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The comparative study of Nd-Fe-B magnetic materials with different Nd content

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For the purpose of better understanding of the effect of different Nd content on the magnetic properties of three types of commercial Nd-Fe-B alloys with 10-12 wt% Nd (Nd-low), 21-25 wt% (Nd-stoich.), and 26-29 wt% Nd (Nd-rich) were simultaneously analyzed using X-Ray and ^{57}Fe Mössbauer spectroscopy analysis. The observation was based on correlation of starting chemical composition with phase composition and magnetic properties of the alloys in optimized magnetic state.

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1. Introduction

Nanocrystalline hard magnetic materials based on Nd-Fe-B alloys are widely used in large number of different applications due to their suitability for tailoring magnets with defined magnetic properties [1]. One of the most important parameters which defines the magnetic microstructure of nanocrystalline Nd-Fe-B in optimal magnetic state and hence their magnetic properties is Nd content. Depending on the starting composition of the alloys, three different microstructures of Nd-Fe-B alloys have been developed by means of melt-spinning method [2] - the alloys with substoichiometric Nd content or the nanocomposite alloys (Nd-low), the alloys with stoichiometric Nd content and the alloys with overstoichiometric Nd content or decoupled magnets (Nd-rich). The Nd-Fe-B alloys with reduced Nd content have multiphase composition and in the optimal magnetic state they are composed of the nano-sized exchange coupled grains of soft and hard magnetic phases. Depending on the alloy composition two types of nanocomposites α-Fe/$Nd_2Fe_{14}B$ and/or Fe_3B/$Nd_2Fe_{14}B$ can be obtained [3]. The stoichiometric and Nd-rich Nd-Fe-B alloys have an almost monophase composition with dominant amount of $Nd_2Fe_{14}B$ phase. While the stoichiometric alloys are characterized by some intergranular exchange coupling between the grains of the same hard magnetic phase [4,5] the Nd-rich alloys are composed of grains of hard magnetic $Nd_2Fe_{14}B$ phase that are magnetically isolated (decoupled) by the intergranular layer of Nd-rich phases [6]. The influence of Nd content on microstructure and magnetic properties of three kinds of commercial Nd-Fe-B alloys was analyzed by comparing phase composition and magnetic properties in optimized magnetic state.

2. Experimental

The commercial melt-spun Nd-Fe-B alloys having 10-12 wt% Nd (Nd-low), 21-25 wt% (Nd-stoich.) and 26-29 wt% Nd (Nd-rich) were simultaneously analyzed. The chemical composition of the starting Nd-Fe-B powders after quenching and crystallization are presented in Table 1.

Table 1. The chemical composition (wt. %) of investigated Nd-Fe-B alloys – as given by producer.

Element	Sample		
	Nd-low	Nd-stoich	Nd-rich
Nd	10-12	21-25	26-29
Fe	> 80	> 65	> 69
B	< 5	< 1.5	< 1.3
Co	-	3-5	-
Zr	-	3-5	-
Si	1-3	-	-

The basic magnetic characteristics of the materials studied are presented in table 2. The phase compositions of the investigated alloys in optimized magnetic state were determined by X-ray diffraction analysis (XRD) and ^{57}Fe Mössbauer spectroscopy (MS) at room temperature. X-ray diffraction measurements were performed on an X'Pert PRO MPD multi-purpose X-ray diffraction system from PANanalytical using Co K_α radiation. Mössbauer spectra were taken in the standard transmission geometry using a ^{57}Co(Rh) source. The calibration was done against α-iron foil data. For the MS fitting and decomposition, the CONFIT software package was used [7]. The computer processing yielded intensities I of components, their hyperfine inductions B_{hf}, isomer shifts δ and quadrupole splittings σ. The contents of the iron containing phases are given as intensities of the corresponding spectral components. However, the exact quantification of the phase contents could be done only when possible differences in values of Lamb-Mössbauer factors were considered. The phase analysis published in [8–10] was applied.

The SQUID (Superconducting Quantum Interference Device) magnetometer was used to perform the magnetic measurements of investigated alloys. A magnetic field ranging from -5.0 T to +5.0 T at room temperature was used to generate hysteresis loops.

Table 2. Basic magnetic characteristics of the analyzed alloys –as given by producer.

Property	Sample		
	Nd-low	Nd-stoich	Nd-rich
Br [kG]	8.35	6.40	6.03
Hcb [kOe]	2.55	4.51	4.70
Hcj [kOe]	3.09	8.57	11.91
$(BH)_{max}$ [MGOe]	6.58	7.50	7.17

3. Results and discussion

The obtained X-Ray diffractograms and Mossbauer spectra presented on Fig 1. and Fig 2 illustrate phase composition of investigated Nd-Fe-B alloys in optimal magnetic state.

The results of both of phase analysis show that the magnetically hard $Nd_2Fe_{14}B$ phase is present in all three investigated alloys. The appearance and identification, actually in small amounts, of non-ferromagnetic boride phase $Nd_{1.1}Fe_4B_4$ is the consequence of the fact that in the investigated alloys boron content is above 4.2 at% [11].

The Nd-Fe-B alloy with substoichiometric Nd content (Nd-low) is multiphase. Besides the main hard magnetic phase $Nd_2Fe_{14}B$, the predominant presence of soft magnetic phases with high magnetization such as Fe_3B is determined. The hard magnetic phase $Nd_2Fe_{14}B$ with magnetically soft Fe_3B phase forms the exchange coupled nanocomposite structure. The formed nanocomposite $Fe_3B/Nd_2Fe_{14}B$ is directly responsible for the enhancement of remanence.

In the alloy with the near stoichiometric $Nd_2Fe_{14}B$ composition besides the main hard magnetic phase minor amounts of other phases like $Nd_{1.1}Fe_4B_4$ are also detected, as well as limited amount of paramagnetic iron, probably in a phase with Zr (X-Ray analysis). These phases are probably nanocrystalline and their influence on the magnetic properties is negligible. The small amount of Zr contributes to the further refinement of the hard magnetic grain structure [12] thus promoting the remanece enhancement via the interaction of exchange coupling between the grains.

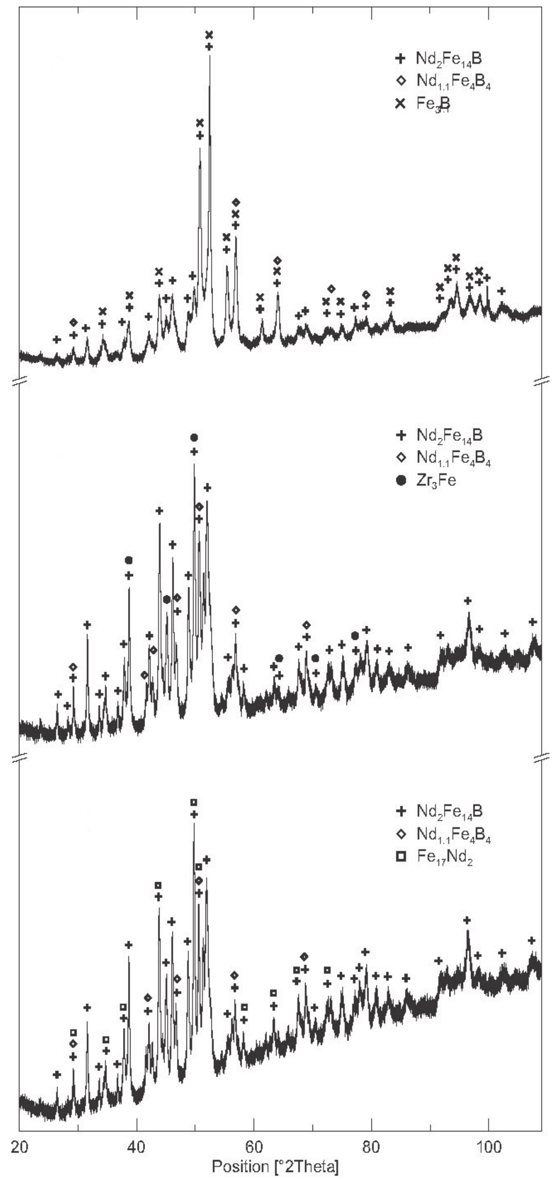

Fig. 1. X-Ray phase analysis of the investigated melt-spun alloys.

In addition to the dominant amount of hard magnetic $Nd_2Fe_{14}B$ phase determined in the Nd-rich alloy, the $Fe_{17}Nd_2$ phase is identified. This phase can be understood as a representative of some minor amount of a Fe(Nd) solid solution. In the corresponding Fe (Nd) B Mössbauer component (Fig. 2), non-magnetic Nd and B atoms are almost undistinguishable. Surprisingly, no traces of any thermal or other decomposition e.g. presence of α-Fe, Fe_2B phases were found.

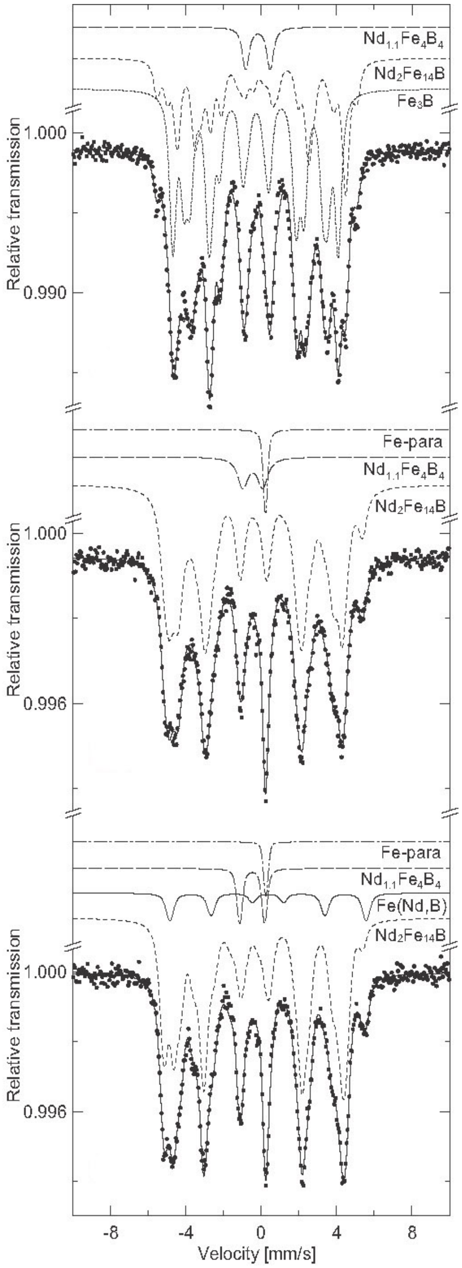

Fig. 2. Mössbauer phase analysis of the investigated melt-spun alloys.

It is known that the phase composition of the studied alloys is not very simple [13-15]. As the every supposed phase is represented by several components in Mössbauer spectrum, the final model of each spectrum is rather complex, including possible surface/interface components as well. Nevertheless, the presence of supposed main phases was confirmed both by XRD and MS analysis.

The phase composition of investigated Nd-Fe-B alloys obtained by MS phase analysis is given in Table 3. For simplicity, proportionality between intensity of the Mössbauer lines and amount of relevant Fe atoms is supposed.

Table 3. Phase composition and relative fractions as taken from MS spectra.

Phase	Sample		
	Nd-low	Nd-stoich.	Nd-rich
Fe_3B	0.58	-	-
$Nd_2Fe_{14}B$	0.38	0.92	0.87
$Nd_{1.1}Fe_4B_4$	0.04	0.05	0.05
Fe(Nd,B)	-	-	0.08
Fe-para	-	0.03	(<<0.01)

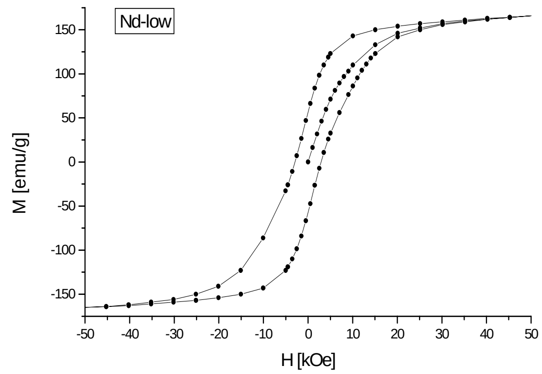

Fig. 3. Hysteresis loop for investigated Nd-Fe-B alloy with 10-12 wt% Nd.

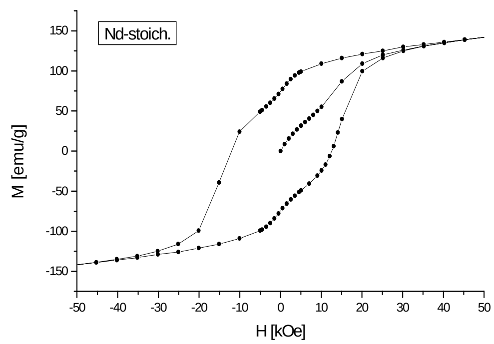

Fig. 4. Hysteresis loop for investigated Nd-Fe-B alloy with 21-25 wt% Nd.

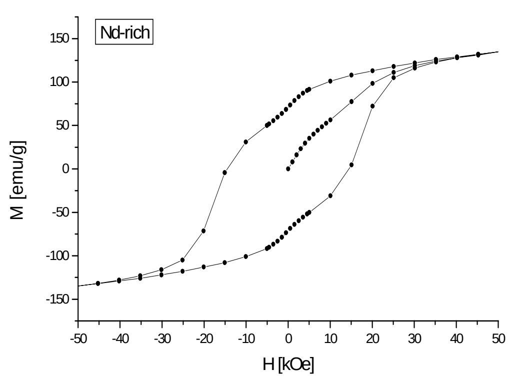

Fig. 5. Hysteresis loop for investigated Nd-Fe-B alloy with 26-29 wt% Nd.

Hysteresis loops obtained by SQUID magnetometer for all investigated alloys are presented on Figs 3-5. The shape of SQUID hysteresis loops correspond to the structure and phase composition of the Nd-Fe-B alloys with reported Nd content in optimal magnetic state and illustrate difference in magnetic properties (behaviour) depending on Nd content. Measured magnetic properties (Table 2, Figs 3-5) demonstrate that the increase of the Nd content causes the increase of coercive force and decrease of remanence. However, the determined values of maximal energy product (BH)max (Table 2) for all three investigated Nd-Fe-B alloys are comparable, which suggest that the alloy with the lowest Nd content has exchange coupled nanocomposite structure.

4. Conclusions

Phase analysis, both XRD and MS have determined the presence of magnetically hard $Nd_2Fe_{14}B$ phase in all three investigated alloys. In the Nd-low, it is accompanied with the magnetically soft Fe_3B phase, building the nanocomposite structure. On the other side, in the Nd-rich sample the overstoichiometric Nd atoms seem to build separate phase of Fe-Nd solid solution. All the three studied hard magnetic materials are of high quality, as none of the materials contain any significant content of "parasitical" phases (e.g. α-Fe or other products of thermal decomposition) degrading the most important magnetic characteristics, with an exception of minor quantities of $Nd_{1.1}Fe_4B_4$ phase. No oxidation products can be seen in the Mössbauer spectra.

The presented results demonstrate the influence of the Nd content on structure and phase composition and consequently on magnetic properties of the analyzed Nd-Fe-B alloys and facilitate the selection of the particular material according to preferred characteristics of magnetic hardness.

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