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# STUDY OF MICROSTRUCTURE AND MAGNETIC PROPERTIES OF OPTIMALLY ANNEALED R/Q $Nd_{4.5}Fe_{77}B_{18.5}$ ALLOY

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## Abstract

The rapid-quenched (R/Q) and subsequently optimally annealed Nd-Fe-B alloy with 12 wt% Nd was characterized using the X-Ray diffractometry (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HREM) and superconducting quantum interference device (SQUID) magnetometer. It was found that microstructure of the investigated alloy mainly consist of $Fe_3B$, $Nd_2Fe_{14}B$ phases and minor content of $\alpha$-Fe phase, with mean crystal grain sizes being below 30 nm. The ferromagnetic exchange coupling between the grains of identified hard and soft magnetic phases has direct influence on the magnetic properties as it is illustrated by SQUID hysteresis loop. Correlation of the measured magnetic properties with results of microstructure analysis indicates that the investigated rapid-quenched Nd-Fe-B alloy has the nanocomposite structure in optimal magnetic state.

*Key words: nanocomposite Nd-Fe-B alloys, exchange coupling, phase composition, crystal grain size, magnetic properties*

## 1. Introduction

The nanocomposite Nd-Fe-B permanent magnetic materials are of great commercial interest as no magnetic alignment is needed and less of the costly neodymium is required [1]. These high energy density magnets are essentially assemblies of hard magnetic and soft magnetic phases in which the former provides high coercivity and the latter provide high magnetization [1-3]. Most common way for production of these nanocrystalline materials is rapid-quenching with subsequent controlled nucleation or crystallization. Magnetic properties of the nanocomposite Nd-

Fe-B materials are under significant influence of the interaction of ferromagnetic exchange coupling between the crystal grains of hard and soft magnetic phases [3-5]. This coupling causes deviation of the magnetization around the boundaries of the crystallites, whose easy axes are unfavorably aligned with respect to the original magnetizing field, thus providing the remanence enhancement. It was found that this intergranular interaction becomes more pronounced at the nanoscale. Given that the degree of remanence enhancement depends on the effectiveness of the exchange coupling the significant research efforts are put into optimization of the microstructure. The main condition for obtaining nanocomposite structure is uniform distribution of soft and hard phase in a magnetic matrix where size of the crystal grains should be less than 40 nm [5]. Depending on the starting chemical composition the Nd-low Nd-Fe-B alloys in optimal magnetic state can have $Fe_3B/Nd_2Fe_{14}B$ and/or $\alpha$-$Fe/Nd_2Fe_{14}B$ nanocomposite structure.

Experimental results obtained in the course of presented study were used for analysis and discussion of structure and magnetic properties of the investigated R/Q Nd-Fe-B alloy with 12 wt.% Nd after optimal heat treatment.

## 2. Experimental

The rapid-quenched Nd-low Nd-Fe-B alloy ($Nd_{4.5}Fe_{77}B_{18.5}$) with 12 wt.% Nd was selected for the realized study. The investigated alloy was synthesized using the centrifugal atomization method and then annealed at 660°C for 5 minutes. The applied heat treatment regime was optimized in previous investigations [6-10]. Basic magnetic characteristics of the investigated alloy after annealing to the optimized magnetic state ($_jH_c$ = 2.8 kOe, $B_r$ = 10.9 kG, $(BH)_{max}$ = 10.7 MGOe) were measured on a vibrating sample magnetometer (VSM) under external magnetic field of 50 kOe. Phase composition of the investigated alloy after applied optimal heat treatment regime was determined by the X-ray analysis (XRD). X-ray diffraction measurements were performed on an X'Pert PRO MPD multi-purpose X-ray diffraction system from PANanalytical using Co K$\alpha$ radiation. Mean grain size and quantitative composition of the identified phases were calculated from XRD data by the FullProf computer program [11]. The X-Ray line broadenings were analyzed through refinement of the Thompson Cox Hastings-pseudo Voight (TCH-pV) function parameters, which in this case was the most reliable peak-shape function. The microstructure of the investigated alloy in optimal magnetic state was analyzed using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HREM) on JEOL JEM 200CX and PHILIPS CM200 microscopes, respectively. The samples for TEM and HREM analysis were prepared using focused ion beam microscopy (FIB). Hysteresis loops of the samples of investigated Nd-Fe-B alloy were obtained on the temperature of the ambient, on a Quantum Design MPMS 5XL Superconducting Quantum Interference Device magnetometer (SQUID) with magnetic field strength of 50 kOe.

## 3. Results and discussion

The results of XRD phase analysis of the investigated $Nd_{4.5}Fe_{77}B_{18.5}$ alloy after optimal heat treatment at 660°C for 5 min (Fig.1 and Table 1) show 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. Since the intensities of obtained diffraction peaks of FeB phases are very low (Fig.1), 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 was not determined. The contents and mean crystal grain sizes of main magnetic phases, determined using FullProf software, are presented in Table 1. The calculated mean grain size of analyzed phases confirms the nanocrystalline structure of the investigated alloy, with grain sizes below 30 nm. Together with the obtained phase composition, this nanocrystalline structure provides necessary conditions for more effective interaction of ferromagnetic exchange coupling between the grains of hard and soft magnetic Fe-rich phases, giving the raise to the remanence enhancement.

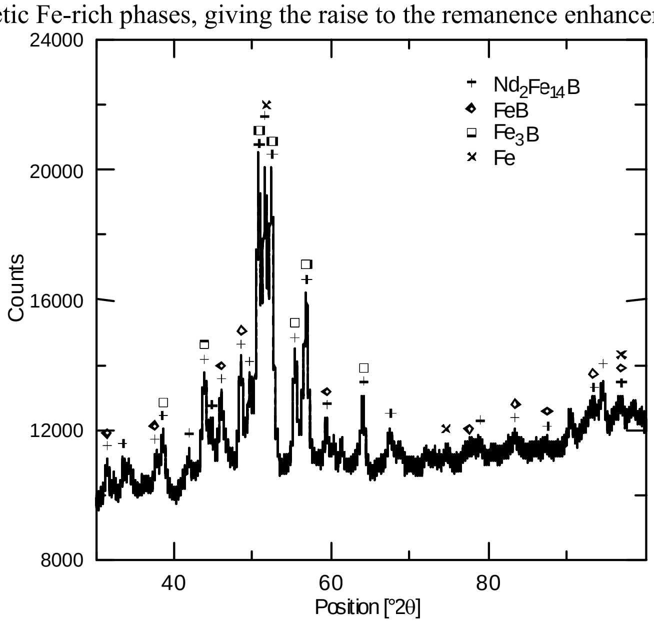
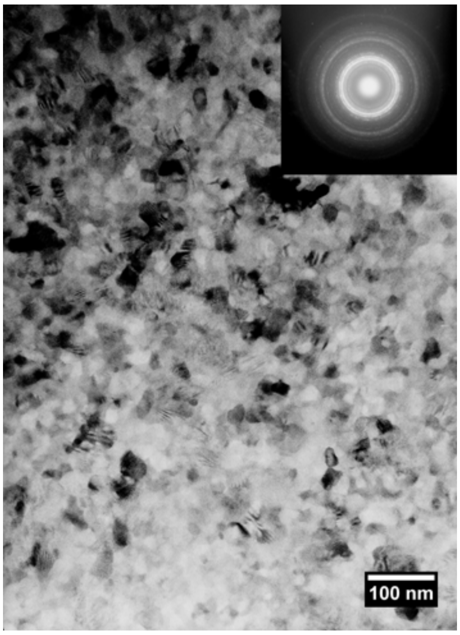
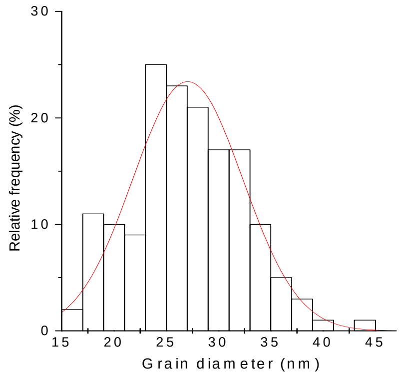



*Fig. 1. X-Ray diffractogram of the investigated rapid quenched $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in the optimal magnetic state*

*Table 1. Phase composition and mean crystal grain size of the investigated $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in the optimal magnetic state*

| **Phases** | **Content** [wt. %] | **Grain size** [nm] |
|---|---|---|
| $Nd_2Fe_{14}B$ | 43.63 | 12.4 |
| α - Fe | 16.54 | 5 |
| $Fe_3B$ | 39.83 | 24 |
| FeB | identified | - |




*Average = 27.0522 nm;*
*St. Dev. = 5.283*

*Fig 2. Bright field TEM micrograph of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in optimal magnetic state with grain size distribution*

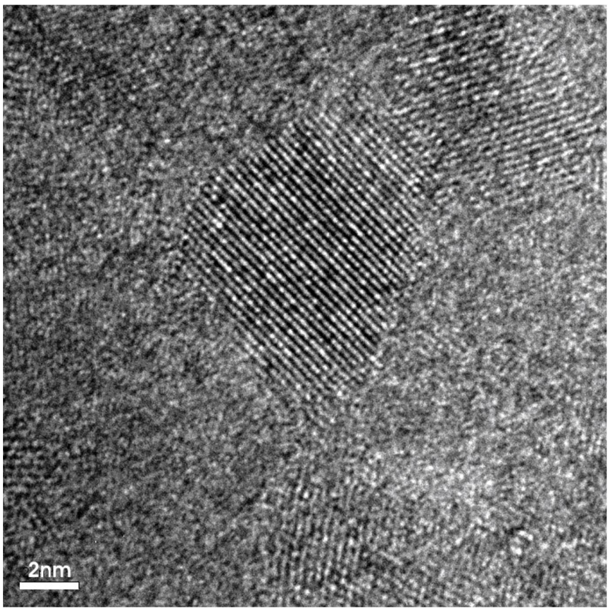



*Fig.3 HREM nanograph of the investigated Nd-low Nd-Fe-B alloy in optimal magnetic state*

The results of TEM analysis validate the mean grain size determined by XRD analysis, as it can be seen on presented bright field TEM micrograph (Fig. 2) showing the microstructure of the analyzed alloy in the optimal magnetic state. The average grain size determined by TEM analysis is also below 30 nm, while the corresponding grain size distribution indicates that the majority of grains have sizes in the range 20-30 nm. Taken together, the obtained results of XRD and TEM analysis imply that the investigated alloy in the optimal magnetic state has a nanocomposite structure of $Fe_3B/Nd_2Fe_{14}B$ and partly of α-$Fe/Nd_2Fe_{14}B$ type.

The HREM analysis (Fig.3) of the investigated R/Q Nd4.5Fe77B18.5 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.

The shape of the hysteresis loop obtained by magnetic measurements on SQUID magnetometer is in correspondence with the verified microstructure of the investigated alloy in the optimal magnetic state.

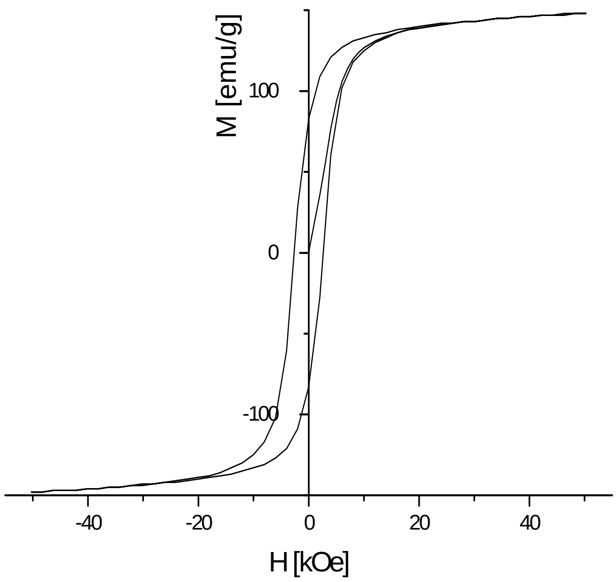



*Fig. 4. Hysteresis loop of the investigated rapid quenched $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in the optimal magnetic state*

The hysteresis loop of the Nd-low alloy presented on Fig. 4 indicates the presence of the interaction of ferromagnetic exchange coupling between the grains of hard and soft 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 and calculated remanence ratio (Jr/Js = 0.6) that is higher than the theoretical limit given by the Stoner-Wohlfarth theory [5] for an assembly of isotropic non-interacting single domain particles for which remanence *Jr* is half of the saturation polarization Js.

## 4. Conclusion

Characterization of the rapid-quenched $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in the optimal magnetic state using XRD, TEM and HREM analysis has confirmed the nanocomposite structure of the investigated alloy, with dominant presence of $Fe_3B/Nd_2Fe_{14}B$ and partly of $\alpha$-$Fe/Nd_2Fe_{14}B$ nanocomposites. The mean crystal grain size of the constituent phases was found to be below 30 nm. Furthermore, experimentally determined value of remanence ratio Jr/Js from the obtained SQUID hysteresis loops is higher than the theoretical limit, which confirms the presence of the interaction of ferromagnetic exchange coupling between the grains of hard magnetic phase $Nd_2Fe_{14}B$ and identified soft magnetic Fe-rich phases with high saturation magnetization. Formed nanocomposites, via the intergranular interaction of ferromagnetic exchange coupling, are responsible for high value of remanence and obtained magnetic energy despite the reduced Nd content compared to Nd-Fe-B alloys with stoichiometric and overstoichiometric composition.

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