The science and technology of mechanical alloying

C. Suryanarayana a, *, E. Ivanov b, V.V. Boldyrev c

a The George S. Ansell Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401-1887, USA
b Tosoh SMD, Inc., Grove City, OH 43213-1895, USA
c Institute of Solid State Chemistry and Mechanochemistry, Russian Academy of Sciences, Novosibirsk, Russia

Abstract

Mechanical alloying (MA) is a powder metallurgy processing technique involving cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill, and has now become an established commercial technique to produce oxide dispersion strengthened (ODS) nickel- and iron-based materials. MA is also capable of synthesizing a variety of metastable phases, and in this respect, the capabilities of MA are similar to those of another important non-equilibrium processing technique, viz., rapid solidification processing (RSP). However, the “science” of MA is being investigated only during the past 10 years or so. The technique of mechanochemistry, on the other hand, has had a long history and the materials produced in this way have found a number of technological applications, e.g., in areas such as hydrogen storage materials, heaters, gas absorbers, fertilizers, catalysts, cosmetics, and waste management. The present paper discusses the basic mechanisms of formation of metastable phases (specifically supersaturated solid solutions and amorphous phases) by the technique of MA and these aspects are compared with those of RSP. Additionally, the variety of technological applications of mechanically alloyed products are highlighted. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mechanical alloying; Supersaturated solid solutions; Amorphous phases; Rapid solidification processing; Applications of mechanically alloyed products

1. Introduction

Non-equilibrium processing of materials has attracted the attention of a number of scientists and engineers due to the possibility of producing better and improved materials than is possible by conventional methods [1]. Rapid solidification processing (RSP) and mechanical alloying (MA) are two such processing methods with somewhat similar capabilities. RSP has started as an academic curiosity in 1960 and matured into an industrially accepted technology with its use for the production of amorphous ferromagnetic sheets for transformer core applications by AlliedSignal. On the other hand, MA started as an industrial necessity in 1966 to produce oxide dispersion strengthened (ODS) nickel- and iron-based superalloys for applications in the aerospace industry and it is only recently that the science of this “apparently” simple processing technology has begun to be investigated. While the scientific basis underlying RSP was investigated in detail from the beginning, applications for the products of RSP were slow to come about mostly because of the limitations on the size and shape of the RSP materials. Thus, invention of the melt spinning technique to produce long and continuous ribbons and of the planar flow casting method to produce wide ribbons accelerated the applications of RSP alloys. Even today use in transformer core laminations remains the major (and most voluminous) application of the RSP alloys. The developments in the science of RSP and the applications of RSP products can be found in several monographs and proceedings of the RQ conferences (see, e.g., [2–6]). In contrast, the technique of MA was used for industrial applications from the beginning and the basic understanding and mechanism of the process is beginning to be understood only now. There have been several reviews and conference proceedings on this technique too [7,8], but the present status of MA has been most recently reviewed by Suryanarayana [9]. The MA literature available up to 1994 has been collected together in an annotated bibliography [10]. Fig. 1(a) presents the growth of publications in the field of MA during the period 1970–1994 and Fig. 1(b) compares the growth trends of publications between MA and RSP. It may be noted that even though the trends for MA and RSP are similar, that for MA is offset by about 15 years from that of RSP. In the present paper, we will first discuss the current scientific understanding of the metastable effects — specifically solid solution formation and amorphization phenomena — achieved by MA and then describe the present and potential applications of MA. A critical comparison will...
be made on the effects achieved by MA and RSP, whenever possible.

2. The technique of mechanical alloying

MA is a dry powder processing technique and has been used to synthesize both equilibrium and metastable phases of commercially useful and scientifically interesting materials. The technique was developed by Benjamin [11,12] around 1966 to develop an alloy combining oxide dispersion strengthening with $\gamma'$ precipitation hardening in a nickel-based superalloy intended for gas turbine applications. Since the oxides cannot be dispersed in the liquid state, a solid-state processing technique was necessary. Thus, MA owes its origin to an industrial necessity. MA is a simple and versatile technique and at the same time an economically viable process with important technical advantages. One of the greatest advantages of MA is in the synthesis of novel alloys, e.g., alloying of normally immiscible elements, which is not possible by any other technique including RSP. This is because MA is a completely solid-state processing technique and therefore limitations imposed by phase diagrams do not apply here.
The process of MA consists of loading the powder mix and the grinding medium (generally hardened steel or tungsten carbide balls) in a stainless steel container sealed under a protective argon atmosphere (to avoid/minimize oxidation and nitridation during milling) and milling for the desired length of time. About 1–2 wt.% of a process control agent (PCA) (usually stearic acid) is normally added to prevent excessive cold welding amongst the powder particles, especially when powders of ductile metals are milled. The types of mills generally used are SPEX mills (wherein about 10 g of the powder can be processed at a time), attritors (where a large quantity of about a few pounds of powder can be processed at a time), or Fritsch Pulverisette mills (where powder in more than one container can be processed simultaneously). The times required for processing are short in the SPEX mills whereas they are longer in the attritors or Fritsch mills. A description of the MA processing and details of the different mills can be found in [9,13].

3. Attributes of mechanical alloying

The formation of an amorphous phase by mechanical grinding of a Y–Co intermetallic compound in 1981 [14], and in the Ni–Nb system by ball milling of blended elemental powders in 1983 [15] brought about the recognition that MA is a potential non-equilibrium processing technique. Since the mid-1980s, a number of investigations have been carried out to synthesize a variety of alloy phases including equilibrium and supersaturated solid solutions, crystalline and quasicrystalline intermediate phases, and amorphous or glassy alloys. Nanocrystalline materials (with a grain size of few nanometers, usually <100 nm) are also produced by MA of powder mixtures. Additionally, it has been recognized that this technique can be used to induce chemical (displacement) reactions in powder mixtures at room temperature or at much lower temperatures than normally required to synthesize pure metals [16]. For example, pure copper metal powder was produced by ball milling a mixture of CuO and Ca powders at room temperature. These attributes of MA are very similar to those of RSP and so frequently comparisons are made of the relative efficiencies of these two techniques.

While the suitability of a particular technique to develop a material depends on the eventual applications for which the product is intended, one fundamental way of comparing these two non-equilibrium processing techniques is to evaluate the departure from equilibrium achieved. Calculations show that the maximum departure from equilibrium is 24 kJ/mol in RSP and it is 30 kJ/mol in MA suggesting that it is possible to achieve greater departure from equilibrium (or “more” metastable effects) during MA.

4. Solid solubility limits

Extended solid solubilities have been achieved by both MA and RSP techniques in several alloy systems. An exhaustive list of the solubility extension values can be found in [9]. Even though the limits of supersaturation have not been established in all the systems by both RSP and MA, based on the available results, a selective comparison is presented in Table 1. It may be seen that a greater extent of supersaturation is obtained by MA than by RSP. A general observation is that the maximum solubility extension achieved by MA is higher than that by RSP when the room temperature solubility is very small or zero [9]. Further, it is also possible to achieve supersaturation in some alloy systems by MA that is not possible by RSP; this is especially true in liquid immiscible systems [9]. Fig. 2(a) compares the maximum equilibrium and extended solid solubilities of different elements in Cu achieved by MA. It may be seen that there is a significant increase in the solid solubility achieved by MA. The increase in solid solubility may be rationalized by the Hume-Rothery rules, where the relative atomic sizes, crystal structures, and electronegativities of the solvent and solute play an important decisive role. A correlation between the solid solubility and atomic radius is presented in Fig. 2(b). It may be noted that increased solid solubility is achieved only when both the atomic size factor (<15%) and similar crystal structure conditions are satisfied. The solid solubility is very limited when these conditions are not satisfied or when the crystal structure is different. Similar results have been obtained in other cases also.

The scientific basis for the formation of supersaturated solid solutions through RSP is reasonably well established. For example, the limit of supersaturation obtainable by RSP has been explained using the concept of $T_0$, the temperature at which the solid and liquid phases have the same free energy. It is possible to obtain a supersaturated solid solution if the alloy melt during RSP is cooled to a temperature below $T_0$. Since the liquid phase is not involved in the MA processing, this concept may not be applicable to explain the formation of supersaturated solid solutions by MA. But, it will be useful to relate the formation of solid solutions by MA to some parameter, say energy input. Since the solid solubility limits increase with increasing solidification rate in RSP alloys, it will be instructive to check whether the
solid solubility limits increase with increasing energy input during MA.

Several theories have been proposed to explain the formation of supersaturated solid solutions by MA. It was reported that the solid solubility could be increased up to the composition when an amorphous phase starts forming, i.e., the solid solubility limit is decided by the metastable equilibrium between the supersaturated solid solution and the amorphous phase [17]. Another theory is that the solid solubility limit is determined by the balance between intermixing due to shearing forces during milling and the decomposition of the solid solution due to thermally activated jumps. If the ratio of these two, referred to as the $\gamma$ factor, is very small thermally activated diffusion will drive the system to equilibrium and no supersaturation is obtained. On the other hand, for very large values of $\gamma$, a fully random solid solution is obtained [18]. It has now been accepted that the most important reason for the increase in solid solubility is the formation of nanostructures during milling [19].

The large volume fraction of atoms in the grain boundaries in these ultrafine-grained materials is expected to enhance diffusion and consequently increase the solid solubility. Even though the above theories explain the solid solubility increases observed in some instances, all the theories are not able to explain the observations in all the alloy systems.

5. Amorphization by mechanical alloying/milling

Amorphization is one of the most frequently reported phenomena in mechanically alloyed powder mixtures. Amorphous phases have been obtained starting from blended elemental powders or mixtures of intermetallics (MA), or stoichiometric compounds (pre-alloyed intermetallics or even pure elements) (referred to as mechanical milling, MM). The number of amorphous phases synthesized by MA is too numerous to list here, but a complete list may be found in [9]. In fact, it has been reported that any alloy
can be made amorphous under the appropriate milling conditions. But, it should be noted that powder contamination during milling could be an important contributing factor in the formation of an amorphous phase by MA, at least in some cases.

Amorphous phases can form from blended elemental powders either directly or via the formation of an intermetallic phase. For example,

\[ mA + nB \rightarrow (A_mB_n)_{\text{amorphous}}. \]

or

\[ mA + nB \rightarrow (A_mB_n)_{\text{crystalline}} \rightarrow (A_mB_n)_{\text{amorphous}} \]

In some instances it has been reported that a solid solution forms in the initial stages of mixing of blended elemental powders, which on continued milling, becomes amorphous. In some other instances it has been reported that the sequence of phase formation is

blended elemental powder \(\rightarrow\) intermetallic

\(\rightarrow\) amorphous phase

Whether an intermetallic or a solid solution forms prior to amorphization depends on the relative free energies of the two competing phases. On the other hand, amorphization in ordered alloys seems to follow the sequence:

ordered phase \(\rightarrow\) disordered phase (loss of long-range order)

\(\rightarrow\) fine-grained (nanocrystalline) phase

\(\rightarrow\) amorphous phase

The times required for amorphization are dependent on the process variables, but they are usually shorter during MM than in MA, because alloying need not occur during MM. Thus, there appear to be many pathways for the formation of an amorphous phase by MA/MM.

The mechanism of amorphization by MA is not clearly understood, but it is now believed that a solid-state reaction similar to that observed in thin films occurs in mechanically alloyed powders. During MM, however, destabilization of the crystalline phase is thought to occur by the accumulation of structural defects such as vacancies, dislocations, grain boundaries, and anti-phase boundaries. The continuous decrease in grain size (and consequent increase in grain boundary area) and a lattice expansion would also contribute to the increase in free energy of the system. Additionally, the theories invoked for the formation of amorphous phases by RSP methods [2–5] (e.g., a minimum solute concentration required for the formation of an amorphous phase, significant size difference between the solvent and solute atoms, etc.) have also been used to explain the amorphization phenomenon by MA. But, in the case of formation of amorphous phases starting from ordered compounds, it was noted that two conditions should be satisfied, viz., that \(T_c\) is higher than \(T_m\) (where \(T_c\) is the critical ordering temperature and \(T_m\) the melting point) and that the ratio of \(\Delta E_{\text{mismatch}} / \Delta E_{\text{ordering}}\) (where \(\Delta E\) is the energy) should be high. Powder contamination is a matter of concern during milling and at least some of the reports on the formation of amorphous phases can be traced to the presence of substantial amounts of impurities. Avoiding the contamination resulted in the formation of only a crystalline phase [20].

The amorphous phases synthesized by MA and RSP techniques have been found to display similar radial distribution functions. The crystallization temperatures of the amorphous phases obtained by MA and RSP are again found to be similar, even though the activation energy for crystallization of RSP alloys is much higher than for MA alloys. But, it has been noted that the composition ranges of the amorphous phases are much wider in alloys produced by MA than in those obtained by RSP. Further, while RSP produces amorphous phases usually around deep eutectic compositions, the composition range in MA amorphous alloys is generally around the eutectic composition [9].

There has been lot of activity in recent times on the synthesis/processing of bulk amorphous alloys [21]. These alloys, characterized by a wide supercooled liquid region (large temperature difference between the crystallization and glass transition temperature), can be easily synthesized at extremely low solidification rates. Such alloys have also been synthesized by MA in multicomponent Zr and Mg-based alloys [22]. Applications for such bulk amorphous alloys include the 3 mm thick faceplate inserts for high-end golf club heads [23]. It is usually observed that it is easier to obtain a metastable phase by MA than by RSP. Additionally, synthesis of nanocrystalline materials is much easier by MA than by RSP.

6. Technological applications of mechanical alloying

6.1. Present applications

The most important application of mechanically alloyed products is in the form of ODS alloys. These alloys have complex compositions and it is difficult to process them through conventional ingot metallurgy (IM) methods.

Mechanically alloyed materials are strong both at room and elevated temperatures. The elevated temperature strength is derived from more than one mechanism. First, the uniform dispersion (with a spacing of \(~100\) nm) of very fine (5–50 nm) oxide particles (commonly used are Y2O3 and ThO2) which are stable at high temperatures, inhibit dislocation motion in the metal matrix, and increase the resistance of the alloy to creep deformation. Another function of the dispersoid particles is to inhibit the recovery and recrystallization processes, which allow a very stable grain size to be obtained. These large grains resist grain rotation during high-temperature deformation. The very homogeneous distribution of alloying elements during MA gives both the solid solution strengthened and precipitation-hardened alloys more stability at elevated temperatures and overall improvement in properties. INCO
produces annually about 350 t of commercial ODS alloys mainly based on nickel, iron, and aluminum. Typical compositions and applications of MA–ODS alloys are listed in Table 2. The reasons for the application of ODS alloys for these applications have been critically discussed in [13].

Apart from the ODS alloys, the technique of MA is also being commercially used to produce PVD (physical vapor deposition) targets for the electronic industry by Tosoh, USA (about 5 t per year). This is because it is easier to produce a chemically homogeneous product by MA rather than by IM methods. Yet another commercial application of mechanically alloyed products is in the use of MRE (Meal, Ready-to-Eat) heaters which have been extensively used during the Desert Storm Operation by the US in 1996. These heaters contain finely ground mechanically alloyed powders of Mg and Fe, which on contact with water, produce heat. This is a very good example of commercialization of a simple process. Recently, it has also been reported [24] that Zoz in Germany and Fukuda Metal Foil and Powder in Japan have joined together in producing about 600 kg per day (about 200 t per year) of mechanically alloyed material for paints and solders. The most important advantage of MA in all these applications is in the production of a highly homogeneous product without any segregation effects being present in them.

### 6.2. Potential applications

Apart from the real applications described above, there have been many suggested applications for MA materials. These include the production of FeSi$_2$, a thermoelectric material, which cannot be processed as a homogeneous bulk polycrystalline alloy by conventional IM methods due to the occurrence of eutectic and peritectoid reactions in the alloy system. MA offers an easy alternative for this. The thermo-e.m.f. of the MA material is 0.2 V against a value of 0.18 V for the powder produced from the ingot [25].

Similarly, it has been suggested that mechanically alloyed Mg-based materials can be used for hydrogen storage. Typical hydrogen storage materials should have a large hydrogen capacity, must have high rates of hydrogenation and dehydrogenation, reduced absorption temperatures, and should require very little or no activation treatments. All these (except for the storage capacity) can be achieved by having a small grain size of the material, easily achieved by MA. Even though pure Mg has a large hydrogen storage capacity (7.6 wt.% hydrogen as a hydride), it gets easily oxidized and so usually Mg alloys are preferred. Production of Mg–Ni alloys containing a small amount of Ni (1–2 at.%) with the Ni dispersed as discrete particles in the Mg matrix is much easier by MA than by IM methods due to the large difference in the melting points of the two metals and the high vapor pressure of magnesium. Mechanically alloyed Mg–1 at.% Ni alloy has a hydrogen storage capacity of 6.1 wt.%.

### 6.3. Mechanochemistry

Mechanochemistry is the term applied to the process in which chemical reactions and phase transformations take place due to the application of mechanical energy. This is a very old process, with the first publication dating back to 1894 [26]. The applications of mechanochemistry include exchange reactions, reduction/oxidation reactions, decomposition of compounds, and phase transformations. Of these, the exchange reactions have received a lot of attention in recent years, especially from Paul McCormick [16] in Australia, while the general phenomenon of mechanical activation of solids has been a popular research topic in the erstwhile USSR and eastern Europe [27].

The exchange reactions studied so far can be represented by an equation of the type:

\[ \text{MO} + \text{R} \rightarrow \text{M} + \text{RO} \]

where a metal oxide (MO) is reduced by a more reactive metal (reductant R) to the pure metal M. Metal chlorides and sulfides have also been reduced to pure metals this way. These reactions are characterized by a large negative free energy change and are thermodynamically feasible at room temperature. Solid-state reactions involve the formation of a product phase at the interfaces of the reactants. Further growth of the product phase involves diffusion of atoms of the reactant phase through the product phase, which constitutes a barrier layer preventing further diffusion. Hence high temperatures are required for the reaction to occur at reasonable speeds. MA can provide the means to increase the reaction kinetics due to the generation of clean and fresh surfaces (a result of fracturing), increased defect density,
and reduction of particle sizes. These mechanochemical reactions have been utilized to produce pure metals, alloys, and compounds at room temperature both in the laboratory and on a commercial scale.

7. Problems in mechanical alloying

In spite of the above-mentioned advantages and simplicity of MA, the technique suffers from some problems. These can be discussed under three groups, viz., powder contamination, limited science content, and limited applications.

7.1. Powder contamination

The contamination of powders during MA is a major concern. The small size of the powder particles, availability of large surface area, and formation of new surfaces during milling all contribute to the contamination of the powder. In addition, the milling conditions (grinding medium, grinding vessel, time of milling, intensity of milling, etc.) and the atmosphere under which the powder is being milled also contribute to the contamination level. In many cases, especially when reactive metals like titanium and zirconium are being milled, the levels of contamination are high and unacceptable. These levels increase with milling time and the highest levels reported are 44.8 at.% oxygen in an Al–6 at.% Ti powder, 26 at.% nitrogen in a Ti–50 at.% Al powder, and 60 at.% iron in a W–5 at.% Ni alloy powder [9]. Although several methods have been suggested to decrease/minimize the powder contamination level, the most effective ones seem to be (a) use of high-purity metals, (b) use of high-purity atmosphere, (c) use of balls and container of the same material that is being milled, (d) self-coating of the balls with the milled material, and (e) shortest milling times allowed.

7.2. Limited science content

As mentioned earlier, the science base for MA has been poor. Although it is known that the technique works and so is useful, one is not very clear how and why the technique works. This is because MA is a complex stochastic process and the number of variables involved is too many. Amongst others, these include the type of mill; size, shape, and weight of the grinding medium; velocity, angle and frequency of media impacts; ball-to-powder weight ratio; milling atmosphere; purity, size, shape, and hardness of the powder particles; milling time; milling temperature; and type and amount of the PCA. In spite of the complexity, some attempts have been made to model the process of MA and limited success has been achieved. For example, it has been possible to establish a relation between the experimentally observed phase formation and some of the process variables. But, it has not been possible to predict the final chemical constitution (type and description of phases) for a given set of milling conditions [28,29]. Some attempts have also been made to conduct deterministic MA experiments in which, instead of milling the powders in an attritor or a shaker mill, one uses thin sheets of metals or rolling of powders under controlled conditions, to evaluate the progress of alloying at each stage [30,31]. This has still not really gone far in enhancing our understanding of the MA process.

7.3. Limited applications

The industrial applications of MA have been few. The most significant applications seem to be about 350 t of ODS materials, 200 t of solder alloy, and 5 t of PVD target (Cr–V) alloys per year. Even though other potential applications have been suggested, many of them have not been industrial realities. The use of mechanochemical reactions in producing pure metals, alloys and compounds, dental filling alloys, catalyst materials, inorganic pigments, and fertilizers has
been known for some time now but needs to be exploited further. Identification of some niche applications for the MA products is likely to accelerate the rate of growth in this field.

8. Concluding remarks

MA is a simple and versatile technique capable of producing different types of metastable effects in a variety of alloy systems. The science base for this technique appears to be limited. The effects of MA are compared with those of RSP — another important non-equilibrium processing technique. The MA products find applications in various industries and these are summarized in Fig. 3. Powder contamination appears to be a serious problem during MA. Powder consolidation to produce bulk shapes results in loss of the metastable effects and thus it appears wise to use the MA powder in the as-produced condition rather than trying to consolidate it into bulk shapes. Consolidated products may be used if the alloys have a high tolerance to gaseous impurities. Search for new applications of MA products becomes easier if one can come up with novel designs of equipment capable of producing large quantities of material, preferably in a continuous mode.

References