Magnetic properties of the Fe\textsubscript{48.75}Pt\textsubscript{26.25}B\textsubscript{25} nanostructured alloy

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Abstract. The Fe\textsubscript{48.75}Pt\textsubscript{26.25}B\textsubscript{25} powder was prepared by high-energy ball milling of the crystalline melt-spun ribbon. The X-ray diffraction and transmission Mössbauer spectroscopy measurements allowed the identification of the tetragonal FePt and orthorhombic FeB phases in the as-quenched alloy. The ball milling of the ribbon led to the transformation of the ordered tetragonal FePt phase into a disordered cubic FePt solid solution with the average crystallites size of about 15 nm. Annealing of the as-milled powder recovered the nanocrystalline tetragonal FePt phase. Differences in magnetic properties between the as-milled and annealed powders were revealed by hysteresis loop and magnetization vs. temperature measurements.

1. Introduction
Nanocomposite materials consisting of hard and soft magnetic phases are widely used in the fabrication of efficient exchange-coupled spring magnets. Such a possibility has been discovered for rapidly quenched Fe-Pt-B alloys in which fine nanocomposite structures can be formed due to annealing, leading to excellent hard magnetic properties [1-4]. Bulk magnets have been obtained in the binary Fe-Pt [5,6] or Fe-Pt-P [6] systems by mechanical alloying and subsequent annealing and sintering processes.

In the present study, the rapidly quenched Fe\textsubscript{48.75}Pt\textsubscript{26.25}B\textsubscript{25} alloy was mechanically milled in order to obtain the powder samples. Structural characterization was performed by X-ray diffraction and Mössbauer spectroscopy techniques as a function of milling time and annealing conditions. The dependence between the structure and magnetic properties of the as-milled and annealed powders was studied by hysteresis loop and magnetization vs. temperature measurements.

2. Experimental details
The Fe\textsubscript{48.75}Pt\textsubscript{26.25}B\textsubscript{25} alloy was prepared in a ribbon form by the melt-spinning technique. About 6 g of the ribbon was subjected to high-energy ball milling for up to 5 h under an argon atmosphere. The Fritsch P5 planetary ball mill with steel vial and balls and 250 rotations per minute was used. Thermal behaviour of the as-milled powder was studied by differential scanning calorimetry (DSC) with the scanning rate of 40 K min\textsuperscript{-1}. The final powder was annealed for 15 min. in vacuum at temperatures
determined from the DSC curve. Structural properties of the ribbon and powder samples were investigated by X-ray diffraction (XRD) and Mössbauer spectroscopy in a transmission geometry. A standard powder diffractometer with CuKα radiation was employed. All Mössbauer spectra were measured at room temperature using a 57Co-in-Rh source. The relative content of the phases present in the nanocrystalline samples was calculated as a ratio of the area of the relevant subspectrum to the total spectral area. A vibrating sample magnetometer and a Faraday balance were used to evaluate magnetic properties of the samples studied with the applied fields up to 2 and 1.5 T, respectively.

3. Results

The as-quenched Fe48.75Pt26.25B25 ribbon has a two-phase structure consisting of the ordered tetragonal (fct) FePt and orthorhombic FeB phases as shown by the XRD pattern in figure 1. The Mössbauer spectrum of the as-quenched sample (figure 2a) confirms the identification of the crystalline phases. Two magnetically split sextets are observed: one with narrow lines and the following hyperfine parameters: hyperfine field $H_{hf}=27.2$ T, isomer shift $\delta=0.28$ mm/s and quadrupole shift, QS, of 0.30 mm/s attributed to the tetragonal FePt phase (relative spectral fraction of 46%), and the other one with slightly broadened lines and $H_{hf}=10.2$ T, $\delta=0.26$ mm/s and QS=0.14 mm/s assigned to the crystalline FeB phase. The large positive value of QS obtained for the non-cubic FePt phase is an evidence for the anisotropic electric charge distribution in the tetragonal structure.

Mechanical milling of the ribbon for up to 5 h results in a gradual transformation of the ordered fct FePt phase into the disordered cubic (fcc) FePt solid solution (figure 1). The average crystallites size of the FePt solid solution is about 15 nm after milling for 5 h (estimated by using the Sherrer formula). In the Mössbauer spectrum of the sample milled for 1 h a new magnetic component appears showing

![Figure 1. XRD patterns of the as-quenched ribbon, the samples after milling for 1 and 5 h and the 5 h milled sample after annealing at 923 K.](image1)

![Figure 2. Mössbauer spectra of the (a) as-quenched ribbon, (b,c) milled samples and (d) sample milled for 5 h and annealed at 923 K.](image2)
broad lines and a distribution of hyperfine fields with the average value of about 30 T and almost zero value of QS (figure 2b). These features indicate the formation of the disordered cubic FePt solid solution.

The mechanically induced phase transformations are summarized in figure 3 that presents the relative abundance of the phases calculated from the Mössbauer spectra vs. milling time. The relative fraction of the solid solution spectral component increases with the increase of milling time at the expense of the sextet related to the ordered FePt. Its contribution reaches about 53% of the total spectral area after 5 h of milling whereas the contribution of the ordered phase is negligible. The relative content of the FeB phase decreases slightly with the progress of the milling process.

Thermal behaviour of the final powder (after milling for 5 h) was studied by the DSC method (figure 4). The DSC curve shows a broad exothermic peak with onset temperature of about 660 K and the maximal effect at 730 K. The final powder was annealed at temperatures of 823, 873 and 923 K for 15 min. The XRD patterns and the Mössbauer spectra of the annealed samples are very similar. The results obtained for the powder annealed at 923 K are shown at the bottom of figure 1 and in figure 2d. Both the XRD pattern and the Mössbauer spectrum reveal two-phase structure consisting of the tetragonal FePt and FeB phases. Thus the annealing caused a complete transformation of the disordered fcc solid solution into the ordered fct FePt phase. This transformation is related to the exothermal effect observed in the DSC curve. The relative abundance of the fct FePt phase calculated from the Mössbauer spectra of the annealed samples is in the range of 50-53%.

Figure 5 presents the temperature variations of magnetization of the powders after final milling and after annealing at 923 K. The room temperature value of the magnetic moment per formula unit decreases after annealing from 0.97 to 0.74 μB for the as-milled and annealed samples, respectively, reflecting the structural changes of the FePt phases. In the case of the as-milled powder the magnetization decreases with increasing the temperature up to about 600 K. The following increase in magnetization is related to the disorder-order transformation of the FePt phase. The temperature dependence of magnetization recorded for the annealed powder containing the ordered FePt phase shows a continuous decrease. The estimated Curie temperatures are 610 and 735 K for the as-milled powder, and 745 K for the annealed sample. The lower value could be related to both the FeB and the fcc FePt phases whereas the larger ones are very close to the Curie temperature characteristic for the fct FePt phase.

Hysteresis loops recorded at room temperature for the as-milled and annealed at 923 K powders are shown in figure 6. The hysteresis of the as-milled sample is typical for soft magnetic materials. The saturation magnetization value determined from the hysteresis is 0.94 T. After thermally induced
4. Conclusions
The as-quenched ribbon was fully crystalline. Its structure was composed of the hard magnetic tetragonal FePt and soft magnetic orthorhombic FeB phases. The high-energy ball milling of the ribbon led to the gradual refinement of the structure. After milling for 5 h the tetragonal FePt phase transformed into the nanocrystalline disordered cubic FePt solid solution. Annealing of the as-milled powder fully recovered the nanocrystalline tetragonal FePt phase whereas the relative abundance of the FeB phase remained almost unaffected. Also the temperature dependence of magnetization of the as-milled sample revealed the ordering of the FePt phase at about 650 K. The hysteresis loop measurements showed that the as-milled powder was magnetically soft whereas annealing caused magnetic hardening of the samples related to the formation of the hard magnetic tetragonal FePt phase.

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