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Scientific paper

VISOKOENERGETSKI NANOKRISTALNI Nd-Fe-B MAGNETNI MATERIJALI – SINTEZA, KARAKTERIZACIJA, PRIMENA

HIGH-ENERGY NANOCRYSTALLINE Nd-Fe-B MAGNETIC MATERIALS – SYNTHESIS, CHARACTERIZATION, APPLICATION

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Izvod

Permanentni magnetni materijali na bazi Nd-Fe-B legura su jedna od najznačajnijih grupa visokoenergetskih nanokristalnih magnetnih materijala. Savremena istraživanja u razvoju ove grupe magetnih materijala su usmerena u tri glavna pravca: povećanje magnetne energije, poboljšanje otpornosti na koroziju i redukovanje sadržaja retke zemlje (Nd) u cilju sniženja cene finalnog magnetnog materijala, ali uz zadržavanje visokih vrednosti magnetne energije. Direktna zavisnost mikrostukture i magnetnih svojstava Nd-Fe-B legura od sadržaja Nd je iskorišćena za razvoj tri osnovna tipa magnetnih nanokristalnih materijala: sa stehiometrijskim sadržajem Nd, sa obogaćenim sadržajem Nd (dekuplovani) i sa redukovanim sadržajem Nd (nanokompoziti). U radu je dat kratak opis svakog tipa materijala, prikaz metoda dobijanja i neki od primera visokotehnološke primene. Za dabranu metodu sinteze dati su procesni uslovi za optimizaciju magnetnih svojstava na bazi dobijenih eksperimetalnih rezultata istraživanja, primenom savremenih i visokorezolutivnih metoda karakterizacije. Dat je takođe kratak osvrt na trendove i izazove u daljem razvoju magnetnih nanomaterijala.

Ključne riječi: *nanostrukturni magnetni materijali, Nd-Fe-B legure, magnetna svojstva.*

Abstract

One of the most widely used high-energy nanocrystalline permanent magnetic materials are Nd-Fe-B alloys. Current R&D of Nd-Fe-B magnets is focused on three major topics: increase of magnetic energy, improvement of corrosion resistance and reduction of rare-earth content as a way of decreasing prices of final magnetic material with still significant magnetic energy. Utilizing the high sensitivity of microstructure and magnetic properties of Nd-Fe-B alloys to the Nd content, three distinctive types of nanocrystalline alloys have been developed: stoichiometric magnets, Nd-rich (decoupled magnets) and magnets with reduced Nd content (nanocomposite magnets). In the presented paper a brief overview of each type of Nd-Fe-B alloy is given, processing methods are outlined and several high technology application examples are presented. Based on experimental results obtained using modern high resolution characterization techniques optimal processing conditions for the selected synthesis method are presented. Trends and challenges in future R&D of magnetic nanomaterials are discussed.

Key words: *nanostructured magnetic materials, Nd-Fe-B alloys, magnetic properties.*

1. INTRODUCTION

Nanocrystalline hard magnetic materials based on Nd-Fe-B alloys play a pivotal role in modern performance oriented industry and they are widely used in large number of different applications due to their suitability for tailoring magnets with defined magnetic properties [1]. The significance of the research and development of high-energy permanent Nd-Fe-B magnetic materials comes from their influence on miniaturization and increase of effectiveness of a wide spectrum of devices, as well as on entirely new constructive solutions in various technical and technological domains. Research and development in the field of magnetic materials based on Nd-Fe-B alloys is directed in three main directions: increase of magnetic energy, increase of corrosion resistance and reduction of amount of rare earth (Nd) in order to reduce the price of final magnetic material while keeping high values of magnetic energy [2-4]. It is known that the performance of Nd-Fe-B magnetic materials is superior when they are engineered on a nanometric scale. 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 [5] - the alloys with reducen 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 [6]. 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 [7,8] 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 [9]. The influence of Nd content on microstructure and magnetic properties of three kinds of commercial Nd-Fe-B alloys was analyzed by comparing microstructure, phase composition and magnetic properties in optimized magnetic state.

2. DESIGN OF NANOCRYSTALLINE ND-FE-B ALLOYS – INFLUENCING PARAMETERS, METHODS OF CHARACTERIZATION

The most common method for production of nanocomposite permanent magnets is method of rapid quenching (melt-spining) [1-4,8]. The advantage of using of method of rapid quenching for production of nanostructured Nd-Fe-B magnetic alloys is possibility of direct influence on the grain size and microstructure by controlling the cooling rate in order to increase coercivity of these magnetic materials. By controlling the cooling rate, wheel speed, ejection conditions and melt temperature a very high frequency of crystal nucleation and relatively low growth rate of the $Nd_2Fe_{14}B$ phase can be achieved which combined leads to the ultra fine grain size of typically 20-50 nm [4,5,7,8,10]. Key for optimization of magnetic microstructure is heat treatment [2,5,11]. Heat treatment directs crystallization flow towards obtaining optimal phase composition and nanocrystalline microstructure which results in optimal magnetic properties. Further reduction of grain size and improvement of magnetic properties can be achieved by the micro alloying of starting alloy, e.g. with Cu and Nb [12]. Various alloying additives change the intrinsic properties of present phases and thus the strength of the intergranular interaction of exchange coupling which depends on the grain size and type of present phases.

For the purpose of better understanding of the influence of the different content of Nd on the formation of the optimal magnetic matrix and defining of interactive intergranular mechanisms which have dominant influence on the magnetic properties, three melt-spun Nd-Fe-B alloys 10-12 wt% Nd (Nd-low), 21-25 wt% (Nd-stoich.) and 26-29 wt% Nd (Nd-rich) were simultaneously analyzed. Heat treatment regime for each Nd-Fe-B alloy was investigated in the temperature interval from 600-700^{o}C [13-17]. Selected and applied heat treatment regimes are: 630^{0}C/3min for Nd-rich; 600^{0}C/3min for Nd-stoich. and 660^{0}C/5min for Nd-low alloy.

In experimental work, different investigation techniques and methods were used. Scanning electron microscopy (SEM) analysis, Transmission electron microscopy (TEM) and High Resolution Electron Microscopy (HREM) were used for study and evaluation of microstructure of the investigated alloys in optimized magnetic state. Phase compositions 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 [18]. 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 [19,20] was applied. Magnetic properties of heat treated samples were measured on Superconducting Quantum Interference Device (SQUID) magnetometer with magnetic field ranging from -5.0 T to +5.0 T at room temperature. Chemical composition of the investigated Nd-Fe-B alloys after quenching and crystallization are presented in table 1.

Table 1. Chemical composition (wt. %) of investigated Nd-Fe-B alloys

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	-	-

Morphology of the investigated alloys is illustrated by the SEM micrograph of Nd-low alloy (Fig 1.). Platelets, that are typical for rapid quenched melt-spun alloys, with width between 80-140 μm and thickness around 25-35 μm can be observed.

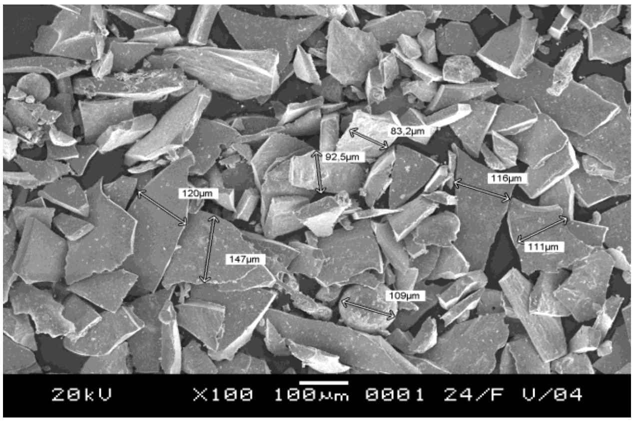


Fig. 1 - SEM micrograph of the investigated melt-spun Nd-low Nd-Fe-B alloy

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

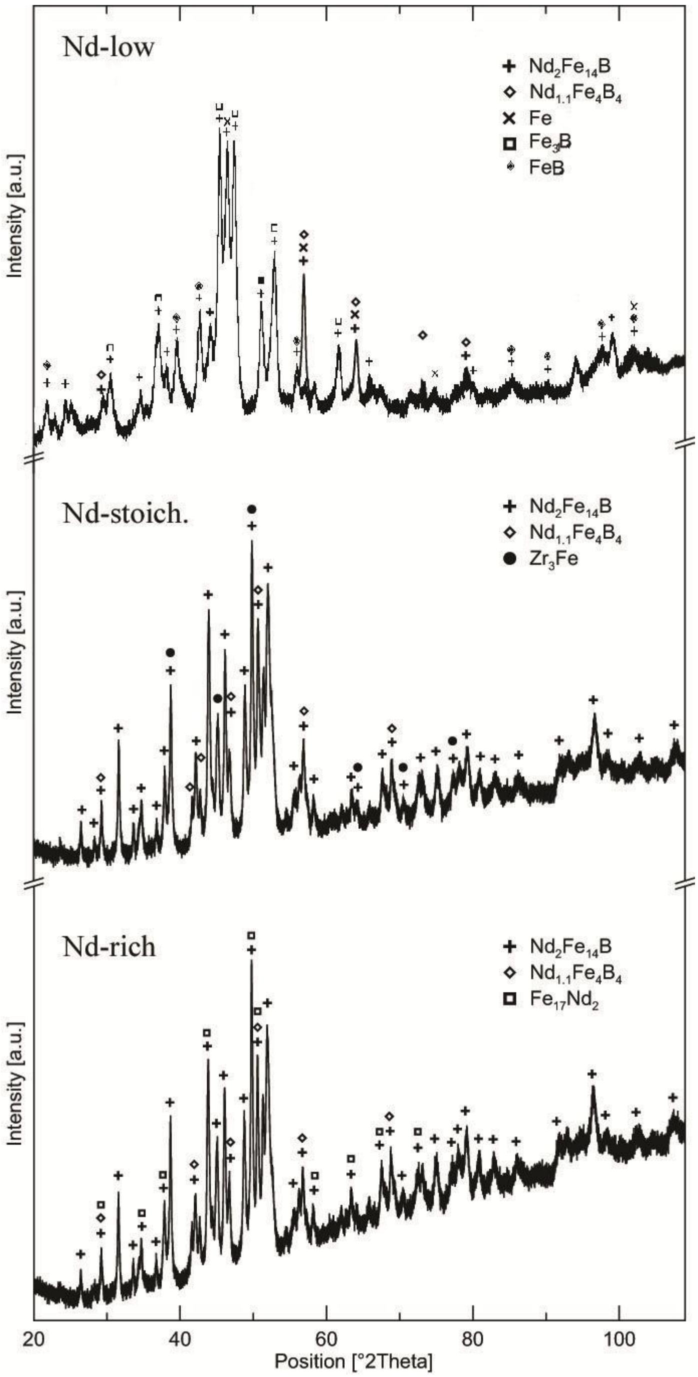


Fig. 2 – X-Ray diffractograms of the investigated alloys

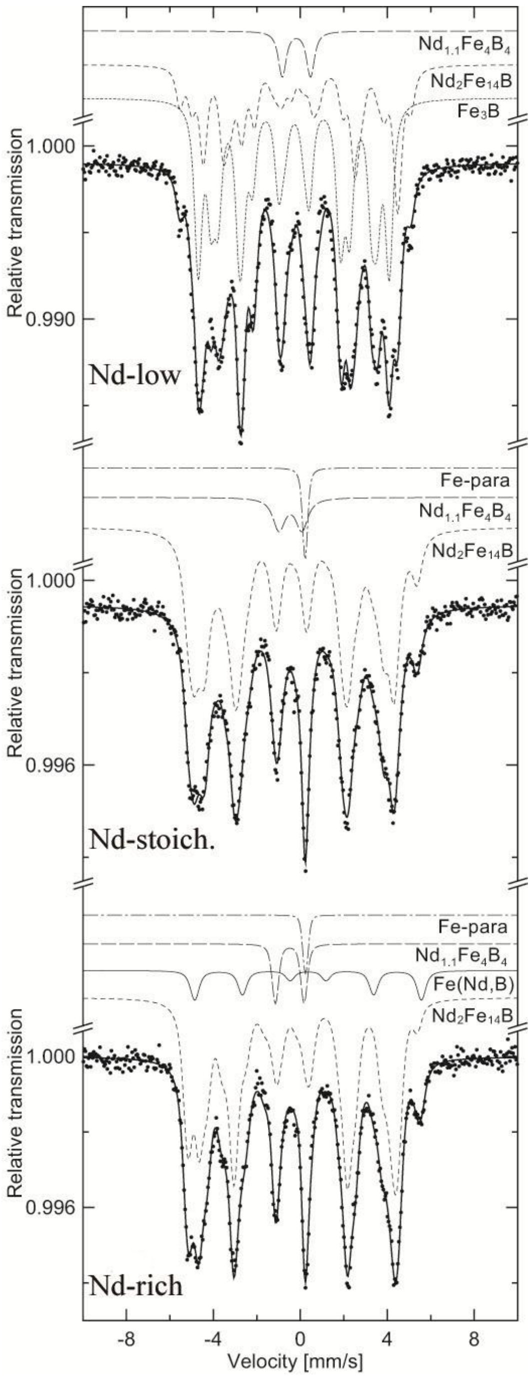


Fig. 3 – Results of MS analysis

By observing the results of XRD analysis of Nd-rich alloy, the hard magnetic phase $Nd_2Fe_{14}B$ is identified as the primary phase. In addition to the hard magnetic $Nd_2Fe_{14}B$ phase and boride phase the $Fe_{17}Nd_2$ phase is identified as well. Due to low reflections intensity and a great number of reflections of the identified primary phase, it was not possible to define by this analysis to which phases the unidentified diffraction maximums belong.

Results of XRD analysis of the alloy with near stoichiometric Nd content in optimized state (Fig. 2) show that this alloy has almost single phase composition with dominant amount of

$Nd_2Fe_{14}B$ hard magnetic phase. Besides the main hard magnetic phase minor amounts of other phases like $Nd_{1.1}Fe_4B_4$ were detected, as well as limited amount of paramagnetic iron, probably in a phase with Zr. 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 [1] thus promoting the remanece enhancement via the interaction of exchange coupling between the grains.

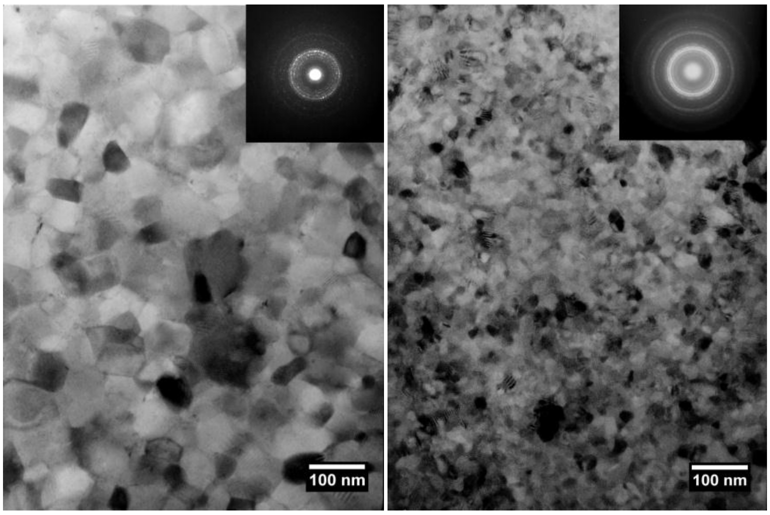
The Nd-Fe-B alloy with substoichiometric Nd content (Nd-low) is multiphase. In addition to the main hard magnetic phase $Nd_2Fe_{14}B$, the predominant presence of soft magnetic phases with high magnetization such as Fe_3B is determined.

For better insight in the phase composition of the investigated melt-spun alloys after the heat treatment the MS analysis was carried out. Given that MS analysis provides more detailed identification of phases containing Fe, apart from main magnetic phases, the presence of other soft and paramagnetic phases was determined as well. The results of MS phase analysis of investigated rapid quenched Nd-Fe-B alloys corroborate the phase compositions determined by XRD. The obtained MS spectra are presented on Fig. 1 and corresponding phase compositions are given in table 2.

Table 2. - 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)

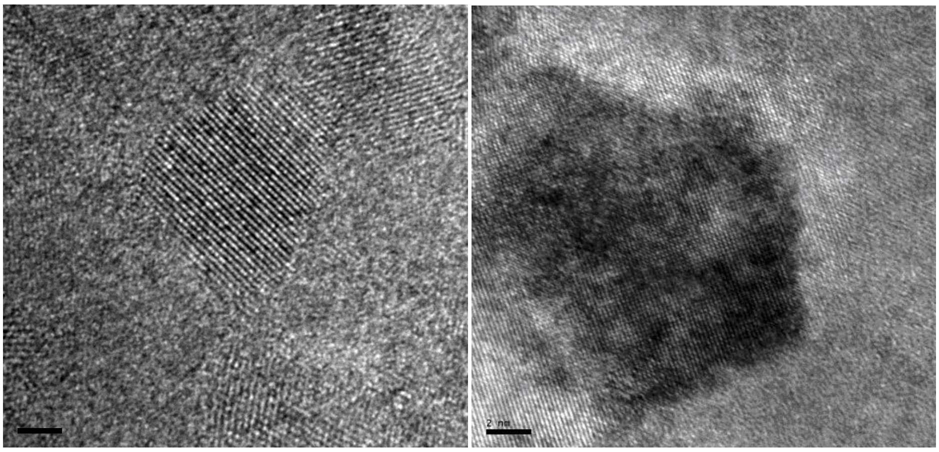
The $Fe_{17}Nd_2$ phase identified in the Nd-rich alloy by XRD can be understood as a representative of some minor amount of a Fe(Nd) solid solution found by MS analysis. In the corresponding Fe (Nd) B Mössbauer component (Fig.3), non-magnetic Nd and B atoms are almost undistinguishable.



a) *b)*

Fig. 4 –TEM images of a) Nd-low and b) Nd-rich alloy in the optimal magnetic state

Microstructures of the investigated Nd-Fe-B alloys with the nonstoichiometric Nd content in the optimized magnetic state are illustrated by TEM and HREM images given in Fig. 4 and Fig. 5. The presented TEM images confirm nanocrystalline structure of the investigated alloys and show that in a case of Nd-low alloy (Fig. 4a) the average crystal grain size is below 30 nm while in the case of Nd-rich alloy (Fig. 4b) the average crystal grain size is about 60 nm. The obtained electron diffraction patterns show very high density of diffraction rings, due to which the reliable identification of present phases was not possible. More detailed analysis of microstructure of the investigated Nd-Fe-B alloys with nonstoichiometric Nd content is given in previous publications [21-23].



a) *b)*

Fig. 5 – HREM images of a) Nd-low and b) Nd-rich alloy in the optimal magnetic state

The HREM analysis (Fig.5a) of the Nd-low alloy in the optimal magnetic state has confirmed that in the microstructure of the alloy there are crystal grains with the sizes about 10 nm and less. The HREM nanograph of the Nd-rich alloy in optimal magnetic state (Fig.5b) illustrates the presence of the crystal grains with the sizes of about 20 nm within the microstructure of the alloy and implies the existence of ***equilibrium structure, since the structure is considered to be equilibrial if the angles between the boundaries of the crystal grains of the same phase are 120^o.***

The shapes of the hysteresis loops obtained by magnetic measurements on SQUID magnetometer (Fig.6) are in correspondence with magnetic microstructure of the investigated alloys in the optimized magnetic state.

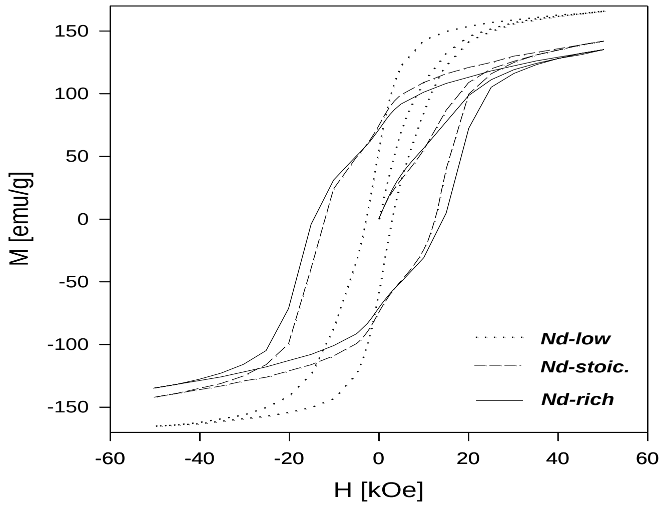


Fig. 6 - Hysteresis loops of investigated Nd-Fe-B alloys in optimized magnetic state

The obtained hysteresis loop of the Nd-rich Nd-Fe-B alloy in the optimized magnetic state (Fig.6) implies the presence of the magnetically decoupled nanocrystalline structure. The obtained high value of coercivity (H_{cj} = 11.91 kOe) supports this and indicates nearly a monophase structure of the alloy with dominant content of main hard magnetic phase $Nd_2Fe_{14}B$.

Values of measured magnetic properties (Table 3.) and the shape of the obtained SQUID hysteresis loop of the Nd-stoich. Nd-Fe-B alloy (Fig.6), enhanced remanence and magnetic energy indicate that microstructure of this alloy provides conditions for the efficient interaction of exchange coupling between the grains of the main hard magnetic phase $Nd_2Fe_{14}B$. It can be assumed that the grains of hard magnetic phase are in direct contact with each other and there are no intergranular phases which would cause the magnetic isolation of the grains and thus disable the exchange interaction. Measured value of coercive force H_{cj} is 8.57 kOe, (Table 3.) is consistent with the theoretical and experimental observations i.e. it decreases with the reduction of Nd content [2,4,6].

Further increase of remanence and magnetic energy is obtained for multiphase Nd-Fe-B alloy with reduced content of Nd by forming nanocomposite structure after application of optimal heat treatment [16, 21, 24]. According to results of phase analysis of the Nd-low alloy (Fig. 2., Fig.3.) besides hard magnetic $Nd_2Fe_{14}B$ phase, soft magnetic Fe_3B and minor quantities of α-Fe phases were identified as well as the whole set of ferromagnetic Fe-Nd phases. Compared to the other two investigated alloys with dominant hard magnetic $Nd_2Fe_{14}B$ phase, remanence of this alloy is increased (*Br* = 8.35 kG) and the shape of hysteresis loop indicates enhancement of remanence.

Based on analysis and correlation of phase composition after applied heat treatment regime, measured magnetic properties as well as experimentally calculated remanence ratio, phase composition of magnetic matrix and type of intergranular mechanism which have dominant influence on the magnetic properties of investigated Nd-Fe-B alloys were defined (Table 3.).

Table 3. - Structure, magnetic properties and intergranular interactions of investigated Nd-Fe-B alloys in optimized magnetic state

Type of alloy	**Structure / phase composition**	**Dominant influence on magnetic properties / Type of intergranular interaction**	**Magnetic properties**		
			Br [kG]	**Hcj** [kOe]	**(BH)max** [MGOe]
Nd - rich	almost monophase $Nd_2Fe_{14}B$	Dominant amount of $Nd_2Fe_{14}B$ / Magnetic decoupled $Nd_2Fe_{14}B$ grains	6.03	11.91	7.17
Nd – stoich.	almost monophase $Nd_2Fe_{14}B$	Dominant amount of $Nd_2Fe_{14}B$ / Exchangecoupling between$Nd_2Fe_{14}B$ grains	6.40	8.57	7.50
Nd - low	multiphase $Fe_3B/Nd_2Fe_{14}B$	Nanocoposite $Fe_3B/Nd_2Fe_{14}B$ / Exchangecoupling between soft magnetic Fe_3B grains and hard magnetic $Nd_2Fe_{14}B$ grains	8.35	3.09	6.58

By correlation of phase composition obtained after optimal heat treatment (Fig. 2., Fig.3.) and measured magnetic properties (Fig. 6, Table 3.), observed enhancement of remanence and significant value of maximal magnetic energy can be attributed to formation of $Fe_3B/Nd_2Fe_{14}B$ nanocomposite i.e. presence of intergranular interaction of ferromagnetic exchange coupling between the grains of soft and hard magnetic phases. Calculated value of remanence ratio *Mr/Ms* of investigated Nd-low alloy obtained by measurements on SQUID magnetometer exceeds theoretical limit [6] and indicates that nanocomposite structure is formed and that the magnetic properties of investigated Nd-low alloy are under the influence of the exchange coupling.

Obtained experimental results summarily presented in tables 2 and 3. of the investigated melt-spun Nd-Fe-B alloys with different Nd content show that after applied heat treatment regimes, phase transformations were completed on the level which enabled formation of optimal magnetic microstructures on nanosclae and provided necessary conditions for intergranular interactions. Final magnetic properties of the Nd-Fe-B permanent magnetic materials determine type and kind of their potential application e.g. while exchange coupled Ne-Fe-B alloys (Nd-low, Nd-rich) are suitable for bonded magnet production [25] decoupled high coercive Nd-rich alloys are more suitable for providing magnetic flux or applications in magnetic field sensing elements [26, 27].

3. CONCLUSIONS

Presented experimental results clearly illustrate influence of Nd content and conditions of heat treatment on formation of optimal nancrystalline magnetic structure and thus on magnetic properties of the investigated melt-spun Nd-Fe-B alloys. Intergranular mechanisms between present phases and their influence on magnetic properties were observed and discussed on the basis of Nd content, phase composition in optimized magnetic state and values of magnetic properties.

On the basis of obtained experimental results it can be concluded that magnetic properties of the investigated Nd rich Nd-Fe-B alloy are under dominant influence of the magnetically isolated grains of hard magnetic $Nd_2Fe_{14}B$ phase. On the other side, magnetic properties of Nd-stoich and Nd-low alloys are under influence of intergranular interaction between the present phases. The nanocrystalline structure and almost monophase composition of the Nd-stoich alloy in the optimal magnetic state have provided conditions for exchange coupling between the grains of hard magnetic phase $Nd_2Fe_{14}B$ which has influenced the enhancement of remanence and maximal magnetic energy with consequent decrease of coercivity comparing to the Nd rich alloy. The enhancement of remanence and consequently magnetic energy despite the significant reduction of Nd content for the Nd-low alloy compared to the investigated Nd-rich and near stoichiometric Nd-Fe-B alloys comes as a consequence of exchange coupling between the grains of soft magnetic and hard magnetic phases i.e. formation of nanocomposite structure.

Research and development in the field of design of the nanocrystalline magnetic materials based on rapid quenched Nd-Fe-B alloys in the first decade of 21^{st} century was focused on defining of correlation between starting chemical composition, synthesis conditions, heat treatment, phase composition and magnetic properties. Realized investigations have covered optimization of heat treatment regimes for the purpose of formation of nanocomposite structures and strengthening of intergranular interaction of exchange coupling which has direct influence on the enhancement of remanence and consequently on the increase of magnetic energy.

Part of these investigations were expanded on the work with amorphous precursor of Nd-Fe-B-aloys which enabled more precise control of the crystalization flow and better control of phase transformations during the heat treatment. Further grain size refinement of present phases, their uniform distribution and therefore increase of the final magnetic properties by micro alloying with different elements from the group of transition metals or/and lanthanides was one of the main focuses and it is still a part of ongoing investigations.

Better understanding of new magnetic concepts of intergranular interactions, especially from the point of view of the role of novel nanocrystalline structures of magnetic materials was enabled by introduction of the new modern high resolution techniques for characterization on nano level and multidiscipline investigative approach.

Focus of further investigations in the field of permanent magnets are development and texturing of new nanocomposite systems, development of new non-equilibrium processing routes as well as texturing techniques which would require all advanced characterization techniques from electron microscopes, atom probe, synchrotron-based spectro–microscopes, neutron scattering, high resolution magnetic imaging to large-scale computational simulations.

According to market analysis data from 2000 to 2008, the average annual growth rate of global rare earth permanent magnet market maintained about 25% with an increase in the first quarter of 2010 to more than 30%. The output of China as the main Nd-Fe-B producing country in the world in 2009 was 94 kilotons. The major Nd-Fe-B manufacturers in China have gradually turned from medium and low-end low value-added application market to high-end application market, for instance, VCM, automobile, wind power, MRI instrument, and so on.

In the following years, there will be a vigorously increasing demand for rare earth permanent magnet in the fields such as wind power, new energy vehicles, and energy-saving home appliances with the improved requirements of energy saving & environment protection as well as the solutions of technical matters.

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