Materials developed by mechanical alloying and melt spinning

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Abstract – *Materials science is a multidisciplinary research topic related to the development of physics and technology. Mechanical alloying of ribbon flakes is a two steps route to develop advanced materials. In this work, a Fe based alloy was obtained using three pathways: mechanical alloying, melt-spinning and mechanical alloying of previously melt-spun samples. Processing conditions allow us to obtain amorphous or nanocrystalline structures. Furthermore, a bibliographic revision of mechanical alloying is here presented.* **Copyright © 2007 Praise Worthy Prize S.r.l. - All rights reserved.**

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I. Introduction

One of the main fields concerning physics research is materials science. Materials science is a multidisciplinary research discipline involving physics, engineers and chemists. The history of the humanity is closely associated to the development of new materials. In fact, materials with a metastable structure (amorphous, nanocrystalline, extended solid solution) present interesting technological applications. Mechanical alloying (MA) and rapid solidification (RS) are two important routes to obtain amorphous or nanocrystalline alloys. The field of rapid solidification ($\sim 10^6$ K/s) of alloys from the liquid state started with Pol Duwez and coworkers successful rapid quenching experiments in 1960 [1]. In these experiments, an extended crystalline solid solution and an amorphous phase, the metallic glass $Au_{80}Si_{20}$, were obtained. One of the typical methods to develop alloys by rapid solidification is the melt-spinning (MS) technique. It is known that Fe-based alloys prepared by rapid solidification techniques in ribbon form can exhibit superior soft magnetic properties [2]. Nevertheless, ribbons not attain a more important level of applicability due to various shortcomings: the ribbon form, the limited alloy compositions (near deep eutectics) and the usually brittle behavior [3]. Recently, mechanical alloying of ribbons is applied as an alternative route to obtain powdered materials [4]-[5]. The MA of bulk amorphous or nanocrystalline metallic glasses may be a two-step procedure in the powder metallurgy industry. In principle, the MA alloys may be consolidated to any desired shape and form.

In this work, we present: a) an historical perspective and analysis of the MA technique and b) a comparison of three routes (MA, MS and MS+MA) to develop a Fe based alloy.

II. Mechanical alloying

II.1. Historical perspective

Mechanical alloying is a processing technique that allows alloys production starting from mixtures of elemental and/or compounds powders (flakes). During MA, a lamellar structure arises in the powders due to the cold welding and fracture of the particles. The MA process produces a refinement of the microstructure and an intimate mixing of the constituents that favors the formation of a metastable structure. MA was developed around 1966 by John Benjamin and coworkers at the Paul D. Merica Research Laboratory of the International Nickel Company (INCO) to produce a material combining oxide dispersion strengthening with gamma prime precipitation hardening in a nickel-based superalloy for gas turbine applications [6]-[7]. Initially, the process was referred to as milling or mixing. The first scientific article was "Dispersion strengthened superalloys by mechanical alloying" [8]. Nevertheless, this process was known 40 years earlier from the work of Hoyt, who reported coating of tungsten carbide, WC, with Co by ball milling. The term "mechanical alloying" was introduced by INCO in a patent [9].

MA has been utilized in several areas of materials processing and applied to obtain different materials, sometimes combined with consolidation techniques to develop bulk materials: oxide dispersion strengthened materials [10], intermetallics [11], nanomaterials [12], composites [13], ceramics [14], polymers [15], amorphous [16], hydrogen storage [17] and extended solid solutions [18]. As an example, figure 1 shows the solubility limits of several elements into Fe bcc structure at the equilibrium state and after MA process.

The recent status of MA has been reviewed in several works [9], [19]-[20]. The MA and related topics literature available up to 2007 has been collected. Figure 2 presents the growth of publications in the field of MA and related topics during the period 1990-2007 [21]. The article amount increases a factor three.
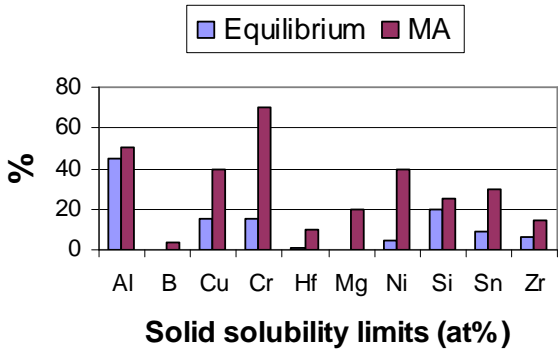

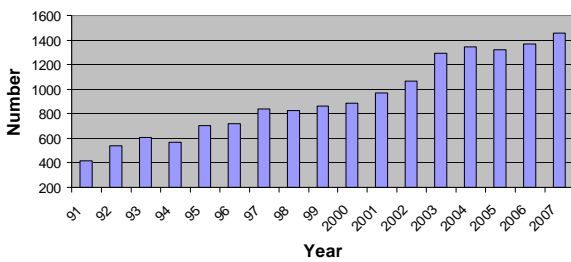Fig. 1. Solid solubility limits of several elements in Fe [22-30].

Fig. 2. Amount of publications concerning materials developed by mechanical alloying.

II.2. Milling parameters

MA is a complex process which depends on many physical, chemical and geometrical factors. Those parameters affect the milling efficiency and the energy transfer. A detailed list must include the geometric and dynamic parameters of mill design, the character of motion of milling media, the physical and mechanical characteristics of milling media, the characteristics of processed substances, the mass ratio of milling balls to powder, the milling time, the temperature of the vial, the milling atmosphere, the selection of process control agents or the filling factor of the vial. The milling time (BPR) and the ball-to powder mass ratio (BPR) are the parameters usually given to characterize an experimental MA setup. It should be pointed that the use of different milling conditions and/or ball mills results in different reaction pathways. The milling intensity is a measure of the milling energy, which is directly proportional to the powder generated in the milling process. The modification of the milling conditions will strongly affect the way by which energy is transferred to the milled powder and, hence, the nature of final alloys. As

an example, using other milling device, and milling alloys of similar composition can be obtained a nanocrystalline or an amorphous phase as main phase [31]. Figure 3 shows the evolution of the crystalline size of a Fe based alloy using different milling intensity. A higher value of the rotation speed (here given in r.p.m.) correspond to a higher milling intensity.

It is necessary to consolidate the nanocrystalline or amorphous materials developed by melt spinning to obtain bulk alloys for practical applications in the powder metallurgy or magnetic sectors. For it, an option is to mill ribbon flakes to produce a material with a like-powdered form. In this moment, consolidation of amorphous or nanocrystalline powders into bulk, full density compacts while retaining final nanoscale grain size is obviously a major challenge [32]. If the original material is amorphous, it can be easier to obtain a nanocrystalline material after consolidation. As an example, bulk amorphous and nanocrystalline FeZrNbB alloys were prepared by consolidating amorphous powders crushed from as-quenched ribbons [33].
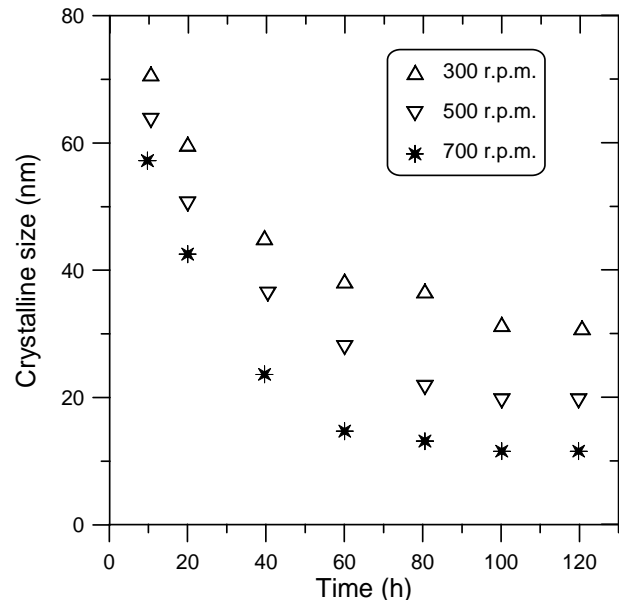

Fig. 3. Crystalline size versus milling time for different milling intensities.

As increasing the milling time, the ribbon pieces were fractured, and the final form corresponds to a powdered-like material. Figure 4 shows the percentage of alloy in ribbon form using a sieving method as a function of milling time. Results show a general diminution of the necessary milling time, considered as the lowest limit time at which powdered particles represents ≥ 95 wt.%, with the increase of the rotation speed. As expected, when increasing the total energy involved in the ribbon fracture, the limit time decreases. A lower milling time favors the technological reliability of this combined route. For ribbon flakes milled at 200, 300 and 400 r.p.m. the times were 24 h, 24 h and 8h, respectively. In previous works [34], only slight

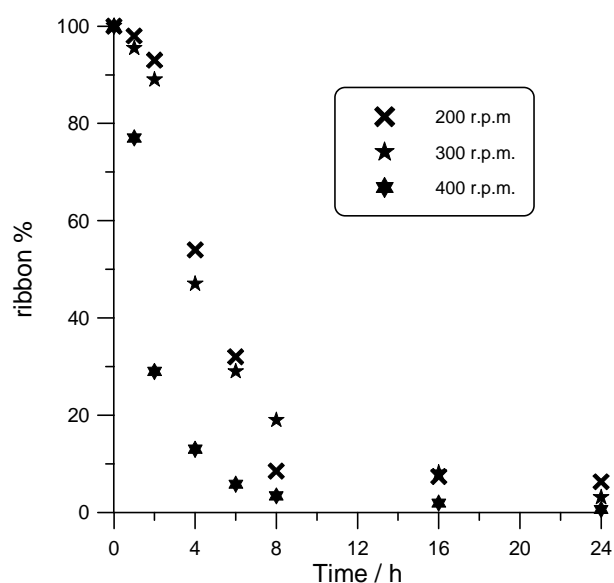differences due to the ball-to-powder weight ratio were found.

Fig. 4. Percentage of alloy in ribbon form as a function of milling time.

III.   Materials and Methods

The composition analyzed in this article is $Fe_{70}Ni_{10}B_{20}$. The alloy was produced directly by milling (MA alloy), by melt spinning (MS alloy) or by the combined route (MS + MA alloy). Milling (MA alloy) was performed in a planetary ball-mill (Fritsch Pulversitte P7) starting from pure element and compound powders (99.7%-purity Fe, with a particle size under 10 μm; 99.8%-purity Ni, with a particle size under 50 μm; and 99.6%-purity B, with a particle size of 50 μm). Powder was loaded into a cylindrical Cr-Ni stainless-steel vial together with balls of the same material in an argon atmosphere. The ball-to-powder ratio was 5:1. The milling process was performed at a speed of 700 r.p.m. at different milling times until 100 hours.

The Fe-Ni based alloy was also produced by melt-spinning (MS alloy). The precursors used were pressed powders of elemental Fe, Ni and B. The ribbon has a size of about 0.1 cm wide and 20 μm thick. The molten alloy was quenched on the surface of a rapidly spinning (about 30 m/s) Cu wheel. The working atmosphere was inert, Ar. The ribbons ulterior milling was performed at 400 rpm during 10 hours (MS + MA alloy). Ribbons were cut into pieces about 0.5 cm large. The size reduction of the ribbons was followed by a sieving method after different milling times, using a 50 μm sieve to control the percentage of original ribbon considered as well fractured or powdered-like.

The sample thermal characterization was carried out by differential scanning calorimetry (DSC) under an argon atmosphere in a Mettler-Toledo DSC30 device. The morphology and composition study was performed by scanning electron microscopy (SEM) in a Zeiss DSM960 A equipment coupled with energy dispersive X-ray microanalysis (EDX). The X-ray diffraction (XRD) patterns were carried out in Siemens D-500 equipment and the analysis of the patterns was performed by Rietveld refinement using MAUD software.

IV.   Results and discussion

Low contamination from the milling tools (< 1.35 at.%) was found by ICP and EDX in the milled alloys (MA and MS + MA). Furthermore, oxygen was detected probably due to the large surface area and the high reactivity of the fine particles. Likewise, MS alloy shows the same nominal composition after and before melt-spinning production. Similar results are reported in other Fe based alloys [35]. Figure 5 shows the X-ray diffraction patterns of the alloy as quenched, the alloy as milled and the as milled ribbon. MS alloy show the typical halos of an amorphous structure. The same structure remains after flakes milling. The microstructure of MA alloy after 100 h milling is nanocrystalline, a bcc Fe solid solution, with a lattice parameter of 0.2865(3) nm and a crystallite size of 12.4 nm.
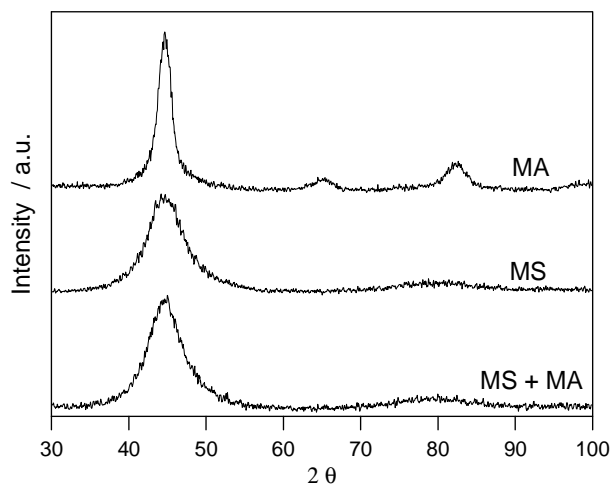

Fig. 5. XRD spectra corresponding to: as milled powders (MA), as quenched (MS) and as milled flakes (MS + MA).

DSC measurements performed support the existence of a metastable structure as determined by XRD. Figure 6 shows DSC scans performed at a heating rate of 10 K/min, for quenched and milled samples. One or two main exothermic processes were detected that are related to the structural relaxation (MA and MS + MA) and crystallization (all samples). The first process is shallow and broad. It is typical for a relaxation process and starts at about 425 K. A crystallization peak starts at high temperature. The crystallization process in the

rapidly solidified samples produces a very sharp exothermic peak. Both, the onset temperature of the main peak and the crystallization enthalpy are comparatively higher for rapidly solidified sample than for samples MA, as expected since the last ones are powders with some remains of crystallinity.
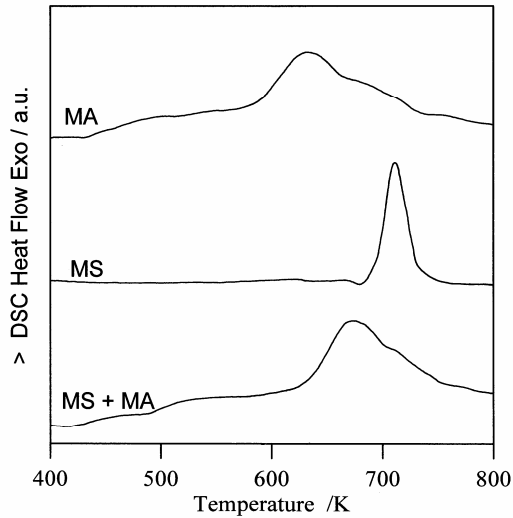

Fig. 6. DSC scans at 10 K/min of: as milled powders (MA), as quenched (MS) and as milled flakes (MS + MA).
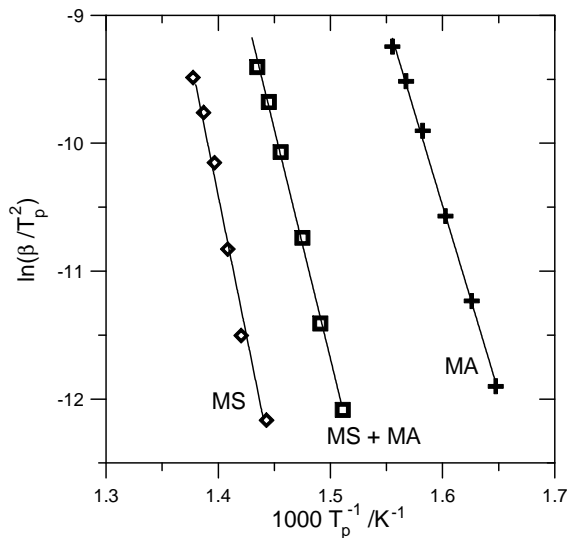

Fig. 7. Kissinger plots to determine the apparent activation energy of the crystallization process.

The apparent activation energies of the crystallization process processes were calculated by the Kissinger's shift peak method [36]. For it, the samples were heated at different rates: β = 2.5-5-10-20-40 K min^{-1}. The value of the apparent activation energy, E, of the crystallization process are 241 $\pm$ 21, 361 $\pm$ 32 and 298 $\pm$ 23 kJ/mol for alloys MA, MS and MS + MA respectively. The values obtained in other alloys were between 230 and 380 K/mol in MA samples, and between 320 and 690 K/mol in MS samples [37]-[38].

The apparent activation energy of the MA alloyed powders seems reasonable to be associated with a grain growth process in the nanocrystalline MA alloy and to nucleation plus crystalline growth in the amorphous alloy obtained by MS or by MS + MA.

The combination of higher activation energy and crystallization temperature is associated to a higher thermal stability. In this work, the alloy produced by MA is nanocrystalline and the alloys produced by MS are amorphous. It is reasonable to expect that structure and properties could be different when using MA, MS or MA + MS methods [39]. Nevertheless, it is also possible to develop amorphous MA alloys by modifying milling conditions [40]. In this moment, it is possible to design advanced materials for specific applications by the combination method of melt-spinning and mechanical alloying [41].

V. Conclusions

In this work, we perform a brief bibliographic revision of mechanical alloying as a technique able to develop metastable materials. This technique can be combined with melt-spinning to obtain powdered materials. In our case, the same Fe-rich alloy was produced by three routes: mechanical alloying (MA), melt spinning (MS) and mechanical alloying of melt-spun sample (MS + MA). Different processing pathways produce alloys with different microstructure (amorphous or nanocrystalline) and thermal stability front crystallization.

Acknowledgements

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