MECHANICAL ALLOYING AND MILLING

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ABSTRACT

The search for new and advanced materials is the major preoccupation of metallurgists, ceramicists, and material scientists for the past several centuries. Significant improvements in mechanical, chemical, and physical properties have been achieved by alloying and through chemical modification and by subjection the materials to conventional thermal, mechanical, and thermo mechanical processing methods. Present paper deals with a brief review of the mechanical alloying questions focusing on the possible processes and apparatuses (mills).

INTRODUCTION

The rapid progress of technology has been constantly putting forward ever-increasing demands for materials that have higher temperatures and in more aggressive environments than is possible with the traditional and commercially available material. This has led to the design and development of advanced materials that are" stronger, stiffer, hotter, and lighter" than the existing materials. Synthesis and development of such materials has been facilitated by exploring the interrelation-ship among processing, structure. Properties and performance of materials the underpinning themes of materials science and engineering.

Mechanical alloying, the subject matter of this literature, is a powder processing technique that was developed in the mid 1960 by John Benjamin to produce nickel-based oxide dispersion strengthened (ODS) superalloys for gas turbine applications [1], also be used to synthesize a variety of both equilibrium and nonequilibrium material at room temperature and starting from blended elemental powders. This processing involves repeated cold welding, fracturing, and rewelding of powder particles in a high-energy ball milling resulting in the formation of alloy phases. This technique is also capable of synthesizing a variety of equilibrium and nonequilibrium alloy phase starting from prealloyed powders.

BASIS OF NONEQUILIBRIUM PROCESSING

The central underlying them to synthesize material in a nonequilibrium state is to "energize and quench" as proposed by Turnbull [2]. Processes such us as solid-state quenching, rapid solidification from the melt, irradiation, and condensation

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from vapor were considered by Turnbull to evaluate the departure from equilibrium. As depicted in (Fig. 2), the process of energization involves bringing the equilibrium crystalline material, with a Gibbs free energy G_0, into a highly nonequilibrium (metastable) state, with a free energy G_2. This could be achieved by some external dynamic forcing, e.g., through increase of temperature T (melting or evaporation), irradiation, application of pressure, or storing of mechanical energy E by plastic deformation [3, 4]. For example, during rapid solidification processing the starting solid material is melted and during vapor deposition the materials is vaporized. The energized material is then ”quenched” into a configurationally frozen state by methods such as rapid solidification processing or mechanical alloying, such that the resulting phase is in a highly metastable condition, having a free energy G_1. This phase could then be used as a precursor to obtain the desired chemical constitution (other less metastable) and/or microstructure (e.g., nanocrystalline) by subsequent heat treatment/processing.

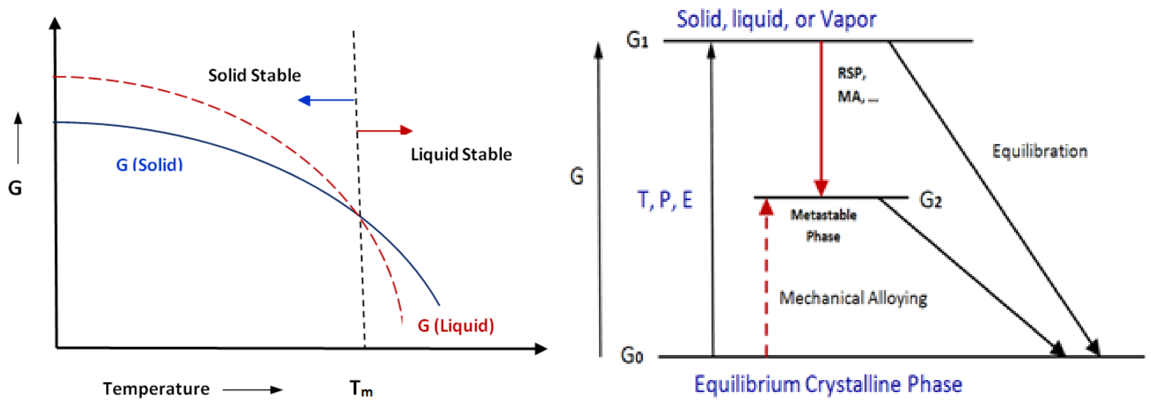


Fig. 1

The basic concept of “energize and quench” to synthesize nonequilibrium materials

Based on, C. Suryanarayana. Mechanical Alloying and Milling, Orlando, 2003, pp 2-3

PROCESSES

Mechanical milling/disordering

Mechanical alloying is the generic term for processing of metal powders in high mills. However, depending on the state of the starting powder mix and the processing steps involved, it describes the process when mixtures of powders (of different metals or alloys/compound) are milled together. Thus, if powders of pure metals A and B are milled together to produce a solid solution (either equilibrium or supersaturated), intermetallic, or amorphous phase, the process is referred to as MA. Material transfer is involved in this process to obtain a homogeneous alloy.

When powders of uniform composition, such as pure metals intermetallics, or prealloyed powders, are milled in a high mill, and material transfer is not required for homogenization, the process has been termed mechanical milling (MM). It may be noted that when a mixture of two intermetallics is processed, and then alloying occurs, this will be referred to as MA because material transfer is involved. However, if a pure metal or an intermetallic is processed only to reduce particle (or grain) size and increase the surface area, then this will be referred to as MM because material transfer is not involved [5].

Reaction milling (RM)

Reaction milling (RM), pioneered by Jangg et al, is the AM process accompanied by a solid-state reaction. In this process the powder is milled without the aid of any process control agent to produce fine dispersions of oxides and carbides in aluminum [6]. The dispersion of carbides is achieved by adding lamp black or graphite during milling of aluminum. Adjusting the oxygen content via close control of the milling atmosphere (oxygen, argon, nitrogen,air, etc.) results in production of the oxides.

Cryomilling

The milling operation is carried out cryogenic (very low) temperatures and/or milling of materials is done in a cryogenic medium such as liquid nitrogen.
In this process, the vessel is cooled by a continuous flow of liquid nitrogen through the “water cooling” jacket of the mill. In addition, or alternatively, liquid nitrogen could be introduced into the milling chamber itself throughout the run. After completion of the milling run, the power is removed from the mill in the form of a slurry and transferred to a glove box containing dry argon. When the liquid nitrogen is allowed to evaporate, a residue of the milled powder is left behind [7].

Rod milling

Rod milling hat was is the technique developed in Japan [8], essentially to reduce powder contamination during the processing stage. In this process, the grinding medium is in the form of rods rather than spherical balls. In a conventional ball mill, impact forces scratch the surface of the milling media and the debris from the milling media contaminates the being milled. On the other hand, if shear force predominate, they are more effective in kneading the powder mixtures and the resulting powder is much less contaminated. To achieve this minimized contamination, the balls were replaced long rods in the rod mill because long rods rotating in a cylindrical vial predominantly exert shear forces on the material.

Mechanically activation annealing

Mechanically activation annealing (M2A) is a process that combines short MA duration with a low-temperature isothermal annealing. The combination of these two steps has been found to be effective in producing different refractory materials such as silicides based on niobium, molybdenum, etc [9]. For example, MA of molybdenum and silicon powders for 1-2 h in a planetary ball mill followed by a 2 to 24 h annealing at 800˚C produced the MoSi2 phase. A consequence of this method is that optimization of the M2A process could lead to a situation in which isothermal annealing can be carried out inside the milling container to avoid air contamination of the end product.

Double mechanical alloying

Double mechanical alloying (dMA) involves two stages of milling. In the first stage the constituent elemental powder size are refined and uniformly distributed as an intimate mixture. This mixture is then subjected to a heat treatment at high temperature during which intermetallic phase is formed. The size of the intermetallic formed ranges forms less than 1 μm to a few micrometers. During the second stage, the heat-treated powder is milled again to refine the powder size of the intermetallic phases and reduce the grain size of the matrix [10].

Mechanically activated self-propagating high- temperature synthesis

Another recently coined is mechanically activated self-propagating high-temperature synthesis (MASHS), which is based on a combination of MA and self-propagation high-temperature synthesis (SHS) processes. SHS is a well-know method to produce advanced material as a practical alternative to the conventional methods. SHS offers advantage with respect to the process economics and process simplicity. In the typical SHS reaction, the mixed reactant powder are pressed into a pellet of certain green density and subsequently ignited to the ignition temperature. In the MASHS process the powder mixture is mechanically alloyed to produce a structure and then the SHS reaction is initiated by pressing the powder into a pellet and igniting it in furnace [11, 12].

Oxidation-attrition milling-reduction

Oxidation-attrition milling-reduction (OMR) is another term that has been used recently in the literature. In this method, the commercially available powders (of micrometer size) are oxidized at appropriate temperature to produce brittle oxide powders. These powders are subjected to attrition milling to obtain nanoscale oxide powders. Which are subsequently reduced to metallic powders with nanometer grain size. This method should be particularly useful to produce nanocrystalline powders of ductile metals and materials [13]. It’s necessary to ensure that the oxides of such materials are brittle and that they can also be easily reduced to pure metals.

Mechanochemical processing

Mechanochemical processing (MCP) or mechanochemical synthesis is the term applied to powder processing in which chemical reactions and phase transformations take place during milling due to application of chemical energy [13, 14]. An important feature of the process is the plastic deformation and chemical processes occur almost simultaneously. The mechanochemical reactions could result in the synthesis of novel materials, reduction/oxidation processes, exchange reaction, decomposition of compound, and phase transformations in both organic and inorganic solids. The materials produced in this way have already found application areas such as hydrogen storage materials, gas absorbers, fertilizer, and this technique has become a large effort in the general field of mechanical alloying and milling.

RAW MATERIAL

The raw materials used for (MA) are the widely available commercially pure powders that have particle size in the range of 1-200 μm. However, the powder particle size is not very critical, except that it should be smaller than the grinding ball size, this is because the powder particle size decreases exponentially with milling time and reaches a small value of a few micrometers only after a short period (typically a few minutes) of milling. The raw powders fall into the broad categories of pure metals, master alloys, prealloyed powders, and refractory compounds. The oxygen content of the commercially pure metal powders ranges from 0.05 to 2 wt% therefore, if one is interested in studying phase transformations in the milled powders, it is necessary to choose reasonably high-purity powders for the investigations. This is important because most commonly the nature and amount of impurities in the system decides the type of formation [15].

EQUIPMENT FOR MECHANICAL ALLOYING

Different types of high-energy milling equipment are used to produce mechanically alloyed/milled powder. They differ in their design, capacity, efficiency of milling, and additional arrangement for cooling, heating, and so forth.

Spex Shaker Mills

Shaker mills, such as SPEX mills, which mill about 10-20 g of the powder at a time, are most commonly used for laboratory investigation and for alloy screening purposes. These mills are manufactured by SPEX CerPrep. The common version of the mill has one vial, containing the powder sample and grinding balls, secured in the clamp and swung energetically back and forth several thousand times a minute. The back-and-forth shaking motion is combined with lateral movements of the ends of the vial, so that the vial appears to be describing a figure of 8 or infinity symbol as it moves. With each swing of the vial the balls impact against the sample and the end vial, both milling and mixing the sample. Because of the amplitude (about 50 mm) and speed (about 1200 rpm) of the clamp motion, the ban velocities are high (on the order of 5 m/s) and consequently the force of the ball’s impact is unusually great. Therefore, these mills can be considered as high-energy variety [16].

Planetary Ball Mills

Another popular mill for conducting MA experiments is the ball mill (referred to as Pulverisette) in which a few hundred grams of the powder can be milled at the same time. These are manufactured by Fritsch Gmbh. The planetary ball mill owes its name to the planet-like movement of its vials. These are arranged on a rotating disk, and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk both act on the vial contents, consisting of the material to be ground the grinding balls. Since the vial and the supporting disk rotate in opposite direction, the centrifugal forces alternately act in like and opposite direction [17].

Attritor Mills

A conventional ball mill consists of a rotating horizontal drum half-filled with small steel balls. As the drum rotates the balls drop on the metal powder that is being ground; the rate of grinding increases with the speed of the rotation. At high speed, however, the centrifugal force acting on the steel balls exceeds the force of gravity, and the balls are pinned to the wall of the drum. At this point the grinding acting stops [18]. An attritor (a ball mill capable of generating higher energies) consists of a vertical drum containing a series of impellers. The impellers energize the ball charge, the dry particles are subjected to various forces such as impact, rotation, tumbling, and shear. This causes powder size reduction because of the collisions between balls and container wall, and between balls, agitator shaft, and impellers. Therefore, micrometer-rang fine powders can be easily produced. Attritors are the mills in which large quantities of the powder (from few pounds to about 100 Ib). The velocity of the grinding medium in the attritors is much lower (about 0.5 m/s) than in the planetary or SPEX mills, and consequently the energy of milling in the attritores is low.

PROCESS AND OPERATING PARAMETERS

Selection of grinding medium

Proper selection of the nature, size distribution of the grinding medium is an important step in achieving efficient milling of powder particles. The selection depends on the several factors, some of which are interrelated.

Specific gravity

In general, high-density media give better result. This is because the kinetic energy of the balls is higher and consequently higher amount of energy are transferred to the milled powder. The media should be denser than the powder being ground. Also, highly viscous material require with a higher density to prevent floating.

Initial feed size

Since smaller media cannot break up large particles, the grinding media should be large than the powder particle size. A mixture of different size of the grinding balls helps to improve the efficiency of the attritor.

Final particles size

The grinding medium should be smaller when very fine particles are desired; the smaller the grinding medium, the smaller is the final particle size.

Hardness

The harder the media the lesser is the powder contamination, and consequently the medium lasts longer. However, the medium is brittle, then edges of the medium may be chipped off and get incorporated into the milled powder and contaminate it.

Discoloration

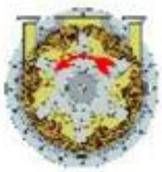
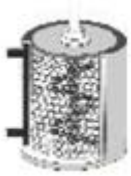
Certain media result in color development and are, therefore, not suitable in the production of some materials such as white coatings.

Cost

Media that are two to three times more expensive may last considerably longer. These may be well worth the extra cost over the long run.

Table 1

Compares most corresponding devices that are in use for high kinetic processing (HKP) with respect to size and maximal velocity of the milling tools

device	Simoloyer®	Planetary Ball Mill	Attritor®	Drum(ball)mill
max. diameter [m]	0.9	0.2	1	3
max. total volume [l]	400	8	1000	20000
max. rel. velocity [m/s]	14	5	4.5-5.1	<5
graphic (cross section)				

Source: Reactive Dry-Milling for Environmental Protection, Simo40-paper.DOC, page 1/12

CONCLUSIONS

1. One of the greatest advantages of (MA) is in the synthesis of novel alloys that are either impossible or difficult to prepare by any other technique, this because MA is a completely solid-state processing technique and limitations imposed by phase diagrams does not apply here.
2. MA is a complex process that involves many variables, and many of them are interdependent. Therefore, modelling of the MA process is difficult, one has to go much farther in developing models that can reach the final goal of predicting the nature of phase produced under a given set of milling conditions.
3. There is so much more to learn about the “science” of MA that the future of MA is assured for several years to come.

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