

Hard-magnetic melt-spun R–Fe–B alloys on the base of light rare-earth metals (R=La, Nd)

O.M.Bovda, V.O.Bovda, L.V.Onischenko, O.S.Tortika, O.O.Kostin, A.G.Ravlik, B.A.Avramenko*, A.S.Aseev*, V.M.Baumer***

National Scientific Centre "Kharkiv Institute of Physics and Technology",
1 Akademicheskay Str., 61108 Kharkiv, Ukraine
*NTU "KhPI", 21 Frunze Str., 61002 Kharkiv, Ukraine
**SSI ISC, 60 Lenin Ave., 61178 Kharkiv, Ukraine

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Effects of La addition on microstructure and magnetic properties of $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ (wt. %) melt-spun ribbons and isotropic bonded magnets were systematically studied. X-ray diffraction and DSC data revealed that addition of La led to the formation of highly refined and inhomogeneous La-rich phase. It was shown that the average grain size and volume fraction of the main magnetic $(La,Nd)_2Fe_{14}B$ phase depend on La concentration. For better $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ x = 2.5 and 5 wt. % bonded samples, the room-temperature magnetic properties of H_{ci} = 1343 kA/m and 1300 kA/m, and B_r = 0.61 T and 0.614 T were obtained. Magnetic flux aging loss for alloys with appropriate La content (x = 5–10 wt. %) did not exceed 5 % in the range of 100–125°C, which is typical for conventional ternary Nd–Fe–B melt-spun magnets.

Проведено систематическое исследование влияние добавок La на микроструктуру и магнитные свойства быстрозакаленных лент и изотропных магнитопластов на основе сплавов $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ (мас. %). Данные рентгеноструктурного анализа и калориметрических исследований показали, что добавка La приводит к образованию высокодисперсной и неоднородной фазы обогащенной La. Показано, что средний размер зерна и объемная доля основной магнитной фазы $(La,Nd)_2Fe_{14}B$ зависит от концентрации La. Наибольшие магнитные свойства H_{ci} = 1343 кА/м и 1300 кА/м, B_r = 0,61 Тл и 0,614 Тл получены на магнитопластах с x = 2.5 та 5 мас. % La. Величина потерь магнитного потока для образцов с x = 5–10 мас.% La соизмерима со значением для традиционного быстрозакаленного тройного сплава Nd–Fe–B и не превышает 5 % в диапазоне температур 100–125°C.

I. Introduction

Recently, a commercial success of Nd–Fe–B magnets has been realized not only due to excellent intrinsic magnetic properties of $Nd_2Fe_{14}B$ phase but also to the fact that its elemental constituents have been economically attractive. However, rare-earth crisis puts pressure on the cost and availability of strategic metals such as Nd, Dy, Tb, which are critical for production of $Nd_2Fe_{14}B$ based permanent magnets. Attempts to overcome the problem have been taken in several directions. One of them is to develop technological improvements [1, 2] and another one is to search for inexpensive raw materials [3, 4] having hard magnetic properties which are intermediate between those of ferrites and Nd–Fe–B.

It is well known that $Ln_2Fe_{14}B$-type phase is formed with all lanthanides (Ln) [5], among which La and Ce are more abundant than highly-valued Nd, Dy and Tb. Recent studies on the effects of La substitution in α-Fe/$Nd_2Fe_{14}B$ exchange-coupled alloys [6,7] suggest that La substitution will effectively refine the grain size, as well as decrease of crystallization temperature of the over-quenched ribbons. Although, there are a lot of scientific papers which study influence of La and Ce additions on magnetic properties of (Nd,R)–Fe,T–B (R = Dy + La + Ce, T = Co,Cr,Ga) alloys [4–9], the specific role of La can be hardly singled out in the case of multi-component systems.

The effect of La substitution on $Nd_2Fe_{14}B$ melt-spun alloy has not been well understood yet, especially its role in improving magnetic properties and microstructure evolution in the melt-spun alloys. Thus, the present study is focused on the above two points of $(Nd,La)_2Fe_{14}B$ melt-spun magnets, aiming at understanding the role of La addition in microstructure control and magnetic properties of both melt-spun alloys and bonded magnets at room and elevated temperatures.

2. Experimental

Alloys with nominal compositions of $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ x = 0–25 wt. % were arc-melted for three times under argon atmosphere to insure homogeneity. Ribbons were prepared from initial ingots by melt-spinning on the Cu wheel at speed of 25 m/s. Isotropic epoxy bonded magnets were made of crashed melt-spun flakes with typical density of samples about 4.7 g/cm^3.

Magnetic properties of melt-spun ribbons were measured by VSM. Bonded magnets were pulse magnetized with 5 T, and measured by a hysteresisgraph. The flux aging loss was measured by Helmholtz coil on bonded magnets exposed up to 300°C for up to 1 h. Structural and microstructural studies were carried out using a Siemens D 500 X-ray diffractometer (XRD). Correction of the instrumental broadening was measured on a LaB_6 standard. The data were collected in the 2θ range of 10 to 90 degrees at a step of 0.04 degrees during 120 sec. Analysis of the X-ray data was performed by Rietveld method using FullProf [10].

The crystallization behavior was studied by DSC-7 to identify the grain boundary melting temperatures of the melt-spun samples.

3. Results and discussion

Fig. 1 illustrates the room temperature magnetic properties of the melt-spun ribbons. It can be seen that $La_xNd_{33-x}Fe_{65.9}B_{1.1}$

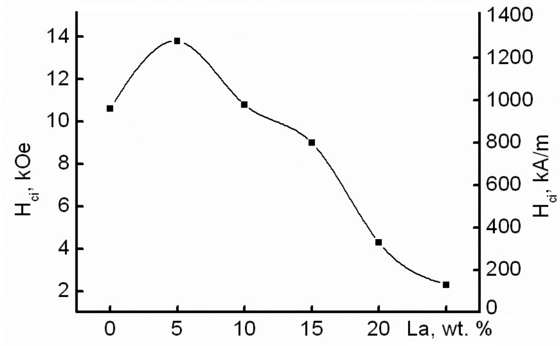

Fig. 1. H_{ci} of melt-spun $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ ribbons.

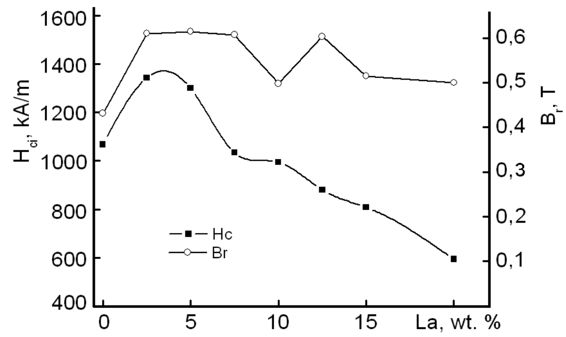

Fig. 2. H_{ci} and B_r of bonded $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ magnets.

x = 5 wt. % alloy has higher magnetic performance than the other compositions, indicating the beneficial effect of small La additions. The ribbons with x = 10 wt. % show magnetic properties comparable with non-doped ternary $Nd_{33}Fe_{65.9}B_{1.1}$ flakes. However, further La substitution for Nd leads to the drastic decrease of room temperature H_{ci} value.

Table 1 and Fig. 2 give in detail the magnetic properties of $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ isotropic bonded magnets. While the concentration dependence of H_{ci} has a little variation for compositions with x = 7.5–10 wt. %, it goes

Table 1. Magnetic properties of $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ bonded magnets

Sample	H_{ci}, kA/m	B_r, T
x = 0	1067	0.431
x = 2.5	1343	0.610
x = 5	1300	0.614
x = 7.5	1034	0.607
x = 10	994	0.498
x = 12.5	880	0.603
x = 15	808	0.515
x = 20	593	0.500

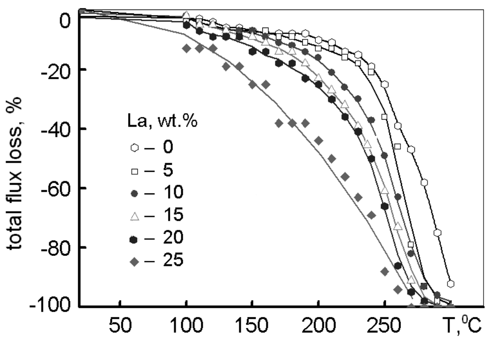

Fig. 3. Total flux loss of $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ bonded magnets.

through a sharp maximum to lower values for compositions within $x = 12.5–25$ wt. %. Large H_{ci} and Br values are obtained with a narrow concentration range near $x = 2.5–5$ wt. %. Such coercitivity behavior coincides with one of the melt-spun ribbons.

Fig. 3 shows the flux aging loss of the bonded magnets prepared from $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ $x = 0–25$ wt. % melt-spun alloys and aged at various temperatures from 100 to 300°C. One can see that La additives at concentrations of $x = 5–10$ wt. % allow to have magnet's operating temperature in the range of 100–125°C with conventional flux aging loss limit of 5 % [11]. Thus, the maximum operating temperature of $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ $x = 5–10$ wt. % alloys bears strong similarity with ternary $Nd_{33-x}Fe_{65.9}B_{1.1}$ magnets. It is also should be noted that $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ $x = 5–10$ wt. % melt-spun ribbons may be used in applications within the 120–170°C temperature range with no more than a 10 % loss of magnetic flux.

In Fig. 4, X-ray diffraction data for three La containing samples are displayed. For the case of low La content $x = 5$ wt. %, it can be seen that the alloy is composed of $Nd_2Fe_{14}B$ type phase. For higher La composition $x = 15$ wt. % the XRD pattern indicates the presence of two crystalline phases: β-La and the hard magnetic $Nd_2Fe_{14}B$ type phase. Further La doping leads to formation of the additional phases such as $Nd_2Fe_{23}B_3$ and Fe_2B. A multi-component Rietveld analysis of Fig. 4 yields mass fractions and grain sizes of constituent phases. The results of this study are summarized in Table 2. According to X-ray analyses (see Table 2), La doping results in the formation of $(Nd,La)_2Fe_{14}B$ solid solution which accompanied by the lattice parameters raise even after β-La phase precipitation. For the samples with $x = 15$ and 25 wt. %, the strongest diffraction peak ($2\theta = 29.1°$) of β-La phase shows prominent asymmetry attributed to the highly refined and inhomogeneous structure. Whereas the grain size of $(Nd,La)_2Fe_{14}B$ phase increases up to 38 nm for $x = 15$ wt. % sample, the grain growth is suppressed for the sample with higher La concentration ($x = 25$ wt. %).

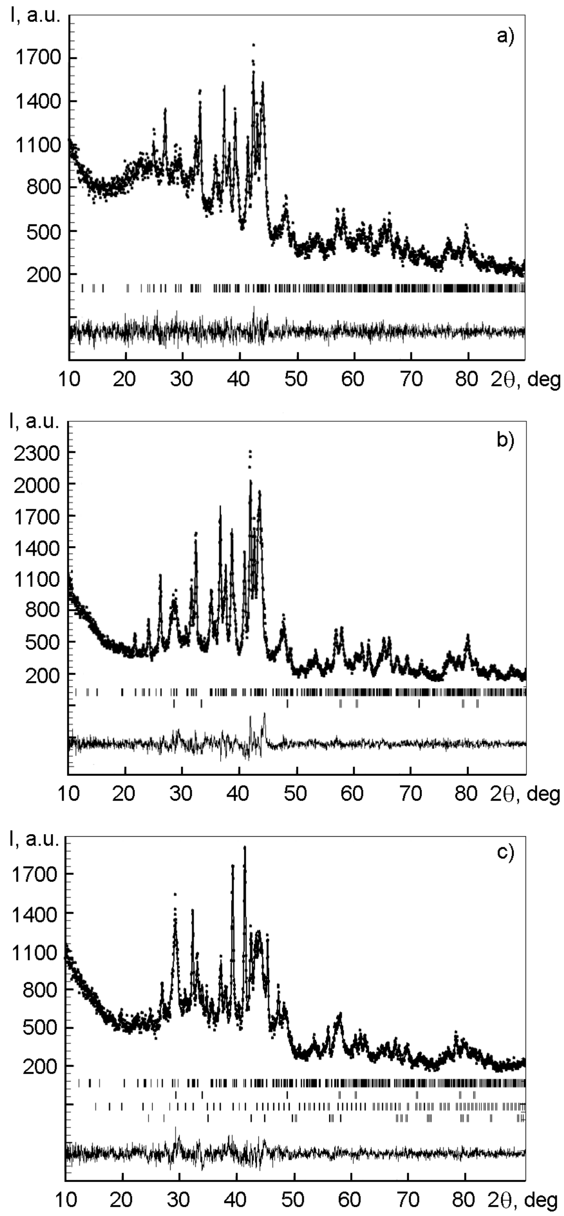

Fig. 4. X-ray diffraction patterns for $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ ribbons: a) $x = 5$ wt. %, b) $x = 15$ wt. %, c) $x = 25$ wt. %.

From these results it is clear that substitution of La for Nd in the range of 2.5–7.5 wt. %, which made up about 22 % of total rare-earth metal, improves the mag-

Table 2. X-ray data for $La_xNd_{33-x}Fe_{65,9}B_{1,1}$ melt-spun alloys.

Alloy $La_xNd_{33-x}Fe_{65,9}B_{1,1}$	Phases	Mass fraction	Lattice parameters (A)	V (A3)	Estimated grain size./ micro-strain, nm/%
x=5	$Nd_2Fe_{14}B$	100.0 (1.6)	a=8.7999(7) c=12.2325(12)	947.264(12)	29/0.15
x=15	$Nd_2Fe_{14}B$ β-La	92.8(1.3) 7.2(6)	a=8.8089(5) c=12.2673(8) a=5.3011(15)	951.91(10) 148.97(7)	38/0.16 8/0.25
x=25	$Nd_2Fe_{14}B$ β-La $Nd_2Fe_{14}B$ Fe_2B	52.7(1.3) 17.3(6) 26.8(1.0) 3.2(4)	a=8.8196(8) c=12.3226(15) a=5.3117(7) a=14.2035(10) a=5.1625(18) c=4.276(3)	958(18) 149.87(3) 2865.4(4) 113.97(11)	29/0.27 16/0.66 106/0.15 25/—

netic properties of the melt-spun and bonded magnets. Despite the fact that intrinsic magnetic properties of $La_2Fe_{14}B$ phase ($4\pi M_s$ = 13.8 kG, H_a = 20 kOe at 295 K, T_c = 530 K) are inferior to those of $Nd_2Fe_{14}B$, it did not show any strong detrimental effect on magnetic performance at room and elevated temperatures. Chang et al. [12] observed similar behavior for exchange-coupled α-Fe/$(La,Nd)_2Fe_{14}B$ magnets and showed that high total rare-earth content not only increases the volume fraction of $R_2Fe_{14}B$ phase in the melt-spun alloys, but also decreases the average grain size of constituent phases, which subsequently enhance the intrinsic magnetic properties of the ribbons.

The other reason for H_{ci} enhancement might be caused by the modification of the grain boundary phase which provided greater resistance to domain movement. Fig. 5 presents grain boundary melting temperatures calculated from the DSC curves. The grain boundary phase melting temperatures were indicated by endotherms in the DSC scans between 450 and 600°C. All alloys showed appreciable tendency for lowering boundary melting temperature with increasing La content. This implies that the La–Nd–Fe–B alloys might be suitable for hot die-upsetting process at lower temperatures than the ternary Nd–Fe–B compounds, and have a longer and more favorable period in which the $(La,Nd)_2Fe_{14}B$ grains have to align [13].

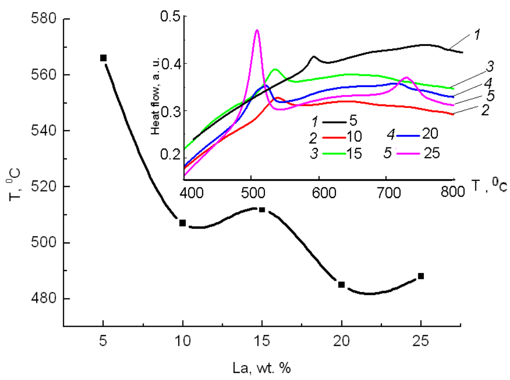

Fig. 5. Grain boundary melting temperatures and DSC scans of melt-spun $La_xNd_{33-x}Fe_{65.9}B_{1.1}$ ribbons.

4. Conclusions

In summary, isotropic bonded magnets prepared from melt-spun La–Nd–Fe–B alloys exhibit high room temperature H_{ci} and Br, and relatively cost-attractive La element can be used. The alloys with La, x = 2.5–7.5 wt. %. also show improved coercitivity and reduced irreversible flux aging losses which did not exceed 5 % at T = 120°C. Thus, the high-valued Nd metal in the isotropic bonded magnets can be replaced by less expensive La up to 22 % without strong deterioration of magnetic properties up to T = 120°C.

References

1. Yasuhiro Une, Masato Sagawa, *J.Jap. Inst. Metals*, **76**, 12 (2012).
2. R.S.Sheridan, R.Sillitoe, M.Zakotnik et al., *J. Mag.Mag.Mat.*, **324**, 63 (2012).
3. J.F.Herbst, M.S.Meyer, F.E.Pinkerton, *J. Appl.Phys.*, **111**, 07A718 (2012).

4. W.Tang, Y.Q.Wu, K.W.Dennis et al., *J.Appl. Phys.*, **109**, 07A704 (2011).
5. S.Sinnema, R.J.Radwanski, J.J.M.Franse et al., *J. Magn. Magn. Mater.*, **44**, 333 (1984).
6. W.C.Chang, S.H.Wu, B.M.Ma, C.O.Bounds, *J. Appl. Phys.*, **81**, 4453 (1997).
7. W.C.Chang, S.H.Wu, B.M.Ma, C.O.Bounds, *J. Magn. Magn. Mater.*, **167**, 65 (1997).
8. K.Y.Ko, S.Yoon, S.W.Ko, *J.Phys.: Conf. Ser.*, **266**, 012036 (2011).
9. K.Y.Ko, S.Yoon, J.G.Booth et al., *J. Mat. Sci.*, **37**, 1421 (2002).
10. J.Rodriguez-Carvajal, T.Roisnel, FullProf.98 and WinPLOTR: New Windows 95/NT Applications for Diffraction. Commission for Powder Diffraction, International Union of Crystallography, Newsletter, No.20 (May-August) Summer (1998).
11. P.Campbell, D.N.Brown, Z.M.Chen et al., in: Proc. of HPMA04 Workshop., **1** (2004), p.31.
12. W.C.Chang, D.Y.Chiou, S.H.Wu et al., *J. Appl. Phys.*, **83**, 6271 (1998).
13. D.N.Brown, Y.K.Lim, R.A.Remoroza, D.J.Miller, *J. Appl. Phys.*, **109**, 07A742 (2011).

Швидкозагартовані магнітожорсткі сплави R-Fe-B на базі легких рідкісноземельних металів (R=La, Nd)

О.М.Бовда, В.О.Бовда, Л.В.Онищенко, О.С.Тортіка, О.О.Костін, А.Г.Равлік, Б.А.Авраменко, А.С.Асеєв, В.М.Баумер

Проведено систематичне дослідження впливу добавок La на мікроструктуру і магнітні властивості швидкозагартованих стрічок та ізотропних магнітопластів на базі сплавів $La_xNd_{33-x}Fe_{65,9}B_{1,1}$ (мас. %). За даними рентгеноструктурного аналізу та калориметричних досліджень встановлено, що додавання La призвело до формування висoкодисперсної та неоднорідної фази збагаченої на La. Показано, що середній розмір зерна та об'ємна доля основної магнітної фази $(La,Nd)_2Fe_{14}B$ залежить від концентрації La. Найбільші магнітні властивості H_{ci} = 1343 кА/м і 1300 кА/м, та B_r = 0,61 Тл і 0,614 Тл отримано для магнітопластів з x = 2,5 та 5 мас.% $La_xNd_{33-x}Fe_{65,9}B_{1,1}$. Втрати магнітного потоку у зразках з x = 5–10 мас.% La відповідають традиційному потрійному швидкозагартованому сплаву Nd–Fe–B та не перевищують 5 % у діапазоні температур 100–125°C.