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# A Comparative Thermomagnetic Study of Melt-spun Nd-Fe-B Alloys with Different Nd Content

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***Abstract:***

*Changes in the phase composition and magnetic properties of three types of commercial Nd-Fe-B alloys with different Nd content – low (10-12 wt%), near stoichiometric (21-25 wt%) and rich (26-29 wt%) caused by thermomagnetic analysis (TM) were observed in regard to optimal magnetic state. Phase compositions of investigated alloys before and after TM measurement up to 800 ℃ were compared using $^{57}Fe$ Mössbauer spectroscopy and X-Ray analysis. The TM measurements decompose all three materials and the main products of decomposition process α-Fe and $Fe_2B$ phase. Observed changes in structure and phase composition had direct influence on magnetic properties. Loss of magnetic properties induced by thermal decomposition is clearly illustrated on corresponding SQUID hysteresis loops.*

***Keywords:*** *Nd-Fe-B alloys; Thermomagnetic measurements; Phase composition; Structure; Magnetic properties;*

## 1. Introduction

The studies of nanocrystalline Nd-Fe-B hard magnetic materials have become very significant over the last few decades due to the fact that subtle changes in microstructures allow a tailoring of magnets with defined magnetic properties [1]. Alloy compositions and processing conditions have a strong influence on the microstructure of melt-spun Nd–Fe–B ribbons in optimal magnetic state and hence on their magnetic properties [2]. The Nd–Fe–B alloys could be analyzed according to Nd content [3].

The alloys with reduced neodymium content (nanocomposite alloys) have multiphase composition and in the optimal magnetic state they are composed of the nano-sized exchange coupled grains of soft and hard magnetic phases. Depending on the alloy composition two types of nanocomposites α-Fe/$Nd_2Fe_{14}B$ and/or $Fe_3B$/$Nd_2Fe_{14}B$ can be obtained [4].

The stoichiometric and Nd-rich Nd-Fe-B alloys have an almost monophase composition with dominant amount of $Nd_2Fe_{14}B$ phase. While the stoichiometric alloys are characterized by some intergranular exchange coupling between the grains of the same hard magnetic phase [5,6] the Nd-rich alloys are composed of grains of hard magnetic $Nd_2Fe_{14}B$ phase that are magnetically isolated (decoupled) by the intergranular layer of Nd-rich phases [7,8].

The influence of Nd content on microstructure and magnetic properties of three types

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of commercial Nd-Fe-B alloys was analyzed by comparing phase compositions and magnetic properties in optimized magnetic state and in state after thermomagnetic measurements up to 800°C.

## 2. Experimental

The chemical composition and basic magnetic properties of the investigated commercial melt-spun Nd-Fe-B powders after quenching and crystallization are presented in Tab. I. The magnetic powders, having a particle size in range 74 to 177 μm, used in this study, were supplied by Xiamen Yuxiang Magnetic Materials Ind. Co. Ltd, China.

**Tab. I** The chemical composition and magnetic properties of the investigated melt-spun Nd-Fe-B powders given by producer

| Sample | Magnetic property | | | | Element (wt %) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $B_r$ [kG] | $H_{cb}$ [kOe] | $H_{cj}$ [kOe] | $(BH)_{max}$ [MGOe] | Nd | Fe | B | Co | Zr | Si |
| Nd - L | 8.35 | 2.55 | 3.09 | 6.58 | 10-12 | >80 | <5 | - | - | 1-3 |
| Nd - S | 6.40 | 4.51 | 8.57 | 7.50 | 21-25 | >65 | <1.5 | 3-5 | 3-5 | - |
| Nd - R | 6.03 | 4.70 | 11.91 | 7.17 | 26-29 | >69 | <1.3 | - | - | - |

The phase compositions of the investigated alloys in optimized magnetic state were determined by X-ray diffraction analysis (XRD) and $^{57}$Fe Mössbauer spectroscopy (MS) at room temperature. X-ray diffraction measurements were performed on an X'Pert PRO MPD multi-purpose X-ray diffraction system from PANanalytical using Co K radiation. Mössbauer spectra were taken in the standard transmission geometry using a $^{57}$Co(Rh) source at room temperature. The calibration was done against α-iron foil data. For the spectra fitting and decomposition, the "CONFIT" program package was used [9]. The computer processing yielded intensities I of components, their hyperfine inductions $B_{hf}$, isomer shifts δ and quadrupole splittings σ. The contents of the iron containing phases are given as intensities of the corresponding spectral components. However, the exact quantification of the phase contents could be done only when possible differences in values of Lamb-Mössbauer factors were considered. The phase analysis published in [10-12] was applied. Thermomagnetic properties of the samples were measured on the EG&G Vibrating Sample Magnetometer (VSM), in the field of intensity of 50 Oe under vacuum (0.1 Pa). The investigated powders were cold-pressed into small Tab.ts having diameter of about 3 mm. The samples were heated up to 800°C with heating and cooling rate of 4 K/min.

In order to investigate the changes in structure and phase composition that have direct influence on magnetic properties, caused by TM measurements, after the TM, the MS and XRD analysis were repeated.

Magnetic properties of investigated alloys in optimal magnetic state and after TM measurements were measured at the room temperature using Superconducting Quantum Interference Device (SQUID) magnetometer with magnetic field strength in range −50 to 50 kOe.

## 3. Results and discussion

The qualitative results of XRD phase analysis of investigated Nd-Fe-B alloys in state before and after TM measurements, obtained from corresponding X-ray diffraction spectra,

are summarized and presented in Tab. II. The role of XRD analysis was to identify and explain the constitution of some phases, e.g. oxides, that could not be identifiable from Mössbauer spectra and to confirm the presence of others.

**Tab. II** Qualitative results of the X-Ray analysis for investigated alloys in state before and after TM measurements

| | X-Ray before TM | | | X-Ray after TM | | |
|---|---|---|---|---|---|---|
| Sample | Nd-L | Nd-S | Nd-R | Nd-L | Nd-S | Nd-R |
| Phases | $Nd_2Fe_{14}B$ | $Nd_2Fe_{14}B$ | $Nd_2Fe_{14}B$ | $Nd_2Fe_{14}B$ | $Nd_2Fe_{14}B$ | $Nd_2Fe_{14}B$ |
| | $Nd_{1.1}Fe_4B_4$ | $Nd_{1.1}Fe_4B_4$ | $Nd_{1.1}Fe_4B_4$ | $Nd_2BFe_{12}Si_2$ | $Nd_{1.1}Fe_4B_4$ | $Nd_{1.1}Fe_4B_4$ |
| | $Fe_3B$ | $Zr_3Fe$ | $Fe_{17}Nd_2$ | $Fe_2B$ | $Fe_2B$ | - |
| | - | - | - | $Fe_3B$ | $B_{12}Zr$ | - |
| | - | - | - | α - Fe | α - Fe | α - Fe |

The obtained Mössbauer spectra illustrate phase composition of investigated Nd-Fe-B alloys in optimal magnetic state and after TM measurements. The Mössbauer spectra of the three magnetic powders taken before the TM measurement are presented in Fig. 1.

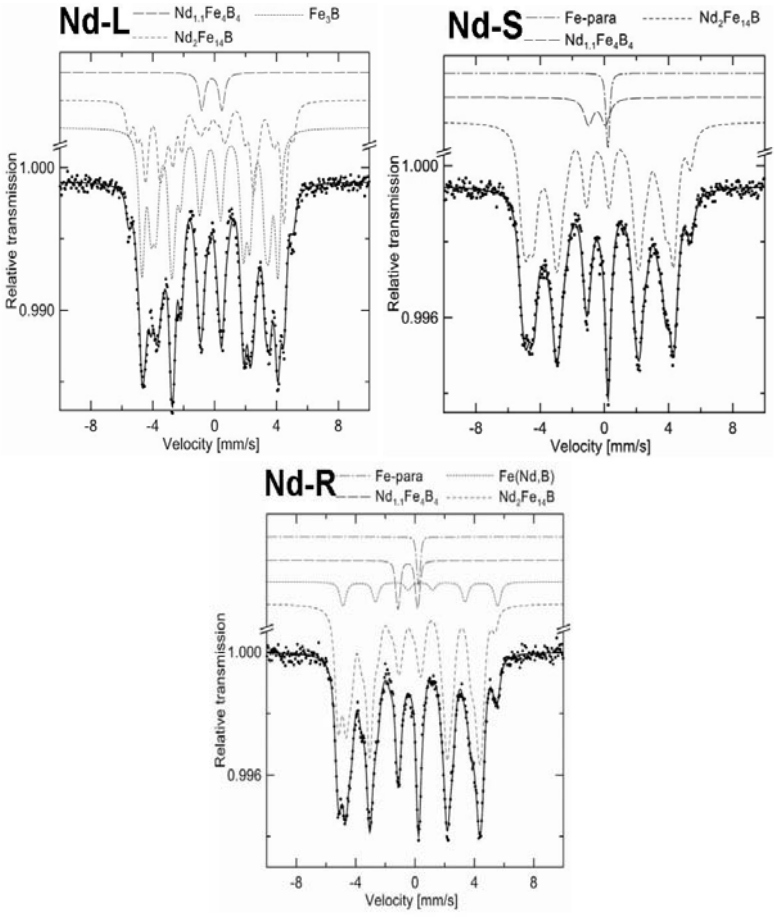


**Fig. 1.** Mössbauer spectra of the investigated Nd-Fe-B alloys in optimal magnetic state (before TM measurements)

The relative amount of identified phases obtained from related MS spectra are given in Tab. III. For simplicity, proportionality between intensity of Mössabuer lines and amount of relevant iron atoms is supposed.

According to the results obtained both by XRD and MS phase analysis, it is obvious that the magnetically hard $Nd_2Fe_{14}B$ phase is present in all three investigated alloys. The appearance and identification, actually in small amounts, of non-ferromagnetic boride phase $Nd_{1.1}Fe_4B_4$ is the consequence of the fact that in the investigated alloys boron content is above 4.2 at% [13]. It was found that the boride phase $Nd_{1.1}Fe_4B_4$ has not uniform grain distribution with high density of defects, with the approximately the same dimensions as grains of $Nd_2Fe_{14}B$ phase [14]. Given that Curie temperature is very low (Tc=13 K), $Nd_{1.1}Fe_4B_4$ phase does not have ferromagnetic properties at room temperature environment and as a consequence, it decreases overall magnetic properties.

**Tab. III** The relative phase content, as taken from Mössbauer spectra for the state before and after TM measurements

| Phase | before TM | | | after TM | | |
|---|---|---|---|---|---|---|
| | Nd-L | Nd-S | Nd-R | Nd-L | Nd-S | Nd-R |
| $Nd_2Fe_{14}B$ | 0.38 | 0.92 | 0.87 | - | 0.64 | 0.92 |
| $Nd_{1.1}Fe_4B_4$ | 0.04 | 0.05 | 0.05 | - | 0.03 | 0.03 |
| $Fe_3B$ | 0.58 | - | - | 0.34 | - | |
| $Fe_2B$ | | | | 0.42 | 0.13 | - |
| Fe(Nd,B) | - | - | 0.08 | - | - | |
| Fe-para | - | 0.03 | <<0.01 | 0.03 | - | |
| α - Fe | | | | 0.21 | 0.12 | 0.05 |

The alloy with low Nd content (Nd-L sample) has a multiphase structure and consists predominantly of soft magnetic $Fe_3B$ phase in addition to the main hard magnetic $Nd_2Fe_{14}B$ phase (Tab. II, Tab. III, Fig.1). In general, the nanocrystalline Nd low alloys are characterized by the ferromagnetic exchange coupling between the grains of hard and magnetically soft phases building the well known nanocomposite structure. The formed nanocomposite $Fe_3B/Nd_2Fe_{14}B$ is directly responsible for the enhancement of remanence.

In the Nd-S sample with the near stoichiometric $Nd_2Fe_{14}B$ composition besides the main $Nd_2Fe_{14}B$ phase, minor amounts of other phases like $Nd_{1.1}Fe_4B_4$ are also detected, as well as limited amount of paramagnetic iron, probably in a phase with Zr – identified by XRD. These phases are most likely nanocrystalline, hence their influence on the magnetic properties is negligible. The small amount of Zr contributes to the further refinement of the hard magnetic grain structure [15] thus promoting the remanence enhancement via the interaction of exchange coupling between the grains. In regard to the starting composition of this alloy (Nd-S), it is obvious that this sample contains a certain amount of Co, substituting iron. Unfortunately, phases with Co (without Fe) could not be identified by $^{57}Fe$ MS analysis. On the other side, such phases were not detected by XRD as well. Even small amount of Co has a role to increase the Curie temperature of alloy. However, the addition of Co to Nd-Fe-B alloy lowers its coercivity and thus the temperature stability is not actually improved by Co addition alone [16, 17].

In addition to the dominant amount of hard magnetic $Nd_2Fe_{14}B$ phase determined in the Nd-rich alloy (Nd-R) in the optimal magnetic state, the $Fe_{17}Nd_2$ phase is identified by XRD (Tab. II). This phase can be understood as a representative of some minor amount of a Fe(Nd) solid solution. In the corresponding Fe (Nd, B) Mössbauer component (Fig 1, Tab.

III), non-magnetic Nd and B atoms are almost inappreciable. Very interesting fact is that no traces of any thermal or other decomposition e.g. presence of α-Fe, $Fe_2B$ phases were found.

Analyzing the obtained TM curves (Fig. 2), new information about phase transformations for three alloys with different Nd content was derived [18,19,20]. The differences between three analyzed materials are demonstrated in the absence of $Fe_2B$ phase and presence of α-Fe phase in the Nd-rich material, which is in agreement with MS and XRD results (Tab. II, Tab. III).

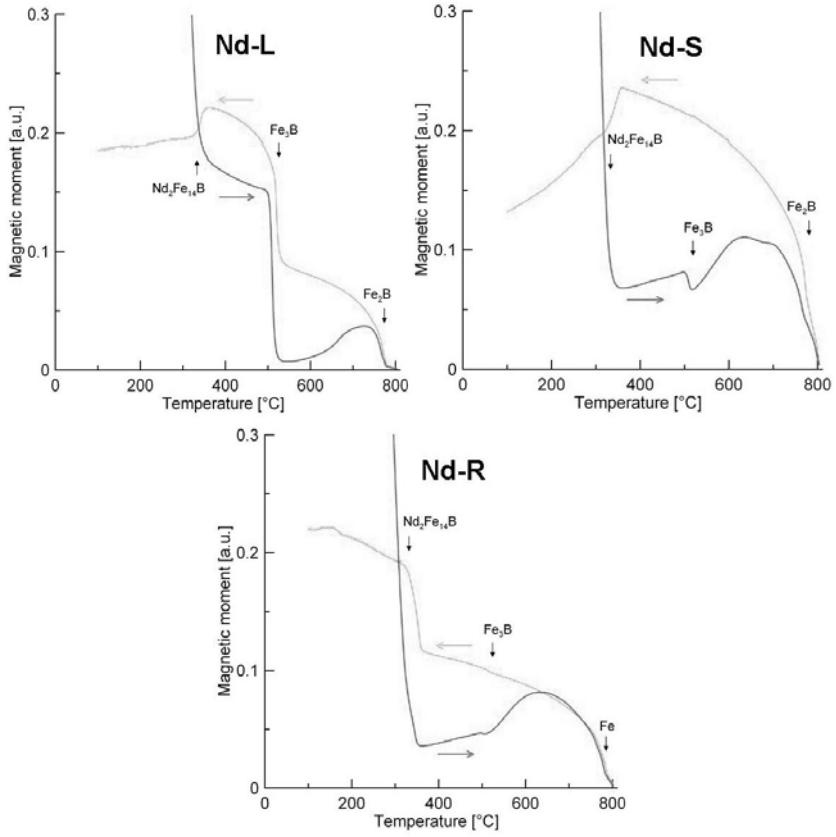


Fig. 2. Thermomagnetic curves of the investigated melt-spun Nd-Fe-B alloys

For better understanding of the magnetization measurements, some fundamental data ($T_c$, $\mu_o M_s$) of phases identified by TM are given in Tab. IV.

**Tab. IV** Literature values for Curie temperature and saturation magnetization of listed phases

| Phase | $\mu_o$Ms [T] | $T_c$ [K] |
|---|---|---|
| $Nd_2Fe_{14}B$ [21] | 1.61 | 585 |
| $Fe_3B$ [22] | 1.62 | 820 |
| $Fe_2B$ [23] | - | 1015 |
| α-Fe [24] | 2.15 | 1043 |

To estimate the level of thermal decomposition of investigated materials during the TM measurement, XRD and MS methods were applied once again. The phase compositions determined by the XRD analysis are presented in Tab. II. The resulting Mössbauer spectra are

shown on Fig 3 and the corresponding phase composition are given in Tab. III.

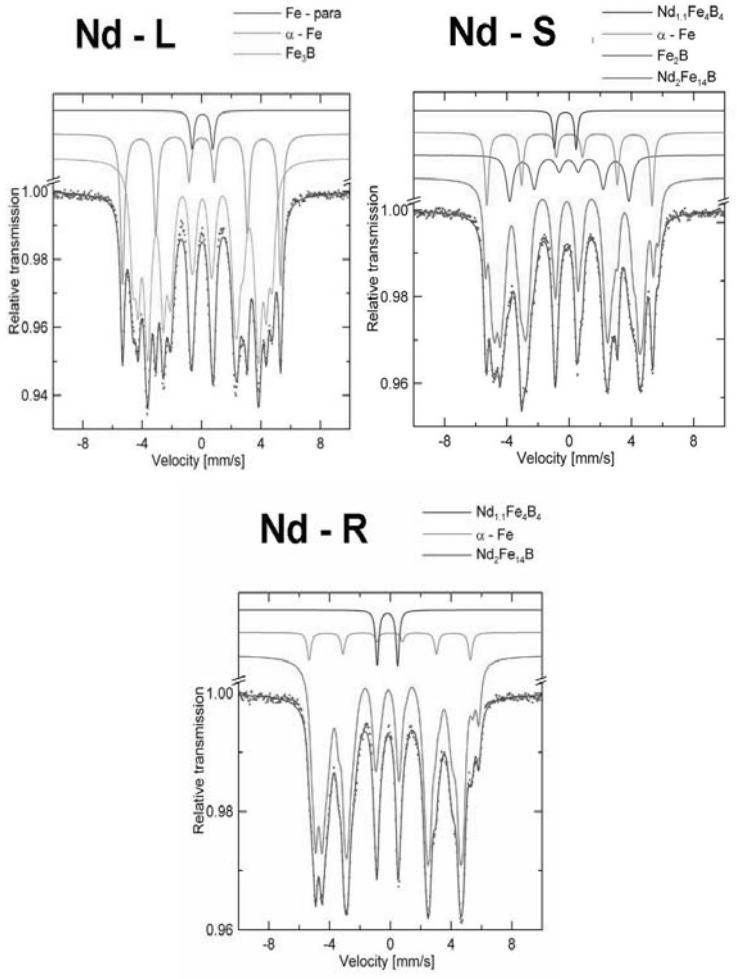


**Fig. 3.** Mössbauer spectra of the investigated Nd-Fe-B alloys after TM measurements

The obtained results for all three investigated alloys could be used as a confirmation that α-Fe phase and whole set of Fe-B phases were formed after thermal decomposition caused by TM experimentation. Observed decrease of the amount of hard magnetic $Nd_2Fe_{14}B$ phase directly induces deterioration of magnetic properties. According to both MS and XRD results, the main decomposition product is α-Fe phase. This soft magnetic phase is accompanied by a number of different Fe–B phases, predominantly of the tetragonal $Fe_3B$ structure.

After TM measurements, in the Nd-L alloy, the substitution of Fe atoms in $Nd_2Fe_{14}B$ phase with Si can be observed and multipart phase $Nd_2BFe_{12}Si_2$ was identified (Tab. II). Usually, the small addition of Si leads to a very fine and homogeneous grain size distribution which has a direct influence on remanence enhancement [25,26]. More recent studies show that the magnetization decreases linearly with increasing Si content [27].

As it could be already supposed from the TM curves (Fig 2.), the high amount of $Fe_2B$ phase was determined in Nd-L and Nd-S alloys after thermal decomposition.

The results for Nd-R sample show that amount of hard magnetic $Nd_2Fe_{14}B$ phase increases after TM measurements, which it is not entirely true; because the whole set of neodymium compounds could not be identified. The calculated amount of $Nd_2Fe_{14}B$ phase

probably includes also the paramagnetic (Nd, B) phases and/or Nd-rich phase, as well as oxides of neodymium formed during the TM measurements. In agreement with the thermomagnetic curve analysis the process of thermal degradation of the material is situated to the intergranular layer mainly, leaving the $Nd_2Fe_{14}B$ phase almost unchanged. The iron solid solution marked as Fe(Nd,B) phase looses the diluted elements and they may move to the separate phase(s), not detecTab. by Mössbauer effect. In spite of conservation of the main phase volume, the final state of the material is different from the optimal so deterioration of hard magnetic properties can be expected.

Although the samples were under the vacuum during the TM measurements, in order to suppress the oxidation process as much as possible, the presence of oxides can be expected in the samples after the TM measurements. In the X-ray spectra some oxidation products can be found ($Fe_3O_4$ and also $Nd_2O_3$); however, intensity of the peaks was just on the threshold of acceptability and without support of MS, since the $^{57}Fe$ Mössbauer spectroscopy is not able to detect $Nd_2O_3$ phase (no iron) and therefore they were not included. This is the main reason why the quantitative results of MS analysis presented in Tab. III should be taken as relative phase compositions.

Hysteresis loops obtained by SQUID measurements (Fig 4.) illustrate the substantial difference between the optimal magnetic state and after thermomagnetic measurements up to 800°C. It is obvious that the magnetic properties of investigated alloys have very strong relationship with their phase composition.

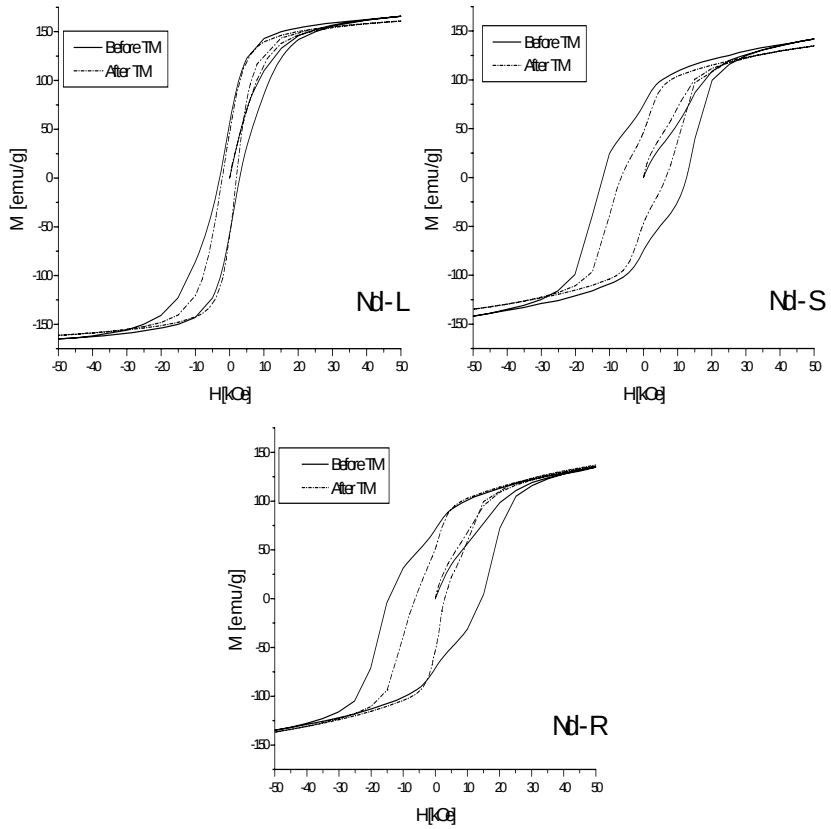


**Fig. 4.** Hysteresis loops of investigated Nd-Fe-B alloys with 10-12 wt% Nd (Nd-L), 21-25 wt% Nd (Nd-S) and 26-29 wt% Nd (Nd-R), in optimal magnetic state and after TM measurements

The thermal decomposition is the main reason for the degradation of hard magnetic quality of investigated Nd-Fe-B materials. Generally speaking, all three hysteresis loops after TM measurements show considerable deterioration of magnetic properties (decrease of both remanence and coercivity) compared with the optimal magnetic state.

## 4. Conclusion

The magnetic behavior of the investigated rapid quenched Nd-Fe-B alloys during TM measurements corresponds to the phase transformations which are clearly illustrated by obtained experimental results.

In the optimal magnetic state, the analyzed magnetic materials are high quality, as none of the materials contain any significant content of "parasitical" phases (e.g. α-Fe, $Fe_2B$ or other products of thermal decomposition) degrading the most important magnetic properties, with an exception of minor quantities of $Nd_{1.1}Fe_4B_4$ phase. The shapes of obtained SQUID hysteresis loops are characteristic for each type of investigated Nd-Fe-B magnetic materials and measured values of magnetic properties can be explained by the different phase composition of alloys governed by Nd content.

The TM measurement decomposes all three materials in similar manner and the main products of the decomposition process are α-Fe and $Fe_2B$ phases. The substantial difference between the state with optimized magnetic properties and the state after the thermal decomposition induced by thermomagnetic measurement was confirmed by MS and X-Ray phase analysis as well as magnetic measurements on SQUID magnetometer.

The thermal decomposition is the main reason for the loss of the hard magnetic properties of investigated materials. Comparing the obtained results of magnetic measurements and phase analysis for all three investigated Nd-Fe-B magnetic materials, it could be concluded that the thermal decomposition is more pronounced on the sample enriched with neodymium - Nd-R.

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***Садржај:*** *Истраживане су промене фазног састава и магнетних својстава у односу на оптимално магнетно стање за три типа комерцијалних Nd-Fe-B легура са различитим садржајем неодијума – ниским (10 – 12 mas %), блиским стехиометријском (21-25 mas %) и високим (26-29 mas %), проузрокованих термомагнетним (TM) мерењима. Фазни састави истраживаних легура пре и после TM мерења до 800℃ су поређени коришћењем $^{57}Fe$ Mössbauer спектроскопске фазне анализе и рендгенско-дифрактометријске анализе. Услед термомагнетних мерења долази до декомпозиције сва три истраживана материјала и као основни продукти декомпозиције настају α-Fe и $Fe_2B$ фазе. Посматране промене у структури и фазном саставу имају директан утицај на магнетна својства. Губитак магнетних својстава настао услед термичке декомпозиције је јасно илустрован одговарајућим SQUID хистерезисним петљама.*

***Кључне речи:*** *Nd-Fe-B легуре, термомагнетна мерења, фазни састав, структура, магнетна својства;*