SmCo$_5$+20%Fe magnetic nanocomposites have been obtained by mechanical milling in a planetary mill and subsequent annealing. The influence of the milling and annealing conditions on the magnetic and structural behaviour of SmCo$_5$/α-Fe has been studied by X-ray diffraction, electron microscopy, magnetic measurements and Mössbauer spectrometry.

Key words: magnetic nanocomposite, inter phase exchange coupling, mechanical milling, spring magnets.

1. INTRODUCTION

The low remanence, normally expected for isotropic magnets, $M_r \leq M_s/2$ (where $M_r$ is the remanent magnetisation and $M_s$ represents the saturation magnetisation), could be enhanced by interfacial exchange coupling, between soft and hard magnetic phases at nanometer scale in the so called exchange-enhanced nanocomposites magnetic materials [1, 2]. It has been demonstrated [3–6] that the crystallite sizes of both phases, in particular the soft one, are important in determining remanence enhancement and coercivity. It was found that, the microstructure and the phase composition, of the nanocomposites ribbons based on R$_2$Fe$_{14}$B hard phase and Fe and Fe$_3$B soft phases, have a strong influence on the soft
phase hardening by exchange interactions [6]. The micromagnetic modelling and experimental investigations on recrystallised Nd$_3$Dy$_{1}$Fe$_{86}$Co$_{10}$B$_{20}$ amorphous rods evidenced the optimum microstructure for 15 min at 630°C devitrification [7]. The dependence of the macroscopic properties of the soft layer on the hard-layer magnetization and microstructure in exchange spring bilayers has been investigated and modelled using a Preisach-type two-dimensional model. This model was successfully applied in order to explain the dependence of the soft layer loop parameters on the hard layer magnetization [8]. The analytical calculations and the numerical micromagnetic simulations [9], show that the values of the critical nucleation and depinning fields, in composite exchange coupled spring systems, depend on the thickness of the layers and determine the shape of the corresponding hysteresis loop. The studies of different combinations of hard/soft layer compositions and thicknesses consisting of CoPt/(Fe-Co) or Sm$_2$Co$_7$/Fe, Co, or Ni) found that the dominant factors determining the interlayer exchange coupling are the exchange constant $A_h$ and anisotropy constant $K_h$ of the hard layer and the saturation magnetization $M_s$ is the essential parameter of the soft layer that governs the exchange interaction [10]. In exchange-spring magnets with temperature-induced interfacial intermixing, differences in the diffusion lengths of constituent elements typically lead to local compositional changes. In order to avoid this effect, it has been shown that in Sm–Co/Fe exchange-spring permanent magnets, adding an artificially created intermixed layer enhances the exchange coupling effectiveness without modifying the local composition of the Sm–Co layer [11]. Mechanical alloying/milling has been extensively applied to synthesize various metastable phases exhibiting exciting magnetic properties, including spring magnets [12–20]. The Mössbauer spectroscopy on SmCo$_5$/Fe nanocomposite obtained by mechanical milling show a partial alloying of Fe and Co. It has been found that the fractional volume of α-Fe(Co) solid solution tends to increase at the expense of the initial α-Fe phase upon progressive milling [18]. The coercive field of the magnetic nanocomposite increase for powders milled with surfactant [18]. An increasing of Co in α-Fe soft phase was shown also by Ito et al. [19] in (SmCo$_{1-x}$)Fe$_x$ powders obtained by mechanical milling and annealing. A maximum value of $(BH)_{max}$, 105.8 kJ/m$^3$, was obtained for the (SmCo$_3$)$_2$Fe$_{25}$ powder. Zhang et al have shown that the coercivity mechanisms of as-milled SmCo$_5$+α-Fe milled powders annealed at 550°C for 30 min are all controlled mainly by domain wall pinning [20].

The influence of the milling and annealing conditions on the magnetic inter-phase coupling of mechanically-milled SmCo$_5$ hard magnetic phase and α-Fe soft phase will be presented. By Mössbauer spectroscopy it was evidenced the existence of two main Fe contributions which results by milling: one of α-Fe and the second one of the Fe in SmCo$_5$ phase [14]. One question that needs to be addressed is whether the iron phase remains essentially pure after the milling and annealing and the evolution of Mössbauer spectra comes from Fe at the interface with hard phase
grains, or a progressive alloying of Fe with Co and of SmCo$_5$ with Fe occurs during these processes. In order to address this question, SEM, TEM and EDX studies of the microstructure are presented. Samples milled for 6 and 8 hours and annealed between 450 and 650°C, which gave the best hysteresis behaviour will be discussed. The structural, microstructural and magnetic studies will be taken into consideration in order to explain their magnetic behaviour.

2. EXPERIMENTAL DETAILS

An alloy ingot with the SmCo$_5$ nominal composition was prepared by induction melting under argon atmosphere. An excess of Sm was used in order to compensate the preferential evaporation of Sm during melting and the sensitivity of Sm to oxidation during milling and annealing. 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, whose grain size was below 40 µm, in a ratio of 80 (SmCo$_5$)/ 20 (Fe) weight percent. The mixture was mechanically milled under argon atmosphere using a high-energy planetary mill. 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 temperatures ranging from 450 to 650°C for 0.5 or 1.5 hours. Note that the chosen maximum annealing temperature of 650°C is smaller than the recrystallisation temperature of the phases involved.

X-ray diffraction patterns were recorded in the angular range 2θ = 25–100°. For these experiments a SIEMENS D500 powder diffractometer with the Kα1 radiation of copper (λ = 1.5406 Å), was used. Scanning electron microscopy (SEM) and X-ray microanalysis studies were performed on a Jeol-JSM 5800LV microscope equipped with an EDX spectrometer. Transmission electron microscopy was performed on a Hitachi HNAR-9000 TEM (accelerating voltage 300kV, Scherzer resolution 0.18 nm). The magnetisation curves were recorded at 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

As we showed before [14, 15], the SmCo$_5$+20 wt% α-Fe mechanically milled nanocomposite, milled for 6 or 8 hours and annealed at about 550°C present interesting magnetic properties, coercivity $\mu_0H_c = 0.81$ T and remanence $M_r = 82$ emu/g, given by
a good exchange coupling between SmCo$_5$ hard phase and $\alpha$-Fe soft phase. The physical behaviour of those two series of magnetic nanocomposites will be further analysed by supplementary microstructure studies. The X-ray diffraction patterns for 6 and 8 hours as-milled samples and for samples annealed at 600$^\circ$C for 30 minutes (6 h milled sample) and at 550$^\circ$C for 1.5 h (8 h milled sample) are presented in Figure 1. The X-ray pattern for SmCo$_5$ hard magnetic phase milled two hours 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$_5$ hard phase, the width of the diffraction peaks increases and the high angle peaks become progressively undetectable. For the composite SmCo$_5$/$\alpha$-Fe samples, the Bragg peaks corresponding to SmCo$_5$ and $\alpha$-Fe phases are also broadened by milling. The diffraction peaks are better resolved after annealing. The annealing temperature being smaller than the recrystallization temperature, this refinement of the structure and microstructure can be attributed to the decrease of the internal stresses. It is important to note that even after 8 hours of high energy milling the X-ray patterns of as-milled and annealed samples show the presence of both starting phases: SmCo$_5$ and $\alpha$-Fe. No additional peaks are evidenced. The diffraction peaks of the 8 h milled sample are larger than those of the 6 h milled sample, proving the decreasing of the crystallite dimension by milling. The mean sizes of the Fe nanocrystallites were calculated from Full-Width-at-Half-Maximum, FWHM, of the diffraction peaks according to Scherrer’s formula [23]. The grain size is derived to be of about 18 ($\pm$2) nm in the 8 h milled sample.

Fig. 1 – X-ray diffraction patterns of the SmCo$_5$ +20% Fe composite samples milled for 6 and 8h as milled and annealed at indicated temperature and time, compared to that of SmCo$_5$ milled for 2 hours.
The hysteresis curves for 6 h and 8 h as-milled samples and for samples annealed at 600°C for 30 minutes (6 h milled sample) and at 550°C for 1.5 h (8 h milled sample) are presented in Figure 2. For comparison, the hysteresis curve of the hard phase SmCo₅ milled for 2 hours is also given. A net improvement of the coercivity and of the remanence was obtained in annealed samples. The coercivity and remanence evolution versus milling time and annealing conditions (time, temperature) were discussed elsewhere [14]. The coercivity is higher for the 6 h milled sample annealed at 600°C for 30 minutes, 0.93 T, compared with 0.76 T for the 8 h milled sample annealed at 550°C. The remanence has an opposite behaviour, Mᵣ having a value of 0.75 emu/g and 0.89 emu/g for the 6 h and 8 h milled and annealed samples respectively. This behaviour can be explained by the improvement of the exchange coupling between soft and hard magnetic phases for long milling times. The stronger soft/hard magnetic coupling will increase the remanence by the contribution coming from the exchange enhanced soft magnetic phase. Obviously, this coupling will slightly decrease the coercivity of the hard phase. The characteristic features of interphase exchange coupling are well illustrated in the dM/dH vs. H curves, Figure 3. When the peak is thin and it is observed at high negative field, this corresponds to a narrow crystallite grain.

Fig. 2 – Hysteresis loops for the SmCo₅+20% Fe nanocomposites milled for 6 and 8 h as milled (open symbols) and annealed (filled symbols) at indicated temperature and time, measured at 300 K, compared to that of the SmCo₅ hard phase milled for 2h. The lines are guide for the eye.

Fig. 3 – Room temperature dM/dH versus H curves for SmCo₅+20% Fe nanocomposites milled for 6 and 8h as milled (open symbols) and annealed samples (filled symbols) at indicated temperature and time, calculated from M vs. H curves measured at 300 K. The lines are guide for the eye.
distribution and a stronger exchange coupling. The as milled composites present a maximum at very low field, given by a low coercivity for both phases, proving that the coercivity of the hard phase is destroyed by milling. The annealed samples present a maximum at rather high field, which bears witness to the occurrence of a significant coercivity. Since two distinct maxima are expected for uncoupled hard and soft phase mixture, the presence of only one maximum proves the good coupling between the hard and the soft phase. Consequently, the width of these dM/dH peaks can be interpreted as an estimation of the efficiency of hard/soft inter-phase exchange coupling: the narrower the peak the better the exchange coupling between the soft and hard phase. The large peaks and the long tails testify about the percentage of crystallites which are not well coupled by exchange to the hard phase. The little peak near zero field for 6 h milled and annealed sample proves that not all Fe crystallites are coupled by exchange. This behaviour could be due to the larger Fe crystallites. The curves for 8h milled and annealed samples in figure 3 testify that a great majority of the Fe crystallites are coupled by exchange with the hard phase. The significant width of this peak proves a wide range of crystallite dimensions, which present different degree of exchange coupling.

The room temperature Mössbauer spectra of the 6 and 8 h milled samples, as well as the ones of the samples milled for 8h and annealed at 450°C for 0.5 and 10 hour. The experimental data are represented by the crosses and the interpolated continuous line. The Mössbauer contribution of the Fe from Sm-(Co,Fe) phase is also displayed for each spectrum.
• the magnetic contribution of the α-Fe phase, with the possibility of milling and/or induced insertion of Co in Fe structure, named α-Fe(Co)
• a magnetic contribution attributed to Fe atoms in Sm-Co–rich regions, named Sm-(Co,Fe)
• a paramagnetic contribution attributed to some nanocrystallites with a superparamagnetic behaviour.

The comparison of the Mössbauer spectra of the 6 and 8 h milled samples shows that the intensity of the Sm-(Co,Fe) contribution (9% and 17% for the two samples, respectively) increases with the milling time. This indicates that as the milling time increases, the number of Fe atoms that diffuse in the Sm-Co-rich regions increases. Annealing at 450°C leads to a further increase of the intensity of the Sm-(Co,Fe) contribution (22% and 28% for 0.5 and 10 hours, respectively). Progressive increasing of the intensity of the Sm-(Co,Fe) contribution by increasing the milling time, can be presumably attributed to a replacement of Co by Fe in SmCo₅ phase. This interpretation has been confirmed by recent tomographic atom probe investigations [24].

Scanning electron microscopy images obtained with backscattered electrons signal of 6 and 8 h milled samples annealed at 600 and 550°C respectively are presented in Figure 5. We can mainly distinguish two phases represented by: a majority grey area on the black background and small white spots inside the grey regions. The grey phase is attributed to the SmCo₅/α-Fe composite and the white spots can be associated to isolated SmCo₅ particle not mixed in the composite. This assumption is sustained by the fact that the density and the surface of the white spots in 8 h milled samples are drastically reduced in comparison with the 6 h milled sample, Figure 5.

(a)                                                                      (b)
Fig. 5 – Room temperature scanning electron microscopy: a) image of 6 h milled samples annealed at 600°C, b) image of 8 h milled sample annealed at 550°C.
The EDX studies confirm this hypothesis. These chemical analyses of the grey region give the following atomic composition: ≈ 13.1% Sm, ≈ 60.9% Co and ≈ 26% Fe. Having in mind that SmCo₅ + 20 wt% α-Fe composite consists in 12.6 at % Sm, 62.9 at % Co and 24.5 at % Fe, we conclude that by milling, the Fe percentage increases as a consequence of the contamination with Fe from the bowls and the balls made of stainless steel. The EDX chemical analysis of the white region gives approximately the following atomic composition: 17.6% Sm, 80.3% Co and 2.1% Fe. The iron content of the white region should be attributed to a progressive alloying of SmCo₅ phase with Fe, as was suggested by Mössbauer study. The Co/Sm ratio is about 4.6 in both cases, white and grey regions. The discrepancy between the Co/Sm atomic ratio of 4.6 found by EDX measurements and the value of 5 presumed in SmCo₅ phase can be explain by the experimental errors and also by the excess of Sm quantity added in the bulk SmCo₅ alloys preparation.

The transmission electron microscopy observations on 6 hours milled samples annealed at 450 °C for 0.5 hours show the presence of nanocrystallites ranging from 5 to 15 nm, Figure 6. This result is in rather good agreement with the mean crystallite sizes deduced from X-ray diffraction measurements [14].

4. CONCLUSIONS

The influence of the milling and annealing conditions on the magnetic behaviour of mechanically-milled and annealed 80 wt% SmCo₅ + 20 wt% α-Fe spring-magnet composites have been studied by structural, microstructure, magnetic and Mössbauer spectroscopy studies. This research was focussed on 6 and 8 h milled samples, where the interphase exchange coupling is well realized by appropriate annealing. The demagnetization curve for SmCo₅/α-Fe nanocomposite
milled 6 or 8 h and annealed between 500 and 600°C exhibits a smooth shape testifying for a good coupling between the hard SmCo5 and soft Fe magnetic phases. A maximum value \((BH)_{\text{max}}\) of 84 kJ/m\(^3\) was obtained for SmCo5+20 wt% \(\alpha\)-Fe powders milled for 8 hour and annealed at 550°C for 1.5h. The \(dM/dH\) vs. \(H\) curves present mainly one peak for the optimum milled and annealed samples. This proves the existence of efficient exchange coupling between the soft and hard magnetic phases. The peak in the \(dM/dH\) curves for the optimal samples is rather large due to the particle size distribution. We consider that a narrower particle size distribution, near optimum size, would represent a valuable way to improve the interphase exchange interactions, which will result in a higher coercivity and a better remanence. The Mössbauer analysis shows that Fe/Co interdiffusion occurs during milling, interdiffusion that increases during annealing. EDX analysis, scanning and transmission electron microscopy support both the Fe diffusion in the SmCo5 phase and the Co diffusion in the \(\alpha\)-Fe phase, hypothesis initially inferred from Mössbauer spectroscopy.

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