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A comparative study of the Fe-based amorphous alloy prepared by mechanical alloying and rapid quenching

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ABSTRACT

This paper presents a comparative study regarding the preparation of Fe-based amorphous alloys via mechanical alloying (MA) and rapid quenching (RQ). The obtained samples (powders and ribbons) were characterised by X-ray diffraction (XRD), in-situ high-temperature X-ray diffraction (HT-XRD), differential scanning calorimetry (DSC), thermogravimetry (TG) and vibrating sample magnetometry (VSM). By using elemental powders of Fe, Si and B, it was found that amorphisation cannot be achieved by dry MA or RQ. Wet MA using benzene as process control agent (PCA) led to the alloy amorphisation after 20 h of milling. It was proved that the amorphisation via wet MA is possible due to the extra amount of C atoms provided by the PCA decomposition. Using powders obtained by wet MA or a mixture of Fe, Si, B and C elemental powder, amorphous ribbons were obtained by RQ. During the amorphous samples crystallisation, a mixture of α-Fe(Si) and Fe borides is formed. The magnetic measurements showed that the magnetic characteristics of the samples are strongly influenced by the technique used for their preparation.

1. Introduction

In the past decades, amorphous materials have become a subject of great interest from the scientific and industrial perspective. Because of the absence of atomic long range order and crystalline defects, the amorphous materials are characterised by interesting properties such as excellent soft magnetic characteristics, high mechanical strength, high hardness and high corrosion resistance [1]. In the attempt to save energy or to convert it more efficiently, Fe-based amorphous alloys represent important candidates in almost all energy-related technologies. They are characterised by excellent soft magnetic properties such as high magnetic permeability, high saturation magnetisation, low coercivity and low magnetic core losses.

Fe-based amorphous alloys have been produced via a series of techniques such as rapid quenching (RQ), water/gas atomisation, plasma processing and mechanical alloying (MA) [2–5]. Among these, the most widely used technique is RQ and a series of techniques using the principles of rapid cooling from the liquid state have been developed: melt spinning, high pressure die casting, copper mould casting, suction casting etc. [1,5–8]. To achieve amorphisation via RQ, cooling rates of 10^5–10^6 K/s and proper chemical composition must be assured. Generally, the chemical composition of the alloys is limited to a narrow range of compositions that are close to deep eutectics. By RQ, ribbons, wires and small ingots can be prepared [5]. These shapes (simple geometries) limit the application of amorphous soft magnetic materials in electromagnetic devices where often 3D geometries (sometimes complicated 3D shapes) are required.

Besides RQ, MA has begun to be intensively used to produce amorphous alloys of various compositions [9–11]. Upon high energy ball milling, a mix of elemental powders of the constituents is subjected to repeated severe plastic deformation, cold welding and fracturing phenomena. Due to many defects induced by milling, the solid-state reaction between constituents takes place, leading to the alloy formation. The first amorphous alloy prepared by mechanical alloying, $Ni_{60}Nb_{40}$, was reported in 1983 [12] and since then, numerous studies were devoted to the amorphisation of binary, ternary or multicomponent alloys [13]. The products of

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mechanical alloying are in powder form, allowing thus through proper compaction techniques, such as hot pressing or spark plasma sintering, the preparation of 3D shapes [14,15]. Compared to RQ techniques, MA can produce amorphous alloys even when their composition is far from that corresponding to deep eutectics or if the heat of mixing of constituents is positive. In some cases, when ductile elements are subjected to mechanical alloying, to avoid excessive cold welding (formation of large particles), process control agents (PCA) are used. The PCA are organic or inorganic substances that act as surfactant reducing the amount of cold welding processes. If the amount and type of PCA are properly chosen (generally not larger than 5 wt.% of processed powder), a balance between cold welding and fracturing phenomena is established [13,16]. Alternatively, mechanosynthesis was proved to be an effective technique to prepare Fe-based powders by milling of the amorphous ribbons obtained by rapid quenching technique [17,18].

The purpose of this study is to present our results concerning the preparation of $Fe_{75}Si_{20}B_5$ at.% amorphous alloys via RQ (melt spinning) and MA and the influence of preparation techniques over the characteristics of the alloy. A comparative structural, calorimetric, thermogravimetric and magnetic study of the alloys prepared by the above-mentioned techniques is presented. It was shown that the preparation technique have a strong influence on the structural characteristics of the products as well as on their magnetic and thermal properties.

2. Experimental

In order to prepare amorphous $Fe_{75}Si_{20}B_5$ at.% alloy via MA or RQ, a mixture of elemental powder of Fe, Si and B was used. To ensure the starting mixture's homogeneity, the elemental powders were homogenised in a turbula-type blender for 30 min. The composition of the starting mixture (starting sample) was: 75 at.% Höganäs NC 100.24 iron powder, 20 at.% silicon powder 99.9% (Alfa Aesar) and 5 at.% boron powder 99.9% (Alfa Aesar). This mixture was then processed in a high-energy planetary ball mill (Fritsch Pulverisette 6). The following milling parameters were used for all MA experiments reported in this study: milling vials capacity - 500 ml, milling vials material - tempered steel, milling balls diameter - 14 mm, ball to powder weight ratio (BPR) - 16:1, filling factor - 60%, disc rotational speed - 350 rpm, milling atmosphere - high purity argon, process control agent used - benzene (4 ml).

The master alloys used for RQ experiments were prepared by arc melting in an argon atmosphere. The mixture of elemental powder or amorphous powder prepared by wet MA was melted several times to ensure the alloy's homogeneity. The amorphous powder prepared by wet MA was used to ensure identical chemical composition for amorphous powders and ribbons. The parameters of the RQ experiments were the following: the wheel was manufactured by copper, tangential wheel speed was in the range of 25–32 m/s, the crucible was made from quartz, the melting of the sample was made by induction, the diameter of the nozzle was 600–800 μm, the distance between nozzle and rotating wheel was 200 μm and high purity argon was used as atmosphere. The above-mentioned parameters lead to ribbons of 10–15 μm thickness and 0.9–1 mm width.

The structural characterisation of the powders and ribbons was made by XRD in the angular range of $2\theta = 20–110°$. The equipment used was an Inel Equinox 3000 powder diffractometer, working with Co Kα radiation ($\lambda = 1.7903$ Å). In-situ high-temperature X-ray diffraction (HT-XRD) patterns were recorded up to 900 °C using an Anton-Paar equipment (HTK 1200 N advanced high-temperature chamber). The heating rate was 10 °C/min and the atmosphere used was preliminary vacuum (10^{-2} Torr). The frequency of the XRD spectra acquisition was one diffraction per minute.

The thermal stability of the amorphous samples was investigated by differential scanning calorimetry (DSC). The equipment used was a Setaram Labsys apparatus using as reference high purity alumina powder. The measuring range was 20–750 °C, with a heating/cooling rate of 20 °C/min under argon atmosphere. The thermogravimetric (TG) measurements were made using a Setaram Labsys apparatus up to 750 °C in a hydrogen atmosphere with a heating rate of 20 °C.

The hysteresis loops of amorphous samples were recorded using a vibrating sample magnetometer (VSM) from Lake Shore Cryotronics Inc. The maximum applied field was 800 kA/m.

3. Results and discussions

Using a mixture of elemental powders of Fe, Si and B, an attempt to prepare amorphous powders was made via dry MA and RQ. In Fig. 1 are presented the XRD patterns of powders prepared by dry MA and ribbons prepared by RQ (melt spinning). Concerning the powders prepared by MA, in the XRD pattern of starting sample (ss), only the peaks of Fe and Si can be observed. The Bragg reflexions of B are not visible due to its relatively low scattering factor. After 5 h of milling, a Fe-based solid solution is formed. Increasing the milling time leads only to the diminution of the crystallite size (observable by the increase of the full-width at half maximum of the XRD peaks) and no amorphisation was achieved. It can be observed, in the case of the samples prepared by RQ that, regardless of the parameters of melt spinning process, amorphous samples were not obtained. The XRD patterns of the ribbons reveal several peaks corresponding to Fe_3Si and Fe_2B phases.

To achieve the alloy amorphisation, a second set of experiments was performed consisting of wet MA and melt spinning experiments. In the case of wet MA, benzene was used as process control agent (PCA). Contrary to dry milling experiment, powder amorphisation was achieved after 20 h of wet mechanical alloying. The XRD pattern of the powder wet milled up to 20 h is presented in Fig. 2a. The XRD pattern of this powder consists in a single broad peak that is given by the lack of long-range atomic order characteristic of the amorphous materials. Considering that both milling experiments were performed using identical process parameters, the use of PCA is the only factor that can affect the structural characteristics (the crystallinity) of the final product. It was reported that wet milling can alter the chemical composition of the materials processed [16]. Due to the severe thermomechanical conditions that occur during the milling process, the decomposition of the PCA can be expected. The as resulted atomic species are further processed together with the powders leading to their contamination. The most reported atomic species that contaminates the processed powders are C, O, N etc. [16,19]. In the present case, a contamination with C resulted for the benzene decomposition can be expected. To prove this hypothesis, a TG measurement was performed using a hydrogen atmosphere due to its decarburising effect. The TG curve of the powders wet milled up to 20 h is given in Fig. 2b. It can be noticed that for temperatures above 375 °C, an important mass loss phenomenon occurs. This was mainly attributed to the decarburising of the powders during heating in a hydrogen atmosphere. A small part of the mass loss observed on TG curve can be also attributed to the deoxidation phenomena (reduction of the oxide layer formed on the particles surface during milling).

According to the measurement, the carbon content of the wet MA powders is about 2.3 wt.%. The successful amorphisation of the powders via wet MA can be explained considering the contamination with carbon of the processed powder. The carbon atoms are metalloids atoms, and the increase of the amount of metalloid elements will lead to enhanced chances to induce amorphisation.