Novel materials synthesis by mechanical alloying/milling

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An account is given of the research that has been carried out on mechanical alloying/milling (MA/MM) during the past 25 years. Mechanical alloying, a high energy ball milling process, has established itself as a viable solid state processing route for the synthesis of a variety of equilibrium and non-equilibrium phases and phase mixtures. The process was initially invented for the production of oxide dispersion strengthened (ODS) Ni-base superalloys and later extended to other ODS alloys. The success of MA in producing ODS alloys with better high temperature capabilities in comparison with other processing routes is highlighted. Mechanical alloying has also been successfully used for extending terminal solid solubilities in many commercially important metallic systems. Many high melting intermetallics that are difficult to prepare by conventional processing techniques could be easily synthesised with homogeneous structure and composition by MA. It has also, over the years, proved itself to be superior to rapid solidification processing as a non-equilibrium processing tool. The considerable literature on the synthesis of amorphous, quasicrystalline, and nanocrystalline materials by MA is critically reviewed. The possibility of achieving solid solubility in liquid immiscible systems has made MA a unique process. Reactive milling has opened new avenues for the solid state metallothermic reduction and for the synthesis of nanocrystalline intermetallics and intermetallic matrix composites. Despite numerous efforts, understanding of the process of MA, being far from equilibrium, is far from complete, leaving large scope for further research in this exciting field. IMR/323

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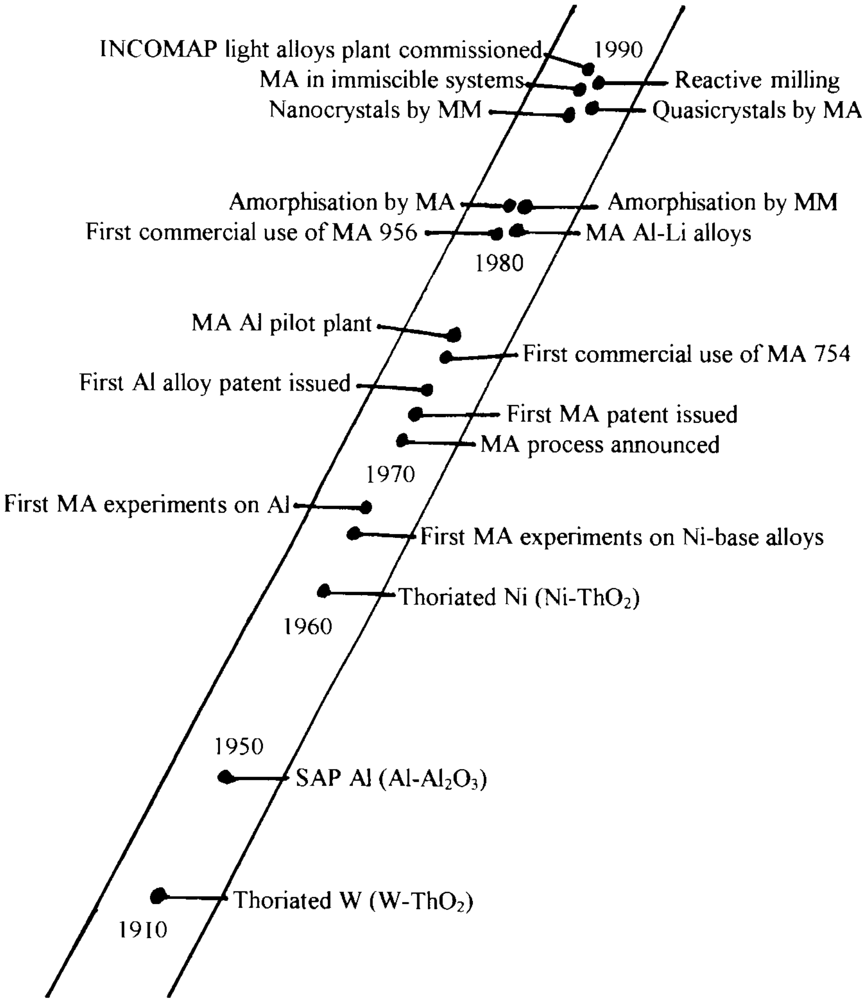
Introduction

Mechanical alloying (MA) is a high energy ball milling technique, in which elemental blends are milled to achieve alloying at the atomic level. In addition to elemental blends, prealloyed powders and ceramics, such as oxides, nitrides, etc., can also be used to produce alloys and composites by this technique. This technique was developed around 1966 (Ref. 1) by Benjamin and his co-workers at the Inco Paul D. Merica Research Laboratory as a part of the programme to produce oxide dispersion strengthened (ODS) Ni-base superalloys for gas turbine applications. The initial experiments by Benjamin's group were aimed at coating the oxide particles with Ni by ball milling. Such a process was known 40 years earlier from the work of Hoyt,[2] who reported coating of WC with Co by ball milling. In 1966, attention was turned by Benjamin's group to the production of alloys by high energy ball milling. The first experiments in this direction were on the production of thoria dispersed nickel (commonly known as TD nickel) and Ni–Cr–Al–Ti alloy with thoria dispersions. The success of both these experiments led to the first patent on this process (Fig. 1). The process was initially referred to as 'milling/mixing'. The term 'mechanical alloying' was actually coined by Ewan C. McQueen, a Patent Attorney for Inco.[3]

Figure 1 (Refs. 4 and 5) shows the chronological evolution of the MA process. Most of the work on MA before the early 1980s was concentrated on the production of ODS superalloys (Ni- and Fe-base) and Al alloys. In 1983, a paper by Koch and his group from Oak Ridge National Laboratory[6] triggered off such a chain reaction that MA has become a field of research all over the world in many laboratories. In this seminal work, Koch *et al.*[6] reported the formation of amorphous phase by the MA of an elemental blend of Ni and Nb of $Ni_{60}Nb_{40}$ composition. While Benjamin is the pioneer of MA, Koch can be considered as the father of present face of MA. Two years before the invention of Koch, a Russian group led by Yermakov demonstrated the amorphisation of intermetallic compounds in Y–Co (Ref. 7) and Gd–Co (Ref. 8) by milling in a planetary mill. This also opened up a new area which is now commonly referred to as 'amorphisation by mechanical milling (MM)' as against that reported by Koch *et al.*,[6] in which the MA of dissimilar elements leads to amorphisation ('amorphisation by MA'). 1983 can be considered the birth year for 'solid state amorphisation' (SSA) with two more papers appearing on amorphisation by low temperature diffusion annealing of multilayers of Au and La (Ref. 9) and that of Zr_3Rh by hydrogenation.[10] Codeformation (rolling) of pure metal foils of Ni and Zr followed by low temperature annealing was also reported to result in the formation of an amorphous alloy.[11,12] Severe plastic deformation under hydrostatic pressure is also reported to have led to the alloying of elemental blends.[13,14] All these techniques, including amorphisation by irradiation[15] are now considered as variations of SSA. In the past decade many reports have appeared on solid state amorphisation by all the above routes; the most popular routes being MA and MM.

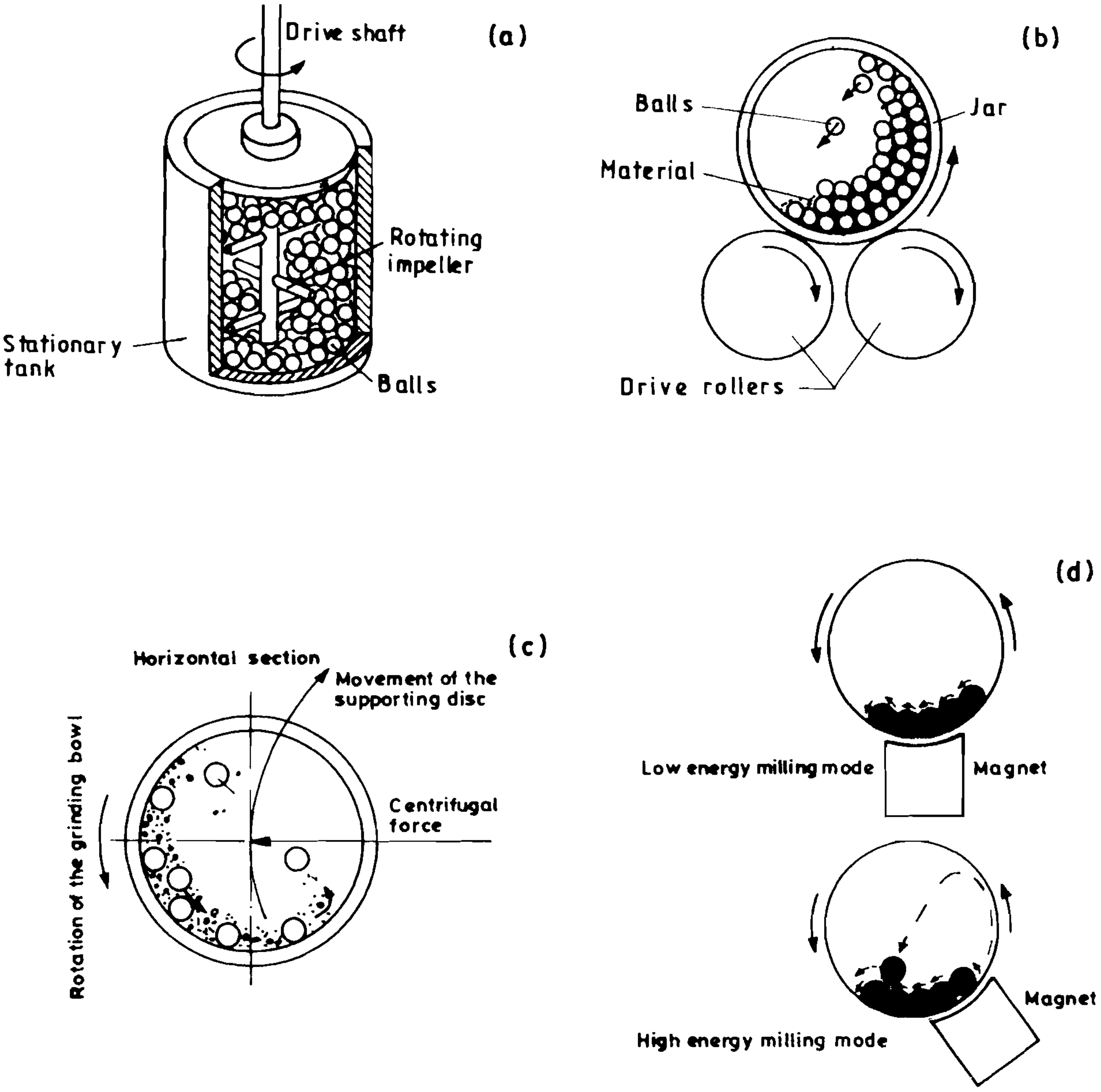
Even though Benjamin developed the MA technique originally for ODS alloys, almost all the stable and metastable structures produced by rapid solidification processing (RSP) have been realised by MA. In addition, extended solid solution and amorphous phase formation in the case of liquid immiscible systems have been observed by MA which are difficult



1 **Chronological evolution of MA process (after Ref. 4)**

to obtain by RSP, making the MA process superior to RSP in many respects. There were also successful attempts to combine MA with RSP in order to exploit a synergistic effect.[16–18] Mechanical alloying has also been widely used for the synthesis of nanocrystalline metals, alloys, intermetallic compounds, ceramics, and nanocomposites in recent years.[19] In addition, quasicrystalline phases have also been synthesised in many metallic systems by MA.[20] A new area that started in late 1980s is reactive milling/combustion synthesis. Taking clues from the first work of Schaffer and McCormick (reduction of CuO by Ca during milling),[21] a large amount of work has been carried out to check the feasibility of using high energy ball milling in the area of chemical refining. High energy ball milling has also been used for the production of various intermetallics and nanocomposites *in situ*, by milling metallic powders in reactive atmospheres.[22,23]

A number of international conferences have been organised on the subject covering various aspects related to MA/MM.[24–27] In addition, a few conferences were dedicated to a particular aspect of this very wide field such as ODS alloys,[28–32] amorphisation,[33–36] disordering,[37] and mechanochemistry.[38] The subject has been deliberated at length in all the 'Rapid quenching (RQ)' conferences since RQ6 in 1987.[39–42] The three international conferences held so far on nanostructured materials[43–45] and other similar conferences on nanophase materials[46–56] have also given considerable importance to the nanocrystalline materials prepared by MA/MM. The subject has been given its due respect in the powder metallurgy world congresses held from time to time[57–62] and in Titanium '92.[63] Mechanical alloying/milling has also been the subject of special issues in a few journals.[64,65] A new journal, *Int. J. Mechanochemistry and Mechanical Alloying*[66] has recently been started to serve the work that is being published in the field of MA. There are a number of general reviews[67–72] as well as reviews on specific aspects related to MA/MM, such as, ODS alloys,[73–78] amorphisation,[79–89] disordering,[90] quasicrystals,[20] intermetallic compounds,[91–94] nanocrystals,[19,95,96] reactive milling/combustion synthesis,[22,23,97–99] and modelling of energy transfer during milling.[100–103] Suryanarayana[104] has recently brought out a bibliography on MA and MM covering all the reports that appeared in this field during 1970–94. The last comprehensive review on MA/MM was that of Koch[68] which appeared in 1991. This rapidly growing field deserves at least one comprehensive review every five years to keep the readers well informed about the developments in this field. The present review attempts to cover all the aspects of MA/MM with the goal of having a comprehensive and critical review of the state-of-art in this field.



a attritor (Ref. 68); *b* tumbler mill (Ref. 68); *c* planetary mill (Ref. 100); *d* uniball mill (Ref. 105)

2 Schematic of ball movement in typical ball mills used for MA/MM

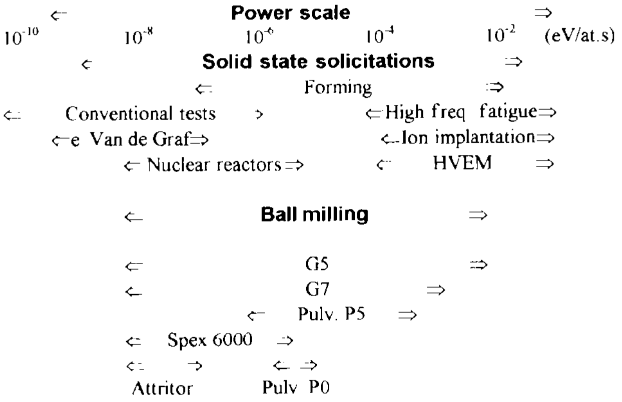
Mechanical alloying: devices and process

High energy ball mills

Mechanical alloying/milling is usually carried out in high energy mills such as vibratory mills (Spex 8000 mixer/mill), planetary mills (Fritsch and Retsch mills), and attritor mills (Szegvari attritor). The energy transfer to the powder particles in these mills takes place by a shearing action or impact of the high velocity balls with the powder. An attritor was the first high energy ball mill used for MA by Benjamin.[1] The attritor was invented in 1922 by Szegvari for a quick dispersion of fine sulphur particles during the vulcanisation of rubber. The attritor has a vertical cylindrical tank in which the powder and balls are charged. The movement of the balls and powder is achieved by the horizontal impellers attached to a vertical shaft which is made to rotate (Fig. 2*a*).[68] Set progressively at right angles to each other, the impellers energise the balls causing the size reduction of powder by impact. Owing to the higher capacity of these attritor mills (Table 1), they are usually preferred in industry rather than in research laboratories. The tumbler mills (Fig. 2*b*),[68] which are traditionally used in mineral processing, can also be used for MA if their diameters are sufficiently large (of the order of metres) and if

Table 1 Comparison of various high energy ball mills

Type of mill	Capacity (Ref. 100)	Ball velocity, $m\ s^{-1}$	Refs.
Mixer	Up to 2 × 20 g	<3·9	101
Planetary	Up to 4 × 250 g	<11·24	102, 103
Attritor	0·5–100 kg	<0·8	101
Uniball	Up to 4 × 2000 g	...	...



3 Power scale for various ball mills in comparison with other solid state solicitation processes (after Refs. 69, 112)

mills are operated close to the critical speed beyond which the balls are pinned to the inner walls of the mill because of the centrifugal force dominating over the centripetal force. For large scale production, tumbler mills are more economical when compared with the attritor and other high energy ball mills.[106] Vibratory tube mills[107] are also used for pilot scale production in which a cylindrical container with the powder and ball charge is vibrated.

The laboratory mills, though with smaller capacities,[108] offer a higher velocity for the balls.[109–111] The capacities and linear velocities of the balls in various high energy ball mills are compared in Table 1. Figure 3 (Refs. 69, 112) compares the injected power levels in various mills. Among the laboratory mills, the Spex 8000 shaker mill and Fritsch Pulverisette are most widely used. In the Spex mill, most widely used in USA, the vial containing the balls and powder is vibrated in three mutually perpendicular directions with an amplitude of 50 mm and a frequency of 20 Hz. In the Fritsch planetary mill, commonly used in European countries, the disc on which the vial is mounted rotates in the opposite direction to that of the vial; this gives a centrifugal force to the balls (Fig. 2*c*).[100] In the basic models (P5 and P7) the speeds of the vial and disc can not be independently varied; however, this has been achieved in the modified versions (G5 and G7).[111,113] Even though the linear velocity of the balls in the Fritsch mill is higher than that of the Spex mill, the frequency of impacts is much greater in the Spex mill,[109,110] which makes it a higher energy mill in comparison with the Fritsch mill. Owing to the low energies of milling in the case of the attritor, it takes longer to achieve alloying when compared with laboratory mills. It has been shown[114] in the Ti–Mg system that alloying takes place after 16 h in the Spex mill, while the attritor took 100 h to achieve the same result.

Another high energy ball mill which is widely used at present by the Australian investigators is the Anutech uniball mill.[105,115] This mill consists of a stainless steel horizontal cell with hardened steel balls. The movement of the balls is confined to the vertical plane by the cell walls and is controlled by an external magnetic field whose intensity and direction can be adjusted. Depending on the position of the magnet, the mill can run in either high energy mode (impact prominent) or in low energy mode (shear prominent) (Fig. 2*d*).[105] Another interesting feature of this mill is that the impact velocity and frequency can be independently controlled[105] which is not usually possible in the other mills unless some modifications are incorporated.[111,113] In addition to the above mills several other mills such as a single large ball in a vibrating frame mill,[116] rod mill,[117] modified rod mill,[118] and other specially designed mills[119,120] have been used for MA/MM. In some cases[121,122] a combination rolling and ball milling is also used to achieve MA.

Milling parameters

The kinetics of alloying and other phase transformations induced during MA/MM depend on the energy transferred to the powder from the balls during milling. The energy transfer is governed by many parameters such as the type of mill, milling speed, type, size and size distribution of the balls, ball/powder weight ratio, extent of filling of the vial, dry or wet milling, temperature of milling, atmosphere in the mill and finally, the duration of milling. The kinetic energy of the balls is higher with higher speeds of milling and with heavier balls (tungsten carbide better than steel). A number of investigators[123–126] have reported an increase in the glass forming composition range (GFR) with an increase in milling speed. Joardar *et al.*[127] have recently shown that NiAl formation and its disordering tendency during MA are enhanced with increasing milling intensity. It has also been reported recently,[128] that the reaction rate for the formation of TiC during MA increases exponentially with the density of the balls. The size and size distribution and the number of the balls should be chosen so as to achieve an optimum packing of the vial. Too dense a packing of the balls decreases the mean free path of the ball, while a loose packing minimises the collision frequency. Ball/powder weight ratios of 5:1–10:1 are widely used and are effective.

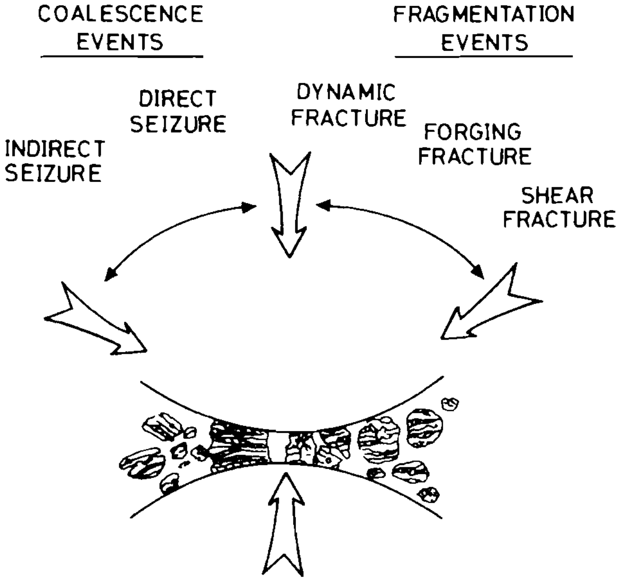
High energy ball milling is characterised by repeated welding and fracturing of the powder. The extent of welding and fracturing is decided by the deformation behaviour of the powder and the temperature of milling. Thus, the nature of phase transitions during milling are, to a large extent, a function of the temperature of milling. Lee *et al.*[129] have shown that the rate of amorphisation increases with an increase in milling temperature; however, the reasons for such an effect are not yet fully understood. Klassen *et al.*[130] have very recently reported alloying the Ag–Cu system, a system with positive enthalpy of mixing, at low milling temperature while higher milling temperatures have favoured decomposition of the solid solution. During the milling, a part of the energy of the balls is dissipated as heat which raises the temperature of the powder. This aspect is discussed in detail in the section 'Temperature effects during milling' below. Mostly MA is carried out in a dry condition under an inert atmosphere to prevent the oxidation of the powders. In the case of ductile materials such as Al and Sn, to prevent excessive welding of the particles to the balls and the inner walls of the vial and to achieve proper balance between welding and fracture, some process control agents (PCAs) are used.[131–134] These PCAs are mostly organic materials such as stearic acid, methanol, and toluene.[74] Radlinski *et al.*[135] have shown that milling in presence of PCAs can drastically affect the solid state reactions in the Al–Mg system. They (PCAs) could also reduce the Fe contamination during milling, the reactivity of Ti–Cu and Al–Ti powders towards oxygen after milling, and improve the magnetic properties of $(Co–Fe)_{75}Si_{15}B_{10}$.[135] In certain cases milling is performed in a wet condition in order to avoid completely excessive welding and oxidation.[136] Excessive welding can also be prevented by changing the deformation characteristics of the powder by carrying out the MA at subzero temperatures where the fracturing of the particles is more pronounced.[137]

Alloying process

The MA process is characterised by repeated welding and fracturing of the powder particles trapped between the colliding balls during milling. The extent of these individual microprocesses (welding and fracturing) depends mainly on the mechanical behaviour of the powder components. Hence, the powder components are usually classified as (a) ductile/ductile, (b) ductile/brittle, and (c) brittle/brittle systems.

Ductile/ductile systems

A large number of elemental blends that are mechanically alloyed so far fall in this category. The mechanism of alloying when both components of the blend are ductile was first given by Benjamin and Volin[131] and was dealt with by Benjamin in detail in later reports.[3,73,74,138,139] According to these, the MA process can be conveniently divided into five stages based on optical microscopic observations. Figure 4 (Ref. 140) shows a schematic of the events occurring when the powder particles are trapped between two colliding balls. In the first stage of MA, the equiaxed ductile particles are flattened by microforging resulting in flaky and platelike particles. The increased surface area of the particles results in extensive cold welding of powder components on further milling (second stage) resulting in sandwichlike microstructure and an associated increase in the average particle size. On further milling, the particle size decreases because of further fracturing and the particles tend to become equiaxed (third stage). The increase in the hardness of the particles because of strain hardening is the reason for fracturing to dominate in this stage. The fourth stage is called random welding orientation in which a number of lamellar colonies of random orientation develops in each composite particle. The hardness and particle size tend to reach saturation in the final steady stage (steady state) suggesting that welding and fracturing frequencies are balanced. There is a continuous decrease in the interlamellar distance in each particle with milling and the lamellae become unresolved under the optical microscope in the fifth stage of MA. Alloying starts by the diffusion of one element into the other towards the end of the third stage because of the formation of fine alternate layers of the constituent elements and is further aided by the rise in temperature and the short-circuit diffusion paths created by the deformation induced defects during milling. Alloying is complete in the fifth stage of the MA process. A number of metallic systems such as Ni–Cr, Cu–Ni, Cu–Zn, Ni–Al, etc., fall in the category of ductile/ductile systems. The MA of Nb and Sn also falls in this category which has led to the formation of superconducting Nb_3Sn,[73,141] by choosing the blend in the stoichiometric ratio. The formation of MnBi (Ref. 142) by the MA of Mn and Bi is also an example of this category.



4 Schematic of events occurring during ball to powder collision (after Ref. 140)

Ductile/brittle systems

The early work of Benjamin and his group on the ODS alloys is a typical example of a ductile/brittle system. In such a system, the ductile metallic particles such as Ni or Al are flattened and welded to each other during milling, while the brittle phase such as oxide particles is fragmented and embedded in the layers of the ductile phase.[73,74] As milling proceeds, the layers of the ductile phase come closer and ultimately become unresolved, while the brittle phase is uniformly distributed as fine particles in the matrix of the ductile phase. In the case of Ni-base ODS alloys, the brittle intermetallics, added to Ni and other elemental powder blends, become fragmented and finally, are alloyed with the Ni matrix, in contrast to the inert oxide particles.

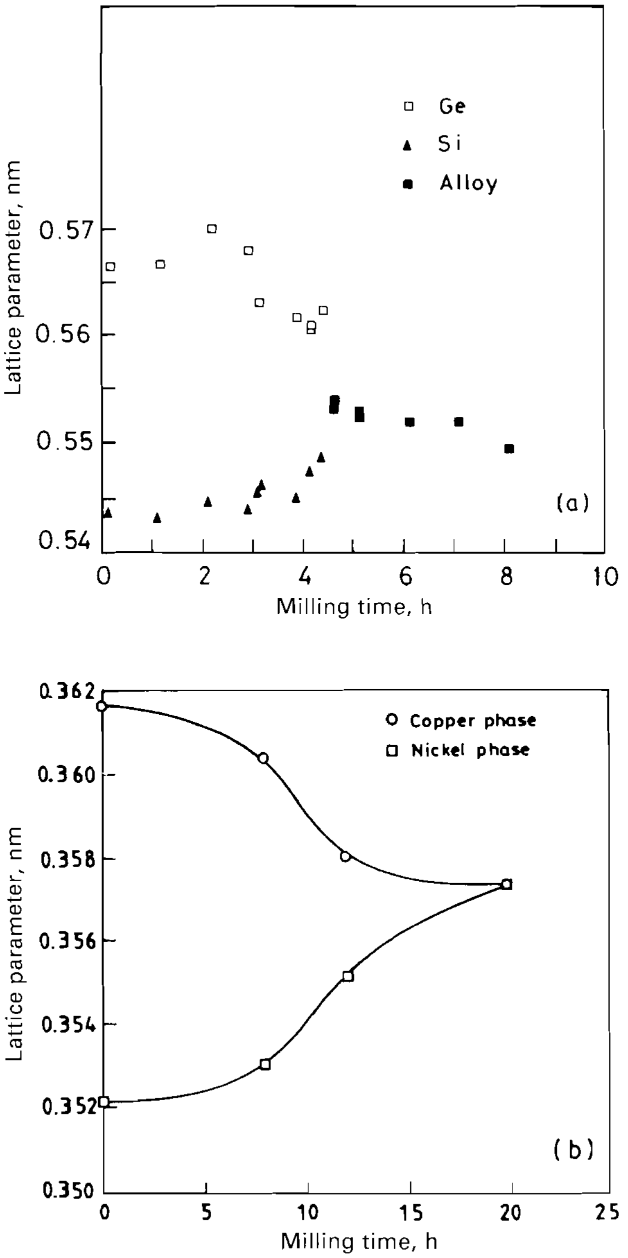
Nb_3Ge, Nb_5Ge_3 (Ref. 141), and TiB_2 (Ref. 143) have been produced by the MA of ductile/brittle components. Another example of MA of this group was the formation of amorphous Ni–24 at.-%Zr alloy, when Zr and $NiZr_2$ powders were milled together.[144] Ball milling of brittle amorphous B with Fe did not result in alloying and the B particles remained dispersed in the ductile Fe matrix, while alloying could be observed in the Fe–Si system.[145] These differences could be attributed to the differences in the equilibrium solid solubility of B and Si in Fe. Silicon has significant solubility in Fe, while B has negligible solubility. Thus it appears that to achieve alloying during the milling of ductile/brittle components, the brittle component not only needs to be fragmented to a small size to shorten the diffusion distances but also should have some equilibrium solubility in the ductile counterpart.

Brittle/brittle systems

In the initial stages of development of the MA technique, it was thought that the milling of brittle/brittle components would result only in the fragmentation of the individual components to the limit of comminution without any alloying. However, alloying has been successfully demonstrated in the Si–Ge system[146] with the formation of solid solution during the ball milling of a powder mixture of Si–28 at.-%Ge. Amorphous alloys were obtained by milling mixtures of intermetallic compounds[84] such as $NiZr_2$ and $Ni_{11}Zr_9$ (Refs. 147, 148). All the above examples suggest that alloying and material transfer is possible during the high energy ball milling of brittle/brittle systems. However, the mechanism of alloying in such systems is not yet clearly understood. The microstructural features in these systems with granular morphology during MA were found to be very different from ductile/ductile systems with their lamellar morphology. Material transfer in these systems is thought to be due to diffusion caused by the rise in temperature during milling. This is supported by the evidence that MA in the Si–Ge system could not be achieved when the elemental blend was milled in a vial cooled by liquid nitrogen.[145] In contrast, alloying could be achieved in a ductile/ductile system such as Ni–Ti at 233 K (Ref. 149) and in a ductile/brittle system such as Nb–Ge at 258 K (Ref. 141). This could be due to the enhanced diffusion paths in these systems caused by deformation induced defects which are expected to be insignificant in brittle/brittle systems.

Mechanical alloying – true alloying?

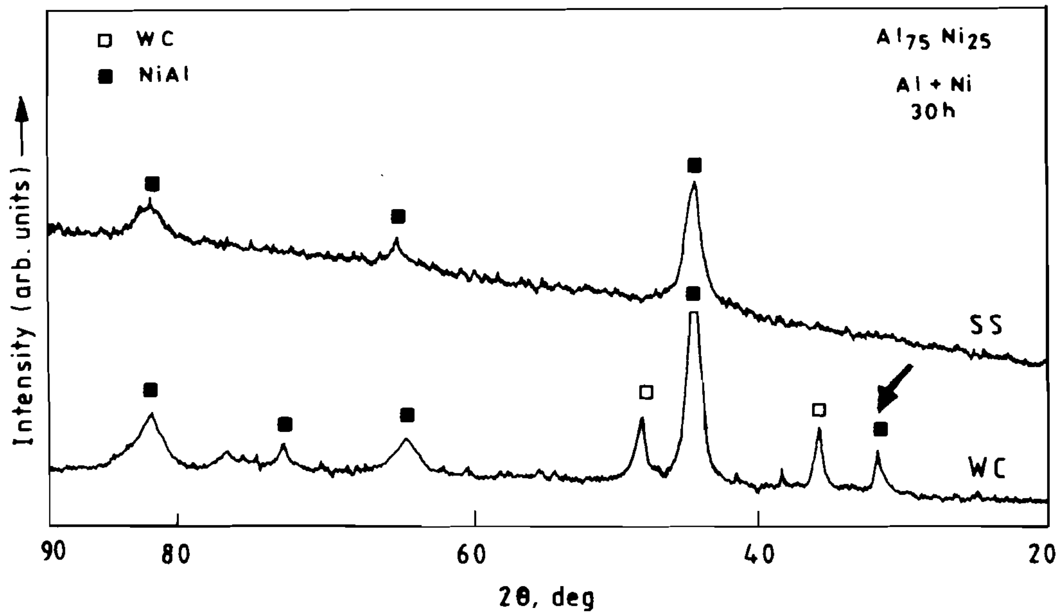
The first work that cleared the doubts whether the MA process results in only a fine mechanical mixture of the constituents of the elemental blend or forms true alloys was that of Benjamin.[73] He could show from magnetic measurements that a Ni–Cr alloy prepared by MA behaves exactly in the same way as that produced by the ingot metallurgy route. Once Cr dissolves in Ni the latter loses its ferromagnetic property and becomes paramagnetic depending on the concentration of Cr. This would not happen if Ni and Cr remained as a mechanical mixture of fine powder. The formation of diamond cubic solid solution in the Si–Ge system was shown by lattice parameter measurements of Ge and Si during MA using X-ray diffraction.[145] Figure 5*a* (Ref. 146) shows the variation in lattice parameters of Si and Ge when an elemental blend of Si–28 at.-%Ge was milled in a Spex mill. The lattice parameters of Ge and Si approached each other in the course of milling and merged after 5 h of milling. On further milling, the lattice parameter essentially remains constant suggesting that alloying was complete within 5 h. Figure 5*b* (Ref. 150) shows similar lattice parameter changes leading to solid solution formation in the Cu–Ni system during MA. The formation of intermetallic compounds[74,141,142,146] and amorphous phases[6,84] on the MA of elemental blends also has proved that alloying at the atomic level occurs during high energy ball milling. A typical example is the formation of β-brass (bcc) during the MA of an elemental blend of Cu (fcc) and Zn (hcp).[151,152]



5 Lattice parameter variation of *a* Ge and Si during MA of Si–28 at.-%Ge in Spex mill (Ref. 146) and *b* Cu and Ni during MA of Cu–50 at.-%Ni (Ref. 150)

Contamination during milling

Most of the MA work reported so far has been carried out using stainless steel (SS) or hard chrome steel (CS) milling media (balls and container). These can introduce a large amount of Fe contamination into the milled powder. It has been shown that during the synthesis of NiAl from an Ni and Al blend using



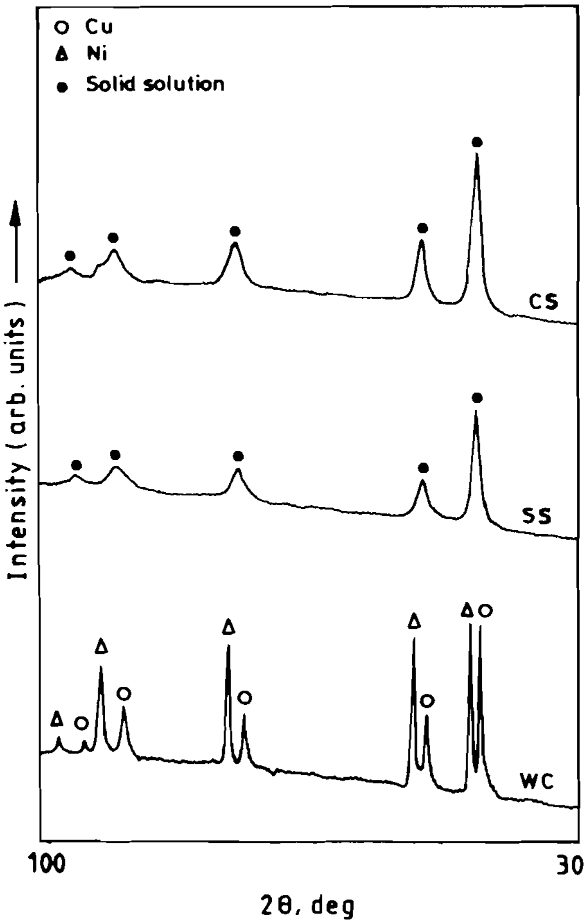
6 **XRD patterns of elemental blend of $Al_{75}Ni_{25}$ after MA for 30 h in stainless steel (SS) and WC milling media showing formation of NiAl (arrowhead indicates {100} superlattice reflection) (after Ref. 154)**

SS milling media that the Fe contamination is of the order of 18 at.-%.[153] However, with CS milling media (having better wear resistance than SS), the contamination level was about 5 at.-%.[153] The level of contamination not only depends on the milling media but also on other milling parameters such as the type of mill and milling speed, etc. Contamination levels are expected to be greater in high energy ball mills such as the Spex mill. In order to minimise contamination, less energetic mills such as the vibratory mill may be used.[68] Contamination can be avoided by milling the powders with a milling media made up of the same material as that of the powders being milled.[68] However, this proposal is difficult to put into reality in many cases.

It has been shown recently[150,152,153] that Fe contamination from milling media can be a blessing in disguise. During the MA of elemental blend of Ni and Al, it was observed that completely disordered (long range order parameter, $S = 0$) nanocrystalline NiAl forms when milled with SS media, while partially ordered NiAl ($S = 0{\cdot}55$) forms when milled in tungsten carbide (WC).[153] Milling with CS media has resulted in NiAl with intermediate S (0·48).[153] Figure 6 (Ref. 154) shows the X-ray diffraction (XRD) patterns of Ni,Al powder mixture of $Al_{75}Ni_{25}$ composition milled in a Fritsch Pulverisette (P-5) at 300 rev min^{-1} for 30 h using SS and WC milling media. The presence of the {100} superlattice reflection of NiAl can be clearly seen (indicated by arrowhead in the figure) in the case of WC and is absent when milled with SS. In recent years, it has been argued that some ductility can be introduced into the otherwise brittle intermetallic compounds by grain refinement[155] and/or by introduction of disorder.[156] Iron is known to reduce the ordering energy of NiAl (Refs. 156, 157). Thus, it is not surprising that Fe contamination during milling has resulted in the formation of disordered NiAl (Refs. 153, 154). The above results suggest that Fe contamination from milling media can be helpful in inducing ductility in some otherwise brittle aluminides by introducing disorder.

Another example of the usefulness of Fe contamination was observed during the MA of Cu–Ni elemental blends.[150] Complete alloying and the formation of solid solution was observed when an elemental blend of $Cu_{50}Ni_{50}$ was milled in a Fritsch Pulverisette (P-5) at 300 rev min^{-1} for 20 h in SS and CS milling media while no alloying was observed when milled in WC under identical conditions (Fig. 7).[150] Another interesting feature was that in the case of CS and SS milling media, the Cu and Ni crystallites become nanocrystalline (<20 nm) during milling, while in the case of WC they remained coarse (>200 nm) even after 20 h of milling. This could be attributed to the change in the deformation characteristics of Cu and Ni due to Fe contamination during milling in SS and CS media. It is also evident from this study that nanocrystallisation is probably a prerequisite for alloying during high energy ball milling, at least in slow diffusing systems such as Cu–Ni.

Another potential source of contamination during high energy ball milling is the milling atmosphere. In order to avoid oxygen contamination, most of the researchers carry out milling either in argon or in wet conditions. The contamination of oxygen is most severe for reactive metals such as Al, Ti, and Zr and contamination to the extent of 10% is possible in Zr- and Ti-base alloys. The oxygen concentration tripled during the milling of Al after 3 h (Ref. 134) and doubled in Ni_3Al after 6 h (Ref. 158) when milled in an impure argon atmosphere. Koch *et al.*[6] observed that the amorphous phase obtained in the Ni–Nb system has a lower crystallisation temperature when milled in air when compared with that obtained by milling Nb and Ni powder mixture in helium. Lee and Koch[159] reported faster amorphisation in air than in argon or helium; they attributed this to the



7 **XRD patterns of elemental blend of $Cu_{50}Ni_{50}$ after MA for 20 h in stainless steel (SS), chrome steel (CS), and WC milling media showing formation of solid solution in first two cases (Ref. 150)**

oxygen contamination. Oxygen contamination has also been reported to have led to crystallisation of amorphous phase during MA in the Ni–Ti system.[160] Ivison *et al.*[161] have shown that hydrogen contamination can act as a catalyst for the amorphisation reaction in the Ti-rich compositions in the Cu–Ti system during MA and that the reaction was inhibited in its absence. During the MA of $Ti_{50}Al_{50}$ Suryanarayana and Froes[162] have shown that amorphisation occurs in 30 h when milled in nitrogen while it takes 100 h in argon. Guo *et al.*[163] have attributed the formation of metastable fcc phase during the MA of $Ti_{95}Al_5$ and $Ti_{50}Al_{50}$ to the high oxygen and nitrogen contamination during milling. Atmospheric contamination can be minimised by milling in high purity argon either by filling the container with it and sealing it, by enclosing the mill in an argon filled glove box, by carrying out wet milling in a reducing medium such as toluene, or by milling in vacuum.[164]

Another source of contamination is the process controlling agents added during milling of ductile metals such as Al in order to minimise excessive welding. It was shown[165] that PCAs such as Nopcowax-22DSP get incorporated into the metal powder within 25 min resulting in contamination of the powder. However, the PCAs are usually added in very small quantities (<1%) and hence are not a cause for much concern.

Physics of mechanical alloying/milling

If one looks at the large amount of experimental results available in the field of high energy ball milling, it becomes clear that the nature and kinetics of phase transformations are quite sensitive to the milling conditions. This has prompted a number of investigators to attempt the most difficult and crucial study in the field of high energy ball milling, i.e. to study the physics/mechanics of milling so as to understand the results of MA and to predict, if possible, the outcome of a MA experiment, given the experimental conditions. Benjamin and Volin[131] were the first to attempt at a semi-empirical solution for the time required for alloying during MA. Based on microhardness measurements on the particles at various milling times, they arrived at an expression for the variation of the lamellar thickness of the composite as a function of milling time. Their analysis was based on the assumptions that the rate of energy input and the rate at which material is trapped between colliding balls during MA are independent of milling time and that the energy required per unit strain is a linear function of instantaneous hardness of the powder particle. The time at which the lamellar thickness reached the resolving power of the optical microscope was considered to be the time required for alloying. Very recently, Pabi *et al.*[166] have developed a rigorous mathematical model based on the modified isoconcentration contour migration method to predict the kinetics of diffusive intermixing during MA. They have successfully correlated the kinetics of alloying to the melting temperature in the Cu–Ni system which the ballastic diffusion model[112] failed to establish.

Since the above early work, more sophisticated modelling attempts[167,168] have been made to have a deeper understanding of MA. Five research groups have been mainly involved in this modelling work. They are, Hashimoto and Watanabe[100] from Japan, Maurice and Courtney[101,103,169,170] and Koch *et al.*[70] from the USA, Magini *et al.*[102] from Italy, and Gaffet *et al.*[96] from France. The efforts of various investigators can be classified mainly into two groups, namely, the modelling/simulation approach and the energy maps/milling maps approach.

Modelling/simulation approach

As MA is inherently stochastic in nature, one has to accept that modelling of the process is very difficult. In addition, the motion of balls in various mills used for MA is quite complex in nature and understanding it is crucial to estimate the energy transferred from the balls to the powder. The phase transformations induced during high energy ball milling are mainly dependent on the energy transferred during the collision of the balls with the powder, the frequency of these collisions, and the deformation behaviour of the powder. Owing to the lack of sufficient knowledge about the deformation behaviour of materials at high strain rates, impact velocities, and impact frequencies, one can not expect absolute predictions, but only an order of magnitude prediction and the general trends from these modelling efforts. In addition, one can also identify critical process variables for process optimisation.

The modelling efforts can be classified into local and global models. In local modelling, the extent of plastic deformation, frequency of welding, and fracturing during collision are estimated given knowledge of the impact velocity, impact frequency, and other milling parameters. The impact velocities, frequencies, and angle of impacts being mill dependent, global modelling tries to predict them in a specific milling device. A combination of local and global models can give a more complete picture of what goes on during high energy ball milling.

Local modelling

Maurice and Courtney[140] were the first to attempt this approach. They considered collision involving powder entrapped between milling media. They assumed that the collision between balls coated with powder is similar to the Hertzian collision of uncoated balls and that the coating only slightly perturbs the collision. Essentially, this means that the work involved in the plastic deformation is assumed to be a small fraction of the precollision kinetic energy of the balls. The collision volume was considered to be a cylinder of radius equal to the Hertz radius. Considering collision to be analogous to microupsetting, the Hertz radius, the collision duration, and the strain per collision have been estimated. The Hertz radius, collision time, and strain per collision are proportional to $v^{0\cdot4}$, $v^{-0\cdot2}$, and v, respectively (where v is impact velocity). Assuming that the processing time is related to a critical amount of total deformation,[171] they estimated the processing times to be proportional to $v^{-2\cdot6}$. Benjamin[172] modelled single collision based on the material response of the powder and arrived at similar collision times. Bhattacharya and Arzt[173] in an alternative approach modelled the response of a porous compact and predicted the change in the dislocation density as a function of milling time and intensity. None of the above models deal with powder fragmentation and coalescence. They are 'snapshots' of single collisions and hence do not give much insight into the MA process.

In their later work, Maurice and Courtney[174] attempted a more rigorous treatment of the single collision and developed criteria for welding and fracture. Incorporating the above principles, two computer programs have been developed.[175] The first of these, MAP1, deals with a single species with the option to add dispersoids and the second one, MAP2, considers welding of two species to form a third composite species. The programs describe the changes in the powder size, shape, hardness, and microstructural scale during MA. The programs predict[176] several stages of the MA process described originally by Benjamin and Volin.[131] The predicted particle sizes[176] are in reasonable agreement with the measured ones.[131–133] However, the model[176] underestimates the rate of powder deformation and overestimates impact frequency. The detailed model of Maurice and Courtney[177] shows that the processing time dependence on impact velocity for various combinations of metals of different hardness and fracture toughness is in the range v^{-2}–v^{-3}. The model could also predict quite closely the influence of atmosphere and premilling of Ni on the formation Ni_3Si_2 during MA.[178]

In a separate study Aikin *et al.*[179–181] used kinetic principles to study the fracture and coalescence events. The model predicts the welding and fracturing probabilities and the particle size distribution[179,180] during MA based on the assumption that the fracturing and welding frequencies are species dependant and do not depend on particle size or milling time. They could show[178,179] that the fracturing and welding probabilities scale directly with ball/powder weight ratio and vary almost linearly with mill power. However, all the above models deal with ductile materials only and do not predict the phase transitions induced during MA, in the sense that the atomistic process of MA is not addressed in these models.

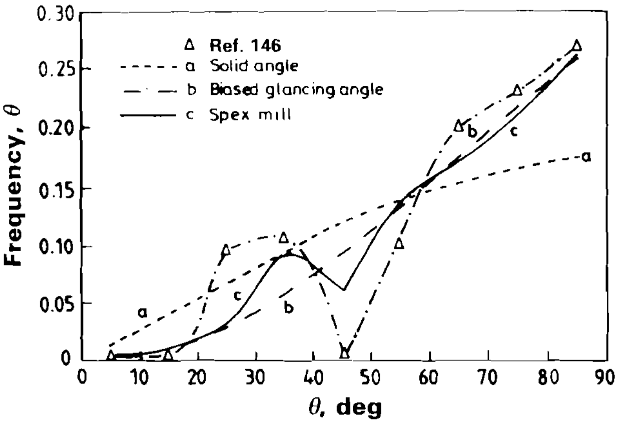
Global modelling

Davis and Koch[146] were the first to model the kinetics of ball milling in a Spex mill. The ball motion in the vial was recorded on a videotape and then analysed by a motion analysis computer translation system. The study showed that the majority of the impacts have an energy dissipation of 10^{-3}–10^{-2} J (Table 2). The impact velocity was predicted to be $\leqslant 6$ m s^{-1}. The model also predicts that the majority of the impacts are glancing in nature and not head-on. This result was later confirmed by the modelling studies of Maurice and Courtney[140] (Fig. 8). Maurice and Courtney[182] have also modelled the milling dynamics in a Spex mill and a hypothetical one-dimensional ball mill. They suggested that most of the collisions result in a modest energy loss, while only 4–7% of the collisions result in an appreciable energy transfer. In an ingenious experiment, Basset *et al.*[183] have estimated the impact velocities from the indentation on a Cu plate fixed at one end of the vial in a Spex mill. Their estimated velocities in the mill were in the range 1·8–3·3 m s^{-1} and found to be strongly dependent on the ball size. Surprisingly this study shows that the impact velocity decreases with an increase in ball diameter while one expects the reverse trend.

Hashimoto and Watanabe[100,184–186] have also analysed the motion of the balls by numerical simulation using Cundall's discrete element method. The effect of adhered powder layer on the balls was expressed

Table 2 Number of impacts for various ball and kinetic energy values in Spex 6000 mill (Ref. 146)

Number of balls	Kinetic energy of impact, J				
	10^{-7}–10^{-4}	10^{-4}–10^{-3}	10^{-3}–10^{-2}	10^{-2}–10^{-1}	10^{-1}–1·0
Mill operated for 0·5 s					
5	0	43	297	3	0
10	0	78	505	13	1
15	4	124	928	24	0
Mill operated for 1·0 s					
5	0	78	612	3	0
10	0	148	1201	13	2
15	4	229	1873	24	0



8 Experimentally determined (Spex mill, Ref. 146) and calculated (Ref. 140) frequency distribution of impact angles during ball milling: $\theta = 0$ refers to head-on collision

by a dashpot spring model.[186] One, two, and three dimensional ball motion[186] in three types of mill, namely, vibratory,[185] tumbler,[186] and planetary[100] mills were studied. In the detailed model of Hashimoto and Watanabe,[184] the translational and rotational motion and viscoelastic, frictional, and gravitational forces were taken into account. The whole motion of the balls was traced contact by contact. The ball motion trajectories, impact velocities, frequencies, and energy consumption during MA were calculated. As with the approach of Maurice and Courtney,[140] Hashimoto and Watanabe[184] used Hertz contact theory to deduce the force-displacement relation. The simulation of ball trajectories for tumbler mills[186] compares quite closely with video observations.

Le Brun *et al.*[187] analysed ball motion in the planetary mill and concluded that the MA process in this mill should be described in terms of attrition and wear and not in terms of impact. They observed three modes of ball motion ranging from chaotic to impact + friction to friction with increasing ratio of the angular velocities of vial and disc. Dallimore and McCormick[188] have used the two-dimensional discrete element method computer program to predict the motion of balls in a planetary mill. The model developed by them is capable of predicting both the changes in ball motion and energy dissipation for any combination of milling parameters. From the study of reaction between CuO and Ni during ball milling they concluded that the distribution of impact energies is of little importance for the propagation of the reaction.

Rydin *et al.*[189] have used high speed cinematography to study the global dynamics of a transparent attritor. They also estimated the impact velocity and frequency of impacts by placing Pb balls in the attritor at specific positions. They observed high velocity direct impacts in the attritor core where the impeller arms are located. Unfortunately, very little powder was observed in these regions. The region where most of the powder was located received low energy impacts by ball sliding. In fact, they observed that most of the powder segregated to the edge of the attritor bottom which is a 'dead zone' because of the lack of ball motion in this region. Thus, the attritor is a very inefficient device of energy transfer. The predominance of sliding is caused by the closed packed array of balls. Rydin *et al.*[189] have suggested many ways of improving the efficiency of energy transfer in the attritor such as modifying the attritor design and using a mixture of different size balls. A study with a mixture of different size balls[190] has shown that both welding and fracturing rates are enhanced.

Recently, Maurice and Courtney[177] have compared the alloying kinetics of the attritor and the Spex mill by combining their local and global models. The average impact velocity and impact frequency are of the order of 0·5 m s^{-1} and 0·88 s^{-1}, respectively, in an attritor. These values are 10% of the corresponding ones in a Spex mill (4 m s^{-1} and 7 s^{-1}). Their model predicted alloying times of 180 and 125 h for 100% and 95% alloying, respectively, in an attritor and 15 min in the Spex mill for a given powder combination. Comstock and Courtney[191] have confirmed the prediction in the case of the Spex mill wherein they observed the alloying time of 20 min for a Cu Nb elemental blend. However, in the case of the attritor, experiments[180] have shown about ×5 8 faster alloying kinetics. The model of Maurice and Courtney[177] also predicts a strong dependence of alloying time on the velocity of the balls while the density changes in the milling media and powder shape factor have only moderate influence on the former. However, the initial powder size does not seem to affect the alloying kinetics. Vityaz *et al.*[192] have also modelled the alloying kinetics considering fractals as energy dissipators.

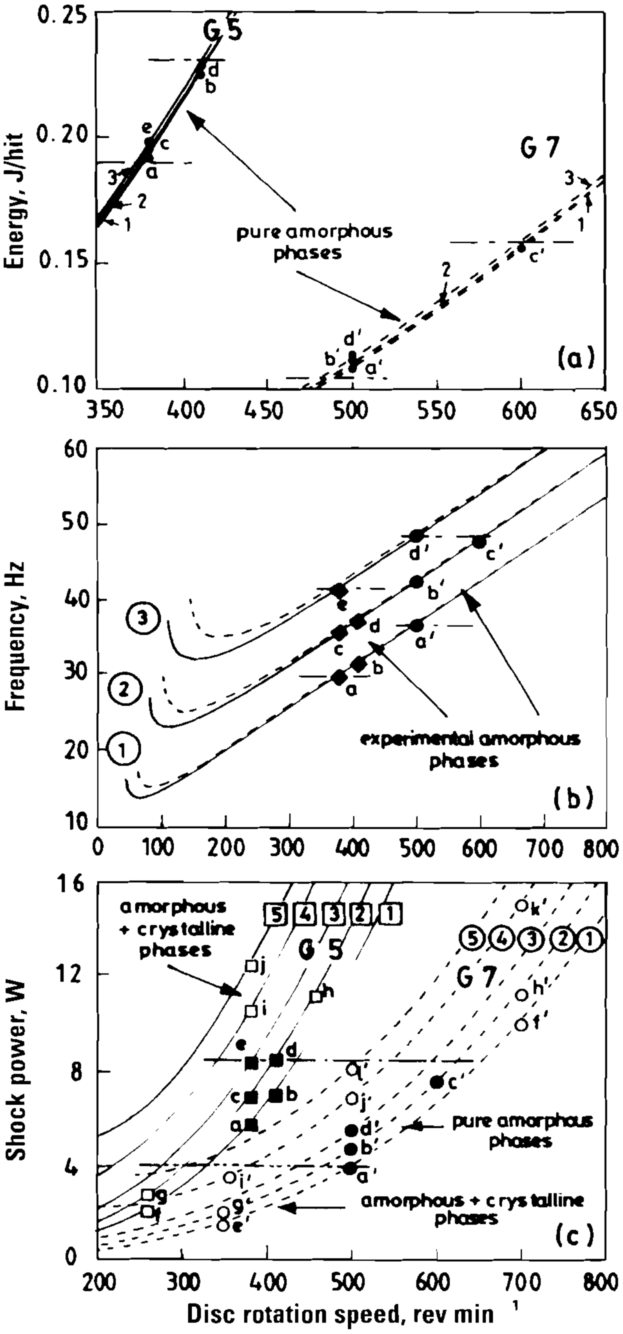
Energy maps/milling maps approach

In the modelling approach, discussed in the section 'Modelling/simulation approach' above, the influence of milling energy on the phase transformations induced during high energy ball milling has not been considered. The energy maps approach has a more practical value as it is aimed at arriving at the conditions under which certain phase transformations are induced by MA. This approach has been used more extensively for amorphisation during MA/MM. Gaffet[193] studied amorphisation by MA in the Ni Zr system for various compositions and concluded that a dynamic equilibrium is reached during milling which depends only on the energy induced during milling and is independent of the nature of initial mixture. In a later study, Gaffet[113] modified the planetary mill in order to vary independently the speeds of the disc Ω and vial w and identified a domain in the two-dimensional Ω w map (parameter phase diagram, PPD) in which amorphisation of $Ni_{10}Zr_7$ and $Ni_{11}Zr_9$ is feasible. He argued that the impact energy of the balls is proportional to Ω^2 and the impact frequency is proportional to w. Thus, by varying Ω and w one can independently vary the impact energy and the frequency of impacts which is not feasible in the conventional planetary mill. Gaffet and co-workers[194 196] also carried out milling at 100, 200, and 300 C and arrived at a three-dimensional

PPD of Ω *v.* *T*, which they have referred to as *E–v–T* (where *E* is impact energy, *v* impact frequency, and *T* temperature) for the amorphisation of $Ni_{10}Zr_7$ and $Ni_{11}Zr_9$. Chen *et al.*[197–199] have also attempted to model the energy transfer in a vibrating frame and concluded that amorphisation in $NiZr_2$ and $Ni_{10}Zr_7$ occurs above a certain injected power.

In the early reports, Gaffet *et al.* have not given any mathematical treatment. After calculating the impact energy, frequency, and the power (product of energy and frequency) for the planetary ball mills (G5 and G7) based on kinematic modelling, Abdellaoui and Gaffet[110,111] concluded that neither the shock energy nor the shock frequency, separately govern but that the shock power alone decides the end product of high energy ball milling. Figure 9 demonstrates this fact for the amorphisation of $Ni_{10}Zr_7$. Calculations for the modified horizontal rod mill[118] have shown that irrespective of the mill used, amorphisation of $Ni_{10}Zr_7$ occurs at shock powers in the range 0·4–0·8 W g^{-1}. The kinetic parameters for various high energy ball mills are compared in Table 3.

In an independent study, Burgio *et al.*[200,201] have derived kinematic equations describing the velocity and the acceleration of the ball in a planetary ball mill. The treatment of Burgio *et al.*[201] is more rigorous than that of Abdellaoui and Gaffet[111] as they have considered not only the detachment velocity of the ball but also the residual velocity of the ball after a succession of impacts. Considering the effect of the degree of filling the vial on the impact energy of the ball, Burgio *et al.*[201] have derived an expression for the effective impact energy of the ball. In addition, they have also calculated the total power released by the balls during milling by considering that the frequency of impacts is proportional to the difference in the angular velocities of the disc and the vial. Various milling parameters such as the size and number of balls, the ball/powder weight ratio (charge ratio, CR), etc., are included in the two energy parameters. The major assumption in the calculations is that the balls release their energy by collisions with the powder and all the energy released by the balls is transferred to the powder. Based on experiments on the Fe–Zr system with different values of Cr and mill speed, they could identify a domain for amorphous phase formation in the map of impact energy and power. They could also show that beyond a critical impact energy Fe_2Zr intermetallic is preferred to the amorphous phase during MA. At lower impact energies, the end product of MA remains as a pure metal mixture. In another report Padella *et al.*[202] verified the model of Burgio *et al.*[201] in the Pd–Si system by fixing the CR and varying the ball size in a planetary mill. The fact that an increase in the ball size increases the impact energy is verified by the result that with a ball diameter of 8 mm, formation of Pd_3Si intermetallic was observed, while smaller ball sizes result in the formation of the amorphous phase.



9 *a* Kinetic energy, *b* frequency, and *c* power of impacts as function of disc and vial speeds for $Ni_{10}Zr_7$ in G5 (full curves) and G7 (broken curves) planetary ball mills: numbers 1–5 near curves correspond to vial speeds of 1:150, 2:250, 3:350, 4:500, and 5:600 rev min^{-1}; data points *a–e* (G5) and *a′–d′* (G7) refer to amorphous phase formation and data points *f–j* (G5) and *e′–i′* (G7) refer to mixture of amorphous and crystalline phases (after Ref. 111)

In most of the models discussed so far collision is considered as the main energy transfer event and the roll of attrition is neglected. Magini *et al.*[203,204] argued that such an assumption is valid when the degree of filling is low and when the mill is operated at a high speed. Based on free fall experiments, on a flat surface, of bare balls and balls milled with a powder mixture of $Ti_{50}Al_{50}$, Magini *et al.*[204] measured the rebound yield and estimated the energy dissipated during impact for various ball sizes, heights of fall, and for different milling times. The balls milled with $Ti_{50}Al_{50}$ are expected to have a thin coating of powder and the rebound yield of these coated balls was very low

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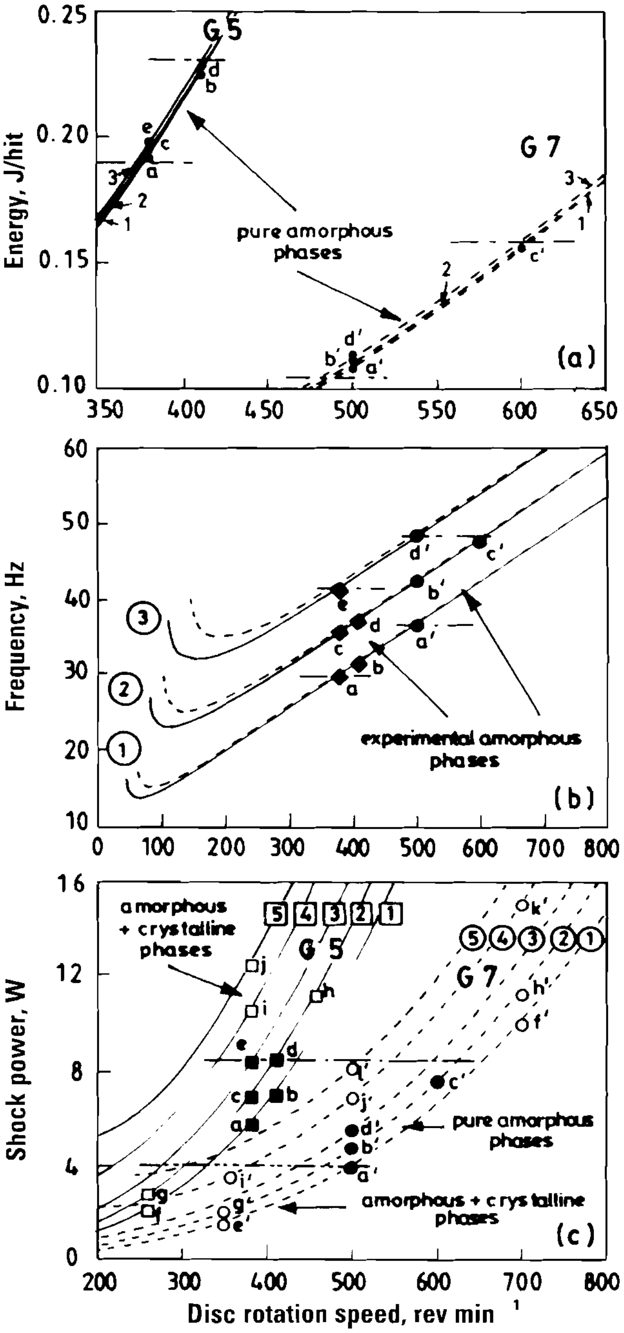

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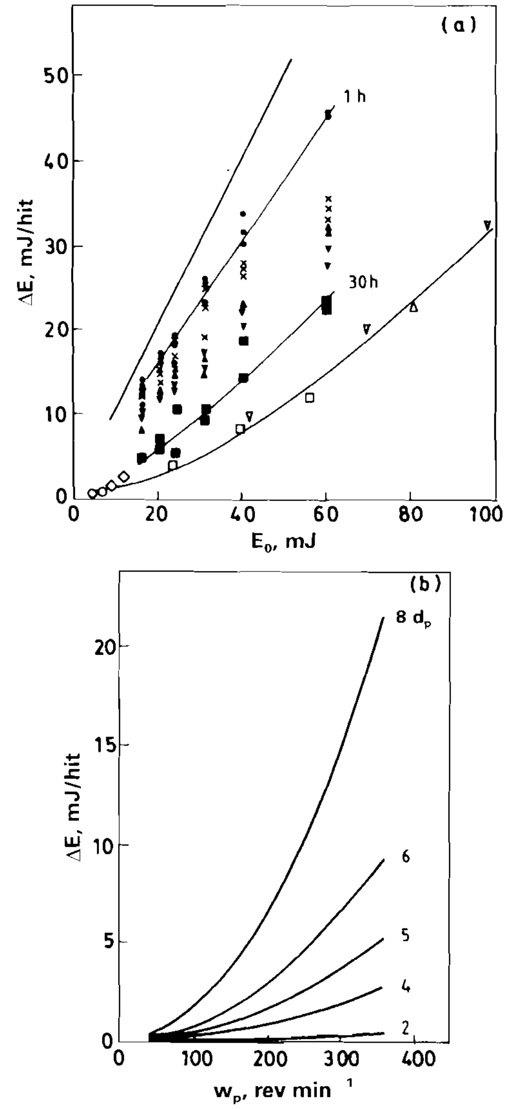
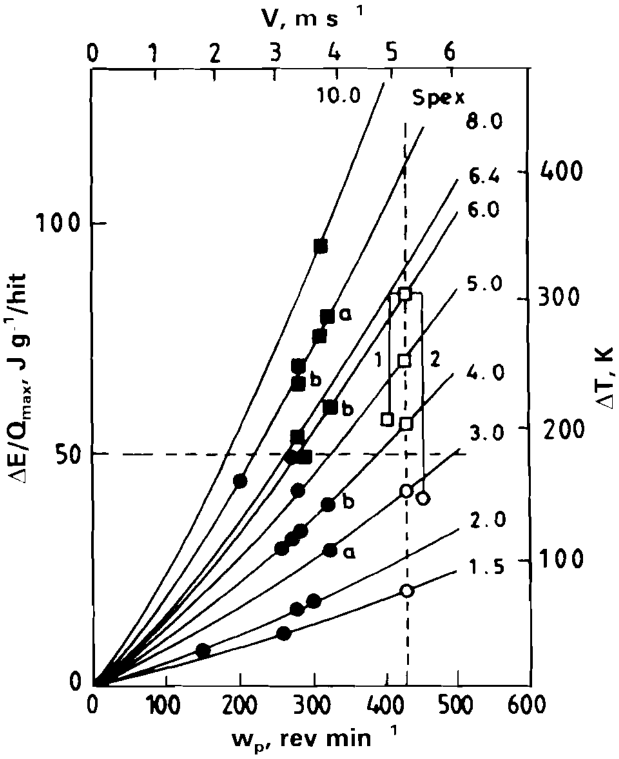


10 *a* **Energy dissipated during impact ΔE plotted against impact energy of ball E_0: open symbols refer to bare balls while solid symbols refer to balls milled with powder for various durations, upper straight line represents total energy dissipation and** *b* **variation of energy dissipated during impact with speed of mill and ball diameter d_p in mm (after Ref. 204)**



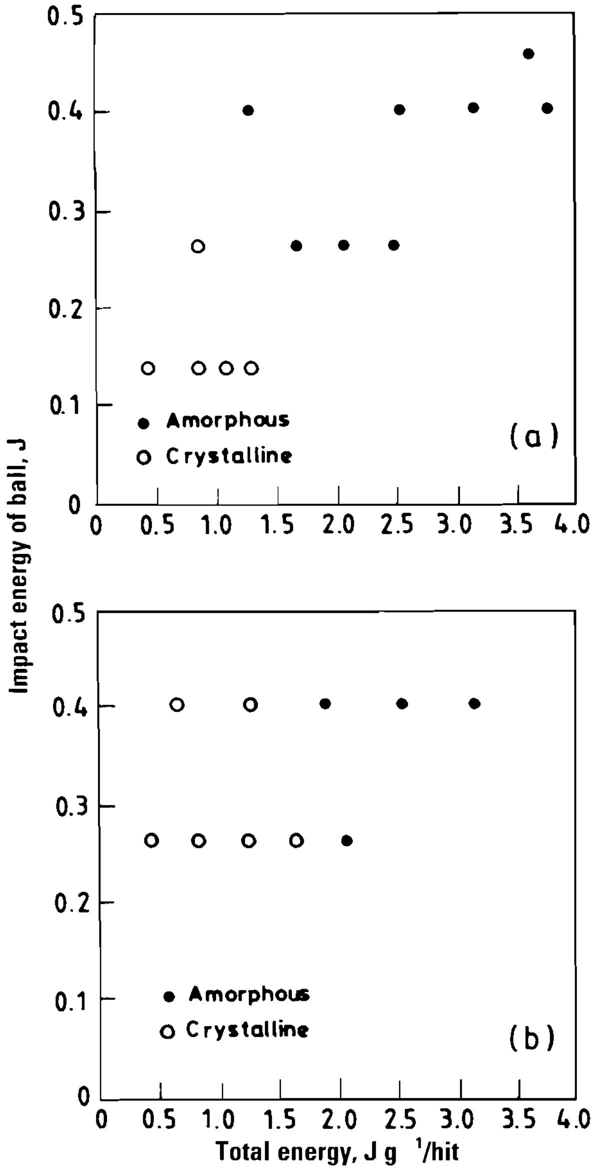
11 Energy map showing phases formed during MA in Pd–Si system: all data points refer to $Pd_{80}Si_{20}$ excepting (a) = $Pd_{86\cdot5}Si_{13\cdot5}$ and (b) = $Pd_{83}Si_{17}$, solid symbols are for experiments carried out in planetary mill and open symbols for those in Spex mill, horizontal broken line refers to critical energy dissipation above which intermetallic formation is observed. Numbers against each curve refer to ball diameter in mm (after Ref. 102)

when compared with the bare balls. The energy dissipated for various initial energies of the balls (both bare and coated balls) is shown in Fig. 10*a*. It can be clearly seen that in the early stages of milling (1 h) the situation is close to total anelastic dissipation ($\Delta E = E_0$): for long periods of milling, the energy dissipation is similar to that of the bare balls. Thus, it can be assumed that in the initial hours of milling the kinetic energy is totally dissipated in the impact. Under the conditions of anelastic impact, the energy dissipated in each collision would be proportional to d_b^3 and w_p^2 (where d_b is the diameter of the ball and w_p the speed of the disc in the planetary mill) as shown in Fig. 10*b*. Magini *et al.* have also estimated the surface density of the powder coating by measuring the weight of the balls at different milling times.

Based on experiments in the Pd–Si system, Magini *et al.*[205] could conclude that the formation of the Pd_3Si intermetallic compound occurs when the energy dissipated is greater than a critical value (Fig. 11). Figure 11 also gives the adiabatic temperature rise during impact. In a later report, Magini *et al.*[206] have measured the power absorbed during milling using an electric power meter and could show that the

Table 3 Kinetic energy, shock frequency, and shock power for various mills for $Ni_{10}Zr_7$ (Ref. 118)

	Vibratory mills			Planetary mills			Horizontal rod mill
	Attritor	P0	Spex	P5	G5	G7	
Velocity of the ball (m s)	0–0·8	0·14–0·24	<3·9	2·5–4·0	0·24–6·58	0·28–11·24	0–1·25
Kinetic energy (10 ^{3} J hit)	<10	3–30	<120	10–400	0·4–303·2	0·53–884	0–190
Shock frequency (Hz)	>1000	15–50	200	~100	5·0–92·4 (5 balls)	4·5–90·7 (5 balls)	0–2·4 (1 rod)
Power (W g ball or rod)	<0·001	0·005–0·14	<0·24	0·01–0·8	0–0·56	0–1·60	0–0·1



a $Ti_{50}Ni_{50}$; *b* $Ti_{50}Cu_{50}$

12 Milling maps identifying domain of amorphous phase formation (solid symbols) during MA (after Ref. 208)

measurements match very well with those predicted by the collision model. By direct measurements of applied torque to the motor, Iasonna and Magini[207] have confirmed the above conclusion. Both the models of Iasonna and Magini[207] and Abdellaoui and Gaffet[111] predict the same power absorption variation with mill speed (both being based on the collision model). Iasonna and Magini[207] have also established the importance of filling factor on the energy transfer during milling.

Modifying the energy expressions of Burgio *et al.*[201] to suit their mill configuration, Murty *et al.*[208] could generate a milling map of impact energy and the total milling energy by including all the milling parameters in the two energy parameters. Murty *et al.* could identify the glass forming conditions for the Ti–Ni and Ti–Cu systems in such a milling map (Fig. 12). A minimum impact energy of about 0·2 J and a minimum total energy of 1·5 J g^{-1}/hit are identified as necessary for amorphisation in these systems.[208] Suryanarayana *et al.*[209] have also developed a milling map of CR and milling time in which they identified the glass forming regime in the Ti–Al system. Very recently, Joardar *et al.*[127] have developed the milling map for the formation and disordering of NiAl by MA. Based on detailed experimentation, they could successfully show that the formation and complete disordering of NiAl is governed by the total energy input during milling and not by the impact energy of the ball. They could demonstrate that even at very low impact energies, if the total energy imparted to the powder during milling crosses a critical value NiAl forms. Thus, the results of Joardar *et al.*[127] are in agreement with those of Abdellaoui and Gaffet.[110,111] It is interesting that the total energy required for complete formation of NiAl and that for complete disordering are of the same order.[127]

Thus, milling maps can identify the conditions necessary for any given phase transformation induced by ball milling. However, there still exists a controversy – whether the impact energy or the shock power drives the phase transformation. While Abdellaoui and Gaffet[111] have shown that the shock power is the deciding parameter, Iasonna and Magini[207] have shown that the impact energy can change the reaction path at low filling. The work of Joardar *et al.*[127] has also shown that the phase formation during MA is governed by the total energy of milling (shock power). Further work is essential in order to get a better understanding of the energy transferred to the powder during milling.

Temperature effects during milling

Most of the models discussed so far inherently assume that all the energy transferred to the powder is used in bringing microstructural changes in the powder. However, it is logical that a part of this energy is used in increasing the temperature of the powder and the milling media.[210] The temperature during milling can depend on the kinetic energy of the ball and the material characteristics of the powder and milling media. The temperature of the powder influences the diffusivity and defect concentration in the powder thus influencing the phase transformations induced by milling. Higher temperatures are expected to result in phases which need higher atomic mobility (intermetallics) while at lower temperatures the formation of amorphous phases is expected if the energy is sufficient. Low temperature can also enhance the formation of nanocrystalline phases.

There have been a number of reports in which the macroscopic temperature of the mill has been measured. Davis[211] and McDermott[212] have measured the maximum temperature of the Spex mill to be 50°C (40°C without balls) and concluded that most of the heat comes from the motor and bearings. Kimura and Kimura[213] reported a maximum macroscopic temperature of 172°C in the attritor. Borzov and Kaputkin[214] have measured a temperature in the range 100–215°C for an attritor using SiC and diamond sensors. A substantial temperature rise (120 K) is also reported by Kuhn *et al.*[107] in vibratory mills. Thus the macroscopic temperature during milling appears to be low and sensitive to the mill design.[210,215]

The microscopic temperature of the powder just after the impact can, however, be quite high. In fact, Yermakov *et al.*[7,8] have attributed amorphisation during milling to the local melting and rapid solidification of the powders. As it is not possible to measure the microscopic temperature during milling, investigators took two approaches to estimate it. One of the approaches is to calculate it by appropriate models and the other is to infer the temperature from the structural/microstructural changes during milling. There can be a large temperature rise due to some exothermic reactions during milling; however, this is not considered in these models.

Assuming that particles trapped between colliding balls (head-on collision assumed) deform by localised shear, Schwarz and Koch[109] estimated a microscopic temperature rise of about 40 K for $Ni_{32}Ti_{68}$ and $Ni_{45}Nb_{55}$ powders in a Spex mill. Davis and Koch[146] calculated the ball velocities and used the expression and materials of Schwarz and Koch[109] to predict a raise in temperature (ΔT) of $\leqslant 112$ K. They[146] have also calculated the maximum ΔT to be about 350 K. Maurice and Courtney[140] have also developed an expression for the adiabatic temperature rise during milling modelling the deformation of powder to be similar to that of microforging. However, they assumed ΔT to be low such that the material is in the cold working regime. Magini *et al.*[204] have also calculated the adiabatic temperature in a planetary mill and reported the maximum temperature to be of the order of 400 K after calculating the amount of powder trapped between the balls during a Hertzian collision. Bhattacharya and Arzt[216] calculated the contact temperature of the powder compact surfaces, assuming Hertzian elastic collisions, which are higher (350°C) than those calculated by others. However, they show a rapid decrease of the temperature to ambient at the centre of the compact. Davis and Koch[146] calculated the ΔT due to sliding friction to be very low ($\leqslant 10$ K). Miller *et al.*[217] used microsecond time resolved radiometry to observe a temperature raise during impact on various materials. They observed a ΔT of about 400 K.

As it is difficult to model the temperature rise during milling, investigators have tried to infer it from the microstructural changes occurring during ball milling. The observation of deformation bands and slip lines by optical microscopy[73] and the high dislocation densities and deformation bands seen in transmission electron microscopy[218] indicate that the microscopic temperatures are much below the recrystallisation temperature. In some cases, however, it is reported[82,213] that the temperature is above the crystallisation temperature of the amorphous phase. Davis and Koch[146] studied the tempering of martensite in an Fe 1·2C steel during ball milling and concluded the maximum microscopic temperature to be about 275°C. Davis and Koch[146] have also milled Bi powder and concluded that the temperature of milling is below the melting point of Bi (271°C).

The milling temperatures obtained by both calculation and experiment are given in Table 4. The results suggest that there is only a moderate temperature rise during milling and that local melting can be ruled out.

ODS alloys by mechanical alloying

The development of strong ODS alloys has been the prime goal of Benjamin's group, which invented the MA technique. Very fine microstructures and a fine dispersion of oxides in the case of Ni- and Fe-base superalloys and Al alloys by MA have yielded superior mechanical properties over the conventional alloys. Some of these MA ODS alloys have been commercially produced despite strong competition from conventional ODS alloys. The ODS alloys produced by MA can be classified based mainly on the matrix materials as ODS superalloys, Al alloys, Ti alloys, and ODS intermetallics. These are discussed below.

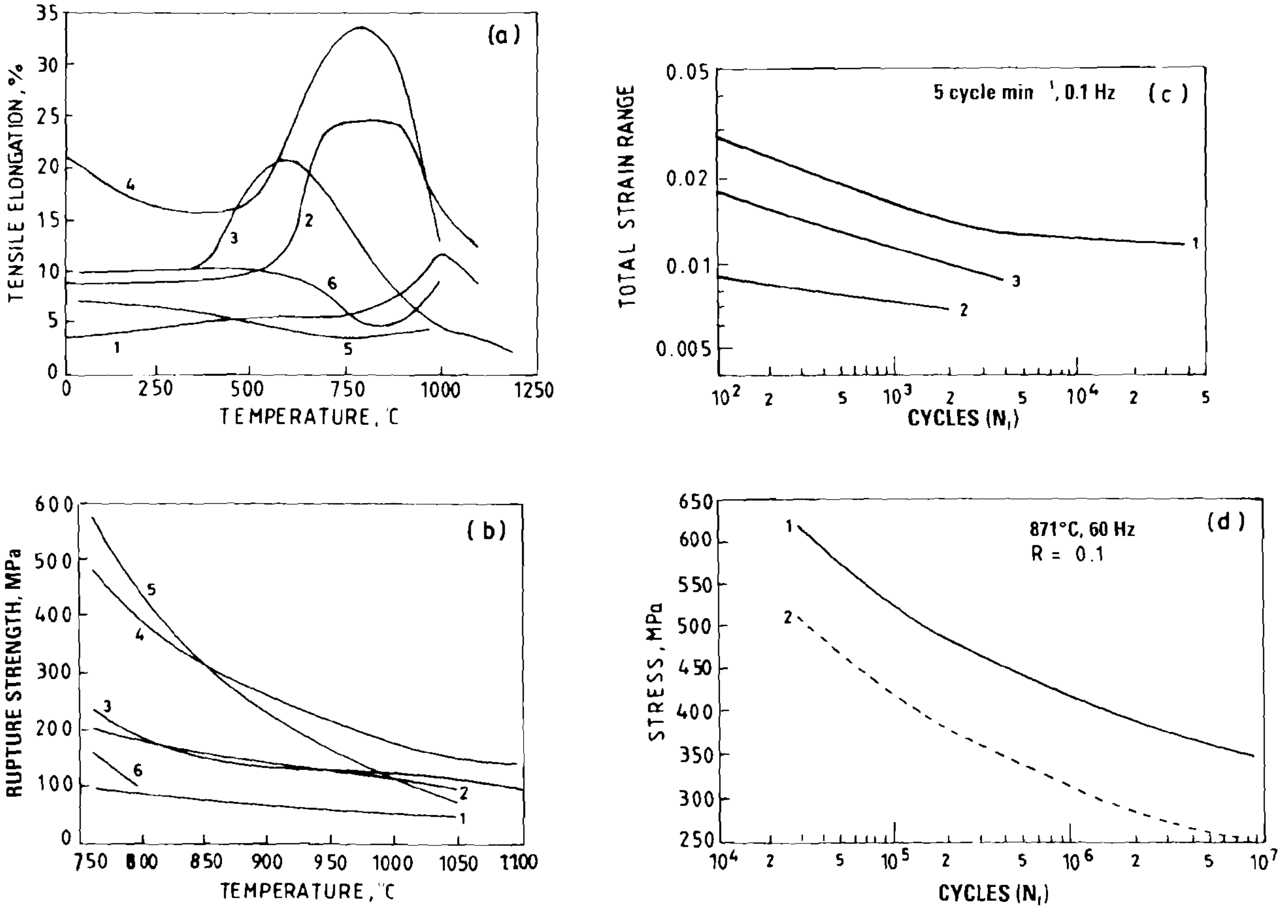
ODS superalloys

Most of the work on the development of ODS superalloys was concentrated on Ni-base alloys. A number of ODS Ni-base superalloys such as Inconel MA754, MA758, and MA6000 have been developed by MA. Among the above alloys, the Inconel MA6000 series alloys developed by Benjamin's group have shown higher tensile elongation and creep rupture strength up to 1373 K when compared with directionally solidified and single crystal Ni-based superalloys (Fig. 13*a* and *b*). The low and high cycle fatigue properties of these alloys are also better than those of the conventional alloys (Fig. 13*c* and *d*).[77] In these MA6000 alloys, the intermediate temperature strength comes from γ' precipitates; Y_2O_3 dispersoids give the high temperature strength; W and Mo act as solid solution strengtheners; while Al and Cr confer oxidation resistance; Ti, Cr, and Ta collectively provide sulphidation resistance.[74] The feasibility of achieving a homogeneous dispersion of oxides like Y_2O_3 and ThO_2 made some of the Ni-base MA superalloys candidates for high temperature coating materials for turbine blades. The MA6000 alloys were also reported to be superplastic in nature,[219,220] thus making their processing easier.

The Fe-base Inconel alloy MA956 was found to maintain its strength levels at temperatures over 1573 K in corrosive atmospheres. Along with high temperature oxidation and corrosion resistance, this alloy is found to have high fabricability when compared with conventional Fe-base superalloys.

Table 4 Estimated temperature rise during milling

Method	Rise ΔT, K	Refs.
Calculation	$\leqslant 10$	145
	40	109
	130	140
	$\leqslant 350$	146
	350	216
	400	204
Experimentation	50	211, 212
	120	107
	100–215	214
	172	213
	<271	146
	400	217



13 *a* **tensile elongation as function of temperature for MA ODS superalloys (1) MA6000, (2) MA753, (3) MA956, and (4) MA754 compared with (5) cast MAR-M200 and (6) directionally solidified MAR-M200;** *b* **1000 h creep rupture strength for MA ODS superalloys (1) MA956, (2) MA754, (3) MA753, and (4) MA6000 compared with (5) cast MAR-M200 and (6) wrought Ni80A;** *c* **low cycle fatigue behaviour of (1) MA6000E compared with (2) cast MAR-M200 and (3) directionally solidified MAR-M200; and** *d* **high cycle fatigue strength of (1) MA6000 compared with (2) directionally solidified MAR-M200 superalloy (after Ref. 77)**

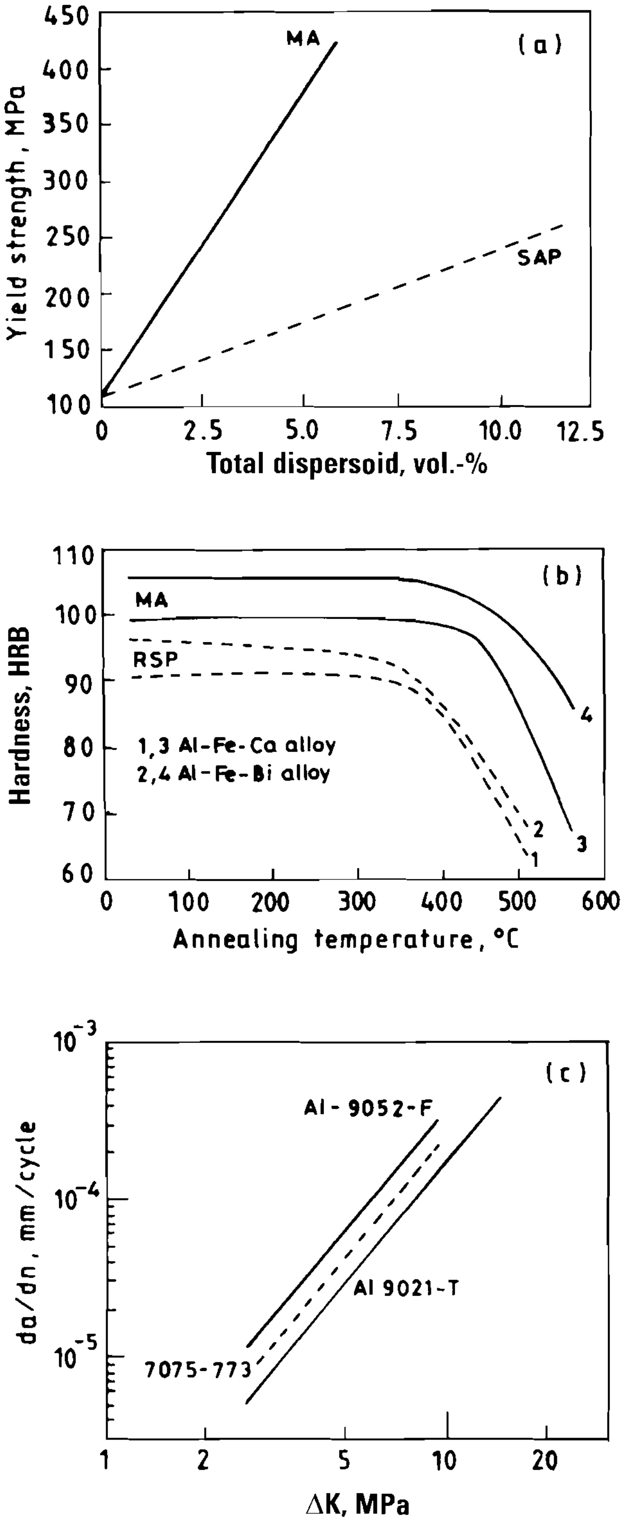
Mechanically alloyed Fe 16Cr (wt-%) alloys with about 2·6%Y$_2$O$_3$ dispersoids have shown better strength than TD nickel and TD Ni-Cr alloy at temperatures below 600 C.[221] Their oxidation resistance was, however, found to be similar to TD Ni Cr alloy.[221]

ODS Al alloys

The ODS Al-base alloys made by MA are found to be much superior to the traditional SAP alloys. Figure 14 shows some of the mechanical properties of MA Al alloys in comparison with SAP alloys.[77] Coupled with high strength and hardness values even at higher temperatures, the fatigue crack growth rates of these MA Al alloys are much lower than those of conventional alloys. Recently, there has been a drive to combine RSP and MA to obtain a synergistic effect.[16,18] Figure 15 shows the improvement in the yield strength obtained by using a combination of these two techniques in the case of Al-8Fe-4Ce alloy.[16] The room temperature and high temperature hardness and tensile strength of the RSP + MA compacts were found to be superior to those of the RSP compacts. The steady state creep in the former case was 2–4 orders lower than the latter in the temperature range 250–400 C. The ductility of the RSP + MA compacts, however, is much poorer than that of the RSP alloy: this could be due to the internal strains of the particles. Al$_3$Ti dispersion strengthened Al-Ti alloys have been successfully produced by MA and their tensile strength was shown to be higher than 7075 and 2024 alloys above 150 C.[222]

ODS Ti alloys

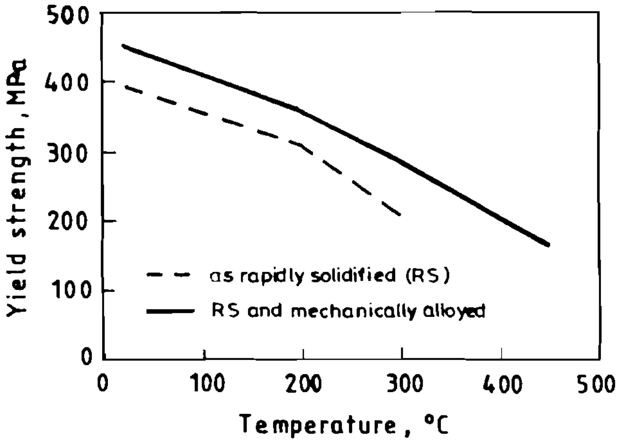
Disperson strengthening of Ti by MA was first attempted by Wright and Wilcox,[223] though unsuccessfully. In this attempt, a homogeneous dispersion of Y$_2$O$_3$ could not be achieved. Baccino *et al.*[224] successfully produced a homogeneous Y$_2$O$_3$ dispersion in a β Ti alloy by MA. Later, Sundaresan and Froes[225] attempted to develop a uniform dispersion of Er$_2$O$_3$ in Ti Al V-Fe alloy by internal oxidation of Er during consolidation. Although a fine dispersion of Er$_2$O$_3$ particles could be obtained, the dispersion was not uniform. Suryanarayana *et al.*[226] have studied the dispersion of Er$_2$O$_3$ in Ti Al Nb V Mo alloy and concluded that optimisation of process parameters is essential to achieve uniform distribution of the dispersoids.



14 *a* Effect of dispersoid content on yield strength of MA and SAP Al alloys; *b* effect of annealing temperature on hardness of MA and SAP alloys, and *c* fatigue crack growth rates of MA Al alloys in dry air compared with conventional alloys (after Ref. 77)

ODS intermetallics

Nickel, Fe, and Ti aluminides are the most prominent intermetallics studied for the development of ODS intermetallics. Jang *et al.*[227] studied the dispersion of Al_2O_3, Y_2O_3, and ThO_2 in Ni_3Al powders by MA.

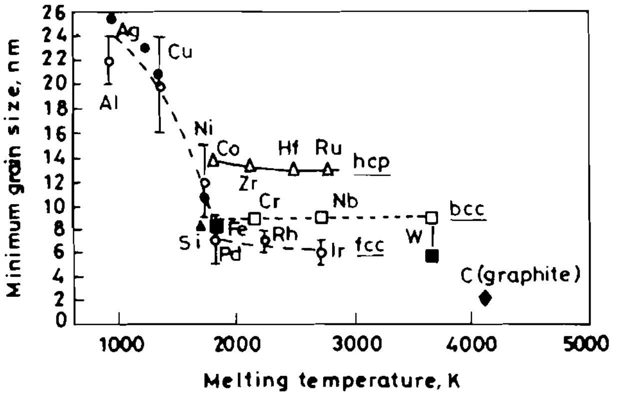


15 Yield strength of Al–8Fe–4Ce alloy produced by RSP and combination of RSP and MA (after Ref. 16)

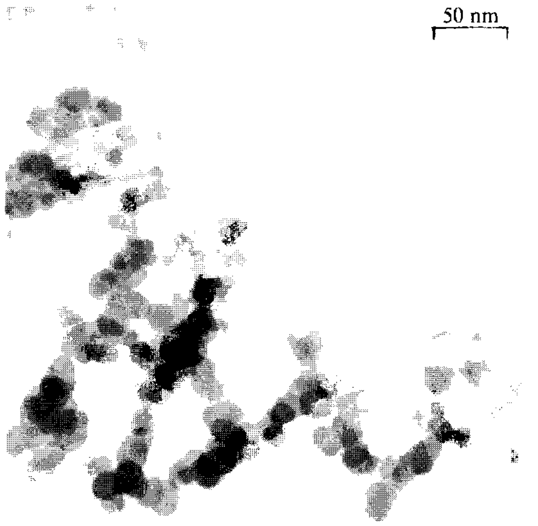
The dispersoids were found to decrease the grain size of the intermetallic and hence increase its yield strength, but the room temperature ductility was reduced. Jang and Koch[228] have also shown improvement in the strength of Ni_3Al with oxide dispersions. In another study, Benn *et al.*[229] have shown improved strength of Ni_3Al up to 600°C due to Y_2O_3 dispersions by MA. A number of composites based on NiAl (Refs. 230–234) have also been successfully synthesised by MA. Vedula and Strothers[235] could improve both the yield strength and room temperature ductility of FeAl by the dispersion of Y_2O_3 by MA. Grain boundary strengthening was maintained in these ODS FeAl alloys up to 827°C.

Nanocomposites by mechanical alloying

In recent years, there have been considerable efforts to produce *in situ* nanocomposites by MA. Zhu *et al.*[236] have synthesised Pb–Al and Fe–Cu nanocomposites by MA. In a similar attempt, Provenzano and Holtz[237] have shown the formation of Ag–Ni and Cu–Nb nanocomposites by MA. Du *et al.*[238] have produced Al–BN composites by high energy ball milling. In an interesting report, Naser *et al.*[239] have shown that no grain growth occurs in the matrix close to its melting point when Cu and Mg are reinforced with nanocrystalline Al_2O_3 by MA. Wu *et al.*[240] have reported the formation of nanocrystalline TiC in an amorphous Ti–Al matrix by MA. A solid state reaction leading to the formation of AlN and AlB_2 was reported by them during further processing of these nanocomposites. $TiAl–Ti_5Si_3$ nanocomposites have been reported by Liu *et al.*[241] by MA followed by thermal treatment. They attribute the formation of these nanocomposites to the crystallisation of the amorphous phase obtained by MA in the Ti–Al–Si system. These nanocrystalline compounds appear to be quite stable and no significant coarsening was observed even after heat treatment for 1 h at 1000°C. Similar nanocomposites have been obtained by Senkov *et al.*[242] by MA and subsequent heat treatment of a mixture of TiH_2 and Al–Si alloy powders. $Al_3Nb–NbC$ nanocomposites have been obtained by the MA of Al and Nb powders.[243]



16 Minimum grain size for nanocrystalline elements as function of melting point (after Ref. 253)



17 Transmission electron micrograph of nanocrystalline NiAl synthesised by MA (Ref. 269)

Interestingly, NbC in this case appears to have formed by the reaction of Nb with the methanol medium in which the milling was performed.

Equilibrium/non-equilibrium phase formation by mechanical alloying/milling

Nanocrystals

Nanocrystals are crystals with a characteristic size of a few nanometres, at least in one direction. Such fine crystals are characterised by a large fraction of atoms residing at the grain boundaries which imparts very special properties for these materials. The novel characteristics of these nanocrystalline materials include high diffusivities, increased solid solubility, high strength, and sufficient formability in the case of ceramics. After the pioneering work of Gleiter,[244] the synthesis and characterisation of these materials attracted wide attention.[245–249]

The formation of nanocrystalline structures by high energy ball milling has widened the scope of MA/MM.[19,250–253] Nanocrystalline structures were obtained by high energy ball milling of a number of elemental powders such as Cr, Nb, W, Hf, Zr, and Co (Ref. 254), Fe (Refs. 255, 256), Ni (Ref. 257), Ag (Ref. 258), and graphite.[259,260] The crystallite sizes of the nanocrystals obtained by MA/MM are usually calculated from X-ray peak broadening after eliminating the strain and instrumental broadening contributions using standard methods.[261,262] The initial results have shown an indication that the minimum crystallite size obtained by MM varies inversely with the melting point of the element. It was argued[254] that in the case of elements with low melting points, the tendency for cold welding dominates, resulting in larger crystallite sizes. Very recently, Koch[253] has compiled the minimum crystallite sizes reported so far for various elements by MM (Fig. 16). The figure clearly brings out the fact that for fcc elements having lower melting points (Al, Ag, Cu, and Ni) the minimum crystallite size varies inversely with their melting point. However, in the case of bcc, hcp, and fcc elements with higher melting points, the minimum crystallite size is virtually insensitive to their melting point. Thus, the understanding of the reasons for the minimum crystallite size is presently at a primitive stage.

Nanocrystalline solid solutions have been synthesised in a number of systems by the MA of elemental powder mixtures such as Ti–Si (Ref. 263), Ti–Ni, Ti–Cu (Ref. 264), Ti–Mg (Ref. 114), and Ti–Al (Refs. 123, 265). Shen and Koch[266] have recently studied the formation of nanocrystalline solid solutions in the Ti–Cu (0–8 at.-%Cu), Nb–Cu (0–20 at.-%Cu), Ni–Cu (0–50 at.-%Cu), Cr–Cu (0–20 at.-%Cu), Fe–Cu (0–15 at.-%Cu), Cu–Ni (0–50 at.-%Ni), Cu–Fe (0–50 at.-%Fe), and Cu–Co (0–50 at.-%Co) systems. They showed that the solid solution hardening or softening is governed mainly by the hardening or softening of the grain boundaries. A number of intermetallic compounds such as NiTi, CuEr, AlRu, SiRu (Ref. 267), TiNi (Ref. 268), Ni_3Al and Ni_2Al (Ref. 263), NiAl (Ref. 269) (Fig. 17) and various electron compounds in the Cu–Zn system[151] have been obtained in the nanocrystalline state by MA/MM. Attempts are being made to commercialise these nanocrystalline materials.[253]

Solid solutions

Extension of solid solubility

The extension of terminal solid solubility by MA has not been studied thoroughly so far, as the emphasis of most of the investigators was more either on ODS alloys or on amorphisation. The limited data available on the extension of terminal solid solubility achieved in different alloy systems by MA are given in Table 5. The formation of solid solution in the entire composition range in the eutectic Ag–Cu system[271] has highlighted the potential of MA in achieving large extensions of terminal solid solubilities even in systems with positive enthalpies of mixing in the solid state. This is supported by the results of Suryanarayana and Froes,[114] in which a terminal solid solubility of 6 at.-% of Mg in Ti has been achieved by MA while these elements are immiscible in the solid state under equilibrium conditions. They attributed this extension of solid solubility to the nanocrystalline structure formed during MA. The large volume fraction of grain boundaries present in the nanocrystalline state are expected to enhance the solid solubility in these materials. Murty *et al.*[264] showed that in the Ti–Ni and Ti–Cu systems the extension of solid solubility is limited by the onset of amorphisation. In another report, Murty and Pabi[285] correlated the limit of extension of solid solubility of NiAl during MA with crystallite size. Thus MA can be used very effectively to extend the solid solubility of one element in the other so as to obtain stronger alloys.

Alloying in immiscible systems

Mechanical alloying has a clear edge over RSP in achieving alloying in liquid immiscible systems. In the initial stages of development of MA, Benjamin[73] could demonstrate the formation of homogeneous mixtures of Fe–Cu and Cu–Pb by MA. Later, a significant solid solubility was reported in the Fe–Cu system by MA.[266,286–292] Alloying has also been reported in the Cu–W (Refs. 293, 294), Cu–V (Refs. 295, 296), Cu–Ta (Refs. 297–299), and Cu–Co (Refs. 300–302) systems by MA. Significantly, Huang *et al.*[303] have reported a continuous series of solid solutions in the Cu–Co system. Alloying in liquid immiscible systems by MA is an interesting phenomenon and there have been efforts to understand the driving force for such a behaviour during high energy ball milling. Yavari *et al.*[287,304] have attributed this to the capillarity effect. They argued that high energy ball milling results in the formation of small fragments with tip radii of the order of 1 nm. The capillarity pressure at these tips forces the atoms on these fragments to dissolve. Gente *et al.*[302] and Huang *et al.*[303] have proposed that formation of homogeneous solid solution is energetically more favoured when the crystallite size of the constituents is reduced below a critical size which is of the order of 1–2 nm. Huang *et al.*[305–307] and Murty *et al.*[150] have shown that nanocrystallisation is a prerequisite for alloying during MA.

Table 5 Estimation of terminal solid solubility by mechanical alloying

		Solid solubility at room temperature, at.-%		
Solvent	Solute	Equilibrium (Ref. 270)	MA	Refs.
Ag	Cu	0·3	100·0	271
	Ni	0·7	3·8	93
Al	Cr	0·0	5·0	272
	Fe	0·0	4·5	93
	Mg	2·1	23·0	93
	Mn	0·0	18·5	273
	Nb	0·0	25–30	93
	Ti	0·0	6·0	123
	Zr	0·0	9·1	93
Cd	Zn	0·0	50·0	72
Co	C	0·0	6·0	274
	Cr	0·0	40·0	275
	V	9·1	33·0	275
	Zr	0·0	5·0	275
Cr	Co	9·0	40·0	275
	Cu	0·0	20·0	266
Cu	Co	0·0	90·0	266, 276
	Fe	0·0	50·0	266
	Hg	0·0	70·0	72
	Zn	30·0	50·0	152
Fe	Al	18·5	50·0	277
	Cu	0·0	15·0	266
	Mg	0·0	20·0	278
	Si	9·0	27·5	279, 280
Mg	Ti	0·0	4·2	93
Mn	Co	4·0	50·0	275
Nb	Al	21·5	60·0	93
	Cu	0·0	20·0	266
	Ni	7·0	10·0	72
Ni	Ag	2·0	9·0	93
	Al	10·0	27·0	72
	C	0·0	12·0	274
	Nb	6·0	15·0	281
Ti	Al	36·0	55·0	282
	Cu	0·0	8·0	266
	Mg	2·9	60·0	114, 283
V	Co	7·0	40·0	275
Zr	Al	0·5	15·0	284
	Co	0·0	4·0	275

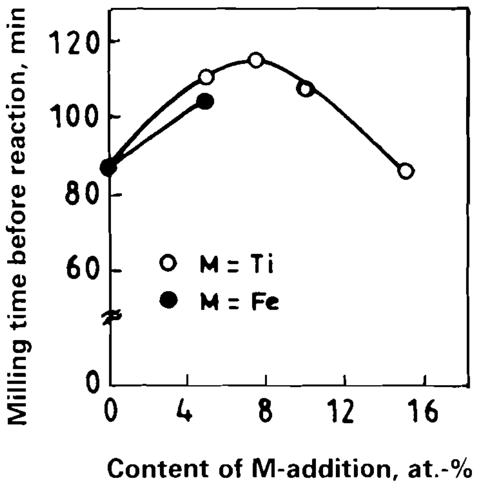
Intermetallic compounds

The intermetallics constitute some of the most technologically prospective engineering materials. This stems from their novel attributes such as excellent high temperature strength, and thermal stability apart from the high corrosion/oxidation resistance and unique electrical and magnetic properties. The high melting temperatures and the poor formability of the intermetallics, however, poses major impediments to their conventional processing. Under this perspective, MA has been regarded as an extremely promising solution. Over the past decade, a considerable volume of work has been reported on the synthesis of a large number of intermetallic compounds via MA. The bulk of these efforts has been on the aluminides and to some extent on the silicides.

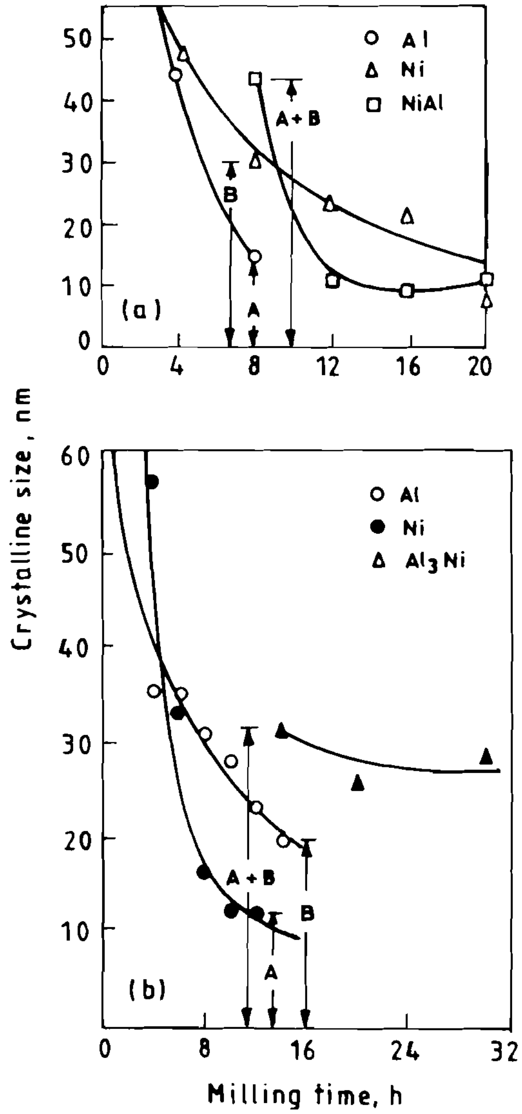
Aluminides

Overwhelming interest in the MA of aluminides has been instigated by their possible applications in aerospace and automotive industries owing to their high specific strength at elevated temperatures. Among all aluminides, the MA of Ni, Ti, and Fe aluminides have so far received major attention.

Ni aluminides The formation of Ni aluminides, such as Al_3Ni, AlNi, and $AlNi_3$ via MA has been established at various compositions in binary Ni_xAl_{100-x} $(32 < x < 90)$ elemental blends.[308] Subsequent efforts[269,309–312] have confirmed the previous results of solid state synthesis in the Ni–Al system. Although a considerable extension of phase fields in $AlNi_3$, AlNi, and even in the line compound Al_3Ni has been observed under intense milling conditions,[269,310] Ni_2Al_3 and Ni_5Al_3 phases were found to be metastable under similar conditions.[269] It is of interest to note that, in a marked contrast to the gradual temperature rise (~348 K) during the MA of Ni aluminides in a laboratory ball mill under air,[308] formation of NiAl in a Spex 8000 mill under an Ar atmosphere[309] was accompanied by an exothermic reaction within a short duration of milling following an interruption after 2 h of continuous milling. A similar observation has also been reported recently[313] on low energy ball milling of $Al_{50}Ni_{50}$. Recent studies by Liu *et al.*[314]



18 Effect of Ti and Fe addition on time of initiation of exothermic NiAl phase formation reaction (after Ref. 314)

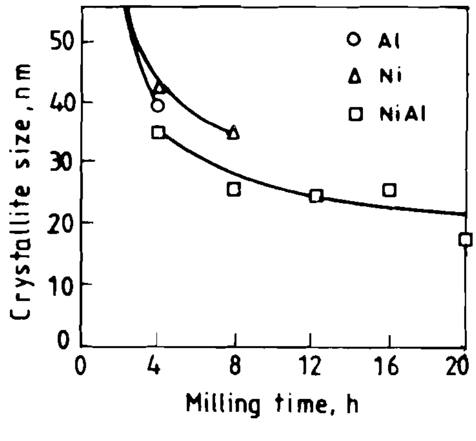


19 Discontinuous additive mixing during formation of *a* AlNi and *b* Al_3Ni by MA (after Ref. 315)

have revealed a delayed initiation of the exothermic NiAl phase formation reaction on addition of ternary alloying elements such as Ti and Fe as indicated in Fig. 18. The occurrence of explosive reaction was also observed on opening the vial following milling.[313] This suggests the possible role of energy liberated during the oxidation of Al in promoting the Al Ni reaction. On the other hand, the absence of catastrophic reaction when milled in air[308] could be attributed to the continuous oxidation of the elements and the slow diffusion between the oxide coated ingredients which results in reduced reaction kinetics.

Interestingly, recent work on alloying mechanism during MA[315] revealed the occurrence of catastrophic mixing via an entirely new mechanism called 'discontinuous additive mixing' in the formation of ordered AlNi and Al_3Ni on MA, only when the ingredients are refined to a certain critical level (Fig. 19). In these cases, no diffusion of one element in the other is observed until their crystallite sizes reach the nanocrystalline state. Once the constituent elements reach a critical crystallite size, the intermetallic forms by a reaction similar to the self-propagating high temperature synthesis. The crystallite size of the intermetallic at the time of its formation was found to be the sum of the crystallite sizes of its constituents before the reaction. The critical crystallite size required for the reaction to initiate was found to increase with a decrease in the enthalpy of formation of the ordered intermetallic. Studies have indicated, however, a switchover to a gradual diffusive mode of mixing once the products become disordered, e.g. $AlNi_3$ or AlNi(Cr), as is evident from Fig. 20.[315,316]

Ti aluminides Investigations on Ti–Al intermetallics have revealed considerable resistance to alloying during MA. For example, prolonged milling for 100 h in a Fritsch P5 planetary mill at a CR of 10 : 1 has failed to produce Ti Al compounds.[317] The formation of Ti Al intermetallics could be achieved on adopting a two stage process involving MA and subsequent annealing.[136] This is evidenced by the MA attempts for the synthesis of AlTi and Al_3Ti, which required annealing of the ball milled ingredients at 873 and 813 K, respectively.[318] Several other reports on the production of Al Ti intermetallics such as Al_3Ti, Al_3Ti_2, AlTi, and $AlTi_3$ through a 'mechanically acti-



20 Continuous diffusive mixing in disordered NiAl(Cr) during MA (after Ref. 316) vated annealing process' involving intense ball milling followed by an annealing process are also available.[319,320] It is, however, quite obvious that the annealing temperatures would vary considerably depending on the final crystallite sizes which dictate the diffusion distance. On the other hand, there also exist some reports of the direct synthesis of Ti–Al intermetallics by MA. For example, the formation of AlTi and $AlTi_3$ have been reported during the MA of $Al_{60}Ti_{40}$ and $Al_{50}Ti_{50}$ elemental blends.[321] Moreover, investigations by Park *et al.*[322] have shown successful synthesis of AlTi and $AlTi_2$ through direct MA in a vibratory mill in stainless steel grinding media with 12·7 and 19·1 mm dia. grinding balls. However, the extent of Fe contamination and its possible role in triggering such a reaction during MA remains to be investigated. Suryanarayana *et al.*[323] have synthesised TiAl by the MA of Al_3Ti and TiH_2.

Fe aluminides Al_3Fe formation during the MA of $Al_{80}Fe_{20}$ and $Al_{75}Fe_{25}$ blends in Fritsch P5 planetary ball mills is quite well documented.[324,325] Interestingly, the initiation of Al_3Fe formation occurred within 40 h in the $Al_{75}Fe_{25}$ blend as against 65 h in $Al_{80}Fe_{20}$. Such a delayed synthesis of Al_3Fe in $Al_{80}Fe_{20}$ is quite explicable because of the off-stoichiometric composition. No intermetallic compound has been detected in Al–12·5 at.-%Fe blend even after 80 h of MA.[324,325] Subsequent annealing at 773 K, however, resulted in Al_3Fe phase. The formation of such non-stoichiometric Al_3Fe may be an indication of an extended Al_3Fe phase field, though any possible Al loss due to oxidation may also play a role in this regard. Mechanical alloying of Fe-rich composition, e.g. Al–75 at.-%Fe, which incidentally lies in the $AlFe_3$ phase field, has been found to produce AlFe instead.[326] Subsequent annealing, on the other hand, has led to B2–$AlFe_3$ instead of the usual DO_3 structure. The formation of AlFe during MA in preference to $AlFe_3$ has been attributed to its lower ΔH_f ($-31·8$ kJ mol^{-1}) when compared with that of $AlFe_3$ (-18 kJ mol^{-1}). The formation of metastable Al_5Fe_2 through MA has also been demonstrated[327] inside 0·5 h in a Spex 8000 mill at a CR of 6 : 1 which finally transformed to a more stable AlFe on MA for 5 h.

Other aluminides Apart from the above mentioned Ni, Ti, and Fe aluminides, the versatility of MA has been demonstrated in the synthesis of several other aluminides including ternary aluminides. Some of these aluminides include Al–Nb, Al–Mo, Al–Zr, Al–Ni–Fe, etc. A list of these mechanically alloyed aluminides is presented in Table 6.

Silicides

The MA of silicides has gained significant interest in recent years,[343] particularly because of their potential applications as structural materials in the field of microelectronics and electrical technology.

Ni silicides The initial efforts by Radlinski and Calka[91] in the synthesis of Ni–Si intermetallics through MA of an equiatomic blend of Ni and Si failed to produce the desired product even after prolonged milling for 1000 h. However, subsequent annealing treatment at 973 K for a period of 1 h did result in the formation of NiSi. On the other hand, studies of the MA of $Ni_{100-x}Si_x$ ($x = 25$, 28, 33, 40, and 50) in a Fritsch P5 mill at a very high vial speed of 642 rev min^{-1} revealed crystalline phase formation for $x = 25$, 40, and 50, and amorphous phases for $x = 28$ and 33.

Fe silicides Mechanical alloying attempts with elemental $Fe_{33}Si_{67}$ blend[345] have shown the formation of a mixture of low temperature tetragonal α-$FeSi_2$, high temperature orthorhombic β-$FeSi_2$, and the cubic FeSi phases. Mechanical alloying studies on $Fe_{100-x}Si_x$ ($x = 5$, 25, 37·5, and 50) in a Fritsch P7 mill at a CR of 12 : 1 have revealed the formation of FeSi, Fe_2Si, Fe_5Si_3, and $FeSi_2$, respectively.[346] However, the MA of Fe–6·5 wt-%Si has shown the formation of a solid solution.[347] In fact, an extremely high intensity MA study by Abdellaoui *et al.*[348] has demonstrated the formation of Fe–Si solid solution over an extended phase field, up to Fe–37·5 wt-%Si. On the other hand, MA studies in the Si-rich composition regimes in an horizontal ball mill[349] have revealed the formation of β-$FeSi_2$ phase for Si > 70 at.-% and $\varepsilon + \beta$-$FeSi_2$ at 50 at.-% < Si < 70 at.-%.

Ti silicides In the initial studies of MA in the Ti–Si system by Veltl *et al.*[350] in a planetary ball mill, no intermetallic formation in the intermediate stages of

Table 6 Aluminides synthesised by mechanical alloying

Phase	Structure	ΔH_f, kJ mol^{-1} (Ref. 328)	Synthesis route*	Refs.
AlCo	B2	−43	MA	329
Al_4Cu_9	$D8_2$	−8	MA	330
Al_3Hf	$L1_2$	−51	MA	331
Al_3Mg_2	fcc	3	MA	332
$Al_{12}Mg_{17}$	A12	3	MA	332
Al_6Mn	Orthorhombic	−15	MA	333
AlMn	B2	−43	MA	333
$Al_{12}Mo$	bcc	−5	MA + HT	334
Al_5Mo	Hexagonal	−10	MA + HT	334
Al_4Mo	Monoclinic	−13	MA + HT	334
Al_8Mo_3	Monoclinic	17	MA + HT	334
$AlMo_3$	Monoclinic	−15	MA + HT	334
Al_3Nb	$D0_{22}$	−29	MA	92, 335
$AlNb_2$	$D8_b$	−36	MA + HT	92
$AlNb_3$	A15	−28	MA + HT	336–338
AlZr	Orthorhombic	−83	MA	92
Al_3Zr_2	Orthorhombic	−80	MA	92
Al–49Ni–2Cr	B2	...	MA	145
Al–46Ni–8Cr	B2	...	MA	145
Al–42Ni–16Cr	B2	...	MA	145
Al–40Ni–20Cr	A2	...	MA	145
Al–Ni–Fe	B2	...	MA	314, 339
Al–49Ni–2Fe	B2	...	MA	145
Al–46Ni–8Fe	B2	...	MA	145
Al–42Ni–16Fe	B2	...	MA	145
Al–40Ni–20Fe	A2	...	MA	145
Al–Ni–Ti	B2	...	MA	310, 314, 340
Al–25Zr–3Fe	$L1_2$	...	MA	92
Al–25Zr–8Fe	$L1_2$	...	MA	341
Al–25Zr–8Ni	$L1_2$	...	MA	341
Ti–24Al–11Nb	B2	...	MA	92, 342
Ti–25Al–25Nb	B2	...	MA	342
Ti–28·5Al–23·9Nb	B2	...	MA	92
Ti–37·5Al–12·5Nb	B2	...	MA	92

* HT: heat treatment. All ternary compostions at.-%.

milling has been detected possibly because of fast amorphisation reaction in the high energy milling. However, the generation of TiSi intermetallic phase before amorphisation during MA has been observed within 4 h in a Vibro mill at higher CR.[351] Mechanical alloying results reported by Oehring and Bormann[352] and Park *et al.*,[353] demonstrate the formation of crystalline Ti_5Si_3 which remained stable even on prolonged milling. Such a high stability of Ti_5Si_3 against amorphisation during milling is in conformity with its large negative free energy of formation (~ -71 kJ mol^{-1} at 673 K). Recent studies on the MA of elemental blends of compositions $Ti_{33}Si_{67}$ and $Ti_{42}Si_{58}$ have shown the formation of crystalline Ti_5Si_3 and Ti_5Si_4 embedded in an amorphous matrix during 60 h of milling in a Vibro mill.[354] $TiSi_2$ and TiSi phases were also detected in the preliminary stages of milling (4 h) in this study which paved the way to the more stable phases with the progress of milling.

Mo silicides Most of the research work on the MA of Mo silicides has been primarily focused on the Mo disilicide ($MoSi_2$), which is a well known refractory intermetallic (melting point 2323 K) with considerable technological importance. Successful synthesis of $MoSi_2$ by MA has been reported by Schwarz *et al.*[355] in a Spex 8000 mill within 70 h. More recently, nanocrystalline $MoSi_2$ has been synthesised by the MA of $Mo_{33}Si_{67}$ in a planetary ball mill (Fritsch P5) at a disc speed of 280 rev min^{-1} (Ref. 356). Interestingly, both the low temperature and high temperature phases, namely α and β $MoSi_2$ occurred during MA, with the extent of β increasing with milling time. Lee *et al.*[357] have reported that the formation of $MoSi_2$ during MA is quite sensitive to the mill used. While both α and β $MoSi_2$ could be obtained by MA in a Spex mill, MA in a planetary mill did not yield the silicide even after subsequent annealing treatment. In a significant report, Liu and Magini[358] have shown that high energy ball milling results in a self-propagating high temperature synthesis (SHS) reaction leading to stable α-$MoSi_2$, while low energy milling leads to metastable β-$MoSi_2$ without any such reaction.

Other silicides The development of silicides other than the Ni, Fe, Ti, and Mo silicides through MA has evoked only limited interest so that few reports are available. Some of these have been on the Pd silicides. It is interesting that while high energy ball milling[359] resulted in the formation of the line compound Pd_3Si along with an amorphous phase from a mixture of composition Pd–16–23 at.-%Si elemental blend, low energy milling[360] of Pd–17 at.-%Si led only to an amorphous phase. The direct synthesis of Pd_2Si has been reported on the MA of Pd–Si blends with Si > 33 at.-% while at Si > 50 at.-%, the initial product of Pd_2Si is destabilised on prolonged milling and gradually transformed to the high temperature PdSi phase.[361] Nb_5Si_3 and Ta_5Si_3 compounds have also been synthesised through the MA of elemental blends.[362] Lou *et al.*[363] have shown that milling without interruption leads to the abrupt formation of $NbSi_2$, while regular interruption results in its gradual formation. Unlike $MoSi_2$ in which prolonged milling resulted in the transformation of the low temperature phase (α) to the high temperature phase (β), the progress of MA of Nb_5Si_3 in a Spex mill[364] led to the formation of more of the room temperature phase (α) at the expense of the high temperature phase (β).

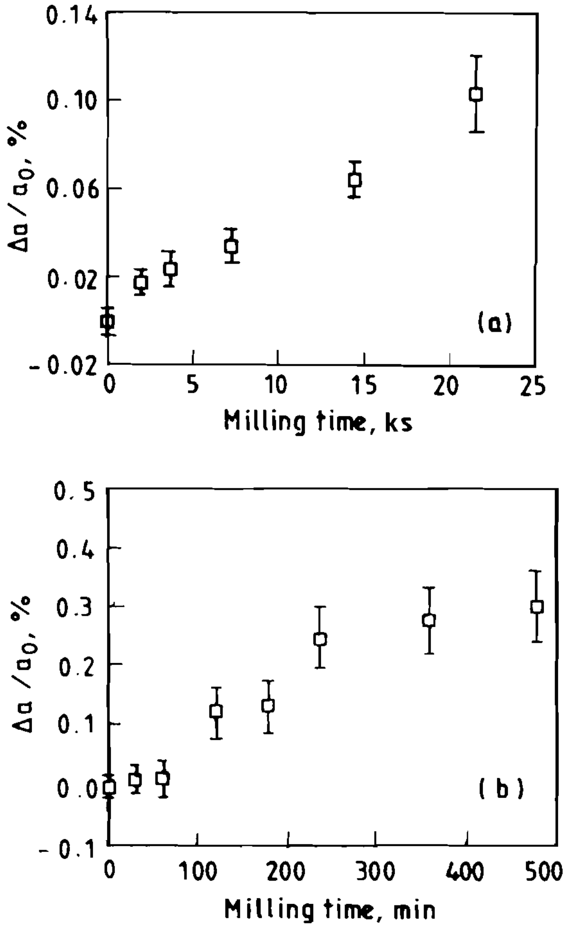
Other intermetallics

Although the aluminides and silicides have stolen the limelight of MA research in the field of intermetallics, several other intermetallics deserve mention because of fundamental aspects as well as technological importance. The formation of various compounds in the Cu–Zn system, namely β-CuZn, γ-Cu_5Zn_8, and ε-phases, through MA has been extensively studied over the past decade.[151,152,365] Studies have shown that a sequence of phase formation is maintained during the milling of elemental Cu–Zn blends in a Fritsch P5 mill, in which the Zn-rich phases, e.g. ε and/or γ, are always the first to form.[152] This is attributed to the high diffusivity of Cu in Zn rather than *vice versa*.[152] The progress of milling has shown the gradual formation of the Cu-rich phases through a continuous diffusive mechanism. The synthesis of superconducting intermetallics by MA, e.g. Nb_3Sn has also been successful,[126] and efforts on the MA of the superconducting Nb–Ge system have led to successful production of a number of phases, namely Nb_3Ge, Nb_5Ge, and $NbGe_2$, depending on the composition of the starting blend.[134,366] Various other intermetallic phases are also known to have been produced by MA. A list of non-aluminide and non-silicide intermetallics produced by MA is presented in Table 7.

Table 7 Intermetallics synthesised by mechanical alloying other than aluminides and silicides

Phase	Structure	ΔH_f, kJ mol^{-1} (Ref. 328)	Synthesis route*	Refs.
Co_3C	Hexagonal	+6	MA	367, 368
Cr_7C_3	Hexagonal	−13	MA + HT	369, 370
Cr_3C_2	Orthorhombic	−16	MA + HT	369, 370
Cr_2Nb	C15	10	MA	371
β-CuZn	B2	−8	MA	151, 152, 365
γ-Cu_5Zn_8	$D8_2$	−4	MA	151, 152
ε-$CuZn_4$	Hexagonal	−2	MA	151, 152
Fe_3C	Orthorhombic	+25	MA	368
$FeSn_2$	C16	−1	MA	372
Fe_3Sn_2	Monoclinic	−2	MA + HT	372
FeSn	B35	−2	MA + HT	372
Fe_3Sn	DO_{19}	2	MA	373
Fe_3Si	DO_3	21	MA	373
FeTi	B2	−25	MA	374
Fe_3Zn	$D8_2$	−2	MA	373
Mg_2Ge	C1	115	MA	375
Mg_2Ni	Hexagonal	−52	MA + HT	376
Mg_2Si	C1	−79	MA	375
Mg_2Sn	C1	80	MA	375
Nb_3Ge	A15	28	MA	134, 366
Nb_5Ge	Orthorhombic	−19	MA	366
$NbGe_2$	C40	29	MA	366
Nb_3Sn	A15	−16	MA	126
Ni_3B	Cubic	−21	MA	377
Ni_3C	Cubic	+7	MA	367, 368
Ni_3Sn_2	Hexagonal	24	MA	372
TiB_2	Hexagonal	74	MA	90
TiC	$L1_2$	77	MA	378–380
TiNi	B2	52	MA	380

* HT: heat treatment.



a Nb_3Au (Ref. 381); *b* Nb_3Sn (Ref. 382)

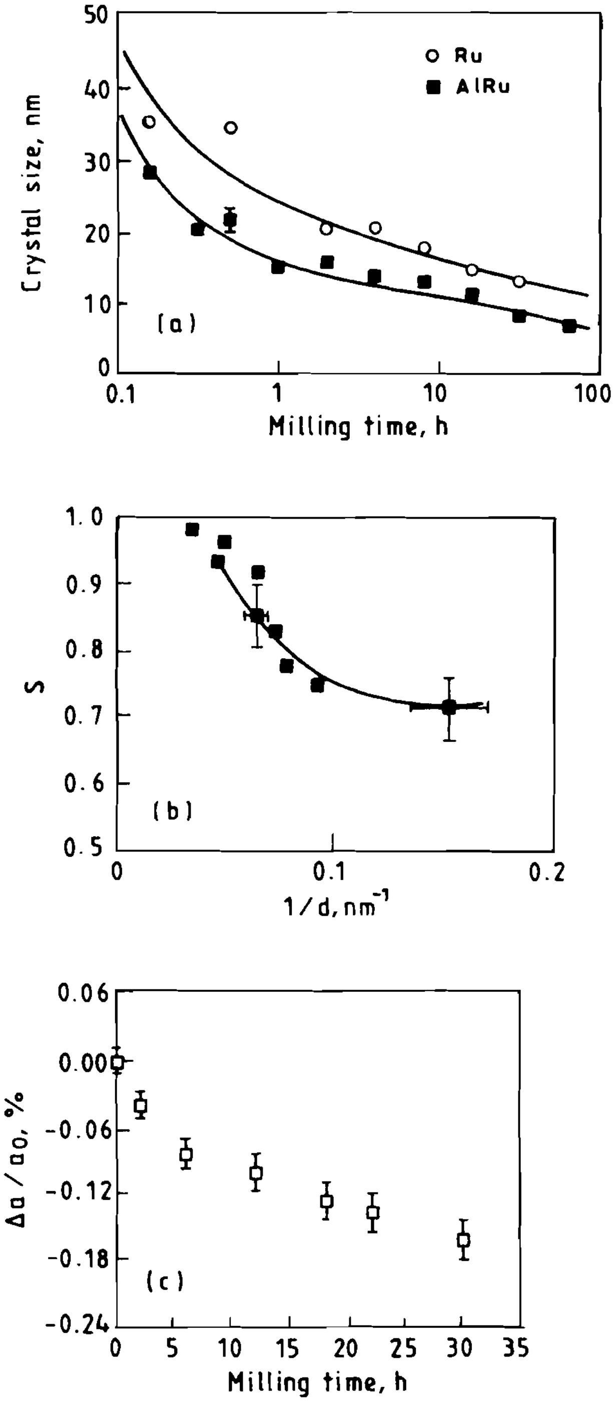
21 Increase in lattice parameter *a* with progress of milling

Disordering of intermetallics by milling

Large plastic deformation is known to induce high defect density, which may trigger a transition to disordered and/or amorphous state in the ordered crystalline intermetallics. It is therefore anticipated that high energy milling can destabilise the ordered structure. So far milling induced disordering in a large number of intermetallic compounds has been reported. The work done in this area so far is presented below on the basis of their structures.

A15 compounds

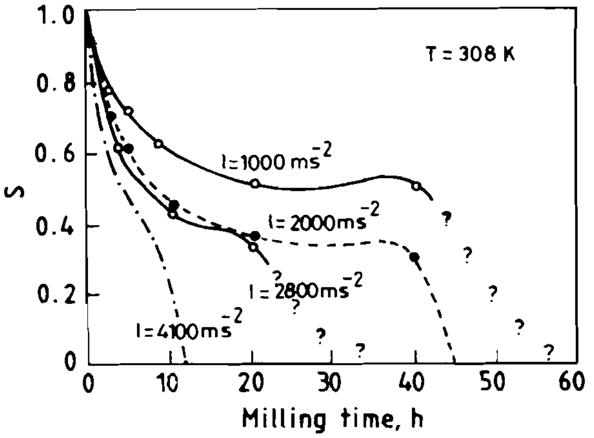
The superconducting property of the A15 compounds aids the monitoring of the disordering characteristics of these intermetallics with the progress of milling by the degradation of the superconducting transition temperature T_c. Investigations on the MM of Nb_3Au (Ref. 381) and Nb_3Sn (Ref. 382) have revealed disordering tendencies with milling as indicated by the variation in T_c. The disordering has been identified as antisite type as exemplified by an increase in the lattice parameter in the course of milling (Fig. 21). Such an increase in the lattice parameter accompanying disordering has been attributed to the accommodation of big Sn/Au atoms on small Nb atom sites. Disordering of V_3Ga and Nb_3Au during MM has also been studied with XRD techniques.[383]



22 Variation in *a* crystallite size with progress of milling and *b* long range order parameter *S* with crystallite size of AlRu (Ref. 384) and *c* lattice parameter of CoAl (Ref. 329) with milling time

B2 compounds

Studies on mechanically induced disorder during the ball milling of B2 intermetallics were initiated with the partial disordering of AlRu as reported by Hellstern *et al.*[384] A gradual drop in the long range order parameter S (Fig. 22*a*) was observed along with the reduction in the crystallite size with progress of milling (Fig. 22*b*); S was determined by the usual XRD technique.[385] Ball milling of B2 intermetallics has so far demonstrated the involvement of two



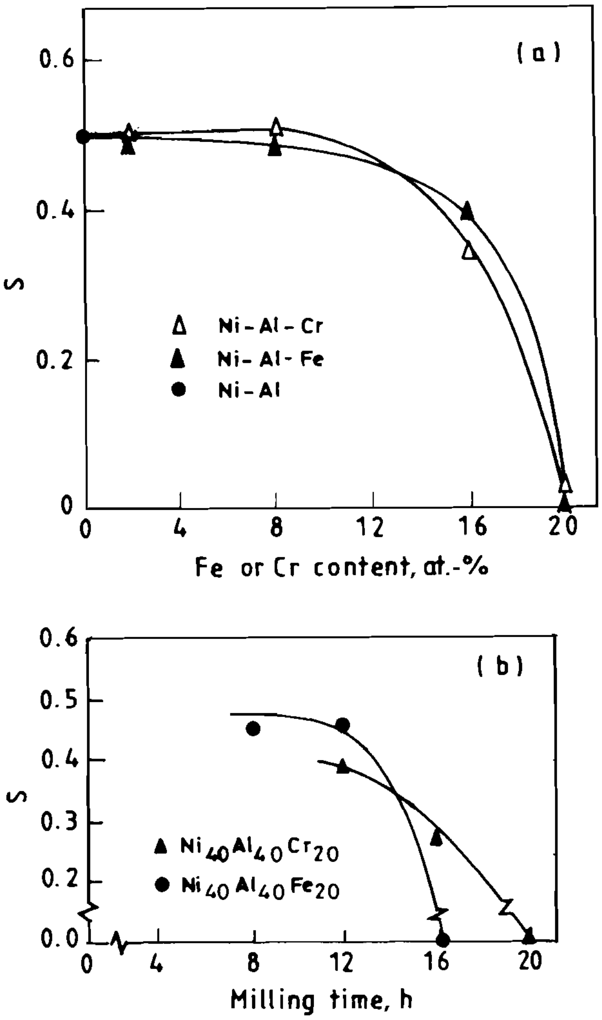
23 Effect of milling intensity on long range order parameter S of FeAl (after Ref. 387)

distinctly different types of disordering, namely antisite disorder and triple defect disorder. Antisite disorder, which is observed in CoZr (Ref. 90) involves an increase in the lattice parameter. On the other hand, the B2 compounds between VIII and IIIA group elements, e.g. CoGa (Ref. 386) and CoAl (Ref. 329) display triple defect disorder where the transition atom fits into the wrong sublattice but the other component remains on its own sublattice. The occurrence of triple defect disorder is indicated by the decrease in the lattice parameter with milling (Fig. 22*c*). The B2 compound in the Fe$_{60}$Al$_{40}$ represents a rare exception where antisite disorder occurs as indicated by the increase in the lattice parameter[90] in spite of the fact that it is a VIII–IIIA compound. Studies by Poecht *et al.*[387] have indicated the formation of total disorder ($S = 0$) of FeAl depending on the choice of milling parameter (Fig. 23), in a Fritsch P0 vibratory mill. The MA/MM of B2 NiAl, on the other hand, manifest high resistance against total disordering[339,388] possibly due to high ΔH_{ord}. Recent work,[153] however, has indicated the possibility of the introduction of total disorder by ternary addition of Fe or Cr to the extent $\geqslant 18$ at.-% (Fig. 24*a*). Moreover, a drop in the value of S of NiAl(Cr) to zero is delayed when compared with that in NiAl(Fe), as evident from Fig. 24*b*.[389] This difference could be attributed to the ease of dissolution of Fe in NiAl owing to the isomorphous nature of NiAl and FeAl which is not the case with Cr.

B8 compounds

B8 compounds are characterised by the general formula $M_{1+x}N$ (where M = transition metal and N = non-transition metal).[90] The filling of the tetrahedral sites (II) depends on the value of x where $0 \leqslant x \leqslant 1$. Two different categories of these compounds are generated, i.e. for $x = 0$, a B8$_1$ structure with all tetrahedral sites vacant is obtained, while for $x = 1$, a B8$_2$ structure with fully occupied tetrahedral sites is obtained. Compounds may, however, have partially filled tetrahedral sites with B8$_2$ structure of formula $M_{1 \cdot 5}N$.

B8$_2$ compounds with $M_{1 \cdot 5}N$ composition Ball milling induced disordering has been observed in B8$_2$ compounds, e.g. Fe$_3$Ge$_2$ and Mn$_3$Sn$_2$.[390] The disordering has been monitored by the change in the magnetisation with milling time at 4·2 K and an applied field of 21 T. Such disordering could be caused by the shift of the transition metal atoms, during milling, from fully occupied sites (I) to the empty sites (II). The contrasting behaviour in the variation of magnetisation accompanying the disordering process in Fe$_3$Ge$_2$ and Mn$_3$Sn$_2$ originates from the difference in the magnetic properties of Fe$_3$Ge$_2$ (ferromagnetic) and Mn$_3$Sn$_2$ (ferrimagnetic).

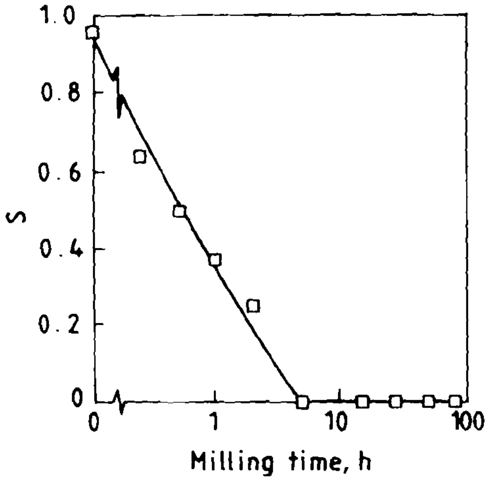


24 *a* Effect of Fe and Cr addition on long range order parameter S of mechanically alloyed NiAl (Ref. 153) and *b* change in S of mechanically alloyed NiAl(Cr) and NiAl(Fe) (Ref. 389) as function of milling time

B8$_2$ compounds with M_2N composition M_2N compounds consist of fully occupied interstices by M atoms and therefore a redistribution of M is practically impossible. Owing to these reasons these compounds have been found to show antisite disorder as observed in ball milled Co$_2$Ge (Ref. 391) and Co$_2$Si (Ref. 392).

L1$_2$ compounds

Among all L1$_2$ intermetallics, the disordering behaviour of Ni$_3$Al has been the most widely studied.[393–395] As is evident from Fig. 25,[393] formation of a fully disordered Ni$_3$Al during MM occurs within 5 h



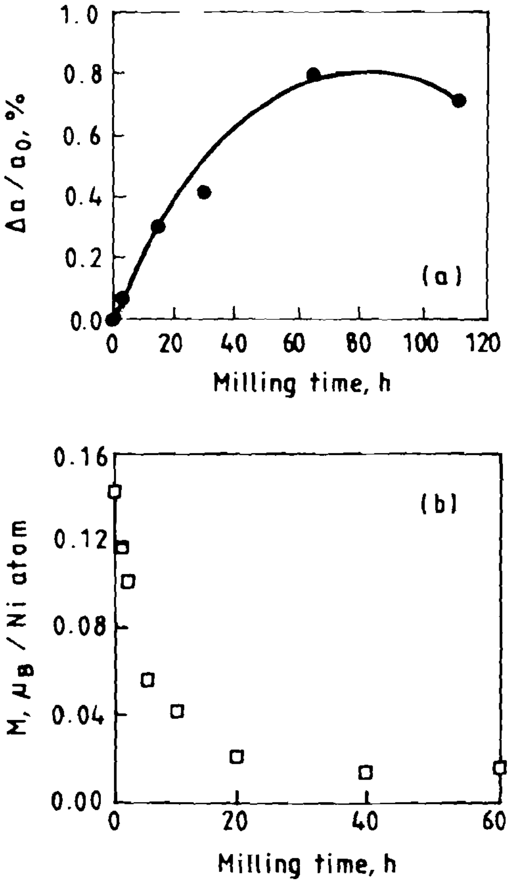
25 Change in long range order parameter *S* of Ni_3Al during ball milling (after Ref. 393)

of milling. An increase in the lattice parameter (Fig. 26*a*) accompanies the decrease in magnetisation (Fig. 26*b*),[393] indicating antisite disorder. The occurrence of antisite disorder in $L1_2$ Fe_3Ge has also been proved by magnetisation studies.[90] Yavari[396] has reported detailed reordering studies of disordered Ni_3Al obtained by MM on subsequent annealing. Disordering of Nb_3Al on MM has also been reported.[397]

Amorphous phases

Metallic glasses possess some special properties such as high strength, good toughness, high corrosion resistance, and low eddy current and magnetic hysteresis losses. The last property makes metallic glasses very good soft magnetic materials. Several books have been written on metallic glasses.[398-400] In general, all the non-crystalline solids that exhibit a glass transition temperature T_g are defined as metallic glasses. Most of the non-crystalline alloys produced by RSP satisfy this definition, while those produced by solid state amorphisation (SSA) rarely show a T_g and therefore, are termed amorphous phases.

Solid state amorphisation is a process by which amorphous phases are produced from crystalline pure metal mixtures and alloys in the solid state without any intermediate melting stage. Barring irradiation induced amorphisation, SSA was first observed by Yeh *et al.*[10] when Zr_3Rh was annealed in a hydrogen atmosphere at low temperature (~473 K). This unusual result was attributed to the anomalously fast diffusivity of hydrogen in Zr_3Rh resulting in an amorphous hydride. Schwarz and Johnson[9] have reported amorphisation during the diffusion annealing of vapour deposited multilayers of Au and La which was attributed to the high diffusivity of Au in La. Later, codeformation of two pure metal foils of Ni and Zr by cold rolling followed by low temperature annealing also resulted in amorphisation.[11] The most widely studied SSA technique is MA which was first demonstrated by Koch *et al.*[6] in the Nb-Ni system. Subsequent work has demonstrated that amorphisation during ball milling can be achieved not only in the pure metal mixtures but also in mixtures of intermetallics and in both these cases some alloying is involved before amorphisation. In addition, amorphisation has also been achieved by milling single phase intermetallics.



26 *a* Increase in lattice parameter *a* of Ni_3Al and *b* simultaneous decrease in its magnetisation of 4·2 K and 21 T, with progress of milling (after Ref. 393)

Amorphisation by mechanical alloying/milling

Amorphous phase formation has been the most widely studied aspect of MA.[84-86] Koch *et al.*[6] were the first to report amorphisation by MA. They have shown that a pure metal powder mixture of composition $Ni_{60}Nb_{40}$ transforms to an amorphous phase after 14 h of MA. They have also shown that milling in air reduces the crystallisation temperature T_x of the resulting glass when compared with milling in an inert He atmosphere, for reasons unknown. During the study of amorphisation of Ni,Zr powders by MA, Weeber *et al.*[401] found that Ni-Zr alloy powder can be amorphised in a shorter time than a mixture of pure Ni and Zr powders. This is mainly due to the reduction of energy requirement for the amorphisation by an amount equivalent to that required for alloying in the former case. Even the crystallisation temperature was higher in the former case due to the reduced chance of oxidation of Zr. Dolgin *et al.*[402] showed that the growth of the amorphous phase follows a $t^{1/2}$ (*t* being milling time) law suggesting that it is diffusion controlled.

During MA, the XRD peaks of the pure metals become continuously broader and less intense and finally, the composite becomes amorphous. In the Ni–Zr system a new type amorphisation reaction has been found[403,404] in which crystalline intermetallic compounds form as intermediate products when a planetary mill is used for MA. Mechanical alloying in a vibratory mill results in the direct formation of amorphous phase without any intermediate stage. In a vibrating frame all the powder in the vial remains as such during the whole milling period, while in a planetary mill the powder forms a thin layer on the milling tools. In the case of the vibrating mill because of the smaller contact surface between ball and powder particles, the high energy of the balls is transferred to a smaller volume, and as the heat can not be removed easily, it results in a higher temperature of particles. Probably, the characteristic time for diffusion through a layer of alloyed Ni–Zr which depends on the local temperature, is longer than that for the nucleation and growth of crystalline compounds in the planetary mill which results in the formation of intermetallic compounds as intermediate products.

Gaffet *et al.*[405] have confirmed the result of Weeber *et al.*[404] in their study on the Ni–Zr system. In contrast, Kim and Koch[366] have observed the formation of Nb_3Sn as an intermediate product of amorphisation of Nb–Sn in a Spex vibratory mill. Similar results have been reported in the Nb–Ge (Ref. 406), Nb–Si (Ref. 407), Fe–Sn (Ref. 408), and Zr–Al (Ref. 409) systems. In an important contribution Eckert *et al.*[125] have reported different glass forming composition ranges (GFRs) at different milling intensities in a planetary mill in the Ni–Zr system. At a milling intensity of 3 ($2\cdot5\ \mathrm{m\ s^{-1}}$) no glass formation was observed indicating that the energy was insufficient for amorphisation. At a milling intensity of 5 ($3\cdot6\ \mathrm{m\ s^{-1}}$) the GFR was found to be 30–83 at.-%Ni, which narrowed down to 66–75 at.-%Ni when the milling intensity was increased to 7 ($4\cdot7\ \mathrm{m\ s^{-1}}$). This clearly indicates that at high milling intensities the temperature during milling rises above the crystallisation temperature of the amorphous phase thus reducing the GFR. Oleszak *et al.*[410] showed that prolonged milling could result in the crystallisation of the amorphous phase formed by MA at shorter milling times. Recently, El-Eskandarany *et al.*[411] have shown an interesting sequence of phase transformations during MA in the Co–Ti system. They observed cyclic amorphous$\rightleftharpoons$crystalline transformation on continuous milling for the $Co_{50}Ti_{50}$ composition. The amorphous phase formed after MA for 22 ks converted into a bcc phase after 86 ks and further transformed into an amorphous phase after milling for 360 ks. This trend of cyclic transformation continued on prolonged milling. They attributed the amorphous to bcc transition to the disability of the amorphous phase to withstand impact and shear forces, while the bcc phase appears to be destabilised on prolonged milling because of the increased defect concentration. Amorphous phase formation by MA has so far been observed in a large number of binary and ternary alloy systems over wide composition ranges as listed in Table 8.

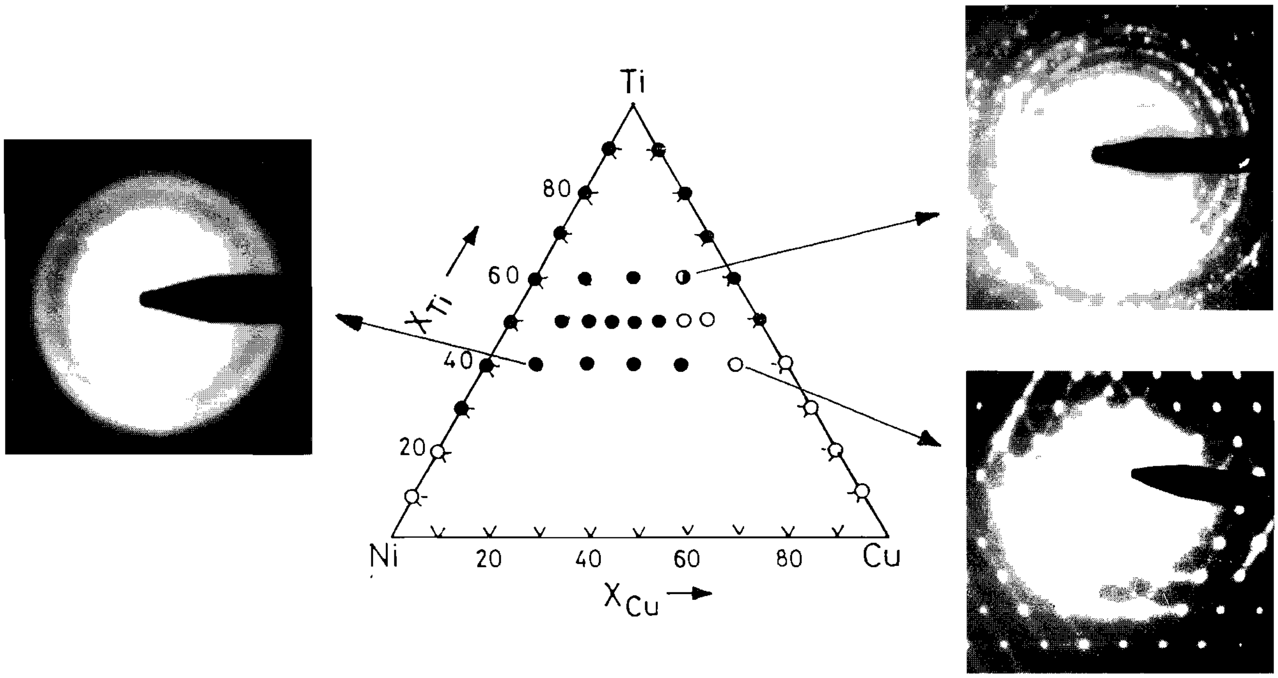
Table 8 Amorphous phases formed by mechanical alloying of pure metal mixtures

System	Glass forming composition range, at.-% solute	Refs.
Ti–Al	10–75	123
Ti–Co	80–85	126
Ti–Cu	10–87	412
Ti–Ni	10–70	124
Ti–Pd	15–58	413
Ti–Si	20–60	414
Ti–Zn	60	415
Zr–Co	27–92	416, 417
Zr–Cu	40–60	417, 418
Zr–Fe	30–78	416, 417, 419
Zr–Ni	27–85	416, 417, 420–423
Zr–Pd	45–60	424
Hf–Cu	30–70	425
Hf–Ni	15–65	425
Nb–Co	35–85	426
Nb–Cr	32–70	426
Nb–Fe	35–75	426
Nb–Ge	25–27	427
Nb–Ni	20–80	428, 429
Nb–Mn	35–60	426
Nb–Si	25	427
Nb–Sn	25	430
Cu–Nb–*X*	$Cu_{44}Nb_{42}X_{14}$ (X = Si, Ge, Sn)	430
Fe–Zr–B	$(Fe_{75}Zr_{25})_{100-x}B_x$ (x = 0–15)	431
Nb–Ge–Al	$Nb_{75}Ge_{25-x}Al_x$ (x = 6, 12, 19)	427
Ti–Ni–Al	$Ti_{50}Ni_xCu_{50-x}$ (x = 10, 25)	432
	$Ti_{60}Ni_xCu_{40-x}$ (x = 15, 20)	432
Ti–Ni–Cu	$Ti_{72}Ni_{16}Cu_{12}$	433
	$Ti_{40}Ni_{60-x}Cu_x$ (x = 0–40)	124
	$Ti_{50}Ni_{50-x}Cu_x$ (x = 0–30, 50)	124
	$Ti_{60}Ni_{40-x}Cu_x$ (x = 0–20, 40)	124, 434

Even though amorphisation by MA has been studied widely in the case of binary alloy systems, studies on ternary alloy systems are very few.[427,430–433] The present authors[124] have demonstrated a wide GFR in the Ti–Ni–Cu system which extends from $x = 0$–40 for $Ti_{40}Ni_{60-x}Cu_x$; $x = 0$–30 and 50 for $Ti_{50}Ni_{50-x}Cu_x$; and $x = 0$, 20, and 40 for $Ti_{60}Ni_{40-x}Cu_x$ alloys after 40 h of MA in a planetary mill at a milling intensity of 6 (Fig. 27).

Apart from its simplicity the MA technique has many other advantages over the RSP technique. The GFR in the case of RSP is in general restricted to the deep eutectics because of kinetic constraints. But in MA the GFR is centred at the equiatomic composition and is much wider in many systems. Figure 28 shows the GFR obtained by MA in the Ni–Nb system in comparison with other techniques.[429] It is quite clear from the figure that the GFR is much wider by MA when compared with melt quenching. Only by RF sputtering and pico second laser was the GFR obtained wider and comparable to that obtained by MA. Murty *et al.*[435] clearly showed in the Ti–Ni–Cu system that the glass forming ability of an alloy is governed by entirely different factors in RSP and MA. While in MA the thermodynamic aspects appear to dominate, the kinetic factors appear to decide the glass forming ability during RSP.

Amorphisation by melt spinning is very difficult in systems with shallow eutectics, cascade of peritectics, and in immiscible systems with positive heats of mixing. In recent years, MA has been used successfully to obtain amorphous phases in such systems (Table 9). El-Eskandarany *et al.*[439] have shown a very wide GFR of 10–90 at.-%Ta in the Al–Ta system,



27 Glass forming composition range in Ti–Ni–Cu system after 40 h of MA; solid, open, and half solid circles represent amorphous, crystalline, and mixture of amorphous and crystalline phases, respectively: inset electron diffraction patterns represent each of above states (Ref. 124)

which is the widest GFR obtained in any system so far by MA. Glass formation has not been observed so far by melt spinning in this system. Al–Ti is another such system where glass formation has not been feasible by RSP. The present authors[123] have obtained a wide GFR of 25–90 at.-%Ti in this system by MA. Figure 29 shows the electron diffraction patterns from $Al_{50}Ti_{50}$ at different stages of MA. With increasing milling time the powders become much finer, more deformed, the lattice defect concentration also increases and finally, the powder becomes completely amorphous after 40 h of milling at a milling intensity of 6 (Fig. 29*d*).

Table 9 Amorphous phases formed by mechanical alloying in systems with positive heat of mixing

System	Glass forming composition range, at.-% solute	Refs
Ag-Cu	50	436
Al-C	20-50	437
Al-Cr	15	272
Al-Fe	20-50	436
Al-Nb	50	438
Al-Ni	70-75	308
Al-Ta	10-90	439
Al-Ti	25-90	123
Al-Zr	60-85	284
Ta-Co	10-80	440
Ta-Cu	30-50	298, 299, 441, 442
Ta-Fe	20-60	443
Ta-Ni	10-80	440, 444
V-Cu	50	295
V-Fe	50	445
V-Ni	30-55	446
V-Zn	50	447
W-Fe	50	448, 449

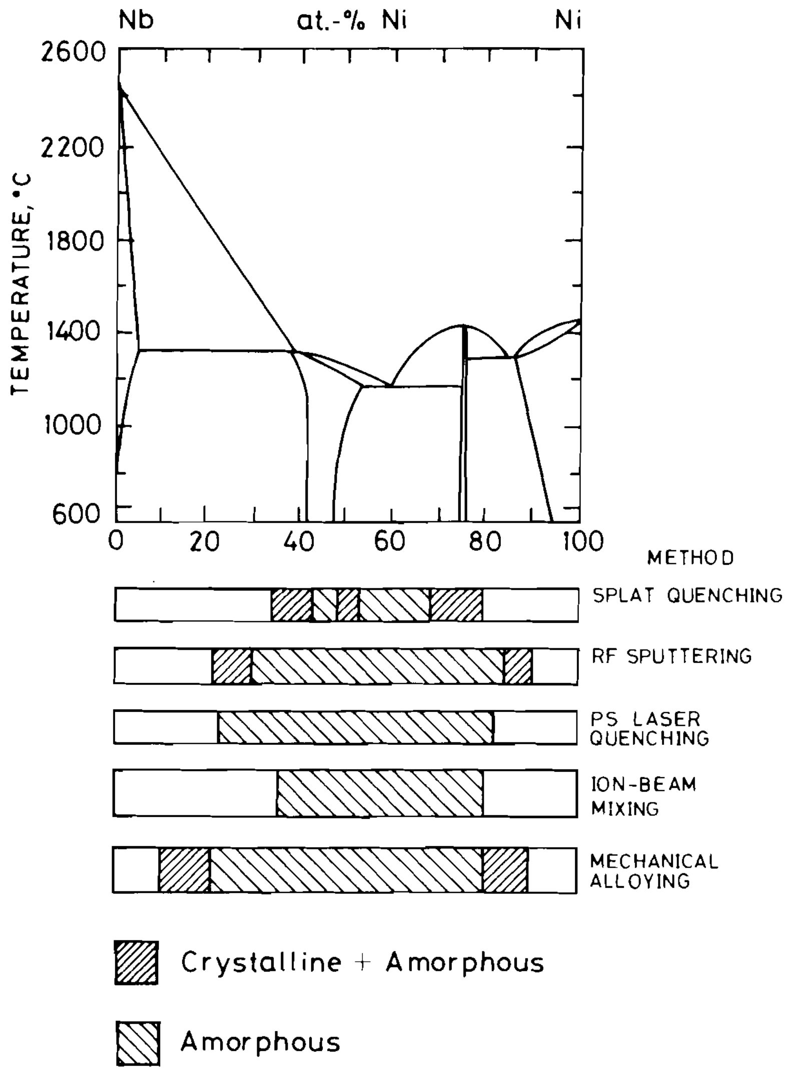
One more restriction of the RSP regarding glass formation is that the compositions corresponding to stable intermetallic compounds are very difficult to amorphise. This problem has been overcome by using MA. Many intermetallic compounds and mixtures of intermetallic compounds have been amorphised in recent years by MA (Table 10).

Theory of amorphisation by mechanical alloying/milling

For any transformation a driving force is required. Solid state amorphisation, which is a crystal to amorphous transformation, can be considered as an intermediate stage of transformation of a metastable crystalline state to an equilibrium crystalline state as

Table 10 Amorphous phases formed by milling of intermetallic compounds or mixture of intermetallic compounds

System	Intermetallic mixture of intermetallics	Alloy composition, at.-% solute	Refs.
Cu-Zr	CuZr	50	418
	$CuZr_2$	67	418
Nb-Ge	Nb_3Ge	25	427
Ni-Al	Ni_3Al	25	394
Ni-Nb	Ni_6Nb_7	55	108
Ni-Ti	NiTi	50	450
	$NiTi_2$	67	108
Ni-Zr	$NiZr_2$	67	451
Ti-Co	CoTi + Co_2Ti	60	452
Ti-Cu	$CuTi_2$ + CuTi	40	452
Ti-Fe	FeTi + Fe_2Ti	60	452
Ti-Mn	Mn_2Ti + $Mn_{52}Ti_{48}$	62	452
Ti-Ni	NiTi + Ni_2Ti	60	452
Y-Co	YCo_3, YCo_5	75, 84	7
Zr-Cu	$CuZr_2$ + $Cu_{51}Zr_{14}$	60	452
Zr-Ni	$NiZr_2$ + $Ni_{11}Zr_9$	40, 50	452
	Ni_5Zr + Ni_7Zr_2	61, 78	453

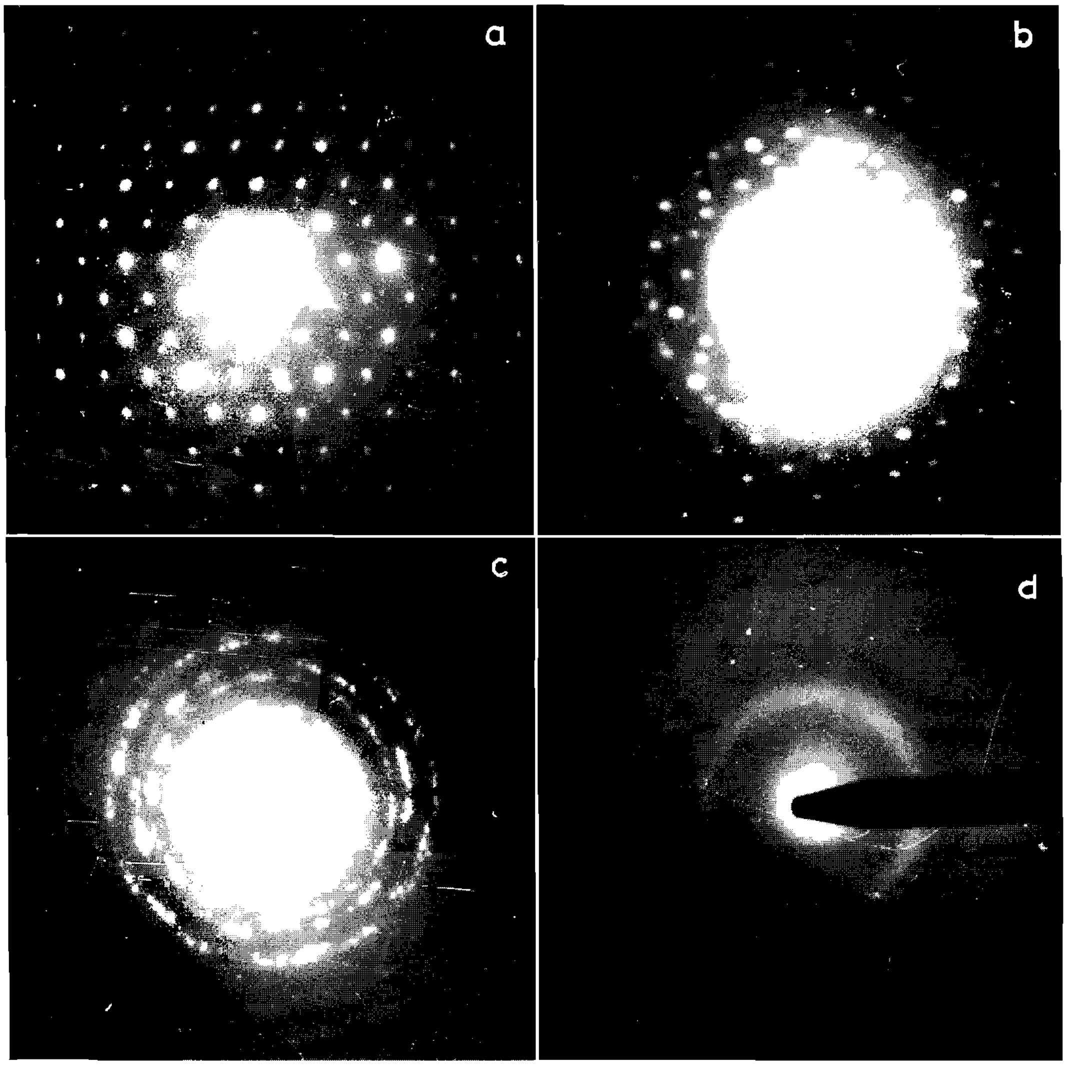


28 Glass forming composition range obtained in Ni–Nb system by different processing routes (after Ref. 429)

shown in Fig. 30.[80] Thus the thermodynamic condition for SSA by MA is that the free energy of the amorphous phase must be lower than that of the initial pure metal mixture and the terminal solid solutions in that system ($G_a < G_c$). For the amorphous phase to form in preference to the more stable intermetallic compounds ($G_i < G_a$), the time scale for the formation of the former τ_{c-a} should be much shorter when compared to that of the latter τ_{c-i}. Also, as the amorphous phase is metastable, the time scale τ_{a-i} should be much longer than τ_{c-a} so that the amorphous phase formation can be observed. Thus the kinetic conditions for SSA are that $\tau_{c-a} \ll \tau_{c-i}$ and $\tau_{c-a} \ll \tau_{a-i}$.

In other words, these conditions define the kinetic constraints for the formation of intermetallic compounds during SSA. This kinetic constraint is provided by the anomalous diffusion of one element in the other. If $D_{A\ in\ B} \gg D_{B\ in\ A}$, the amorphous phase can grow at sufficiently low temperatures where there is no possibility of nucleation and growth of intermetallic compounds. It is in general known that late transition elements with smaller atomic size (e.g. Cu, Ni, Au) have very high diffusivities in early transition elements having larger atomic size (e.g. Zr, Hf, La, Ti). Calculation of the diffusivities from standard data[454] for the Al–Ti system at room temperature has shown[136] that the self-diffusivity of Al and Ti are $2{\cdot}9 \times 10^{-25}$ and $6{\cdot}0 \times 10^{-32}$ cm^2 s^{-1}, respectively, while the chemical diffusivity of Al in α-Ti is $8{\cdot}7 \times 10^{-23}$ cm^2 s^{-1}, which is nine orders higher than the self-diffusivity of α-Ti. This provides the kinetic constraint for the nucleation and growth of an intermetallic compound and aids in amorphisation. An exception to this rule was amorphisation by MA in a slow diffusing V–Zr system.[445,455]

In the transformation of a crystalline pure metal mixture to an amorphous phase during MA the driving force is provided by the large negative ΔH_{mix} of the amorphous phase. The importance of the thermodynamic factors was pointed out by Hellstern and Schultz[456] in their study of the glass forming ability of transition metal Ti alloys by MA. While Ni–Ti, Co–Ti, and Cu–Ti alloys could be completely amorphised because of their large negative ΔH_{mix} of the liquid, Fe–Ti, Mn–Ti, and Cr–Ti could only be partially amorphised because of their smaller ΔH_{mix} of liquid.[457] The V–Ti alloy did not form glass at all

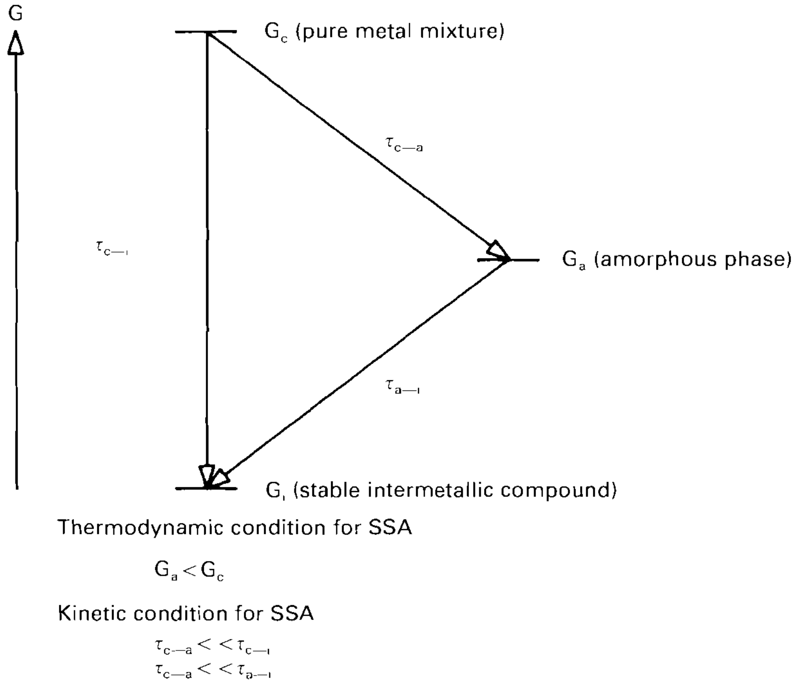


29 Electron diffraction patterns of $Al_{50}Ti_{50}$ after *a* 4 h, *b* 8 h, *c* 16 h, and *d* 40 h of MA representing evolution of amorphisation during MA (Ref. 123)

in the time period of their study as this system is isomorphous and a solid solution is always favoured at lower temperatures.

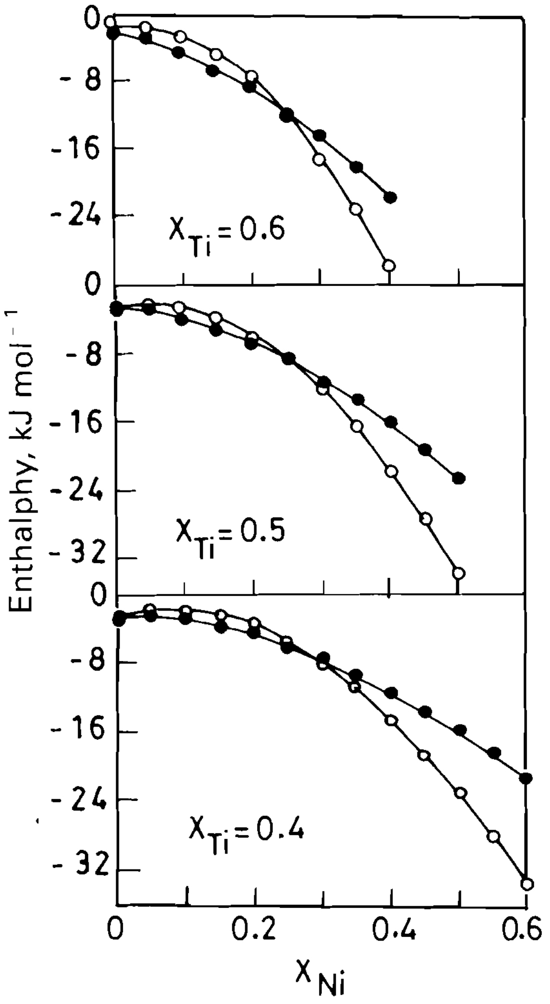
Thermodynamic criteria for glass formation have been worked out by Murty *et al.*[458,459] for unary and binary systems. The thermodynamic approach has been extended by Murty *et al.*[124] to calculate the GFR in the ternary Ti–Ni–Cu system using Miedema's approach.[457,460] In this approach the ΔS_{mix} is neglected as its contribution to the free energy is found to be negligible in comparison with the contribution of ΔH_{mix} at the temperature of 300 K and thus the driving force for amorphisation comes mainly from the enthalpy contribution. In these calculations crystalline pure metals were chosen to be the standard state and their enthalpy was assigned to be zero. Figure 31 shows the enthalpy–composition diagram for the amorphous phase and solid solution for the three groups of alloys $Ti_{40}Ni_{60-x}Cu_x$, $Ti_{50}Ni_{50-x}Cu_x$, and $Ti_{60}Ni_{40-x}Cu_x$ which have been studied by MA by Murty *et al.*[124] The calculated GFR (Fig. 32) was found to be $x = 0$–30 and 58–60 for $Ti_{40}Ni_{60-x}Cu_x$ alloys; $x = 0$–24 and 49–50 for $Ti_{50}Ni_{50-x}Cu_x$ alloys; and $x = 0$–15 for $Ti_{60}Ni_{40-x}Cu_x$ alloys and compares fairly well with that obtained experimentally (Fig. 27).

The mechanism of anomalous diffusion and the concept of negative heat of mixing can not be used for the amorphisation of intermetallic compounds as it can be seen clearly from Fig. 33 that there is no chemical driving force for the amorphisation of an intermetallic compound (reaction path 3→2). The increased free energy of the crystalline phase because of the lattice defects produced by severe plastic deformation during milling could be higher than the free energy of the amorphous phase, thus driving the amorphisation reaction. A similar explanation has been given by Lee *et al.*[452] for the amorphisation of a mixture of intermetallic compounds (Fig. 34). In this case the free energy of the initial mixture of intermetallic compounds G_0 is lower than that of the amorphous phase G_4. Owing to the deformation induced defects during milling the free energy of the individual intermetallic compound rises (G_1 and G_2) and thus the free energy of the mixture of intermetallic compounds after milling G_3 would be higher than that of the amorphous phase G_4 thus providing the required driving force for amorphisation.

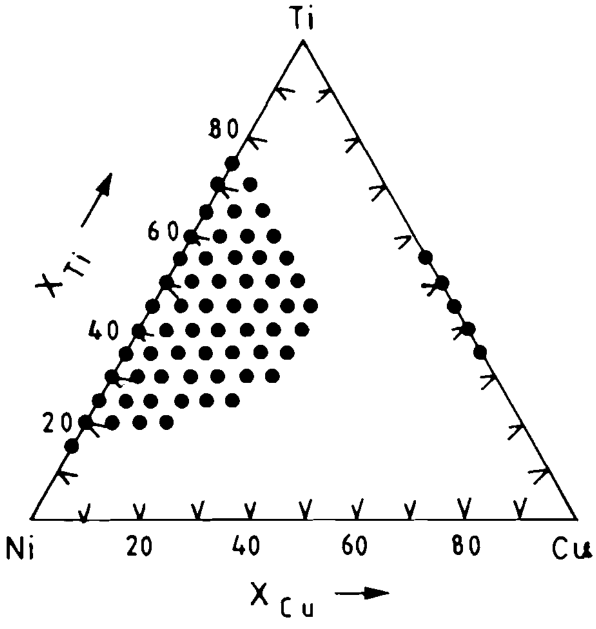


30 Schematic free energy diagram indicating criteria for solid state amorphisation (after Ref. 80)

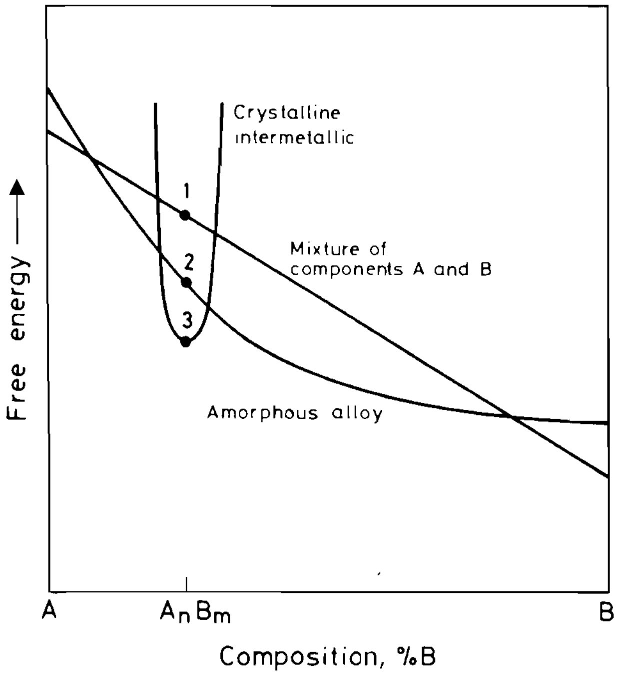
The results on the amorphisation of intermetallics have proved that a negative ΔH_{mix} for the amorphous phase is not a necessity for amorphisation by MA.[461–463] But SSA by annealing of multilayers of pure metals requires a negative ΔH_{mix} for the amorphous phase as mixing of the elements can not take place otherwise. This is the most important advantage of MA and this concept has been utilised in amorphisation in liquid immiscible systems. Yavari and Desre[461,462] have attributed amorphisation in systems with positive heats of mixing to the development of



31 Enthalpy-composition diagrams for solid solution (open circles) and amorphous phase (solid circles) in Ti-Ni-Cu system (after Ref. 124)



32 Glass forming composition range in Ti-Ni-Cu system, calculated using Miedema's model; solid circles represent amorphous phase (after Ref. 124)



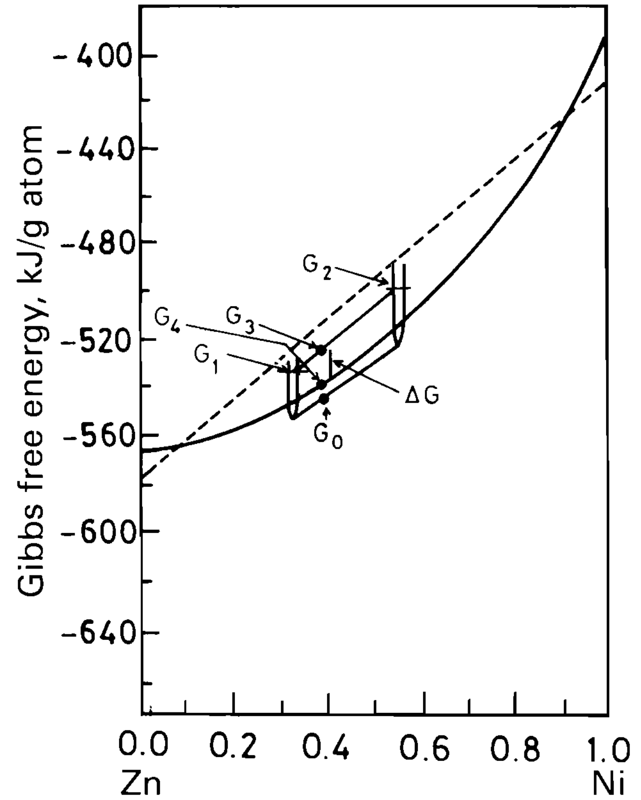
33 Schematic free energy–composition diagram showing absence of driving force for amorphisation of an intermetallic compound (after Ref. 109)

steep concentration gradients during MA. Alternately, as shown in Fig. 35 the heavy deformation during MA increases the free energy of the pure metals and the interfacial energy arising from the lattice defects and the new grain boundaries created raise the free energy of the solid solution above that of the amorphous phase thus aiding in amorphisation. In this figure the term G_d refers to the free energy increase due to deformation.

Solid state amorphisation has also been explained using polymorphous phase diagrams.[464] The T_0 and T_l^s curves in Fig. 36 are the isofree energy and isentropic curves for the liquid and solid phases, respectively: T_{g0} is the ideal glass transition temperature.[465] At any temperature below T^* if the composition of the alloy is higher than c^*, the crystal catastrophically transforms to an amorphous phase. During MA, because of the anomalous diffusivity of one element in the other and the enhanced diffusivities arising from increased defect concentration, once the concentration of the fast diffusing element in the relatively immobile element crosses the critical concentration c^*, the amorphisation occurs catastrophically. A number of investigators[466–470] have introduced the thermodynamic parallels between melting and SSA.

Quasicrystals

The first report on the formation of a quasicrystalline phase by MA was by Eckert *et al.*[471] in the Al–Cu–Mn system. They have shown that a powder mixture of composition $Al_{65}Cu_{20}Mn_{15}$ transforms to a quasicrystalline phase on MA in a planetary mill after 90 h of milling. Following this report there have been a few other reports on quasicrystalline phase formation by MA which are summarised in Table 11. In a very interesting report Eckert *et al.*[476] have shown the formation of different metastable phases at different milling intensities (milling speeds) in the Al–Cu–Mn system. At a milling intensity of 5 (3·6 m s^{-1}) they observed amorphous phase formation and at a milling intensity of 7 (4·7 m s^{-1}) a 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 localised temperatures generated at different milling intensities. They also observed transformation of these phases into one another on further milling at various milling intensities (Fig. 37).



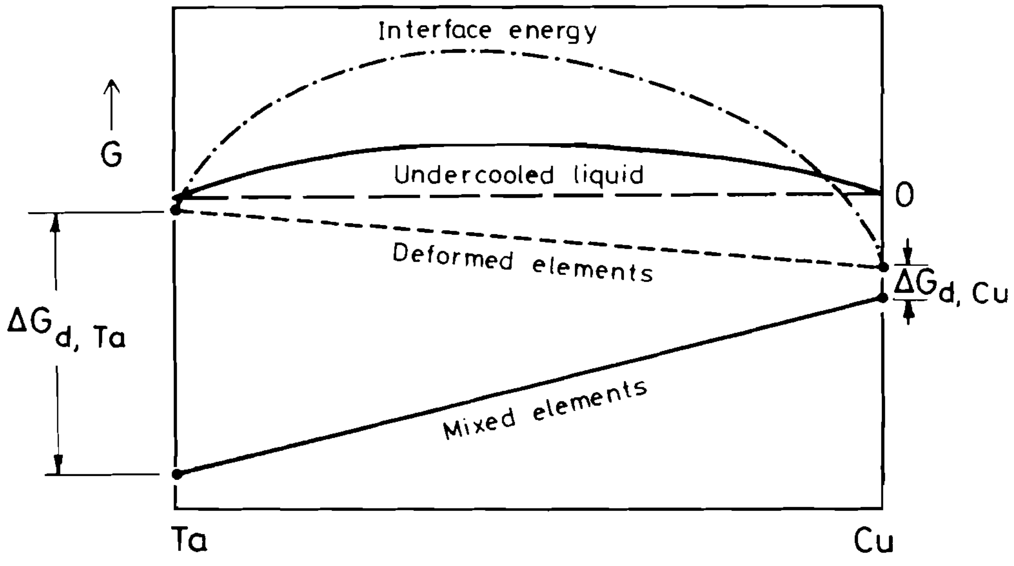
34 Schematic free energy–composition diagram demonstrating creation of driving force for amorphisation of mixture of intermetallic compounds (after Ref. 452)

Crystallisation of metallic glasses by milling

This section deals with a transformation which is the reverse of that dealt with in the section 'Amorphous phases' above. The literature dealing with the crystal-

Table 11 Quasicrystalline phases formed by mechanical alloying

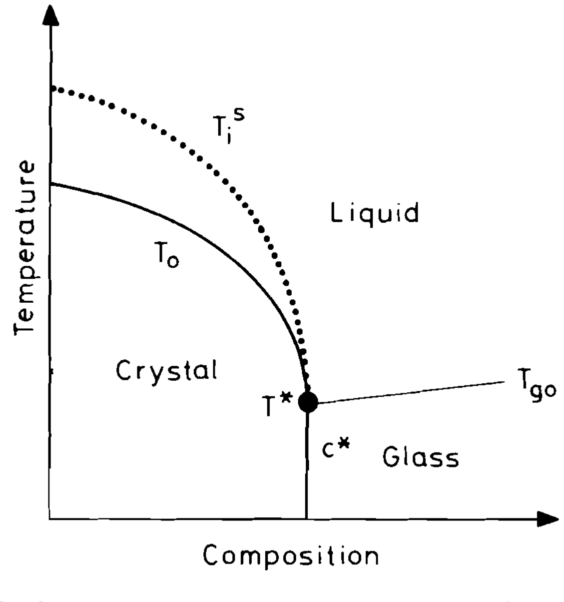
System	Composition	Refs.
Al-Cu-Fe	$Al_{65}Cu_{20}Fe_{15}$	472
Al-Cu-Mn	15–25 at.-%Cu 10–20 at.-%Mn	20, 471
Al-Cu-Ru	$Al_{65}Cu_{20}Ru_{15}$ $Al_{70}Cu_{12}Ru_{18}$	473
Al-Pd-Mn	$Al_{70}Pd_{20}Mn_{10}$	474
Mg-Cu-Al	$Mg_{32}Cu_8Al_{41}$	475
Mg-Zn-Al	$Mg_3Zn_3Al_2$	475



35 **Free energy–composition diagram for liquid immiscible Cu–Ta system showing feasibility of amorphisation of solid solution due to stored energy induced by MA (after Ref. 298)**

lisation of amorphous phases by MM is much less than that of amorphisation by MA/MM. The limited literature available in this area can be classified into two groups. The first group deals with crystallisation through the MM of metallic glasses made by RSP. The second group includes those reports in which the amorphous phases made by MA/MM under certain milling conditions crystallise on continued milling with changed milling conditions.

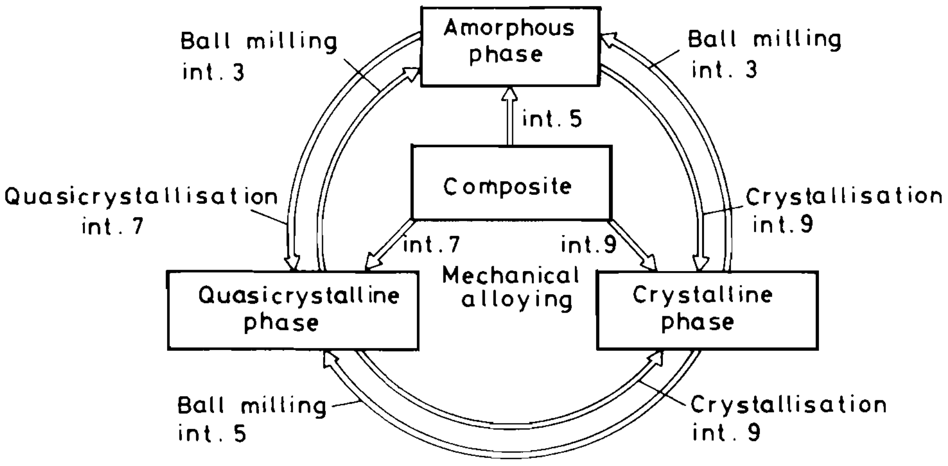
Trudeau *et al.*[477] have milled Metglas 2605Co ($Fe_{66}Co_{18}Si_1B_{15}$) and Metglas 2605S-2 ($Fe_{78}Si_9B_{13}$) and found that both crystallise on milling, with Co-containing metallic glass crystallising at shorter milling times. The crystallisation of these glasses during milling was attributed to the local rise in the temperature during ball milling, while the early crystallisation of the Co-containing glass was thought to be due to its lower crystallisation temperature (441 C cf. 553 C of Metglas 2605S-2). In an interesting experiment, they have mechanically alloyed Co and Ni to Metglas 2605S-2 and found that addition of Co induces rapid crystallisation while Ni stabilises the amorphous phase. This is interesting because Ni addition is known to lower the crystallisation temperature of Metglas 2605S-2 to 375 C. This work has suggested that a lower crystallisation temperature of a metallic glass is not sufficient for it to be crystallised during high energy ball milling. Crystallisation of metallic glass in the Fe–B–Si system by MM has been observed by several other investigators.[478,479]



36 **Schematic polymorphous phase diagram showing possibility of crystal to glass transition at low temperature (after Ref. 464)**

Eckert *et al.*[125] have shown that a high milling intensity (milling speed) causes the amorphous phase obtained in the Zr–Ni system at a lower milling speed to crystallise. Matsuki *et al.*[430] have reported similar results in the Nb–Sn system. Mechanical alloying in this system at 180 rev min^{-1} resulted in an amorphous phase while milling at 250 rev min^{-1} yielded Nb_3Sn phase. These results were assumed to be due to the high temperatures generated during milling at higher milling speeds. Earlier work on SSA by the low temperature annealing of multilayers[79] has shown that an increase in the annealing temperature results in the formation of intermetallic compounds. The difficulty in the formation of these crystalline phases during low temperature annealing of the multilayers has been attributed to the anomalously high diffusivity of one of the constituents of the diffusion couple in the other which makes the nucleation and growth of intermetallic compounds very difficult at low temperatures.

Kimura and Kimura[213] have measured the temperature of the attritor during the MM of NiTi. At 450 rev min^{-1} they observed a temperature of 180 C and the product of milling was crystalline. Milling at 300 rev min^{-1} resulted in the formation of an amorphous phase and the temperature of the mill was 100 C. Mizutani and Lee[480] obtained an amorphous phase



37 Phase transitions in Al–Cu–Mn system induced by MA at various milling intensities (int.) (after Ref. 476)

during the MA of Ni,Zr powders corresponding to $Ni_{50}Zr_{50}$ and $Ni_{70}Zr_{30}$ compositions and continued milling resulted in the crystallisation of the amorphous phase: oxygen contamination was believed to be the cause of this effect. Petzoldt[428] observed an interesting sequence of phase formation during the MM of a mixture of intermetallics in the Ni–Zr system. The sequence of phase formation with increasing milling time was: mixture of intermetallics → amorphous phase → amorphous + metastable crystalline phase → amorphous phase. This was attributed to the free energy changes in the system. In an interesting experiment, Gaffet[194] found that changing the vial temperature from room temperature to 200 C did not influence the product of milling of $Ni_{10}Zr_{90}$ powder while the variation of the milling speeds of disc and vial in the planetary mill has a strong bearing on the milled products.

Thus, it appears that temperature rise during milling alone can not explain the crystallisation of amorphous phases observed during milling. Chemistry changes during milling and the local temperature rise during milling can enhance the crystallisation kinetics. It is possible that the defects introduced during milling accelerate the diffusion and in turn the crystallisation kinetics during milling.

Reactive milling

The milling process during which chemical reactions take place leading to the metallothermic reduction and/or resulting in the formation of compounds is termed 'reactive milling'. Schaffer and McCormick[21,481] were the first to report the reduction of metal oxides by reactive metals. They have shown that reduction of CuO by Ca is feasible by ball milling the powders together. An exothermic reaction resulting in an abrupt rise in the temperature of the vial by 140 K during dry milling was reported by them. They calculated the adiabatic rise in the temperature due to the reaction from the enthalpy change of the reaction (-473 kJ mol^{-1}) and the heat capacities of the reactants to be 4000 K which is much above that required for self-sustaining combustion (~2300 K). They have also shown[481] the formation of β-CuZn phase by the simultaneous reduction of CuO and ZnO with Ca. However, it is clear from their results that the reactions have not gone to completion. Schaffer and McCormick, in their subsequent publications[482,485] have shown similar metallothermic reduction reactions in a number of systems. Table 12 gives a list of various reactions reported so far during milling. The kinetics of these reactions have also been studied by Schaffer and McCormick,[485] who have shown an increase in the rates of the reaction at higher milling energies. Lu *et al.*[488] have reported the reduction of Fe_3O_4 with Al during milling which resulted in the formation of ferromagnetic Fe and superparamagnetic Fe particles. El-Eskandarany[487] has given another dimension to the subject when he reported the formation of nanocrystalline Cu and TiO_2 particles by the reduction of Cu_2O with Ti.

There have been reports of reduction of chlorides also during high energy ball milling. McCormick *et al.*[491] have shown the reduction of $TiCl_4$ with Mg and formation of not only Ti but also alloys such as Ti–3Al, Ti–6Al–4V, TiAl, and Ti_3Al by changing the proportions of the constituents. The reactants used

Table 12 Chemical reactions observed during milling

Reaction		Refs.
$Ag_2O + Al$	$\rightarrow Ag + Al_2O_3$	484
$CuO + Al$	$\rightarrow Cu + Al_2O_3$	484
$CuO + Ca$	$\rightarrow Cu + CaO$	21, 481
$CuO + Fe$	$\rightarrow Cu + FeO$	484–486
$CuO + Mg$	$\rightarrow Cu + MgO$	484
$CuO + Mn$	$\rightarrow Cu + MnO_2$	484
$CuO + Ni$	$\rightarrow Cu + NiO$	484
$Cu_2O + Ti$	$\rightarrow Cu + TiO_2$	487
$Fe_2O_3 + Ca$	$\rightarrow Fe + CaO$	482
$Fe_3O_4 + Al$	$\rightarrow Fe + Al_2O_3$	488
$PbO + Si$	$\rightarrow Pb + SiO_2$	489
$V_2O_5 + Ti$	$\rightarrow V + TiO_2$	482
$ZnO + Ca$	$\rightarrow Zn + CaO$	484
$ZnO + Ti$	$\rightarrow Zn + TiO_2$	484
$CuCl_2 + Na$	$\rightarrow Cu + NaCl$	490
$FeCl_3 + Ca$	$\rightarrow Fe + CaCl_2$	490
$FeCl_3 + Na$	$\rightarrow Fe + NaCl$	490
$TiCl_4 + Mg$	$\rightarrow Ti + MgCl_2$	491
$ZrCl_4 + CaO$	$\rightarrow ZrO_2 + CaCl_2$	492

for the formation of these alloys were $TiCl_4$, $AlCl_3$, Mg, and V. However, they have not observed any combustion reaction in these cases. In another report, Ding *et al.*[490] have shown the reduction of $FeCl_3$ and $CuCl_2$ with Na and Ca which has led to the formation of nanocrystalline Cu and Fe powders. In an interesting study, Suryanarayana *et al.*[323] have shown the formation of TiAl by the reactions between Al_3Ti and TiH_2. However, the reaction did not go to completion during milling (55 vol.-% of TiAl after 52 h) and 95 vol.-% of TiAl was obtained after hot isostatic pressing.

There have been quite a number of reports on the formation of nitrides and oxynitrides by milling elemental powders in liquid nitrogen (LN_2) (cryomilling). Perez *et al.*[493] have produced nanodispersions of Al_2O_3 and AlN in Fe–10 wt-%Al alloy by the cryomilling of Fe and Al together. Huang *et al.*[494] have obtained a similar dispersion in NiAl by the MA of Ni and Al in LN_2. Aikin *et al.*[495] have produced AlN by the cryomilling of NiAl. Ball milling of metals by sealing the vial with nitrogen gas has also led to the formation of various nitrides such as Fe_2N (Ref. 496) NbN (Ref. 497), Ti_2N (Ref. 498), TiN (Refs. 499, 500), SiN (Ref. 501), TaN (Ref. 502), ZrN (Ref. 503), and (Ti,Al)N (Refs. 500, 504). Nitrides have also been produced by milling the elemental powders in an ammonia atmosphere.[16,505,506]

Although, the results reported so far are encouraging and can have a strong impact on industry, one has to check the feasibility of these reactions on a large scale production. In addition, one needs to look into ways of improving the reaction rates so that they go to completion.

Materials for special applications

Mechanical alloying has also been used to produce special materials such as hard magnets, superconductors, catalysts, materials for hydrogen storage, and materials with giant magnetoresistance (GMR) properties. Schultz *et al.*[507,508] have produced excellent permanent magnetic materials, $Nd_{15}Fe_{77}B_8$ by the MA of an elemental blend followed by annealing. While alloying of Nd with Fe could be easily achieved by MA, amorphous B particles remained after MA. Annealing for 1 h at 600°C resulted in the completion of the alloying process and the formation of $Nd_2Fe_{14}B$ phase. The material thus produced has excellent permanent magnetic properties such as H up to 13 kOe and BH_{max} up to 12·8 MOe. In their later reports, Schultz's group have shown the formation of other permanent magnets such as $Sm_2Fe_{17}N_{2\cdot7}$ (Ref. 509), $Sm_2Fe_{17}C_2$ (Ref. 510), $SmCo_5$ (Ref. 511), Sm_2Co_{17} (Ref. 511), and SmFeTi.[512] Sui *et al.*[513] successfully produced $Nd_2Fe_{14}C$ by the MA of an elemental blend of $Nd_{16}Fe_{84-x}C_x$ ($x = 8{\cdot}0$, $8{\cdot}2$, $9{\cdot}0$), while optimum magnetic properties were obtained for 8·2 at.-%C after a heat treatment at 900°C. Ding *et al.* have reported the formation of $Sm_2Fe_{17}N_{2\cdot7}$ (Ref. 514), and $Sm_2(Fe,Ga)_{17}C_2$ (Ref. 515) by MA. Ito *et al.*[516] have reported that the grain sizes (20 nm) obtained by MM are smaller than the magnetic domain size (200 nm) in the case of $Sm_2Fe_{17}N_x$ magnets. Interestingly, the magnetic properties were found to be sensitive to the grain size even when they are finer than the domain size.

A15 superconductors such as Nb_3Al (Ref. 337) and Nb_3Sn (Ref. 126) have been successfully synthesised by MA. It is interesting to note that such compounds are difficult to produce by the conventional ingot metallurgy route because of the large difference in the melting points of the constituents. In addition, as these compounds form by a peritectic reaction which is very sluggish, heavy coring and inhomogeneity are usually observed when they are made by the melting route. Mechanical alloying provides an easy way of producing such compounds with good homogeneity. Yuon *et al.*[517] could produce YBa_2Cu_3 precursor to superconductor by the MA of CuY and CuBa intermetallic compounds. Batalla and Zwarz[518] could produce similar precursors by the MA of Cu,Y, and Ba powders. Inoue and Masumoto[519] could produce high T_c oxide superconductors by MA followed by oxidation. They could successfully prepare precursors for oxidation in the immiscible Ba–La–Cu system by MA. However, the $LnBa_2Cu_3O_{7-8}$ (Ln = Y, Gd, Ho, Er) formed by oxidation (920°C in oxygen) of mechanically alloyed precursor did not show any better superconducting properties than the conventionally made superconductors.

Another area where a significant amount of work has been carried out is in the production of alloys for hydrogen storage through MA. Ivanov *et al.*[520–523] have developed Mg-base alloys with Ni, Fe, Co, or Ce for hydrogen storage by MA. All the above alloys have shown significant reactivity with hydrogen. Mechanically alloyed Mg alloys with 5–20 wt-%Fe (or Ni, Ti, Cu) have also been found to be supercorroding. These alloys have been developed by the US Naval Civil Engineering Laboratory for short-circuited galvanic cells to react rapidly and predictably with sea water to produce heat and hydrogen gas for marine applications.[524] The hydrogen storage alloys produced by MA were found to be much better than conventional alloys.[524–526] Moelle and Fecht[527] have shown enhanced hydrogen solubility in nanoparticles produced by milling. Singh *et al.*[528] have observed superior hydrogenation behaviour in the case of nanocrystalline Mg_2Ni produced by MA. Nohara *et al.*[529] have shown that modification of the surface of MgNi with graphite by MA can improve its rate of hydrogen absorption.

The feasibility of producing nanocrystalline materials in a easy way by MA/MM has opened up a new synthesis route for the production of catalysts which are expected to have better reactivity in the nanocrystalline state. However, the efforts in this direction have been limited probably because of the possible adverse effects of contamination of the surface of these nanocrystalline powders during milling. Miani *et al.*[530] produced carbides of Fe by MA which have shown significant catalytic activity for CO_2 hydrogenation. Schulz *et al.*[531] could produce nanocrystalline Ni–Mo alloys with high catalytic activity by MA. Catalytic activity has also been observed in mechanically alloyed Ti_2Ni and $Al_{65}Ni_{35}$ by Benameur *et al.*[532] They have also shown that catalytic activity decreases in the order of amorphous, nanocrystalline, and crystalline states. Recently, there have been reports that the nanocrystals obtained by MA in the Cu–Co (Refs. 533, 534) and Cu–Ag (Ref. 535) systems show giant magnetostriction. This has given another dimension to the field of MA.

Concluding remarks

The possibility of synthesising a variety of materials as mentioned above has made MA an exciting field to work in for many investigators. Although most of the work carried out so far is 'academic' in nature, some of the alloys produced by MA such as ODS alloys and hydrogen storage materials could see the light of commercialisation. Even after 25 years since Benjamin's work on MA, the atomistic mechanism of alloying during high energy ball milling has not yet been clearly identified. Most of the models reported so far discuss alloying at the microscopic level and not at the atomistic level. The highly non-equilibrium nature of the process makes it almost impossible to arrive at an atomistic mechanism. Although there are indications that the defects induced during milling have a significant role to play in the alloying process, the nature and concentration of these defects remains among the many questions to be answered. Amorphisation of intermetallic compounds during MM and alloying in immiscible systems are usually attributed to the defects generated during milling. However, a quantification of the defects and the resultant increase in the free energy of the constituents of milling has not yet been done systematically. In spite of a large amount of work reported on the formation of amorphous phase and intermetallics by MA/MM, prediction of their formation and composition for a given system before carrying out the experiment and identification of the milling conditions that can lead to its formation are far from reality. Only recent works have started concentrating on a solution for this problem. It is very clear that alloying during MA depends strongly on the deformation behaviour of the constituents. However, no serious efforts have been made so far to quantify the influence of any of the mechanical properties of the constituents on the alloying kinetics.

Most of the work carried out on MA so far has been restricted to the reporting of various phases formed during the MA/MM of the powders. Very few investigators have tried to go further than the production of powders and study the mechanical and physical properties of the compacts. The compaction of the MA powders poses a problem because of the heavily strained state of the powder. However, the advent of techniques such as shock wave compaction allow this hurdle to be overcome. The poor ductility of the MA compacts in some cases also poses a practical problem which needs further investigation. Every application needs the components in bulk form and serious efforts are warranted in the direction of the production of near net shaped mechanically alloyed products without significant loss of their special properties. Similarly, most of the mills available so far are of laboratory size and hence attempts should be made to build large capacity mills without sacrificing the energy of the mill to a large extent. This calls for the involvement of design engineers, thus giving the field a multidisciplinary facet. Another major problem of high energy ball milling is the chance of contamination from the milling tools and milling atmosphere. Although a variety of process control agents are being used to reduce the contamination, a solution to the problem is far from complete.

In spite of all the above drawbacks, MA attracts the attention of a large group of researchers and technologists basically because of its potential to produce a variety of materials in the simplest possible way. A variety of equilibrium and non-equilibrium phases which are difficult to produce by the conventional ingot metallurgy route and even by rapid solidification processing have been successfully synthesised by this technique. Mechanical alloying/milling definitely has a bright future as a solid state processing route.

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