Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 75 (9) 1271–1277 (2010)
JSCS–4050
UDC 546.657'72'27:66.017+
537.622:621.318.12
Original scientific paper

An overstoichiometric Nd–Fe–B hard magnetic material

TOMÁŠ ŽÁK[1]*, NADEŽDA M. TALIJAN[2#], VLADAN R. ĆOSOVIĆ[2#], JASNA T. STAJIĆ-TROŠIĆ[2#] and ALEKSANDAR S. GRUJIĆ[2#]

[1]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, v.v.i., Žižkova 22, 616 62 Brno, Czech Republic and [2]Institute of Chemistry, Technology and Metallurgy, Department of Materials and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

(Received 17 February, revised 16 April 2010)

Abstract: A commercial Nd-rich Nd–Fe–B-based hard magnetic material was studied. The obtained results were compared before and after recording of the thermomagnetic curve up to 800 °C. The curve itself showed clearly besides Curie points of the $Nd_2Fe_{14}B$ phase and α-Fe also another critical temperature. Mössbauer spectroscopic (MS) phase analysis and X-ray diffraction analysis (XRD) showed in addition to the commonly known phases $Nd_2Fe_{14}B$ and $NdFe_4B_4$ also some paramagnetic and ferromagnetic iron atoms (MS) and $Fe_{17}Nd_2$ intermetallics (XRD). During the exerted thermal treatment, the content of the $Nd_2Fe_{14}B$ and $NdFe_4B_4$ phases remained almost unchanged, while iron atoms from remnant minor phases built a separate α-Fe phase. The XRD pattern also showed the presence of some minor Nd phase. The results of Squid magnetic measurements suggest a nanocrystalline decoupled structure of the Nd-rich alloy in the optimized magnetic state. Measurement of the magnetization loop showed, in spite of small changes in the phase composition, that magnetic properties of the quality material deteriorated during the thermal treatment.

Keywords: rapid quenched Nd–Fe–B; overstoichiometric Nd content; Mössbauer phase analysis; XRD; magnetic properties.

INTRODUCTION

Permanent magnetic materials are key components of numerous electronic, data processing and medical devices, and recently, significant amounts are also required in the automotive.[1] 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, which has a large saturation

* Corresponding author. E-mail: zak@ipm.cz
# Serbian Chemical Society member.
doi:10.2298/JSC100217058Z

magnetization and high anisotropy field, as the principal phase.[2,3] Hence, studies of Nd–Fe–B hard magnetic materials have become very significant over the last few decades.[4] Besides alloys with lowered neodymium contents exhibiting nanocomposite character, Nd–Fe–B alloys with enhanced qualities arising through the use of overstoichiometric Nd atoms are employed. Overstoichiometric (Nd-rich) Nd–Fe–B alloys have an almost monophase composition with the $Nd_2Fe_{14}B$ phase being dominant. Grains of this phase are magnetically isolated (decoupled) by intergranular layers of Nd-rich phases.[5–7] This structure leads essentially to a magnetic decoupling and each hard magnetic grain behaves like a small permanent magnet, which results in high coercivities.[1,8] The superior magnetic performance of this type of Nd–Fe–B alloy arises from the higher values of coercivity compared to nanocomposite Nd–Fe–B alloys[9,10] and ferrite-based magnetic materials.[11,12] In addition, their resistivity to higher temperatures is better than that of nanocomposite Nd–Fe–B alloys with a low Nd content.[13]

EXPERIMENTAL

The influence of the content of overstoichiometric Nd on the microstructure of commercial Nd–Fe–B alloy (Xiamen Yuxiang Magnetic Materials Ind. Co. Ltd, China) was analyzed by comparing the phase composition in the optimized magnetic state and after thermomagnetic measurement. The nominal composition of the material was >26 wt. % of Nd and < 1.3 wt. % of B, with the balance being Fe; the particle size was between 74 and 177 μm, the induction B_T = 0.603 T, the coercivities H_c(B) = 0.374 MA m^{-1} and H_c(J) = 0.974 MA m^{-1} and the energy product $(BH)_{max}$ = 57.1 kJ m^{-3}. The thermomagnetic curve was measured on an EG & G vibrating sample magnetometer in the field of 4 kA m^{-1} in vacuum. The heating and cooling rate was 4 °C min^{-1} with 30 min. hold at the maximum of 800 °C. Interpretation of comparable thermomagnetic measurements can be found in a previous investigations.[14] Mössbauer spectra were taken at room temperature in the standard transmission geometry using a ^{57}Co(Rh) source. The calibration was realized against an α-iron foil. The "Confit" program package[15] was used for spectra fitting and deconvolution,. Omitting the possible influence of the Lamb–Mössbauer factor, the relative content of the iron containing phases was derived from the intensities of the corresponding spectral components. The phase analysis was realized in manner similar to that described in Hinomura *et al.*[16] The X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro MRD diffractometer from PANanalytical with Co Kα radiation operated at 40 kV and 30 mA. For routine characterization, diffraction data was collected in the range of 2θ Bragg angles (20 to 110°, step 0.08°). All XRD measurements were performed with powder samples at ambient temperature. For a quantitative analysis and determination of the crystallite size, HighScore plus with Rietweld structural models based on the ICSD database was used. The magnetic properties of the alloy *i.e.*, the corresponding hysteresis loops, were obtained at ambient temperature using Quantum Design MPMS 5XL superconducting quantum interference device (SQUID) magnetometer with magnetic field strength in range −4 to 4 MA m^{-1}.

RESULTS AND DISCUSSION

The curve of the thermomagnetic measurement, coming out from the optimized state, is presented in Fig. 1. It was completed taking into account the Curie

temperature of phases. Questionable is the FeB phase with a Curie temperature at about 325 °C, as it was detected neither in the optimized state nor in the final one. However, its intermediate presence during the heating process cannot be excluded. The rapid increase of the magnetic moment during cooling can be assigned, in addition to the structural changes, to the field cooling process. From the magnetically disordered state, during cooling the moments tend to minimize energy against the external magnetic field and the final state results in an anisotropic moments distribution, appearing externally as an enlargement of the bulk magnetic moment.

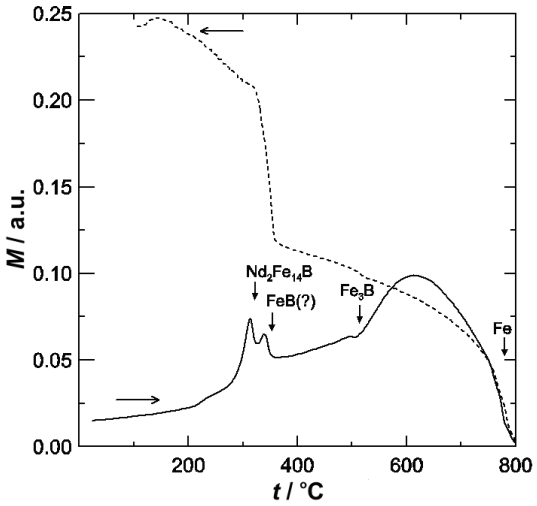

Fig. 1. The thermomagnetic curve measured on the Nd-rich Nd–Fe–B material in vacuum at a field of 4 kA m^{-1}. Heating: solid line, cooling: dotted line. The heating and cooling rates were both 4 °C min^{-1}.

The results of the Mössbauer phase analysis are presented in Figs. 2 and 3, and quantitatively in Table I. The original material was of high quality with a high content of the hard magnetic $Nd_2Fe_{14}B$ phase and a small amount of the $NdFe_4B_4$ phase. The presence of these crucial phases was confirmed by XRD analysis.

The kind and amount of other the phases correspond to the fraction of overstoichiometric Nd atoms. The Fe(Nd) solid solution component in the Mössbauer spectrum, with a spectral contribution looking like a "slightly broadened α-Fe phase", consists of a few sextets originating from iron atoms with 0, 1, 2, *etc.* neodymium atoms as nearest neighbors. Assuming an absence of atomic order, it is possible to plot theoretical relative intensities of such components depending on the concentration of Nd atoms as derived from the binomial distribution. The content of Nd atoms was then estimated by comparing these plots with the measured intensities to roughly 10 at.%. The $Fe_{17}Nd_2$ intermetallics structure found in XRD pattern (Fig. 4) is of a very similar composition. we cannot It is impossible to determine which atoms brought the iron of the phase labeled as Fe-para

into the paramagnetic region, especially as it has no evident match in the XRD pattern.

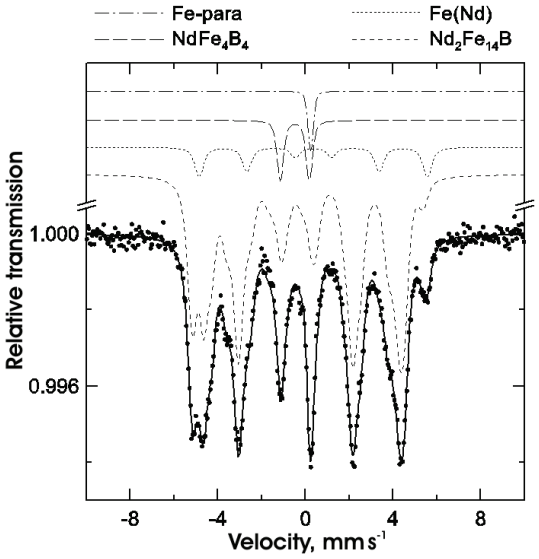

Fig. 2. Mössbauer phase analysis of the sample in the optimized state.

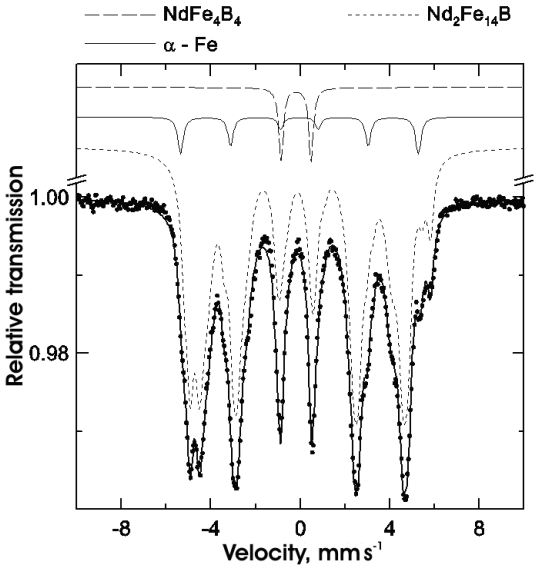

Fig. 3. Mössbauer phase analysis of the sample after thermomagnetic measurement.

Contrary to the data obtained by S. C. Wang and Y. Li,[6] no Nd oxide phases were distinguished using the XRD method. The thermal treatment during the thermomagnetic measurement brought an insignificant change in content of the dominating $Nd_2Fe_{14}B$ phase and of the $NdFe_4B_4$ phase. As the main decompo-

sition product, a weak component of the magnetically soft α-Fe phase was found, simultaneously giving rise of a separate Nd phase, as obvious from the XRD results only (Fig. 5).

TABLE I. The relative amount of iron-containing phases as determined from the Mössbauer spectra in the optimized state and after thermomagnetic measurement

Phase	Optimized state	After annealing
$Nd_2Fe_{14}B$	0.87	0.92
$NdFe_4B_4$	0.05	0.03
Fe(Nd)	0.08	–
α-Fe	–	0.05

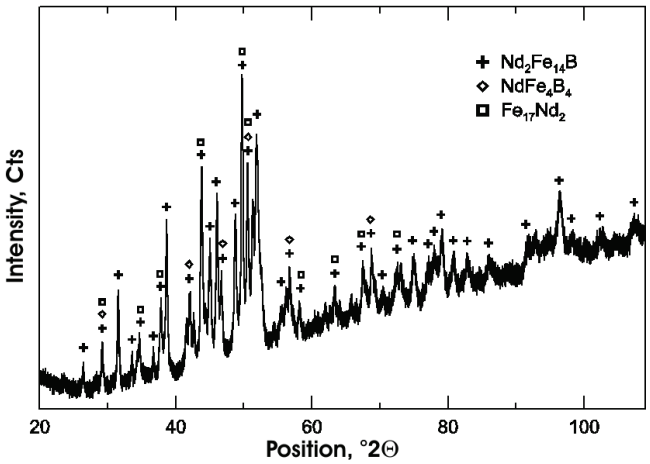

Fig. 4. The XRD pattern of the sample in the optimized state.

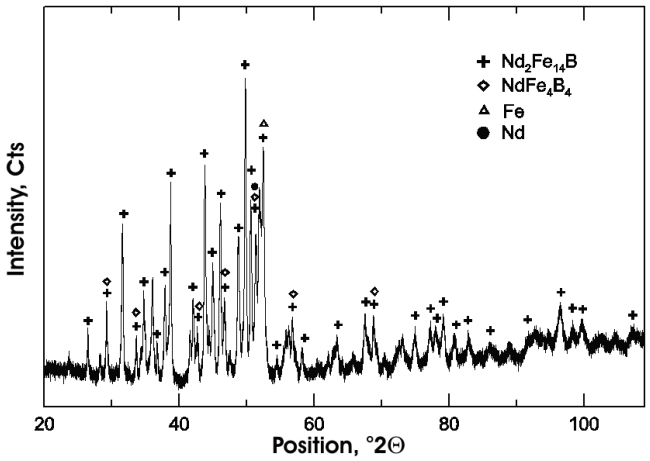

Fig. 5. XRD Pattern of the sample after thermomagnetic measurement.

The shape of the Squid hysteresis loop of the Nd-rich Nd–Fe–B alloy (Fig. 6) in the optimized magnetic state implies the presence of a magnetically decoupled nanocrystalline structure. The obtained high value of coercivity supports this and indicates a nearly monophase structure of the alloy with a dominant content of the main hard magnetic phase $Nd_2Fe_{14}B$. From the magnetization loop measurement (Fig. 6), it follows that, in spite of small changes in phase constitution, the thermal treatment during thermomagnetic measurement deteriorated the magnetic properties of the quality hard magnetic material.

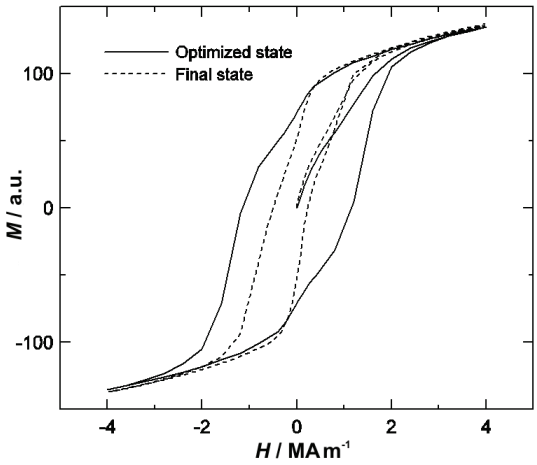

Fig. 6. Hysteresis loops of the samples in the optimized state and after thermomagnetic measurement.

CONCLUSIONS

In agreement with the thermomagnetic curve analysis, the process of thermal degradation of the material mainly occurred in the intergranular layer, leaving the dominant $Nd_2Fe_{14}B$ phase and the minor $NdFe_4B_4$ phase almost unchanged. The iron–neodymium phase underwent decomposition and both elements moved to separate phases, whereby the neodymium was not detectable by the Mössbauer effect but could be distinguished in XRD pattern. Thus, from a magnetic point of view, the main thermal decomposition product was the soft magnetic α-Fe phase. In spite of the conservation of the volume of the $Nd_2Fe_{14}B$ phase, the final state of the material was different from the optimal and deterioration of the magnetic properties (of magnetic hardness) was evident. It is obvious that the magnetic properties of the investigated alloy are in strong relationship to its structure and phase composition.

Acknowledgments. This work was supported by the Czech Ministry of Education, Youth and Sports, Project 1M0512, and by the Ministry of Science and Technological Development of the Republic of Serbia under Project OI 142035B.

И З В О Д

НАДСТЕХИОМЕТРИЈСКИ Nd–Fe–B ТВРДИ МАГНЕТНИ МАТЕРИЈАЛИ

ТОМÁШ ŽÁК[1], НАДЕЖДА М. ТАЛИЈАН[2], ВЛАДАН Р. ЋОСОВИЋ[2], ЈАСНА Т. СТАЈИЋ-ТРОШИЋ[2] и АЛЕКСАНДАР С. ГРУЈИЋ[2]

[1]*Institute of Physics of Materials, Academy of Sciences of the Czech Republic, v.v.i., Žižkova 22, 616 62 Brno, Czech Republic и* [2]*Институт за хемију, технологију и металургију, Центар за материјале и металургију, Универзитет у Београду, Његошева 12, 11000 Београд*

Испитиван је комерцијални магнетно-тврди материјал на бази Nd–Fe–B легуре обогаћене неодијумом. Добијени резултати испитивања материјала у оптималном стању и после термомагнетних (ТМ) мерења до 800 °C поређени су и дискутовани. На добијеној термомагнетној кривој се, поред јасно видљивих Кири температура фаза $Nd_2Fe_{14}B$ и α-Fe, може уочити и још једна критична температура. Применом Mössbauer-ове спектроскопске (МС) фазне анализе и методе дифракције X-зрака (XRD) утврђено је, поред присуства очекиваних $Nd_2Fe_{14}B$ и $NdFe_4B_4$ фаза, и присуство парамагнетних и феромагнетних јона Fe (МС), као и $Fe_{17}Nd_2$ интерметалних једињења (XRD). У току примењеног термичког третмана удео $Nd_2Fe_{14}B$ и $NdFe_4B_4$ фаза је остао скоро непромењен, док су атоми Fe из осталих фаза са мањим уделом формирали засебну α-Fe фазу. Резултати магнетних мерења на Squid магнетометру указују на нанокристалну декупловану структуру легуре обогаћене на неодијуму у оптималном магнетном стању. Из добијених хистерезисних петљи се може видети да је и поред малих промена у фазном саставу термички третман довео до делимичног губитка магнетних својстава испитваног материјала.

(Примљено 17. фебруара, ревидирано 16. априла 2010)

REFERENCES

1. O. Gutfleisch, *J. Phys. D: Appl. Phys.* **33** (2000) R157
2. N. C. Koon, B. N. Das, M. Rubinstein, J. Tyson, *J. Appl. Phys.* **57** (1985) 4091
3. C. Abache, H. Oesterreicher, *J. Appl. Phys.* **57** (1985) 4112
4. J. J. Croat, J. F. Herbst, R. W. Lee, F. E. Pinkerton, *J. Appl. Phys.* **55 (**1984) 2078
5. I. Ahmad, H. A. Davies, R. A. Buckley, *J. Magn. Magn. Mater.* **157**–**158** (1996) 31
6. S. C. Wang, Y. Li, *J. Magn. Magn. Mater.* **285** (2005) 177
7. A. Grujić, N. Talijan, A. Maričić, J. Stajić-Trošić, V. Ćosović, V. Radojević, *Sci. Sinter.* **37** (2005) 139
8. D. Goll, H. Kronmüller, *Naturwissenschaften* **87** (2000) 423
9. N. Talijan, V. Ćosović, J. Stajić-Trošić, A. Grujić, T. Žák, Z. Lee, V. Radmilović, *Mater. Trans. JIM* **50** (2009) 2302
10. V. Ćosović, N. Talijan, A. Grujić, J. Stajić-Trošić, T. Žák, Z. Lee, V. Radmilović, *Sci. Sinter.* **41** (2009) 209
11. D. Gingasu, I. Mindru, L. Patroni, S. Stoleriu, *J. Serb. Chem. Soc.* **73** (2008) 979
12. J. Ding, W. F. Miao, P. G. McCormick, R. Street, *J. Alloys Compd.* **281** (1998) 32
13. N. Talijan, T. Žák, J. Stajić-Trošić, V. Menushenkov, *Metalurgija – J. of Metall.* **8** (2002) 201
14. N. Talijan, V. Ćosović, J. Stajić-Trošić, T. Žák, *J. Magn. Magn. Mater.* **272**–**276** (2004) e1911
15. T. Žák, Y. Jirásková, *Surf. Interface Anal.* **38 (**2006) 710
16. T. Hinomura, S. Nasu, H. Kanekio, M. Uehara, S. Hirosawa, *Mater. Trans. JIM* **12 (**1997) 1106.