High Energy Ball Mill Processing

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Abstract: The technique named mechanical alloying has been historically used for designating many different process routes, in spite of involving various kinds of materials and purposes. The aim of this work is to make a review of this technique, with special emphasis on the differences between those routes. Based on that, a suggestion for the classification of the various routes is presented. The high-energy ball mill processing can be divided in three main groups according to the mechanisms involved and/or the purpose envisaged: Mechanophysical conditioning, Mechanochemical synthesis and mix processes. In the first group, dissimilar or similar materials can be processed. In the second group, the materials can be synthesized with or without bonding changes during the process. The third one is a combination of the two first processes. Some examples are also presented.

Introduction

The High-Energy Ball Mill Processing have been used in the last 30 years for processing several materials, including metallic powder alloys, composites, intermetallics and ceramics which can result in nanocrystalline or amorphous materials. Its commercial use appears in the middle of the sixties after Benjamin and coworkers [1] produced superalloy powders reinforced by oxide dispersion using a technique denominated "milling/mixing". The term "mechanical alloying" appeared only at the end of the same decade; it was set down by Ewan C. MacQueen and patented by International Nickel Company (INCO™). According to Benjamin, mechanical alloying is a high-energy milling process, done dry, for producing metal-matrix composite powders with controlled microstructure. It o ccurs b y s uccessive w elding a nd fracture o f p articles o f a mixture containing metallic and non-metallic powders under high energetic impact of the mill balls. Although limited this definition had been well suited for usage of this technique at that time. Nowadays it seems too restrict, due to the fact that a high number of materials can be processed by high-energy mills. This former definition is not also adapted because the use of dry processing conflicts with examples of moist process of some materials [2].

A wider definition w as proposed by Schwarz [3], for whom mechanical alloying is a high-energy ball mill technique employed to prepare powder alloys with unequal microstructure. On the other hand, for Gachon [4], in a definition based on processing equipments, mechanical alloying is any process that produces the combination or alloying of two or more chemical elements, applying mechanical methods for deforming (milling, rolling and pressing), that direct or indirect produces the desired alloy. The last two definitions would be well suited if the mechanical alloying was restricted to metallic alloys production. However, this term has been historically applied to several different processes, not only concerning to the processed materials, but specially to the active mechanism in each situation.

·   This paper presents a short review of the High Energy Ball Mill Processing; hereafter referred to as **HEBMP**, and purposes a classification taking into account the different actuating

mechanisms in the processes.

HEBMP – A Flexible Technique

The main mechanism of the HEBMP is the competition between the generation of crystalline defects, due to the plastic deformation, and its thermally activated recover.

This technique was employed commercially as a forerunner production process to obtain iron-based superalloys, as well as powders for deposition on catalyzers.

The HEBMP can be done using different types of mills. The vibrator and planetary mills have been used for processing small amounts of materials (less than 100g) during times of the order of minutes. The attritor mills, horizontal and vertical, can process higher quantities of powders (between 100g and 10Kg) in some hours. When the goal is the production of amounts of the order of tones, such as in commercial production, mill diameter having orders of meters and even days of processing time have been required [3].

The high energy ball mill can impose to the balls, velocities of the magnitude of meters per second. It h as b een s tated t hat t he i mpact o f t hese b alls a t 3 .6m/s c ould c orrespond t o a kinetic energy of about 30mJ and a powder temperature increase of 250°C.

Mechanical Dispersion

The HEBMP have been used for producing metal-matrix composites with oxide dispersion (ODS composites). Generally, these composites have only 1-2vol.% of oxide particles [1]. The first usage in order to produce MMC's was the mechanical dispersion of oxides in nickel superalloys [5], in which the particles distribution were fine and homogeneous, providing efficient pinning points to the grain boundaries and to dislocations and resulting in a general improvement of mechanical properties, such as toughness, ultimate tensile strength and wear resistance.

Interface Formation

The interface formation is also an important characteristic of this process that can reach values of about $600m^2/cm^3$ due to the decrease of the mean particle size and the formation of smaller grain sizes. Thus, due to the large fraction of atoms segregated at the grain boundaries, this technique can be used to increase the solubility of some elements; to obtain nanocrystals, and transform some crystalline powders in amorphous [6-8].

Table 1- Comparative values of elements solubility (%at.) in materials produced by HEBMP and by simple solidification [9].

Solid Solution	Maximum Solubility (room temperature)	Solubility after HEBMP
W in Ni	11	21
Mg in Ti	< 0.2	6
Hg in Cu	< 1	70
Al in Ti	12	75
Sn in Nb	0	25
Sn in Fe	0	66
Al in Pd	15	50
Cu in Al	0	33
Co in B	0	50
Ga in As	0	50

An example of supersaturated solid solution produced by HEBMP can be seen in the Table 1. It has been assumed that nanocrystalline structures obtained are mainly responsible for the solubility increase in the so processed materials [9].

Fetch and coworkers [6], studying the production of pure nanocrystalline metals by milling, obtained fcc metals (Fe, Cr, Nb, W) and hc metals (Zr, Hf, Co, Ru) with grain sizes of the order of 9nm and 13nm respectively. Pure metals, in general, can not be transformed into amorphous materials, exception made for some transition elements (e.g.: Ni, Co, Cr, Fe, Mn) that can be amorphous when deposited from vapor over substrates at very low temperatures (e.g. 4.2 K).

Koch [10] asserts that only intermetallic compounds having very narrow compositions, in other words, having its occurrence with small amounts of a second metal, can become amorphous by milling, otherwise it is quite impossible.

Microstructural Refining and Alloys Synthesis (Ductile Metals)

Using elemental powders which similar chemical composition and structure, the resulting mixture obtained by HEBMP are, in general, alloys with very fine microstructure.

The alloy formation process of ductile metals using HEBMP starts with a multilayer structure, where the composing metal powders are arranged in alternate layers. This layers tend to become continuously thinner as the plastic deformation increases until a point where its thickness allows the interdiffusion process [11,12] This interdiffusion between layers is assisted by the increase of temperature and the increase of crystalline defects induced by the milling action.

An example is the binary system Ni-Cu where the alloys present complete solid solution. Using elemental powders to produce these alloys by HEBMP, one can verify the alloying reaction advance taking mixture samples periodically during the process and analyze it by x-ray diffraction, as exemplified in Fig. 1 [13].
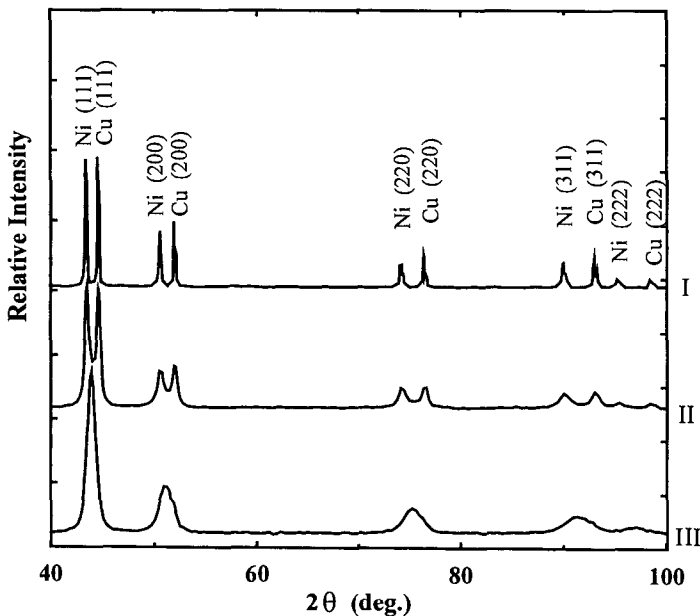

Fig. 1 – X-rays diffraction patterns of: (I) elemental powder mixture, (II) powder processed for 5h with wax and (III) powder processed for 5h without wax [13].

Intermetallic and Ceramic Compounds

The HEBMP allows solid state reactions from the mixing of elemental powders, resulting in intermetallic compounds such as aluminates, silicides, carbides, borates and nitrides.

Several systems have been studied with a special attention to the ones which formation enthalpies are extremely negatives. However, it is possible the production of compounds with positive enthalpy of formation, such as Ni_3C ($\Delta H = 43KJ/mol$ between $273K < T < 2000K$), Fe_3C ($\Delta H = 25KJ/mol$) [14]. Its occurrence is influenced by the high density of defects, which can have significant influence on the free energy of different phases, as well as on the kinetics of solid state reactions.

The main mechanism acting during these compounds formation is a self-heat sustained reaction where the mechanical impacts contribute to that, delivering the energy related to the heat of formation. In such case, when the heat generated by the system exceeds the dissipation heat rate, this exceeding energy could be used as an activation energy for the reaction that can propagate through the system. Such mechanism requires a nucleation time because it depends on the particle size diminution and on increasing contact between the reagents.

Some systems do not present the formation of these compounds by mechanical action, due to the insufficient transference of energy to the powder and then needing a posterior heating. The energy transfer by sphere collisions depends on the operational parameters, e.g. balls diameter, angular speed and ball/powder mass ratio [15]. For instance, in order to obtain the intermetallic Nb_3Al from a powder mixture containing Al-75%atNb, one have to heat during 2 hours at 825°C a powder already mixed by 5 hours via HEBMP. On the other hand, the intermetallic compound $NbAl_3$, having formation enthalpy more negative than the previous one, can be obtained directly from the HEBMP after 15 hours processing [16].

Synthesis of Metals and Alloys by Oxide-Reduction Reactions

The synthesis of metals can do by reduction of its metals oxides by other metals under the main condition that its formation enthalpy present intense negative values. For example, the reduction of cooper oxide by other metals can be done according to Eq. 1, where Z can be Al, Ca, Mg, Ti, Mg, Fe or Ni [17].

$$Cu_xO + yZ = xCu + Z_yO \qquad ....Eq. 1$$
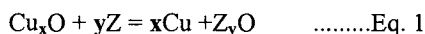
The β-brass production by HEBMP of a mixture of CuO, ZnO and Ca is one of the various examples of the process potentiality. The resulting products (oxides and metals) are generally separated by chemical processes.

"In situ" Composite Formation

α-Al_2O_3-M nanocrystalline composites, where M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, W, were obtained by Matteazzi [18] by mixing oxide metal M_xO_y and Al via HEBMP. There is also the possibility of the production of α-Al_2O_3-M-$M_{ceramic}$ nanocomposites by a two stage processing: metallic oxide reduction by aluminum and subsequent synthesis of the metallic carbide by carbon addition.

A commercial process that uses the same technique to the "in situ" formation of aluminum base composites is known as DISPAL™, where additions of carbon and oxygen, in the ranges of 0 to 3%wt. and 0.4 to 2.5 wt.%, respectively, produce dispersions of nanometric particles (18 to 25 nm) of Al_4C_3 and aluminum oxide in a matrix containing subgrain sizes between 0.6 and 1.5 μm.

After thermomechanical processing (e.g. extrusion) these composites present excellent microstructural stability even at relatively high temperatures. For instance, depending on the dispersion content at 400°C, such alloys present superior creep resistance, elongation between 3 and 19% and yield strength of 74 to 156MPa [19].

Another example is the MMC Al-20%vol.SiC$_p$ obtained by HEBMP for 2 hours and consolidated by hot extrusion. This composite presents a microstructure free of SiC clusters, with smaller SiC particles and significant higher yield stress and ultimate tensile stress, maintaining the same order of elongation, when compared to the composite produced by simple mixture [20].

The "in situ" production of composites does not occur only in the solid state. Calka [12], using aluminum and ammonia in a planetary ball mill, provided with an special magnetic mill control, obtained a nanocrystalline composite Al-AlN, containing 88wt. %AlN. Wu et alli [21], obtained the compounds Ti(C,N), Ti(O,N) and Ti(O,C,N) by HEBMP after 48 hours, starting from a mixture of Ti and C powders under atmospheres of N_2, NH_3 and even air.

Final Considerations

From the above discussion it is proposed a classification based on different fabrication methods as presented in Fig. 2.
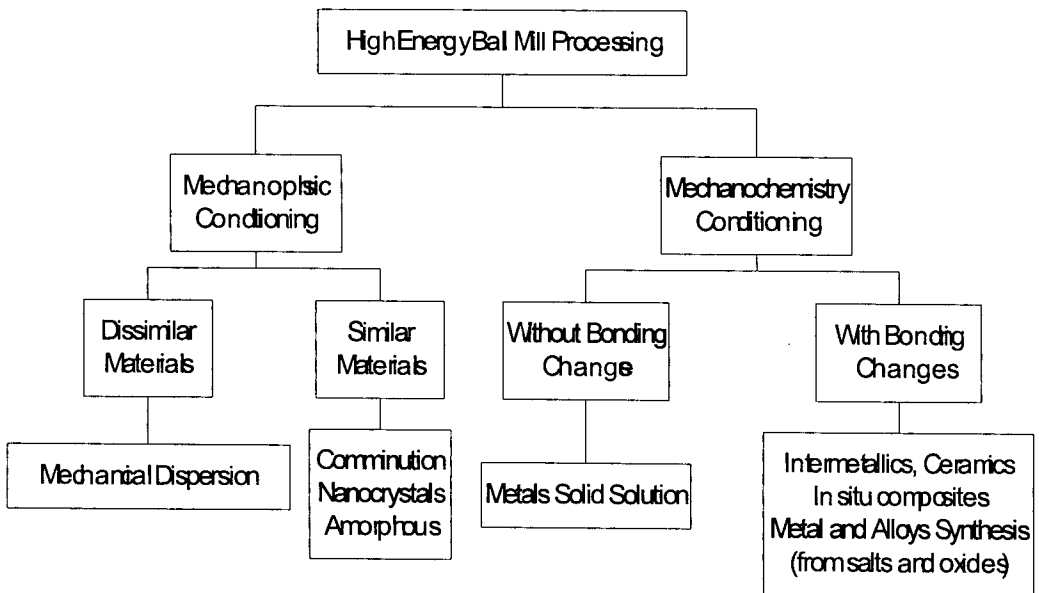

Fig. 2 – Proposition of HEBMP classification.

The HEBMP can be basically classified in three main groups:
-Mechanophisic conditioning;
-Mechanochemistry conditioning;
-Mix processes.

In the mechanophisic conditioning there is no change concerning the chemical bonding types, occurring only changes of the elements or an intimate mechanical contact between the matrix

and the ceramic phase introduced as dispersion particles. The main characteristic is the refined microstructure, d ue to a dispersion of one ceramic phase in a metallic matrix, for example, or a significant increase of interfacial area, both of them improving the possibility of nanocrystalline or amorphous materials formation. The energy stored in these materials, originated from the milling action, can be released by heating without the formation of new phases.

In the mechanochemistry synthesis there are changes concerning the types of chemical bonding, which can occur by the change of the next neighbor atoms and/or by a true change of the type of bonding. When some metallic bonds are broken and new ones are formed, a substitutional solid solution is obtained. Also in this group there is the compound formation, where a metallic bond is replaced by a covalent or ionic bond, as occur in some intermetallic or ceramic compounds.

Finally, in the mix processes both previous processes can obtain the final product; for example, an "in situ" composite can be obtained from the mixture of an oxide, e.g. Fe_2O_3, and a reducing agent, e.g. Al, presenting a nanometric dispersion of aluminum oxide particles in an iron matrix.

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