Structural, magnetic and thermal characterization of $Fe_{50}Se_{50}$ powders obtained by mechanical alloying

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Abstract

$Fe_{50}Se_{50}$ alloys has been produced from the elementary powders in a high-energy ball mill. The influence of milling times on the microstructures, structure and thermal proprieties have been studied by scanning electron microscopy (SEM) coupled with (EDS) microanalysis, X-Ray diffraction (XRD) and differential scanning calorimetry (DSC).

The interaction hyperfine and magnetic proprieties are investigated by transmission Mössbauer spectroscopy (TMS) and thermomagnetic measurements (VSM) respectively. For milling times up to 6 h, the Rietveld refinement of the X-ray diffraction spectra shows the formation of the hexagonal β-FeSe phase, amorphous selenium and also nanocrystalline α-Fe, the (DSC) curves shows several exothermic and endothermic picks, such as the crystallization the selenium amorphous at 103°C For milling times 39 h; the XRD shows the emergence of new phase, also in nanometric scale, a typical of α-FeSe phase tetragonal which has technological interest because is a superconducting phase.

The Mössbauer spectroscopy confirmed to formation the two phase's paramagnetic hexagonal β-FeSe and $\alpha-$FeSe tetragonal, in according the XRD and DSC. Measurement of magnetization (VSM) shows that saturation magnetization (M_S) decreases by increasing the time of milling.

Keywords: FeSe alloys; X-Ray diffraction; nanostructured materials; Magnetic proprieties; Mechanical alloying.

1 Introduction

The Iron Selenide, (FeSe) alloys, attracts more and more considerable attention of researches due to its electrical, optical and magnetic proprieties[1-2], the FeSe alloys are usually structured in several crystalline forms, such as $FeSe_2$ that has an orthorhombic marcasite structure, the hexagonal Fe_7Se_8 phase, $\beta-$FeSe phase with hexagonal NiAstype structure,$\alpha-$FeSe phase with tetragonal PbO-like structure and monoclinic Fe_3Se_4 phase, the various structure gives very interesting properties that make iron selenide a very promising alloy for applications in different fields in the industry for example solar cells [3], superconductivity and in optoelectronics [4].

FeSe samples can be prepared by various techniques spray pyrolysis [5-6], selenisation of iron films [7], hydrothermal method [8], metal organic chemical vapor deposition [9], microwave synthetic method [10] and solid-state reaction [11]. Many works have been done to obtain FeSe using mechanical alloying[12-15], owing the large melting points of iron 1535 °C and selenium 217°C can be the volatilization of Se, makes obtaining difficult the Fe-Se alloys structure at specific stoichiometry by these techniques.

The mechanical alloying (MA) technique was considered as the most useful tool for the development of nanostructured of variety of alloys elementary powders [16]. The materials obtained by this technique are homogeneous and are in the form of powder, therefore easy to industrialize by powder metallurgy, during (MA), the powders particles are subjected to severe plastic deformation and are repeatedly deformed, cold welded and fractured, the high-energy ball-milling process used for refining of microstructure, also for inducing chemical reactions between elements chemical. The interdiffusion between elements can be facilitated by the creation of structural defects, where the repeated shocks between balls-powders and the inner wall of the vial, creates numerous crystalline defects as grain boundaries, vacancies, interstitials and dislocations.

In this work, we targeted the development of nanostructured powders of $Fe_{50}Se_{50}$ composition by mechanical allowing in high energy Ball-Milling, the samples obtained were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) coupled with (EDS) microanalysis. Transmission Mössbauer spectroscopy (TMS) and magnetization measurements (VSM), whose objective is to determine the structural, magnetic and thermal properties of milled mixtures.

2 Experimental

2.1 Materials and methods

High purity Fe and Se powders (99.98at. %, particle size ~10µm) and (99.95at. %), particle size ~10µm) respectively were used to synthesize $Fe_{50}Se_{50}$ nanostructured powders in a Pulverisette P 7 planetary ball-mill. The powder-to-ball ratio for the mechanical alloying was 1:10. To prevent any oxidation of powders, loading, sealing, and unloading of powders into and from the vial were carried in high purity argon atmosphere. The milling process was interrupted after every 30 minutes of milling for 10 minutes, to avoid the elevation of the temperature in the interior of the vial, in order to minimize the cold welds between the powder particles and the wall of the vial.

Structure of powders were performed with X-ray diffraction (XRD) using SIEMENS D501diffractometer (with CuKα radiation $\lambda_{k\alpha}$ = 0.154185 nm in a $\theta - 2\theta$ geometry). In order to perform the analysis, XRD patterns were analyzes using MAUD program [17], which is based on the Rietveld and Warren-Averbach methods in combination with Fourier analysis [18-19]. The procedure consists in modeling the diffraction profiles by analytical functions in order to characterize the microstructure of the powders. During fitting procedure, the background and peak profiles for all phases are evaluated.

The morphology of the powders was followed by scanning electron microscopy (SEM) (Model: JEOL JSM-6360) equipped with a thermo electron corporation energy dispersive X-ray detector (EDS) for compositional chemical analysis. The thermal analysis of the milled powders was made by DSC using a Perkin–Elmer DSC 7, were carried out from 30 °C to 600 °C in continuous heating mode (10 °C/min) under a pure argon atmosphere. The magnetic properties was identified in a vibratory sample magnetometer (VSM) at 300k in an external field up to 10KOe such as the intrinsic coercivity (H_{CI}) and the saturation magnetization (M_S) are discussed as a function of milling time.

The technique of Mössbauer spectroscopy is widely used to investigate the magnetic properties and hyperfine interaction, the Mössbauer spectra measurement was done in the transmission mode with ^{57}Co diffused into Rh matrix as the source moving with constant acceleration. The spectrometer (Wissel) was calibrated by means of a standard α–Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The samples were measured at room temperature. The fitting of the spectra was performed with the help of the NORMOS program using Lorentzian profiles.

3. 1 Scanning microscopy and analyses

The morphological evolution of the $Fe_{50}Se_{50}$ powder particles as a function of the milling time is shown in Fig1. As can observed a change in the shape of the particles because of the repetition of the phenomena of fracture and welding during milling, for un-milled powders, the shapes are identical, some particles one is a form of spheres irregular. At 3h of milling, we see the appearance of flattened forma and large particle, which shows the phenomenon of welding, is the dominant. In addition, some with a lamellar structure formed of alternating arrangement of Fe and Se layers. During milling and under the effect of repeated shocks between the particles and balls-balls and the inner wall of the vial, the lamellar structure is destroyed and refined and becomes small particles with different sizes depending on the time of milling and the power of shocks.

After 6 hours of milling, the morphology of the powders looks small and homogeneous in size, we continue milling, the powders are subjected to repeated flattening, fracturing, and re-welding, and the particles will undergo more and more plastic deformation, which leads to a change in their morphology.

For all time of milling 12h at 39h, the milled powders show an agglomeration of the particles and fine particles with irregular contours or not homogeneous but with a size distribution, the balance between cold welding and fracturing among the powders is responsible for morphological changes that occur in them.

EDS analysis in Fig 2, shows energy peaks correspond to the elements in the sample Se and Fe, they are narrow and strong the ratio 32.79: 29.86 and 33.37: 32.27 for 6h and 39h the milling respectively shows the homogeneity of the composition $Fe_{50}Se_{50}$. The EDS measurement reflect that no contamination by milling tools and the presence of carbon due to the sample holder of the device. The oxygen present only on the surface, not up to the reaction with Se or Fe.

3.2 X-Ray diffraction and analyses

The structural evolution of the powders $Fe_{50}Se_{50}$ during milling process has been investigated by XRD. Fig 3 shows the X-ray diffraction patterns of samples at different milling times.

For powders un-milled we distinguish the peaks of Bragg corresponding the crystalline structures of iron $\alpha - Fe$ (Ref. Code 00-006-0696) and selenium trigonal (Ref Code 00-006-0362). The peaks of selenium disappeared at 3h of milling, from the XRD analysis we can state that part of the Se is now amorphous and the rest of the selenium is reacted with iron and the β-FeSe phase with hexagonal (*space group P63/mmc*) NiAs type nanostructured structure is formed. Likewise, the peaks of iron phase are broadened and their intensity is reduced. For the powder milled 6 hours, we distinguish the evolution of the peaks of the β-FeSe phase, and the progress of milling above 6h at 12 and 24h causes a broadening and decrease intensity of the peaks, usually indicates the reduction of crystallite size (L) and increase of microstrain deformation (σ).

During the development of system iron selenide, many phases can be formed, according to Okamoto [20] the FeSe alloys system can structure in eleven crystalline different phases that complicates the study of their structure after elaboration.

And the new diffraction peaks for powder milled at 39h indexed to α-FeSe phase nanostructured with tetragonal structure PbO-like (*space groupP4nmm*), the emergence the α-FeSe, explain the transition or decomposition some β-FeSe to α-FeSe, the phase transition during mechanical allowing can be explained by the changes of Gibbs free energy. [21]. In addition, it is noted that the tetragonal phase is formed at higher temperatures, by comparison of the formation temperature of the hexagonal phase.

According to J-C. Grivel et al [22], the formation β-FeSe phase from Fe and Se involves the successive formation of different phase intermediate products and β-FeSe transforms into $\delta-$FeSe at ~500°C.

The tetragonal α-FeSe phase type PbO [23-24] mentioned by some others researchers β-FeSe [25-27] represents an interesting type of material whose potential has been proven in many fields because of its electrochemical properties [28] and the magnetic properties [29] significantly the discovery of its superconductivity [23] generated more and more attention for the preparation and the study of properties of this phase.

R.A.et al [30] developed FeSe system by chemical vapor deposition method; the crystalline structures formed are the tetragonal and hexagonal superconducting phases in agreement with our results found by XRD.

X-ray diffraction (XRD) pattern analysis is not applied only for the identification of crystalline structures, but also to determine the microstructural parameters of nanostructured materials. Fig 4 shows the Rietveld refinements of the experimental spectra of powders un-milled, has been made by introducing two phases, Fe (Ref Code 00-006-0696) with a lattice parameter a = 0.2865nm) and Se trigonal (Ref.Code00-006-0362 with lattice parameter a = 0.4355nm and c = 0.4948nm).

For milling times 3h at 6h, the appearance or disappearance of peaks, due to the emergence of new phases, which indicate the interdiffusion between Fe and Se, the best Rietveld refinements (Fig 5) is obtained by amorphous-like Se phase, nanocrystalline Fe, and β-FeSe hexagonal NiAs type structure. For 39 h of milling the Rietveld refinement (Fig 6) is realized with two nanostructured phases hexagonal β-FeSe and $\alpha -$ FeSe tetragonal and also the nanocrystalline Fe. Because of the widening of the diffraction spectra and the decrease of their X-ray intensity with the increase of milling time which to an explanation by the reduction of the size of the crystalline size and the increase of the micro-deformation, for all the Rietveld refinement of spectra we used the model Popa rules.

The best Rietveld refinement of mixtures $Fe_{50}Se_{50}$, allowed us to well estimated the lattice parameters, average crystallite size <L>, microstrains ($<\sigma^2>^{1/2}$) and relative fraction of phases formed as a function of the milling, and (Table 1) grouped all the parameters that are deduced from the refinement. N. Chen et al [31], developed the tetragonal phase α-FeSe by solid -state reaction, with a = b = 3,772Å and b = 5,522 Å according with our results.

S.B. Harris et al [32], are found that the two phases FeSe tetragonal and hexagonal are grown simultaneously. S. Zhang et al [33], they found that the growth of the phase α-FeSe tetragonal, accompanied by the presence of the structure β-FeSe hexagonal.

The average crystallites size <L> decreases rapidly during the first hours of milling, and to reach a value of 25 nm after 39 hours of milling for the $\alpha - Fe$. Thus, the average size of the crystallite obtained by MA depends on the milling conditions, namely: the type of high-energy ball mill, the number and the diameter of the balls, the mass ratio of powders / balls and the milling intensity.

On the other hand, the microstrain average ($\langle\sigma^2\rangle^{1/2}$) vary in the same way as the size of the crystallite but inversely: they increase rapidly during the first hours of milling and stabilize around a stationary value of the order of (0.9 ± 0.1%).

3.3 Mössbauer Spectroscopy

The Mössbauer spectra measurement was done in the transmission mode with^{57}Cothe room temperature. The fitting of the spectra was performed with the help of the NORMOS program [34] using Lorentzian profiles. Mössbauer spectra of samples $Fe_{50}Se_{50}$ at different milling time are shown in (Fig .7). For all milling times 3 h at 24 h, the Mössbauer spectra showing two components, a sextet corresponds the $\alpha - Fe$ (sub spectrum 1 – sextet) with a mean hyperfine field B_{hf}, equal 33T, sextet intensity decreases with increasing milling time, the other component is a doublet which is paramagnetic at room temperature with isomer shift $\delta =$ 0.43 at 0.46 mm/s, are attributed to phase β-FeSe (sub spectrum 2 –doublet) [33], their intensity increases with increase milling time, in according with the work of A. Sklyarova, et al [35].

For sample milled at 39h, Mössbauer spectra contains tow doublets (sub spectrum 2and sub spectrum 3), and one sextet (sub spectrum 1 –sextet), that the second doublet corresponding the tetragonal phase α-FeSe with isomer shift δ=0.54mm/s.

A. Błachowski et al [36], are found tetragonal α-FeSe structure by applying direct reaction between Fe and Se (in stoichiometric $Fe_{1.04}Se$). The study by Mössbauer spectroscopy at different temperature shows that the isomer shift δ is varied from 0.5476 (120k) to 0.5640 (4.2k), these results are in agreement with what we found.

The work of Y. Mizuguchi et al [37], Mössbauer spectra analyses shows the paramagnetic behavior of the tetragonal phase FeSe, with the doublet of(isomer shift; δ or IS = 0.5380mm / s). The appearance of superparamagnetic, owing to formation of phases nanocrystallite, in good agreement with the calculations from the XRD. The hyperfine parameters of all phases determined from Mössbauer spectra (site or sub spectrum, isomer shift IS, hyperfine field B_{hf}, quadrupole splitting, and relative area) are given in (Table II).The relative fraction of the iron phase decreased by increasing the milling time, accompanied by the growth of the formed phase, by interdiffusion between elements Fe and Se.

3.4 Magnetization measurements

The variation in the magnetic proprieties usually originate from the structure, microstructure and they, are attributed to the important fraction atoms of atoms residing in the interfaces and / or grain boundaries, linking single-domain crystallites [38].

The magnetic hysteresis loops, taken at 300 K, for samples collected after 6h, 12h, 24h and 39 h of milling are presented in (Fig 8). From 6 up to 12h of milling, all of them have similar shapes, the sigmoidal hysteresis cycles are usually observed in nanostructured powders with short magnetic domains. This is owing to the presence of structural distortions insides particles. The small cycles hysteresis losses de proprieties generally desired in soft magnetic materials. The intrinsic coercivity (H_{CI}) values of the $Fe_{50}Se_{50}$ powders were measured at various milling. Fig 9 shows the changes in the (H_{CI}) as a function of milling time. As can be seen, (H_{CI}) increases with increasing milling time, the (H_{CI}) gradually increased with increasing mechanical alloying and peaked at ~4.38 ± 0.2ka/m. Increasing is maybe due to the decreasing crystallite and particle size, increasing lattice strain and redistribution of Fe and Se elements to facilitate phase change(s) during alloy formation. Fig 10: shows the variation of the saturation magnetization as a function of milling time, it is observed a monotonic decrease of (M_S) from 0. 85097 to 0. 41530 emu/g at 39 h of milling.

Recently T. Ashokkumar et al [39] in a study of an FeNi alloy obtained by ball milling have shown that the saturation of magnetization (M_S) is dependent on the crystallite size and particle size. A. Rathi et al [40], they showed that the milling under argon atmosphere appeared to have a stronger influence on the saturation magnetization than the milling media.

3. 5 DSC Measurements.

Fig.11shows the DSC thermograms of powders milled at 3,6, 12 and 39hdetermined by using heating rate 10°C/min. the exothermic peaks located at 98 -99°C for powders milled 3h and 6h respectively, that correspond to the crystallization of amorphous selenium produced by the milling process. The formation of the amorphous phase of selenium in the $Fe_{50}Se_{50}$ mixture was confirmed by X-ray diffraction. This exothermic peak was also observed in the results of A. Chebli et al. [41]; however, the endothermic peak found at 54 - 55 °C is attributed to the glass transition of selenium (T_g), in agreement with the published literature [42]. Therefore, the peaks located at 150°C and 280°C for sample milled 3h represent the structural relaxation of β-FeSe hexagonal and $\alpha-$Fe nanostructured [41], confirming XRD results. The DSC curves also show an endothermic peak, at 221-224°C, that corresponds to the selenium melting temperature; in close agreement with the temperature of the selenium, 217°C. The same phenomena have been found by G. Liu et al [43], showing the mixture of FeSe and $FeSe_{0.7}Te_{0.3}$, the emergence of an endothermic peak at temperatures 217-225°C. At 6h of milling, the exothermic stress relaxation process does not appear. This effect is probably due to the stress release associated to the amorphous phase disappearance (between 3 and 6h of milling the amorphous Se phase percentage is reduced from 20 to 4 at%).

For the milling time 39h, the DSC curve shows, an exothermic peak at 368 °C, that is attributed to the tetragonal FeSe phase, in agreement with the results obtained by S. Zhang et al. [44]. The endothermic peak at 480 and 482°C, for milling time 12h and 39h respectively, is related to decomposition of the β-FeSe phase. The DSC curve at 6 h of milling shows, a broad endothermic peak at 520 °C, probably due to a solid-state transformation (β-FeSe transform to $\delta -$FeSe) [12, 22]. The results obtained by the thermal analysis are consistent with those obtained by XRD and Mössbauer spectroscopy

4 Conclusions

The morphology, structure, thermal, magnetic and hyperfine proprieties of the iron selenide $Fe_{50}Se_{50}$ powders obtained by mechanical allowing have been studied by means of X-ray diffraction, scanning microscopy electronic coupled by microanalysis (EDX), scanning calorimetry, vibration scanning manometer and Mössbauer spectroscopy, the mechanical allowing of elemental Fe and Se powders in High-energy in composition $Fe_{50}Se_{50}$ resulted in formation nanocrystalline alloys. The Rietveld refinement of XRD patterns for powders form 3 at 6h indicates Fe nanostructured, β-FeSe and Se amorphous. For 39h, the XRD reveals FeSe tetragonal phase.

MS confirmed the coexistence of two phases, the tetragonal FeSe phase and the hexagonal phase with paramagnetic behaviour in $Fe_{50}Se_{50}$ powders synthesized by high-energy mechanical alloy. The DSC thermograms show several peaks endothermic and exothermic, corresponding to glass transition, crystallization, melting and phases relaxation. The results extract from XRD, DSC and MS are in very good mutual agreement.

Acknowledgements

Financial support from High School of Technological Education (ENSET) –Skikda is acknowledged.

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Figures captions:

Fig. 1. SEM micrographs of $Fe_{50}Se_{50}$ powders prepared by mechanical alloying before and after different milling times.

Fig2. EDS microanalysis corresponding to 0, 6, and 39h milling.

Fig. 3: XRD patterns of the $Fe_{50}Se_{50}$powders milled for various times.

Fig 4: Rietveld refinement of the XRD of powders $Fe_{50}Se_{50}$un-milled experimental (dots) and calculated (full line) patterns are shown, difference is given below (Gof=1.11)

Fig 5: Rietveld refinement of the XRD of powders $Fe_{50}Se_{50}$milled 3h and 6h experimental (dots) and calculated (full line) patterns are shown, difference is given below (Gof=1.13)

Fig 6: Rietveld refinement of the XRD of powders $Fe_{50}Se_{50}$milled 39h experimental (dots) and calculated (full line) patterns are shown, difference is given below (Gof=1.13).

Fig. 7: Mössbauer spectra of $Fe_{50}Se_{50}$ powder mixtures milled for 3h ,6h 12 h and 39h

Fig 8: hysteresis loop of $Fe_{50}Se_{50}$ samples milled for 3;6,12,24 and 39h

Fig 9: Plots of saturation magnetization (M_S) at various milling times of $Fe_{50}Se_{50}$ powders

Fig 10: Plots of intrinsic coercivity (H_{CI}) at various milling times of $Fe_{50}Se_{50}$ powders

Fig 11: DSC curves of $Fe_{50}Se_{50}$ powder mixtures milled for 3h, 6h 12 h and 39h

Tables captions:

Table. 1. Lattice parameters, average crystallite size <*L*>, microstrains ($<\sigma^2>^{1/2}$) and relative fraction of phases as a function of the milling.

Table. 2. Mössbauer parameters as a function of milling time for mixture $Fe_{50}Se_{50}$