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STUDY OF THERMOMAGNETIC BEHAVIOR, PHASE COMPOSITION AND STRUCTURE PARAMETRES OF NANOCRYSTALLINE $Nd_{4.5}Fe_{77}B_{18.5}$ ALLOY

Aleksandar S. Grujić
Jasna T. Stajić-Trošić
Nadežda M. Talijan
Vladan R. Ćosović
Institute of Chemistry, Technology and Metallurgy
Njegoševa 12, 11000 Belgrade, Serbia

Tomáš Žák
Institute of Physics of Materials, Academy of Sciences of the Czech Rep., v.v.i.,
Žižkova 22, 616 62 Brno, Czech Republic

ABSTRACT
The influence of phase composition and structure parameters on the magnetic properties of rapidly quenched nanocrystalline Nd-low Nd-Fe-B alloy was studied. Thermomagnetic behavior of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy was observed by measurement of thermomagnetic curves (TM) in temperature interval 20–800 ^oC. Phase composition and crystallite size of the investigated alloy in optimized magnetic state and after TM were determined using X-ray diffraction (XRD) method. The determined mean grain size in optimal magnetic state, both by XRD and TEM analysis was below 30 nm, and the nanocomposite structure consisted of $Fe_3B/Nd_2Fe_{14}B$ and partly of α-Fe. Based on determined increase of the amount of main decomposition product α-Fe and presence of Nd_2O_3 and number of different Fe-B phases as well as increase of mean grain size after the TM, it can be assumed that these are the main reasons for the quality loss of hard magnetic properties
Keywords: nanocomposite Nd-Fe-B alloy, thermomagnetic behaviour, X-ray, SQUID

1. INTRODUCTION
The Nd-Fe-B alloys with reduced Nd content have the multiphase microstructure. Beside the main hard magnetic phase $Nd_2Fe_{14}B$, soft magnetic phases with high saturation α-Fe and/or Fe_3B phase exist, as well as whole set of phases of Fe-B type. An optimum magnetic microstructure consists of a homogenous dispersion of a hard phase in a soft phase [1]. The mean grain sizes of the $Nd_2Fe_{14}B$, Fe_3B or α-Fe phases are ultra fine (< 40 nm) [2]. Formed nanocomposites $Fe_3B/Nd_2Fe_{14}B$ and α-Fe/$Nd_2Fe_{14}B$ in alloys with reduced amount of Nd are characterized by the presence of intergranular interaction of ferromagnetic exchange coupling which is directly responsible for the increase of remanence and consequently the increase of magnetic energy [3,4]. It is known that magnetic properties of nanocomposite Nd-Fe-B permanent magnetic materials are very sensitive to grain size and phase composition, since the exchange coupling effect is sensitive function of grain size. Increase in grain size would generally result in decrease of remanence enhancement [5].
The scope of the presented investigations is to study the changes of magnetic properties of nanocomposite $Nd_{4.5}Fe_{77}B_{18.5}$ alloy induced by the thermomagnetic measurements by comparing the experimentally determined phase composition, crystallite sizes and magnetic properties in the optimized magnetic state and after TM.

2. EXPERIMENTAL

Magnetic characteristics of the investigated $Nd_{4.5}Fe_{77}B_{18.5}$ alloy after subsequent annealing to the optimized magnetic state are presented in Table 1.

Table 1. Origin and basic magnetic characteristics of investigated alloy

Alloy	Preparation	Treatment	$_iH_c$ (kOe)	B_r (kG)	$(BH)_{max}$ (MGOe)
$Nd_{4.5}Fe_{77}B_{18.5}$	centrifugal atomization	660°C/5 min.	2.8	10.9	10.7

Thermomagnetic behavior of investigated alloy has been studied by measurement of thermomagnetic curves (TM) in temperature interval 20–800^{o}C using an EG&G vibrating sample magnetometer in the field of intensity of 50Oe under vacuum (0.1Pa) with the heating and cooling rate kept at 4 K/min. For the TM measurements the material was cold pressed into small tablets with the diameter of about 3 mm. Phase composition and grain size of the investigated $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in optimized magnetic state and after TM were determined by X-ray diffraction (XRD) method using an X'Pert PRO MPD multi-purpose X-ray diffraction system from PANanalytical with Co K_α radiation. Size-strain analysis and qualitative phase analysis of the obtained X-ray diffraction data were done by the FullProf computer program and the X-ray line broadenings were analyzed through refinement of the TCH-pV (in this case the most reliable peak-shape function) function parameters. Microstructure of the investigated Nd-low Nd-Fe-B alloy in optimized state was observed by a transmission electron microscope (TEM), JEOL JEM-2000, operated at 200 kV. The TEM samples were prepared by mechanical grinding and ion beam thinning. Magnetic properties of the investigated alloy were measured on the temperature of the ambient using the Superconducting Quantum Interference Device (SQUID) magnetometer with magnetic field strength μ_0H of 5T.

3. RESULTS AND DISCUSSION

Thermomagnetic behavior of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy and appropriate phase transformations have been observed by thermomagnetic measurements. Obtained TM curves are presented on Figure 1.

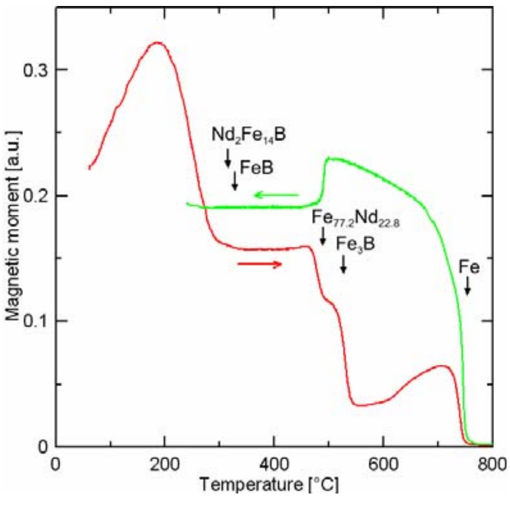
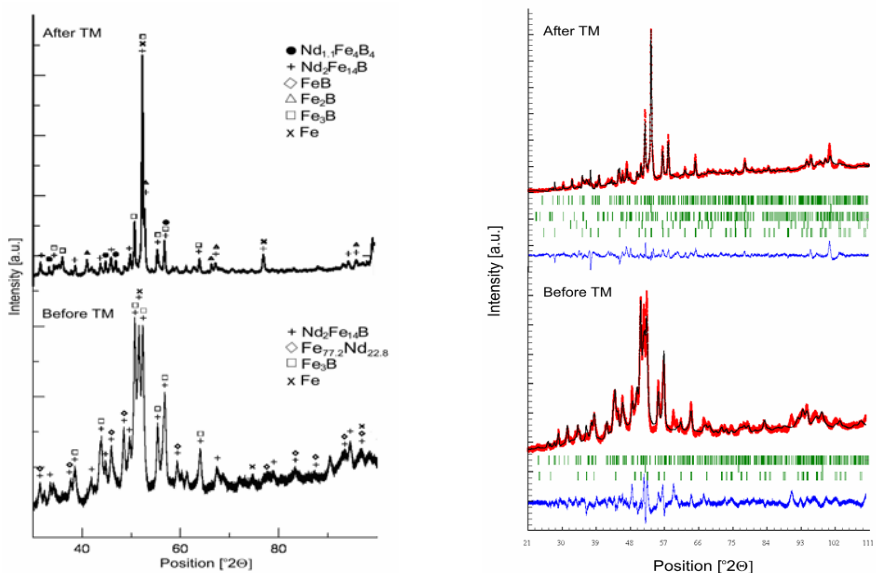


Figure 1. TM curves of investigated $Nd_{4.5}Fe_{77}B_{18.5}$ alloy

By XRD analysis of the alloy in optimized state Fe_3B, $Nd_2Fe_{14}B$, $Fe_{77.2}Nd_{22.8}$ and α-Fe phases were identified as shown in Figure 2a. Analysis of XRD spectra suggests that $Nd_2Fe_{23}B_3$ and α-Fe are present in traces [6,7]. The present $Fe_{77.2}Nd_{22.8}$ phase is to be understood more as a representative of Fe(Nd,B) components. After the TM measurements (20-800^{o}C) according to XRD results Figure 2a., the main decomposition product is the α-Fe, this phase is accompanied by $Nd_2Fe_{14}B$ phase, Fe_3B and a number of different Fe-B phases as well as the boride phase $Nd_{1.1}Fe_4B$

For better understanding of the influence of content and grain size of individual phases on the magnetic properties of investigated alloy before and after the TM, the size-strain and quantitative phase analysis of X-ray data were done. Comparisons between observed and calculated intensities before and after the TM are presented on Figure 2b. The vertical bars indicate positions of reflections and the difference patterns are given below. Summarized results are presented in Table 2.



a) b)

Figure 2. a) XRD diffractograms, b) comparison between observed and calculated intensities of the investigated alloy before and after TM

Table 2. Phase composition and mean grain sizes for the $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in the state before and after thermomagnetic measurements obtained by size strain analysis using FullProf software

Phase	Before TM		After TM	
	Amount [%]	Grain size [nm]	Amount [%]	Grain size [nm]
$Nd_2Fe_{14}B$	43.63	12.4	17.95	38
α - Fe	16.54	5	36.77	29
Fe_3B	39.83	24	28.16	34
Nd_2O_3	-	-	8	7.9
Fe(O)B	-	-	9	11.3

From the results of XRD analysis (Figure 2a and Table 2) it is obvious that after TM, the amount of soft magnetic phases has increased, predominantly α-Fe, as well as the increase of grain size of all identified phases. The presence of Nd_2O_3 phase is also confirmed. Practically, the increase of amount of soft magnetic phases and grain size of present phases has the direct influence on reduction of magnetic properties.

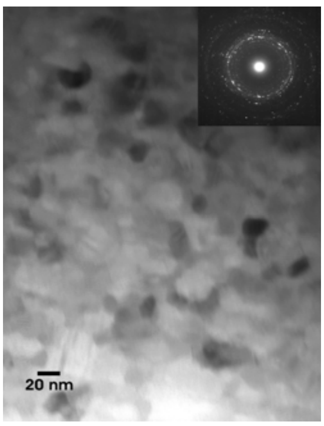


Figure 3. Bright field transmission electron micrograph of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in optimized magnetic state. The insert figure is the electron diffraction pattern of the selected area.

From the TEM micrograph (Figure 3.) it can be noticed that the average grain size in optimized magnetic state is below 30 nm which confirms the mean grain size calculated by the size-strain analysis of XRD data. A microdiffraction analysis gave evidence of mixture of nanocrystalline phases. This implies that the alloy has the nanocomposite structure of $Fe_3B/Nd_2Fe_{14}B$ and partly α-Fe.

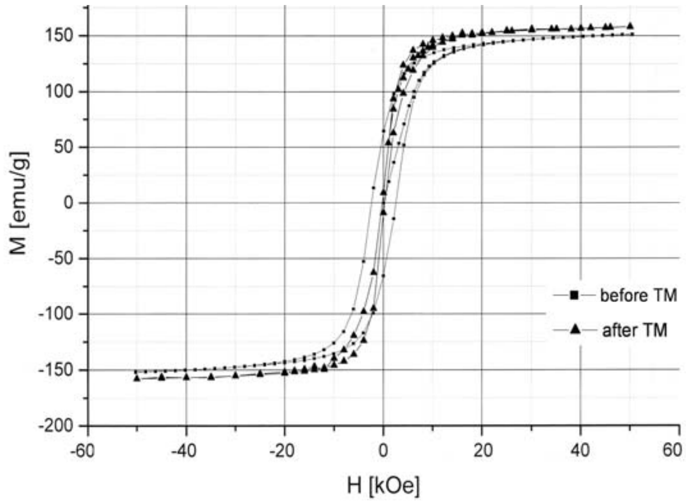


Figure 4. SQUID hysteresis loops of the investigated rapid quenched $Nd_{4.5}Fe_{77}B_{18.5}$ alloy in the optimized state and after the thermomagnetic measurements

Magnetic behaviour of investigated alloy before and after TM is presented with the corresponding SQUID hysteresis loops on Figure 4. The calculated value of remanence ratio Jr/Js>0.5 for the alloy in optimized magnetic state suggest that interaction of ferromagnetic exchange coupling between grains of soft and hard magnetic phases has the direct influence on the magnetic properties. The change of magnetic behavior after the thermomagnetic measurements, which is clearly illustrated as the shape of SQUID hysteresis loops, corresponds to the changed phase composition and increased grain sizes determined by XRD. Hence, it can be assumed that the thermal decomposition is the main reason for the quality loss of investigated hard magnetic material.

4. CONCLUSION

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 $Nd_{4.5}Fe_{77}B_{18.5}$ alloy. Magnetic properties of the alloy in optimized magnetic state correspond to the nanocomposite structure of the alloy. The fact that the calculated remanence ratio from SQUID hysteresis loop for the alloy in the optimized magnetic state is higher than theoretical limit (Jr/Js=0.6) confirms this assumption. 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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6. ACKNOWLEDGEMENT

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