Nanocrystalline (Pr,Dy)-(Fe,Co)-Zr-Ti-B magnets produced directly by rapid solidification

P Pawlik¹, K Pawlik¹, H A Davies², J J Wysłocki¹, W Kaszuwara³

¹Institute of Physics Czestochowa University of Technology, Al. Armii Krajowej 19, 42-200 Częstochowa, Poland

²Department of Engineering Materials, Center for Advanced Magnetic Materials and Devices, The University of Sheffield, Sheffield S1 3JD, UK

³Department of Engineering Materials, Nanocenter, Warsaw University of Technology, ul. Wołoska, 141 Warsaw, Poland

E-mail: pawlik@wip.pcz.pl

Abstract. Hard magnetic thick ribbon samples of a series of Pr₉₋ₓDyₓFe₆₀Co₁₃Zr₁₊yTi₁₋₃ₓyB₁₄ alloys (where x=0;1 and y=0;1) (having average thicknesses tₗ of~ 140 µm) were produced directly by the melt-spinning technique under an Ar atmosphere. The phase constitution of the samples in the as-cast state was determined by X-ray diffractometry and Mössbauer spectroscopy. Hysteresis loops measurements at room temperature indicated very good hard magnetic properties for the alloys, which the coercivity attaining a maximum values of 1.58 MA/m. This is comparable with the coercivities of commercial NdFeB magnets based on melt spun ribbon and with those for nanocrystalline Nd-Fe-B magnets produces by other processes such as mechanical alloying or HDDR.

1. Introduction

In recent years intensive investigations of RE-Fe-Co-B-type bulk glassy alloys (where RE=Nd, Pr, Dy) has been driven by possibility of producing nanocrystalline magnets by annealing of the amorphous precursors. It has been shown [1,2], that the addition of 1 at. % of Zr to (Pr,Dy)₄₋₅(Fe,Co)₇₃₋₅Zr₁₋₂₀B₂₀-type alloys allows the processing of fully glassy cylindrical rods of diameter 1 mm and tubes with outer diameters up to 3 mm and having wall thicknesses of ~ 0.3 mm. Processing of the tube samples by a suction-casting technique was facilitated by adjusting the ingot volume and the applied suction pressure [3-5]. However, due to the relatively low volume fractions of the hard magnetic phase in the nanocomposites, obtained by the appropriate annealing of amorphous precursors, rather low values of coercivity Jₜ (≈180kA/m) and maximum energy product (BH)ₘₐₓ (~47kJ/m³), were achieved.

Hirosawa et al. [6] have demonstrated the possibility of processing thick ribbons (tₗ~100 µm) for Nd-Fe-Ti-C-B alloys containing 8.5-9 at.% of Nd, which were nanocrystalline in the as-cast state and which showed significant hard magnetic properties. Further heat treatment at elevated temperatures resulted in improvement of Jₜ and (BH)ₘₐₓ. These results triggered our effort to produce nanocrystalline Pr-based alloy magnets by the rapid solidification processing. Suitable compositional
modifications resulted in the formation of alloys containing 9 at. % of Pr and with addition of Ti and Zr. We have reported previously [7] the microstructure and magnetic properties of 1 mm diameter cylindrical rods and 3 mm thin-walled tubes produced for the Pr$_8$Fe$_6$Co$_{13}$Zr$_1$Ti$_3$B$_{14}$ alloy. The aim of the present study was to investigate the influences of Zr, Ti and Dy additions on the magnetic properties and phase constitution of directly quenched nanocrystalline melt-spun ribbons (of thickness $t_r \sim 140 \, \mu m$).

2. Samples preparation and experimental methods
Small button ingots of Pr$_{9-x}$Dy$_x$Fe$_{60}$Co$_{13}$Zr$_{1+y}$Ti$_{3-y}$B$_{14}$ alloys (where $x=0;1$ and $y=0;1$), were prepared by argon arc-melting and then melt-spun at circumferencial roll speed of $\sim 6 \, m/s$ under an Ar atmosphere, to yield ribbons of thickness $t_r \sim 140 \, \mu m$. The phase constitution was determined by X-ray diffractometry (XRD) using CoK$_\alpha$ radiation. XRD scans were carried out on both surfaces of the ribbons. Mössbauer spectroscopy in the transmission mode, with constant acceleration of the $^{57}$Co source within a Rh matrix, was used for quantitative phase analysis of the samples. The magnetic properties were measured at room temperature using a vibration sample magnetometer operating in a magnetic field up to 5 T.

3. Results and discussion
The X-ray diffraction patterns obtained for as-cast ribbons ($t_r \sim 140 \, \mu m$) of Pr$_{9-x}$Dy$_x$Fe$_{60}$Co$_{13}$Zr$_{1+y}$Ti$_{3-y}$B$_{14}$ alloys (where $x=0;1$ and $y=0;1$) are shown in figure 1. For all four alloy compositions the XRD traces show evidence of crystalline peaks of relatively low intensities superimposed on the broad halo of the amorphous matrix. This feature was present on both the roll-contact and the free surfaces of the ribbon samples. For the alloys containing 1 at % of Zr, much larger signals from the amorphous matrix are evident in the XRD traces taken from both surfaces of the ribbon (figure 1a,b) than for the Zr-free alloy ribbons. The resolved crystalline phase components are marked on the traces.

Figure 1. XRD traces for the rapidly solidified thick ribbon samples of Pr$_{9-x}$Dy$_x$Fe$_{60}$Co$_{13}$Zr$_{1+y}$Ti$_{3-y}$B$_{14}$ alloys (where $x=0;1$ and $y=0;1$), taken from roll-contact and non-contact surfaces of the ribbon.
Analysis of crystalline peak positions shows the presence of the Pr\(_2\)(Fe,Co)\(_{14}\)B phase. Broadening of the crystalline peaks indicates a nanoscale structure for this magnetic phase. No other crystalline phases were detected for any of the investigated alloy ribbons. In order to confirm the XRD results and also to perform quantitative analysis of the phase compositions, Mössbauer spectroscopy was used. The samples were crushed to powder in order to obtain specimens representative of the whole volume of the ribbon in each case.

In the fitting procedure for the Mössbauer spectra, the contribution from the hard magnetic Pr\(_2\)Fe\(_{14}\)B phase was considered. In the elementary cell of this crystalline phase, six magnetically nonequivalent positions of Fe atoms are present, which in the Wyckoff notation are labeled as: 16k\(_1\), 16k\(_2\), 8j\(_1\), 8j\(_2\), 4e and 4c. The contribution to the Mössbauer spectra from the surroundings of these Fe positions in the elementary cell, is represented by six Zeeman lines, for which the relative intensity ratios of 4:4:2:2:1:1, were chosen. In order to match theoretical spectra to the experimental data, an additional two spectral components were required. The first one corresponds to a crystalline paramagnetic phase - possibly Pr\(_{1+}\)Fe\(_4\)B\(_4\), which was not detected by X-ray diffraction, while the second corresponds to the continuous hyperfine field distribution. This continuous line in the deconvoluted spectrum is related to the presence of an amorphous phase and also to the interface between the grains of the crystalline phase and the amorphous matrix. The results of the Mössbauer spectra analysis carried out for the ribbon samples of Pr\(_9\)Fe\(_{60}\)Co\(_{13}\)Zr\(_1\)Ti\(_3\)B\(_{14}\) and Pr\(_8\)Dy\(_1\)Fe\(_{60}\)Co\(_{13}\)Zr\(_2\)Ti\(_2\)B\(_{14}\) alloys are shown in figure 2. Quantitative analysis of the spectra allow the determination of the volume fractions of the crystalline phases and the amorphous matrix.

![Mössbauer Spectra](image)

**Figure 2.** Mössbauer spectra together with the hyperfine field distributions corresponding to their continuous line components obtained for the thick as-cast ribbon samples of the Pr\(_9\)Fe\(_{60}\)Co\(_{13}\)Zr\(_1\)Ti\(_3\)B\(_{14}\) (a) and Pr\(_8\)Dy\(_1\)Fe\(_{60}\)Co\(_{13}\)Zr\(_2\)Ti\(_2\)B\(_{14}\) (b) alloys.

It was determined that, for the Pr\(_9\)Fe\(_{60}\)Co\(_{13}\)Zr\(_1\)Ti\(_3\)B\(_{14}\) alloy, up to ~12% of the Pr\(_2\)(Fe,Co)\(_{14}\)B and 9.5% of the Pr\(_{1+}\)Fe\(_4\)B\(_4\) crystalline phases were present within the majority amorphous matrix. Similar volume fractions of the crystalline phases were determined for the Pr\(_8\)Dy\(_1\)Fe\(_{60}\)Co\(_{13}\)Zr\(_1\)Ti\(_3\)B\(_{14}\) alloy samples (12.6% and 12% respectively, for the Pr\(_2\)(Fe,Co)\(_{14}\)B and Pr\(_{1+}\)Fe\(_4\)B\(_4\) phases). For the two other alloy compositions, larger volume fractions of the hard magnetic phase (20.8 % for the x=0 and y=1 alloy and 21.3% for the x=2 and y=1 alloy, respectively) and similar fractions of the paramagnetic phase were detected. Considering these results one can conclude that addition of Dy at the expense of Pr does not significantly change the volume fraction of the hard magnetic crystalline phase within the alloys investigated. However, changes of Zr and Ti to 2 at. % of each element, resulted in doubling of the fraction of hard magnetic crystalline phase in the as-cast ribbon samples.

The basic magnetic parameters for the as-cast ribbons were determined from the hysteresis loops measured at room temperature in external magnetic fields up to 5T. The loops measured for all four
alloy compositions are shown in figure 3. Two-stage demagnetization curves were observed for the 1 at.% of Zr alloys, with a characteristic decrease of the magnetization around the remanence point. This shape of the hysteresis loops is typical for two-phase alloys with large contents of a soft magnetic phase. The Dy addition to the alloy compositions resulted in an increase in $J_H$ from 1.24 MA/m for the $x=0$ and $y=0$ alloy to 1.33 MA/m for the $x=1$ and $y=0$ alloy. In the case of the alloys containing 2 at. % of Zr, a significant increase of the coercive field to 1.58 MA/m was observed for both of the compositions investigated. Furthermore, significant remanence enhancement, together with the square-shaped hysteresis loops were revealed for these samples, which indicates the existence of some exchange interactions between the nanocrystalline grains of the hard magnetic phase and the amorphous matrix.

![Figure 3. Hysteresis loops measured for the ribbon samples of Pr$_{9-x}$Dy$_x$Fe$_{60}$Co$_{13}$Zr$_{1+y}$Ti$_{3-y}$B$_{14}$ alloys (where $x=0;1$ and $y=0;1$).](image)

4. Conclusions
It has been shown that very thick ($t_r ~ 140 \, \mu\text{m}$) as-quenched ribbon samples of Pr$_{9-x}$Dy$_x$Fe$_{60}$Co$_{13}$Zr$_{1+y}$Ti$_{3-y}$B$_{14}$ alloys (where $x=0,1$ and $y=0,1$), consist of two ferromagnetic phases – hard magnetic nanocrystalline grains of the Pr$_2$Fe$_{14}$B and the soft magnetic amorphous matrix and one paramagnetic Pr$_{14}$Fe$_4$B$_4$ phase. The volume fraction of the hard magnetic crystalline phase changes with the Zr and Ti contents. An increase in Zr concentration at the expense of Ti, resulted in an increased volume fraction of the hard magnetic phase from ~12 vol.% for $y=0$ alloys to 21 vol.% for $y=1$ alloys and thus in improvement of magnetic properties.

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