C, and TiB_2 [Khadem *et al*. (2011), Prabhu *et al*. (2006), Khakbiz *et al*. (2009) and Cambronero *et al*. (2003)] to more unconventional reinforcements, such as intermetallics [Chaubey *et al*. (2012)], metallic glasses [Lee *et al*. (2005)], quasicrystals [Fahad Ali *et al*. (2012)], and carbon nanotubes [Perez-Bustamante *et al*. (2008)] have been successfully used as reinforcements in AMCs through mechanical alloying/ mechanical milling (MM) route.

Among hard reinforcements SiC reinforced AMCs have considerable potential as an engineering material and is one of the most widely used dispersoids in Al-based composites. Carreno Gallardo *et al*. (2014) reported that SiC nanoparticles can be uniformly incorporated into AA2024 matrix by milling process and found short milling time (2 h) gave the best response on the mechanical properties of composites. Parvin *et al*. (2008) reported homogenous distribution of the 10 wt.% SiC reinforcement phase in Al6061 matrix using mechanical alloying route and extremely refined microstructure was achieved with increasing milling time. Al reinforced with SiC particulate (SiC_p) with distinct nanocyrstalline characteristics was fabricated by employing high-energy ball milling [Eskandarany (1998)]. The effect of reinforcement particle size, matrix to reinforcement particle size ratio and volume fraction of the reinforcement (0-20 vol.%)

on the microstructure and mechanical properties of Al-6Cu-0.4Mn-SiC_P composites manufactured by powder metallurgy was investigated by Slipenyuk *et al*. (2006) and Khadem *et al*. (2011) investigated structural and morphological evaluation of Al-5 vol.% SiC nanocomposite powder produced by MM and showed that the addition of hard SiC particles accelerates the effect of milling process, leading to faster work hardening rate and fracture of aluminum matrix. Furthermore, aluminum shows better crystallite size refinement during ball milling in the presence of SiC particles. A similar work on Al-1 vol.% SiC nanoparticles reported that the hardness could be increased from 47 $HV_{0.5}$ pure aluminum to 163 $HV_{0.5}$ when milled at highest input energy levels [Lauri Kollo *et al*. (2010)]. Rodrigues *et al*. (2011) have reported that SiC is superior to other reinforcements in relation to strength strengthening by way of higher values of Vickers hardness of the composite.

Among the other potential reinforcement materials, (CNTs) have recently emerged as suitable and ideal reinforcement for metals/alloys [Bakshi *et al*. (2010)] owing to their low density and exceptional mechanical properties, in particular, elastic modulus of about 1 TPa and tensile strength higher than 30 GPa [Iijima (1991), Amal *et al*. (2012) and George *et al*. (2005)]. Multi-walled carbon nanotubes (MWCNTs) reinforced aluminum matrix composites have gained considerable attention due to their extremely high elastic modulus and high tensile strength [Nouri *et al*. (2012)]. Amounts ranging from 0.25 to 5 wt.% of MWCNTs have been incorporated into Al and its alloys. However, a uniform distribution of CNTs within the matrix and the possibility of their agglomeration, caused by the Vander Waals forces between them [Chu *et al*. (2013], are the key issues in metal-MWCNTs composites [Esawi *et al*. (2010), Esawi *et a.l* (2010 a) and Deng *et al*. (2009)].

The mechanical alloying (MA) process has been considered as an effective dispersion technique to achieve well-dispersed MWCNTs-reinforced composite powders for further processing [Esawi *et al.* (2009), Esawi *et al.* (2007), Choi *et al.* (2011), Morsi *et al.* (2010) and Perez-Bustamante *et al.* (2010)]. Table 4.1 summarizes the details of the milling parameters employed by various researchers to obtain Al-MWCNT composites. Morsi and Esawi *et al.*, investigated the effect of MA on the distribution of CNTs and grain size of Al in the Al-based MWCNT nanocomposites. 2–

Table 1.2: Details of MA processing parameters for the synthesis of Al-MWCNT composites.

Reinforcement	**Process parameters**								
Amount	Mill	Milling vial	Milling medium	Speed (rpm)	BPR	PCA	Atmos phere	Milling time (h)	Ref
2.5 wt.%	SPEX 8000	steel	WC-Co	-	5:1	M	Argon	1.5	[a]
0.5-5 wt.%	Planetary ball mill	SS	SS	400	10:1	M	Argon	0.5	[b]
2 wt.%	Planetary ball mill	SS	SS	200	10:1	M	Argon	6	[c]
0.25-0.75 wt.%	SPEX 8000M	HS	HS	-	5:1	-	Argon	2	[d]
10 vol.%	SPEX 8000	WC	WC	1200	10:1	SA	Argon	5	[e]

[a-Morsi *et al.* (2010), b-Esawi *et al.* (2010), c-Esawi *et al.* (2009), d- PerezBustamante *et al.* (2010) and e-Poirier *et al.* (2009)]

5 wt.% MWCNTs were introduced into the Al matrix by milling. The authors reported that MA could avoid agglomeration of the CNTs in the composite; they observed individual CNTs embedded in the Al-matrix after milling for 48 h [Esawi *et al*. (2007)]. The authors also noted that the particle size changed with milling time due to the dynamic balance between cold welding and fracturing events and that the use of methanol as a PCA helped in producing more rounded and finer particles, especially at low CNT contents [Moris *et al.* (2007)]. The effect of changing the weight fraction of CNTs on the mechanical properties of mechanically alloyed Al–MWCNTs was investigated. It was reported [Perez-Bustamante *et al.* (2008)] that higher strength and hardness were achieved with increasing milling time and increasing weight fraction of the CNTs. The strength of pure Al increased significantly with milling time even without any MWCNTs present in it. Further, it was noted that the effect of MWCNTs on the strength properties was more important as the milling time increased. As is well known, good bonding between the matrix and the reinforcement is necessary to achieve satisfactory mechanical properties of composites. The excellent mechanical properties of the composite were reported to be due to the formation of an amorphous layer between the Al matrix and the MWCNTs, which could have led to a better wetting behavior of CNTs by the Al matrix [Perez-Bustamante *et al.* (2010)]. Al-Aqeeli *et al.* (2012) investigated the alloying behavior of multi-walled CNTs in Al–Si–Mg alloys through mechanical milling in a Fritsch pulverisette planetary ball mill. They chose two prealloyed A–7Mg–0.3Si and Al–12Mg–0.3Si (wt.%) powders to which they had added CNTs at concentration levels of 0.5-2.0 wt.% and milled them for different periods of time. It was noted that without prior sonication, the CNTs were getting agglomerated during milling; this was more predominant at higher CNT levels and also

occurred sooner. Further, while the dispersion of sonicated CNTs was uniform at short milling times, agglomeration took place on milling for longer periods of time. Lastly, when milling was conducted for 5 h, the CNTs got comminuted to such small sizes that it was difficult to detect their presence through SEM investigations; energy dispersive spectroscopy (EDS) methods, however, were able to detect their presence. Perez-Bustamante *et al.* (2012) found a tremendous enhancement in mechanical properties for CNT reinforced AA2024 aluminum alloy, in particular, hardness to about 30% over unreinforced alloy. Other investigators [Perez-Bustamante *et al.* (2008) and (2014)] showed that the MWCNTs reinforced Al-alloy based nanocomposites exhibit considerably higher hardness compared to that for pure Al (57 HV) and the MWCNTs content plays an important role on the increase in the mechanical properties. Recently, Bradbury *et al.* (2014) have reported that MWCNTs reinforced aluminium matrix nanocomposite, prepared by planetary ball milling and hot compaction, showed an increase in the hardness of about 151 HV.

1.7 Strengthening mechanisms in particulate reinforced MMC’s

The strengthening effect in particulate-reinforced metal matrix composites is attributed to three main factors involving: (i) Orowan strengthening effect, (ii) enhanced dislocation density caused by the difference in the coefficients of thermal expansion between the matrix and particles, and (iii) load-bearing effect of the hard reinforcement [Zhang *et al.* (2006)].

1.7.1 Orowan strengthening

Orowan strengthening, caused by the resistance of closely spaced hard particles to the passing of dislocations, is important in aluminum alloys. Second phase particles or reinforcing ceramic particulates serve as obstacles to dislocations motion and thus increase the strength of the material [Llyod (1994) and Ibrahim *et al.* (1991)]. For relatively large and stiff particles, the dislocations bow out so as to pass around the particles, leaving dislocation loop in their wake. Thilly *et al.* (2001) observed Orowan loop mechanism and used it to simulate the good mechanical properties of Cu/Nb nanocomposites. It is clear that plastic deformation has occurred during synthesis of MMC's and Orowan loops are expected to exert a back stress on dislocation sources [Dieter (1986)]. Therefore, it is necessary to take into consideration the Orowan strengthening in the modeling of MMC's.

1.7.2 Thermal mismatch

In MMC's, the increased interfacial area between the reinforcement and matrix contributes to the enhanced mechanical properties due to the nanosized particles. Also because of the thermal mismatch between the reinforcement and the matrix, which are in the thermal equilibrium only at the temperature at which they are brought into contact during the process, on cooling from the processing temperature thermal stresses around the nanoparticles large enough to cause plastic deformation are generated in the matrix, especially in the interface region [Vaidya *et al.* (1994)]. These stresses reduce quickly with increasing distance from the boundary, which generate small defects such as dislocations in the close vicinity of the nanosized particles [Choi *et al.* (2005)]. The presence of a high dislocation density near the interface between the matrix and reinforcement particles has been experimentally observed [Dunand *et al.* (1991) and Arsenault *et al.* (1986)].

1.7.3 Load transfer

Due to the nanosize of the reinforcement particles and the sound synthesizing method, there is a strong cohesion at the atomic level between the matrix and particles, i.e., the nanosized particles are directly bonded to the matrix [Liu *et al.* (1997), Zhang *et al.* (2002) and Liu *et al.* (1997a)]. In general, the yield strength of a composite material is the stress required to operate dislocation sources and is governed by the presence and magnitude of all the obstacles that restrict the motion of dislocations in the matrix.

By taking into consideration the above strengthening effect, Zhang and Chen [Zhang and Chen (2007)] and Ramakrishnan (1996) proposed an analytical expression to predict the yield strength by the following equation:

$$\sigma_{yc} = \sigma_{ym}(1 + f_l) + (1 + f_d) + (1 + f_{Orowan}) \text{ and } \sigma_{yc} = \sigma_{ym}(1 + f_l + f_d + f_l f_d) \tag{1.1}$$

$$f_l = 0.5\, V_p \tag{1.1a}$$

$$f_d = \frac{1.25 G_m b}{\sigma_{ym}} \sqrt{\frac{12(T_{proc} - T_{test})(\alpha_m - \alpha_p)V_p}{bd(1-V)_p}} \tag{1.1b}$$

$$f_{Orowan} = \frac{0.13 G_m b}{\sigma_{ym} d_p \left[\left(\frac{1}{2V_p} \right)^{1/3} - 1 \right]} ln \frac{d}{2b} \tag{1.1c}$$

Where σ_{yc} is the yield strength of MMCs, σ_{ym} is the yield strength of the monolithic matrix under the same processing conditions as those of MMCs, f_l is the improvement factor due to the load-bearing effect, f_d is the improvement factor associated with the enhanced dislocation density in the matrix induced by the thermal mismatch between the matrix and the reinforcement particles, f_{Orowan} is the improvement factor due to the Orowan strengthening effect, G_m is the shear modulus of the matrix, b is the Burgers vector of dislocations in the matrix, T_{proc} is the processing temperature, T_{test} is the test temperature, α_m is the coefficient of thermal expansion of the matrix, α_p is the coefficient of thermal expansion of the reinforcement phase, V_p is the volume fraction of reinforcement particles and d is the grain size.

1.8 Intermetallics

Intermetallic phases /compounds are chemical compounds of metals the crystal structures of which are different from those of the constituent metals [Gerhard Sauthoff (1995)]. The composition of an intermetallic may vary within a restricted composition range known as homogeneity range. This homogeneity range may be narrow or vanishing as is the case for a line compound and such phases are usually addressed as intermetallic compounds. Phases with a wide homogeneity range are usually addressed as intermetallic phases. These compounds have emerged as materials with vast potential for application in a wide range of technologically important areas [Darolia (1991)]. The enormous potential of intermetallics especially aluminides stems from their many attractive properties, such as high oxidation and corrosion resistance and relatively low densities, combined with their ability to retain strength and stiffness at elevated temperatures [Busso *et al.* (1994) and Jayram *et al.* (1994)]. These materials are already indispensible in many applications and offer the possibility of providing additional breakthroughs in performance in, for example, high temperature structural materials, magnetic materials, and hydrogen storage materials.

A number of nanocrystalline intermetallic compounds have been synthesized as a by-product of amorphization studies or alloying development, a major driving force for producing nanocrystalline intermetallics is improvement in ambient temperature mechanical properties. Bohn *et al.* (1991) have suggested that nanocrystalline intermetallic compounds may have improved mechanical properties. Their arguments cover several possible advantages for nanocrystalline intermetallics including improved strength and ductility. While the strength of elemental nanocrystalline metals can be increase by factors of 4-5 over conventional grain size materials [Jang *et al.* (1990)] strengthening effects in some hard intermetallics are more modest of the order of 10-20% [Koch *et al.* (1992)].

1.9 Al-Fe intermetallics

Considering all excellent physical and mechanical properties of aluminum, it has become an important element in intermetallics. Iron (Fe) and aluminum (Al) alloys rank among the most important engineering materials because they provide good properties at low material cost in many applications [Ashby (2005)]. Density of these engineering materials is compared with some light and heavy metals in Fig.1.1. Iron

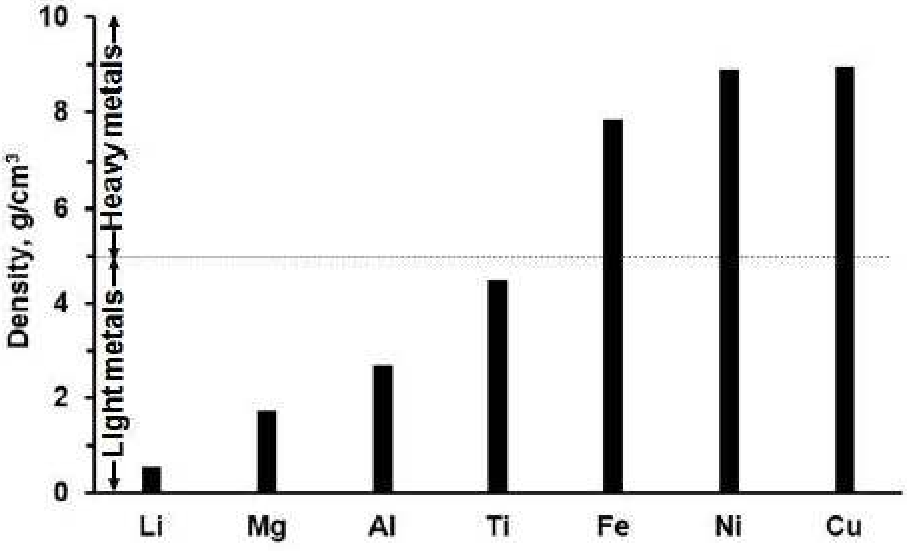

Figure 1.1: Density of some light and heavy metals.

aluminide compounds are solid examples of the use of aluminum in intermetallics industry. Changing aluminum content in iron-aluminum system leads to different iron aluminide compounds. Al-rich iron aluminides are characterised by low density, but also by lower strength and hardness than Fe_3Al or FeAl ones. However, strength and hardness can be improved by grain size refinement, especially to nanometric scale. Nanocrystalline materials exhibit enhanced properties, such as high strength and hardness, compared to the materials with conventional grain size [Gleiter (1992), Nieman *et al.* (1992) and Polmear (1996)]. Having their strength increased, Al-based intermetallics possess high specific strength. Table 1.2 indicates the crystal structure, stability range and hardness for the Al-Fe intermetallic phases.

Table 1.3: Crystal structure, stability range and hardness of intermetallic phases formed in Al-Fe binary systems at room temperature [Richard *et al.* (1994) and Massalski (1994)].

Phases	**Symbol**	**Crystal structure**	**Stability range** (at.%)	**Vickers Hardness** (9.8N)
AlFe	β’’	BCC (Order)	23-55	491-667
$AlFe_3$	β’	DO_3	23-34	344-368
Al_2Fe	ζ	Triclinic	66-67	1058-1070
Al_5Fe_2	η	Orthorhombic	70-73	1000-1158
Al_3Fe	θ	Monoclinic	74.5-76.5	772-1017

1.10 Al-Fe intermetallics by MA/MM

Amorphization of either elemental powder mixtures or powders of intermetallics, by high energy ball milling, has gained an unprecedented interest. It is considered that when the free energy of an intermetallic compound is raised by severe mechanical deformation above that of the amorphous phase, a polymorphous phase transformation from crystalline to amorphous occurs due to an increased volume fraction of grain boundaries and simultaneous disordering [Koch *et al*. (1996)]. Most of the studies on Al-Fe system have been concentrated mainly on mechanical alloying (MA) with individual elements [Mukhopadhyay *et al*. (1995), Krasnowski *et al*. (2010), Hongwei Shi *et al*. (2008), Mhadhbi *et al*. (2011) and Krasnowski *et al*. (2009)]. Binary Al-Fe powder alloys have been prepared in a wide range of composition by the MA [Oleszak *et al*. (1997), Hunag *et al*. (1997), Enzo *et al*. (1998), Cardellini *et al*. (1998), Zou *et al*. (2002) and Krasnowski *et al*. (2006)] and formation of metastable intermetallics, nanocrystalline and amorphous phase [Fadeeva *et al*. (1992), Froes *et al*. (2001), Nayak *et al*. (2006), Sasaki *et al*. (2009) and Nayak *et al*. (2010)] has been reported. Moreover, similar structures have been evidenced for a range of Al content. Zou *et al*. (2002) reported the formation of amorphous phase in Al–25 at.%Fe and Al–30 at.%Fe alloy at early stages of MA. It has also been reported that during prolonged milling amorphous phase undergoes crystallization to form Al_5Fe_2 intermetallics. Further, Zhou *et al*. (1999) reported the formation of amorphous phase in Al–20 at.%Fe alloy after 240 h of MA. Huang *et al*. (1997) observed almost complete amorphous phase in Al- (17-33) at.%Fe system and on the other hand, Enzo *et al*. (1998) and Cardellini *et al*. (1998) observed crystalline phase for Al–34 at.%Fe and Al–25 at.%Fe and Al–25 at.%Fe and Al–20 at.%Fe system respectively. It is noteworthy that despite of same composition of initial powder mixture, various structures can evolve depending on the parameters of the milling process [Suryanarayana (2001)].

In contrast to MA experiments, except the study on the effect of mechanical milling (MM) on the structural evolution of as-cast Al_2Fe and Al_5Fe_2 intermetallic systems for different short milling times by Romero *et al*. (2013) no other reports on systematic investigation on structural evolution of as-cast Al-rich iron aluminide intermetallics by MM are available. So far as intermetallics are concerned, effort has been directed mainly towards development of high strength materials and only a few studies [Chang *et al*. (1991) and Kim *et al*. (1992)] are reported that address the softening behavior in nanoscale microstructures or composite microstructures.

1.11 Powder production

Metal powder production techniques are used to manufacture a wide spectrum of metal powders to meet the requirements of a large variety of applications. Powders of virtually all metals and alloys can be produced [Lynn *et al.* (1998)]. Various powder production processes permit the precise control of the chemical composition and of the physical characteristics of powders and allow tailoring of specific attributes for targeted applications. Development and technical innovation in metal powder production processes are constantly pursued to meet the quality, cost, and performance requirements of existing and emerging applications [Dowson (1989), German (1994) and Sanderow (1998)].

Powder production methods include water and gas atomization, ball milling, electrolysis and chemical methods including the reduction of oxides [Lynn *et al.* (1998)]. Depending on the physical and chemical properties of the material as well as on the required production rate the suitable production method is selected. Ball milling technique which involves mechanical alloying and mechanical milling allows production of homogenous materials starting from blended elemental powder mixtures and from prealloyed powders or intermetallics respectively is a powerful powder processing technique. This method for powder synthesis can circumvent many of the limitations of conventional alloying and allows the preparation of alloys and composites with unique advantages which cannot be synthesized via conventional casting or rapid solidification routes [Suryanarayana (2004)].

1.12 High energy ball milling

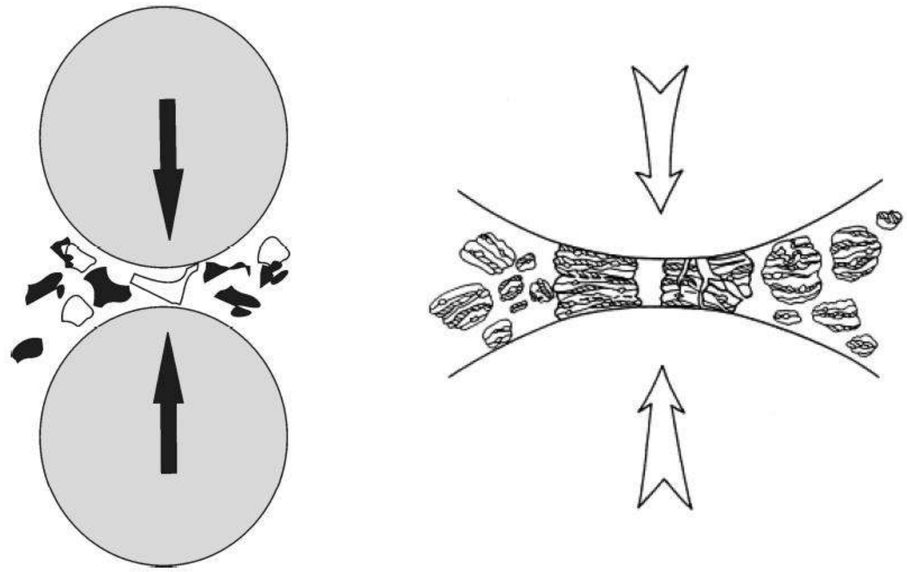

Figure 1.2: Schematic illustration of ball-powder-ball collision of powder mixture [Suryanarayana (2004)].

Ball milling is a powder metallurgy technique that allows production of variety of materials, such as metal alloys and composites, starting from elemental or compound powders [Suryanarayana (2001)]. The central basic event characterizing all type of ball mills is the ball-powder-ball collision. Powder particles are trapped between the colliding balls during milling and undergo deformation and/or fracture processes which define the ultimate structure of the powder as schematically illustrated in Fig. 1.2. Milling process involve leading the blended elemental or prealloyed powder particles along with the grinding medium in a vial and subjecting them to heavy deformation.

The process involves optimization of a number of process variables as schematically presented in Fig. 1.3, to achieve the desired final product, such as the particle size distribution, the degree of disorder, or amophization, and the required stoichiometry.

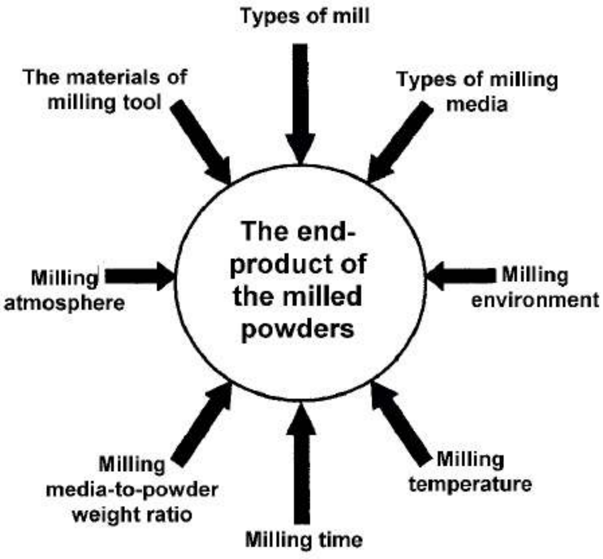

Figure 1.3: Important variables affecting the final constitution of the milled powders [Eskandarany (2001)].

Of the chief controlling factors, milling time is one of the most important parameters in milling of powders. The milling time required to develop a given microstructure is a function of the characteristics of the pristine materials, and of the equipment and parameters employed. Nevertheless, in most cases, the rate of refinement of the internal structure varies roughly varies with the logarithm of the milling time and the grain size of the initial particles is relatively irrelevant as in a few minutes to an hour, the crystallite (or grain) size is refined to the nanometer scale (Fig. 1.4).

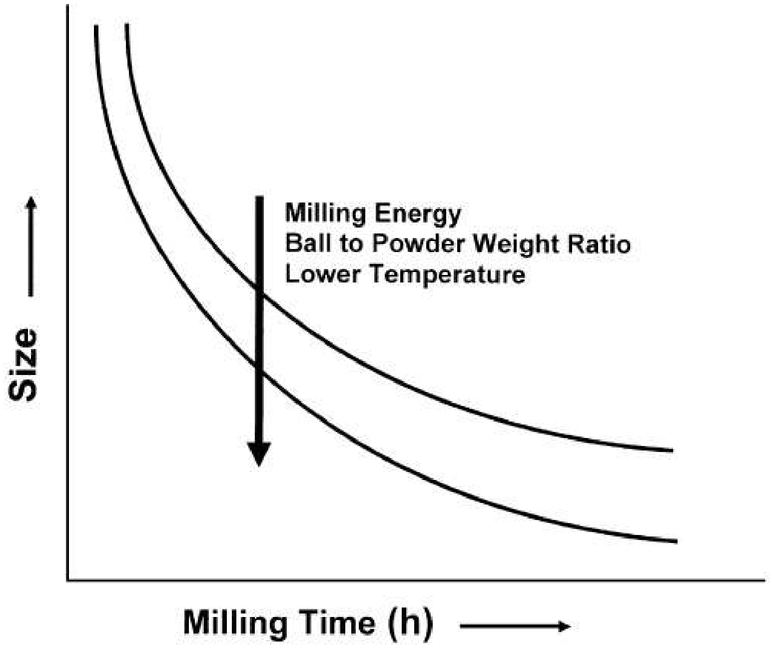

Figure 1.4: Refinement of crystallite or grain size as a function of milling time [Suryanarayana (2001)].

Though the process was first developed in the late 1960’s to produce oxide-dispersion-strengthened alloys it received greater attention in the early 1980’s due to the discovery of amorphous alloys. Since then ball milling has become a powerful tool for milling single composition powders (such as intermetallic compounds) to synthesize non-equilibrium structures/microstructures including amorphous alloys, extended solid solutions, meta-stable crystalline phases, nanocrystalline materials, and quaiscrystals [Koch (1991)]. Though the process was first developed in the late 1960’s ball milling of powders was first developed as a powder metallurgy technique to produce dispersion strengthened alloys by J.S. Benajamin and colleagues at the International Nickel Company [Benajmin (1970 & 1976)]. Prior to this milling was an integral part of the ceramic processing and powder metallurgy industries, where it was used to reduce particle size, mix, blend and change particle shapes. In the later years, milling gained a lot of importance as a powerful non-equilibrium method that can synthesize a variety of metastable structures. It has been shown that milling produces metastable structures such as amorphous [Koch *et al.* (1983)] and quasicrystalline materials [Eckert *et al.* (1989)]. Ball milling has achieved great success as a processing technique for preparation of alloyed powder or composites in powder form [Suryanarayana (2001& 2008)]. In the early 1980's the era of the Solid State Amorphization (SSA) was started by using this technique [Yadav *et al.* (2012)] which did not confine on the SSA materials only, but also it drove up and spreaded to include many different synthesized materials, such as nanocrystalline materials [Koch (1993)], stable and metastable materials [Suryanarayana (2001)], composites and nanocomposites materials [Stawovy *et al.* (1998) and Wensley (2005)] and intermetallic compounds.

1.13 High energy ball mills

Different types of high-energy milling equipment are used to produce mechanically alloyed/milled powders. The stresses responsible for effective grinding includes compression, shear (attrition), impact (stroke) and impact (collision). The milling equipment differs in their design, capacity, efficiency of milling, and also on additional arrangements for cooling, heating and so forth. Fig. 1.5 shows the schematic diagram of ball mill used for high energy milling of materials [Suryanarayana (2004)].

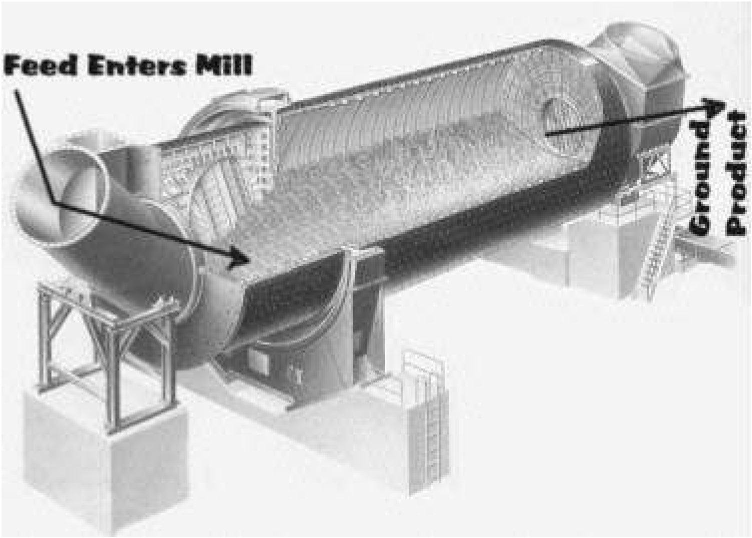

Figure 1.5: Schematic diagram of ball mill used for high energy milling operations [Ganguli *et al.* (1997)].

The material to be ground is filled with the grinding media and made to rotate around a horizontal axis. An internal cascading effect reduces the material to a fine powder. Industrial ball mills can operate continuously fed at one end and discharged at the other end. The grinding works on principle of critical speed. The critical speed can be understood as that speed after which the steel balls start rotating along the direction of the cylindrical device. Thus cause no grinding further. In general the mills are operated at 65 to 75 percentage of the critical speed. Compression stress and impact stress acting between the colliding balls and ball and powder, powder particles and walls of the cylinder are the prime stresses in milling operations.

(a) Vibratory ball mill

The vibratory ball mill is another kind of high energy ball mill that is used mainly for preparing amorphous alloys. It can be divided into vibratory frame grinder and shaker mill. The vials capacities in the vibratory mills are smaller (about 10 ml in volume) compared to the other types of mills. In this mill, the charge of the powder and milling tools are agitated in three perpendicular directions (Fig. 1.6) at very high speed, as high as 1200 rpm. The mill is evacuated during milling to a pressure of 10^{-6} Torr, in order to avoid reactions with a gas atmosphere. Subsequently, this mill is suitable for mechanical alloying of some special systems that are highly reactive with the surrounding atmosphere, such as rare earth elements. Most of the research related to understanding on the fundamental of MA has been carried out using SPEX shaker mills. Maurice and Courtney, has reported that in case of a vibrant mill SPEX 8000, the balls reach a speed as high as several m/s and that the shocks developed can lead to very high instant pressure [Maurice *et al.* (1990)].

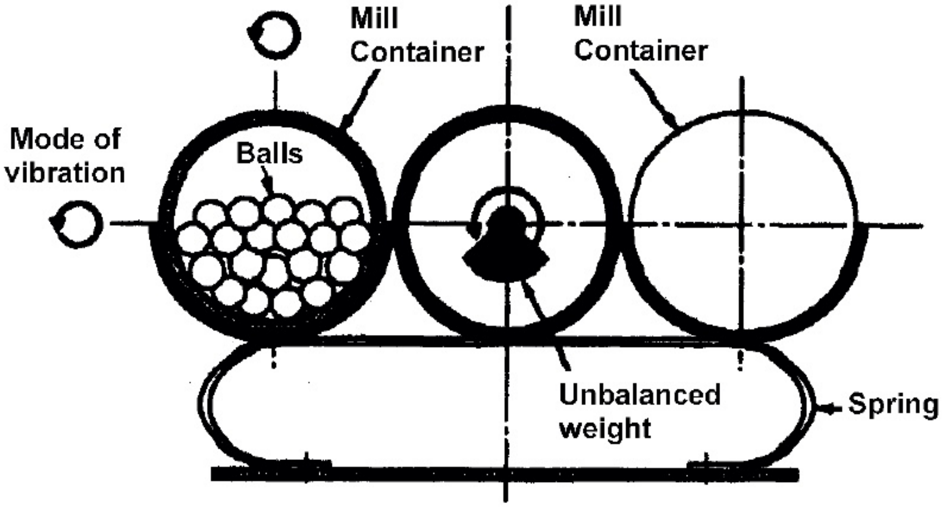

Figure 1.6: Schematic drawing of a high-energy vibratory ball mill [Hashimoto *et al.* (1992)].

(b) Tumbler ball mill

The tumbler ball mills date back to 1876 and are characterized by the use of balls (made of iron, steel, or tungsten carbide) as milling media. The capacities of these mills are governed by several variables (ratio of mill length to diameter, speed of mill, size of balls, particle size, etc.) that should be adjusted and balanced. In these mills, the useful kinetic energy can be applied to the powder particles of the reactant materials [Taggart (1927)] (Fig. 1.7) by collision between the balls and the powders, pressure loading of powders pinned between milling media or between the milling media and the liner Impact of the falling milling media, shear and abrasion caused by dragging of particles between moving milling media, shock wave transmitted through crop load by falling milling media. The tumbler ball mills have been successfully used for preparing several

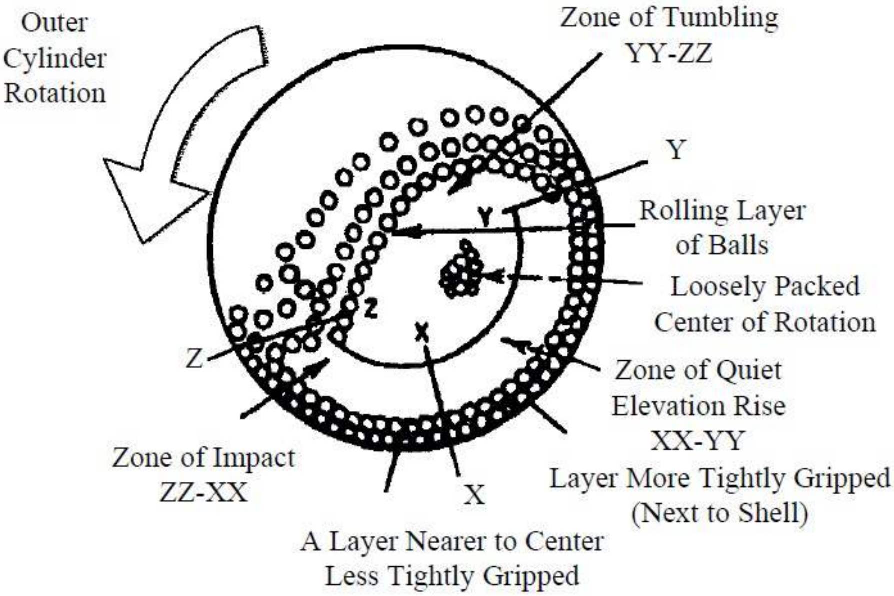

Figure 1.7: Schematic cross-section of tumbler ball mill showing ball movement [Taggart (1927)].

kinds of mechanically alloyed powders. However, this kind of low-energy mill may lead to an increase in the required milling time for a complete MA process, it produces homogeneous and uniform powders. In addition, it is cheaper than those of the high-energy mills and can be self-made with lower costs. Moreover, tumbling mills are operated simply with low maintenance requirements.

(c) Attritor mills

Attritors are the mills in which large quantities of powder (from about 0.5 to 40 kg) can be milled at a time. Commercial attritor mill are also available from Union Process, Akron, OH. The principle of this mill is different from others because here the vial is static and one or more stirrers are placed inside the vial and their rotation (several hundred rpm) mix the powders and balls together (Fig. 1.8). The friction and shear are then preponderant. The efficiency of such mills is relatively low as compared to the Fritsch or SPEX mills and consequently the energy of the mill is low. Only a small part of the powder lies at the place where an efficient mixing occurs. The powder tends to fall, by gravity, at the bottom of the vial and concentrates near the vial wall, a place where the milling is very limited. Thus, the recent models of attritors present a curved bottom in order to favor the movement of the balls and powders towards more active parts of the vial.

(d) Planetary ball mill

Among various types of ball milling, the planetary ball mill is most popular mills used for synthesizing advanced materials. The planetary mill owes its name to the planet like movement of its milling containers, which are arranged on a rotating support disk with a special drive mechanism that rotates them around their own axes. The centrifugal forces produced by the containers rotating around their own axes and by the rotating support disk, act on the material being processed and on the milling balls. Since the two rotational movements occur in opposite directions, their superimposition gives raise to the so-called coriolis forces: the combined centrifugal forces lift off the milling balls across the inner chamber of the container and make them

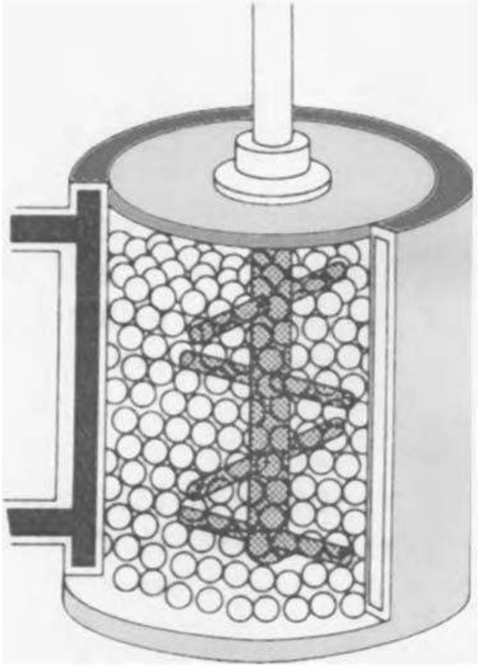

Figure 1.8: Arrangement of rotating arms on a shaft in the attrition ball mill [Suryanarayana (2001)].

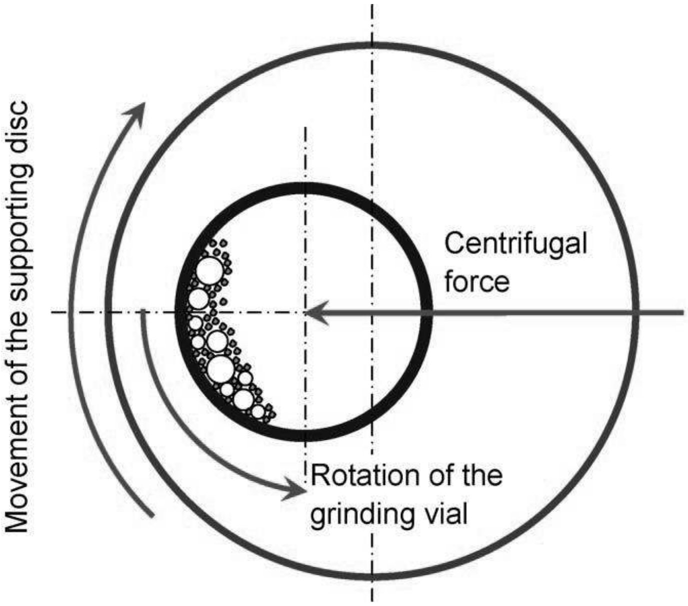

Figure 1.9: Working principle of planetary ball mill [Gu *et al*. (2009)].

collide against the opposing inner wall of the container (Fig. 1.9). The ball trajectory depends on the relative value of the ball speed *vs* container rotation and on the relative size of the support disk *vs* container [Gaffet *et al.* (1995)], rendering the collision either tangential (frictional) or normal (impact) to the container internal wall. The fine interplay between frictional and impact forces in planetary mills can result in a high degree of microstructural refinement.

1.14 Attributes of mechanical milling

MM is a simple and an economically feasible process with important technical advantages.

- Usually, we make alloys by melting together the components, whereas mechanical alloying involves synthesis of materials in solid state by high-energy ball milling.
- Synthesis of novel alloys, e.g., alloying of normally immiscible elements, which is not possible by other technique like rapid solidification. This is because MM is a complete solid state processing technique and therefore limitations imposed by phase diagrams don't apply here.
- Extended solid solubility was achieved by MM in some alloy system. This technique can be used to induce chemical displacement reactions in powder mixtures at room temperature or at much lower temperature than normally required to synthesize pure metals.
- MM can be used for the refinement of the matrix microstructure down to nanometer range. These nanostructures obtained not by clustered assembly but by the structural decomposition of coarser grained structures as the result of severe plastic deformation.
- Amorphous phase formation is one of the most frequently reported phenomena in MA/MM powder mixtures.

1.15 Nanostructured materials

Nanostructured materials are important class of metastable materials that are produced by ball milling. Materials are considered as nanostructured if the crystallite size is of the order of few nanometers (typically 1-100 nm). A novel way of transforming a material to a metastable state is to reduce its grain size from micrometers to nanometers, when the proportion of atoms at the grain boundaries is equal to or higher than those inside the grains. Because of the very fine grain size of these materials, and consequently the large volume fraction of atoms in or near the grain boundaries, these materials exhibit properties that are often superior, or sometimes completely new, in comparison to those of conventional coarse-grained materials.

In 1987, Thompson and Politis first reported the formation of a nanostructured material synthesized by MA [Thompson *et al.* (1987)], although Shingu, in 1988 reported the formation of "nanometer order crystalline structures produced by mechanical alloying" [Shingu *et al.* (1988)]. In 1993 Koch has summarized the results on the synthesis and structure of nanocrystalline structures produced by mechanical attrition [Koch *et al.* (1993)]. Mechanical alloyed pure metals, intermetallics and alloys (if they continue to be crystalline) have resulted in nanometer dimension size grain sizes. There have not been many investigations to explain why and how the nanometer-sized grains are obtained in these materials. Mechanism for the formation of nanostructures by MA/MM has been reported [Hellstern *et al.* (1989)].

In 1992 Li *et al.* proposed a relation between grain size and time of milling by a model for the refinement of grain size during ball milling [Li *et al.* (1992)].
It is given by:

$$d = Kt^{-2/3} \tag{1.2}$$

Where d is the grain size, t is the time, K is a constant.

It has been suggested that the minimal grain size achievable by milling is determined by the balance between defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes. This gives a lower bound for the grain size of pure metals and alloys and suggests that a small grain size itself provides a limit for further grain refinement by milling. Once the whole material has the nanocrystalline structure, further deformation can only be accomplished by grain boundary sliding, which does not lead to microstructural refinement anymore. It was proposed that the limiting grain size is determined by the minimal grain size that can sustain a dislocation pile-up within a grain and by the rate of recovery [Eckert *et al.* (1992)].

1.16 Grain size refinement

Milling can facilitate the formation of materials with very fine grains of nanometric size. The grain size of materials decreases with milling time and reaches a saturation level when a balance is established between the fracturing and cold welding event. The nanostrucured grain size of materials obtained by mechanical milling can be determined using X-ray line broadening or transmission electron microscopy (TEM). Koch reported a common observation that the crystallite size decreases with milling time using X-ray line broadening technique [Koch (1997)]. The grain size achievable by milling is determined by the competition between the plastic deformation via dislocation motion that tends to decrease the grain size, and the recovery and recrystallization behavior of the material that tends to increase the grain size [Eckert *et al.* (1992) and Borner *et al.* (1996)]. The reduction of grain size is also limited by the minimum grain size where no nucleation or propagation of cracks is allowed within grains.

To explain the nanocrystalline formation, a mechanism similar to dynamic recrystallization occurs during grain reduction. This is due to the fact that during hot working, grains are formed by the annihilation of dislocations and the transformation of subgrains into grain by grain rotation and subgrain boundary sliding. These grains maintain their nanometric size since the milling temperature is relatively low for grain growth to take place. The final grain size can be reached once equilibrium between dislocation accumulation and dynamic recovery is established. In other approaches, some experiments suggested that the minimum grain size is inversely proportional to melting temperature. However, this appears valid for some FCC crystals with $T_m >$ 1800 K but cannot be generalized. Some studies suggested that the nanograins nucleate and grow in a relatively slow rate due to the low temperature encountered during milling [Zhang (2004)].

The mechanism for formation of nanostructured grain size by ball milling was proposed by Fecht *et al*. (1995) via three different stages that can be summarized as:

1. Localized deformation and increase in dislocation density.
2. Movement of dislocations, annihilation/rearrangement to form a cell with nanometer scales.
3. Random orientation of grains [Koch (1997)].

Fecht *et al*. (1995) have described the development of nanocrystalline microstructure during milling in three basic stages.

Stage 1: Deformation localization in shear bands containing a high dislocation density.

Stage 2: Dislocation annihilation/recombination/rearrangement to form cell/subgrain structures with nanoscale dimensions-further milling extends this structure throughout the sample.

Stage 3: The orientation of the grains becomes random i.e., low angle grain boundaries change to high angle grain boundaries by grain boundary rotation, sliding.

1.17 Amorphization

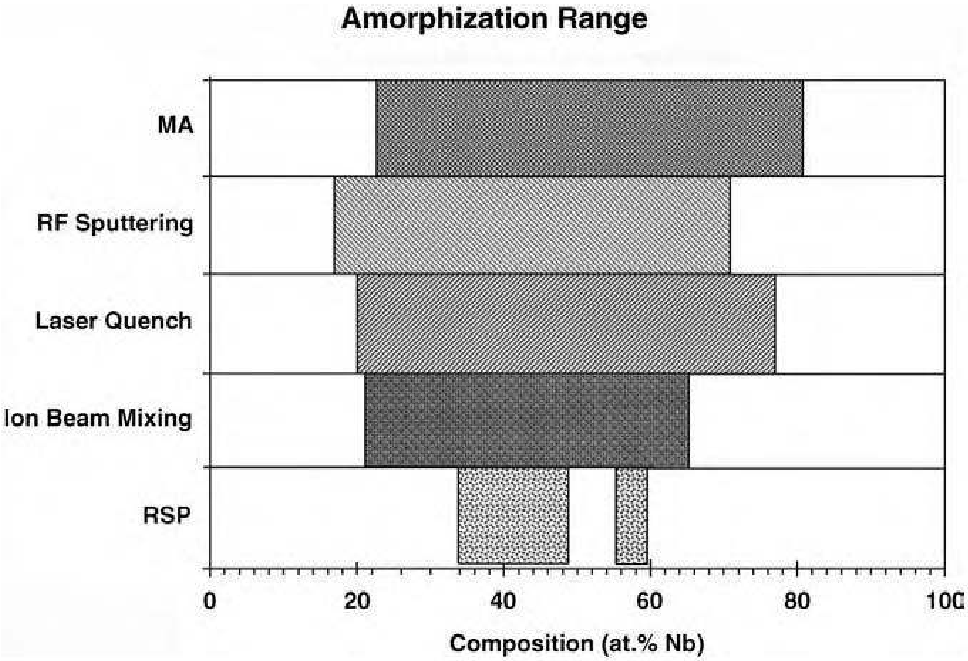

Figure 1.10: Composition of amorphous phase forming range achieved in the Ni-Nb system by different non-equilibrium processing routes [Suryanarayana (2004)].

One of the discoveries that resulted in an increased interest in MA/MM was the development of amorphous phase from crystalline elemental powders and intermetallics. Amorphous alloys can be formed in alloy systems by different nonequilibrium processing techniques but the homogeneity range for the formation of the amorphous phase is quite wide for the mechanically alloy powder as shown in Fig. 1.10.

The synthesis of amorphous material by MA starting from blended powders was first reported in 1983 by Koch *et al.* 1983. The amorphization of intermetallic compounds by mechanical milling was found by Yermakov *et al*. (1981) or a number of Y-Co compounds such as YCo_3, Y_2Co_7, YCo_5. Further a more detailed investigation has been performed by Schwarz and Petrich for $NiTi_2$ compound [Schwarz *et al.* (1985)]. Today a large increase of general interest on the amorphization of intermetallics and of mixtures of intermetallics by mechanical milling is found [Weeber *et al.* (1988), Loeff *et al.* (1988) and Askenazy *et al.* (1988)].

Amorphous phases can be formed by either of two possible routes i.e., from blended elemental powders (A and B) directly or by the formation of an intermetallic phase (A_mB_n). For example,

$mA + nB \rightarrow (A_mB_n)$ amorphous

$mA + nB \rightarrow (A_mB_n)$ crystalline $\rightarrow (A_mB_n)$ amorphous

Amorphization is faster in case of MM than MA, as alloying need not occur during MM. Nevertheless, the mechanism of amorphization is not clearly understood. A possible explanation for the amorphization process of the compound may be the accumulation of internal strain in the crystallite grains during the milling process. Formation of a crystalline intermetallic phase has been reported to occur before amorphization [Pan *et al.* (1994) and Cho *et al.* (1993)]. In some instances, it has also been reported that a solid solution forms first which on continued milling becomes amorphous [Eskandarany (1996) and Sheng *et al.* (1999)]. In some systems, the MA of the blended elemental powder mixture results, with increasing milling time, in the sequential formation of phases of solid solution, followed by an intermetallic and finally an amorphous phase [Bonetti *et al.* (1990)]. The formation of intermetallic or solid solution phase before amorphization depends on the relative free energies of the competing phases; the phase with the lower free energy forms first. On the other hand, if the amorphous phase has the lowest free energy of all these phases, it forms directly without any other phase forming prior to amorphous.

1.18 Solid state phase transformations

During MA/MM two different processes can occur. First, the free energy of the system can be raised by the accumulation of different types of crystal defects. Second the free energy can be lowered by activating a phase transformation to a more stable state. The phase formed during milling process can be a stable or metastable phase depending on the milling conditions. Phase transformations were first reported in 1997 by El-Eskandarany *et al*. [Eskandarany *et al.* (1997) & (1999)] during high-energy ball milling of elemental Co and Ti. In a very interesting report Eckert *et al*. (1990) have shown the formation of different metastable phases at different milling intensities (milling speed) in Al-Cu-Mn system. At a milling intensity of 5 (3.6 m s^{-1}), they observed the amorphous phase formation and at the milling intensity of 7 (4.7 m s^{-1}), quasicrystalline phase resulted and at a still higher milling intensity of 9 (5.8 m s^{-1}) an intermetallic compound was formed. These results were attributed to the different localized temperatures generated at different milling intensities. They have also observed transformation of these phases into one another on further milling at various milling intensities [Fig. 1.11].

1.19 Criteria for phase transformations during milling

Phase transformations that occur during milling are mostly dependent on the energy transferred to the powder and the reactions that place in them and can be better understood by considering both thermodynamic and kinetic aspects of phase transformation [Schultz *et al.* (1994)] as shown schematically in Fig. 1.12 which

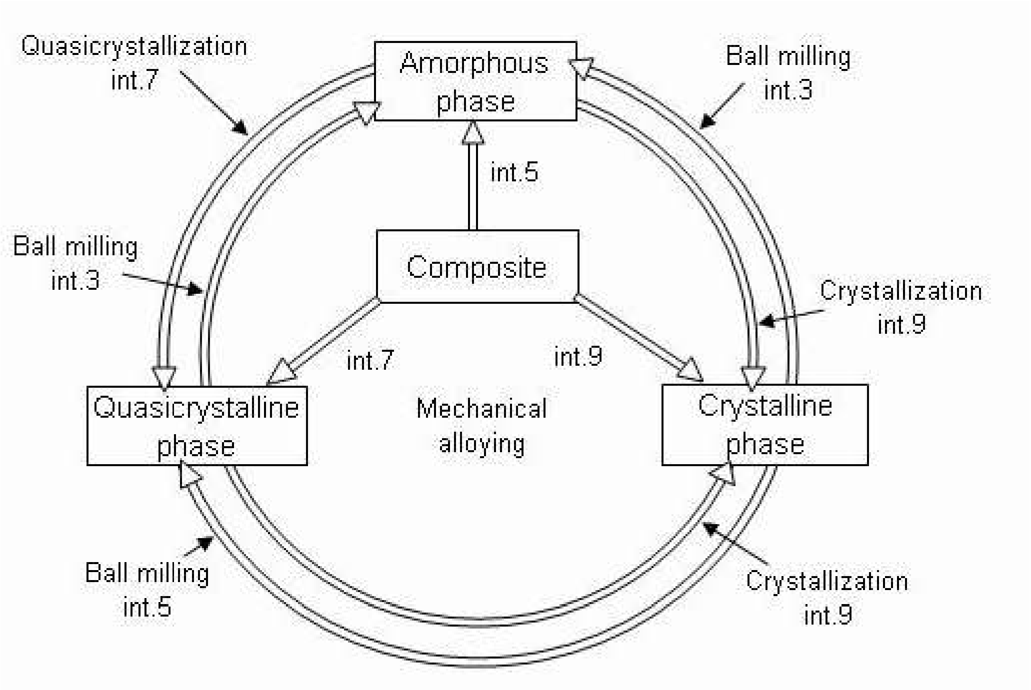

Figure 1.11: Phase transformation in Al-Cu-Mn system at various milling intensities in a planetary mill [Eckert *et al.* (1990)].

displays the Gibbs free energies of the equilibrium (G_{eq}) and metastable (G_{meta}) phase. To form a metastable phase by ball milling, the free energy of the equilibrium phase has to risen above the metastable to a state G_0. This high energy state can be achieved by mechanical milling. The free energy of the system can then be lowered form G_0 either by the formation of the metastable or by the formation of the equilibrium phase.

The formation of the equilibrium phase is thermodynamically favored because of the large driving force involved

$$\Delta G_{eq} = \left(G_0 - G_{eq}\right) > \Delta G_{meta} = \left(G_o - G_{meta}\right) \qquad (1.3)$$

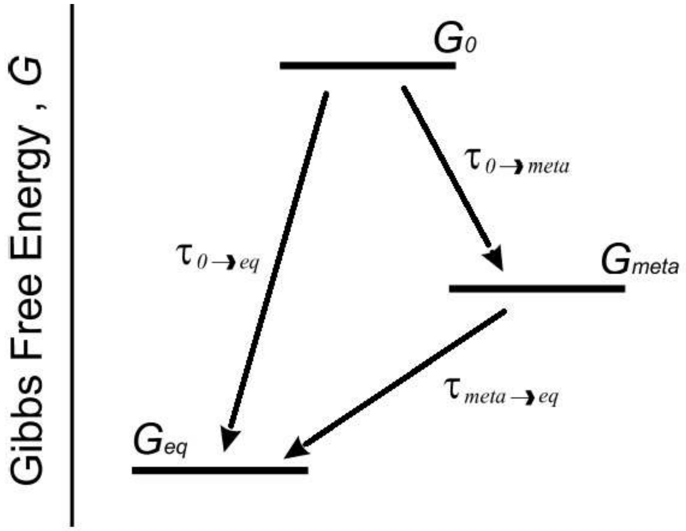

Figure 1.12: Schematic representation on formation of metastable phase during ball milling [Schultz (1988)].

However, the formation of the metastable phase from the initial state G_o is possible if the characteristic reaction time for its formation ($\tau_0 \rightarrow meta$) is much shorter than that of the equilibrium phase ($\tau_0 \rightarrow eq$). At the same time, the rate of formation of the equilibrium phase from G_{meta} ($\tau_{meta} \rightarrow eq$) must be longer than that of metastable phase formation. These kinetic constraints can be summarized as [Schultz *et al.* (1994)]

$$\tau_0 \rightarrow meta \ll \tau_0 \rightarrow eq \qquad (1.4)$$

$$\tau_0 \rightarrow meta \ll \tau_{meta} \rightarrow eq \qquad (1.5)$$

1.20 Mechanical properties of nanostructured materials

Mechanical property is an important consideration for the application of materials and depends fundamentally upon their microstructure on a variety of length scales and the nature of bonding among their constituent atoms. Mechanical deformation can be either elastic or plastic. Elastic deformation is effected through reversible changes in the interatomic spacing or the bending and stretching of bonds between atoms; it is governed by the elastic constants or moduli of a material. For metals, such deformation is in general relatively easy owing to the non-local nature of metallic bonding, but for materials with strong covalent or ionic bonding such as intermetallic compounds it is difficult. Mechanical properties of nanocrystalline materials display an increasing interest. Reducing the grain sizes not only create a big impact on the microstructures of the nanocystalline materials, but also alters their mechanical properties significantly. The most important mechanical properties of nanocrystalline metals and alloys include significantly increased hardness, strength and ductility, etc. with respect to the decreasing grain sizes [Siegel *et al.* (1995)]. The mechanical properties of NC materials not only depend on the average grain size, but also on the grain size distribution and the microstructure, such as grain boundary structures have critical effect on their mechanical properties.

1.21 Hardness and strength

Grain sizes with nanometer dimensions have been observed in almost all MA/MM pure metals, intermetallics and alloys. Literature review shows that the mechanically alloyed/milled nanocrystalline materials unveils unique features of deformation different from that of polycrystals and shows 4-5 times hardness higher than that of the conventional coarse-grained counterparts [Maung *et al.* (2012), Meyers *et al.* (2006) and Tang *et al*. (2013)]. Conventional polycrystals have long been known to exhibit a strong dependence of strength (or hardness) on grain size. This behavior of size effect on strength has been observed to agree with the classical well known Hall-Petch (HP) [Hall (1951) and Petch (1953)] relation

$$\sigma = \sigma_0 + kd^{-\frac{1}{2}} \tag{1.6}$$

where σ_0 is the frictional stress resisting the motion of dislocations or the internal back stress, *k* is the Hall-Petch slope related to the measure of resistance for the movement of dislocations from one grain to another and *d* is the average grain size. A similar expression for hardness is given as [Mukhopadhyay *et al.* (2006) and Furukawa *et al.* (1996)]

$$H = H_0 + \mathrm{k_H} d^{-\frac{1}{2}} \tag{1.7}$$

Where H_0 is the intrinsic hardness dependent on lattice frictional stress. These unusual properties have been attributed to a high area fraction of grain boundaries (GB) which inherently act as strong barriers to dislocation motions. The strengthening effect has been ascribed to the pileup of dislocations and the resistance of the dislocations to slip transfer [Armstrong (1983), Lasalmonie *et al.* (1986) and Mukhopadhyay *et al.* (2006)].

1.22 Inverse Hall-Petch behavior

As suggested by the H-P relationship, the hardness or strength of the materials increases monotonously with the inverse of the square root of the grain size. However, as the grain size is decreased to the submicrometer range, the *k* value (HP slope) tends to decrease; and when the grain size is decreased to less than 100 nm, the *k* value often becomes negative. The relationship between the strength of the nanostructured material and the grain size is very complicated. Since dislocation activity is almost absent in these materials, below a critical grain size the HP relation becomes invalid. Deviations from the Hall-Petch relation was first reported by Chokshi *et al.* (1989) on nanocrystalline copper and palladium and this softening behaviour for nanocrystalline materials is the so called inverse Hall-Petch effect i.e., hardness and strength decrease with a decrease in grain size. At the nanoscale grain size where dislocation activity is believed to be absent [Koch *et al.* (2001)], below a critical grain size, k the HP slope becomes negative implying that the materials get softened. The breakdown in the Hall-Petch trend has been attributed to different deformation mechanisms that become dominant once the grain size is reduced down below a critical value [Koch (2003)]. The major interest involving the studies of strength has been to see if the HP relation holds at smallest grain sizes. Literature shows varied results that can be separated into three classes:

(a) Hall-Petch relation holds even at small grain sizes with essentially the same Hall-Petch slope that is seen at large grain sizes.

(b) Hardness increases with decreasing grain size but the Hall-Petch slope has a lower value than that observed for coarse-grained material.

(c) A negative Hall-Petch slope is observed at small grain sizes.

1.23 Deformation mechanisms of nanostructured materials

The expansion of the understanding of deformation of conventional polycrystalline materials to materials with grain sizes on the scale of nanometer is, at present, an evolving process. Experimental finding on inverse Hall-Petch has prompted various researches to propose models pertaining to their mechanism of deformation. Of the proposed models, two deformation mechanisms related to this work are discussed below:

(a) Pile-up breakdown

The concept of pile-ups has been at the root of the traditional explanation for the HP effect. As the grain size decreases, the number of dislocations piled up against a grain boundary decreases. At a critical grain size, the concept of a pile-up can no longer be used to explain the plastic flow. Fig. 1.13 shows pile-ups for a grain size in the micrometer and nanometer range. For grains on the scale of micrometer or larger, the dislocation sources are assumed to be in the centre of the grain, leading to positive and negative dislocation pile-ups generated by the activation of a Franck-Read source. It is generally accepted that conventional dislocation sources such as the Frank-Read source cease to operate in nanocrystalline materials, and the grain boundaries become the potential sources and sinks. Thus the multiplying effect on the stress field is lost [Meyers *et al.* (2006)].

Wadsworth and Nieh [Nieh et al. (1991)] predicted the grain size in various materials at which the Hall–Petch relationship would break down by assuming that there is a point at which each individual grain in a polycrystalline sample will no longer be able to support more than one dislocation. The critical equilibrium spacing between dislocations, l_c from their calculation is

$$l_c = \frac{3Gb}{\{(1-v)H\}} \tag{1.8}$$

where H is the hardness. In principle, when the grain size, d is smaller than l_c, there will be no dislocation pile-ups and the Hall–Petch relation will break down. Thus,

$$d_c = \frac{Gb}{\{(1-v)H\}} \tag{1.9}$$

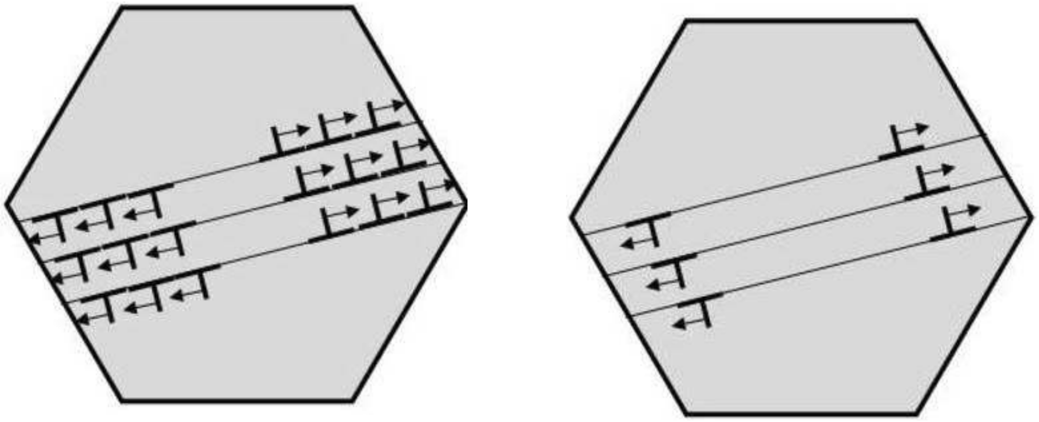

Figure 1.13: Breakup of dislocation pile ups: (a) microcrystalline regime and (b) nanocrystalline regime.

(b) Grain-boundary sliding

The phenomenon of superplasticity has led to detailed study of grain-boundary sliding as the dominant deformation mechanism [Ball *et al.* (1969)]. For nanocrystalline materials, this has been proposed to be the dominant deformation mechanisms at grain sizes < 50 nm. Hahn *et al.* (1997) proposed two hardness relationships,

$H_V = H_0 + \frac{k}{\sqrt{d}}$ in the dislocation dominated regime and (1.10)

$H_V = H_0 - \frac{m_1}{d}(d - m_2)^{1/2}$ in the grain boundary sliding regime (1.11)

where m_1, $m_2$and k are material parameters and d is the grain size. By employing the concept of thermally-activated shear, Conard *et al*. [Conard *et al.* (2000)] proposed that the macroscopic shear rate produced by the independent, atomic shear events at the grain boundaries is given by

$$\dot{\gamma} = N_V A b v exp\left[\frac{-\Delta F(\tau_e)}{kT}\right] \tag{1.12}$$

where N_V is the number of places per unit volume where thermally-activated shear can occur. A is the area swept out per successful thermal fluctuation, b the atomic diameter, ϑ the frequency of vibration and ΔF the Helmholtz free energy, which is a decreasing function of the effective shear stress $\tau_e = \tau - \tau_0$ where τ is the applied stress and τ_0 threshold stress or critical stress.

Reasonable expansions for the parameters on the right side of equation 1.12 are $N_V = \frac{\delta}{db^3}$, where $\delta = 3b$ is the grain boundary width, $A = b^2$, v_D the Debye frequency ($\approx 10^{13}\text{s}^{-1}$), ΔF is the Helmholtz free energy, V the activation volume pertaining to the thermally activated grain boundary shear event equals b^3. It is expected that the value of ΔF will be approximately that for an atom-vacancy interchange in the lattice or grain boundary diffusion Q_b. Inserting the above values into equation 1.12 and considering both forward and backward jumps, gives;

$$\dot{\gamma} = \frac{2bv_D}{d} \sinh\left(\frac{V\tau_e}{kT}\right) exp\left(\frac{-\Delta F}{kT}\right) \tag{1.13}$$

where $\sinh X \approx X$ for $X \leq 0.5$ and $\sinh X \approx \frac{1}{2}\exp X$ for $X \geq 2$, equation 1.10 thus gives that τ_e is proportional to d for small values of $\left(\frac{V\tau_e}{kT}\right)$ and varies as ln (d) with large values.

Experimental observations and molecular dynamic simulations [Duran *et al.* (1996) and Swygenhoven *et al.* (1999)] show that grain boundary sliding is the primary deformation mechanism in nanocrystalline materials and that such a sliding mechanism results in a buildup of stress across neighboring grains. This stress, in turn, is relieved by grain boundary and triple junction migration. The degree to which this occurs depends on grain size since for small grain sizes, less planar interfaces provides reduced steric hindrance to concurrent grain sliding. Such grain-boundary sliding activity is mainly facilitated by atomic shuffling and stress-assisted free volume migration [Kim *et al.* (1999)].

1.24 Scope for the present work

From the literature review it is clear that aluminum is the most promising light weight structural material due to their low density, high specific strength and high ductility but suffer from poor strength/hardness. Aluminum based composites and intermetalllics are gaining tremendous importance because of their potential application in various fields as a light weight structural materials. Many investigations are now being carried out by researchers to explore the potential of aluminum based composites and intermetallics. Aluminum matrix composites are considered to be one of such promising materials and are on the forefront of research and have been widely investigated and are attracting unprecedented interest due to their possible applications in high performance structural and functional components. The properties of AMCs in particular strength can be tailored by suitable combinations of the matrix alloy, type of reinforcement, volume fraction and processing routes to meet specific applications. Discontinuously-reinforced AMCs are particularly attractive due to their easer fabrications routes, lower costs and nearly isotropic properties. It can be successfully prepared by powder metallurgy (P/M). The main advantage of P/M over other methods, such as liquid phase processing, is the microstructure control of the phases (e.g. volume fraction, size and morphology of matrix and reinforcement) that is virtually absent from the liquid phase route. In addition, the relatively low processing temperature of P/M may avoid undesired interfacial reactions between matrix and reinforcement. In this line reinforcing the matrix by thermally stable reinforcements the strength and hardness at elevated temperatures can be improved.

The present work is aimed at investigating the improvement in properties after reinforcing hard industrial by-product such as garnet and carbon nanotube with specific aluminum alloy using mechanical milling and compare with those of unreinforced alloy and pure aluminum. Effect of individual reinforcement type has been studied by comparing the composites. Attempts have also been made to understand the strengthening effects involved in garnet/MWCNT particulate reinforced metal matrix composites. Alloys based on intermetallic phases with high aluminum content are synthesized and characterized Microstructural refinement to nano level has been exploited as a means of producing materials with increased strength. The relationship between the strength of the nanosturctured material and the grain size has been investigated. Since dislocation activity is almost absent in nanostructured materials the strength decreases with decrease in grain size. The motivation is to synthesize equilibrium intermetalllic phases from Al-Fe alloy system and subsequently nanostructured phases after subjecting them to mechanical milling in order to understand the phase stability with milling time and the effect of the consequent nano-phases on the mechanical properties of the alloy. Possibility of formation of phases has been explored using improved Miedema's model. Attempts have been made at investigating the possible factors and deformation mechanism leading to softening behavior involved in nano-intermetallics.