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PHASE COMPOSITION, CRYSTALLITE SIZE AND MAGNETIC PROPERTIES OF RAPID QUENCHED Nd-RICH $Nd_{14}Fe_{79}B_7$ ALLOY

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ABSTRACT
The paper presents the research results concerning the phase composition, grain size and magnetic properties of rapid quenched $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state (after annealing at 650^oC/3min). Phase composition and crystallite size of investigated alloy in optimized magnetic state were determined using the X-ray diffraction analysis (XRD). Microstructure of the Nd-rich Nd-Fe-B alloy was furthermore investigated by a transmission electron microscope (TEM). The $Nd_2Fe_{14}B$ crystallite size determined both by the TEM and by the size-strain analysis of XRD data was about 60 nm. The results of XRD analysis show that the investigated alloy is almost single phase alloy with dominant amount of $Nd_2Fe_{14}B$ hard magnetic phase (~ 95 mass %). Also, according to the results of magnetic measurements it is obvious that some small amount of Nd-rich and other non-magnetic phases are situated on grain boundaries causing the magnetic isolation of $Nd_2Fe_{14}B$ grains.
Keywords: nanocrystalline decoupled Nd-Fe-B alloy, phase composition, crystallite size, magnetic properties

1. INTRODUCTION

Rapid quenched Nd-Fe-B alloys are an important class of permanent magnets because of their excellent magnetic properties originating from the ferromagnetic $Nd_2Fe_{14}B$ compound as a principal phase [1], which has a large saturation magnetization and high anisotropy field [2]. In general, nanocrystalline decoupled or high-coercive Nd rich Nd-Fe-B alloys are characterized by the presence of paramagnetic phases such as $Nd_{1.1}Fe_4B_4$ and Nd-rich phases in the grain boundary regions [3,4]. The single crystallites of the hard magnetic phase are more or less separated by a paramagnetic Nd-rich boundary phase and this separation can cause de-coupling of magnetic $Nd_2Fe_{14}B$ grains, thus reducing the remanence enhancement by reducing the exchange-coupling effect. This phase at least partly insulates the $Nd_2Fe_{14}B$ grains and this is considered to act to dump the nucleation of reverse domains and, for nanoscale $Nd_2Fe_{14}B$ grains, to also reduce the degree of exchange coupling. The other important parameter is the grain size, since an increase in grain size generally results in decrease of coercivity and remanence enhancement.

In this work, the rapid quenched Nd-rich $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state was characterized by determination of phase composition, grain size and magnetic properties using the X-ray, TEM, VSM and SQUID. Summarized experimental results obtained by mentioned methods are presented and discussed.

2. EXPERIMENTAL

The composition of the starting Nd-Fe-B alloy was Nd - 32 mass%, Pr - 0.5 mass%, B - 1.2 mass%, Al - 0.3 mass%, Fe – balance. The powder was prepared by centrifugal atomization process and optimally treated at 650°C/3min. The investigated alloy was in the powder form, suitable for the X-ray diffraction. The phases present in optimized magnetic state were determined by X-ray diffraction 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_α radiation. Based on X-Ray diffraction data for optimized magnetic alloy mean crystallite size of identified phases was determined by size-strain analysis using the FullProf computer program. Microstructure of the material was also investigated by a transmission electron microscope (TEM), JEOL JEM-2000, operated at 200 kV. Magnetic properties of the optimized magnetic alloy were measured at 300 K on a vibrating sample magnetometer (VSM) with a maximum external field of 50 kOe and on the SQUID magnetometer with external magnetic field μ_0H that can be varied from -5 to 5 T.

3. RESULTS AND DISCUSSION

Based on previous investigations [5] the optimal heat treatment of the investigated Nd-rich Nd-Fe-B alloy (650°C for 3 min) was chosen. Origin and magnetic properties of the investigated alloy in the optimized magnetic state are presented in Table 1.

Table 1 Origin and magnetic properties of investigated alloy in optimized state

Alloy	Preparation	Treatment	${}_iH_c$ (kOe)	B_r (kG)	$(BH)_{max}$ (MGOe)
$Nd_{14}Fe_{79}B_7$	centrifugal atomization	650°C/3 min.	16.2	7.4	10.6

The X-ray diffractogram of $Nd_{14}Fe_{79}B_7$ powder in optimized magnetic state is shown on Figure 1.

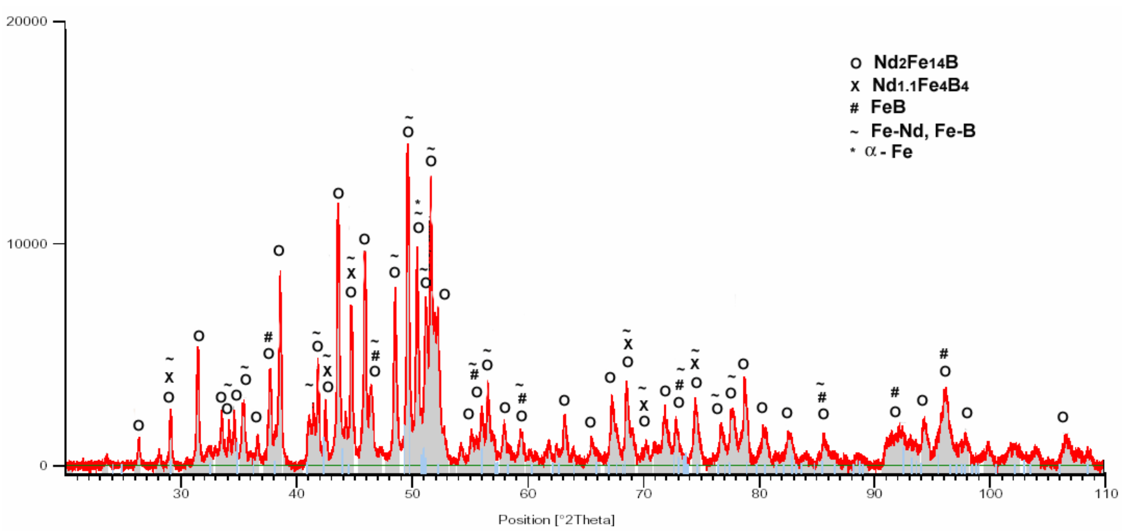

Figure 1. The X-ray diffractograms of $Nd_{14}Fe_{79}B_7$ powder in optimized magnetic state

By observing the results of XRD analysis, the hard magnetic phase $Nd_2Fe_{14}B$ is identified as the primary phase. Fe-Nd corresponds to the ferro-magnetically ordered Fe-Nd phases, up to the $Fe_{17}Nd_5$ intermetallics and to the paramagnetically ordered Fe-Nd phases with higher Nd content. They obviously represent remnant minor paramagnetic phases, predominantly those of high Nd content being situated on grain boundaries [5,6]. The presence of a non-magnetic phases $Nd_{1.1}Fe_4B_4$ and α–Fe was detected as well as some small amount of unidentified components. Due to low reflections intensity and a great number of reflections of the identified primary phase, it was difficult to strictly define by this analysis to which phases the unidentified diffraction maximums belong. Appearance and identification, actually in small amounts, of non-magnetic boride phase $Nd_{1.1}Fe_4B_4$ is the result of an increased B content of about 7 at% in the investigated alloy.

For better understanding of the influence of content and grain size of individual phases on the magnetic properties after optimal heat treatment, the size-strain and quantitative phase analyses of X-ray data were done. Summarized results are presented in Table 2.

Table 2. Phase composition with crystallite sizes of the $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state

Phase	Content [%]	Crystallite size [nm]
$Nd_2Fe_{14}B$	95	57
α - Fe	5	59

From the results of XRD analysis (Figure 1 and Table 2) it is evident that the investigated alloy is almost single phase alloy with dominant amount of $Nd_2Fe_{14}B$ hard magnetic phase (95 mass %). The mean crystallite size determined by the size-strain analysis of XRD data was about 60 nm.
Microstructure of the Nd-rich Nd-Fe-B alloy in optimized magnetic state was also investigated by a transmission electron microscope (TEM). From the TEM micrograph (Figure 2) it can be seen that the average grain size complies with the mean crystallite size of identified phases calculated by the size-strain analysis of XRD data of the investigated alloy.

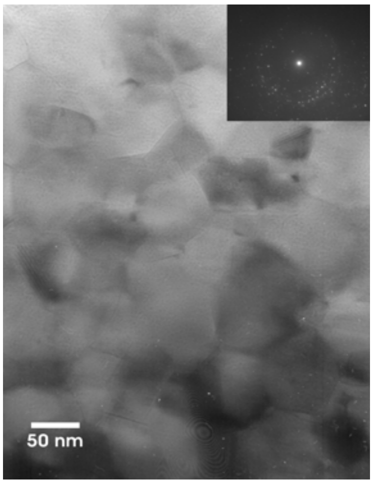

Figure 2. Bright field transmission electron micrograph of $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state. The insert figure is the electron diffraction pattern of the selected area.

Measured values of magnetic properties suggest that in the optimized state the optimal phase composition and optimal microstructure were obtained. Magnetic behaviour of investigated alloy is illustrated on Figure 3 with the corresponding SQUID hysteresis loop.

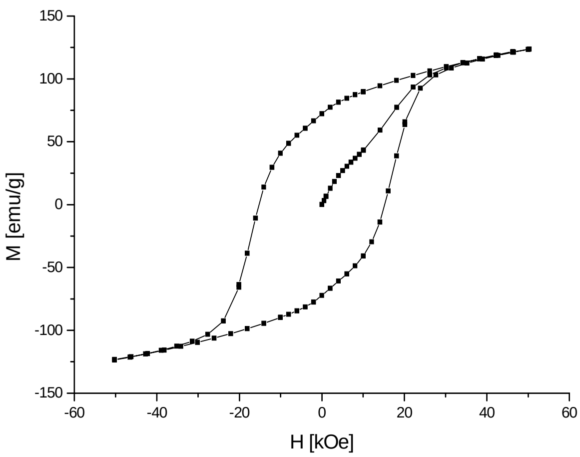

Figure 3. SQUID hysteresis loop of $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state

As previously mentioned, the $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state has about ~ 95mass% of hard magnetic $Nd_2Fe_{14}B$ and according to literature the expected saturation magnetization of the alloy is 15.6 kG, corresponding to 90mass% $Nd_2Fe_{14}B$ and the value of saturation magnetization for $Nd_2Fe_{14}B$ phase is 16 kG [7]. The measured values were below the expected value, probably because the maximum magnetic field of 50 kOe, is not high enough for measurement of the saturation magnetization of $Nd_2Fe_{14}B$ due to its high anisotropy field [8]. Therefore, although the remanence ratio Mr/Ms = 0.582 calculated from the SQUID hysteresis loop has different value than expected, it is obvious that the maximum strength of the applied magnetic field is not enough for the total saturation.
High value of coercive force of the investigated alloy in the optimized magnetic state is consequence of the magnetic isolation of the $Nd_2Fe_{14}B$ grains by the small amount of Nd-rich and other present phases that are situated on grain boundaries.

4. CONCLUSION

According to the results of XRD analysis it is evident that the investigated alloy is almost single phase alloy with dominant amount of $Nd_2Fe_{14}B$ hard magnetic phase (95 mass %) 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. The $Nd_2Fe_{14}B$ grain size determined both by the TEM and by the size-strain analysis of XRD data was about 60 nm which suggest nanocrystalline structure of the alloy in the optimized magnetic state. Also, according to the results of magnetic measurements on SQUID magnetometer (although measured value of remanence does lightly exceed 0.5 $4\pi J_s$ of the $Nd_2Fe_{14}B$ compound) it is obvious that single grains of the hard magnetic phase are more or less separated by a paramagnetic RE-rich boundary phase. This separation causes de-coupling of magnetic $Nd_2Fe_{14}B$ grains, thus reducing the remanence enhancement by reducing the exchange-coupling effect.

5. REFERENCES

[1.] Guthfleisch O., J. Phys. D: Appl. Phys. 33 (2000) 157.
[2.] Koon N.C., Das B.N., Rubinstein M., Tyson J., J. Appl. Phys. 57 (1985) 4091.
[3.] Gronefeld M., Kronmuller H., J. Magn. Magn. Mater. 99 (1990) L267.
[4.] Harland C.L., Davies H.A., Journal of Alloys and Compounds 281 (1998) 37.
[5.] Talijan N., Ćosović V., Stajić-Trošić J., Žák T., J. Magn. Magn. Mater. 272 (2004) e1911.
[6.] Grujić A., Talijan N., Maričić A., Stajić-Trošić J., Ćosović V., Radojević V., Sci. of Sint. 37 (2005) 139.
[7.] Ding J., Lee Y., Yong P.T., J. Phys. D: Appl. Phys. 31 (1998) 2745.
[8.] Kneller E.F., Hawig R., IEEE Trans. Magn. 27 (1991) 3589.

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