Conference materials
UDC 537.622.4, 537.9, 54.057
DOI: https://doi.org/10.18721/JPM.153.106

Effect of Co substitution on the microstructure and magnetic properties of Nd-($Fe_{1-x}Co_x$)-B particles synthesized by a modified Pechini-type chemical method

V. Yu Samardak [1], S. A. Azon [1], A. Yu Samardak [1], E. K. Papynov [1],
A. S. Samardak [1], A. V. Ognev [1] ✉

[1] Far Eastern Federal University, Vladivostok, Russia
✉ ognev.av@dvfu.ru

Abstract: Magnetic Nd-(Fe, Co)-B powders prepared by a modified Pechini-type chemical method are investigated. The effect of 0–100 at.% Co concentration on magnetic properties is shown. The structure and morphology of the powders are studied by electron microscopy. The average particle size is determined by electron microscopy. The internal structure of the nanoparticle agglomerates was explored by transmission electron microscopy. The $Nd_2Fe_{14}B$ phase was determined by spot electron diffraction. The dependence of saturation magnetization and coercive force of $NdFe_{1-x}Co_xB$ powders on the cobalt content is investigated and discussed. An increasing coercive force is observed as a result of the increase in Co content. It is shown that the absence of phase purity leads to a decrease in the coercive force in comparison with the Nd-based hard magnetic obtained by metallurgical methods.

Keywords: NdFeCoB magnets, powders, Pechini method, microstructure, elemental analysis, magnetic properties

Funding: The study was supported by the Russian Science Foundation (project 19-72-20071). A. S. Samardak thanks Ministry of Science and Higher Education of the Russian Federation for providing funding as part of State Assignment (project no. 0657-2020-0013) to cover analysis of the surface morphology. A. Yu. Samardak thanks the Government of the Russian Federation for providing funding for project no. 075-15-2021-607 to cover measurement and analysis of magnetic properties.

Citation: Samardak V. Yu, Azon S. A., Samardak A. Yu, Papynov E. K., Samardak A. S., Ognev A. V., Effect of Co substitution on the microstructure and magnetic properties of Nd-($Fe_{1-x}Co_x$)-B particles synthesized by a modified Pechini-type chemical method. St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.1) (2022) 38–43. DOI: https://doi.org/10.18721/JPM.153.106

Материалы конференции
УДК 537.622.4, 537.9, 54.057
DOI: https://doi.org/10.18721/JPM.153.106

Влияние Co на микроструктуру и магнитные свойства частиц Nd-($Fe_{1-x}Co_x$)-B, синтезированных модифицированным методом Печини

В. Ю. Самардак [1], С. А. Азон [1], А. Ю. Самардак [1], Е. К. Папынов [1],
А. С. Самардак [1], А. В. Огнев [1] ✉

[1] Дальневосточный Федеральный Университет, г. Владивосток, Россия
✉ ognev.av@dvfu.ru

Аннотация. Исследованы порошки Nd-(Fe,Co)-B, синтезированные модифицированным методом Печини. Показано влияние на магнитные свойства и структуру изменение концентрации Co от 0 до 100 ат. %. Методами электронной микроскопии изучены структура и морфология порошков. По данным сканирующей электронной микроскопии определен средний размер частиц. Методом просвечивающей электронной микроскопии установлена внутренняя структура агломератов наночастиц. С помощью локальной дифракция обнаружена фаза $Nd_2Fe_{14}B$. С помощью вибромагнетометрии при комнатной температуре получены зависимости намагниченности насыщения и коэрцитивной силы порошков $NdFe_{1-x}Co_xB$ от содержания кобальта. Установлено возрастание коэрцитивной силы за счет увеличения содержания Co. Показано, что отсутствие фазовой чистоты приводит к понижению коэрцитивной силы в сравнении с магнитожесткими материалами на основе Nd, полученными металлургическим методами.

Ключевые слова: NdFeCoB, порошковые материалы, метод Печини, микроструктура, элементный анализ, магнитные свойства

Финансирование: Исследование выполнено при поддержке Российского научного фонда (проект 19–72-20071). Самардак А.С. благодарит Минобрнауки России за поддержку по государственному заданию (проект № 0657–2020-0013) в части анализа морфологии поверхности. Самардак А.Ю. благодарит Правительство Российской Федерации за государственную поддержку по проекту № 075-15-2021-607 в части измерения и анализа магнитных свойств.

Ссылка при цитировании: Самардак В. Ю., Азон С. А., Самардак А. Ю., Папынов Е. К., Самардак А. С. Влияние Co на микроструктуру и магнитные свойства частиц Nd-($Fe_{1-x}Co_x$)-B, синтезированных модифицированным методом Печини // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.1. С. 38–43. DOI: https://doi.org/10.18721/JPM.153.106

Introduction

Hard magnetic materials based on $Nd_2Fe_{14}B$ are widely used in automotive transport, generators, micromotors, and microelectronics [1–3]. This is due to their unique technical characteristics, and first, the maximum energy product $(BH)_{max}$ among all permanent magnets [4]. The most promising are composite magnetic materials in which there are two phases: a magnetically hard phase (for example, $Nd_2Fe_{14}B$), including a magnetically soft phase [5]. To form such compounds, we used Nd-based powders made of nanocrystalline alloys with subsequent grinding (top-down approach) or chemical synthesis (bottom-up approach).

At the top-down approach during the ball milling process, it is possible to introduce additives (Tb, DyCo, Cu + DyCo, Al + DyCo, Cu) using mechanosynthesis, which increase the energy product, reduce the degradation of magnetic parameters during sintering [6–8]. These methods also have disadvantages associated with the heterogeneity of the compounds, caused by a wide spread in particle size, segregation of impurities, for example, carbon, oxidation during the manufacturing process, and the high cost of initial pure raw materials.

Bottom-up approaches are based on the synthesis of magnetic powders by chemical methods, which makes it possible to more precisely control the size and structures of particles from nano- to micro-sizes. Different methods are used, for example, sol-gel Pechini [9,10], sol-gel auto combustion [11], and the microwave technique [12]. The powders of magnetic nanomaterials obtained by chemical synthesis are potentially applicable in biomedicine [13] and to solve environmental problems (waste treatment) [14].

In this paper, we present the results of a study of the structure and magnetic properties of $Nd_2(Fe_{1-x},Co_x)_{14}B$ powders with a change in Co concentration from 0 to 100%, obtained by the modified Pechini method. It is shown that the addition of Co leads to the formation of the Fe-Co alloy and increases the coercive force.

Materials and Methods

The synthesis of oxidized Nd-($Fe_{1-x}Co_x$)-B powders was carried out according to the procedure described in [15]. The reduction of the mixture of oxides was carried out by mixing this powder with calcium hydride CaH_2 (weight ratio 1:1.5) in an argon atmosphere and pressing the resulting mixture into a tablet and subsequent calcination in vacuum (pressure 10^{-3}—10^{-4} Torr) at 800 °C according to the following stepwise heating scheme. The product obtained after heat treatment is subjected to washing from impurities of metallic calcium and its oxide in an aqueous solution of ammonium chloride (NH_4Cl).

The structure and morphology of the powders were studied using a Tecnai G^2 30 transmission electron microscope (TEM) and a Quanta 200 Pegasus scanning electron microscope (SEM).

Magnetic parameters (hysteresis loops, temperature dependences of magnetization) were measured on a Lakeshore 7400 vibromagnetometer.

Results and Discussion

Fig. 1 and 2 show electron microscopic images and elemental microanalysis data of nanopowders with Co content: 0, 30, 60, and 100%. The powder particles in the sample without Co have an asymmetric shape; additionally, 15 µm in size and larger agglomerates are formed. Agglomerates have a loose structure with particles of various sizes and types. The average size of the powders is 870 nm. According to the local elemental analysis, Ca, Cl, O and Si were in the samples, which may have remained due to the powder preparation method (Fig. 2, *a*).

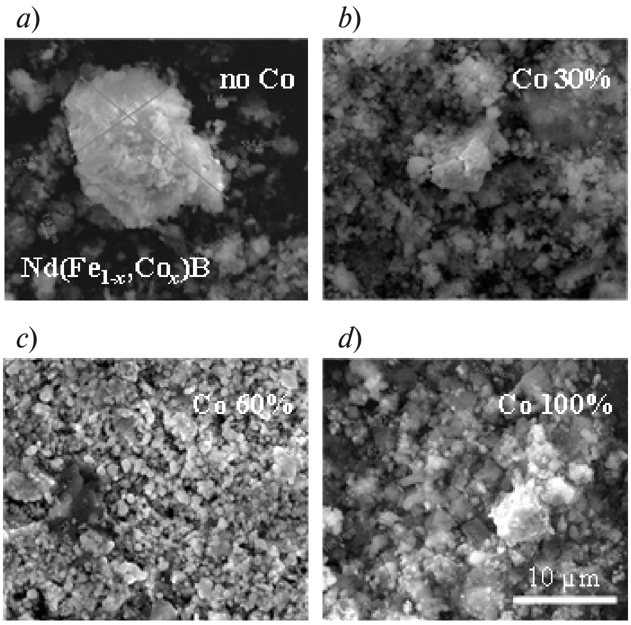


Fig. 1. SEM images of $NdFe_{1-x}Co_xB$ particles without Co (*a*) and the declared percentage of cobalt: 30 (*b*), 60 (*c*), 100% (*d*)

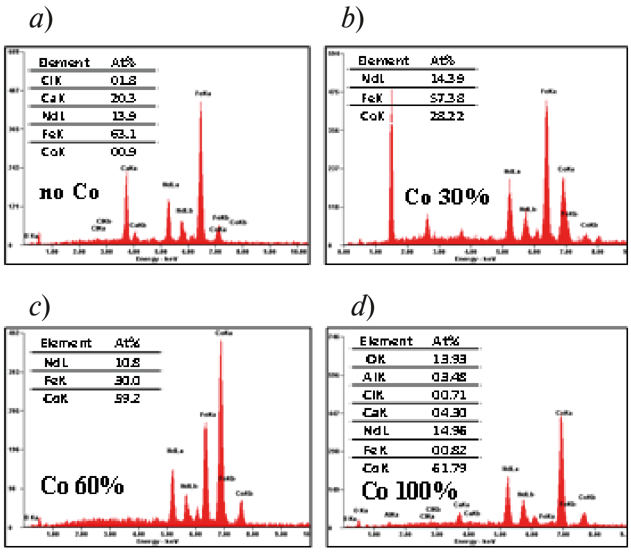


Fig. 2. EDX analysis of $NdFe_{1-x}Co_xB$ particles without Co (*a*) and declared percentage of cobalt: 30 (*b*), 60 (*c*), 100% (*d*)

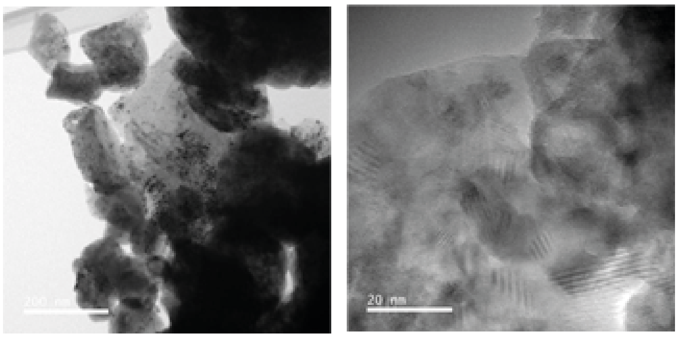
Fig. 1, *b* shows the SEM image of a sample with 30% Co. The average size of the powders is 690 nm. According to the initial elemental analysis, the composition approaches the expected composition (Fig.2, *b*). For samples with 60% Co, images against the background of agglomerates show mainly 'smooth' particles that do not have sharp protrusions. It can be seen that the particles are fairly close in size. The average particle size is about 550 nm. According to the data of local elemental analysis, the samples predominantly contain the elements Nd, Fe and Co equal to 10.8, 30.0, and 59.2 at%, respectively, without taking into account the content of contaminating elements Ca, Cl and O (Fig. 2, *c*).

In a sample with 100% Co, that is, without iron, particles with clear boundaries and surface relief are observed (Fig. 1, *c*). There are agglomerates and individual particles of different sizes. The average size of the powders is about 620 nm. According to the data of local elemental analysis, Ca, Cl, and O are present in the samples (Fig. 2, *d*). The local content of Co in an individual particle is 61.8 to 78.7 at.%.

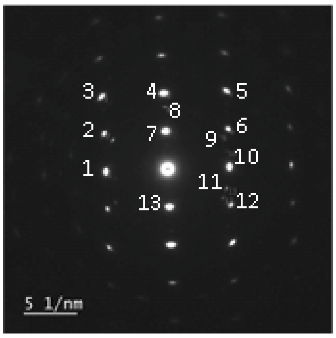
Thus, the SEM method showed that the powders contain both individual particles, mostly irregular in shape, and agglomerates. The most uniform in size structure of the powder in the sample with 60% Co. According to the data from local elemental analysis, all of the studied samples contain Ca, Cl, O, and Si, which may have remained due to the powder preparation method. In general, the content of Nd, Fe, and Co in individual particles corresponds to the declared ones.

A TEM study showed (Fig. 3) that the powders contain both individual particles of mostly irregular shapes and agglomerates. In this case, the particle sizes range from 25 to 1500 nm. Some large particles contain smaller particles of the order of (5–20) nm. The nanoparticles in NdFeB samples without Co were identified as the $Nd_2Fe_{14}B$ phase (a = 0.88 nm, c = 1.22 nm), see Fig. 3, *c*.

a) *b*)



c)



№	d-Spacing (nm)	$Nd_2Fe_{14}B$
1	0,1716	511(334)
2	0,147	416
3	0,1087	448
4	0,1409	515
5	0,1095	448
6	0,1473	416
7	0,2817	222
8	0,1734	510(325)
9	0,1731	510(325)
10	0,18	216
11	0,1727	510(325)
12	0,1721	510(325)
13	0,2775	222

Fig. 3. TEM images of NdFeB particles (without cobalt): bright-field image (*a*), direct resolution of the microstructure (*b*); as well as microelectron diffraction pattern of the NdFeB nanopowder microstructure and its interpretation (*c*)

Fig. 4 shows the magnetic hysteresis loops measured on a vibromagnetometer at room temperature. The maximum value of the specific magnetization σ_{17}, measured in a magnetizing field of 17 kOe, reaches a value of approximately 125 G cm³/g and the coercive force H_c = 260 Oe of the corresponding powder. Although the cobalt sublattice in the $Nd_2Co_{14}B$ compound has an easy-plane anisotropy, an increase in the coercive force is observed with increasing Co concentration (see the inset in Fig. 5), but the H_c values are not typical for magnetically hard materials (usually several kOe and higher).

Fig. 5 shows the dependence of the maximum specific magnetization σ_{17} and the coercive force H_c of the

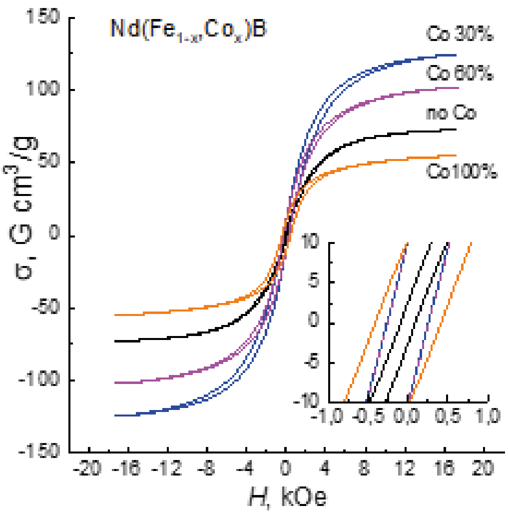


Fig. 4. Magnetic hysteresis loops of $NdFe_{1-x}Co_xB$ powders, depending on Co concentration: 0, 30, 60, and 100. The inset shows enlarged fragments of hysteresis loops

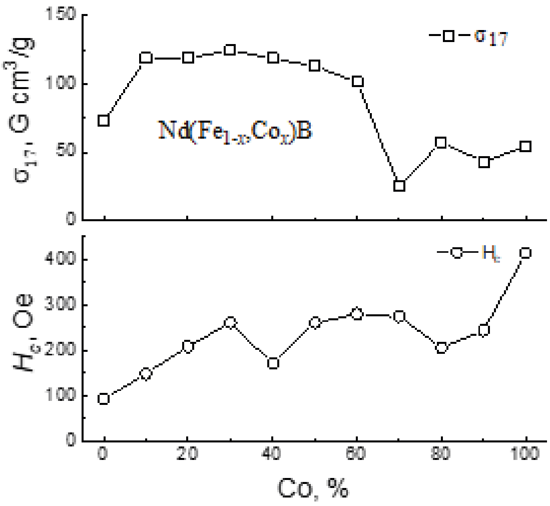


Fig. 5. Dependence of saturation magnetization σ17 and coercive force Hc of $NdFe_{1-x}Co_xB$ powders on cobalt content

$NdFe_{1-x}Co_xB$ powders on the content of cobalt, which replaces iron. After the addition of Co, there is a sharp increase in the magnetization, which decreases with the substitution of iron. The value of H_c increases from 10 to almost 415 Oe with increasing Co concentration.

Thus, $NdFe_{1-x}Co_xB$ powders were obtained, in which nanoparticles of a predominantly magnetically soft phase are formed. It follows from the TEM results that the indicated method can form particles with a magnetically hard $Nd_2Fe_{14}B$ phase. It is theoretically predicted that the maximum values of NS and energy product can be achieved in nanocomposite materials consisting of soft and hard phases [16]. It is likely that the presence of impurities in the samples reduces the purity of the phases, leading to a deterioration in the magnetic properties. A wide spread of particle sizes and their shapes leads to the fact that the magnetization reversal process occurs with the help of different mechanisms (magnetization rotation or domain wall motion). Furthermore, the magnitude of the coercive force in agglomerates of nanoparticles can decrease as a result of magnetostatic interaction. These features appear as a smooth hysteresis loop.

Conclusion

The $NdFe_{1-x}Co_xB$ powders were obtained by chemical synthesis using the modified Pechini method. A series of samples with Co concentrations from 0 to 100% was obtained and studied. The resulting material consists of both individual particles, mostly irregular in shape, and agglomerates (up to 15 μm). The average particle size according to electron microscopy varies from 550 to 870 nm. In this case, particles smaller than 100 nm in size can also be encountered. According to the data from local elemental analysis, all of the studied samples contain Ca, Cl, O, and Si, which may have remained due to the powder preparation method. The content of Nd, Fe, and Co in the particles corresponds to the declared ones. The magnetic properties of powders are typical for soft magnetic materials. An increase in the Co content leads to an increase in the coercive force up to 415 Oe. Probably, such magnetic properties are due to the low phase purity and a wide range of particle sizes.

REFERENCES

1. **Coey J. M. D.,** Magnetic materials, Alloys Compd. 326 (2001) 2–6.

2. **Matsuura Y.,** Recent development of Nd–Fe–B sintered magnets and their applications, J. Magn. Magn. Mater. 303 (2006) 344–347.

3. **Cui J., Kramer M., Zhou L., Liu F., Gabay A., Hadjipanayis G., Balasubramanian B., Sellmyer D.,** Current progress and future challenges in rare-earth-free permanent magnets, Acta Mater. 158 (2018) 118–137.

4. **Coey J.M.D.,** Magnetism and Magnetic Materials, Cambridge University Press, Cambridge, 2010.

5. **Skomski R., Coey J. M. D.,** Giant energy product in nanostructured two-phase magnets, Phys. Rev. B 48 (1993) 15812.

6. **Samardžija, Z., McGuiness, P., Soderžnik, M., Kobe, S., Sagawa, M.,** Microstructural and compositional characterization of terbium-doped Nd-Fe-B sintered magnets. Mater. Charact. 67 (2012) 27–33.

7. **Lee M. W., Bae K. H., Lee S. R., Kim H. J., Jang T. S.,** Microstructure and magnetic properties of NdFeB sintered magnets difusion-treated with Cu/Al mixed Dyco alloy-powder archives of metallurgy and materials 62(2) (2017) 1263–1266.

8. **Samardak V. Yu., Kharitonov V. N., Belov A. A., Shichalin O. O., Papynov E. K., Protasov A. V., Stashkova L. A., Kuranova N. N., Pushin V. G., Samardak A. S., Ognev A. V.,** Structure, Composition and Magnetic Properties of Nd-(Fe,Co)-B Hard Magnetic Copper-Doped Powders. J Supercond Nov Magn 35 (2022) 1703–1708.

9. **Deheri P. K., Swaminathan V., Bhame S. D., Liu Z., Ramanujan R. V.,** Sol-gel based chemical synthesis of $Nd_2Fe_{14}B$ hard magnetic nanoparticles, Chem. Mater. 22 (24) (2010) 6509–6517.

10. **Ahmadpour G., Samardak A. Yu., Korochentsev V. V., Osmushko I. S., Samardak V. Yu., Komissarov A. A., Shtarev D. S., Samardak A. S., Ognev A. V., Nasirpouri F.,** Microstructure, composition and magnetic properties of Nd-($Fe_{1-x}Co_x$)B oxide magnetic particles synthesized by Pechini-type chemical method, Advanced Powder Technology, 32, 11 (2021) 3964-3979.

11. **Ma H. X., Kim C. W., Kim D. S., Jeong J. H., Kim I. H., Kang Y. S.,** Preparation of Nd-Fe-B

by nitrate-citrate auto-combustion followed by the reduction-diffusion process, Nanoscale. 7 (17) (2015) 8016–8022.

12. **Tan X., Parmar H., Chaudhary V., Zhong Y., Ramanujan R. V.,** Synthesis and reaction mechanism of high (BH)max exchange coupled $Nd_2(Fe,Co)_{14}B$/a-Fe nanoparticles by a novel one-pot microwave technique, New J. Chem. 42 (23) (2018) 19214–19223.

13. **Nethi S. K., Bollu V. S., Patra C. R.,** Rare Earth-Based Nanoparticles: Biomedical Applications, Pharmacological and Toxicological Significance. In: Shukla, A. (eds) Nanoparticles and their Biomedical Applications. Springer, Singapore. (2020).

14. **Papynov E. K., Dran'kov A. N., Tkachenko I. A., Buravlev I. Y., Mayorov V. Y., Merkulov E. B., Fedorets A. N., Ognev A. V., Samardak A. S., Drenin A. S., Tananaev I. G.,** Synthesis and Sorption Characteristics of Magnetic Materials Based on Cobalt Oxides and Their Reduced Forms, Russian Journal of Inorganic Chemistry, 65 (6) (2020) 820–828.

15. **Fischer, R., Leineweber, T., Kronmüller, H.,** Fundamental magnetization processes in nanoscaled composite permanent magnets, Phys. Rev. B: Condens. Matter Mater. Phys. 57 (1998) 10723.

THE AUTHORS

SAMARDAK Vadim Yu.
Samardak_vy@dvfu.ru
ORCID: 0000-0002-1919-113X

PAPYNOV Evgeniy K.
papynov.ek@dvfu.ru
ORCID: 0000-0002-1185-7718

AZON Semen A.
azon.sa@dvfu.ru
ORCID: 0000-0003-3129-1499

SAMARDAK Alexandder S.
samardak.as@dvfu.ru
ORCID: 0000-0001-5917-4361

SAMARDAK Alexey Yu.
samardak.aiu@dvfu.ru
ORCID: 0000-0002-0795-374X

OGNEV Alexey V.
ognev.av@dvfu.ru
ORCID: 0000-0002-1619-3666

Received 21.05.2022. Approved after reviewing 01.07.2022. Accepted 05.08.2022.