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$SmCo_5$/α-Fe nanocomposite material obtained by mechanical milling and annealing

V. POP[a,b*], O. ISNARD[b], I. CHICINAŞ[c], D. GIVORD[d], J. M. LE BRETON[e]
[a]*Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania*
[b]*Laboratoire de Cristallographie, CNRS, BP166, University J. Fourier, 38042 Grenoble, Cédex 9, France*
[c]*Materials Sciences and Technology Dept., Technical University of Cluj-Napoca, 103-105 Muncii ave., 400641 Cluj-Napoca, Romania*
[d]*Laboratoire de Magnétisme Louis Néel, CNRS, BP166, F-38042 Grenoble, Cédex 9, France*
[e]*Groupe de Physique des Matériaux, UMR CNRS 6634, Université de Rouen, 76801 Saint Etienne du Rouvray cedex, France*

The influence of the milling and annealing conditions on the structural and magnetic behaviour of mechanically-milled $SmCo_5$/α-Fe alloys has been studied. The structural evolution of the samples was followed by X-ray diffraction. The width of the hard magnetic phase diffraction peaks increases with milling time, then the peaks almost disappear for eight hours of milling. The characteristic diffractions peaks of the $SmCo_5$-type phase are restored during subsequent heat treatment. The coercive field, the remanent magnetisation and the degree of the exchange coupling between the hard magnetic grains and the soft α-Fe grains were studied by magnetic measurements, performed in magnetic fields up to 10 Tesla and temperatures between 4 K and 300 K as well as by Mössbauer spectrometry.

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1. Introduction

The research of nanocrystalline materials has undergone huge development in the last years. The interest in the study of nanocomposite hard magnetic materials begun in the year 1991 when it was shown that an intimate mixture of exchange-coupled magnetically hard nanograins ($Nd_2Fe_{14}B$) and magnetically soft nanograins (Fe_3B and/or α-Fe), could in principle lead to maximum energy products $(BH)_{max}$ higher than those achieved in the existing sintered magnets [1]. The low remanence normally expected for isotropic magnets, $M_r \approx M_s/2$ (where M_r is remanent magnetisation and M_s represents the saturation magnetisation), could be enhanced as an effect of the interfacial exchange coupling existing at the nanometer scale between the soft and hard grains [2, 3]. In addition to this so-called remanence enhancement effect, the coupling between hard and soft grains works against reversal of the soft grain magnetization. This is the so-called exchange-spring phenomenon [4-10]. As a result, spring magnets combine the high anisotropy of hard magnetic phases with the large magnetization which may be found in soft magnetic phases.

There are two basic parameters that characterize the structure of the nanostructured materials: the crystallites diameter, D, and the volume fraction of the nanocrystalline phases, V_{cr}. In hard magnetic nanocrystalline materials full or almost full crystallization is required. The critical dimension for the soft phase, below which the soft phase is rigidly coupled to the hard phase, is found to be roughly twice the width of the domain wall in the hard phase, δ_h [11]:

$$\delta_h = \pi\sqrt{A_h / K_h} \quad (1)$$

where A_h and K_h are the exchange and anisotropy constants of the hard magnetic phase, respectively. From an experimental point of view, a large reversible demagnetization curve in conjunction with a remanence reinforcement, $m_r > 0.5$ ($m_r = M_r/M_s$), may be considered as a criterion characterizing the presence of the exchange spring mechanism.

Several studies were performed in view of obtaining spring magnet type magnetic materials by mechanical alloying (MA) or mechanical milling (MM) [10, 12-18]. Since the discovery of intergrain exchange coupling magnetic material, mechanical alloying has become a widely used preparation technique to obtain nanocrystalline structures. Mechanical alloying involves the synthesis of materials by high-energy ball milling [19], in which elemental blends (or pre-alloyed powders) are milled to achieve alloys or composite materials. We concentrate on the mechanical milling technique to blend two different magnetic phases. In a previous study, mechanical milling was applied to synthesize $SmCo_5$/α-Fe magnetic nanocomposites starting from a mixture of two hours milled $SmCo_5$ and 20 weight percent of elemental iron [20]. The coercivity and the remanence were found to be dependent upon the process conditions and they could

be improved by adjusting the milling and/or heat treatment conditions (time and temperature). In the present study, we proceed to a systematic study of the exchange coupling which is induced by mixing a hard and a soft phase through mechanical milling. We tried to obtain exchange coupling between crystallites of these two phases, without any chemical reactions between the starting magnetic phases.

2. Experimental

MA or MM can be performed in air or under controlled atmosphere. Because the rare earth are very sensitive to the oxygen, for the preparation of rare-earth permanent magnetic materials it is necessary to carry out MM in inert atmosphere in order to avoid rare earth oxidation. Subsequent annealing of MM materials can be used to favour the formation of the desired phases. Also the annealing treatment diminishes the internal stresses induced by milling.

An alloy ingot with the $SmCo_5$ nominal composition was prepared by induction melting under argon atmosphere. The purity of the elements was 99.9%. The ingot was crushed into small pieces and it was subsequently mechanically milled for two hours in a high energy planetary mill under argon atmosphere. The $SmCo_5$ powder thus obtained was mixed with an iron powder (grain size below 40 μm) in a ratio of 80 ($SmCo_5$)/ 20 (Fe) weight percent. The mixture was mechanically milled under argon atmosphere using the above-mentioned high-energy planetary mill. Several milling times were used ranging from 2 to 8 hours. In order to investigate the influence of the annealing on the evolution of the Fe/$SmCo_5$ exchange coupling, samples made of milled powder were sealed inside evacuated silica tubes for further heat treatments. These treatments were performed at temperature ranging from 350 to 650 °C for different times ranging from 0.5 to 10 hours. Note that the chosen maximum annealing temperature of 650 °C is smaller than the recrystallisation temperature of the phases involved in the samples.

X-ray diffraction patterns were recorded in the angular range 2θ = 25 – 100°. For these experiments a SIEMENS D500 powder diffractometer with the $K_{\alpha 1}$ radiation of copper (λ = 1.5406 Å), was used. Scanning electron microscopy (SEM) and X-ray microanalysis studies were performed on a Jeol-JSM 5600 LV microscope equipped with an EDX spectrometer (Oxford Instruments Inca 200 soft). The magnetic ordering temperatures were determined with a Faraday type balance at heating and cooling rates of 5 K per minute. A sample of c.a. 50 to 100 mg was sealed under vacuum in a small silica tube in order to prevent oxidation of the sample during heating. The magnetization curves were recorded between 4 K and room temperature, using the so-called extraction method [21] in a DC magnetic field of up to 10 T.

^{57}Fe Mössbauer spectrometry experiments were performed at room temperature in transmission geometry, using a ^{57}Co source in a rhodium matrix. The Mössbauer spectra were fitted according to a least squares method [22].

3. Results and discussion

The progressive evolution of the structure and microstructure of $SmCo_5$/α-Fe samples at the different stages of the process was checked by X-ray diffraction. The X-ray diffraction patterns for samples milled for two, four, six and eight hours are presented in Fig. 1. These are given for as milled samples and for samples annealed at 450 °C for 0.5 hours. The X-ray pattern for the two hours milled $SmCo_5$ sample is also shown for comparison. As a consequence of the induced internal stresses and decrease of the crystallites dimensions, after two hours of milling of $SmCo_5$ the width of the diffraction peaks increases and the high angle peaks become progressively undetectable. For the composite $SmCo_5$/α-Fe samples, the Bragg peaks corresponding to $SmCo_5$ and α-Fe phases are broadened by milling but no additional peaks are evidenced. The diffraction peaks are better resolved after annealing. The annealing temperature being smaller than the recrystallisation temperature, this refinement of the structure and microstructure can be attributed to the decrease in the internal stresses, already resulting from annealing at moderate temperature. X-ray patterns for the 8 hours milled sample annealed at temperatures between 450 and 650 °C for 0.5 or 1.5 hours are presented in Fig. 2. A narrowing of the diffraction peak and an increase in their intensity are observed after annealing. A similar behaviour was obtained for all milling times. It is important to note that even after 8 hours of milling the X-ray patterns of all annealed samples show the presence of both starting phases: $SmCo_5$ and α-Fe. For high annealing temperature (600 and especially 650 °C) a decrease of the Fe characteristic peaks was observed. It can not be completely excluded that a small Fe amount enters into the hard phase. In Fig. 2, the presence of weak peaks which are characteristic of the Sm_2O_3 phase reveals that partial oxidation occurs during annealing at temperatures above 500 °C. This happens despite the fact that the milling and annealing at appropriate temperatures do not change the nature of the phases present in the studied samples. The mean size of the nanocrystallites was calculated from Full-Width-at-Half-Maximum FWHM of the diffraction peaks according to Scherrer's formula [23]. In order to do so, the resolution of the diffractometer has been determined from the diffraction pattern of a reference sample. Details of this procedure can be found elsewhere [24]. The grain size is derived to be of about 18 nm.

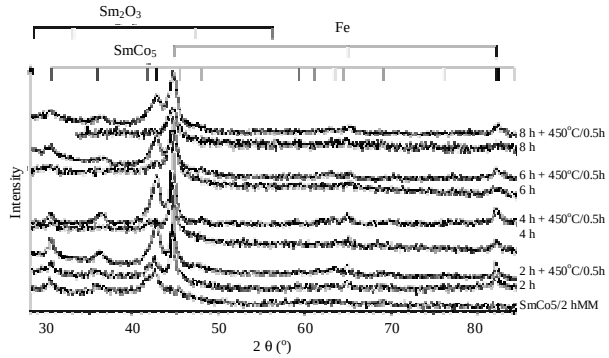


Fig. 1. X-ray diffraction patterns of the $SmCo_5$ +20% Fe composite samples for as milled samples (2, 4, 6 and 8 hours of milling) and samples annealed for 0.5 hours at 450 °C, compared to that of $SmCo_5$ milled for 2 hours.

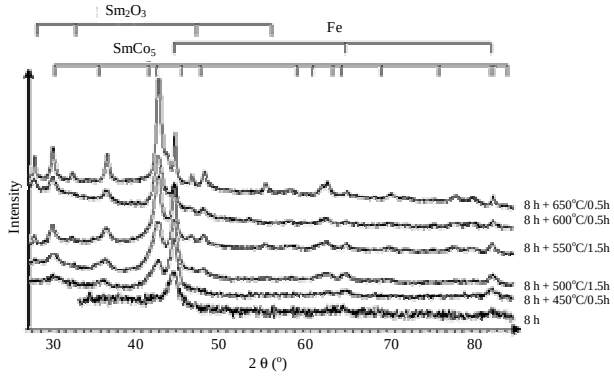
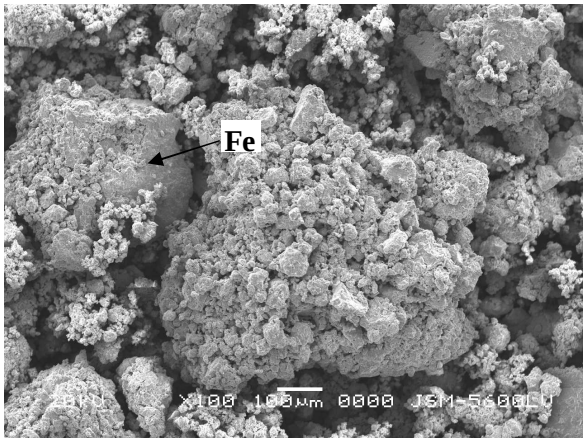


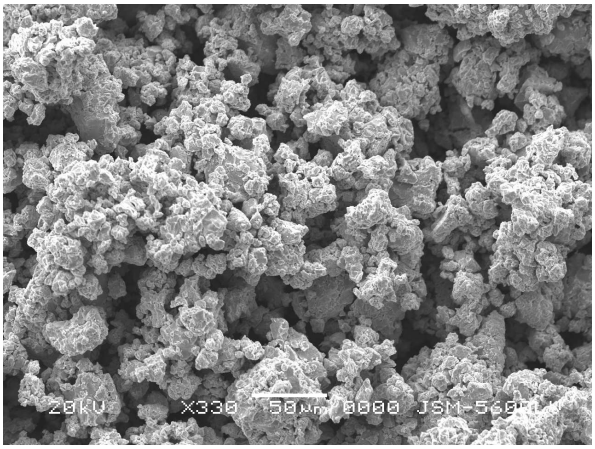
Fig. 2. X-ray diffraction patterns of the SmCo5 +20% Fe composite sample milled for 8 hours and annealed for the indicated time and temperature.

Scanning electron microscopy images of the 2 hours milled $SmCo_5$ hard phase revealed that the corresponding powder is composed of agglomerates (100-200 μm) and the agglomerate particles are formed by grains of about 5-10 μm [20]. The SEM images for $SmCo_5$+20wt%Fe composite powder milled for 2 hours and 8 hours are presented Fig. 3a and Fig. 3b respectively. After 2 hours of milling the $SmCo_5$+20wt%Fe composite powder is not homogeneous. For example in Fig. 3a a large iron particle with flaky shape obtained by MM is well evidenced. By contrast, after 8 hour of milling the particle dimensions are more homogeneous, Fig. 3b. Consequently we do not expect a good magnetic coupling by exchange interactions between hard and soft magnetic phases for 2 hours milled sample, whereas after 8 hours of milling a better coupling is expected a priori.

A quantitative evaluation of the chemical homogeneity for the agglomerates and grains was derived from the EDX measurements. In Figs. 4 and 5 we present the EDX results for two samples, milled for 2 hours and 8 hours respectively. The results presented in these figures show that after 2 hours of milling of the $SmCo_5$ +20 wt% Fe composites, the iron and cobalt distributions are not uniform, Fig. 4. We can see Co rich and especially Fe rich areas located under different grains. After 8 hours of milling, Fig. 5, the distributions of Co and Fe are very similar. This proves a good homogeneity of the mixing of two magnetic phases, $SmCo_5$ hard phase and soft α-Fe phase after 8 hours of milling. These conclusions are in agreement with the results of magnetic measurements discussed below.

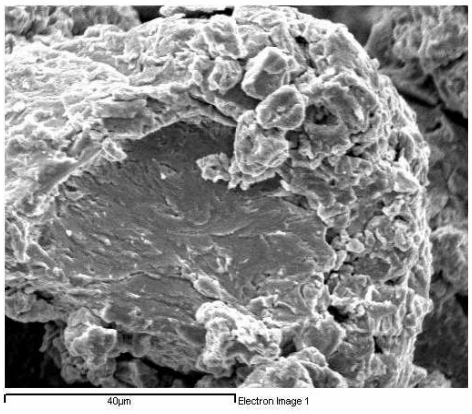


(a)

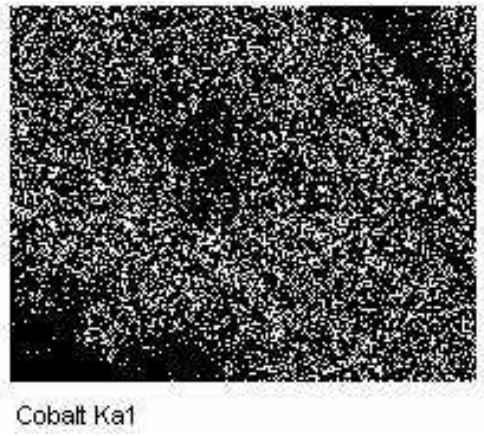


(b)

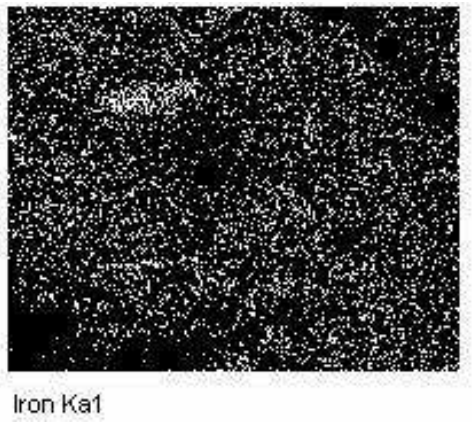
Fig. 3. SEM images for $SmCo_5$+20wt%Fe composite powder milled for 2 hours (a) and for 8 hours (b).



(a)

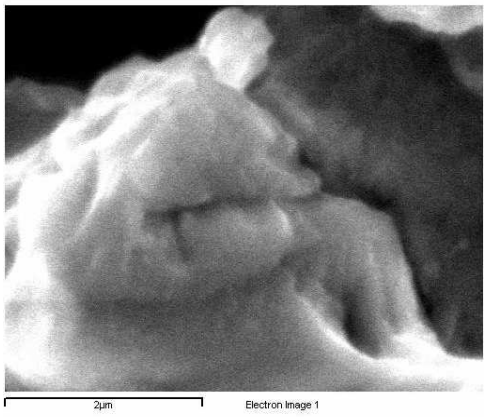


(b)

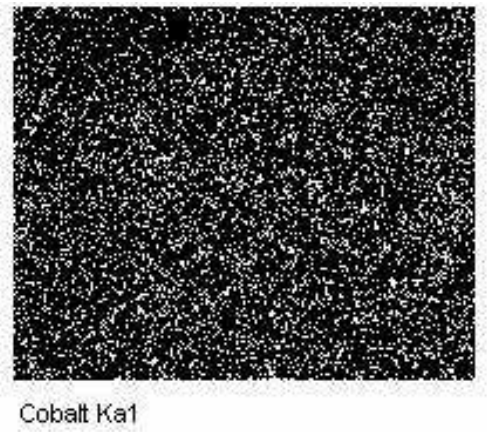


(c)

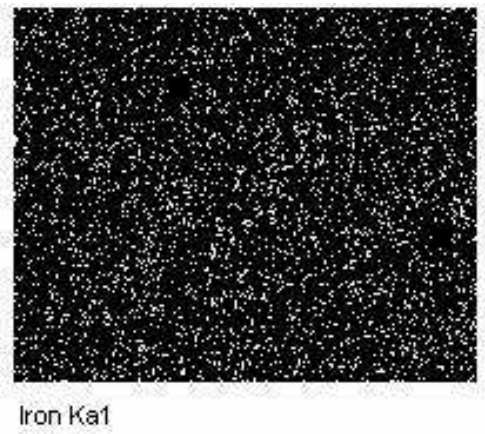
Fig. 4. EDX analysis for Co (b), Fe (c) and the image of the corresponding analysed area (a) for the 2 hours milled $SmCo_5$ +20% Fe composite.



(a)



(b)



(c)

Fig. 5. EDX analysis for Co (b), Fe (c) and the image of the corresponding analysed area (a) for the 8 hours milled $SmCo_5$ +20% Fe composite.

The isothermal magnetisation curves for as milled samples, recorded at room temperature, are plotted in Fig. 6. For comparison, the hysteresis curve of the hard phase $SmCo_5$ milled for 2 hours is also given. As expected for a hard phase, the 2 hours milled $SmCo_5$ compound exhibits

a broad hysteresis cycle with a magnetisation of about 84 emu/g under a field of 10 T. After mixing of the hard $SmCo_5$ phase with the Fe soft magnetic phase and milling, the saturation magnetisation is greatly enhanced up to about 128 emu/g, but the coercivity drops. Indeed, the coercivity decreases from 1.05 T for the 2 h milled $SmCo_5$ to 0.29-0.09 T for $SmCo_5$+20wt%Fe composite samples milled between 2 and 8 hours, Fig. 6. The greater coercivity of the 2 hours milled $SmCo_5$+20wt%Fe sample is actually related to the shape of the demagnetisation curve, which shows that the magnetic coupling between the hard and the soft magnetic phases is poor. This aspect is in agreement with the fact that after 2 hours of milling an inhomogeneous mixture of the two magnetic phases was shown to occur by SEM, Fig. 4. The evolution of the demagnetisation curves shows an improvement of the exchange coupling between Fe and $SmCo_5$ upon increasing milling time. This is associated with a decrease in the coercive field value. The better exchange coupling between two magnetic phases is given by the homogeneity of the long time milled samples, Fig. 5, and the nanosize of the crystallite deduced from X-ray diffraction patterns, Fig. 1 and 2. We also note the poor remanence value measured in samples after the milling process. The drop of the magnetic parameters can be partly overcome by a heat treatment at 450 °C for 0.5 hour, Fig. 7. The magnetic coupling is improved in all the samples. The coercive field increases up to five times. This heat treatment also enables the high magnetisation induced by Fe addition to be preserved. Furthermore the remanence is significantly increased up to 2.5 times. After annealing, the demagnetisation curve exhibits a smooth shape testifying for a good coupling between the hard $SmCo_5$ and soft Fe magnetic phases. The influence of the annealing on the shape of the hysteresis curve and magnetic characteristics for 8 hours milled $SmCo_5$+20 wt%Fe sample is presented in Fig. 8. The increasing of the annealing temperature or the annealing time improves the rectangularity of the hysteresis curve and consequently an increase of the coercivity and of the remanence is observed. The stronger influence was observed in the coercive field. The coercive field increases from 0.09T for the as milled sample up to 0.45, 0.71 or 0.81 Tesla for samples annealed at 450 °C/0.5 hours, 500 °C/1.5 hours or 650 °C/0.5 hours respectively. The remanence increases strongly up to 77 emu/g for the first heat treatment, 450 °C for 0.5 hours. The maximum value of 82 emu/g is obtained in samples annealed at 500 °C for 1.5 hours. Higher annealing temperature induced a slow decreasing of the remanent magnetisation up to 77 emu/g for the sample annealed at 650 °C for 0.5 hours. Also a little shoulder in the demagnetisation curves was observed for the sample milled 8 hours and annealed at 650 °C for 0.5 hours. This behaviour can be understood if one considers that annealing performed up to about 550-600 °C improves the exchange interactions between soft Fe and hard $SmCo_5$ nanocrystallites. For higher annealing temperatures some recrystallisation starts and chemical reaction between the two phases may occur, whereas the exchange coupling becomes poorer.

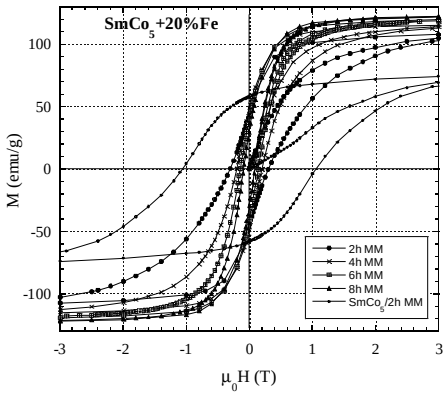


Fig. 6. Room temperature hysteresis cycles recorded for the $SmCo_5$ +20% Fe composite samples milled from 2 to 8 hours compared to that of the hard phase $SmCo_5$ milled for 2 hours.

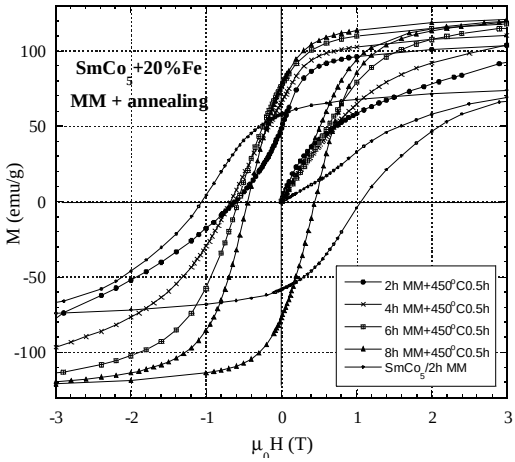


Fig. 7. Room temperature hysteresis cycles recorded for the $SmCo_5$ +20% Fe composite samples milled from 2 to 8 hours and annealed at 450 °C for 0.5 hours. The hysteresis curve of the hard phase $SmCo_5$ milled for 2 hours is given for comparison.

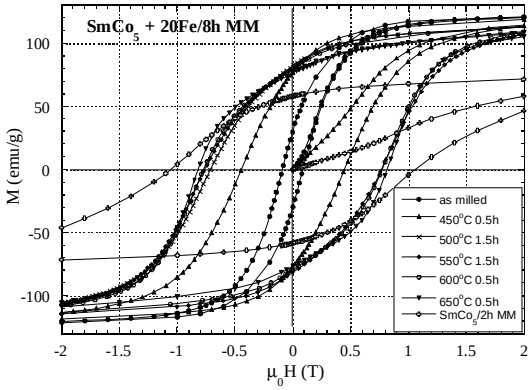


Fig. 8. Room temperature hysteresis cycles recorded for the $SmCo_5$ +20% Fe composite samples milled 8 hours and annealed compared to that of the hard phase $SmCo_5$ milled for 2 hours.

In order to study the influence of the milling and annealing on the physical properties, some samples were analysed by ^{57}Fe Mössbauer spectrometry at room temperature. The Mössbauer spectra of the $SmCo_5$+20wt%Fe composite obtained after 6 hours of milling and annealed at 450 °C for different times are presented in Fig. 9. All the experimental spectra are mainly composed of the magnetic contribution of α-Fe, in agreement with the presence of the soft α-Fe phase. However, a second contribution can also be observed, and must be taken into account for the fit. Consequently all the spectra were fitted with two contributions. The first contribution is composed of two magnetic components with hyperfine fields in the 33-36 T range, and is attributed to the α-Fe type phase. The fact that the hyperfine fields are higher than 33 T (this value corresponds to pure α-Fe) indicates that the phase contains Co atoms, and is thus denoted α-Fe(Co). The second contribution is composed of two magnetic components with hyperfine fields in the 26-33 T range. This contribution has a mean hyperfine field (about 27.7 T) which is reduced compared to that of pure α-Fe, and of the same order as the hyperfine field of iron-rare earth intermetallics. Thus, the second contribution could be attributed to Fe atoms that diffused in the $SmCo_5$ phase during milling, in so-called $Sm(Co,Fe)_5$ regions.

The fittings show that when the milling time increases, the relative intensity of the α-Fe(Co) contribution decreases, while that of the $Sm(Co,Fe)_5$ regions increases, as shown in Fig. 10. This indicates that increasing the milling time leads to an increase of the proportion of Fe atoms in the $Sm(Co,Fe)_5$ regions.

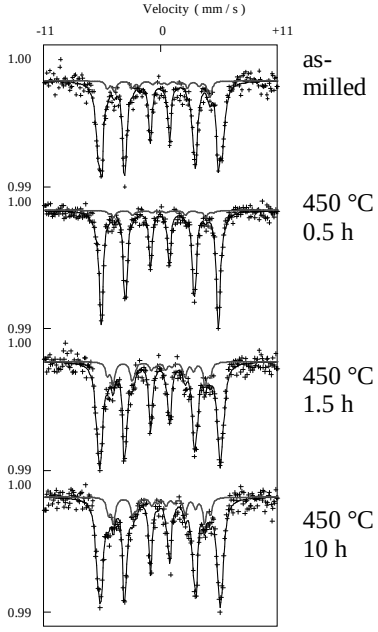


Fig. 9. Room temperature Mössbauer spectra of $SmCo_5$+20wt%Fe composite milled 6 hours and annealed at 450°C for different times. The minority contribution of the $Sm(Co,Fe)_5$ regions is displayed on top.

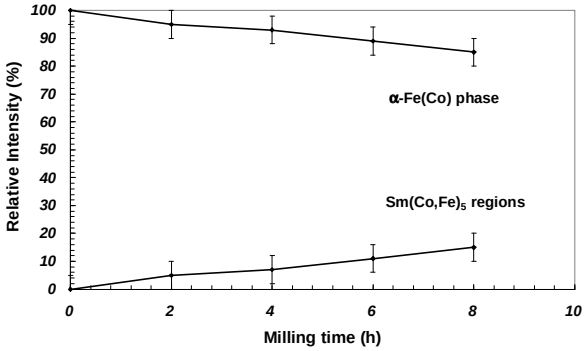


Fig. 10. Mössbauer relative intensities of the two contributions to the Mössbauer spectra of the $SmCo_5$+20wt%Fe composite as a function of the milling time.

It has to be noted that the mean hyperfine field of the α-Fe(Co) contribution increases with the milling time, in relation with an increase of the Co content in the phase. According to the hyperfine field values obtained from the fittings, the Co content is always less that 10%, increasing from 3% in the powder milled 2 hours to 9% in the powder milled for 8 hours. The results of the Mössbauer investigation of samples milled for 6 and 8 hours and annealed at 450 °C show that after annealing, the relative intensity of the supposed $Sm(Co,Fe)_5$ regions slightly increases up to a maximum value of about 27%. This result confirms that annealing at 450 °C induces a refinement of the microstructure, related to the increase of the exchange coupling between the soft and hard phases.

4. Conclusions

$SmCo_5$/α-Fe nanocomposite alloys have been obtained by mechanical milling process. The influence of the milling and annealing conditions on the structural and magnetic behaviour of mechanically-milled $SmCo_5$/α-Fe alloys has been studied. X-ray diffraction has enabled us to follow the structural evolution of the samples versus milling time and annealing conditions. The hard magnetic phase diffraction peaks are broadened with milling time, then the peaks almost disappear for eight hours of milling. The characteristic diffractions peaks of the $SmCo_5$-type phase are restored during subsequent heat treatment. The annealing induces a refinement of the structure and nanosize crystallites are obtained for the long milling time.

After mixing of the hard $SmCo_5$ phase with the Fe soft magnetic phase and milling, the saturation magnetisation is greatly enhanced up to about 128 emu/g but with a drop of the coercivity comparison with that of the starting $SmCo_5$ phase. This has been attributed to the poor exchange coupling between the hard and soft magnetic phases. Measurements of the hysteresis cycles show an improvement of the exchange coupling upon increasing milling time but the remanent magnetization remains poor. After annealing, the demagnetisation curve exhibits a

smooth shape testifying for a good coupling between the hard $SmCo_5$ and soft Fe magnetic phases. The increase of the annealing temperature or the annealing time improves the rectangularity of the hysteresis curve and leads to an improvement of both coercivity and remanence. According to Mössbauer spectrometry investigation, the mean hyperfine field of the soft α-Fe contribution increases with the milling time. This behaviour could be connected with an increase of the Co content in the α-Fe phase. Also, a contribution attributed to Fe atoms that diffused into the $SmCo_5$ phase during milling is evidenced in the Mössbauer spectra of both as-milled and annealed samples. An increase of the milling time leads to an increase of the proportion of Fe atoms in the so-called $Sm(Co,Fe)_5$ regions. In order to elucidate the above problems and to improve the exchange coupling between hard and soft magnetic phases, further study will be devoted to a systematic investigation of the evolution of the structure, microstructure, hysteresis behaviour and of the Mössbauer spectra versus both milling and annealing conditions.

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*Corresponding author: viorel@ phys.ubbcluj.ro