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Structural and magnetic properties of nanocrystalline NiFeCuMo powders produced by wet mechanical alloying

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ABSTRACT

The NiFeCuMo nanocrystalline soft magnetic powders were successfully obtained by wet mechanical alloying route in a planetary ball mill using benzene (C_6H_6) as process control agent (PCA). The milling time used was ranging from 2 up to 20 h. The synthesis conditions and alloy formation have been investigated by X-ray and neutron diffraction as well as their influence on the intrinsic physical properties. Nanometer scale (≈10 nm) crystallites were obtained. A decrease of the samples magnetization has been observed and attributed to the stresses induced during the milling and to the benzene adsorbed on the powders surface. Differential scanning calorimetry investigation shows the presence of an exothermic peak related to the presence of benzene. The adsorbed benzene, internal stresses and crystalline defects removal took place during the heat treatment at 350 °C for 4 h, leading to an improvement of the powders magnetization.

1. Introduction

The Ni–Fe alloys are known for about a century, but they are still widely studied for both fundamental properties and applications. These alloys are intensively used in electrical and electronic devices for their excellent soft magnetic properties. Fe–Ni alloys around the Permalloy composition and Fe–Ni–Mo–(X) alloys, namely Supermalloy, are well known for their high performance as soft magnetic materials. The Permalloy properties can be improved by alloying with other elements such as Cr, Mo, Mn, Cu, Co, etc. [1]. The 77Ni14Fe5Cu4Mo (wt.%) Supermalloy alloy is well known for its high performance as soft magnetic material. It is characterized by high permeability, and low coercivity.

The soft magnetic nanocrystalline materials, discovered by Yoshizawa et al. [2] in 1988 and explained by Herzer [3], have simultaneously low coercivity and high permeability. There is the possibility to combine the interesting properties of the nanocrystalline materials with the high soft magnetic properties of the Ni–Fe alloys. Due to the capacity of mechanical alloying (MA) to obtain nanocrystalline structures, this technique has attracted more and more attention in the last decades in producing nanocrystalline/nanostructured soft magnetic materials.

Mechanical alloying is a versatile technique for preparation of general alloys or composite materials with desired microstructures including solid solutions with extended solubility limits, nanocrystalline and amorphous alloys, and novel crystalline or quasicrystalline phases [4,5]. This technique involves the synthesis of materials by high-energy ball milling, which implies repeated welding, fracturing, and rewelding of the elemental mixtures (or prealloyed powders, oxides, nitrides, etc.) in order to achieve alloys or composite materials. When two ductile materials are processed, there is always the risk that cold welding processes overcome the fracturing processes. In order to avoid this situation a process control agent (PCA) is used [6,7]. The PCAs (usually referred as lubricant or surfactant) are most common organic compounds (solids or liquids) which act as surface active agents. Together with PCA's benefits came also the risk of powders contamination during the milling process with atoms such as carbon, hydrogen and oxygen which are the most common components of the PCAs. The use of benzene as PCA reduces the formation of a thin layer of alloy on the milling media (balls and vial), the reduction of this barrier layer thickness could lead to increase the iron contamination by milling media for very long milling time.

In the last years, several studies devoted to Ni rich Ni–Fe powders [8–12] and Supermalloy powders [13–19] obtained by mechanical alloying were reported. Different mechanical alloying routes and a large variety of parameters have been used to obtain nanocrystalline Ni–Fe–(X) alloys. A review of the Ni–Fe, Ni–Fe–X–Y

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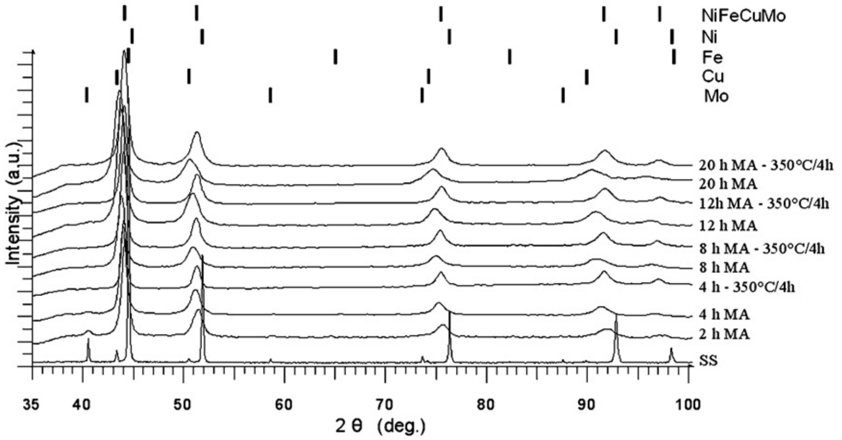


Fig. 1. X-ray diffraction patterns of the as-milled samples after 2, 4, 8, 12 and 20 h of milling and of the samples milled and subsequently annealed at 350 °C for 4 h. ss refers to the starting sample. For clarity, the spectra have been shifted vertically. The Bragg peak positions are shown on the top of the figure for the indicated phases.

magnetic nanocrystalline powders produced by MA techniques was presented in ref. [20]. The coercivity of Supermalloy powders was found to be dependent on the grain size and the domain wall width was determined to be about 15 nm [15]. A minimum in the spontaneous magnetization of Supermalloy vs. milling time was found and it shows that different processes are involved in the alloy formation [16,17]. For a longer milling time (16–32 h) a difference between the Curie temperatures of the Supermalloy MA powders recorded at heating and cooling was observed and it was attributed to the contamination of the milled powder with Fe from the milling media [18]. Also, Permalloy and Supermalloy powders were obtained by mechanical milling of microcrystalline ribbons and swarf respectively [21]. The mechanical milling of NiFeMo alloy causes the creation of Ni_3Fe phase and another phase with higher content of Fe with Curie temperature of 650 °C [21]. Concerning wet MA, ethanol [8] and toluene [9,10] were used as PCA, but the influence of PCA on the alloy formation and on its physical properties has not been discussed.

Our previous papers were focused on the results obtained on the nanocrystalline Ni_3Fe intermetallic compound [11,12] and nanocrystalline Supermalloy (NiFeMo, NiFeCuMo) obtained by dry mechanical alloying and subsequent annealing [13,16–19]. Following these earlier works, the present study is aimed to obtain the nanocrystalline Supermalloy of 77Ni14Fe5Cu4Mo (wt. %) composition by wet-milling (in benzene) and subsequent annealing. Also the benzene influence on alloy formation and spontaneous magnetization of samples is discussed.

2. Experimental

2.1. Sample synthesis

For 77Ni14Fe5Cu4Mo wt.% preparation, a mixture of 123-carbonil nickel, NC 100.24 iron, molybdenum powder produced by chemical reduction and copper powder was homogenized in a Turbula-type apparatus for 15 min. This mixture of elemental powders will be referred as starting sample (ss). The starting sample mixture has been milled in a planetary ball mill apparatus (Pulverizette 4) in argon atmosphere. Benzene was added after every 4 h of milling in order to avoid powders agglomeration. The chosen ball to powder ratio (BPR) was 8:1. After every 2 h of milling a quantity of powder was taken from the vials and characterized. Up to 20 h of wet milling has been performed in order to analyze the influence of the milling time on the structural and the magnetic properties of the alloy. The milled powders were subjected to an annealing at 350 °C for 4 h in vacuum in order to remove the internal stresses and to improve the solid state reaction leading to the new phase synthesis.

2.2. Structural investigation

A D5000 powder diffractometer was used for the X-ray diffraction (XRD) studies. The XRD patterns were recorded in the angular interval $2\theta = 35–100^\circ$ using monochromatic copper radiation Kα1 ($\lambda = 1.5406$ Å). The mean size of the crystallites was estimated from full-width-at-half maximum (FWHM) of the diffraction peaks according to Scherrer's formula. The experimental resolution of the diffractometer has been determined from the diffraction pattern of a reference sample [12].

Neutron powder diffraction patterns were measured at room temperature at the Institut Laue–Langevin (ILL)–Grenoble–France using the D1B instrument. The patterns were recorded in the angular range $2\theta = 30–100^\circ$ using a wavelength of 1.287 Å selected by the (3 1 1) Bragg reflection of a Ge monocromator, the take off angle being 44.2° in 2θ. The two theta step was 0.2° between each of the 400 $_3$He detection cells of the multidetector. The samples were loosely packed in vanadium cylindrical cans. Also, in this case, the instrument resolution was determined from the diffraction pattern of a reference sample.

The particles morphology and chemical homogeneity were investigated by scanning electron microscopy and X-ray microanalysis using a scanning electron microscope type Jeol-JSM 5600 LV, equipped with an EDX spectrometer (Oxford Instruments, Inca 200 soft).

The particle size distribution has been determined using a Laser Particle Size Analyzer (Fritsch Analysette 22-Nanotec), with an analysis field of 10 nm to 2000 μm.

2.3. Thermal and magnetic studies

Differential scanning calorimetry (DSC) investigations were performed using a NETZSCH–DSC 404S apparatus in the 25–700 °C temperature range. The heating speed was 10 °C/min. and the atmosphere used in order to avoid oxidation was Ar + 5% H_2.

The magnetization curves were recorded at room temperature by the extraction method in a continuous magnetic field of up to 8 T. The spontaneous magnetizations have been derived from an extrapolation to zero field of the magnetization obtained in the magnetic field higher than 4 T.

3. Results and discussion

The evolution of the diffractions pattern versus the synthesis conditions (milling time and annealing) is presented in Fig. 1 in order to illustrate the alloy formation induced by wet-milling and annealing. The XRD pattern of the starting sample is compared with the patterns obtained for the as-milled samples for different milling time and for the samples milled and subsequently annealed at 350 °C/4 h. The presence of the (1 1 0) Mo peak after 2 h of milling suggests that in order to obtain the alloy, longer milling time is required.

After 4 h of wet mechanical milling it is easy to observe the vanishing of all peaks corresponding to the elemental powders of Fe, Mo and Cu. This indicates the progressive alloying effect of the

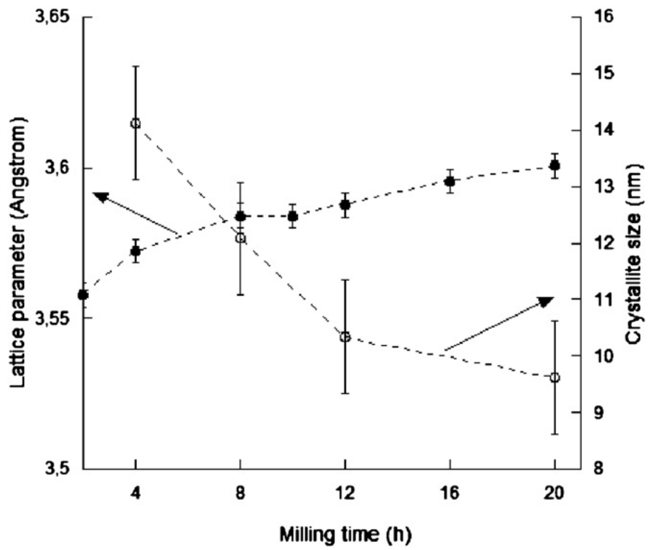


Fig. 2. Evolution of the lattice parameter and crystallites size for as milled samples and as milled and subsequently annealed samples of NiFeCuMo as function of milling time.

mechanical milled powders, since the Bragg reflections are close to the Supermalloy NiFeCuMo ones. Also a shift to the lower angle and the broadening of the Ni Bragg peaks of milled powders is observed after 2 h. This shift to the lower angles is due to the first-order internal stresses and also to the solid-state reaction of alloy formation induced by milling. The decreasing of the crystallites size and second-order internal stresses induced by milling, leads to a significant broadening of the diffraction peaks.

The heat treatment performed on the powders induced the following effects:

(i) a better definition (sharpening) of the X-ray diffraction maxima, as a consequence of the second-order internal stresses removal;
(ii) a shift to higher angles of the peaks due to the predominance of the first-order internal stresses removal effect comparative to the improvement of solid-state reaction of alloy formation effect.

The X-ray diffraction pattern obtained on NiFeCuMo powders after 4 h of mechanical alloying and subsequent annealing show the diffraction peaks corresponding to the bulk alloy of the same composition. We can conclude that the NiFeCuMo alloy is mainly formed after 4 h of wet mechanical alloying followed by 4 h of annealing at 350 °C. In a previous study, the formation of NiFeCuMo by dry mechanical milling was reported to occur after 8 h and subsequent annealing [17]. The wet milling and the milling conditions presented in this study seems to be more efficient for mechanical alloying of NiFeCuMo powders.

The mean size of the crystallites derived from X-ray diffraction pattern led to values ranging from 14 nm to 9 nm for 4 h and 20 h of milling respectively followed by a heat treatment at 350 °C/4 h (Fig. 2).

The lattice parameters for as milled powders of NiFeCuMo were also calculated from X-ray diffraction patterns and are presented as a function of milling time (Fig. 2). Our study shows that a continuous increase of the lattice parameter is observed from ~3.5577 Å for 2 h of milling to ~3.6006 Å for 20 h of milling respectively. The extension of lattice parameter can be explained as a consequence of the alloy formation. Indeed, considering the atomic radii of elements Ni (1.246 Å), Fe (1.274 Å), Cu (1.278 Å) and Mo (1.400 Å) [22] when Ni and Fe are substituted by Mo and Cu in the crystal structure an increase of lattice parameter is expected. Also, it should be considered that the lattice parameter values are influenced by the first-order internal stresses induced during milling.

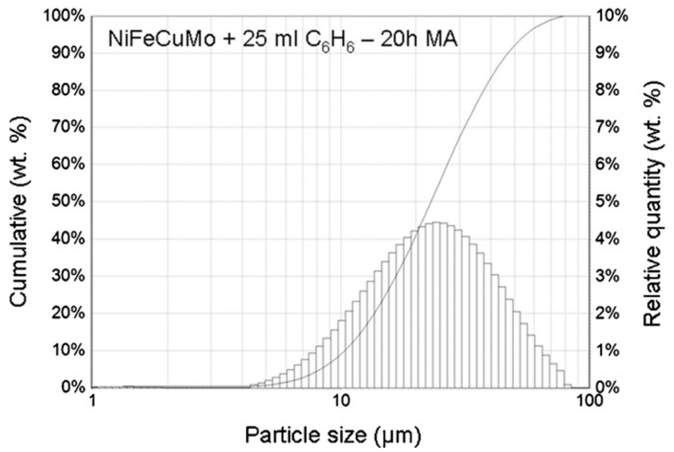


Fig. 3. Particles size distribution of a NiFeCuMo powder wet-milled for 20 h.

An example of the distribution curve of the particle size is given in Fig. 3. The particles size distribution curve of the powders milled for 20 h is shifted towards small particle size classes as can be seen in Fig. 3. This is probably, due to the use of benzene as surfactant and to the presence of molybdenum in the alloy which is a brittle element. This can decrease the malleability of the alloy. The particle size distribution of the 20 h milled powders shows that the median particles diameter (D_{50}) is about 22 μm (Fig. 3). The relatively high percentage (16%) of particles with size larger than 160 μm can be attributed to the agglomeration of smaller particles.

The SEM image of the particles confirms the fact that particles are in fact formed by agglomeration of micrometric and lower than micrometric size particles with polyhedral shape. This fact is clearly evidenced in Fig. 4 by the SEM image of wet-milled particles for 20 h. The X-ray microanalysis performed on the surface of a particle milled for 20 h shows that, within the experimental error limits, the elements distribution maps are very similar as it can be seen in Fig. 5. No cluster of any of these elements has been evidenced by EDX. This conclusion is true as long as the wet-milling duration is equal or superior to 4 h and confirms the analyses of the X-ray

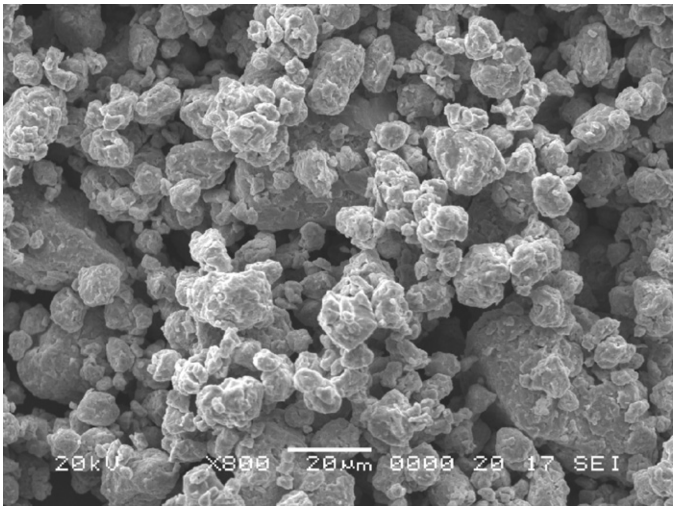
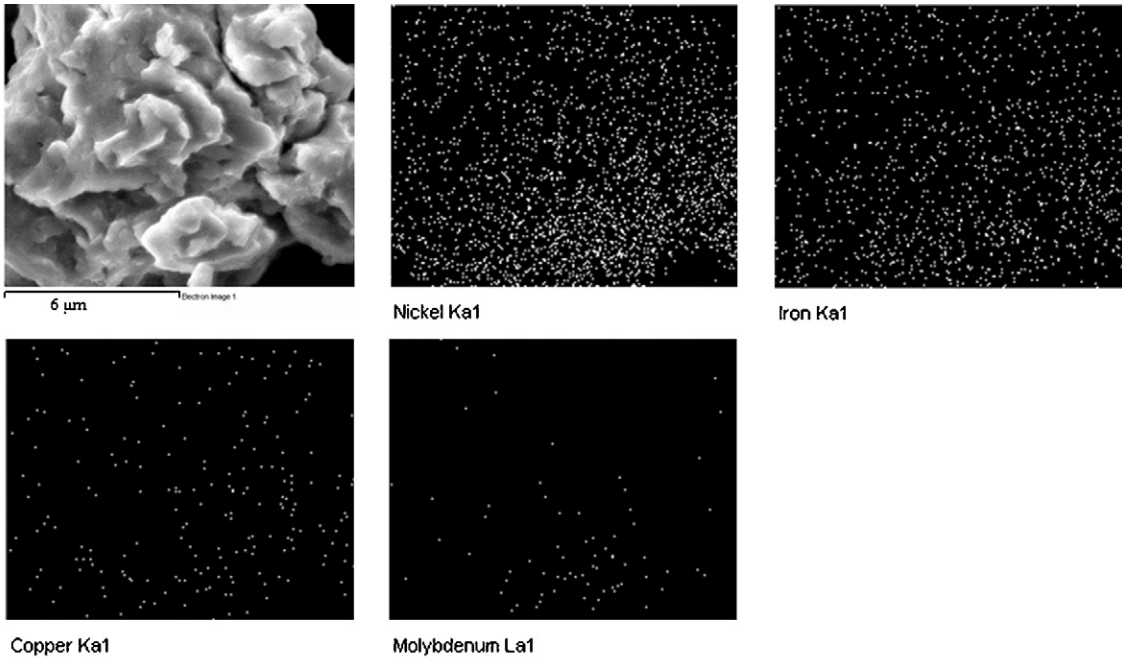


Fig. 4. SEM image of NiFeCuMo powders wet-milled 20 h. The powder is formed by agglomeration of micrometer and sub-micrometric size particles.



Nickel Ka1

Iron Ka1

Copper Ka1

Molybdenum La1

Fig. 5. Distribution maps for Ni, Fe, Cu and Mo obtained on surface of a particle wet milled for 20 h. The X-ray microanalysis performed on the SEM image presented in the upper left side (10,000×).

diffraction. Further, the concentration of Ni, Fe, Cu and Mo determined from energy-dispersive X-ray (EDX) spectroscopy analysis are consistent with the starting sample composition. There are a few remarks concerning the EDX investigation:

(i) the uniform distribution of the elements on the powder surface is not a proof of the alloy formation without an X-ray investigation;
(ii) at milling times shorter than 2 h, inhomogeneous distribution maps of elements was obtained. It is worth to precise that the distribution of the elements clearly depends on the milling time.

A contamination with iron of about 6% was evidenced by EDX investigation for the longer 20 h milled powder.

The influence of the NiFeCuMo alloy formation and the synthesis condition such as the milling time, and the annealing on the magnetic properties of the powders was also investigated. Typical magnetization curves of the synthesized samples are given in Fig. 6. The magnetization curves of the powders milled for 8 and 12 h and annealed at 350 °C/4 h are presented in Fig. 6. The spontaneous magnetizations of the starting sample and of the as cast sample were figured also for comparison.

The decrease of the spontaneous magnetization with increasing the milling time can be attributed to the following phenomena:

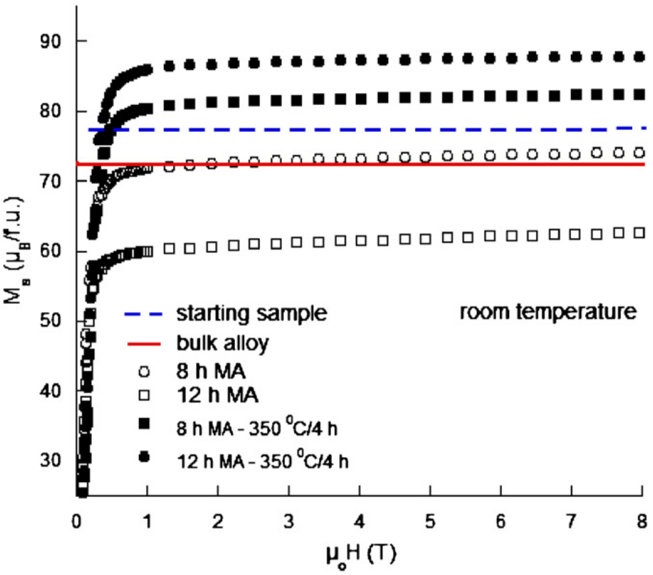


Fig. 6. Room temperature magnetizations curves for as-milled and for milled and subsequently annealed NiFeCuMo samples. The magnetization curves for starting sample and bulk as cast alloy are plotted for comparison.

(i) the alloy formation; as it can be seen from Fig. 6 the spontaneous magnetization of the starting sample is larger than the spontaneous magnetization of the as cast sample so the alloy formation will be accompanied by a reduction of the spontaneous magnetization value;
(ii) the increased density of defects introduced by milling, especially anti-site defects [19,20]; the anti-site defect appears when two atomic species involved in the structure occupy the “wrong” sublattices [4]. As we concluded from the X-ray diffraction pattern, the alloy is mainly formed after 4 h of milling and heat treatment at 350 °C for 4 h. After this period, the density of defects increases, leading probably to the increase of Fe–Fe neighbours pair in detriment of Fe–Ni one. It is well known that Fe atomic moment is amplified if it has a Ni atom as neighbour [23]. Consequently, if the number of Fe–Fe bonds increases, on can expect a decrease of the spontaneous magnetization;
(iii) the presence of a thin layer of benzene obviously non magnetic on the powders surface; On the other hand, due to the ductility of the milled powders and as a result of the fracturing–welding repetitive processes, the traces of benzene can be also included

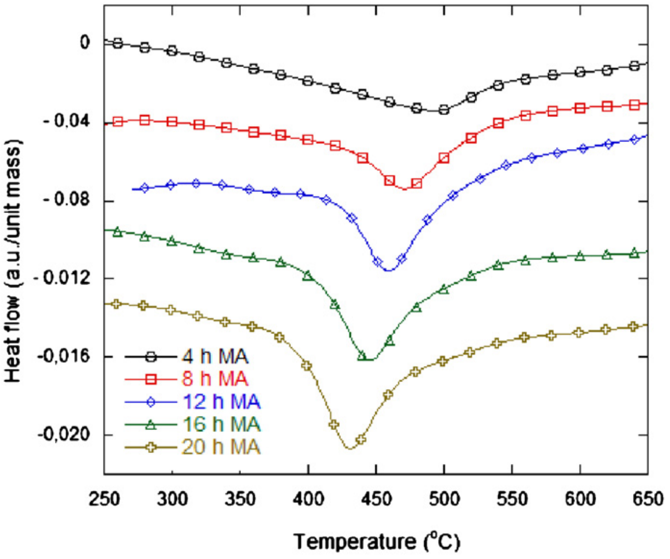


Fig. 7. DSC curves for the as-milled samples. For clarity, the curves are vertically shifted.

inside of agglomerated micrometer and sub-micrometric size particles.

This last hypothesis was confirmed by the DSC measurement since the presence of an exothermic peak for every wet-milled sample can be observed in Fig. 7. This peak was attributed to the benzene removal from the powders surface. The benzene elimination takes place as a consequence of the thermal activation and of the catalytic behaviour of Ni, Fe and Mo on the benzene decomposition [24,25]. A detailed analysis of the nature of the exothermic peak, linked to the presence of the benzene on the samples surface, will be published elsewhere [26].

Both an increase of the DSC exothermic peaks surface (by a factor 4) and a shift towards lower temperatures are observed upon increasing milling time (from 495 °C to 431 °C in the milling interval 4–20 h). The increase of the DSC peaks surface is connected with the increase of the benzene quantity adsorbed in the particles. The quantity of adsorbed benzene increases with increasing the milling time, as a consequence of the increasing of the particles specific surface. Among the different contribution to this exothermic peak, one can cite the presence of benzene first on the surface of the powder (which are known to present a large specific area), second from the interfaces and the grain boundaries, since the agglomerated particles are presenting many interfaces between particles and grain boundaries that may have part of the PCA. In addition, the catalytic power of the powders probably increases with the surface – this will lead to the shift of the peaks towards lower temperatures showing an easier removal/decomposition of the benzene for longer milling time.

Since each particle can be covered with a thin layer of benzene and also can contain the traces of the benzene inside (as a results of the fracturing–welding repetitive processes), it is correct to assume that an increasing error of sample mass considered for magnetic measurement will appear, as a consequence of increasing milling time. The magnetization per unit mass is obviously reduced comparison to conventional bulk alloy due to the presence of C_6H_6 on the surface and inside of the mechanically alloyed particles. As a consequence of this error in ferromagnetic mass considered for the magnetization calculation, we estimated an error in spontaneous magnetization of about 2–5%. We have observed a similar behaviour on the NiFeMo powders obtained by wet milling [19]. It is worth to note that as can be seen from Fig. 6, a heat treatment induces a significant increase of the magnetization of the powders samples. The evolution of the spontaneous magnetization with milling time for samples wet milled up to 20 h and eventually annealed is presented in Fig. 8.

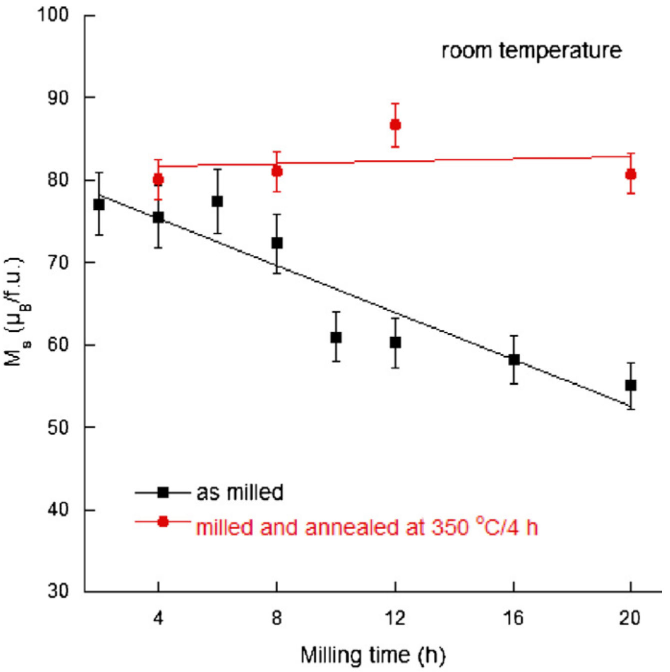


Fig. 8. Evolution of the room temperature spontaneous magnetization vs. milling time for as-milled and for milled and subsequently annealed powders at 350 °C for 4 h.

The influence of an annealing at 350 °C for 4 h leads to an increase of the spontaneous magnetization of the samples. The main two reasons for this evolution of the magnetization could be: (i) the elimination of defects that were introduced during the milling and (ii) the elimination of benzene adsorbed on the powders surface (the DSC curves of the annealed samples do not show the exothermic peaks). Thus, the value of the spontaneous magnetization for the annealed samples is larger than the value of the spontaneous magnetization of the bulk alloy. This can be explained by the contamination with iron of the mechanically alloyed powders, proved by EDX. It is worth to mention that no contamination was evidenced neither by X-ray diffraction (Fig. 1) nor by neutron diffraction (Fig. 9).

The neutron diffraction patterns benefited from very low incoherent scattering from Fe and Ni nuclei and from the constant neutron scattering length whereas X-rays are mainly surface sensitive, neutrons penetrate more into the bulk and one can thus probe deeper in matter. The neutron diffraction is known to have better sensitivity to the small quantities of impurity phases in particular constituted of elements having the largest neutron scattering length like Ni and Fe. Considering this high sensitivity together with the absence of any elementary iron peaks, we can conclude that all iron (including iron introduced by contamination during milling) and nickel have been alloyed in the processed powder even after only 4 h of milling. It has been reported that a contamination with 1–4% Fe should be expected in almost all dry milling experiments performed in steel milling medium [4]. Furthermore, when a dry milling experiment is performed, protective layers cover the milling media (balls and interior surface of the vial), minimizing the contamination. In the case of wet milling this protective layer is very thin and his protective capacity can be expected to be significantly reduced. A higher level of contamination with iron would then be expected in the wet milled

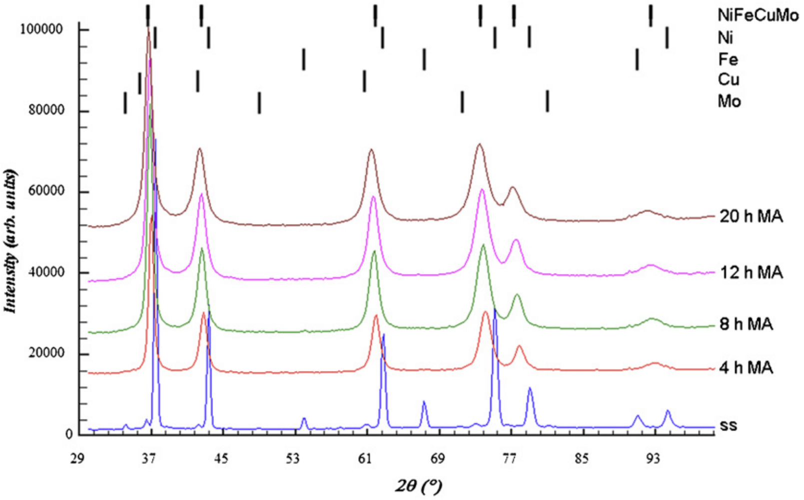


Fig. 9. Neutron diffraction patterns of the as-milled samples (4 h, 8 h, 12 h, and 20 h). ss refers to the starting sample which is a mixture of elemental powder. For clarity, the spectra have been shifted vertically. The position of the neutron diffraction Bragg peaks is shown for the indicated elements and the NiFeCuMo alloy.

powders compared to the same powders dry milled. No presence of α-Fe peaks is detected from the neutron diffraction, even at 20 h of milling, due to effect of mechanical alloying. So, the only proof for such increase of the iron content upon increasing milling time is the slightly higher Fe content as measured by X-ray microanalysis.

4. Conclusions

Nanocrystalline soft magnetic powders of NiFeCuMo were produced by wet milling in argon atmosphere. The X-ray diffraction shows that 4 h of milling and subsequent annealing at 350 °C for 4 h are required in order to achieve the alloy formation. The EDX investigation shows a uniform distribution of the elements Ni, Fe, Cu and Mo on the surface of the particles, but also an increase of the iron content for the longest milling time. A continuous decrease of the spontaneous magnetization per unit mass with milling time was observed. This was attributed to the alloy formation in the first 4 h of milling as well as to anti-site defects induced by milling in the NiFeCuMo alloy structure and to the presence of the benzene adsorbed on the powders surface. Annealing the powders at 350 °C for 4 h, leads to an improvement of the spontaneous magnetization as a consequence of the elimination of the adsorbed benzene and the removal of the internal stresses and crystalline defects induced by milling. A higher value of the spontaneous magnetization of the annealed samples comparison to the value corresponding to the bulk alloy was explained by iron contamination during the milling. In order to avoid or minimize the iron contamination and fully understand the mechanism of benzene elimination during the heat treatment, further experiments are in progress.

Acknowledgements

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