

Phase structure of the nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ magnets with different grain size

Izabela Wnuk,
Jerzy J. Wyslocki,
Anna Przybył

Abstract. The effect of the contents of the magnetically hard and magnetically soft phases on the magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B} + \alpha\text{-Fe}$ nanocrystalline magnets, as produced by the method of mechanical alloying, has been established. The phase composition of specimens was determined using X-ray diffractometry and Mössbauer spectroscopy. The Mössbauer examination showed that as the powder milling times increased, the content of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase increased from 42.8% (after the milling time of 10 h, with a grain size of 44.8 nm) to 66.3% (after the milling time of 48 h, with a grain size of 37.3 nm) and then decreased to 40.3% after 120 h of milling. On the other hand, the content of the magnetically soft phase $\alpha\text{-Fe}$ initially decreased (from 27.7%), reaching a minimum after the milling time of 48 h (17.4%) and then increasing to 36.9% after 120 h of milling.

Key words: $\text{Nd}_2\text{Fe}_{14}\text{B} + \alpha\text{-Fe}$ nanocrystalline magnets • Mössbauer spectroscopy • magnetic properties

Introduction

The basic phase of Nd-Fe-B magnets is the intermetallic phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ containing 11.76 at.% of neodymium [9]. Alloys of an neodymium content greater than stoichiometric (11.76 at.%) in this phase in a state of equilibrium contain an Nd-rich paramagnetic phase, while alloys containing a lower neodymium content have precipitations of the free $\alpha\text{-Fe}$. The magnetic properties of $\text{RE}_2\text{Fe}_{14}\text{B}$ (where RE means rare earths) compounds result from the ferromagnetic coupling of the sublattice magnetic moments of rare earths metals and iron for light RE and the anti-ferromagnetic coupling for heavy RE [3]. The magnetic moments of neodymium and iron are parallel to the c -axis of the tetragonal unit cell, forming a ferromagnetic order, which is in accordance with the rule that the light rare earths are ferromagnetic materials [4]. This is confirmed by Mössbauer [8] and polarized neutron diffraction examinations [2]. The Curie point of the compound is 585 K [2]. Such a combination of the magnetically hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase of high coercivity JH_c with the magnetically soft $\alpha\text{-Fe}$ phase of a high value of magnetic remanence enables good magnetic properties to be obtained in this material. However, the combination

I. Wnuk, J. J. Wyslocki✉, A. Przybył
Institute of Physics,
Department of Materials Processing Technology
and Applied Physics,
Częstochowa University of Technology,
19 Armii Krajowej Str., 42-200 Częstochowa, Poland,
Tel./Fax: +48 34 3250795,
E-mail: wyslocki@mim.pcz.czest.pl

Received: 20 June 2006

Accepted: 6 November 2006

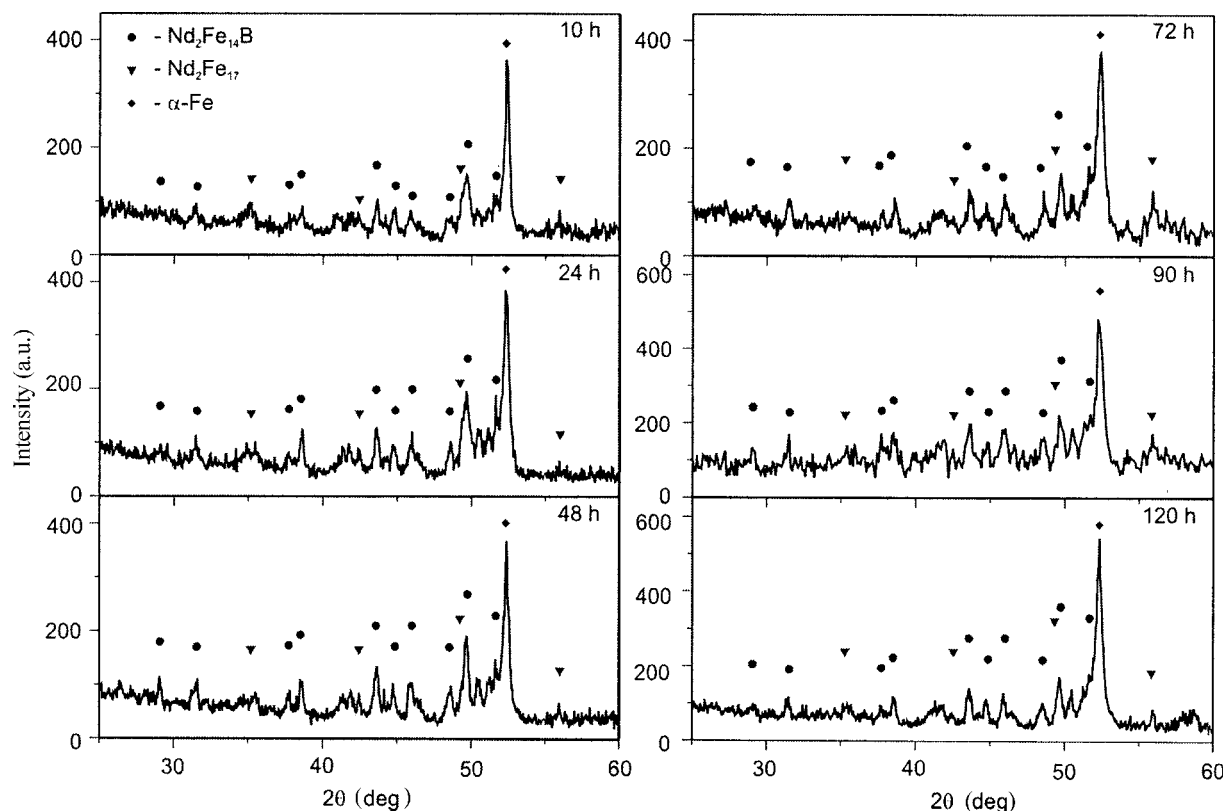


Fig. 1. X-ray diffraction patterns of nanocomposite $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ magnets milled for: 10, 24, 48, 72, 90 and 120 h, respectively.

of the magnetic properties of those phases is only possible at nanometric grain dimensions.

Material and experimental methods

The investigations were carried out on a new class of magnetically hard materials, so-called nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ composite magnets of a different grain size. The test material was prepared by the method of mechanical alloying. Alloys of the basic $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ composition were tested. The starting materials for the preparation of magnets were Nd, Fe powders and the $\text{Fe}_{80}\text{B}_{20}$ alloy. The milling was performed for times varying from 10 to 120 hours. As a result of this process, a characteristic layered metastable structure is formed. Milling of Nd, Fe powders and the Fe-B alloy does not lead to obtain directly the magnetically hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Powders obtained from milling do not have the properties characteristic of magnetically hard materials. The proper phase composition is only obtained during controlled crystallization in the low-temperature annealing process. So obtained material was annealed in a vacuum furnace for the time of 30 min at 923 K (these conditions were considered optimal on the basis of the previous investigation [5]). The next stage of preparation included pressing of the powders under a pressure of 300 MPa. As a result of these processes, $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ nanocomposite magnets were obtained.

The phase composition of the $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ as a function of milling time was determined by XRD and the magnetic properties were measured using a vibrating sample magnetometer. Figure 1 shows the X-ray diffrac-

tion patterns of the magnets, with the marked points corresponding to the angular positions of reflexes corresponding to the identified crystalline phases. The main phase, whose presence was identified, is the magnetically hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Additionally, the following magnetically soft phases occur in the specimens: the $\alpha\text{-Fe}$ phase of a high value of saturation magnetization of $J_s = 2.15$ T and the $\text{Nd}_2\text{Fe}_{17}$ phase of a low value of saturation magnetization below 1 T. These results are in agreement with the results obtained by Schneider *et al.* [10]. The occurrence of these three ferromagnetic phases was observed for all milling times. Such a combination of a magnetically hard phase of great coercivity and a high value of maximum energy product $(BH)_{\text{max}}$ with a magnetically soft phase characterized by high saturation magnetization is very advantageous. It causes that good magnetic properties are achieved in the material.

Using Mössbauer spectroscopy, the effect of milling time on the hyperfine parameters of the $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ magnets was examined. The occurrence of the $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Fe}_{17}$ and $\alpha\text{-Fe}$ phases was observed for all milling times. Figure 2 shows the Mössbauer spectra for the $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ magnets after, respectively, 10, 24, 48, 72, 90 and 120 hours of milling. Six Zeeman sextets were attributed to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, while one sextet to the $\alpha\text{-Fe}$ phase. One Zeeman sextet was attributed to the magnetically soft $\text{Nd}_2\text{Fe}_{17}$ phase. For a complete fitting of the Mössbauer spectrum, a doublet of a very wide line, corresponding to the speromagnetic phase, was used [7]. On the basis of these examinations, the percentage share of the phases forming the magnets was determined (Table 1). As the magnetically soft

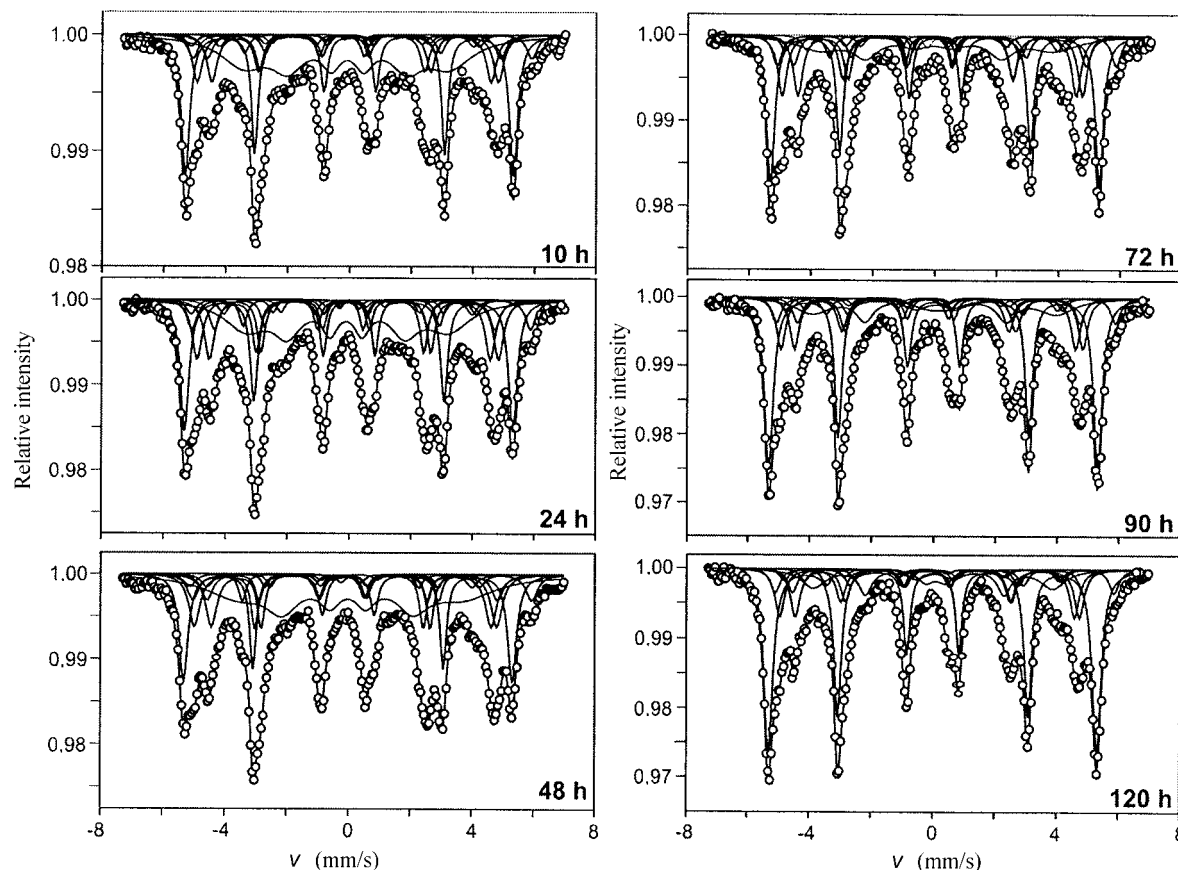


Fig. 2. Mössbauer spectra of Nd₁₀Fe₈₄B₆ magnets milled for: 10, 24, 48, 72, 90 and 120 h, respectively.

Nd₂Fe₁₇ phase has poor magnetic properties (the saturation magnetization of $J_s = 0.88$ T is much lower than the magnetization of the α -Fe phase, and the Curie point is 326 K), the Nd-Fe phase is speromagnetic and its volume fraction of the magnet is small (e.g. after 90 h of milling it amounts to 3.36%), the presence of these phases was disregarded in further considerations.

Using a transmission electron microscope, the grain size distribution was determined. Furthermore, the grain size of the magnetically hard Nd₂Fe₁₄B phase and the magnetically soft α -Fe phase was calculated from the XRD traces using the Scherrer method. Distinct widening of the diffraction peaks on XRD traces was observed for the investigated samples, so that grains smaller than 100 nm wide were observed (Table 2). The

Table 1. Phase composition of the Nd₁₀Fe₈₄B₆ magnet after different milling times (determined from Mössbauer spectroscopy)

Milling time (h)	Phase composition (% volume fraction)		
	α -Fe	Nd ₂ Fe ₁₄ B	Nd ₂ Fe ₁₇
10	27.7	42.8	23.4
24	21.0	60.2	13.4
48	17.4	66.3	13.1
72	23.52	61.1	10.3
90	33.6	44.9	13.2
120	36.9	40.3	12.8

structure obtained in high-energy milling, composed of a mixture of the nanocrystalline grains of the magnetically hard Nd₂Fe₁₄B phase (34.9 nm after 90 hours of milling) and the fine grains of the magnetically soft α -Fe phase (16.2 nm after 90 h of milling) is, according to work [6], the proper structure, in which exchange couplings occur between adjacent grains. Exchange interactions between the grains of the magnetically hard Nd₂Fe₁₄B phase and their adjacent grains of the magnetically soft α -Fe phase cause the parallel alignment of the magnetic moments in the grains of the magnetically soft phase according to the direction of magnetization of the neighbouring grains of the magnetically hard phase. As a result, the remanence enhancement occurs. This effect could be explained by the fact that

Table 2. Average grain size of the hard magnetic phase Nd₂Fe₁₄B and soft magnetic phase α -Fe determined from X-ray diffraction patterns and average grain size on sample surface determined from electron microscopy

Milling time (h)	Grain size		
	Determined from X-ray diffraction		Determined from electron microscopy
	α -Fe (nm)	Nd ₂ Fe ₁₄ B (nm)	Average grain size on sample surface (nm)
10	51.3	44.8	37.6
48	29.3	37.3	23.0
90	16.2	34.9	18.9

Table 3. The effect of milling time on magnetic properties of the $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ magnet, where: J_s – saturation magnetization, J_r – remanence, JH_c – coercive force, $(BH)_{\text{max}}$ – maximum energy product

Milling time (h)	J_r (T)	JH_c (kA/m)	J_s (T)	$(BH)_{\text{max}}$ (kJ/m ³)
10	0.276	62.4	1.98	25.2
24	0.412	116.6	1.81	29.4
48	0.510	149.4	1.96	35.2
72	0.857	198.5	2.1	43.6
90	0.914	251.1	2.12	67.7
120	0.878	178.9	2.06	43.0

a larger volume fraction of the smaller grains of α -Fe phase undergoes the interaction with large grains of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

Discussion of the results and conclusions

It can be concluded that the phase structure of $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ magnets produced by the mechanical alloying, is composed of three phases: the magnetically hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and the magnetically soft α -Fe and $\text{Nd}_2\text{Fe}_{17}$ phases. With increasing milling time, the percentage content of the magnetically hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in the magnets increases (until 48 hours) and then decreases to 40.3% of the alloy ground for 120 hours. On the other hand, the content of the magnetically soft α -Fe phase in the alloy, starting from 10 h, decreases with milling time from 27.7% to 17.4% of the alloy ground for 48 h, and then increases to 36.9% of the alloy after 120 h milling. Increasing share of the magnetically soft phase in the alloy causes an increase in remanence, and thus the maximum energy product $(BH)_{\text{max}}$. According to the results of work [1], the optimal content of the magnetically soft α -Fe phase is 40% with a grain size of 20 nm. Such parameters of microstructure assure the following magnetic properties to be obtained: $JH_c = 0.34 \div 0.36$ MA/m and $J_r = 1.1 \div 1.4$ T [1]. It can thus be found that the effect of milling time on the coercivity and remanence plays an important role. This is associated with the increase in the magnetically soft phase with milling time, which has a high saturation

magnetization. For milling times of 10, 24 and 48 h, the increase in coercivity and remanence is small, but after the milling times of 72 and 90 h a rapid increase in either value occurs (Table 3). The Mössbauer examinations have also confirmed the fact that the milling time and the related grain refinement cause an increase in the content of the magnetically soft α -Fe phase in the alloy, starting from the 48 h of milling. Such parameters of microstructure assure good properties of magnetically hard phases to be obtained. The obtained results have shown that the powder milling time (and thus the grain size) substantially influences the microstructure and magnetic properties of nanocrystalline $\text{Nd}_{10}\text{Fe}_{84}\text{B}_6$ magnets.

References

1. Fidler J, Schrefl T (1998) Micromagnetic calculation of the limits of composite $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha$ -Fe, Fe_3B , Fe_{23}B_6 magnets. In: Proc on 10th Int Symp on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys, Dresden, Germany: 267–276
2. Givord D, Li HS, Tasset F (1985) Polarized neutron study of the compounds $\text{Y}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$. J Appl Phys 57:4100–4103
3. Herbst JF, Croat JJ (1991) Neodymium-iron-boron permanent magnets. J Magn Magn Mater 101:360–362
4. Herbst JF, Croat JJ, Yelon WB (1985) Structural and magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$. J Appl Phys 57:4086–4090
5. Kaszuwara W (2003) Role of chemical composition and processing method in the tailoring of properties of nanocrystalline RE-M magnets. Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa (in Polish)
6. Leonowicz M (1996) Modern hard magnetic materials. Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa (in Polish)
7. O'Handley RC (2000) Modern magnetic materials. Principles and applications. John Wiley & Sons, New York
8. Rosenberg M, Deppe P, Wójcik M (1985) An NMR and Mössbauer study of $\text{Nd}_2\text{Fe}_{14}\text{B}$. J Appl Phys 57:4124–4126
9. Sagawa M, Hirosawa S, Yamamoto H, Fujimura S, Matsuura Y (1987) Nd-Fe-B permanent magnet materials. Jpn J Appl Phys 26:785–800
10. Schneider G, Henig E, Stadelmayer HH, Petzow G (1986) Horizons of powder metallurgy. In: Proc Int Powder Met Conf and Exhibition: "The future of powder metallurgy", Düsseldorf, Germany: 1197