



Mössbauer study of treated $\text{Nd}_2\text{Fe}_{14}\text{B}$

Mieczysław Budzyński,
Virgil C. Constantin,
Ana-Maria J. Popescu,
Zbigniew Surowiec,
Tamara M. Tkachenka,
Kazimir I. Yanushkevich

Abstract. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ cylindrical magnets were treated with water solutions of alkali, acid, and salt. Mössbauer spectroscopy was applied to study the composition and properties of the surface material of the treated magnets. It is shown that the main phase of the permanent $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet partly decomposes. The released $\alpha\text{-Nd}$ at the grain boundaries interacts with water and forms neodymium hydroxide matrix, and the released Fe diffuses into it. The presence of $\text{Fe-Nd}(\text{OH})_3$ is reflected in the paramagnet doublet in the Mössbauer spectra of treated neodymium magnets.

Key words: intermetallics • intergranular corrosion • Mössbauer spectroscopy

M. Budzyński, Z. Surowiec
Institute of Physics,
M. Curie-Skłodowska University,
1 M. Curie-Skłodowska Sq., 20-031 Lublin, Poland

V. C. Constantin, A.-M. J. Popescu
Department of Molten Salts,
“Ilie Murgulescu” Institute of Physical Chemistry,
Romanian Academy,
202 Splaiul Independentei Str., Bucharest, Romania

T. M. Tkachenka✉, K. I. Yanushkevich
Scientific-Practical Materials Research Center
of National Academy of Sciences of Belarus,
19 P. Brovky Str., Minsk, 220072 Belarus,
Tel.: xxxxx, Fax: xxxxx,
E-mail: lttt@physics.by

Received: 18 June 2014
Accepted: 4 November 2014

Introduction

The three-component Nd-Fe-B system is characterized by $\text{Nd}_2\text{Fe}_{14}\text{B}$, NdFe_4B_4 , and Nd_2FeB_3 compounds, but only the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is used to produce magnets with the best characteristics. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets are the most power-intensive ones known so far; they can work in a temperature range from -60 to $+240^\circ\text{C}$ without degradation of the magnet parameters [1] and the way of production allows obtaining magnets of any shape. Therefore, the Nd-Fe-B magnets are widely applicable in electromotors, generators, Hall sensors, medical apparatus, etc.

A serious disadvantage of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets is their poor resistance to corrosive mediums [2–4]. In order to protect the magnetic properties from degradation, it is necessary to understand the degradation processes. Therefore, the purpose of the present work is to study the influence of different corrosive mediums on the structural and magnetic state of $\text{Nd}_2\text{Fe}_{14}\text{B}$. The main experimental method was Mössbauer spectroscopy.

Results and discussion

Several cylindrical permanent $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets for the study were obtained using conventional sintered technology from commercial melt-spun $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders [5]. Then, three identical cylindrical magnet samples were treated with water solutions of alkali

(sample 1), acid (sample 2), and salt (sample 3). The conditions of sample preparation are listed in Table 1. The powder X-ray analysis of the untreated sample shows a tetragonal phase inherent to $\text{Nd}_2\text{Fe}_{14}\text{B}$ with the space group $P4_2/mmm$. The powders for the Mössbauer samples were taken off the surface of each cylindrical magnet.

Mössbauer analyses were performed in usual transmission geometry and a constant acceleration regime. The $^{57}\text{Co}(\text{Rh})$ was used as a source of gamma radiation. The temperatures of the source and samples were 293 K.

Interpretation of the experimental Mössbauer spectrum on the basis of the sample crystal structure is generally accepted. The phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ has a tetragonal crystal structure with 68 atoms in the unit cell [6, 7]. The Fe atoms in $\text{Nd}_2\text{Fe}_{14}\text{B}$ are located in six types of structure-nonequivalent positions: k_1 , k_2 , j_1 , j_2 , e , and c . Two types of positions are occupied by the Nd atoms – f and g , and one type of positions g by the boron atoms. The Mössbauer spectrum of $\text{Nd}_2\text{Fe}_{14}\text{B}$ at ^{57}Fe can be described in the model of six sextets corresponding to the six possible states of Fe atoms [8, 9]. As the populations of the k_1 , k_2 , j_1 , j_2 , e , and c positions are respectively 16, 16, 8, 8, 4, and 4 (56 iron atoms in total), the corresponding subspectra contribute to the total spectrum as 4:4:2:2:1:1. The isomer shift (IS) values were fitted relative to $\alpha\text{-Fe}$. The quadrupole splitting (QS) values were fitted as

$$\varepsilon_Q = \frac{1}{2} eQV_{zz} = \frac{1}{2} (R_{1-2} - R_{6-5})$$

Table 1. The features of $\text{Nd}_2\text{Fe}_{14}\text{B}$ treatment

Sample	Reagent	Concentration of reagent in water solution	Time of exposition [h]
$\text{Nd}_2\text{Fe}_{14}\text{B}$	Untreated	–	–
No. 1	KOH	0.5 M/l	384
No. 2	HClO_4	0.5 M/l	384
No. 3	NaCl	3 wt%	384

Table 2. Mössbauer parameters of untreated $\text{Nd}_2\text{Fe}_{14}\text{B}$

Iron positions	Relative contribution to spectrum	B [T]	IS ± 0.01 [mm/s]	$\varepsilon_Q \pm 0.05$ [mm/s]
$16k_1$	4	28.8	–0.11	0.16
$16k_2$	4	31.0	–0.14	0.09
$8j_1$	2	31.4	0.70	0.21
$8j_2$	2	27.1	–0.15	0.06
$4e$	1	24.2	–0.05	0.21
$4c$	1	20.3	–0.13	–0.11

Table 3. Mössbauer parameters of $\text{Nd}_2\text{Fe}_{14}\text{B}$ treated by water solution of alkali (No. 1)

Iron positions	Relative contribution to spectrum	B [T]	IS ± 0.01 [mm/s]	$\varepsilon_Q \pm 0.05$ [mm/s]
Doublet	5%	–	0.16	0.39
$16k_1$	4	31.0	–0.16	–0.06
$16k_2$	4	27.6	–0.22	–0.01
$8j_1$	2	30.9	0.57	–0.37
$8j_2$	2	28.3	–0.04	–0.16
$4e$	1	22.8	–0.05	–0.16
$4c$	1	15.9	0.69	0.32

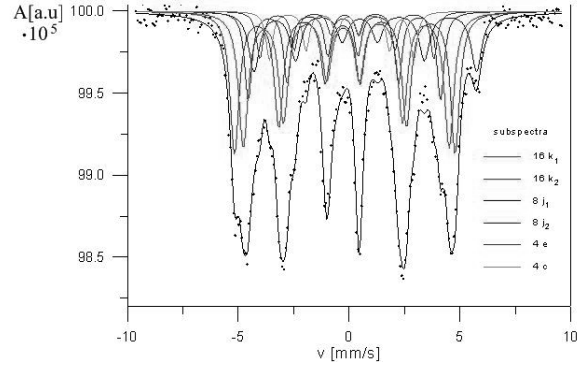


Fig. 1. Mössbauer spectrum of untreated $\text{Nd}_2\text{Fe}_{14}\text{B}$ at room temperature.

where R_{1-2} and R_{6-5} are the 1–2 and 5–6 sextet-line distances.

The Mössbauer spectrum of the untreated $\text{Nd}_2\text{Fe}_{14}\text{B}$ is presented in Fig. 1 and the parameters are given in Table 2. The spectrum is in good agreement with the six-sextet model. No other extraneous phases (metal Fe, $\text{Nd}_2\text{Fe}_{17}$, iron borides FeB, or Fe_2B) have been disclosed. The Mössbauer spectra of treated samples no. 1–3 are shown in Fig. 2; their Mössbauer parameters are given in Tables 3–5.

The experimental spectra of the treated samples cannot be fitted by six sextets similar to that of the untreated sample. Each treated sample spectrum reveals an additional doublet. The total relative contribution of the sextets to the spectrum decreases from sample 1 to 3. The Mössbauer data analysis exhibits no pure iron oxides in the treated samples,

Table 4. Mössbauer parameters of Nd₂Fe₁₄B treated by water solution of acid (No. 2)

Iron positions	Relative contribution to spectrum	B [T]	IS ± 0.01 [mm/s]	$\epsilon_Q \pm 0.05$ [mm/s]
Doublet	12%	–	0.21	0.38
16 k_1	4	32.60	–0.05	–0.04
16 k_2	4	29.64	–0.10	0.07
8 j_1	2	32.54	0.87	0.01
8 j_2	2	29.54	–0.03	–0.14
4 e	1	25.44	–0.04	–0.12
4 c	1	18.34	0.04	0.60

Table 5. Mössbauer parameters of Nd₂Fe₁₄B treated by water solution of salt (No. 3)

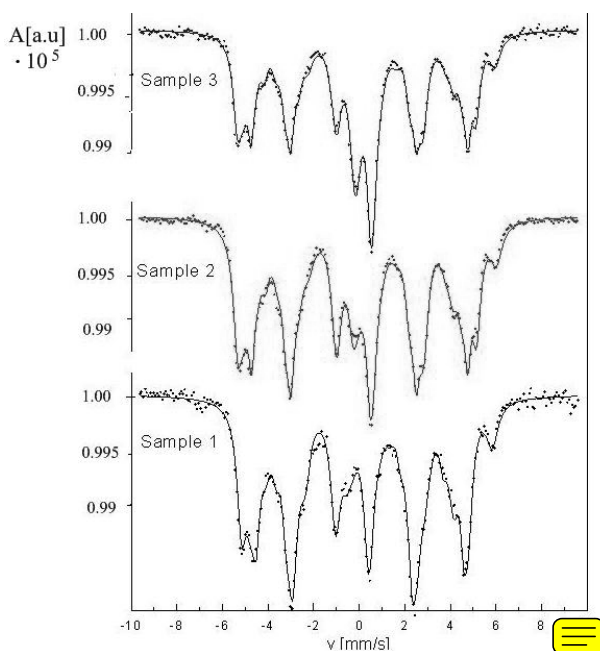
Iron positions	Relative contribution to spectrum	B [T]	IS ± 0.01 [mm/s]	$\epsilon_Q \pm 0.05$ [mm/s]
Doublet	22%	–	0.27	0.37
16 k_1	4	32.50	–0.07	–0.05
16 k_2	4	30.04	–0.11	0.06
8 j_1	2	32.84	0.83	0.01
8 j_2	2	29.64	–0.03	–0.14
4 e	1	25.84	–0.04	–0.12
4 c	1	18.64	0.01	0.06

as there are no subspectra with the appropriate sets of hyperfine parameters in the spectra. There are no iron borides either, as the Mössbauer parameter set for Fe₂B is $B_{\text{eff}} \sim 24$, 2 T, IS ~ 0.40 mm/s; and for FeB, it is 11.8 T and 0.40 mm/s, respectively, and there are no subspectra with such combinations of parameters in the treated sample spectra. It was found that the effective field value at Fe in c -positions decreases in the treated samples. The same change in the magnetic state of iron atoms in c -positions was observed in [10]. We suppose that this is due to the boundary location of c -positions in the unit cell. It is known that the Nd₂Fe₁₄B magnet has a granular structure. The granular material represents the pure Nd₂Fe₁₄B phase and grains have dimensions ca. 200–500 nm, that is, the domain size ca. ~ 300 nm

[1]. The intergranular material is responsible for granular isolation. As the dimensions of the unit cell nearly coincide with those for one grain, the Fe atoms at the grain boundaries are most sensitive to the magnet treatment. The most appreciable field decrease in the hyperfine field at Fe occurs for sample 1 treated with the water solution of alkali. In general, the essentialities described indicate degradation of the macromagnetic characteristics of the Nd₂Fe₁₄B magnet, including coercivity and specific magnetization. This conclusion correlates with the results of investigations of specific magnetization temperature and field dependences.

The paramagnetic doublet in each sample spectrum corresponds to the magnetically disordered phase. The Mössbauer parameters of the doublet are the same for all the treated sample spectra: the isomer shift value is about 0.20 mm/s and the quadrupole splitting value is ~ 0.39 mm/s. The most probable state of the iron atom is Fe³⁺ with $\sigma = 1/2$. An important conclusion is that the composition of the paramagnetic phase is the same for all the treated samples, and does not depend on the sort of reagent dissolved in the water–alkali, acid, or salt. The main reason for this phase origination is the presence of water as a solvent.

To identify the phase corresponding to the doublet, it is necessary to identify the inner structure of the magnet and the possible chemical processes that could occur if the magnet is placed into the water solution of reagent. The intergranular material usually represents the set of Nd-enriched phases. The most probable is the α -Nd phase and the unstable NdO phase. The Nd₂O₅, Nd_{1+x}Fe₄B₄ [1, 11, 12], and Nd₇Fe₃ [13] phases could also be present in the intergranular material but in considerably lower amounts. As the total amount of the intergranular material was negligible relative to the main grain phase, no subspectra except the six sextets in the initial Nd₂Fe₁₄B spectrum were detected. The quadrupole doublet appearing in each treated sample

**Fig. 2.** Mössbauer spectrum of treated sample nos. 1, 2, 3 at $T = 293$ K.

spectrum is the result of destruction of part of the main $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase at the grain boundary. It is known that the rare earth metals, including Nd, can be easily oxidized [13]. It might be supposed that NdO is oxidized to Nd_2O_3 at the grain boundaries and Fe is partly released. The released Fe can diffuse into the Nd_2O_3 matrix. However, the interaction between the α -Nd and the solvent–water at the boundary of the grain seems preferable. As a result, neodymium hydroxide and hydrogen are formed: $\text{Nd} + 3\text{H}_2\text{O} \rightarrow \text{Nd}(\text{OH})_3 + 3\text{H}$. Hydrogen can interact with neodymium loosening the structure ($\text{Nd} + \text{H} \rightarrow \text{NdH}$). Hydrogen can also reduce iron from oxides; this might be one of the reasons why iron oxides are absent in the intergranular material. The formation of $\text{Nd}(\text{OH})_3$ looks feasible assuming that water plays a critical role in the origin of the new intergranular phase. This compound has a relatively low melting point ($\sim 300^\circ\text{C}$) and a hexagonal type of structure. Sometimes, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure is considered as distorted ε -phase type hexagonal nets of Fe atoms separated by basal planes containing Nd and B, [6]. In this approach, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}(\text{OH})_3$ structures are similar. The Fe atoms are partly released from the main phase and embedded into the neodymium hydroxide. The result is visualized as a doublet in all the treated sample spectra with the hyperfine parameters of the doublet not depending on the kind of reagent dissolved in the water. The doublet observed in [14] in the Nd-Fe-B spectrum was assigned by the authors to the $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ phase, but its QS value was about twice larger than that in our work. In the amorphous $\text{Nd}_x\text{Fe}_{81}\text{B}_{19-x}$ ($0 \leq x \leq 19$) spectra [15], the quadrupole doublet also appeared, even in the absence of neodymium. Although the IS value for the doublet was negative and ca. -0.20 mm/s, we suppose that the phases are different from those detected in this work.

Conclusions

Mössbauer spectroscopy was applied to study the structural and magnetic state of iron atoms in $\text{Nd}_2\text{Fe}_{14}\text{B}$ treated with water solutions of alkali, acid, and salt. It was found that all kinds of treatment under the study led to partial erosion of the main $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and an increase in the intergranular material mass. It was demonstrated that the water solutions induced the formation of neodymium hydroxide on the grain boundaries. Here, the material surface contains Fe embedded into the neodymium hydroxide matrix: $\text{Fe-Nd}(\text{OH})_3$. It was shown that, out of the three solutions studied, the salt water solution exerted the strongest negative effect on the magnetic characteristics of $\text{Nd}_2\text{Fe}_{14}\text{B}$.

Acknowledgments. The work was supported in part by Grant No. $\Phi 12\text{A}-007$ (Belarusian Republican Foundation for Fundamental Research).

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