Structure, Phase Composition and Thermomagnetic Behavior of $Nd_{14}Fe_{79}B_7$ Alloy

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Abstract. The results of investigation of the influence of phase composition and microstructure on the magnetic properties of rapid quenched (R/Q) $Nd_{14}Fe_{79}B_7$ alloy are presented and discussed. Thermomagnetic behavior of investigated alloy has been studied by measurement of themomagnetic curves (TM) in temperature interval 20–800°C. Phase composition and grain size of investigated alloy in optimized magnetic state and state after the thermomagnetic measurements were determined using the X-ray diffraction analysis (XRD). Based on X-Ray diffraction data mean grain size of identified phases was determined by size-strain analysis using the FullProf computer program. The investigation by transmission electron microscope (TEM) was done as a confirmation of mean grain size. The substantial difference between the state with optimized magnetic properties and the state after the decomposition, induced by the TM measurements, was illustrated by the corresponding hysteresis loops obtained by measurements on the Superconducting Quantum Interference Device (SQUID).

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 [2,3].

Nd-rich Nd-Fe-B alloys have a paramagnetic Nd-rich phase present at the $Nd_2Fe_{14}B$ grain boundary [4,5]. 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. A small increase in coercivity has also been achieved by reduction of the grain size into the nanocrystalline range [6]. Nanocrystalline materials in general are isotropic concerning the distribution of easy axes in the nanoscaled magnetic grains. In the high-coercive magnets in which the hard magnetic grains are magnetically isolated and therefore exchange decoupled by a paramagnetic intergranular layer, the remanence Jr is limited by the Stoner-Wohlfarth value (Jr = 0.5 Js) [7]. The high-remanent single-phase magnets exhibit remanence values considerably larger than this limit due to effect of exchange coupling between the hard magnetic grains being connected directly without any intergranular layer provided that the average grain size becomes significantly smaller than 50 nm [8,9,10].

Scope of this paper is investigation of microstructure, phase composition and their influence on magnetic properties of the $Nd_{14}Fe_{79}B_7$ alloy in the optimized magnetic state and after the thermomagnetic measurements.

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 630°C/3min. Magnetic properties of the optimized material were measured on a vibrating sample magnetometer (VSM) with a maximum external field of 50 kOe and the obtained values of coercivity, remanence and energy product are 16.2 kOe (1296 kA/m), 7.4 kG (0.74 T) and 10.6 MGOe (85 J/m^3) respectively.

The centrifugally atomized material was in the powder form suitable for the X-ray diffraction. The phases present in state before and after TM were determined by 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 grain size of identified phases was determined by the size-strain analysis using the FullProf computer program.

The thermomagnetic curves were measured in temperature interval 20–800^{o}C using an EG&G vibrating sample magnetometer in the field of intensity of 50 Oe. The heating and cooling rate was kept at 4 K/min. After the TM measurement the XRD analysis was repeated on the material used.

Microstructure of the material was also investigated by a transmission electron microscope (TEM), JEOL JEM-2000, operated at 200 kV.

Magnetic measurements at 300 K for material in state with optimized magnetic properties and the state after the decomposition were performed on the SQUID magnetometer with external magnetic field μ_0H that can be varied from -5 to 5 T.

Results and discussion

The rapid quenched $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state was investigated by thermomagnetic measurement. Fig. 1 shows the thermomagnetic curves that bring the information about phase composition and magnetic behaviour in temperature interval 20–800^{o}C.

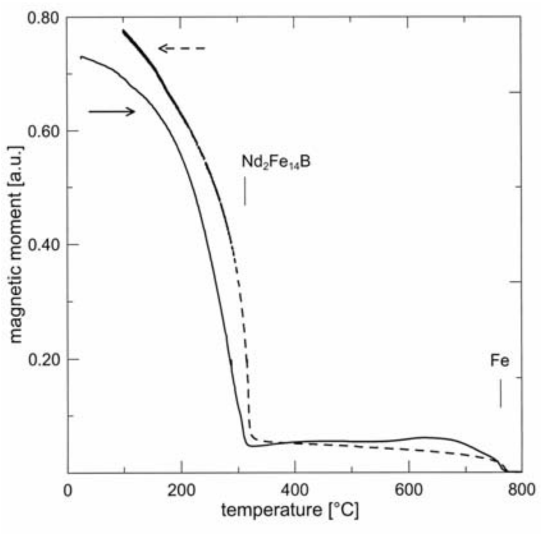

Fig. 1. Thermomagnetic curves of investigated $Nd_{14}Fe_{79}B_7$ alloy.

The X-ray diffractograms of $Nd_{14}Fe_{79}B_7$ powder in state before and after thermomagnetic measurement are shown on Fig. 2. By observing the results of XRD analysis, the hard magnetic phase $Nd_2Fe_{14}B$ is identified as the primary phase [11]. The presence of boride phase $Nd_{1.1}Fe_4B_4$ and α–Fe was also found out and some small amount of unidentified components was also detected. 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. They obviously represent remnant minor paramagnetic phases, predominantly those of high Nd content being situated on grain boundaries [12,13,14]. The Fe-Nd corresponds to ferro-magnetically ordered phases, up to the $Fe_{17}Nd_5$ intermetallics and to the paramegnetically ordered Fe-Nd phases with higher Nd content.

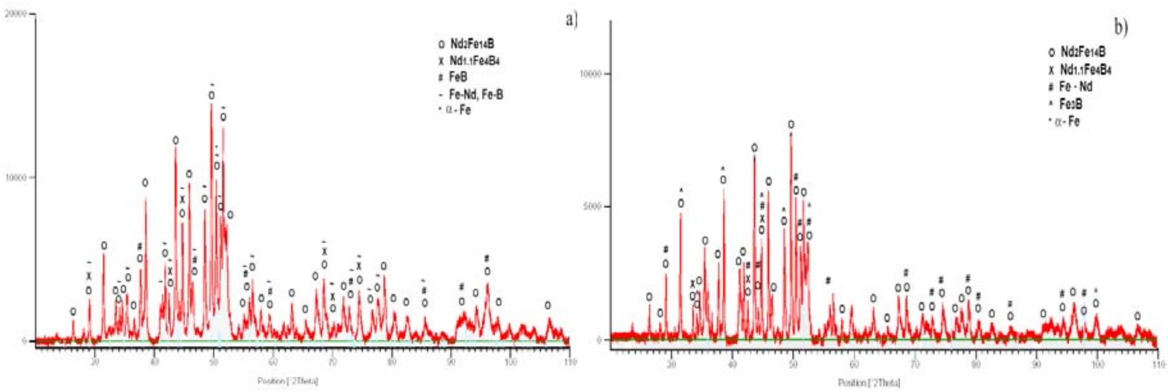

Fig. 2. The X-ray diffractograms of $Nd_{14}Fe_{79}B_7$ powder in
a) optimized magnetic state and b) after thermomagnetic measurements

For better understanding of the influence of content and grain size of individual phases on the magnetic properties before and after the TM, the size-strain and quantitative phase analyses of X-ray data were done. Summarized results are presented in Table 1.

Table 1. Mean crystallite sizes before and after TM measurements

Phase	Before TM		After TM	
	Content [%]	Crystallite size [nm]	Content [%]	Crystallite size [nm]
$Nd_2Fe_{14}B$	95	57	75.0	~ 63.0
α - Fe	5	59	3.3	~ 64.0
$Fe_{17}Nd_5$	-	-	13.8	~ 16.4
Nd_2O_3	-	-	5.7	~ 17.1

From the results of XRD analysis (Fig. 2 and Table 1) it is obvious that after TM, the amount of soft magnetic phases has rapidly increased, predominantly $Fe_{17}Nd_5$. The presence of Nd_2O_3 phase can be explained by oxidation of Nd-rich phases during the TM measurements. The amount of the $Fe_{17}Nd_5$ and Nd_2O_3 phases in the state after TM measurement is about ~ 20mass% with grain size much smaller than hard magnetic phase. Regarding the $Nd_2Fe_{14}B$ phase, the decreasing of amount and the increase of grain size of hard magnetic phase after the TM measurement is obvious. Its content is estimated to 95 mass% in optimally magnetic state and 75 mass% for state after TM measurements. Besides, $Al_{6.3}B_{88}$ and Fe_3B phases were also identified but considering their complex crystal structure they were not considered. Practically, the increase of the amount of the soft magnetic phases and the increase of the grain size of present phases has the direct influence on reduction of magnetic properties.

The single grains of the hard magnetic phase are more or less separated by a paramagnetic RE-rich boundary phase and this separation can cause decoupling of magnetic $Nd_2Fe_{14}B$ grains, thus reducing the remanence enhancement by reducing the exchange-coupling effect. On the other side the isolation of magnetic $Nd_2Fe_{14}B$ grains by non-magnetic phases can lead to the increase of coercivity. The other important parameter is the grain size, since both coercivity and the exchange-coupling effect are the sensitive functions of grain size. An increase in grain size generally results in decrease of coercivity and remanence enhancement [13].

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 micrographs (Fig. 3) it can be seen that the average grain size complies with the mean grain size of identified phases calculated by the size-strain analysis of XRD data of the investigated alloy.

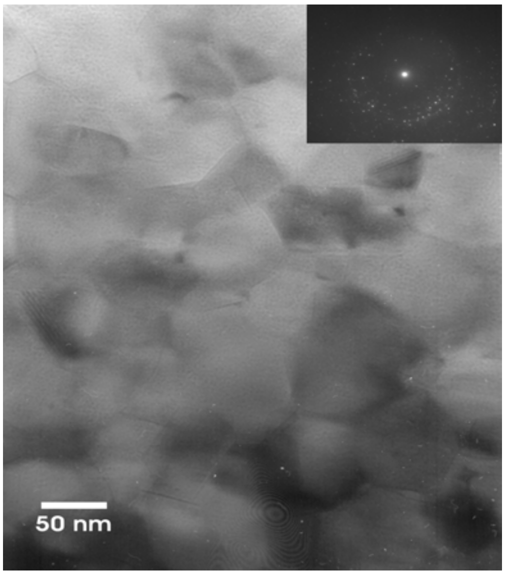

Fig. 3. Bright field transmission electron micrograph of $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state. The insert figure is the electron diffraction patter of the selected area.

For investigated $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state experimentally obtained value of coercive force and remanence measured on VSM are Hci = 16.2 kOe, Br = 7.4 kG. Maximal magnetic energy is 10.6 MGOe, which is expected value for Nd-Fe-B alloy with ~90 mass% of hard magnetic phase [15]. Measured values of magnetic properties suggest that in the state before TM measurement the optimal phase composition and optimal microstructure were obtained. Magnetic behaviour of investigated alloy before and after TM is presented on Fig. 4 with the corresponding SQUID hysteresis loops.

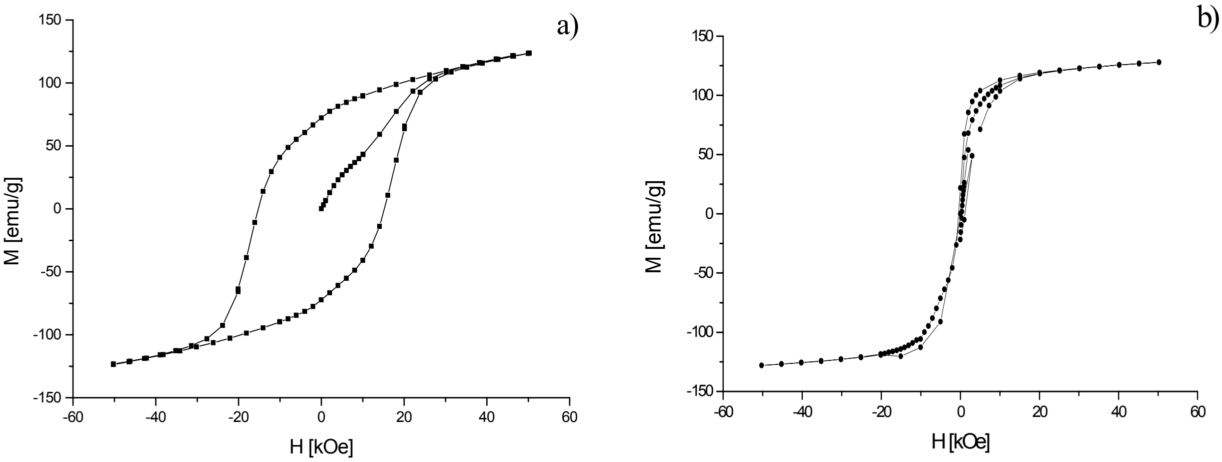

Fig. 4. SQUID hysteresis loops of $Nd_{14}Fe_{79}B_7$ alloy in a) optimized magnetic state and b) after the thermomagnetic measurement

The saturation magnetization of $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state at the maximum magnetic field of 50 kOe (5 T) was 123 emu/g (12.5 kG). The value of saturation magnetization for $Nd_2Fe_{14}B$ is 16 kG [15]. 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 because of high anisotropy field of $Nd_2Fe_{14}B$ [16]. As described in the beginning of this section, the $Nd_{14}Fe_{79}B_7$ alloy in optimized magnetic state consisted of ~95mass% hard magnetic $Nd_2Fe_{14}B$ phase and a mixture of soft magnetic and non-magnetic phases. Due to presence of α-Fe, $Nd_{1.1}Fe_4B_4$, Fe-B, Fe-Nd phases and some non-magnetic phases, the expected saturation magnetization of the samples is 15.6 kG, corresponding to 90 mass% of $Nd_2Fe_{14}B$ [15]. Therefore, the theoretical limit of the remanence is 7.8 kG according to the Stoner–Wohlfarth model (50% of the saturation magnetization). Based on calculated value of remanence ratio Mr/Ms = 0.582 for $Nd_{14}Fe_{79}B_7$ alloy in state before TM measurement that is higher than theoretical limit 0.5, which indicates that despite the evident presence of Nd-rich phase (and other non-magnetic phases) on the grain boundaries, the thickness of this intergranular phase is less than needed for complete magnetic isolation of grains of hard magnetic phase $Nd_2Fe_{14}B$. However, it should be mentioned that calculated Mr/Ms = 0.582 ratio values shows the deviation in relation to the expected because the maximum magnetic field is not enough for full saturation.

After TM measurement, thermal decomposition is evident, so the content of $Nd_2Fe_{14}B$ phase is decreasing to 75 mass%. Nd-rich phases such as Nd_2O_3, $Fe_{17}Nd_5$ (or some non-magnetic phases) and small amount of $Nd_{1.1}Fe_4B_4$ are also present. Value of remanence ratio calculated from the SQUID hysteresis loop for $Nd_{14}Fe_{79}B_7$ alloy after TM measurement is much lower than theoretical limit 0.5. Therefore, it can be assumed that the magnetic properties of thermally decomposed alloy derive from decoupled grains of hard magnetic phase $Nd_2Fe_{14}B$ and higher content of soft magnetic and Nd-rich phases. Decrease of magnetic properties can be also contributed to the growth of grain size of present phases.

Conclusion

According to the results of XRD analysis it is evident that the investigated alloy in optimized magnetic state is almost single phase alloy with dominant amount of $Nd_2Fe_{14}B$ hard magnetic phase (95 mass %) and that this phase has the dominant influence on magnetic properties of the investigated alloy. 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. According to the results of magnetic measurements on SQUID magnetometer (experimentally calculated remanence does lightly exceed 0.5 $4\pi J_s$ of the $Nd_2Fe_{14}B$ compound) which suggests that the thickness of the intergranular Nd-rich phase and other non-magnetic phases in some regions is not sufficient for complete magnetic isolation of $Nd_2Fe_{14}B$ grains which enables the partial exchange coupling between the grains of hard magnetic phase $Nd_2Fe_{14}B$. Nevertheless, this assumption lacks the strong experimental support since the strength of applied magnetic field is evidently not enough for the full saturation of the investigated Nd-Fe-B alloy.The phase transformations and the increase of grain size of present phases which have occurred during the TM measurement have caused the change of magnetic behavior of investigated $Nd_{14}Fe_{79}B_7$ alloy which is clearly illustrated by the shape of SQUID hysteresis loops. Hence, it can be assumed that the thermal decomposition is the main reason for the quality loss of investigated hard magnetic materials. The reduction of magnetic properties after TM is due to increase of amount of main decomposition product α-Fe, presence of Nd_2O_3 and different Fe-B phases, as well as increase of mean grain size.

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References

[1] O. Gutfleisch: J. Phys. D: Appl. Phys. Vol. 33 (2000), p. 157

[2] N.C. Koon, B.N. Das, M. Rubinstein, J. Tyson: J. Appl. Phys. Vol. 57 (1985), p. 4091

[3] C. Abache, H. Oesterreicher: J. Appl. Phys. Vol. 57 (1985), p. 4112
[4] M. Gronefeld, H. Kronmuller: J. Magn. Magn. Mater. Vol. 99 (1990), p. L267
[5] C.L. Harland, H.A. Davies: Journal Of Alloys And Compounds Vol. 281 (1998), p. 37
[6] I. Ahmad, H.A. Davies, R.A. Buckley: J. Magn. Magn. Mater. Vol. 157–158 (1996), p. 31
[7] E.C. Stoner, E.P. Wohlfarth: Phil. Trans. Roy. Soc. Vol. 240 (1948), p. 599
[8] D. Goll, H. Kronmuller: Naturwissenschaften Vol. 87 (2000), p. 423
[9] A. Manaf, R. Buckley, H.A. Davies, M. Leonowicz: J. Magn. Magn. Mater. Vol. 101 (1991), p. 360
[10] R. Fischer, T. Schrefl, H. Kronmuller, J. Fidler: J. Magn. Magn. Mater. Vol. 150 (1995), p. 329
[11] J. Stajić-Trošić: Phd Thesis, University Of Belgrade, 2005.
[12] N. Talijan, V. Ćosović, J. Stajić-Trošić, T. Žák: J. Magn. Magn. Mater. Vol. 272 (2004), p. E1911-E1912
[13] Yu.D. Yagodkin, A.S. Lileev, J.V. Lyubina, at. all: J. Magn. Magn. Mater. Vol. 258-259 (2003), p. 586
[14] A. Grujić, N. Talijan, A. Maričić, J. Stajić-Trošić, V. Ćosović, V. Radojević: Science Of Sintering Vol. 37 (2005), p. 139
[15] J. Ding, Y. Lee, P.T. Yong: J. Phys. D: Appl. Phys. Vol. 31 (1998), p. 2745
[16] E.F. Kneller, R. Hawig: Ieee Trans. Magn. Vol. 27 (1991), p. 3589