Study of Nd-Fe-B Alloys with Nonstoichiometric Nd Content in Optimal Magnetic State

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Abstract:

Characterization of two rapid-quenched Nd-Fe-B alloys with nonstoichiometric Nd content in the optimized magnetic state was carried out using the X-ray diffractometry (XRD), ^{57}Fe Mössbauer spectroscopic phase analysis (MS), electron microscopy (TEM), high resolution TEM (HREM) and Superconducting Quantum Interference Device (SQUID) magnetometer. The experimental results demonstrate the fundamental difference in the structure and magnetic properties of the two investigated alloys in the optimized magnetic state. The Nd-Fe-B alloy with the reduced Nd content ($Nd_{4.5}Fe_{77}B_{18.5}$) was found to have the nanocomposite structure of $Fe_3B/Nd_2Fe_{14}B$ and partly α-$Fe/Nd_2Fe_{14}B$, with mean grain size below 30 nm. On the other side, the overstoichiometric $Nd_{14}Fe_{79}B_7$ alloy has almost a monophase structure with the dominant content of the hard magnetic phase $Nd_2Fe_{14}B$ (up to 95 wt. %) and a mean crystallite size about 60 nm, as determined by XRD and TEM analysis. The results of magnetic measurements on SQUID magnetometer also suggest the nanocomposite structure of the Nd-low alloy and nanocrystalline decoupled structure of the Nd-rich alloy after the optimal heat treatment.

Keywords: Rapid quenched Nd-Fe-B alloys, Nonstoichiometric Nd content, Phase composition, Grain size, Magnetic properties;

1. Introduction

The research and development of high-energy Nd-Fe-B permanent magnetic materials has had a high impact on miniaturization and increase of effectiveness of a wide spectrum of devices, providing entirely new constructive solutions in various technical and technological domains [1,2]. The possibilities of increasing the energy density of nanocrystalline magnets by remanence enhancement by means of intergranular exchange coupling or by texturation, improvement of corrosion resistance and reduction of rare-earth content as a way of decreasing prices of final permanent magnets are one of the major topics of current investigations. Utilizing the high sensitivity of microstructure and magnetic properties of Nd-Fe-B alloys to stoichiometry i.e. mainly to the Nd content, three distinctive types of

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nanocrystalline alloys have been developed: stoichiometric magnets, Nd-rich (decoupled magnets) and magnets with reduced Nd content (composite magnets) [1]. The considerable differences in microstructure and magnetic properties of the alloys with the nonstoichiometric Nd content clearly distinguish them from one another, which makes them rather interesting subject for comparative study.

The Nd-Fe-B alloys with overstoichiometric Nd composition or the Nd-rich alloys in the optimized magnetic state consist predominantly of the main hard magnetic phase $Nd_2Fe_{14}B$ with minor quantities of Nd-rich non-magnetic magnetic phases situated on the grain boundaries of the main magnetic phase. Consequently, the magnetic properties of Nd rich Nd-Fe-B alloys are under dominant influence of the magnetically isolated grains of hard magnetic $Nd_2Fe_{14}B$ phase [2].

On the other side, the microstructure of the nanocomposite permanent magnetic materials based on the Nd-Fe-B alloys with reduced amount of Nd in optimized magnetic state is composed of a mixture of magnetically hard and soft phases. Depending on the alloy composition, the nanocomposite structure can be $Fe_3B/Nd_2Fe_{14}B$ or α-$Fe/Nd_2Fe_{14}B$ or mixture of both. Nanocomposite magnets owe their large saturation magnetic polarization to the presence of soft magnetic phases and high coercivity to the hard magnetic phase. The exchange coupling that occurs between the grains of hard magnetic $Nd_2Fe_{14}B$ phase and the soft magnetic Fe-rich grains explains the total magnetic property [1-4]. It was found that this intergranular interaction, which has significant influence on the magnetic properties, becomes more pronounced on nanoscale. The main condition for obtaining nanocomposite structure is uniform distribution of soft and hard phase in magnetic matrix, where size of crystal grains should be less than 40 nm [1-3]. Hence, the significant research efforts are put into optimization of the microstructure of these alloys.

This paper covers the comparative study of two rapid-quenched Nd-Fe-B alloys with nonstoichiometric neodymium content in optimal magnetic state. On the basis of obtained experimental results, microstructures and magnetic properties of the magnetic materials are discussed.

2. Experimental

Two types of rapid-quenched Nd-Fe-B alloys, Nd-low $Nd_{4.5}Fe_{77}B_{18.5}$ (12 wt.% Nd) alloy and Nd-rich $Nd_{14}Fe_{79}B_7$ (32 wt.% Nd) alloy, were selected for the proposed investigations. The as-quenched powders of these alloys were subsequently annealed to the optimized magnetic state. The applied heat treatment regimes were optimized in previous investigations [5-9]. Basic data concerning preparation method and magnetic properties of both powder samples of the investigated alloys are summarized in Tab. I.

Tab. I. Origin and basic magnetic characteristics of investigated Nd-Fe-B alloys

Alloy	Preparation method	Heat tretment	$_iH_c$ [MA/m]	B_r [T]	$(BH)_{max}$ [kJ/m^3]
$Nd_{4.5}Fe_{77}B_{18.5}$	Centrifugal atomization	660°C/5 min.	0.22	1.09	85.1
$Nd_{14}Fe_{79}B_7$	Centrifugal atomization	630°C/3 min	1.29	0.74	84.4

Phase composition of the investigated alloys after applied heat treatment regimes was determined by the X-ray diffractometry (XRD) and ^{57}Fe Mössbauer spectroscopic phase analysis. XRD measurements were performed on an X'Pert PRO MPD multi-purpose XRD system from PANanalytical using Co Kα radiation. Mean crystal grain size and quantitative composition of the identified phases were calculated from XRD data by the FullProf

computer program [10]. The X-ray line broadenings were analyzed through refinement of the TCH-pV function parameters. Mössbauer spectra were taken in the standard transmission geometry using a ^{57}Co(Rh) source at room temperature. The calibration was done against α-iron foil. For the spectra fitting and decomposition, the "CONFIT" program package was used [11]. Omitting the possible influence of Lamb-Mössbauer factor, the relative content of the iron containing phases was computed from intensities of corresponding spectral components. The microstructure of the alloys in optimized magnetic state was further analyzed using transmission electron microscopy (TEM) and high resolution TEM (HREM) on JEOL JEM 200CX and PHILIPS CM200 microscopes, respectively. For the preparation of samples for TEM and HREM investigation, the H-bar focused ion beam (FIB) technique was used [12]. The magnetic properties of the samples of Nd-Fe-B alloys in optimized magnetic state (Table I) were measured at ambient temperature, on a vibrating sample magnetometer (VSM) with magnetic field strength of 3.98 MA/m. Corresponding hysteresis loops of the investigated alloys were obtained at ambient temperature, on a Quantum Design MPMS 5XL Superconducting Quantum Interference Device (SQUID) magnetometer with magnetic field strength of 3.98 MA/m.

3. Results and Discussion

The obtained XRD patterns of both investigated rapid-quenched Nd-Fe-B alloys in optimized magnetic state are presented on Fig. 1.
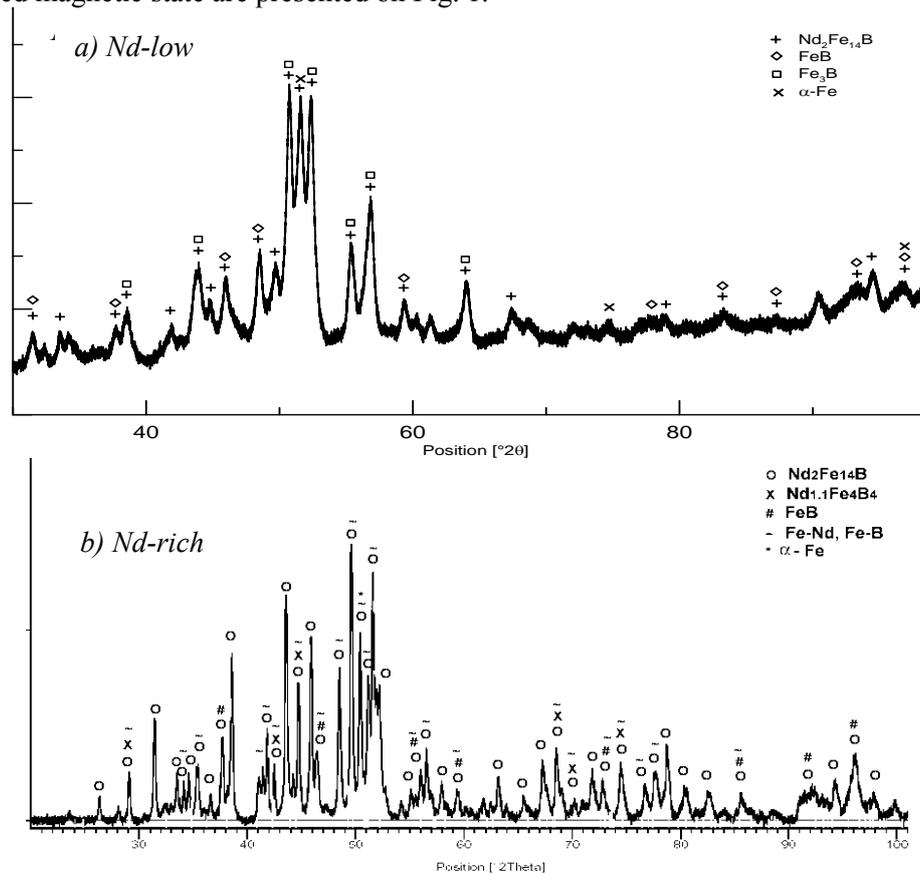

Fig. 1 X-ray diffraction patterns of the investigated $Nd_{4.5}Fe_{77}B_{18.5}$ and $Nd_{14}Fe_{79}B_7$ alloys in optimized magnetic state: a) Nd-low alloy; b) Nd-rich alloy

XRD phase analysis of the $Nd_{4.5}Fe_{77}B_{18.5}$ (Nd-low) alloy after optimal heat treatment at 660°C for 5 min (Fig.1a) confirmed presence of hard magnetic phase $Nd_2Fe_{14}B$, soft magnetic phases with high saturation magnetization, predominantly Fe_3B and partially α-Fe as well as minor quantities of soft magnetic phases of FeB type. The contents and mean grain sizes of main magnetic phases, determined using FullProf software, are presented in Table I Since the intensities of obtained diffraction peaks of FeB phases are very low, it can be assumed that these phases are present in minor quantities and that their influence on magnetic properties is therefore insignificant, which is why their content and mean grain size was not determined.

Tab. II. Phase composition and grain size of the investigated Nd-Fe-B alloys with Nd-low and Nd- rich content in the optimized magnetic state

Alloy		Phases					
		$Nd_2Fe_{14}B$	α - Fe	Fe_3B	FeB	$Nd_{1.1}Fe_4B_4$	Fe-Nd, Fe-B
$Nd_{4.5}Fe_{77}B_{18.5}$	Content [wt.%]	44	16	40	identif.	-	-
	Grain size [nm]	12.4	5	24	-	-	-
	R-factors not corrected for background	$R_{wp} = 2.80$ $R_p = 1.99$ $\chi^2 = 13.7$	$R_{wp} = 2.80$ $R_p = 1.99$ $\chi^2 = 13.7$	$R_{wp} = 2.80$ $R_p = 1.99$ $\chi^2 = 13.7$	-	-	-
	Conventional Rietveld R-factors	$R_{wp} = 20.9$ $R_p = 23.0$ $\chi^2 = 13.7$	$R_{wp} = 20.9$ $R_p = 23.0$ $\chi^2 = 13.7$	$R_{wp} = 20.9$ $R_p = 23.0$ $\chi^2 = 13.7$	-	-	-
$Nd_{14}Fe_{79}B_7$	Content [wt.%]	95	5	-	-	identif.	identif.
	Grain size [nm]	57	59	-	-	-	-
	R-factors not corrected for background	$R_{wp} = 2.00$ $R_p = 1.33$ $\chi^2 = 3.82$	$R_{wp} = 2.00$ $R_p = 1.33$ $\chi^2 = 3.83$	-	-	-	-
	Conventional Rietveld R-factors	$R_{wp} = 16.9$ $R_p = 19.6$ $\chi^2 = 3.82$	$R_{wp} = 25.7$ $R_p = 24.4$ $\chi^2 = 3.83$	-	-	-	-

The calculated mean crystal grain size of analysed phases confirms the nanocrystalline structure in the optimized magnetic state, with grain sizes below 30 nm. Taken together, the obtained phase composition and determined nanocrystalline structure suggest that the necessary conditions for more effective interaction of ferromagnetic exchange coupling between the grains of hard and soft magnetic Fe-rich phases are fulfilled, increasing

the remanence-enhancement effect.

The results of XRD analysis of the Nd-rich $Nd_{14}Fe_{79}B_7$ alloy in the optimized magnetic state (Fig.1b, Table II) suggest that the alloy has almost a monophase composition with dominant amount of hard magnetic $Nd_2Fe_{14}B$ phase. The presence of other soft and paramagnetic phases such as α-Fe, $Nd_{1.1}Fe_4B_4$ and phases of Fe-Nd, Fe-B type were determined as well. Due to similar reasons as in analysis of Nd-low alloy (low intensities of diffraction peaks) the contents and mean grain sizes were calculated only for $Nd_2Fe_{14}B$ and α-Fe phase.

The MS phase analysis of both rapid quenched Nd-Fe-B alloys corroborates the phase compositions determined by XRD. The phase compositions of both alloys obtained from corresponding MS spectra are given in Table III.

Given that MS analysis provides more detailed identification of phases containing iron, apart from main magnetic phases, the presence of other soft and paramagnetic phases was also determined. Although the content of $Nd_2Fe_{14}B$ phase in the Nd-low alloy is much smaller compared to XRD results, its presence can be assumed as the part of the identified phases of Fe-(B,Nd)/Fe(B) type with overall content estimated to 24 wt.%.

The appearance of non-ferromagnetic boron rich $Nd_{1.1}Fe_4B_4$ phase, can be explained as a consequence of high boron content in the investigated alloys (above 4.2 at%)[13]. It was found that $Nd_{1.1}Fe_4B_4$ phase forms in non-uniformly distributed heavily faulted grains of approximately the same dimensions as grains of $Nd_2Fe_{14}B$ phase [14]. Since its Curie temperature is very low (Tc=13 K), the $Nd_{1.1}Fe_4B_4$ phase does not exhibit ferromagnetic behavior at room temperature environment and consequently it is deleterious to the magnetic properties of the magnets [15]. Still, small amounts of this phase can be quite commonly found in Nd-Fe-B magnetic materials, particularly in those based on Nd-rich Nd-Fe-B alloys.

Tab. III. Tentative phase content as taken from Mössbauer spectra

Phase	$Nd_{4.5}Fe_{77}B_{18.5}$	$Nd_{14}Fe_{79}B_7$
	Content [wt.%]	Content [wt.%]
$Nd_2Fe_{14}B$	2	87
Fe-(B,Nd)/Fe(B)	24	-
Fe_3B	67	-
FeB	1	-
α-Fe	2	1
$Nd_{1.1}Fe_4B_4$	4	7
Fe-Nd, Fe-B	-	5

The TEM micrographs (Fig. 2 and Fig. 3), showing the average grain size of both analysed alloys in the optimized magnetic state, confirm the mean crystal grain size determined by XRD analysis. The average grain size of Nd-low alloy in the optimized magnetic state determined by TEM analysis is below 30 nm, while the presented grain size distribution indicates that the majority of grains have sizes in the range 20-30 nm.

A microdiffraction analysis gave evidence for mixing of the nano-crystalline phases. If the results of phase analysis, both XRD and MS are taken into account, this implies that the alloy has a nanocomposite structure of $Fe_3B/Nd_2Fe_{14}B$ and partly α-Fe/$Nd_2Fe_{14}B$ type.
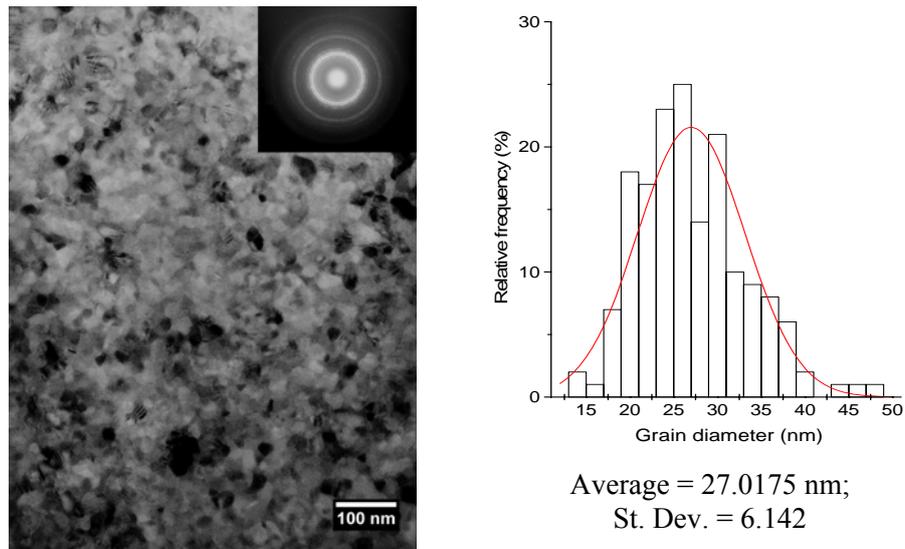
Fig. 2 Bright field TEM micrograph of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in optimal magnetic state with grain size distribution

TEM analysis of the Nd-rich Nd-Fe-B alloy in the optimized magnetic state has revealed the average grain size of about 64 nm. The better agreement between the results of XRD and TEM analysis for Nd-rich alloy can be explained by higher degree of crystallinity of the analysed phases and the fact that the investigated alloy has almost a monophase structure (over 90 wt.% of $Nd_2Fe_{14}B$ phase), involving less complex calculations. The obtained electron diffraction patterns show very high density of diffraction rings, due to which the reliable identification of present phases was not possible [16].
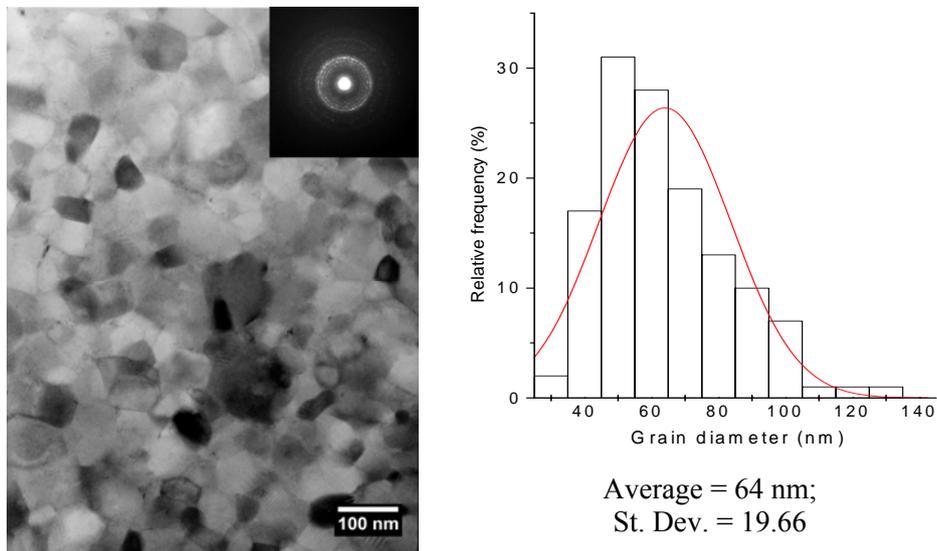

Fig. 3 Bright field TEM micrograph of $Nd_{14}Fe_{79}B_7$ alloy in optimal magnetic state with grain size distribution

The HREM analysis (Fig.4) of the investigated R/Q $Nd_{4.5}Fe_{77}B_{18.5}$ 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, as determined by the XRD analysis.
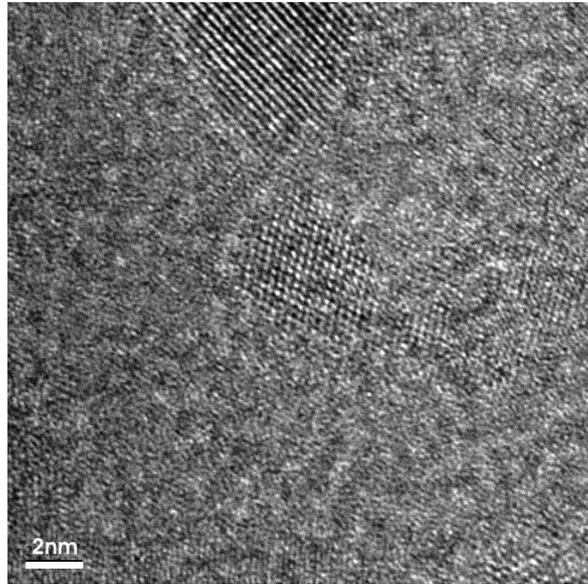
Fig. 4 HREM nanograph of the Nd-low Nd-Fe-B alloy in optimal magnetic state

The HREM nanograph of the $Nd_{14}Fe_{79}B_7$ alloy in optimal magnetic state (Fig.5) illustrates the presence of the crystal grains with the sizes of about 20 nm within the microstructure of the alloy. It is evident that the presented grain still exhibits polygonal structure with the angle between the grain boundaries approximately 120°. From the boundary surfaces morphology point of view this 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°. The presented structure in fact illustrates the presence of triple junctions.
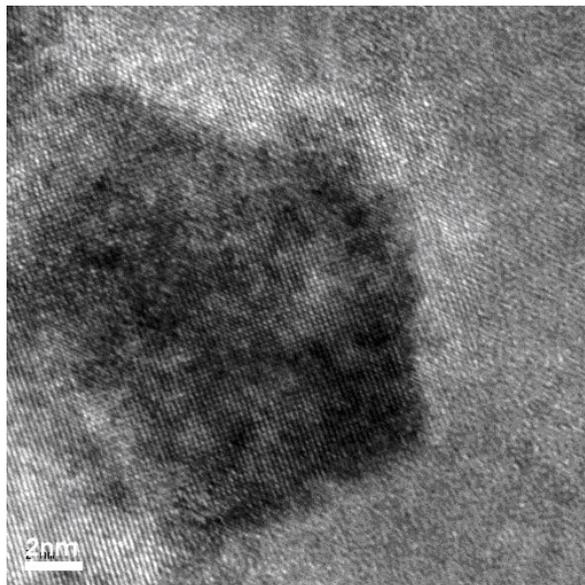

Fig. 5 HREM nanograph of the investigated Nd-rich Nd-Fe-B alloy in optimal magnetic state

When comparing the crystal grain sizes determined by TEM and HREM analysis one should have in mind that the grain size distributions presented on Fig.2 and Fig.3 are based on

the analysis of TEM micrographs that are obtained at relatively low magnification compared to the ones used in HREM analysis. HREM analysis was able to corroborate the results of XRD analysis, that in the microstructures of the alloys there are smaller crystal grains with sizes of only few nanometers.
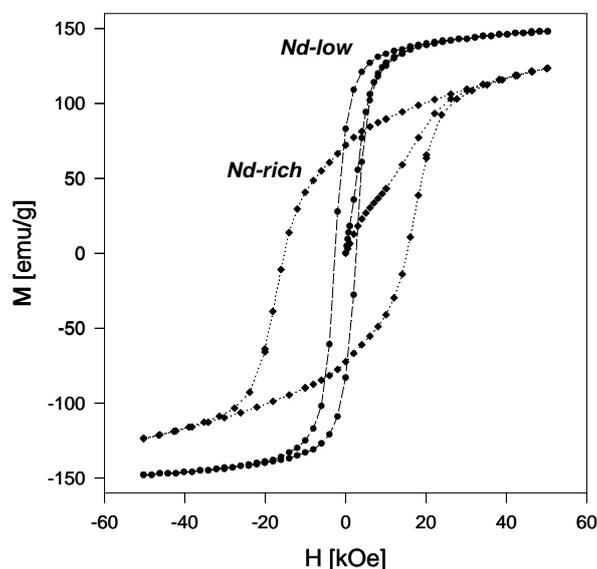

Fig. 6 Hysteresis loops of the investigated rapid quenched Nd-Fe-B alloys in the optimized magnetic state

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

The hysteresis loop of the Nd-low alloy presented in Fig. 6 indicates the presence of the interaction of ferromagnetic exchange coupling between the grains of soft and hard magnetic phases, suggesting the nanocomposite structure of the investigated alloy in the optimized magnetic state. This assumption is supported by the obtained high value of remanence (B_r = 1.09 T) and calculated remanence ratio (J_r/J_s = 0.6) higher than the theoretical limit for the non-interacting magnetic structures given by the Stoner-Wohlfarth theory [17]. The shape of the SQUID hysteresis loop of the Nd-rich Nd-Fe-B alloy (Fig. 6) in the optimized magnetic state implies the presence of the magnetically decoupled nanocrystalline structure. The obtained high value of coercivity ($_jH_c$ = 1.29 MA/m) supports this and indicates nearly a monophase structure of the alloy with dominant content of main hard magnetic phase $Nd_2Fe_{14}B$.

4. Conclusions

Based on results of XRD analysis of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy the dominant content of $Nd_2Fe_{14}B$, Fe_3B and α-Fe main magnetic phases was determined. Due to very low diffraction peak intensities the presence and content of other soft and paramagnetic phases can be omitted from analysis and it can be assumed that they had negligible influence on the magnetic properties of the alloy. The mean grain size of the investigated alloy with reduced Nd content in optimal magnetic state determined both by XRD, TEM and HREM analysis was below 30 nm. The value of the remanence ratio J_r/J_s>0.5, calculated from the SQUID hysteresis loops, suggests that exchange coupling interactions between grains of the soft and

hard magnetic phase exist, which is typical for nanocomposite structures of Nd-Fe-B alloys. Correlation of determined phase composition of the investigated Nd-low alloy in the optimized magnetic state ($Nd_2Fe_{14}B$, Fe_3B and α-Fe phase), the results of microstructural analysis and measured magnetic properties, implies that the alloy has a $Fe_3B/Nd_2Fe_{14}B$ and partly α-Fe/$Nd_2Fe_{14}B$ nanocomposite structure.

On the other side, obtained experimental results suggest that the Nd-rich ($Nd_{14}Fe_{79}B_7$) alloy in the optimized magnetic state has the nanocrystalline magnetically decoupled structure. High value of coercive force measured by the SQUID magnetometer confirms the hard magnetic qualities of this alloy and supports this assumption. In addition, the Nd-rich alloy was found to have almost a monophase composition with the dominant content of the hard magnetic $Nd_2Fe_{14}B$ phase (up to 95 wt.%) and the mean crystal grain size of about 60 nm as determined both by XRD and TEM analysis.

The influence of the Nd content on the magnetic properties of Nd-Fe-B alloys is the most noticeably demonstrated by the shape of the obtained hysteresis loops. The presented study clearly illustrates the substantial difference in the structure, phase composition and corresponding magnetic properties of the rapid-quenched Nd-Fe-B alloys with nonstoichiometric Nd content in optimal magnetic state.

Acknowledgement

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Садржај: Два типа брзо хлађених Nd-Fe-B легура са нестехиометријским садржајем неодијума анализирани су у оптималном магнетном стању применом рендгенско-дифрактометријске анализе (XRD), ^{57}Fe Mössbauer спектроскопске фазне анализе (MS), трансмисионе електронске микроскопије (TEM) и трансмисионе електронске микроскопије високе резолуције (HREM). Магнетна мерења вршена су на SQUID магнетометру. Добијени експериментални резултати указују на фундаменталну разлику у структури и магнетним својствима испитиваних легура у оптималном магнетном стању. Експериментално је показано да $Nd_{4.5}Fe_{77}B_{18.5}$ – легура са редукованим садржајем Nd, има нанокомпозитну структуру типа $Fe_3B/Nd_2Fe_{14}B$ са делимичним учешћем α-Fe фазе и средњу величину кристалних зрна присутних фаза испод 30 nm. Са друге стране, $Nd_{14}Fe_{79}B_7$ - легура обогаћена на Nd, има претежно монофазну структуру са доминантним садржајем тврде магнетне фазе $Nd_2Fe_{14}B$ (до 95 mas. %) и средњу величину зрна око 60 nm, утврђену XRD и TEM анализом. Резултати магнетних мерења на SQUID магнетометру такође указују на нанокомпозитну структуру Nd-Fe-B легуре са редукованим садржајем Nd односно на нанокристалну декупловану структуру легуре обогаћене на неодијуму, после оптималног термичког третмана.
Кључне речи: брзо хлађене Nd-Fe-B легуре, нестехиометријски садржај Nd, фазни састав, величина зрна, магнетна својства;