Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Crystallization Processes of $R_{4.5}Fe_{77}B_{18.5}$ (R = Pr, Nd) Amorphous Alloys

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The amorphous alloys $R_{4.5}Fe_{77}B_{18.5}$ (R=Pr, Nd) were prepared by melt-spinning technique under argon atmosphere on a cooper wheel rotating with surface velocity of 25 m·s^{-1}. The ribbons have been investigated by means of X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Temperatures of crystallization for $Pr_{4.5}Fe_{77}B_{18.5}$, measured at the heating rate 20 K/min, are equal $T_{x1} = 591\,^{\circ}$C for the first exothermic effect and $T_{x2} = 603\,^{\circ}$C for the second one (for $Nd_{4.5}Fe_{77}B_{18.5}$ $T_{x1} = 594\,^{\circ}$C and $T_{x2} = 633\,^{\circ}$C). In the amorphous ribbons the crystallization of Fe_3B phase in the first step, followed by the crystallization of $Pr_2Fe_{23}B_3$ and $Nd_2Fe_{23}B_3$, was observed. Both later phases appear in the process of recrystallization, immediately after Fe_3B formation.

DOI: 10.12693/APhysPolA.126.316

PACS: 61.43.Dq, 65.60.+a, 75.50.Bb

1. Introduction

Annealing of metallic amorphous precursors, also those containing rare-earth elements, can be a powerful procedure for formation of nanocrystalline magnetic materials [1, 2]. Outstanding magnetic properties can be connected with the exchange-coupling between magnetic nanocrystals of two different phases: magnetically soft and magnetically hard. Such coupling is responsible for characteristic properties of each of constituents, such as large remanence and high coercivity. We present the analysis of the crystallization processes in melt-spun $Pr_{4.5}Fe_{77}B_{18.5}$ and $Nd_{4.5}Fe_{77}B_{18.5}$ ribbons. The knowledge of this process is necessary to control the growth of phases, induced by annealing with optimal volume ratio between phases, to tune (control) magnetic properties *via* exchange spring mechanism [1].

2. Experiment

The master alloys were prepared using the arc-melting technique. Subsequently, metallic glasses were synthesized in melt-spinning process with the wheel surface speed of 25 m·s^{-1}. The ribbons were about 25–35 μm thick. Structural information was obtained from X-ray diffraction (XRD) using TUR M-62 diffractometer with CoK_α radiation. The crystallization process of as-quenched glasses was investigated by differential scanning calorimetry (DSC). Measurements were performed from 100 to 830 °C at four different heating rates on Netzsch DSC 404 apparatus.

3. Results

XRD measurements were made for as-quenched samples $Pr_{4.5}Fe_{77}B_{18.5}$ and $Nd_{4.5}Fe_{77}B_{18.5}$ (Fig. 1) to confirm the fully amorphous state of samples. Diffraction patterns allowed us to calculate the sizes of coherently scattered domains L in the amorphous phase from the Scherrer equation [4]. L is equal 0.8 nm and 0.75 nm for $Pr_{4.5}Fe_{77}B_{18.5}$ and $Nd_{4.5}Fe_{77}B_{18.5}$, respectively.

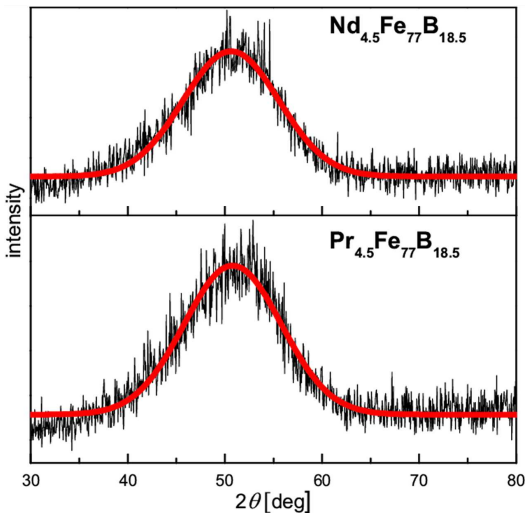

Fig. 1. XRD patterns for of $Nd_{4.5}Fe_{77}B_{18.5}$ and $Pr_{4.5}Fe_{77}B_{18.5}$ amorphous alloys.

The crystallization temperatures of the alloys were determined from the DSC curves (Fig. 2).

The first exothermic peak for $Pr_{4.5}Fe_{77}B_{18.5}$ occurs at 596 °C while for $Nd_{4.5}Fe_{77}B_{18.5}$, at 600 °C. This indicates similar thermal stability of Pr- or Nd-containing alloys.

The Kissinger formula was used to calculate activation energies E for crystallization process, from the slope of the Kissinger plot (Fig. 3). The activation energy for the first crystallization step is 724 ± 20 kJ/mol and for the second one amounts 660 ± 17 kJ/mol.

According to DSC results, Pr- or Nd-containing amorphous ribbons were isothermally annealed far below the first exothermic peak at $T_a = 540\,^{\circ}$C for relatively long

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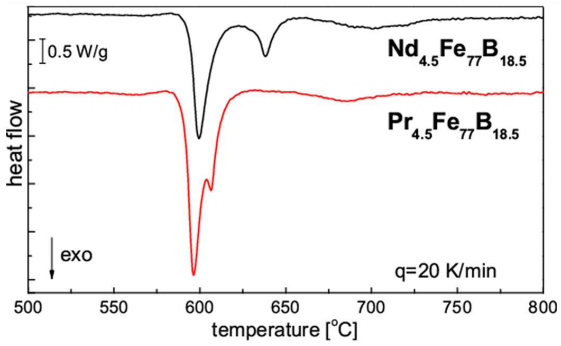

Fig. 2. Calorimetric DSC curves for $R_{4.5}Fe_{77}B_{18.5}$, where R = Pr, Nd at heating rate $q = 20$ K/min..

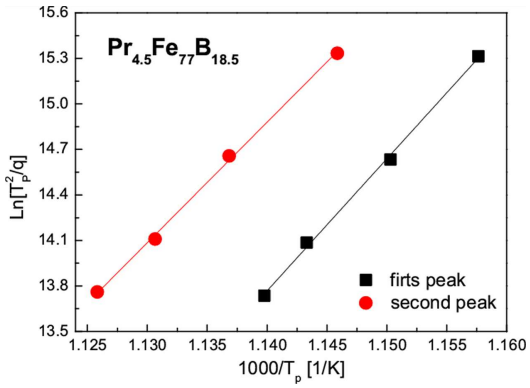

Fig. 3. Kissinger plot for both crystallization event for melt-spun $Pr_{4.5}Fe_{77}B_{18.5}$ ribbon.

time $\tau = 4$ h. Figure 4a and b show XRD patterns of both annealed samples.

In $Pr_{4.5}Fe_{77}B_{18.5}$ the soft magnetic α-Fe and the hard magnetic $Pr_2Fe_{14}B$ phases were identified, as shown in Fig. 4a. According to this figure, it is clear that the main phase is $Pr_2Fe_{14}B$. The crystallization steps for $Pr_{4.5}Fe_{77}B_{18.5}$ glass during isothermal annealing can be described as follows: amorphous phase $\rightarrow$ amorphous + Fe_3B $\rightarrow$ amorphous + Fe_3B + $Pr_2Fe_{23}B_3$ $\rightarrow$ Fe_3B + $Pr_2Fe_{23}B_3$ + $Pr_2Fe_{14}B$ $\rightarrow$ Fe_3B + $Pr_2Fe_{14}B$ + α-Fe $\rightarrow$ Fe_3B + $Pr_2Fe_{14}B$ + α-Fe + $PrFe_4B_4$, which is similar to the scheme described in [5]. Other phases induced by annealing are supposed to be $Pr_2Fe_{23}B_3$ and $PrFe_4B_4$.

As shown in Fig. 4b, after the annealing of $Nd_{4.5}Fe_{77}B_{18.5}$ ribbon, three crystalline phases were identified: two soft magnetic $Nd_2Fe_{23}B_3$, Fe_3B and one hard magnetic $Nd_2Fe_{14}B$. The previous paper suggests that crystallization occurs in two steps only [6]. Our XRD pattern shows three steps crystallization scheme, so the reaction process during isothermal annealing can be written as: amorphous $\rightarrow$ $Nd_2Fe_{23}B_3$ + Fe_3B $\rightarrow$ Fe_3B + $Nd_2Fe_{23}B_3$ + $Nd_2Fe_{14}B$ $\rightarrow$ Fe_3B + α-Fe + $Nd_2Fe_{14}B$.

4. Conclusion

Many techniques have been developed for effective manufacture of commercial materials with hard magnetic properties. Among them, the rapid solidification of molten alloys has been proved to be a reliable route for the synthesis of advanced materials. The melt spinning technique is most favorable because of its simplicity and flexibility. Both analyzed systems reveal relatively high values of effective activation energy and crystallization temperatures. This indicates substantial thermal stability of such amorphous structures stabilized by small amount of rare earth element.

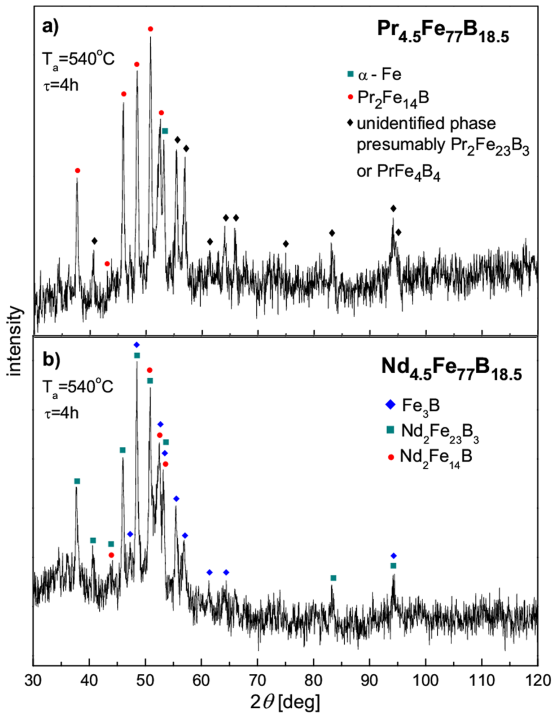

Fig. 4. XRD patterns for the $Pr_{4.5}Fe_{77}B_{18.5}$ (a) and $Ndr_{4.5}Fe_{77}B_{18.5}$ (b) ribbons annealed isothermally.

Acknowledgments

This work was supported by the National Centre for Research and Development within the project no. POKL.04.03.00-00-015/12 and partially (Z.Ś.) by the Polish Ministry of Science and Higher Education (Iuventus Plus grant IP2011 055671).

References

[1] B. Idzikowski, M. Wolf, D. Eckert, A. Handstein, K.-H. Müller, *Mater. Sci. Eng. A* **226-228**, 672 (1997).

[2] B. Idzikowski, M. Wolf, A. Handstein, K. Nenkov, H.-J. Engelmann, F. Stobiecki, K.-H. Muller, *IEEE Trans. Magn.* **33**, 3559 (1997).

[3] H.P. Klug, L.E. Alexander, *X-ray Diffraction Procedures* , 2nd ed., John Wiley &Sons, New York, 1974.

[4] Y.-C. Jung, Y. Ohmori, K. Nakai, S. Hirosawa, H. Kanekiyo, *Mater. Trans.* **42**, 2102 (2001).

[5] M. Rajasekhar, D. Akhtar, M.M. Raja, S. Ram, V. Chandrasekaran, *J. Phys. D* **42**, 095009 (2009).

[6] Y. Jung, Y. Ohmori, K. Nakai, S. Hirosawa, H. Kanekiyo, *Mater. Trans.* **43**, 660 (2002).