Magnetic properties and structure of Nd–Fe–B melt-spun alloys for isotropic bonded magnets

B.A.Avramenko[*], *O.M.Bovda*, *V.O.Bovda*, *E.A.Chernov*[*], *A.A.Kostin*, *D.V.Kutniy*, *A.G.Ravlik*[*], *L.V.Onischenko*, *O.S.Tortika*

National Scientific Center "Kharkiv Institute of Physics and Technology", National Academy of Sciences of Ukraine, 1 Akademicheskaya St., 61108 Kharkiv, Ukraine
[*]National Technical University "Kharkiv Polytechnic Institute", 21 Frunze St., 61002 Kharkiv, Ukraine

The phase evolution and magnetic properties of both melt-spun $Nd_xFe_{98.9-x}B_{1.1}$ x = 10–39 mass % ribbons and isotropic bonded magnets have been investigated. A high coercivity and remanence has been shown to be attainable even in the as-spun state with Nd in the range of x = 28–30 mass % without heat treatment. The influence of heat treatment in the 530 to 730° C range on magnetic properties of melt-spun ribbons has been studied. A well-expressed effect of Nd concentration on the lattice volume of $Nd_2Fe_{14}B$ ($P4_2/mnm$) phase and volume fraction of secondary phases has been revealed. It was shown that exchange-coupling effect plays important role in the hard magnetic properties of the alloys with low Nd content, but melt-spun alloys with high remanence along are not sufficient to guarantee high magnetic performance.

Исследованы магнитные свойства и структура быстрозакаленных сплавов $Nd_xFe_{98.9-x}B_{1.1}$ x = 10–39 mass % и изотропных магнитопластов. Высокие значения коэрцитивной силы и остаточной индукции могут быть получены уже непосредственно в исходном состоянии для сплавов $Nd_xFe_{98.9-x}B_{1.1}$ с содержанием Nd x = 28–30 масс. %. Установлена зависимость магнитных параметров сплавов от температуры отжига в диапазоне от 530°C до 730°C. Отмечена четкая связь между концентрацией неодима и объемом элементарной ячейки фазы $Nd_2Fe_{14}B$ ($P4_2/mnm$), а также объемной долей фаз, которые образовываются в сплавах. Показано, что эффект обменного взаимодействия играет важную роль для магнитожестких свойств сплавов с низким содержанием неодима, хотя высокое значение остаточной индукции само по себе не гарантирует высоких магнитных свойств.

Nanocomposite magnetic materials based on Nd–Fe–B melt-spun alloys attract a considerable attention due to their outstanding magnetic properties [1]. These alloys can be subdivided into two categories by composition. One group consists of $Nd_2Fe_{14}B$ hard magnetic phase and the other one consists of hard magnetic phase exchange-coupled to a soft magnetic phase. The isotropic bonded magnets using both single-phase and two-phase melt-spun alloys continue to enable important new applications in actuators and sensors for storage media, consumer electronics and automotive industry. The magnetic, corrosion and thermal properties of such materials continue to be improved. The technical insentive to use of Nd–Fe–B melt-spun alloys is stimulated by various combinations of intrinsic magnetic properties, low flux aging loss, good thermal and corrosion stability. But the best magnetic performance of the bonded magnet also depends on the type of polymer resin and volume fraction of the magnetic material. Experimental results [2–4] and micro-scale magnetic calculations [5–7] show that the magnetic properties of such materials depend heavily on the microstructure, especially on the grain size and phase distribution.

A typical feature of Nd–Fe–B ternary systems is non-equilibrium solidification of alloys. In this case, the reactions typical of equilibrium crystallization remain incomplete or even are completely suppressed. This is especially true for peritectic reactions, that are typical of the Nd–Fe–B system and are controlled by the diffusion of elements in the solid state. For example, the main hard magnetic $Nd_2Fe_{14}B$ phase is formed by peritectic reaction. Hence, increase of the alloy crystallization rate results in suppression of peritectic reaction and thus in the extension of the temperature range and increase of the concentration range where the primary iron crystals are precipitated [8]. The non-equilibrium crystallization has been evidenced in experiment by various techniques (phase analysis and differential thermal analyses) under studying vertical polythermic cross-cut of ternary diagram along the line corresponding to Nd:B = 2:1 ratio traversing the concentration plane point that corresponds to the $Nd_2Fe_{14}B$ phase stoichiometry.

Other effects of non-equilibrium crystallization are observed in the area where the primary crystallization fields of Fe, Fe_2B, $Nd_2Fe_{14}B$, $NdFe_4B_4$ phases meet the projection of liquidus surface on concentration plane [9]. Moreover, the quenching rate of alloys during melt-spinning process can reach 10^5–10^6 K/s and this should result in the formation of metastable amorphous or nanocrystalline soft magnetic phases and thus deteriorate the magnetic properties of alloys. In addition, the $Nd_2Fe_{14}B$ phase non-stoichiometry may affect heavily the as-quenched microstructure, which in turn will influence the crystallization pathway during annealing. In order to understand the effect of alloy composition on the crystallization behavior and observe the crystallization pathways in both types of Nd–Fe–B melt-spun nanocomposites, we performed a comprehensive study including magnetic measurements and X-ray diffraction (XRD) experiments of melt-spun and heat-treated Nd–Fe–B alloys.

Alloy ingots with compositions of $Nd_xFe_{98.9-x}B_{1.1}$ and x = 10–39 wt % were produced by arc melting under purified argon atmosphere. The quenched ribbons were obtained by melt-spinning in Ar atmosphere at a roll speed of 20 m/s. Typical ribbon thickness was about 30–70 μm. The as-spun ribbons were examined in the initial

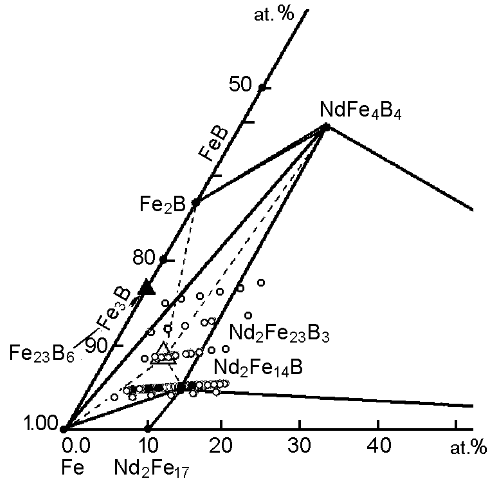

Fig. 1. Fe-rich corner of Nd–Fe–B system. The diagram shows compositions of $Nd_xFe_{100-x-y}B_y$ (x = 10–40, y = 0.9–4) mass %. Note $Nd_2Fe_{23}B$ and Fe_3B are metastable phases (circles are experimental alloys).

state and then were annealed in the temperature range from 530 to 730°C for 5–10 min under vacuum to develop the desired nanocrystalline microstructure. The bonded magnets were made by mixing the ground melt-spun ribbons with formaldehyde resin, pressing the mixture at 10 tons/cm^2 and then curing at 175°C for 30 min. The bonded magnets were 10 mm in diameter and 5 mm in length. The magnetic properties of the ribbons were measured by vibrating sample magnetometer (VSM) with an amplitude magnetic field up to 2 T, and the characteristics of the bonded samples were determined by hysteresimeter with pulse field magnetization. The crystal structure was examined by X-ray diffractometer DRON-2 in Co K_α radiation.

Fig. 1 shows the location of experimental melt-spun alloys in the Nd–Fe–B ternary phase diagram. The compositions of interest are located along the line of constant B concentration (1.1 mass %) and cross the common vertex of α-$FeNd_2Fe_{14}B$–$Nd_2Fe_{23}B_3$ and $Nd_2Fe_{14}B$–$NdFe_4B_4$–Nd triangles. The main phases would be α-Fe and $Nd_2Fe_{14}B$ (at low Nd content) and $Nd_2Fe_{14}B$ (at high Nd content). The metastable phase $Nd_2Fe_{23}B_3$ in compositions of low Nd content can be expected, too. Fig. 2a illustrates the relationship between H_C measured normal and parallel to the ribbon plane for samples with various Nd content. Fig. 2b–2d represent typical hysteresis loops for some melt-spun ribbons registered in the field parallel to

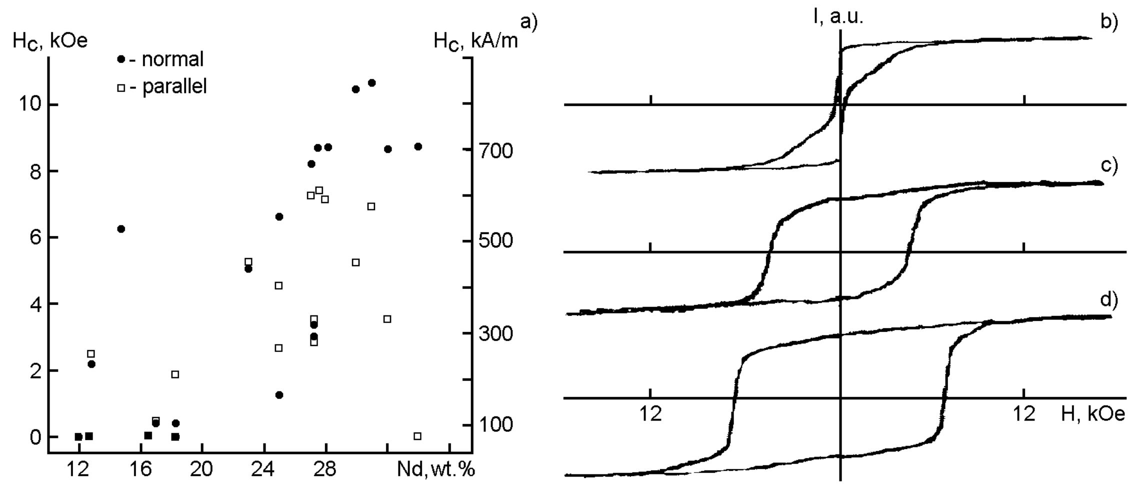

Fig. 2. H_c vs. Nd content for $Nd_xFe_{100-x-y}B_y$ (mass %) melt-spun ribbons (a) and hysteresis loops of the ribbons with various Nd content (wt %); (b) (x = 18.3); (c) (x = 23); (d) (x = 28).

the ribbon plane. It can be seen that a smooth hysteresis loop with decent magnetic properties of M_r/M_s = 0.77 and H_c = 450 kA/m has been obtained in the alloy with x = 23 mass %. The highest coercivity was obtained in the samples with high Nd content (x = 28 and 31 mass %). Hysteresis curves of the melt-spun ribbons with Nd in the range from 18.3 to 26.5 mass % obtained from VSM measurements show saturation remanence ratio M_r/M_s in the range of 0.7–0.77. Therefore, the intergrain exchange-coupling effect should play an important role in the alloy.

The effect of Nd content on the magnetic properties of isotropic bonded $Nd_xFe_{98.9-x}B_{1.1}$ magnets, remanence B_r and H_{ci}, is shown in Figs. 3a and 3b, respectively. Fig. 3c presents hysteresis loops of some bonded samples. According to Fig. 3, three coercivity regions can be distinguished. The coercivity appears to remain at about 100 kA/m in the range x = 10–18 mass %, then increases slightly up to 300 kA/m when x is raising to 26.5 mass % and finally raises considerably up to 1300 kA/м for alloy with x = 29–36 mass %. Changes of coercivity are caused by peculiarities of melt-spun alloy phase composition and reflects clearly the transitions between different tie lines of phase diagram. Remanence does not show any significant dependence on composition of the samples. It should be noted that there is sharp decrease of Br for samples with x = 17 mass % and x = 27 mass %. There is one possible reason for the variation of the remanence for alloys with x = 29–39 mass % due to it considerable sensitivity to the manufacturing conditions during bonding process (crushing and compacting). Although the $Nd_xFe_{98.9-x}B_{1.1}$ bonded magnets at x = 18–26.5 mass % show moderate coercivity in the range 300–450 kA/m, a poor squareness appears in the demagnetization curves causing a much lower $(BH)_{max}$ (see Fig. 3c). Moreover, the squareness of hysteresis loops of the ribbons (Fig. 2c) measured in-plane is essentially higher than the squareness of bonded magnets (Fig. 3c). There are two possible reasons on such behavior. One reason is the poor squareness in this alloy may arise from the fact that α-Fe is a magnetically soft phase with inappropriate size and/or distribution which interferes exchange-coupling between adjacent $Nd_2Fe_{14}B$ and α-Fe grains. The other possible reason may be related to the isotropic distribution and low volume fraction of the ribbons in the bonded magnets, which deteriorate both squareness and remanence.

Fig. 4 shows XRD patterns for $Nd_xFe_{98.9-x}B_{1.1}$ (x = 14, 18.5, 21, 26.5, and 29) ribbons. For the x = 14, 18.5 and 21 alloys, X-ray phase analysis indicates that the alloys contain mainly magnetically hard $Nd_2Fe_{14}B$ phase and α-Fe soft phase. The main appreciable feature in the XRD patterns is the peak broadening which is the indication of fine grain size. As is seen in Fig. 4, the volume fraction of α-Fe phase gradually decreases with increasing Nd content. The Rietveld refinement of the XRD shows that the lattice volume of $Nd_2Fe_{14}B$ ($P4_2$/mnm) phase increases from 921(2) Å^3 for x = 14.5 mass % to 947(2) Å^3 for x = 29 mass% melt-spun alloys.

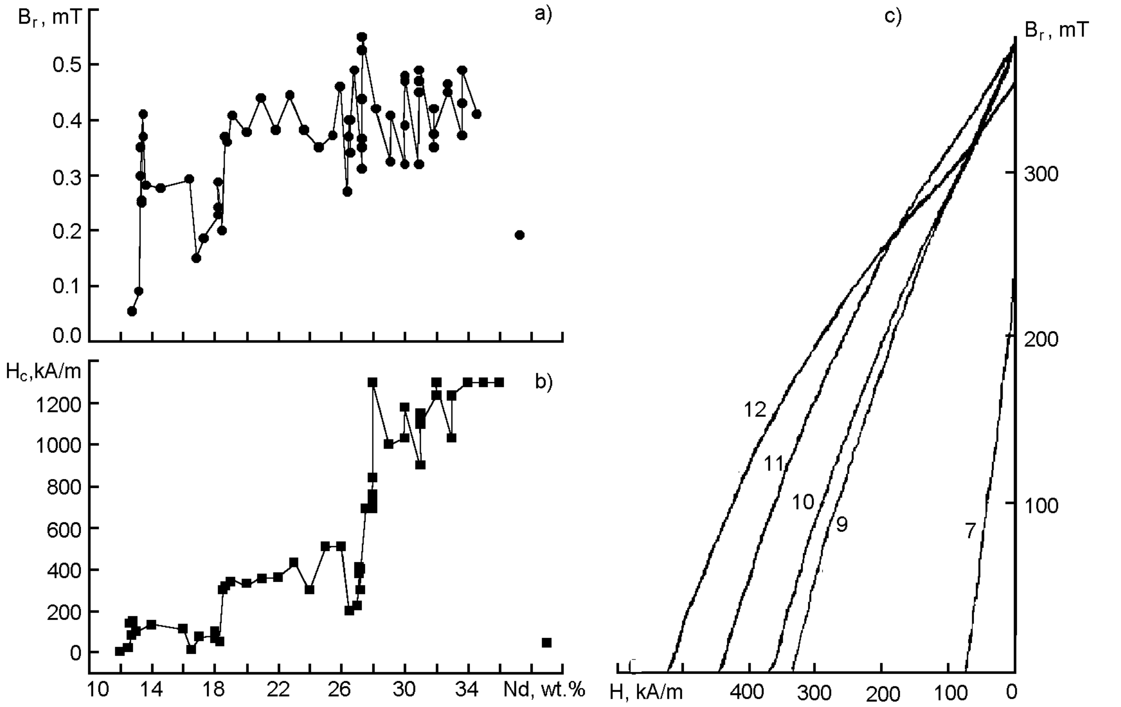

Fig. 3. Remanence (a) and coercivity (b) as functions of Nd content for $Nd_xFe_{100-x-y}B_y$ bonded magnet samples prepared from as-spoon ribbons. Demagnetization curves of some samples (c): *7* (x = 18); *9* (x = 20); *10* (x = 22); *11* (x = 24); *12* (x = 26 mass %).

Melt-spun ribbons were annealed to optimize microstructure and to improve magnetic properties. Magnetic properties of isotropic bonded magnets manufactured from melt-spun ribbons annealed at different temperatures are shown in Fig. 5a–c. The heat treatment at temperatures range of 530–730°C does not show considerable improvement of coercivity for melt-spun alloys with Nd content below $x = 28$ mass %, except for the sample with $x = 22$ mass%. The coercivity of $H_C = 600$ kA/m is obtained for the sample annealed at $T =$ 650°C. It can be seen that $Nd_xFe_{98.9-x}B_{1.1}$ ribbons with higher Nd content (x = 28–39 mass %) annealed at temperature below T = 650°C do not show any coercivity improvement. Moreover, a further increase of annealing temperature up to T = 730°C decreases coercivity from H_c = 1300 kA/m to 780 kA/m for x = 32 mass % and x = 34 mass % samples. An increase of heat treatment temperature to T = 730°C may cause recrysllization and growth of $Nd_2Fe_{14}B$ grains, which might account for the drop in coercivity of samples with high Nd content ($x > 30$ mass %).

On the other hand, the remanence increases after heat treatment at 530°C to 0.33 T for melt-spun samples with $x =$

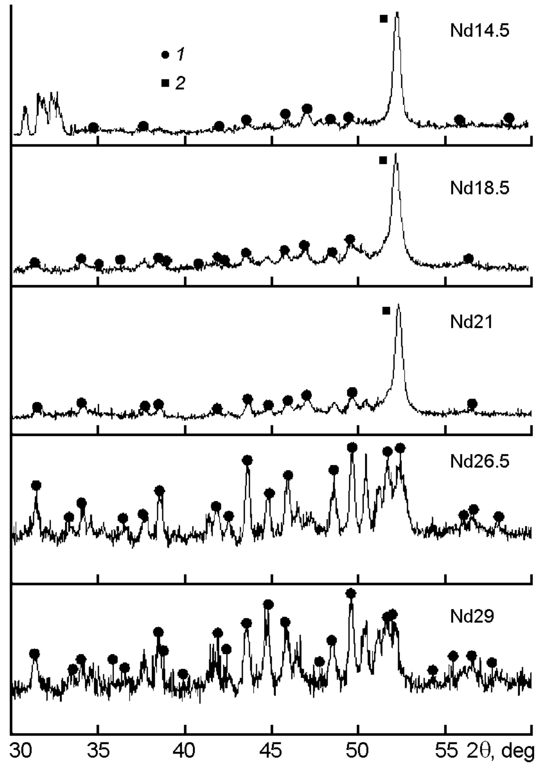

Fig. 4. XRD patterns of the $Nd_xFe_{100-x-y}B_y$ (x = 14.5; 18.5; 21; 26.5; 29 mass %) melt-spun ribbons: *1* – $Nd_2Fe_{14}B$, *2* – α–Fe.

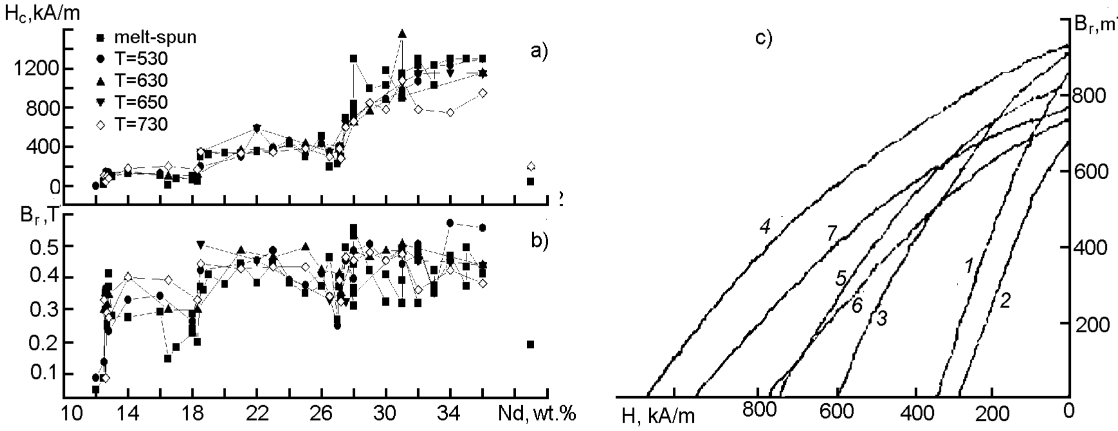

Fig. 5. Coercivity (a) and remanence (b) as functions of Nd content for $Nd_xFe_{100-x-y}B_y$ bonded magnet samples prepared from the ribbons annealed at 530–730°C. Demagnetization curves of some samples (c): x = 18.5, 26.5, 27.5, 31, 32, 34, 36 mass %) for the 1, 2, 3, 4, 5, 6, 7 samples, respectively.

14 mass % and x = 16 mass %. The highest remanence of 0.56 T and 0.5 T have been achieved in the bonded samples with x = 34 mass % and x = 36 mass %, respectively. Heat treatment at 730°C increases remanence to 0.4 T in samples with x = 14 mass % and 16 mass %. One possible reason for remanence improvement at high annealing temperatures in the samples with x = 12.5–18 mass % can be the α-Fe phase grain growth. However, the grain growth due to the high temperature annealing is too excessive. This may explain why coercivity of the $Nd_xFe_{98.9-x}B_{1.1}$ ribbons with x = 12.5–18 mass % annealed at 730°C is so poor. Typical demagnetisation curves of heat-treated bonded samples are shown in Fig. 5c.

The alteration of coercivity in the melt-spun alloys with variation of Nd content clearly indicates the development of particular structure and its influence on magnetic properties. Increasing Nd content results in increased volume fraction of high-anisotropic $Nd_2Fe_{14}B$ phase in the melt-spun alloys and hence affects coercivity. The alloys in the range x = 18.5–26.5 mass % (x = 26.5 mass % being the $Nd_2Fe_{14}B$ stochiometric composition) are of special interest because these alloys are located near $Nd_8Fe_{86}B_6$ composition and used for producing exchange-spring magnets combining magnetically hard phase and magnetically soft one. This explains why magnetic properties of the $Nd_xFe_{98.9-x}B_{1.1}$ ribbons in the range x = 18.5–26.5 mass % containing only $Nd_2Fe_{14}B$ and α-Fe phases show moderate magnetic characteristics due to the exchange coupling between the magnetically soft and hard grains.

It is known that the remanence of nanocomposite increases with the increasing amount of soft magnetic phase, but it should also be noted that such an improvement does not favor the increas of magnetic performance of α-Fe/$Nd_2Fe_{14}B$ nanocomposites. The nominal compositions of those alloys vary along the $Nd_2Fe_{14}B$ and α-Fe tie line. As expected, B_r increases and H_{ci} decreases with increasing α-Fe amounts. Despite the increase in B_r, the $(BH)_{max}$ unexpectedly decreases with the increasing amount of α-Fe, (in spite of the well-known dependence $(BH)_{max} \approx B_r/2$). Thus, a high B_r value alone is insufficient to guarantee a high $(BH)_{max}$ for the nanocomposite. To obtain a nanocomposite with high $(BH)_{max}$, one must balance the B_r, H_{ci} and demagnetization curve squareness. Although alloying elements are known to refine Nd–Fe–B nanocomposite microstructures to yield improved overall magnetic performance [10, 11], the demagnetization curve squareness of nanocomposites is, in general, inferior to near-stochiometric $Nd_2Fe_{14}B$ compositions produced by melt-spinning technique.

To conclude, the $Nd_xFe_{98.9-x}B_{1.1}$ (from x = 10 to x = 39 mass %) melt-spun alloys have been studied comprehensively. High coercivity and remanence could be obtained in as-spun $Nd_xFe_{98.9-x}B_{1.1}$ samples with x = 28–30 mass %. The X-ray analysis has revealed that $Nd_xFe_{98.9-x}B_{1.1}$ melt-spun alloys in the range of compositions x = 18–26 mass % consist of hard-magnetic $Nd_2Fe_{14}B$ phase and soft-magnetic α-Fe one. The exchange coupling plays an important role in the hard magnetic properties in the alloys. The effect of annealing on magnetic properties of as-spun $Nd_xFe_{98.9-x}B_{1.1}$ ribbons has been established. The heat treatment of $Nd_xFe_{98.9-x}B_{1.1}$ (x = 12–18 mass %) melt-spun alloys in the 530–730°C range results in a significant improvement of remanence due to recrystallization of α-Fe grains, as this phase is the major one in these alloys. Heat treatment of $Nd_xFe_{98.9-x}B_{1.1}$ (x = 19–39 mass %) melt-spun alloys does not show any pronounced effect on remanence and coercivity, except for the alloys with high Nd content (x = 32–39 mass %) which show a drop in H_C after annealing at 730°C.

References

1. P.Campbell, D.N.Brown, Z.M.Chen et al., in: Proc. 18th Int. Workshop on High Performance Magnets and their Applications, Annecy, France (2004), p.67.
2. A.Manaf, R.A.Buckley, H.A.Davies, *J.Magn. Magn.Mater.*, **128**, 302 (1993).
3. G.Mendoza-Suarez, H.A.Davies, *J.Alloys Compd.*, **281**, 17 (1998).
4. Z.Q.Jin, H.Okumura, Y.Zhang et al., *J.Magn. Magn.Mater.*, **248**, 216 (2002).
5. R.Skomski, *J.Appl.Phys.*, **76**, 7059 (1994).
6. R.Fischer, T.Schrefl, H.Kronmueller, J.Fidler, *J.Magn.Magn.Mater.*, **150**, 329 (1995).
7. H.Fukunaga, H.Nakamura, *Scr.Mater.*, **44**, 1341 (2001).
8. I.V.Belaev, M.V.Pikunov, O.V.Bondarenko, A.G.Savchenko, *Izv.RAN, Ser.Metally*, No.3, 147 (1994).
9. V.P.Menushenkov, A.G.Savchenko, in: Proc. on Mater. Sci. and Metallurgy: Prospective Technologies and Equipment, Moscow (2003), p.158 [in Russian].
10. W.C.Chang, D.M.Hsing, B.M.Ma, C.O.Bounds, *IEEE Trans.on Magn.*, **32**, 4425 (1996).
11. Z.Chen, Y.Q.Wu, M.J.Kramer et al., *J.Magn. Magn.Mater.*, **268**, 105 (2004).

Магнітні властивості та структура швидкозагартованих сплавів Nd–Fe–B для ізотропних магнітопластів

Б.О.Авраменко, О.М.Бовда, В.О.Бовда, Є.О.Чернов, А.А.Костін, Д.В.Кутній, А.Г.Равлік, Л.В.Онищенко, О.С.Тортика

Досліджено магнітні властивості та структуру швидко загартованих сплавів $Nd_xFe_{98.9-x}B_{1.1}$ x = 10–39 mass % і ізотропних магнітопластів. Високі значення коерцитивної сили та залишкової індукції можна отримати вже безпосередньо у вихідному стані для сплавів із вмістом Nd x = 28–30 мас. %. Встановлено залежність магнітних параметрів сплавів $Nd_xFe_{98.9-x}B_{1.1}$ від температури відпалу у діапазоні температур від 530°C до 730°C. Відмічено чіткий зв'язок між концентрацією неодиму та об'ємом елементарної комірки $Nd_2Fe_{14}B$ ($P4_2$/mnm), а також об'ємним вмістом фаз, що утворюються у сплавах. Встановлено, що ефект обмінної взаємодії грає важливу роль у магнітожорстких властивостях сплавів з низьким вмістом неодиму, хоча висока залишкова індукція таких сплавів не є гарантією високих магнітних властивостей.