Effect of milling time on the structural, microstructure and magnetic properties of nanocrystalline Fe90Sb10 powders obtained by high energy ball milling

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Abstract

Nanocrystalline binary powders Fe$_{90}$Sb$_{10}$ (wt.%) have been elaborated by high energy ball milling in order to study the effect of the milling time on the microstructural and magnetic properties of these alloys. The evolution of structural, morphological and magnetic properties were investigated, as a function of milling time, using the X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray spectrometry (EDX) and the vibrating sample magnetometer (VSM). A disordered Fe (Sb) solid solution with body centered cubic (bcc) crystal structure is formed after twelve hours of milling from XRD results. When the milling time increases, the lattice parameter progressively increases from 0.2861 nm for the Fe$_{90}$Sb$_{10}$ (zero hour milling) compound down to 0.2870 nm for thirty six hours of milling. The sample with the longest milling time has exhibited the lowest value for the mean grain size of 18.16 nm as well as the microstrain of 0.19%. Grain morphology of the powders at different formation stages was examined using scanning electron microscopy (SEM). The chemical composition homogeneity the powder form Fe$_{90}$Sb$_{10}$ (wt.%) were studied done with EDX experiments. For Fe-10Sb (wt.%) nanostructured powders, magnetisation saturation, coercive fields and remnant magnetisation derived from the hysteresis curves were discussed as a function of milling time.

1. Introduction

The elaboration of nanomaterials has known an evolution this last years, the nanomaterials present more often some originals comportment, which differ considerably from those massifs materials with the same chemical composition [1–6].

It exists many development methods of the nanomaterials elaboration: sol-gel method [7, 8], arc discharge method [9], chemical vapor deposition (CVD) [10], sputtering [11], Reverse micelle methods [12], mechanical alloying [13, 14]...etc.

Mechanical alloying (MA) is a powder metallurgy processing technique that involves repeated coldly welding, fracturing, and rewelding of powder particles in a high-energy ball mill. Due to the specific advantages offered by this technique, MA was used to synthesise a variety of advanced materials [15–21].

In recent years, nanostructured Fe-Sb alloy powder is fabricated by various methods including heat treatment of rapidly solidified melt and mechanical alloying (MA) [22, 23]. In this regard, WANG WeiLi et al. [22] investigated by rapidly solidified melt the phase formation α-Fe(bcc) in Fe-10%Sb alloy. M.Kis-Varga et al. [23] after various milling times were obtained nanocrystalline α-Fe(bcc) phase by stainless steel vibrating mill of Fe$_{90}$Sb$_{10}$ powders for a milling times above 100 hours.

The main objective of our work consists on analysing the nanopowders obtained after transformations by mechanical alloying and studying theirs physicals behaviours. In our work, we have chosen the Fe-Sb
This last form a magnetic permanent base from one part and it's used in various applications, on the other hand.

The first step of our work is the elaboration of Fe$_{90}$Sb$_{10}$ alloy by high-energy ball milling of one powder mixing (composed of iron and the antimony). The second step consists on charactering the elements obtained after different milling times by X-ray diffraction (XRD) followed by the Rietveld refinement in the aim to study the microstructural variation, the scanning electron microscope (SEM) was used to characteristic the microstructure such as morphology and the magnetisation measurements by the vibrating sample magnetometry (VSM). These operations allows us to study the behaviour of the magnetisation saturation and the coercive field with the crystalline size.

2. Materials And Methods

High purity (> 99%) and average particle size < 100 µm iron and antimony commercially obtained were used as raw materials. The mechanical alloying process was performed in planetary high-energy ball mill Retsch PM 400. After ensuring that the milling will be performed in an inert atmosphere, the powders were sealed in a cylindrical vial with stainless steel balls having 12 mm in diameter. The ball-to-powder weight ratio is 15:1 and the vial rotation speed was 350 rpm. The milling time was ranged from 0 to 36 hours (0, 2, 4, 8, 12, 16, 25 and 36 h) to investigate its effect on the properties of the obtained powders. The milling process was carried out with a one hour sequence of milling following by 30 min of pause to avoid excessive heating during milling operation.

The milled powders were analysed by X-ray diffraction (XRD) for examining the phase transformations as a function of the alloy composition by a Bruker D8 Advance Eco diffractometer. The diffraction parameters were collected with 2θ ranging from 10° to 130° with a step size of 0.02 and Cu-Kα ($\lambda = 1.5418$ Å) radiation. The MAUD software (version 2.22) [24], based on the Rietveld method [25], was adopted to refine the structural and microstructural parameters of nanostructured powders. Each peak was fitted by a formula of the pseudo-Voigt function expressed by a weighted sum of Gaussian(G) and Lorentzian (L) functions:

$$\Omega(2\theta) = \eta \cdot L(2\theta, H_L) + (1 - \eta) \cdot G(2\theta, H_G)$$

where L and G are, respectively, the Lorentzian and Gaussian components of width at half height, respectively $H_G$ and $H_L$. The parameter $\eta$ which defines the shape of the diffraction peak, has two limit values: $\eta = 0$ or Gaussian limits and $\eta = 1$ or limit Lorentzienne.

In the procedures of refining experimental diagrams, the adjustable parameters, apart from the position and the intensity of the peaks are $H$ and $\eta$ respectively.

These can be substituted by the two widths $HG$ and $HL$ which are directly related to the average microstructural parameters of the sample, namely the size of the mean grains, $\bar{D}$ [26], and mean level of
microstrains, $\varepsilon$ [27], by relations:

$$< D > = K \frac{\lambda}{\beta_L \cos \theta}$$

where $K$ represents the shape factor which varies with crystal shape, $\lambda$ is the wavelength of the radiation used, $\theta$ is the Bragg angle and $\beta_L$ is the width of the peak halfway between the continuous bottom background and the top of the peak expressed in radians.

$$< \varepsilon^2 >^\frac{1}{2} = \frac{1}{2\sqrt{2\pi}} \frac{\beta_G}{\tan \theta}$$

where $\beta_G$ is the breadth of the Gaussian contribution to the peak, which has its origin in the presence of microstrains. Microstructure analysis and morphology observations were carried using Quantum 250–FEI electron microscope (SEM) equipped with an energy-dispersive X-ray microanalysis (EDX). The magnetic properties of the obtained materials, specific magnetisation saturation ($M_s$), coercivity ($H_c$) and remanent magnetisation ($M_r$), were measured using a MicroSense V7 vibrating sample magnetometer (VSM) with a maximum applied field of 18 kOe.

3. Results And Discussion

3.1. Structural Characteristics

Figure 1 presents a series of XRD patterns of the Fe–10Sb (wt.%) powder mixtures after MA for different times obtained at room temperature. Recording of the XRD peaks of pure iron and antimony of the starting powder mixture (labelled 0 h in Fig. 1) showed corresponding reflections for elements with a central cubic structure (CC) for Fe by the plans (110), (200), (211), (220) and (310) and rhombohedral structure for Sb by the plans (012), (104), (040), and (116). After 12 h of milling, we observed that the Sb peaks disappear completely, whereas the peaks related to Fe slightly shift towards small angles (Fig. 2). This proves that Sb atoms dissolve in the Fe lattice leading to the formation of bcc solid solutions (Fe–Sb). The slightly angular shift is attributed to the formation of (Fe–Sb) solid solution and to the first order internal stress induced by milling. The first-order of angular stress acts as a macroscopic level by modifying the lattice parameter and consequently produces an angular shift of XRD peaks [28–29].

All XRD spectra of the milled powders were analysed by the Rietveld refinement. An example of refinement is presented in Fig. 3 for the powder milling at 12 h. We have shown that the diffraction peaks corresponding to (rhombohedral) Sb and (bcc) $\alpha$-Fe disappears after 12 h of milling, and that only the (bcc) $\alpha$-Fe (Sb) phase with a group space Im3m is presented.
Figure 4 presents the change of lattice parameter (a) versus milling time (t) for Fe$_{90}$Sb$_{10}$ samples. As the milling time increases and due to more Sb diffusion, the lattice parameter increases from 0.2861 ± 0.0001 nm for the pure Fe to 0.2870 ± 0.0001 nm after 36 h of milling (Table 1). Such a variation of the lattice parameter is due to the difference between the atomic radii of Fe and Sb since the atomic radius of Sb ($R_{\text{Sb}} = 0.145$ nm) is greater than the atomic radius of Fe ($R_{\text{Fe}} = 0.126$ nm). Generally, the increase of lattice parameter with milling time is due to the solid solution formation. Moreover, in nanostructured materials produced by mechanical alloying, the increase of lattice parameter may also be due to the defects introduced in the interfaces [30].

Figure 5 shows the evolution of the mean grain sizes $<D>$ (nm) and the mean level of microstrains as a function of the milling time. We have noticed that the mean grain size decreases monotonically with increasing milling time. This decrease in $<D>$ is accompanied by an increase in the rate of microstrain $<\varepsilon>$ with milling time.

Indeed, the mean grain size decreases from 59.95 nm (0 h) to 18.16 nm after 36 h while the rate of microstrain increases from 0.076% (0 h) to 0.19% at 36 h. The decrease of $<D>$ and the increase of $<\varepsilon>$ can be explained by the hard character that FeSb powders acquire with increasing milling time, so that the process of grain fragmentation is favoured and gives rise to smaller crystallite size [31]. We can also cite the work of M.Kis-Varga et al. [23] who have observed the decrease of the rhombohedral Sb peaks with a slight broadening of all reflections upon milling up to 10 hours and they almost disappear after MA for 100 h and the formation of a solution solide of the (bcc) $\alpha$-Fe (Sb) phase (the pure crystalline antimony phase is spent) for Fe$_{90}$Sb$_{10}$ samples performed in a stainless steel vibrating mill. The authors calculated from peak widths the grain size value obtained after 200 h of milling was 8.5 nm [23]. The value of $<D>$ (nm) = 18.16 nm obtained in this work after 36 h of milling it is quite logical well with that reported of M.Kis-Varga et al. [23] for the vibrating milled Fe$_{90}$Sb$_{10}$ alloy.

### 3.2 Microstructure characteristics

Before milling, Fig. 6 shows the SEM image of the starting powder, which is an elemental mixture of primary Fe and the Sb powder of the Fe-10Sb alloy (wt.%). Iron particles have a spherical-like morphology and have an average size of about 6 µm, while antimony particles have an irregularly shaped morphology and have an average size of 20–30 µm.

The morphological evolution of the macroscopic powders indicates considerable changes with increasing milling times, as shown by SEM micrographs (Fig. 7). It is well known that the phenomenon of repeated cold welding and fracture is ensured by the action of the balls-powder-balls and balls-powders-wall of the jar during mechanical milling leads to an observable change in the shape and the particle size of the powder obtained [32].

Figure 7 shows SEM images of Fe$_{90}$Sb$_{10}$ powders particles mechanically alloyed for 2 h, 4 h, 8 h, 12 h, 16 h, 25 h and 36 h, of milling. During the milling process (2 and 4 hours), the particles of the mixed
powders, caught between the balls or between the balls and the walls of the jars, are subjected in a way on a continuous basis, to the repeated effects of fractures and welding (Fig. 7(a) and (b)).

During the first milling times (2 and 4 hours), the compressive force and the plastic deformations crush the powder particles. The magnification of the particles during this initial stage of milling shows that the phenomenon of cold welding is dominant, because the powder is relatively tender at the start of milling. The clusters that form are not yet homogeneous and the different particles only seem to be stuck to each other. It is noted that the morphological changes of this period are already important after 4 hours of milling. This type of behavior is in good agreement with some previous references that have shown that in the early stages of mechanical alloying; the phenomenon of the agglomeration, which change the morphology typically the size, and shape of the composites is started [33,34]. After 8 h of milling (Fig. 7(c)), you can may clearly see the phenomena of fracture and welding of the particles and which are specific to mechanosynthesis. In addition, we have noticed the particle refinement continues and the particle shape changes to a form of laminar structure (multi-layered structure) consisting of an overlay of Fe and Sb multilayers. This structure is similar to the materials produced by mechanical grinding from ductile or fragile elements, observed by Davis et al. [35] and Djekoun et al. [36]. The mechanism of formation of this type of lamellar structure is the repetitive result of condensation of powders by cold welding and then fracture, as shown in Fig. 7(c) by the shape of a relatively large flat particle. The Fig. 7(d) represents the micrographs obtained after 12 h of milling. We noted that the majority of the particles possess a lamellar shape and average size between 5 and 15 µm. The decrease in particle size in this stage can be explained by the manner way: The milling process is a balance between fracture and cold welding. The cold welding process results to an increase in the particle size. Those information indicates the formation of a phase of the (bcc) α-Fe (Sb) and which corresponds perfectly to the diffraction of X-rays. For milling times between 16 and 25 hours, see Fig. 7(e) and (f), it is observed that the ground particles become smaller and that there are fine particles, of a size of the order of 5 µm and have a more or less homogeneous aspect characteristic of a balance between the phenomena of fracture and welding. In this stage the bonding forces of the powder particles are stronger when the size of the grains is small, the deformations are no longer possible because they require a great force to fracture the particles it is noticed that the size of the grains decreases with time of grinding, this decrease is due to the process of fracture and welding due to the collision between the powder, the balls and the inner wall of the jar. After 36 hours of milling (Fig. 7(g)), large agglomerates of very fine particles were observed, these particles being finer and smaller for longer grinding times [37].

These results show that after 36 hours of grinding, we produce very small conglomerates compared to the time that preceded it, and their particles are smaller, more homogeneous than the agglomerates obtained at previous grinding times. It is important to note that the fracture process dominates the mechanosynthesis process in this step, which caused a reduction in particle size.

Figure 8 shows the percentage point evolution of iron and antimony in the Fe$_{90}$Pb$_{10}$ system by SEM images and energy-dispersive X-ray (EDX) analyzes performed on all samples and the values of chemical composition of Fe$_{90}$Pb$_{10}$ powder mixtures after several milling times obtained from the EDX are given in
Table 2. SEM and EDX analysis of the mixture without grinding (Fig. 8 (a) and (b)) clearly shows the iron and Sb particles yet separated from each other and with different morphology. Selected area 1(Fig. 8(a)) corresponding to Fe shows a very high massic percentage of iron (100%). On the other hand, selected area 2 (Fig. 8(b)) corresponding to Sb shows a very high massic percentage of antimony (95.53%). This confirms the result of the XRD concerning the presence of Fe, and Sb elements before milling process. During the first milling times of 2 to 4 hours, it is observed that the morphological changes of Fe and Sb are already significant (Fig. 8(c) and (d)). However, we can observe the separate presence of Fe and Sb (the small iron particles are welded to the surface and also become large as well as the antimony particles are reduced by intense breaking), and the FeSb compound already begins to form. With the increase of the times milling from 8 to 36 hours, the chemical composition varies slightly, it is close to the nominal composition Fe$_{90}$Sb$_{10}$, as reported in Fig. 8(e)–(i). Indeed it becomes difficult to distinguish the particles of Fe and the particles of Sb, this indicates a homogeneous distribution of the elements between them, and the formation of the solid solution (Fe,Sb). These results are in good agreement with those found by X-ray diffraction[15,34]. It is very important to note that there are no other peaks other than those of the elements present in the powders, this indicates that there is no impurities and no contamination possibly introduced during the grinding operation (the balls and the internal wall of the jars) [38].

3.3. Magnetic Properties

In our measurements to obtain the hysteresis cycles of the samples, the external magnetic field H is continuously varied between two extreme values, -1.8 kOe and + 1.8 kOe. These values allow us to reach the magnetisation saturation of the material. With the gradual cancellation of the external magnetic field, the material remains in a stable state of residual magnetization. Then, with the increase of the external magnetic field applied in the opposite direction, the magnetisation gradually reaches the state of reverse saturation. For a particular value of the applied field, called coercive field $H_c$, the magnetisation is canceled. Several parameters, such as the coercive field $H_c$, the magnetic moment $m$, the magnetisation saturation $M_s$ and the remanent magnetisation $M_r$ are extracted from the hysteresis curves.

The Fig. 9 shows the room temperature hysteresis loops (M-H) of Fe$_{90}$Sb$_{10}$ powders for different milling times.

We note that all the cycles hysteresis have a sigmoid shape and are generally observed in nanostructured magnetically soft samples with small magnetic domains(see box in Fig. 9). This is due to the presence of structural distortions within the grains. Low hysteresis losses are properties generally sought after in soft magnetic materials. The curves of magnetisation - field loops have been used to determine the values of the magnetisation saturation ($M_s$), coercive fields ($H_c$), remanent magnetisation ($M_r$) and squareness ratio ($M_r/M_s$) (see in Table 1).

In a ferromagnetic material, the orientation of atomic magnetic moments can occur spontaneously, even in the absence of an external magnetic field, provided that the temperature of the material is lower than the critical temperature called ferromagnetic curie temperature. The region of the material or the magnetic
moments have the same orientation and they are called magnetic domains or Weiss domains. When one
passes from the magnetic field to the neighbouring field, the magnetic moments gradually change
orientation over a short distance. This interface where occurs this transition is called a block wall.

In a material that is not subjected to any excitatory magnetic field, the vector sum of magnetic moments
associated with the Weiss domains is zero, that is to say that the material macroscopically presents no
magnetisation.

If the material is subjected to an exciting magnetic field \( H \), the domains whose magnetic orientation is
close to that of the exciting field \( H \), enlarge to the detriment of the less well-oriented domains, which
gradually disappear when the intensity of the excitatory field increases.

There is a higher value of the excitation field called the saturation field for which the single crystal or the
grain will then consist of a single Weiss domain whose magnetisation \( M \) will have the same orientation
as the exciter field \( H \). The corresponding magnetisation is the magnetisation saturation \( M_s \).

The values of \( M_s \) are also included in Table 1. The evolution in magnetisation saturation \( M_s \) as a
function of the milling time (Fig. 10) shows a decrease from 213.73 emu/g after 2 h of milling, then, an
increases to about 226.03 emu/g after 4 h of milling. Finally, a rapid decrease is recorded up to 36 hours
of milling to reach 156,95 emu/g.

The reason for the decrease in magnetisation saturation is attributed to the electronic transfer of the
antimony atoms which fill partially the third band of Fe giving rise to lower values for the magnetic
moment of these atoms [39]. This effect result in the reduction of \( M_s \) is linked to the existence the non-
magnetic elements (Sb) in the vicinity of the Fe atoms. The presence of Sb in the vicinity of Fe causes the
decrease in the magnetic moment of iron. We take note that the increase in \( M_s \) can be attributed to the
reduction in magnetocrystalline anisotropy which leads to an easier rotation of spins [40,41].

The changes in the magnetic properties of nanomaterials ferromagnetic, such as the remanent
magnetisation \( (M_r) \) and the coercivity \( (H_c) \), are usually originate from the microstructure and are
attributed to the large fraction of atoms present at the grain and the grain boundaries.

Further, the remanence \( M_r \) represents the resistance of a material to demagnetisation.

Variation of \( H_c \) and \( M_r \) as a function of milling time is shown in Fig. 11. It was observed that the residual
magnetisation behaves in a similar manner to that of the coercion. It has been observed two stages of
variation for the coercivity of \( H_c \) (and \( M_r \) : an increase during the first four hours of milling, followed by a
rapid decrease for longer times (36 hours). The increase in coercivity of \( H_c \) (and \( M_r \)) is linked to the
irreversible displacement of the walls of magnetic domains following the introduction of different types
of defects (dislocations, grain boundaries and precipitates) and the formation of borides. Also, the
increase in coercivity of \( H_c \) (and \( M_r \)) reflects on the high value of magnetic anisotropy at the milling start
(magnetocrystalline, shaped and magnetoelastic).
The decrease of the coercivity $H_c$ during the second stage depend on the refinement of the grain size which leads to an easier rotation of the magnetic vector, as explained in G. Herzer's model [42]. It should be noted that this model indicates that the grain size for all the samples is less than the magnetic exchange length of the iron-based alloys which is $L_{\text{ex}} = 20-30\text{nm}$ [43], which is probably the main cause of saturation observed in coercive field around $98-121.69\text{Oe}$ (see in Table 1). In the present study, the grain size of the $\alpha$-Fe (Sb) alloy is at the second stage of processing approaches. The exchange length (which is between 18 and 25 nm), the average magnetocrystalline anisotropy of the randomly oriented crystallites do not offer resistance to Bloch walls and the coercivity approaches to the low value characteristic of mild ferromagnetic alloys.

The $Mr / Ms$ ratio is essentially the square measure of the hysteresis loop (M-H). It is related to the level of inter-grain interaction. The evolution with milling time of remanence-to-saturation ratio, $Mr/Ms$ of $\text{Fe}_{90}\text{Sb}_{10}$ powder mixture is shown in Fig. 12. It is observed that a gradual increase the square ratio $Mr/Ms$ to reach a value of around 0.057 after 2h milling, then decreases rapidly from 0.056 at 4h to 0.042 at 25h. After 36 hours of milling, the $Mr/Ms$ undergoes a slight increase to reach 0.044 (Table 1). All samples treated by MA have a $(Mr/Ms)$ ratio between 0.04 and 0.06 which is much lower than that of a single domain particle. The Stoner-Wolfarth model [44] predicts that in single-field particles with uniaxial anisotropy, the low residual is in the order of $Mr/Ms = 0.5$.

Magnetic anisotropy is linked to two microscopic origins: the first is due to the dipolar interaction which is a long range interaction ($\sim r^{-3}$) and which will lead to shape anisotropy, and the second is the spin-orbit interaction which is the coupling between magnetic moments and the crystal lattice. These two interactions are going to play a very important role for small particles.

However, the free energy of magnetic anisotropy depends on the macroscopic shape of the material and its crystal axes. Each type of crystal lattice will give a privileged direction of the alignment of magnetic moments, this is the axis of easy magnetisation.

The magnetocrystalline anisotropy constant ($K$) of the $\text{Fe}_{90}\text{Sb}_{10}$ powder mixture as a function of milling time is obtained by using the relation based on Brown's model between the magnetisation saturation ($Ms$) and coercivity ($Hc$) [45]:

$$K = \frac{H_C \times M_S}{0.96}$$

4

The values of magnetocrystalline anisotropy constant for all the samples are listed in Table 1.

Evolution of anisotropy magnetic constant $K$ and magnetisation saturation $M_S$ as a function of milling time is shown in Fig. 13. It was observed that the anisotropy magnetic constant $K$ behaves in a similar manner to that of the magnetisation saturation $M_S$. We can observe three stages: a slight decrease in the magnetic anisotropy constant $K$ during two hours of grinding, then an increase between 2 and 4 hours of
milling, a slight decrease in the magnetic anisotropy constant K during two hours of grinding, then an increase between 2 and 4 hours of milling, and finally a rapid decrease until reaching a low value of around 16021.97 after 36 hours of milling (Table 1). The increase in K is tributary on the hardening of the system and introduction of an important density of crystal defects. However, the decrease in K may be related to the decrease of the frome anisotropy due to the decrease in the shape distribution of particles during milling[46–48]. Furthermore, it is presumed that the decrease in apparent anisotropy following to grain size refinement cannot produce effectively with the existence of non-magnetic phases along the joints of grains. This refinement prevents exchange coupling between the grains.

With the decrease in dimensionality, the effects related to surfaces become more and more important because the fraction of atoms of surfaces on atoms of volumes is no longer negligible. Thus, it is necessary to hold on into account a term related to the surface of the nanostructure.

The virgin curve (or initial magnetisation curve) reflects the magnetic behaviour of demagnetised samples with increasing applied field. The Fig. 14 shows at room temperature the M (H) virgin curves of Fe$_{90}$Sb$_{10}$ powders for different milling times. We observe that all the virgin curves pass through the origin and show a linear evolution of the magnetisation for low values of the magnetic excitation and from a certain value, the magnetisation increases less quickly, the Fe$_{90}$Sb$_{10}$ powders for the different milling times begin to saturate. It is also noted that the magnetisation saturation Ms as a function of the milling time by increasing the values of the magnetic excitation decrease from 212.46 emu/g after 2 h of milling, then increases to about 224.17 emu/g after 4 h of milling. Finally a rapid decrease up to 36 hours of milling to reach 156.36 emu/g.

The increase in magnetisation saturation can be correlated with that of the crystalline parameter which can be influenced by plastic deformations and the density of defects produced by high energy mechanical milling. On the other hand, the decrease in Ms can be related to the change in the magnetic moment following the modification of the electronic configuration of the closest neighbours of the Fe atom. The decrease in Ms with the increase in the grinding time can be explained by the antiparallel coupling of iron and antimony spins.

### 4. Conclusions

The experimental work presented in this article concerns the preparation of nanostructured Fe$_{90}$Sb$_{10}$ (wt.%) powders using high-energy ball milling from pure elemental Fe and Sb powders in a Retsch PM400 types planetary mill for different milling times up to 36h. The structural, microstructural and magnetic characterisations were made by X-ray diffraction using a structural refinement program (MAUD) based on the method of Rietveld, scanning electron microscopy (SEM) coupled to EDX and Vibrating Sample Magnetometer (VSM). The XRD results reveal the formation of (bcc) α-Fe(Sb) solid solution by the gradual diffusion of Sb atoms into (bcc) α-Fe. After 12h of milling, only the (bcc) α-Fe(Sb) phase is detected. The results of the lattice parameter calculation show that the latter increases slightly from its initial value corresponding to that of (bcc) α-Fe until reaching a final value of 0.2870 nm after 36 hours of
milling. In addition, we have noticed that the average grain size decreases with increasing milling time. This decrease in $<D>$ is accompanied by an increase in the rate of micro-distortions $<\varepsilon>$ with milling time. In fact, the final values of the mean grain size and of the micro-distortions reached 18.16 nm and 0.19%, respectively. The study of the morphology of the Fe$_{90}$Sb$_{10}$ (wt.%) powders allowed us to observe the change of the shape as well as the size of the particles after the grinding. It seems like for long grinding times, the mode used as well as the grinding conditions favor the existence of round-shaped particles. The maps produced by EDX allowed us to follow the evolution of the formation of the alloy according to the grinding time. From the hysteresis curves, we studied the values of the saturation magnetisation (Ms), the coercive field (Hc), remanent magnetization (Mr), the square ratio Mr/Ms and the magnetocrystalline anisotropy constant (K). Ms, Hc and Mr show a rapid decrease for times of 4 up to 36 hours of milling to reach values of 156.95 emu/g, 980e and 6.95 emu/g respectively. Furthermore, we note that in the Mr / Ms ratio, the samples produced during 36 hours of grinding are multidomain. The values of the Mr / Ms ratio is between 0.044 and 0.057. These Mr / Ms values, which are less than 0.1, corresponds to multidomains. From the magnetocrystalline anisotropy constant (K), exhibits a behaviour similar to that of Ms at room temperature.

**Declarations**

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Nassima GUEMMOUD (PhD Student): validation, investigation, resources, writing – original draft, writing - review & editing, visualization.

Dr. Ali HAFS (Supervisor): conception, methodology, resources, review & editing, visualization, supervision, validation.

Dr. Toufik HAFS (Research Collaborator): validation, writing – review & editing, visualization,

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Tables

**Table 1**
Structural parameters and magnetic properties for Fe$_{90}$Sb$_{10}$ powder mixture.

| Milling time (h) | a (nm) (±10$^{-4}$) | <D> (nm) (±2) | ε (%) (±10$^{-3}$) | $H_C$ (Oe) | Mr (emu/g) | Ms (emu/g) | Mr/Ms | K (erg/cm$^3$) |
|------------------|----------------------|---------------|-------------------|------------|-----------|-----------|-------|---------------|
| 0                | 0,2861 59,95         | 0,076         | 121,81 12,2      | 240,35     | 0,05      | 30496,90 |
| 2                | 0,2864 25,31         | 0,13          | 135,98 12,37     | 213,73     | 0,057     | 30273,96 |
| 4                | 0,2865 23            | 0,15          | 137,11 12,69     | 226,03     | 0,056     | 32282,26 |
| 8                | 0,2867 21,96         | 0,16          | 121,69 11,15     | 201,26     | 0,055     | 25511,80 |
| 12               | 0,2868 20,94         | 0,17          | 110,15 9,14      | 189,46     | 0,048     | 21738,56 |
| 16               | 0,2869 19,26         | 0,18          | 107,27 7,76      | 181,21     | 0,042     | 20248,32 |
| 25               | 0,2870 18,63         | 0,19          | 106,89 7,17      | 167,56     | 0,042     | 18656,75 |
| 36               | 0,2870 18,16         | 0,19          | 98 6,95          | 156,95     | 0,044     | 16021,97 |

**Table 2**
Evolution of chemical composition of Fe$_{90}$Sb$_{10}$ powder mixture with milling time.
| Milling time (h) | Elements | Theoretical [wt%] | Experimental analysis [wt%] | Error [%] |
|------------------|----------|-------------------|-----------------------------|-----------|
| 2                | Fe       | 90                | 94.79                       | 1.49      |
|                  | Sb       | 10                | 5.21                        | 2.97      |
| 4                | Fe       | 90                | 93.41                       | 1.32      |
|                  | Sb       | 10                | 6.59                        | 3.48      |
| 8                | Fe       | 90                | 91.44                       | 1.46      |
|                  | Sb       | 10                | 8.56                        | 3.04      |
| 12               | Fe       | 90                | 90.85                       | 1.56      |
|                  | Sb       | 10                | 9.15                        | 2.75      |
| 16               | Fe       | 90                | 89.73                       | 2.06      |
|                  | Sb       | 10                | 10.27                       | 3.27      |
| 25               | Fe       | 90                | 89.42                       | 1.45      |
|                  | Sb       | 10                | 10.58                       | 2.82      |
| 36               | Fe       | 90                | 89.87                       | 1.95      |
|                  | Sb       | 10                | 10.13                       | 2.86      |

**Figures**

**Figure 1**
XRD patterns of the Fe–10Sb (wt.%) powders milled for various times.

![XRD patterns of Fe–10Sb powders](image)

**Figure 2**

Deconvolution of the most intense peak for different milling time.
Figure 3

Rietveld refinement of XRD patterns corresponding to the sample milled for 12 h

Figure 4

Lattice parameter, \( a \) (nm), versus milling time for Fe\(_{90}\)Sb\(_{10}\) powders after 36h of milling time.

Figure 5

Evolution of the average crystallite size, \(<D>\) (nm), and mean internal strain \(<\varepsilon>\) (%), of Fe\(_{90}\)Sb\(_{10}\) powders versus milling time.
Figure 6

SEM image showing the morphology of Fe$_{90}$Sb$_{10}$ alloy without milling.
Figure 7

SEM images showing the shape evolution of the Fe$_{90}$Sb$_{10}$ powder mixtures at different milling times (a) 2 h, (b) 4 h, (c) 8 h, (d) 12 h, (e) 16 h, (f) 25 h and (g) 36 h, respectively.
Figure 8

SEM micrographs and EDX plots of the Fe$_{90}$Sb$_{10}$ powder mixtures for various milling times (a) and (b) 0 h (un-milled), (c) milled for 2 h, (d) milled for 4 h, (e) milled for 8 h, (f) milled for 12 h, (g) milled for 16 h, (h) milled for 25 h and (i) milled for 36 h.
Figure 9

Hysteresis loops (M–H curves) at room temperature of the Fe$_{90}$Sb$_{10}$ powders milled for 0, 2, 4, 8, 12, 16, 25, and 36 h.
Figure 10

Variation of saturation magnetisation of Fe$_{90}$ Sb$_{10}$ powder mixture as function of milling time.
Figure 11

Variation of coercive field and remanent magnetisation of Fe<sub>90</sub>Sb<sub>10</sub> powder mixture as a function of milling time.
Figure 12

Evolution with milling time of remanence-to-saturation ratio, Mr/Ms of Fe$_{90}$Sb$_{10}$ powder mixture

Figure 13

Evolution with milling time of anisotropy magnetic constant $K$ and saturation magnetisation $M_S$ of Fe$_{90}$Sb$_{10}$ powder mixture
Figure 14

Initial magnetisation (virgin) curve at room temperature for the Fe$_{90}$Sb$_{10}$ powders milled for 0, 2, 4, 8, 12, 16, 25, and 36 h (starts at $H = 0$ for demagnetised samples).