Phase Transformations and Structure of Rapid Quenched Nd-Fe-B alloy during the Thermal Treatment

Vladan Ćosović[1], Nadežda Talijan[1], Vojislav Spasojević[2], Jasna Stajić-Trošić[1], Aleksandar Grujić[1], Vladimir Menushenkov[3]

[1]Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia & Montenegro, cmm@tmf.bg.ac.yu
[2]Institute of Nuclear Sciences "Vinča", 11000 Belgrade, Serbia & Montenegro
[3]Moscow State Institute of Steel and Alloys, Leninskij prospect 4, 119991 Moscow, Russia

Keywords: permanent magnet; Nd-Fe-B – low Nd content; heat treatment; nanocomposite; crystallization behavior; exchange coupling

Abstract. Evolution of the microstructure and the processes for obtaining optimal magnetic microstructure of Nd-Fe-B alloy with the low Nd content were studied. The influence of different heat treatment regimes was correlated with phase transformation and measured magnetic properties. The heat treatment regime which provided the microstructure which improves exchange interactions between grains of soft and hard magnetic phases and, consequently, enhances magnetic energy was defined.

Introduction

Recent investigations of permanent magnetic materials based on Nd-Fe-B alloys are 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 permanent magnets with still significant magnetic energy [1,2,3]. Permanent magnetic materials based on Nd-Fe-B alloys with reduced Nd content are the new type of nanocomposite permanent magnetic materials [1-3]. Unlike monophase $Nd_2Fe_{14}B$ magnetic alloys, these materials have a multiphase microstructure. In order to obtain optimal magnetic microstructure which is the key to improvement of hard magnetic properties, heat treatment is needed. By heat treatment crystallization is aimed at the formation of the so called magnetic microstructure, in this case nanocomposite structure which provides optimal magnetic characteristics. Enhancement of magnetic properties of investigated R/Q Nd-Fe-B alloys with low Nd content after heat treatment, according to most authors, is the result of "exchange coupling" between neighboring grains of soft Fe_3B and hard $Nd_2Fe_{14}B$ magnetic phases. Necessary conditions for exchange coupling, are that these phases should be crystalographically coherent and the mean grain size should be below 40 nm [4]. The effect becomes more pronounced with the decrease of the mean grain size which leads to the higher values of the energy product $(BH)_{max}$. Magnetic properties of this type of alloys as a function of heat treatment are the current scope of investigations, especially phase and structural transformations aimed at optimization of magnetic properties.

Scope of this paper was investigation of the influence of heat treatment on the magnetic properties of R/Q Nd-Fe-B alloy with the low Nd content (12 mass%). Thermal behavior was observed through phase transformations and the evolution of the microstructure during different regimes of heat treatment and parallel measurements of the magnetic properties.

The goal of the paper was also to determine the optimal heat treatment regime based on the composition of the alloy, applied heat treatment and microstructural and magnetic properties.

Experimental

Investigated $Nd_{4.3}Fe_{76.2}B_{19.5}$ alloy was produced by melt spinning method under the argon atmosphere. Optimal cooling rate Vs was 20 - 25 m/s. Cooling rate corresponds to the rotation speed of the copper wheel. Process parameters and cooling rate were optimized in the previous investigations [3]. Influence of heat treatment on phase composition and magnetic properties of R/Q Nd-Fe-B alloy was studied in the temperature interval from 600 to 700°C. Samples were annealed at 600, 660 and 700°C for 5 min. Different investigation techniques were used for the realization of the planned investigations. Phase transformations during the heat treatment were observed with combined use of the X-ray diffraction (XRD) analysis and Mössbauer ^{57}Fe spectroscopic (MS) phase analysis. Magnetic properties of heat treated samples were measured at the ambient temperature, on the vibrating sample magnetometer (VSM) with magnetic field strength of 50 kOe and on the superconducting quantum interference device (SQUID) magnetometer with magnetic field strength μ_0H ranging from -5T up to 5T.

Results and discussion

Experimental results of XRD analysis, MS phase analysis and magnetic measurements on VSM are summarized in Table 1.

Table 1. ***Summarized experimental results***

Heat treatment regime	XRD	MS phase analysis	Magnetic properties (VSM)
600°C / 5 min	$Nd_2Fe_{14}B$ $Nd_2Fe_{23}B_3$ Fe_3B $Nd_{1.1}Fe_4B_4$ α - Fe		Br 12.0 kG Hci 2.4 kOe $(BH)_{max}$ 8.0 MGOe
660°C / 5 min	Fe_3B $Nd_2Fe_{14}B$ $Fe_{77.2}Nd_{22.8}$ α - Fe	39% Fe_3B 6% $Nd_2Fe_{14}B$ 4% $Nd_{1.1}Fe_4B_4$ 2% α - Fe 49% Fe-Nd fero	Br 10.9 kG Hci 2.8 kOe $(BH)_{max}$ 10.7 MGOe
700°C / 5 min	$Nd_2Fe_{14}B$ Fe_3B $Nd_{1.1}Fe_4B_4$ α - Fe		Br 11.0 kG Hci 2.7 kOe $(BH)_{max}$ 8.8 MGOe

According to the results of XRD analysis the following phases are present after annealing at 600°C for 5 min: Fe_3B, $Nd_2Fe_{23}B_3$ and α-Fe phases as well as minor quantities of $Nd_2Fe_{14}B$ and boride phase $Nd_{1.1}Fe_4B_4$. Remanence of this sample (600°C/5min) measured on VSM shows the highest value of remanence. This can be explained by a large amount of soft magnetic phases with high saturation magnetization, i.e. Fe_3B and α-Fe.

X-ray diffractogram of $Nd_{4.3}Fe_{76.2}B_{19.5}$ alloy after annealing at 660°C for 5 min is presented in Fig.1.

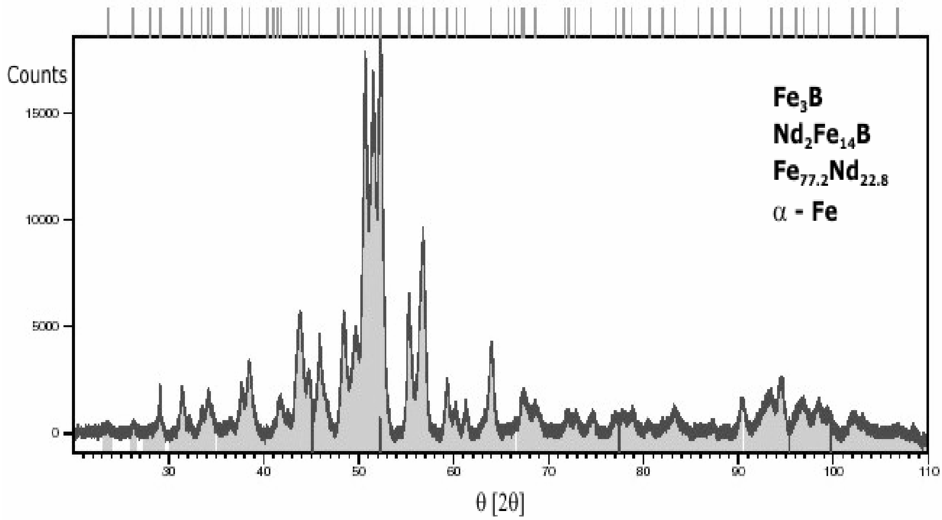

Fig.1. *X-ray diffractogram of the investigated alloy $Nd_{4.3}Fe_{76.2}B_{19.5}$ after annealing at 660°C/5 min*

As shown in Fig.1, Fe_3B, $Nd_2Fe_{14}B$, ferromagnetic phase $Fe_{77.2}Nd_{22.8}$ and α-Fe phases were identified after annealing at 660°C for 5 min. High coercivity of this sample is due to the formation of the hard magnetic phase $Nd_2Fe_{14}B$. Analysis of obtained XRD spectra suggests that $Nd_2Fe_{23}B_3$ and α-Fe are present in traces. Intermedial metastable phase $Nd_2Fe_{23}B_3$ in further process of heat treatment decomposes into the main hard magnetic phase $Nd_2Fe_{14}B$ and the lower amount of the soft magnetic phase α-Fe. Increase of the amount of the hard magnetic phase $Nd_2Fe_{14}B$ in alloy with the increase of the annealing temperature from 600°C to 660°C leads to the higher coercivity of the sample (from 2.4 kOe on 600°C to 2.8 kOe on 660°C) and consequently to the higher energy product $(BH)_{max}$ (from 8.0 MGOe on 600°C to 10.7 MGOe on 660°C).

MS phase analysis provided identification and calculation of relative ratio of individual phase contents in the investigated regime of heat treatment. The CONFIT software package for the spectra fitting and decomposition was used [5]. Present phases were identified by correlation of data obtained by CONFIT program and the data found in the literature [6]. Analysis of the MS spectra of $Nd_{4.3}Fe_{76.2}B_{19.5}$ alloy confirmed the presence of the Fe_3B, $Nd_2Fe_{14}B$ and $Nd_{1.1}Fe_4B_4$ phases and the whole set of Fe-Nd ferromagnetic phases.

A significant increase of energy product $(BH)_{max}$ from 8.0 MGOe for 600°C/5min up to 10.7 MGOe for 660°C/5min and calculated value of reduced remanence $Jr/Js > 0.5$ suggest that interaction of intergranular exchange coupling between Fe_3B and $Nd_2Fe_{14}B$ grains has the direct influence on the magnetic properties of the investigated alloy with low Nd content.

Fig. 2 represents hysteresis loop of $Nd_{4.3}Fe_{76.2}B_{19.5}$ alloy after annealing at 660°C for 5 minutes measured on SQUID magnetometer.

Increase of the annealing temperature at 700°C for 5 min resulted in decrease of energy product $(BH)_{max}$ due to the higher content of soft magnetic α-Fe phase and other identified and unidentified soft magnetic phases compared to content of the hard magnetic phase $Nd_2Fe_{14}B$. Owing to a rather significant content of the $Nd_2Fe_{14}B$ phase a considerable value of coercive force was measured. Presence of boride phase $Nd_{1.1}Fe_4B_4$ in all samples after annealing, although in small amounts, is a consequence of high boron content, above 4.2 at% [3,7]. Magnetic properties suggest that this phase was formed in nanosize and with the negligible influence on the magnetic properties of the investigated R/Q Nd-Fe-B alloy.

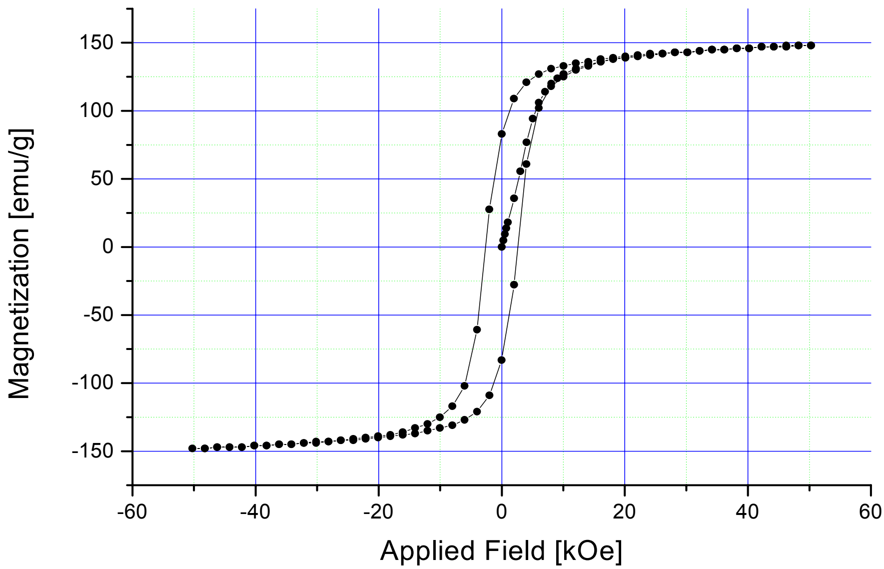

Fig. 2. *Hysteresis loop of $Nd_{4.3}Fe_{76.2}B_{19.5}$ alloy after annealing at 660^{o}C for 5 min*

Conclusion

Calculated relative ratio of individual phase contents, high content of soft magnetic phase with high saturation magnetization Fe_3B (39 mas%), presence of hard magnetic phase $Nd_2Fe_{14}B$ and measured magnetic properties indicate that nanocomposite $Fe_3B/Nd_2Fe_{14}B$ was formed after annealing at 660^{o}C for 5 min. The fact that remanence ratio calculated from SQUID hysteresis loop (Jr/Js = 0.58) for the alloy annealed at 660^{o}C for 5 minutes is higher than the theoretical limit Jr/Js < 0.5 confirms this assumption. Experimentally determined remanence ratio Jr/Js for alloy with low the Nd content corresponds with the theoretical considerations for this type of R/Q Nd-Fe-B alloys predicting the possibility of enhancement of magnetic properties despite the reduced rare earth content.

Acknowledgement

This work has been supported by the Ministry of Science and Environmental Protection of Serbia (Project OI 1212).

References

[1] Z. Cheng, B. Shen, Phys. Rev. B, 52 (13) (1995) 9427.
[2] S. Hirosawa, Y. Shigemoto, T. Miyoshi, H. Kanekiyo, Scripta Mat., 48 (2003) 839.
[3] V. Ćosović, M. Sc Thesis, University of Belgrade, 2004.
[4] E.F. Kneller, R. Hawig, IEEE Trans. Magn., 27 (1991) 3589.
[5] T. Žák, "CONFIT for Windows® 95", *Mössbauer Spectroscopy in Material Science,* M. Miglierini and D. Petridis (eds.), Bratislava, 1999, pp. 385-390.
[6] T. Hinomura, S. Nasu, H. Kanekiyo, S. Hirosawa, J. Japan. Inst. Metals, 61 (1997), 184.
[7] N. Talijan, T. Zák, J. Stajić-Trošić, V. Menushenkov, J. Magn. Magn. Mater., 258-259 (2003) 577.