

Hybrid approach to the synthesis of FePt / Fe₃B nanocomposite magnets

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Exchange coupling between alternatively dispersed hard and soft magnetic phases, gives rise to exchange spring magnets with enhanced energy product $(BH)_{\max}$ that are believed to represent a novel class of permanent magnets with improved properties. The synthesis of a hybrid nanocomposite system made of soft magnetic Fe₃B melt spun ribbon and hard magnetic Fe-Pt thin film, obtained by e-beam co-deposition in ultrahigh vacuum onto the ribbons, is reported. Scanning electron microscopy, transmission electron microscopy and X-ray diffraction are used for structural characterization of these hybrid samples. Magnetic measurements provide observation of a drastic decrease of the saturation magnetization, compatible with the exchange coupling between hard and soft magnetic phases in the melt spun / thin film samples.

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1. Introduction

The development of a novel class of permanent magnets, the so-called “exchange spring” or enhanced remanence nanocomposite magnets has begun since it was predicted [1,2] that nanostructures made of soft and hard magnetic regions, suitably disposed and with sizes comparable to the exchange correlation length, may retain huge energy products $(BH_{\max})$ compared with traditional Nd-Fe-B magnets. These enhanced magnetic properties are due to the exchange coupling between the grains of hard phase through the soft regions [3]. These modern magnetic materials may be synthesized as thin films, multilayers or nanogranular materials [4], depending on the specific applications where these magnets are needed. Industry requires more and more advanced nanomagnets with good high temperature behavior and highly resistive to corrosion. Up to now, the lack of reproducibility of the desired hard-soft microstructure needed for an enhanced energy product, not-so-high energy products compared to the predicted one [5], as well as the chemical instability of nanocrystalline phases has prevented the development of such nanocomposite magnets by methods cost-effective and suitable for industrial applications, such as melt spinning.

Here we report on the synthesis by a hybrid approach of systems made of γ_1 -FePt hard magnetic thin film coupled to a Fe₃B soft magnetic matrix as homogeneous ribbon. The structural and magnetic properties of these magnetic hybrid nanocomposite thin-film/melt-spun ribbon systems are also presented. The choice of Fe-Pt (or CoPt) as hard magnetic phase is justified on one hand by its high corrosion resistance and on the other hand by the high magnetocrystalline anisotropy (7 MJ/m^3) of its $L1_0$ ordered face-centered-tetragonal γ_1 phase [6, 7]. Moreover, exchange coupled 3D nanocomposite magnets made of self-organized FePt and Fe₃Pt nanoparticles [8] and Fe-Pt

thin films [9] but also FePtB-based nanocomposite magnets from amorphous precursors obtained by melt spinning [10] have been recently reported.

2. Experimental

The Fe₃B ribbons were synthesised using the rapid solidification (melt spinning) technique starting with powders of high purity that have been melted together several times in an induction furnace. The melt was then purged through a circular nozzle of 0.5 mm using an Ar overpressure of 40 kPa, onto the surface of a 40 cm diameter Cu wheel rotating with 2000 rot/min. The melt solidifies with a cooling rate of about 106 K/min producing homogeneous ribbons of about 15 micrometers in thickness, 2-3 mm width and several decimeters long. An annealing treatment at 450 °C for 1 h was performed to induce the formation of the Fe₃B soft magnetic phase. The ribbons, carefully chosen to ensure the necessary straightness, were then cut in equal segments and aligned to form a planar rectangular “substrate”. On this “substrate”, Fe and Pt were simultaneously co-deposited by e-beam evaporation with equal, strictly controlled, deposition rates (0.15 nm/sec), to form the Fe₅₀Pt₅₀ alloy on top of the Fe₃B ribbons. The co-deposition was performed at 600 °C in order to have the FePt in its $L1_0$ state. Two hybrid nanostructures were thus obtained, with different thickness of the co-deposited FePt layer: (i) 25 nm Fe + 25 nm Pt on Fe₃B annealed ribbons, and (ii) 100 nm Fe + 100 nm Pt on Fe₃B annealed ribbons. Structural characterization of all the samples (both before and after FePt deposition) was performed with X-ray diffraction using a Bruker G8 diffractometer. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been used for the study of the structure and morphology of the as-obtained ribbons and hybrid composites. TEM images have been recorded

using two JEOL microscopes (JEM 100CX-100 kV-resolution ~ 2 nm and JEM 2010-200 kV-resolution ~ 0.2 nm, respectively). SEM images were taken with a JEOL JSM-840A with a resolution of 0.35 nm, with maximum magnification 300000 $\times$ and acceleration voltage of 0.5–40 kV. Magnetic measurements were carried out with an Oxford Instruments vibrating sample magnetometer (VSM) at room temperature under an applied field up to 1 Tesla. The hysteresis loops were recorded with the field applied parallel to the sample plane.

3. Results and discussion

Fe₃B ribbons

As-cast Fe₃B ribbons present a homogeneous microstructure with dendritic formation of microcrystals, as observed by scanning electron microscope (SEM) imaging (Fig. 1a).

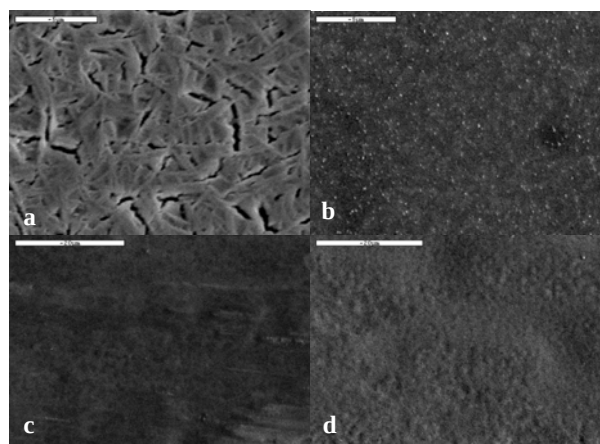


Fig. 1. Scanning electron micrographs of a) as-cast Fe₃B ribbons; b) Fe₃B ribbons annealed at 450°C for 1h; c) FePt(100)/Fe₃B and d) FePt(25)/Fe₃B hybrid system.

The purpose of the post-casting annealing treatment was, as mentioned above, to ensure the formation of Fe₃B soft magnetic phase but also to refine the grain structure and to relax the mechanical stresses induced by the casting procedure. Indeed, after annealing, a well-refined, homogeneous dispersion of nanograins is obtained, as seen from SEM image (Fig. 1b) and the dendritic microcrystals are no more evidenced. These observations were confirmed by transmission electron (TEM) images. Figs. 2a and b show the as-cast and annealed Fe₃B ribbon images taken in bright field imaging mode.

It is remarkable that in both cases the microstructure is made of faceted, agglomerated grains with a quite large size distribution. After annealing, a process of slight crystal growth may be noticed, as expected. Various contrast images observed for the nanograins may be an evidence for the random packing and random anisotropy orientation, as is the case in the amorphous and nanocrystalline Fe-based alloys. Corresponding electron diffraction patterns (insets in Figs. 2a and 2b) were

indexed to the body-centered-cubic b.c.c. α -Fe and orthorhombic Fe₃B phases.

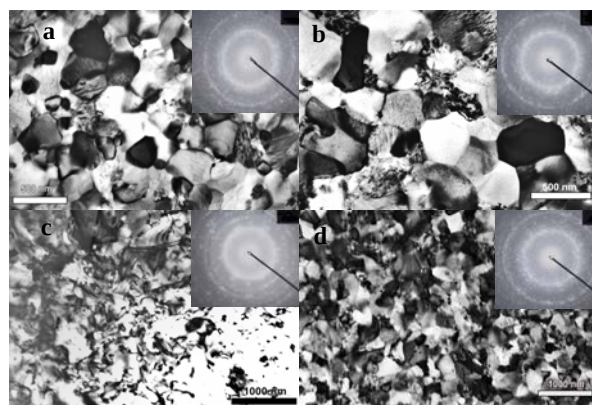


Fig. 2. Bright field transmission electron micrographs of a) as-cast Fe₃B ribbons; b) Fe₃B ribbons annealed at 450°C for 1h; c) FePt(100)/Fe₃B and d) FePt(25)/Fe₃B hybrid system, together with the correspondent electron diffraction patterns.

The occurrence of these phases in the annealed Fe₃B ribbons is confirmed also by X-ray microdiffraction (XRD). The XRD spectra (Fig. 3a) of the annealed Fe₃B ribbons show that the sample is entirely crystallized. A Rietveld-type refinement analysis performed on the diffraction lines provided quantitative information about the phase structure of the ribbons. The b.c.c. α -Fe and orthorhombic Fe₃B phases are shown to occur, in agreement with the EDP observations. The nanograin mean size obtained with the Scherrer's method was 16.7 nm for α -Fe and 19.8 nm for the orthorhombic Fe₃B.

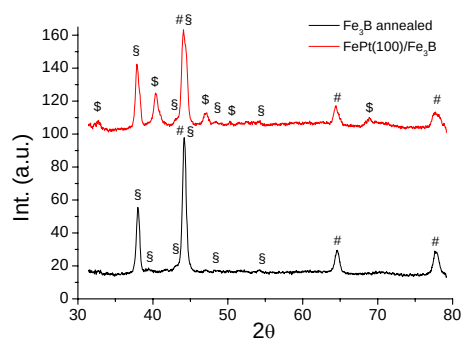


Fig. 3. X-ray diffractograms of Fe₃B ribbons annealed at 450°C for 1h and FePt(100)/Fe₃B hybrid systems: Indexed phases: (#) – b.c.c. α -Fe; (\$) – tetragonal L10 FePt; (§) – orthorhombic Fe₃B.

FePt/Fe₃B hybrid systems

As mentioned above, the deposition of the FePt onto the Fe₃B ribbons was done by e-beam co-evaporation of Fe and Pt with equal deposition rate of 0.15 nm, in a UHV deposition chamber. Two systems were prepared: the first one made of 100 nm Fe + 100 nm Pt on Fe₃B ribbons

annealed at 450 °C (hereafter named FePt(100)/Fe₃B) and the second one made of 25 nm Fe + 25 nm Pt on as-cast Fe₃B ribbons (hereafter named FePt(25)/Fe₃B). The SEM images of the two hybrid systems are presented in the Figs. 1c and d while the bright field TEM images are presented in Figs. 2c and d. For the sample FePt(25)/Fe₃B, it is observed that the homogeneous layer of FePt deposited onto the Fe₃B substrate covers partly the rough granular microstructure, yet the details of the original ribbon microstructure are still observed. For the sample FePt(100)/Fe₃B one can see an extremely homogeneous image, characteristic for thin films and the granular ribbon microstructure is hardly observed. This is due to the refinement of the initially coarse as-cast microstructure by the annealing and also to the higher thickness of the co-deposited FePt layer that covers almost completely the granular Fe₃B microstructure.

The hysteresis loops, recorded with applied field parallel to the sample, for the two hybrid samples as well as those of Fe₃B as-cast and annealed samples are displayed in Figs. 4. In Fig. 4a it can be seen comparatively the hysteresis loops of as-cast Fe₃B ribbon and FePt(25)/Fe₃B hybrid sample (in other words the loops of the Fe₃B ribbon before and after deposition of the FePt thin film).

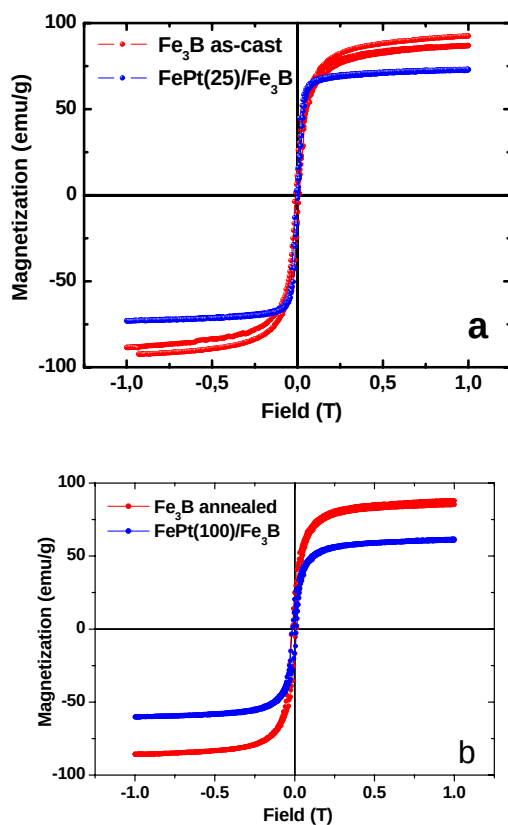


Fig. 4. Hysteresis loops for: a) as-cast Fe₃B and FePt(25)/Fe₃B hybrid system; b) annealed Fe₃B and FePt(100)/Fe₃B hybrid system.

It can be observed that the saturation magnetization decreases with about 20 % after deposition of the (25 nm + 25 nm) FePt thin film. Such strong decrease of the saturation magnetization and also the slight enhancement of the hard magnetic character (slightly higher remanent magnetization and closeness of the loop) is somehow surprising, taking into account the very low content of hard phase in the sample (thickness of FePt: about 50 nm, thickness of the soft magnetic ribbon: about 15 microns). The occurrence of an exchange spring mechanism at the hard-soft interface with the soft magnetic moments pinned by the hard magnetic moments of the FePt may be the only explanation for such different hysteresis loop. Nevertheless, the exchange coupling between hard and soft magnetic phases is not effective, since no noticeable increase of coercivity and energy product is observed after FePt deposition. A similar situation may be observed in the case of (100 nm + 100 nm) FePt thin film. In Fig. 4b, are depicted the hysteresis loops of annealed Fe₃B and hybrid sample FePt(100)/Fe₃B (before and after deposition of the FePt thin films). In this case the decrease of the saturation magnetization is even greater (33%) than in the previous case, due to the higher content of hard magnetic phase FePt but again, no increase of coercivity is observed. One solution to obtain an effective exchange spring mechanism in such hybrid systems is to increase the thickness of the FePt thin film and to enhance the exchange coupling between the hard and soft magnetic regions.

4. Conclusions

A hybrid approach, promising for developing exchange spring magnets with Fe₃B soft magnetic ribbons obtained as melt spun ribbons and FePt hard magnetic phase, obtained by simultaneous co-deposition of Fe and Pt with equal deposition rates onto the ribbons, is reported. SEM and bright field TEM images indicate a uniform and homogeneous deposition of the FePt film onto the polycrystalline Fe₃B ribbons. Both X-ray diffraction and electron diffraction patterns show the occurrence of b.c.c. Fe and orthorhombic Fe₃B as soft magnetic phases in the ribbons whereas FePt is in its tetragonal, hard magnetic state. The room-temperature hysteresis loop of the FePt/Fe₃B hybrid systems show a pronounced decrease of the saturation magnetization compared to the Fe₃B ribbons, typical for the hard-soft exchange coupled systems. The exchange spring mechanisms are not effective since no noticeable increase of the coercivity was observed. The exchange spring effect in such hybrid system is related to the promotion of the L10 FePt phase and, consequently, to a better interfacial exchange coupling between hard and soft regions.

Acknowledgements

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