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Original Research Paper

Structural and magnetic characteristics of Co-based amorphous powders prepared by wet mechanical alloying

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ABSTRACT

Amorphous soft magnetic powder of $Co_{70}Fe_4Ni_2Si_{15}B_9$ (at.%) was obtained by wet mechanical alloying starting from elemental powders using benzene as process control agent (PCA). After 40 h of milling, full amorphisation of the powder was achieved as proved by XRD investigations. The evolution of the mean particle size and specific surface of the particles versus milling time was explained in the light of the phases evolutions and their specific properties. A decrease of the powder magnetisation was observed during its progressive amorphisation as a result of changes of the magnetic moments environment and the presence of benzene in the samples. According to DSC studies the amorphous powder present a two steps crystallisation leading to the formation of Co-fcc, Co_2Si and Co_2B phases. Annealing of the powder at 300 °C for 1, 2 and 3 h leads to a substantial increase of the saturation magnetisation.

1. Introduction

The lack of long range atomic order that characterises the amorphous materials gives them a series of superior physical properties compared to their polycrystalline counterparts. The high mechanical strength, large elasticity, low Young's modulus, high corrosion and wear resistance of the amorphous materials make them suitable for a series of industrial applications in a number of fields such as energy, aeronautic, chemistry and medicine [1].

The amorphous soft magnetic materials have lower saturation induction as compared to their crystalline counterparts due to the presence in their composition of a relatively large amount of metalloid atoms. On the other hand, the lack of the magnetocrystalline anisotropy given by the absence of long range atomic order and their high electrical resistivity make them very attractive for AC and DC applications such as electric transformers and sensors [2].

The Co-based amorphous alloys presents near zero magnetostriction and magnetocrystalline anisotropy that gives them outstanding soft magnetic properties such as low coercivity, high permeability and low hysteresis losses [3].

Over the years, several synthesis routes were used to produce amorphous soft magnetic materials as the following: melt spinning, gas atomisation, mechanical alloying/milling, copper mould casting, vapour deposition, plasma processing, etc. [1]. The most common route used for amorphous materials preparation is melt spinning, thus leading to amorphous ribbons. Due to these ribbons, limited 3D geometries can be obtained, somehow reducing the application field of these materials. Mechanical alloying is another route frequently used in order to prepare amorphous materials, leading to powder samples. In this technique, a mixture of elemental powders or pre-alloyed powders is subjected to high energy ball milling process. As a result of the large number of defects induced by milling and a slight increase of the temperature during milling, the atomic inter-diffusion take place, and finally the alloy is formed [4]. In some cases, together with the milling bodies and powders to be milled, a certain quantity (not larger than 5 wt.% of total processed mass powder) of process control agent (**PCA**) is added [5,6]. The PCA acts as surfactants reducing the number of cold welding processes leading to the achievement of a balance between cold welding and fracturing phenomena [7]. A major advantage of the mechanochemistry route is that this technique can be successfully used to produce amorphous materials in some systems where conventional routes such as melt spinning prove to fail or to be difficult in achieving material amorphisation. Different authors have demonstrated the effectiveness of mechanical alloying to promote the amorphisation of different Co-based alloys, such as Co–Nb [8], Co–B [9], Co–B–Si [10], Co–Cr–Mo [11], Co–Fe–Si–B [12], Co–Fe–Ta–B [13], Co–Fe–(Zr,Ti)–B [14] and

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Co–Nb–Zr–B [15]. In the case of $Co_{40}Fe_{22}Ta_8B_{30}$, it has been reported that increasing milling time leads to the deterioration of the magnetic properties such as saturation magnetisation and coercivity due to the residual stresses, grain refinement, amorphous phase formation, surface anisotropy and particles surface irregularities [13]. It was found that, in the case of Co–Fe–(Zr,Ti)–B system, time to achieve amorphisation increases with the Fe content and the substitution of Ti or Zr for Nb in Co–Fe–Nb–B alloys is not so effective to widen the supercooled liquid region [14].

In this paper, we report on the preparation of $Co_{70}Fe_4Ni_2Si_{15}B_9$ (at.%) amorphous powder via wet mechanical alloying route. The milling time required for alloy amorphisation, evolution of the median particles diameter (D_{50}), magnetic properties and thermal stability of the powders are presented and discussed.

2. Experimental details

In order to obtain $Co_{70}Fe_4Ni_2Si_{15}B_9$ (at.%) amorphous powder, a mixture of elemental powder was prepared. The mixture of elemental powder contains particles of: Co (produced by Alpha-Aesar, 99.8% purity, particle size range 45–150 μm), Fe type NC 100.24 (produced by Höganäs, 98.5% purity, particle size <150 μm), Ni type 123-carbonyl (produced by Inco, 99.8% purity, particle size <7 μm), Si (produced by Alpha-Aesar, 99.9% purity, particle size <150 μm) and amorphous B (produced by Alpha-Aesar, 99.8% purity, particle size <45 μm). The elemental powders were homogenized in a Turbula-type apparatus for 15 min. in order to obtain a uniform distribution of powder particles. The mixture of elemental powders will be referred as starting sample (ss). The as-obtained mixture was wet milled in a planetary ball mill (Pulverisette 6) in the argon atmosphere using 500 ml vials made from tempered steel. The ball to powder ratio (BPR) was 16:1. The diameter of the used grinding ball was 15 mm and the extent of filling the vial was about 50%. The rotational speed of the disc was 350 rpm. In this mechanical alloying experiment, 1 ml of C_6H_6 was added after each sampling procedure in order to supply the quantity of benzene that evaporates. The total quantity of benzene that was added during the entire milling experiment was 5 ml. Benzene was used as PCA in order to minimize the cold welding between particles. Benzene was chosen as PCA due to the relative high stability of its molecule (aromatic ring). This reduce the contamination risk with atoms resulted from the decomposition of the PCA. In order to perform the annealing, the powder was sealed in a quartz tube under vacuum.

A Siemens D5000 powder diffractometer working in reflexion mode was used for the X-ray diffraction (XRD) studies. The XRD patterns were recorded using monochromatic cobalt radiation in the angular range $2\theta = 20–120°$ in reflexion mode. The mean crystallite size was calculated by Scherrer method for the most intense peaks of each solid solution: (111) peak for Co-based fcc solid solution and (101) peak for Co based hcp solid solution.

Differential scanning calorimetry (DSC) investigations were performed using a Setaram Labsys apparatus in the 25–900 °C temperature range. The heating speed was 20 °C/min and the atmosphere used in order to avoid oxidation was Ar.

In order to perform the thermomagnetic measurements ($M(T)$), the powder was sealed in a quartz tube under vacuum (10^{-2} Torr). The heating/cooling rate was 20 °C/min. The measurements were carried out using a home-made equipment.

The particle size distribution has been determined using a Laser Particle Size Analyzer (Fritsch Analysette 22-Nanotec), with an analysis field of 10 nm–2000 μm. The specific surface area of the powder was automatically calculated by particle size analyzer taking into account the shape factor of the particles and the theoretical density of the alloy.

The particles morphology was investigated by scanning electron microscopy using a Jeol-JSM 5600 LV scanning electron microscope.

The magnetisation curves, $M(H)$, were recorded at room temperature using the extraction sample method in a continuous magnetic field of up to 10 T. The saturation magnetisations have been derived from the magnetisation curves for a magnetic field higher than 5 T.

3. Results and discussion

Fig. 1 presents the X-ray diffraction patterns of the starting sample (ss) and the samples milled for 2, 5, 10, 20, 25 and 40 h. The (hkl) indices for the most intense peak of each phase are indicated in the figure. The starting sample is composed by a mixture of elemental Co, Fe, Ni, Si and B powders. The elemental boron powder from starting mixture is in the amorphous state and so no Bragg reflection of this phase is noticeable. In the diffraction pattern of the starting sample, the Bragg reflections of the Co and Si phases are clearly identified. In the case of Co are noticed the peaks of two types of structures: hexagonal – hcp from P63/mmc (#194) space group and cubic – fcc from Fm–3m (#225) space group.

The co-existence of these two allotropic forms is a usual characteristic of the elemental cobalt at the room temperature [16]. The most intense peak of Fe (110) and the most intense peak of Ni (111) are superposing to the most intense one of the Co-fcc. Also, the amount of Fe and Ni are much lower as compared to the amount of Co, and, therefore, the contribution of these phases to the intensity of the peak is also lower. These Bragg reflections cannot be certainly identified in the diffraction pattern, but in the figure are indicated the theoretical peaks positions for Fe and Ni for a good evaluation of the powder evolution. It can be noticed that the most intense peak of Co-hcp (101) has a higher intensity as compared to the most intense peak of Co-fcc (111) suggesting that the hexagonal cobalt is the preponderant one. After only 2 h of milling in the diffraction pattern are identified Bragg reflections corresponding to the Co-hcp and Co-fcc phases, and it is hardly visible the most intense Si peak (111). This indicates that during milling up to 2 h in material started to form two types of cobalt based solid solutions that have hcp and fcc structures respectively. Also, at this milling time according to the diffraction pattern, the Co-fcc structure becomes the main one instead of Co-hcp structure. This can be assigned to the following main phenomena:

- refinement of the crystallites induced by milling process;
- Co-fcc phase is stabilised by Fe and Ni elements.

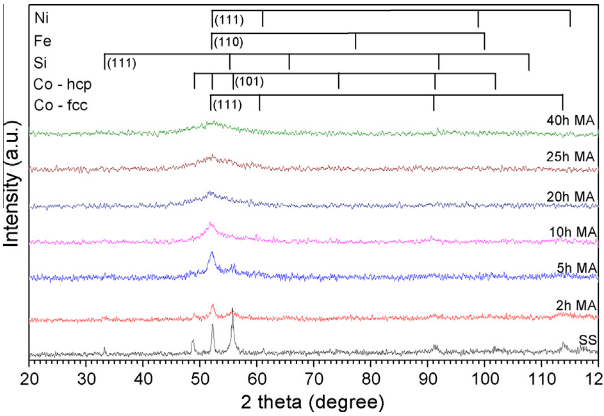

Fig. 1. X-ray diffraction patterns of the starting sample and the samples milled for 2, 5, 10, 20, 25 and 40 h. The patterns have been vertically shifted for clarity, and the (hkl) indices for the most intense Bragg reflection of each phase are marked.