# STRUCTURE AND MAGNETIC PROPERTIES OF CoFeB ALLOYS PREPARED BY BALL MILLING

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**SUMMARY**

*X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and magnetization measurements performed by vibrating sample magnetometer (VSM) were used to observe the evolution of the structure and magnetic properties of the $Co_{70.3}Fe_{4.7}B_{25}$ alloys prepared by ball milling of microcrystalline ribbon and of a mixture of pure powders. For both starting materials ball milling produces nanocrystalline structure with nanometer sized crystals. The both series of $Co_{70.3}Fe_{4.7}B_{25}$ alloys are the ferromagnetic materials.*

*The $(Co,Fe)_3B$ phase was detected in milled $Co_{70.3}Fe_{4.7}B_{25}$ microcrystalline ribbon by means of XRD. This phase is stable during the whole process of milling. Long-time milling up to 1500 hours causes magnetic moment to decrease monotonously and reduces its value by 50 %. Observed decrease of magnetic moment is due to the decrease of powder size as seen from XRD and SEM observation and because of high level of structural defects which are generated during the milling process. The coercivity of milled ribbon at the beginning of milling process steeply rises and reaches its maximum at 24 kA/m for 200 hours of milling, then it decreases very slowly with milling time.*

*XRD diffractograms, show, that at early stages of milling two cobalt allotropes, i.e. hcp-Co and fcc-Co, are present in the structure of milled mixture of powder elements Co(70.3 at. %), Fe(4.7 at. %) and B(25 at. %). After 800 hours of milling the CoO phase appears and its amounts increases with further milling up to 1600 hours. The magnetic moment of pure powders mixture decreases with the milling time more steeply compared to milled ribbon and milling reduces its value by 70 %. Similarly to the previous case, this decrease of magnetic moment is caused by the decrease of the powder size and the high level of structural defects. Another reason for such a kind of behaviour is the fact that the phase CoO is antiferromagnetic with Neel temperature 271 K [10]. As its amount with milling time increases, certain amount of cobalt is trapped in the CoO phase and therefore the total magnetic moment is lowered. The coercivity shows rather complicated behaviour which is characterized with maximum at 20.6 kA/m for 800 hours of milling.*

***Keywords:*** *mechanical milling and alloying, XRD, SEM, magnetic moment, coercivity*

## 1. INTRODUCTION

New amorphous and crystalline materials prepared by mechanical alloying or by mechanical milling have been investigated for a number of alloys [7]. The cobalt- and iron-based amorphous alloys are known to exhibit soft magnetic properties [5]. Ball milling is an effective technique to prepare the metal – metalloid alloys [8].

Soft magnetic materials prepared by melt spinning technique have restricted field of applications because of their shape. Therefore the preparation of magnetic materials by compaction of powder is a very promising chalenge for physics and technology, since it is one of the ways how to produce bulk material. We assume that non-magnetostrictive alloys are very suitable for the preparation of bulk samples by high-pressure compression, because mechanical stress does not induce additional magnetic anisotropy in the ferromagnetic material prepared by such a way.

For our investigations we have chosen material with chemical composition $Co_{70.3}Fe_{4.7}B_{25}$. Alloy of this composition has balanced concentration of Co, Fe and metalloid, and could be in principle non-magnetostrictive (for example amorphous $Co_{70.5}Fe_{4.5}Si_{10}B_{15}$ alloy has zero magnetostriction constant [4]). This paper presents part of our work focused on the preparation of the Co-based soft magnetic materials in the bulk form.

## 2. EXPERIMENTAL

Milling processes were performed on two materials with composition $Co_{70.3}Fe_{4.7}B_{25}$ : microcrystalline ribbon and a mixture of powder elements. Microcrystalline ribbon with thickness of 40 μm produced by the melt spinning technique was cut into pieces about 10 mm x 5 mm. As the second starting material for ball milling a mixture of powders of pure elements of desired atomic composition was used. Both samples were milled in a hardened-steel mortar (inner diameter 9.3 cm) of a vibratory micromill

Pulverisette 0 Fritsch, under argon atmosphere up to 1500 hours. Milling was performed with one ball inside the mortar and the ball to powder ratio was 25:1. The milling process has been interrupted after desired time to remove a part of milled material for further investigations.

The morphology and microstructure of milled powders at the different stages of milling were examined by SEM with energy dispersive X-ray (EDX) analysis facility. Microanalyses were performed using SEM fitted with EDX and average data were obtained from three independent measurements.

The structure of milled materials was studied by XRD using filtered $CoK_{\alpha 1,2}$ radiation with wavelength $\lambda$=0.17902 nm. XRD patterns were recorded at room temperature. Rietveld refinements were carried out using the program package GSAS [3].

Magnetic properties of milled powders were studied using VSM. Magnetic moment and coercivity were determined from M-H loops traced at room temperature with the maximum magnetic field of 480 kA/m.

## 3. RESULTS AND DISCUSSION

### 3.1. Microcrystalline ribbon

Fig. 1 shows the SEM micrographs of ball milled microcrystalline ribbon at different stages of milling. The milling causes the change in morphology of milled powder and after long time milling the spherical shape is dominant. For longer milling times the aggregation of powder particles is characteristic, which has electrostatic or magnetostatic nature (see third picture in Fig. 1).

The crystal structure of the samples was refined using the Rietveld method and it was found to be single phase ($Co_3B$). As it could be seen from XRD patterns (see Fig. 2) this phase is stable during the whole process of milling. With the increase of milling time diffraction lines become more broader what is mainly caused by reducing the average grain size and by increasing the microstrain in the grains. As a result of the crystal structure refinement procedure we were able to obtain numerical values of parameters which characterize the broadening process quantitavely. The results are presented in Fig. 3. It could be concluded from XRD investigations that ball milling of microcrystalline ribbon produces very fine powder with nanocrystalline structure composed of $(Co,Fe)_3B$ phase.

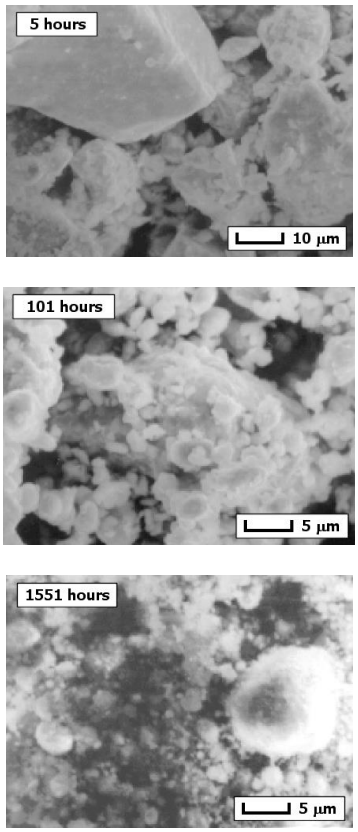


**Fig. 1** SEM micrographs of ball milled microcrystalline ribbon.

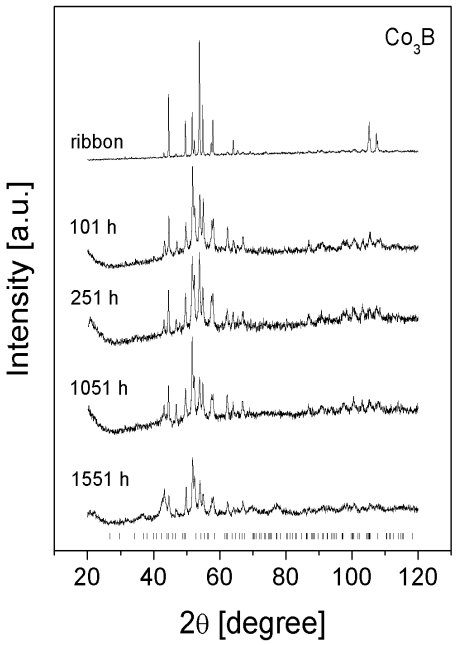


**Fig. 2** XRD patterns of ball milled $Co_{70.3}Fe_{4.7}B_{25}$ microcrystalline ribbon.

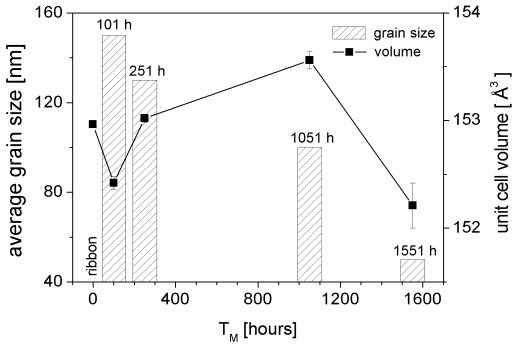


**Fig. 3** Evolution of the grain size and unit cell volume during the ball milling of microcrystalline ribbon.

Fig. 4 shows behaviour of magnetic moment and coercivity of milled ribbon during the ball milling. Another evidence for the presence of the $(Co,Fe)_3B$ phase in ribbon is the value of its magnetic moment which we found to be 1.13 $\mu_B$ per Co atom. This value is in a good agreement with the value 1.1 $\mu_B$ per Co atom for crystalline $Co_3B$ as referred in [2].

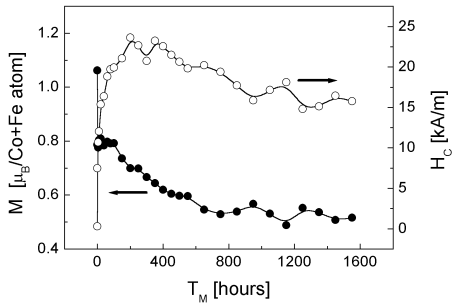


**Fig. 4** Magnetic moment and coercivity vs. milling time.

Long-time milling up to 1500 hours causes magnetic moment to decrease monotonously and reduces its value by 50 %. Observed decrease of magnetic moment is due to the decrease of powder size as seen from XRD and SEM observation and because of high level of structural defects which are generated during the milling process. Because the phase $(Co,Fe)_3B$ is stable during the whole milling process and new phases were not detected (see Fig. 2), the main probable reason for the observed decrease of magnetic moment with milling time is superparamagnetic behaviour of small particles. The coercivity of milled ribbon at the beginning of milling process steeply rises and reaches its local maximum at 24 kA/m for 200 hours of milling time. This is caused by the fact, that with the decrease of the powder size the magnetization process is realised more and more by the rotation of magnetization vectors and the domain wall motion becomes less significant. If we assume that after 200 hours of milling, milled powder consists of single domain particles, coercivity can be expressed in the form

$$H_C \approx K/I_S \,, \qquad (1)$$

where $K$ represents the magnetic anisotropy constant and $I_S$ is the saturated magnetic polarization [1]. Further increase of milling time is accompanied by a slow decrease of coercivity because the anisotropy constant $K$ of milled powder (see equation (1)) decreases steeper than its magnetic polarization $I_S$ [6].

### 3.2. Mixture of pure powders

In Fig. 5 it is clearly visible that the size of powder particles in ball milled mixture of powders decreases with milling time. After long-time milling the spherical shape of the particles is dominant.

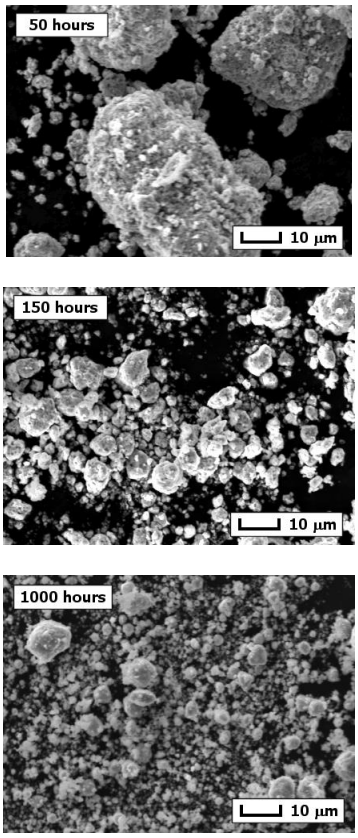


**Fig. 5** SEM micrographs of milled powders mixture.

Quantitative analysis of two powder samples (after 50 and 1000 hours of milling) was performed in order to find out the composition of selected powder particles. Results from EDX quantitative analysis are collected in Tab. 1. Sample milled for 1000 hours contains quite

large amount of oxygen. This contamination by oxygen is due to the large surface area and longer exposition to the atmosphere when taking samples for measurements. We suppose that oxides cover the surface of powder and since the SEM-EDX analysis picks up the signal from surface layers several tenth nanometers thick, that is why the average oxygen concentration in sample is significantly lower than the detected one.

| | 50 hours | | 1000 hours | |
|---|---|---|---|---|
| | wt % | at % | wt % | at % |
| **O** | 2.51 | 8.23 | 21.90 | 49.45 |
| **Fe** | 34.07 | 33.25 | 6.48 | 4.54 |
| **Co** | 63.42 | 58.52 | 71.62 | 46.01 |

**Tab. 1** Results of quantitative analysis of 50 and 1000 hours milled pure powders mixture obtained by SEM-EDX.

The structure of milled pure powders mixture at the early stages of ball milling contains two cobalt allotropes, hcp-Co and fcc-Co (see Fig. 6). Similar results are referred in [9]. After 800 hours of milling the CoO phase appears and its amount increases with further milling (see Fig. 6). After 1600 hours of milling the structure of milled powder consists of nanocrystalline hcp-Co, fcc-Co mixture and very fine grains of CoO.

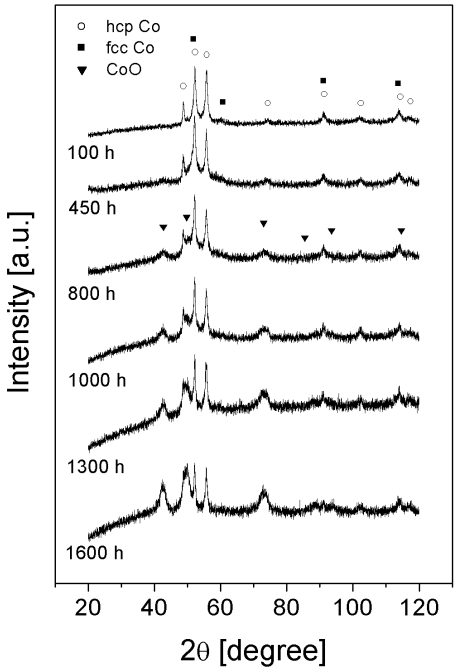


**Fig. 6** XRD patterns of ball milled $Co_{70.3}Fe_{4.7}B_{25}$ pure powders mixture.

Magnetic moment and coercivity of milled pure powders mixture as a function of milling time are shown in Fig. 7. Magnetic moment of pure powders mixture decreases with milling time more steeply compared to milled ribbon and milling reduces its value by 70 %. Similarly to the previous case, this decrease of magnetic moment is caused by decrease of powder size and due to high level of structural defects.

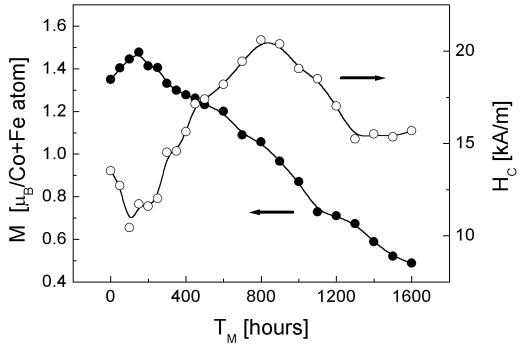


**Fig. 7** Magnetic moment and coercivity vs. milling time.

Magnetic moment gradually decreases because of continuous antiferromagnetic CoO formation. Neel temperature of CoO is 271 K [10]. As its amount increases with milling time, certain amount of cobalt is trapped in the CoO phase and therefore the total magnetic moment is lowered. Coercivity shows rather complicated behaviour. Except small drop at the beginning of the milling, coercivity increases and reaches its maximum at 20.6 kA/m for 800 hours of milling. Further milling causes the coercivity to decrease and after 1300 hours of milling coercivity saturates with value 15.5 kA/m.

## 4. CONCLUSIONS

The structure and magnetic properties of $Co_{70.3}Fe_{4.7}B_{25}$ powders were investigated during the ball milling. From our observations we can conclude that:

- ball milling of microcrystalline ribbon produces nanocrystalline powder composed of $(Co,Fe)_3B$ phase
- during ball milling of pure powders mixture cobalt forms a nanocrystalline mixture of hcp and fcc-Co phases with the simultaneous appearance of CoO oxide phase
- grain size and the amount of structural defects generated during the ball milling strongly influence the behaviour of magnetic moment and coercivity of milled materials

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## BIOGRAPHY

Jozef Bednarčík was born on 6.10.1976. He graduated (MSc.) with distinction from the Faculty of Natural Science at the University of P.J. Šafárik in Košice in 2000. Since 2000 he is a PhD student at the Department of Experimental Physics at the University of P.J. Šafárik in Košice. His scientific research is focused on the structure and magnetic properties of cobalt-based alloys prepared by ball milling. He graduated from the Department of Informatics at the University of P.J. Šafárik in Košice in 2002.