14th Czech and Slovak Conference on Magnetism, Košice, Slovakia, July 6–9, 2010

The Bulk Glass Forming Ability and Magnetic Properties of $Pr_9Fe_{50+x}Co_{13}Zr_1Nb_4B_{23-x}$ ($x = 0, 2, 5, 8$) Alloys

K. Pawlik, P. Pawlik and J.J. Wysłocki

Institute of Physics, Częstochowa University of Technology

al. Armii Krajowej 19, 42-200 Częstochowa, Poland

In the present study the rapidly quenched $Pr_9Fe_{50+x}Co_{13}Zr_1Nb_4B_{23-x}$ ($x = 0, 2, 5, 8$) alloy samples produced in a form of 100 mm^2 plate of various thicknesses were investigated. The X-ray diffraction revealed changes in the phase constitution of as-cast samples depending on the alloy composition and plate thickness. The presence of hard magnetic $Pr_2(Fe,Co)_{14}B$ phase was observed in 0.5 mm thick plates of the $x = 8$ alloy, while fully glassy structure was shown in 0.5 mm thick plates of the $x = 0$ alloy. It was shown in the present paper that magnetic properties of annealed samples originated from different microstructure of as-cast samples.

PACS numbers: 75.50.Ww, 75.50.Kj, 71.20.Eh

1. Introduction

The suction-casting process that consists of suction of the arc-molten alloy into the water cooled copper mould under an Ar atmosphere allows to process bulk glassy RE–(Fe–Co)–B (RE = Nd, Pr, Dy) alloys samples in a form of rods and tubes [1–3]. It was shown that annealing of bulk samples of $(Pr,Dy)_{4.5}(Fe,Co)_{74.5}Zr_1B_{20}$ alloys leads to their nanocomposite microstructure and hard magnetic properties [4]. Nevertheless, rather low coercivity field $_JH_c$ of ≈ 180 kA/m and maximum energy product $(BH)_{max}$ of ≈ 47 kJ/m^3 were measured for these samples due to relatively low volume fraction of the hard magnetic $Pr_2Fe_{14}B$ phase in the composite alloy. Recently, the rapidly solidified bulk samples of RE–Fe–Co–B alloys, containing 9 at.% of RE atoms (where RE = Nd, Pr, Dy), doped with Zr, Ti, C and Nb, were studied [5, 6]. Admixture of 4 at.% of Nb to the $Nd_{10}Fe_{70}B_{20}$ alloy allowed to produce partially amorphous 1.5 mm diameter rods [7]. Further heat treatment resulted in formation of nanocrystalline microstructure and significant rise of coercive field up to 1100 kA/m, while the $(BH)_{max}$ increased to 33 kJ/m^3. Therefore the aim of present work was to study the influence of iron to boron ratio on glass forming abilities (GFA) and magnetic properties of novel $Pr_9Fe_{50+x}Co_{13}Zr_1Nb_4B_{23-x}$ ($x = 0, 2, 5, 8$) alloys.

2. Samples and experimental methods

The ingot samples of base $Pr_9Fe_{50+x}Co_{13}Zr_1Nb_4B_{23-x}$ ($x = 0, 2, 5, 8$) alloys were prepared by arc-melting of the high purity elements with pre-alloyed Fe–B of known composition, under an Ar atmosphere. Rapidly solidified 0.5 mm and 1 mm thick plates (of the surface area ≈ 100 mm^2) were produced by suction-casting of the melt into a water cooled copper die, under the Ar atmosphere. The phase constitution was determined using X-ray diffractometry (XRD) with Co K_α radiation, while magnetic properties were measured at room temperature, using the vibration sample magnetometer in external magnetic field up to 2 T.

3. Results and discussion

The X-ray diffraction patterns measured for as-cast 0.5 mm and 1 mm thick plates of $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ and $Pr_9Fe_{52}Co_{13}Zr_1Nb_4B_{21}$ alloys are shown in Fig. 1a. For the $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ alloy, 0.5 mm plates were fully amorphous, while 1 mm plates contained a small fraction of crystalline phase within the amorphous matrix. In the XRD scans of both 0.5 and 1 mm thick plates of the $Pr_9Fe_{52}Co_{13}Zr_1Nb_4B_{21}$ alloy, the peaks of higher intensity, related to crystalline precipitates and broad bump corresponding to the amorphous phase, were observed. Similar diffraction scans were measured for the 0.5 mm thick plates of the other alloy compositions.

Short time annealing at 983 K for 5 min led to nucleation and growth of crystalline phases in the $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ alloy plates. The XRD scans measured for annealed plates of $Pr_9Fe_{50+x}Co_{13}Zr_1Nb_4B_{23-x}$ ($x = 0, 2$) alloys are shown in Fig. 1b. Positions of peaks corresponding to the identified constituent phases are marked in the figure. The phase analysis showed presence of paramagnetic $Fe_4Pr_{1+x}B_4$ and hard magnetic $Pr_2Fe_{11.2}Co_{2.8}B$ phases in all investigated samples. For other alloy compositions, the increase of peak intensities corresponding to these crystalline phases, was observed. However no other crystalline phase was detected. Lack of the signal related to the amorphous phase in the XRD scans of the samples with higher Fe content is due to the decomposition of this phase during annealing.

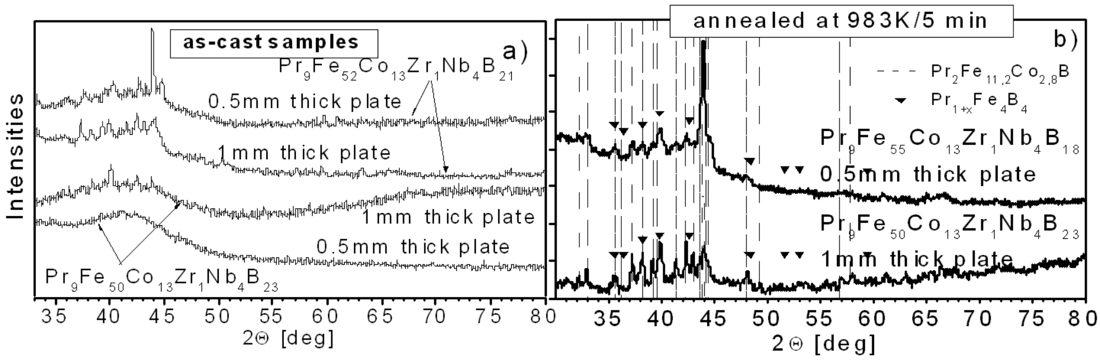

Fig. 1. XRD scans measured for the 0.5 and 1 mm thick plates of $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ and $Pr_9Fe_{52}Co_{13}Zr_1Nb_4B_{21}$ alloys in the as-cast state (a) and for the 0.5 mm thick plate of the $Pr_9Fe_{52}Co_{13}Zr_1Nb_4B_{21}$ alloy and 1 mm plate of the $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ alloy annealed at 983 K for 5 min (b).

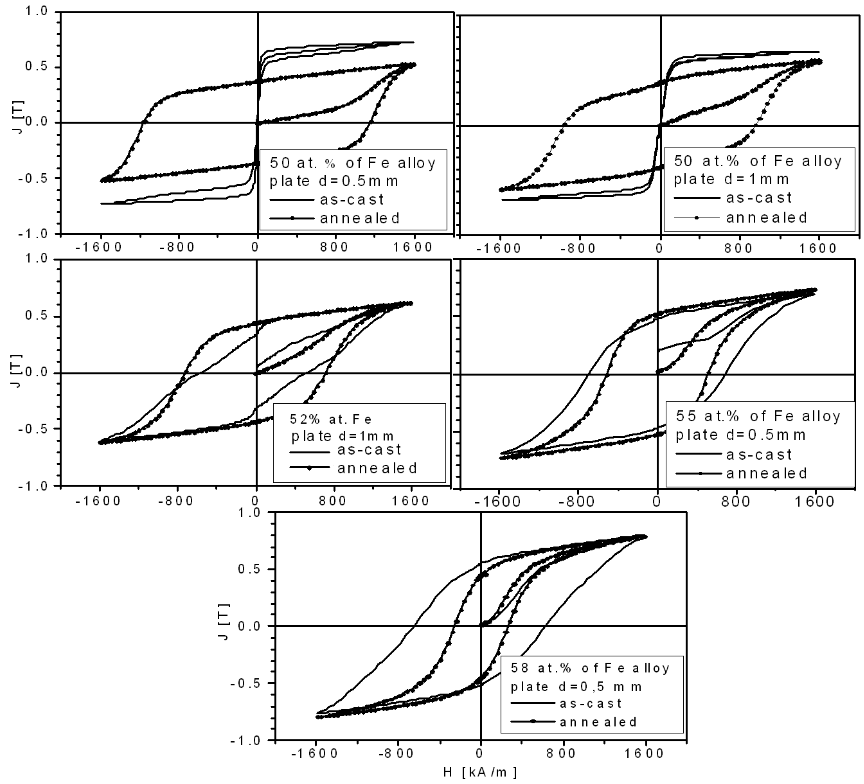

Fig. 2. Hysteresis loops measured on plate samples in the as-cast state and after annealing at 983 K for 5 min of $Pr_9Fe_{50+x}Co_{13}Zr_1Nb_4B_{23-x}$ alloys (where $x = 0, 2, 5, 8$).

The hysteresis loops measured for as-cast and annealed at 983 K/5 min plates of all alloy compositions are shown in Fig. 2. Due to mainly amorphous microstructure of the as-cast 0.5 mm and 1 mm plates of the $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ alloy, the hysteresis loops are typical for soft magnetic materials. However, annealing of this alloy samples at 983 K for 5 min resulted in significant rise of the coercive field ${}_JH_c$ up to ≈ 1150 kA/m, that is due to the nucleation of hard magnetic $Pr_2Fe_{11.2}Co_{2.8}B$ phase. Furthermore, application of the maximum external magnetic field 1600 kA/m does not saturate the samples, so that the measured ${}_JH_c$ are lower than those which could be measured for the saturated samples. It was shown by XRD analysis that both 0.5 mm and 1 mm thick plates of the $Pr_9Fe_{52}Co_{13}Zr_1Nb_4B_{21}$ alloy contained hard magnetic crystalline phase in as-cast state, that resulted in their hard magnetic properties. However, short time annealing of these samples led to the increase of the ${}_JH_c$ and significant change of hysteresis loop shapes and thus increase of the maximum magnetic energy product $(BH)_{max}$.

Changes of the remanence J_r, coercivity ${}_JH_c$ and $(BH)_{max}$ with the alloy composition are shown in Fig. 3. The 0.5 mm thick plate of the $Pr_9Fe_{58}Co_{13}Zr_1Nb_4B_{15}$ al-

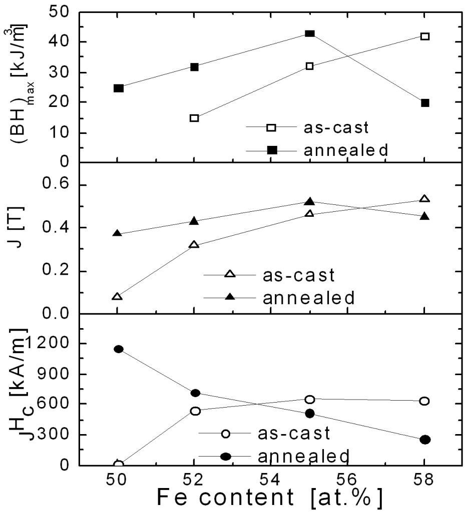

Fig. 3. Dependences of coercivity field ${}_JH_c$, remanence J_r and maximum energy product $(BH)_{max}$ on the alloy composition measured for $Pr_9Fe_{58-x}Co_{13}Zr_1Nb_4B_{15+x}$ (x = 0, 3, 6, 8) alloys plates in as-cast state and annealed at 983 K for 5 min.

loy has the highest ${}_JH_c$ of $\approx$ 650 kA/m and $(BH)_{max}$ of $\approx$ 42 kJ/m^3 in a group of as-cast samples (Fig. 3). However, short time annealing of these alloy samples resulted in a decrease of both ${}_JH_c$ and $(BH)_{max}$. With increase of Fe content in the alloy composition of annealed samples, rise of J_r and $(BH)_{max}$ while decreases of the ${}_JH_c$ were observed. The highest $(BH)_{max}$ was obtained for the $Pr_9Fe_{55}Co_{13}Zr_1Nb_4B_{18}$ alloy samples, which is due to the highest remanence measured for these samples.

4. Conclusions

In the present paper the influence of Fe vs. B ratio on GFA and eventually on the magnetic properties of nanocrystalline magnets, produced by devitrification annealing of bulk glassy plates at 983 K for 5 min was shown. In case of the $Pr_9Fe_{50}Co_{13}Zr_1Nb_4B_{23}$ alloy, processing of glassy plates of the thickness up to 1 mm was possible by suction casting technique. Further annealing of the samples resulted in the crystallization of hard magnetic $Pr_2Fe_{11.2}Co_{2.8}B$ phase. With the increase of Fe content in the alloy composition, subsequent increase of the remanence was observed. The highest $(BH)_{max}$ value of $\approx$ 43 kJ/m^3 was measured for annealed 0.5 mm plates of the $Pr_9Fe_{55}Co_{13}Zr_1Nb_4B_{18}$ alloy. However, relatively large $(BH)_{max}$ of $\approx$ 42 kJ/m^3 was measured for the as-cast $Pr_9Fe_{58}Co_{13}Zr_1Nb_4B_{15}$ alloy plate samples.

Acknowledgments

Work supported by the Polish Ministry of Science and Higher Education for the period 2008–2011 (research project No. NN507 372 735).

References

[1] P. Pawlik, H.A. Davies, *J. Non-Cryst. Solids* **329**, 17 (2003).

[2] P. Pawlik, H.A. Davies, M.R.J. Gibbs, *Appl. Phys. Lett.* **83**, 2775 (2003).

[3] A. Inoue, T. Zhang, *Mater. Trans. JIM* **37**, 185 (1996).

[4] P. Pawlik, H.A. Davies, W. Kaszuwara, J.J. Wysłocki, *J. Magn. Magn. Mater.* **290-291**, 1243 (2005).

[5] S. Hirosawa, H. Kanekiyo, Y. Shigemoto, T. Miyoshi, in: *Proc. 18th Int. Workshop on High Perf. Magn. and Their Appl., Annecy (France) 2004*, Eds. N.M. Dempsey, P. de Rango, p. 655.

[6] P. Pawlik, K. Pawlik, H.A. Davies, J.J. Wysłocki, W. Kaszuwara, *J. Phys., Conf. Series* **144**, 012060 (2009).

[7] J. Zhang, K.Y. Lim, Y.P. Fenga, Y. Li, *Scr. Mater.* **56**, 943 (2007).