Substituted (Nd,Pr)$_2$Fe$_{14}$B alloys: structural features and magnetic properties

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Abstract. In this work the magnetic properties of (Nd,Pr)$_2$Fe$_{14}$B alloys have been investigated in a wide range of temperatures (4.2 – 700 K) and magnetic fields (up to 14 T). The features of the structure were studied using two methods: SEM and AFM/MFM. Magnetic phase transition diagram was constructed. In the region of magnetic phase transitions (Curie and spin-reorientation transition temperatures) the value of the magnetocaloric effect was determined as an entropy change. The constancy of the magnetocaloric effect value for (Nd,Pr)$_2$Fe$_{14}$B alloys has been established.

1. Introduction
In recent years there has been increasing interest in investigation of materials suitable for use as permanent magnets in the low-temperature region [1-3]. The basis of such materials is usually taken by the widely known alloy Nd$_2$Fe$_{14}$B [4-6]. Fundamental magnetic properties (spontaneous magnetization, magnetic anisotropy, hysteresis, spin reorientation, etc.) of this compound may be relatively easy regulated in wide limits by various atom substitutions and additives both in the rare-earth and iron sublattice [7-12]. As an example [13], using praseodymium instead of neodymium in Nd-Fe-B-based permanent magnet (PM) composition enables to avoid application limitations due to spin reorientation (SR) transition at 135 K in Nd$_2$Fe$_{14}$B (such transition does not exist in Pr$_2$Fe$_{14}$B). At the same time, partial substitution of Pr for Nd (which form continuous solid solutions) in the magnetic (Nd,Pr)$_2$Fe$_{14}$B alloys allows one to reduce the SR temperature [14-16]. In addition, partial substitution of Pr for Nd allows one to increase the coercive force of the compound and to substantially affect the magnetic coupling, the magnetic properties of nanocomposite magnets [17, 18]. Despite the fact that the magnetic properties of these technically important alloys have
already been studied a lot, almost no attention has been paid to magnetocaloric phenomena in the region of magnetic phase transitions [19, 20].

A detailed knowledge and a complete understanding of the magnetic microstructure of materials are very important for the development of high performance permanent magnets. The knowledge of magnetic domain behaviour in relation to macroscopic parameters and the physical microstructure of magnets are essential for the theoretical modelling of magnetic properties. So, magnetic force microscopy technique is successfully used for imaging magnetic domain structures of hard magnetic materials [21-26].

This work is devoted to the study of structural and magnetic properties of the (Nd,Pr)\textsubscript{14}Fe\textsubscript{14}B alloys, namely, the study of crystalline and domain structure, magnetization in a wide temperature range (4.2-700 K) and magnetic fields (up to 14 T) and also the study of MCE near magnetic phase transition temperature.

2. Experimental details

The alloys of (Nd\textsubscript{1-x}Pr\textsubscript{x})\textsubscript{14}Fe\textsubscript{14}B (x = 0, 0.25, 0.5, 0.75, 1) were prepared by induction melting of rare-earth metals (99.9 % purity) and precursor Fe\textsubscript{81}B in argon gas atmosphere. The ingots were turned several times and kept in molten state for about 1 h in order to ensure a good homogeneity. Then Single crystals of (Nd\textsubscript{1-x}Pr\textsubscript{x})\textsubscript{14}Fe\textsubscript{14}B were grown by a modified Czochralski method in a tri-arc furnace. The crystal of 20 mm length and 4 mm diameter was pulled out at 10 mm/h pulling speed using a tungsten rod as a seed. Back-scattered Laue patterns were used to confirm the single-crystalline state of the ingot and to orient it for magnetization measurements. Phase purity was checked by standard X-ray diffractometry (XRD) on powders prepared from the ingot.

The elemental composition was assessed by energy dispersive X-ray spectroscopy with a simultaneous study of the microstructure. The studies were conducted on a VegaII Tescan XMU scanning electron microscope (SEM) (Czech Republic) equipped with detectors of reflected and secondary electrons and an energy dispersive X-ray detector INCA-sight (Oxford Instrument, UK) (accelerating voltage 20 kV, current of absorbed electrons at Co - 0.1 nA, probe size 100 nm).

Microstructure and domain structure was investigated by the atomic force (AFM) and magnetic force microscopy (MFM) methods on the polished surface of the specimens using a SMENA scanning probe microscope (Solver platform, ZAO NT-MDT, Russia) at room temperature. The scanning was carried out using standard HA_NC ETALON silicon cantilevers with resonant frequencies F = 137–235 kHz in a semi-contact mode at room temperature. The obtained images were processed with Nova_1443 and Nova_Px 2.0 visualization and analysis software.

Magnetization measurements were performed using a vibrating sample magnetometer (VSM) between 4.2 and 250 K in magnetic fields up to 14 T. The magnetic field was applied both along and perpendicular to the c-axis. High-temperature magnetization measurements (thermomagnetic analysis) were carried out using a commercial PPMS-14 magnetometer (Quantum Design, USA). The magnetocaloric effect in this work was studied by an indirect method. The magnetic entropy change was calculated from the magnetization isotherms by integrating the Maxwell’s relation [19].

3. Results and discussion

3.1. Elemental and phase composition. Surface morphology.

Our XRD data show that (Nd\textsubscript{1-x}Pr\textsubscript{x})\textsubscript{14}Fe\textsubscript{14}B (x = 0, 0.25, 0.5, 0.75, 1) crystallizes in a tetragonal crystal structure (space group P42/mnm) of the Nd\textsubscript{2}Fe\textsubscript{14}B type. However, the amount of the main phase in the resulting alloys varies from 86 to 98 %. In alloys with x = 0.75 and 1, a large amount of the alpha-iron phase was detected (up to 13 %).

It is known that the properties of hard magnetic materials are largely determined by the interfaces between the grains and the phases. The obtained SEM image (figure 1) clearly shows the grain boundaries and the grains themselves, 50–100 μm in size. The elemental compositions of the grains were determined by an energy dispersive X-ray detector on polished surfaces at the indicated points.
Figure 1. SEM image of (Nd₀.₅Pr₀.₅)₂Fe₁₄B surface.

Table 1. Electron microprobe analysis data for the (Nd₀.₅Pr₀.₅)₂Fe₁₄B (local analysis).

| Element (wt.%)/Phase | Fe  | Pr   | Nd   | Dy  | O    | Ni   | Cu   |
|---------------------|-----|------|------|-----|------|------|------|
| Phase 1             | 70.41 | 11.63 | 14.3 | 2.74 | 0    | 0    | 0    |
| Phase 2             | 2.23  | 44.65 | 33.31 | 1.18 | 5.26 | 2.42 | 10.64|
| Phase 3             | 0.79  | 38.79 | 29.35 | 0    | 19.44 | 0    | 0    |
| Phase 4             | 0.51  | 40.64 | 30.56 | 0.7  | 19.41 | 0    | 0    |

Figure 2. Topography (left) and magnetic property distribution (right) for (Nd₀.₅Pr₀.₅)₂Fe₁₄B surface.
(1-4) (Table 1). The iron content of the main grain (point 1) was 70.41 wt. %, while it is 30–130 times less at the grain boundaries (points 2) and in the inclusions (points 3, 4). Elements such as Cu and Ni were present in the boundary region, and oxygen in the inclusions. The presence of oxygen in the inclusions (points 3, 4) indicates the presence of oxides of rare-earth metals (Pr and Nd). The presence of dysprosium was revealed in a small amount everywhere, except point 3.

The strip domain structure is clearly visible in the SEM image in the secondary electrons (figure 1(left)). The domain structure of the alloy in the nanoscale was studied by magnetic force microscopy. MFM technique is used for imaging magnetic domain structures of hard magnetic materials such as Nd-Fe-B [22-26]. The description of such magnetic structures has long been widely known. Figure 2 shows an MFM-image of the polished surface of a (Nd0.5Pr0.5)2Fe14B sample, revealed a classical uniform labyrinth domain structure, characteristic of these alloys, with domain sizes of 1.5–2.0 μm.

3.2. Magnetic and magnetocaloric properties.

The temperature dependencies of magnetization were measured at fixed external dc magnetic field. The thermomagnetic curves M(T) of the (Nd1-xPrx)2Fe14B system samples measured in a field of 0.1 T is given in Figure 3(left). The temperatures of magnetic phase transitions were determined as extremes of the temperature dependence of the derivative of the magnetization dM/dT. The Curie temperatures (T_C) of all investigated alloys were determined. Spin reorientation phase transitions were detected in alloys with concentration of x = 0, 0.25, 0.5, 0.75 and its temperature (T_{SR}) were determined. The Pr2Fe14B, as is known, does not have a spin reorientation over the entire temperature range. Figure 3(right) shows the magnetic phase diagram of the investigated system. It can be seen that with an increase in the praseodymium content, the values of both the Curie temperatures and the SR transition temperatures decrease almost linearly. Moreover, the rate of reduction of T_C is 2/10 at.%, while T_{SR} - 13/10 at.%.  

![Figure 3. Temperature dependence of magnetization (left) and magnetic phase diagram (right)](image)

During the work were obtained magnetization isotherms of the (Nd1-xPrx)2Fe14B (x = 0, 0.25, 0.5) single crystals, measured at temperatures from 4.2 to 250 K in static fields up to 14 T. Figure 4 (left) shows the isotherms of (Nd0.3Pr0.7)2Fe14B single crystal as an example. The nature of the curves clearly demonstrates that in this compound at 4.2 K an "easy cone" anisotropy takes place, while at 77 K it is already an "easy axis".

Previously [20], we conducted MCE studies in the compound Nd2Fe14B and its hydrides by direct method (measurement of adiabatic temperature change ΔT_{ad}). It was found that the largest value (ΔT_{ad} = 0.9K/T) MCE reaches in the T_C region figure 4(right). It can be seen that the adiabatic temperature variation in the region of the Curie temperature is almost four times higher than the similar change in the region of spin reorientation.
Obtaining the set of field dependences of the magnetization in the region of the spin-reorientation phase transition made it possible to calculate the magnitude of the magnetocaloric effect by an indirect method also. The set of magnetic isothermal M(H) curves (the magnetic field was applied along to the c-axis of single crystals) were measured near T_{SR} in steps of 2 K with increasing and decreasing magnetic field up to 14 T. The magnetic entropy change $\Delta S_M$ was calculated from the magnetization isotherms M(H,T) by integrating the Maxwell’s relation (inset figure 4). We can see that the maximums of magnetic entropy change $\Delta S_M$ are observed at T = T_{SR}. In doing so no signs of hysteresis were observed over the whole temperature range. We have previously conducted a detailed analysis of the observed MCE in the region of spin reorientation for the (Nd_{0.5}Pr_{0.5})Fe_{14}B single crystal [16]. It is found that the rescaled $\Delta S_M$ curves around T_{SR} under different magnetic field changes collapse onto nearly the same universal curve, suggesting that the phenomenological construction of the universal curve can be applied to materials with spin reorientation transitions. Now shown, that in (Nd_{1-x}Pr_{x})Fe_{14}B system compounds the maximum value at $T = T_{SR}$ does not change significantly with varying content of praseodymium. This magnetocaloric characteristics obtained for substituted (Nd,Pr)Fe_{14}B alloys are important for the development of hard magnetic materials for lowtemperature applications. The constancy of the magnetocaloric effect value for other multicomponent alloys has been established in [27, 28].

4. Conclusions
In conclusion, we have investigated the structure and magnetic properties of (Nd,Pr)Fe_{14}B alloys. It was found that the amount of the main phase in the samples ranged from 86 to 98%. The features of the structure were studied using two methods: SEM and AFM/MFM. Based on magnetometric measurements, a magnetic phase diagram was constructed. In the field of magnetic phase transitions, the MCE has been investigated.

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References
[1] Huang J C, Kitamura H, Yang C K, Chang C H, Chang C H and Hwang C S 2017 Phys. Rev. ST Accel. Beams 20 064801
[2] Benabderrahmane C, Bertaud P, Valle’au M, Kitegi C, Tavakoli K, Be’chu N, Mary A, Filhol J M and Couprie M E 2012 Nuclear Instruments and Methods in Physics Research A669 1
[3] Hara T, Tanaka T, Kitamura H, Bizen T, Marêchal X, Seike T, Kohda T and Matsuura Y 2004 Phys. Rev. ST Accel. Beams 7 050702
[4] Haskel D, Lang J C, Islam Z, Cady A, Srajer G, van Veenendaal M and Caneld P C 2005 Phys. Rev. Lett. 95 217207
[5] Pastushenkov Y G, Suponev N P, Dragon T and Kronmoller H 1999 J. Magn. Magn. Mater. 196 (Suppl. C) 856 - 858
[6] Wolfers P, Bacmann M and Fruchart D 2001 J. Alloys and Compounds 317 39-42
[7] Herbst J F 1991 Reviews of Modern Physics 63 4 819-898
[8] Kostyuchenko N V, Tereshina I S, Gorbunov D I, Tereshina E A, Andreev A V, Doerr M, Politova G A and Zvezdin A K 2018 Intermetallics 98 139-142
[9] Neznakhin D, Politova G, Ivanov L, Volegov A, Gorbunov D, Tereshina D I and Kudrevatyk N 2018 Defect and Diffusion Forum 386 125-130
[10] Toshin A M and Spichkin Y I 2003 The magnetocaloric effect and its application (eds Coey, J. M. D. et al.) 401–417 (Bristol: Institute of Physics Publishing)
[11] Burkhanov G S, Tereshina I S, Politova G A, Pelevin I A, Koshkidko Yu S, Paukov M A and Drulis H 2017 Doklady Physics 62(1) 10-13
[12] Andreeva N V, Naberezhnov A A, Tomkovich M V, Nacke B, Kichigin V, Rudskoy A I, Filimonov A V 2016 Metal Science and Heat Treatment 58 (7-8) 479-482
[13] Yazid M M, Olsen S H and Atkinson G J 2016 IEEE Trans. Mag. 52 6 2100610
[14] Folks L and Woodward R C 1998 J. Magn. Magn. Mater. 190 28-41
[15] Politova G A, Tereshina I S, Kaminskaya T P, Paukov M A and Dobatkin S V 2018 Russian Metallurgy 9 859-866
[16] Zhou W and Wang Z L Scanning 2007 Microscopy for Nanotechnology. Techniques and Application (Springer)