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PHASE COMPOSITION, STRUCTURE AND MAGNETIC BEHAVIOUR OF LOW NEODYMIUM Nd-Fe-B PERMANENT MAGNETS

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ABSTRACT

Phase composition, structure and magnetic behaviour of two low neodymium hard magnetic materials differing in way of preparation, centrifugal atomization and melt spinning, were compared using Mössbauer spectroscopy, X-ray diffraction, thermomagnetic analysis and SQUID magnetic measurements. Better hard magnetic characteristics of the melt-spun material are explained on the basis of the differences in content of surface and/or interface Fe(Nd,B) phases. Their remarkable presence in the centrifugally atomized material lowers the content of Fe_3B, Fe_2B, α-Fe, and $Nd_2Fe_{14}B$ phases that are responsible for the magnetic qualities of the material. There are just subtle differences in the phase composition of both materials after thermomagnetic measurement, where the α-Fe phase prevails as a product of thermal decomposition.

Key words: Nanocomposite permanent magnets; Mössbauer spectroscopy; X-ray diffraction; thermomagnetic curve; SQUID

INTRODUCTION

The classical $Nd_2Fe_{14}B$ sintered permanent magnets or just $Nd_2Fe_{14}B$ based rare-earth hard magnetic materials have large magnetization and high Curie temperature. The newer nanocrystaline magnetic materials based on Nd(Pr)-Fe-B alloys prepared by the rapid quenching of the liquid are predominantly known as exchange-coupled nanocrystaline composite hard magnetic materials [1] having high remanence and magnetic energy despite reduced amount of expensive rare earth Nd up to three times comparing to above mentioned magnets, exceeding them in many aspects. Such a material is composed of nano-sized grains of soft and hard magnetic compounds. In our case, the soft magnetic phases are mostly formed as (tetragonal) Fe_3B, Fe_2B, and α-Fe and $Nd_2Fe_{14}B$ crystalizes as hard magnetic phase [2]. Nanocomposite magnets have large saturation magnetic polarization due to the soft magnetic phase, and also have high coercivity because of the hard magnetic phase. The exchange coupling between soft and hard magnetic phases explains the total hard magnetic property. The main condition for obtaining nanocomposite structure is uniform distribution of soft and hard phase in magnetic matrix where size of grains should be between 5 and 20 nm because intergranullar coupling between them becomes more pronounced only at the nano scale [3]. The final qualities of the material depend mainly on starting composition, method of synthesis and heat treatment. In the present work, two ways of material preparation are compared: centrifugal atomization and melt-spinning, both realized on the material of

the same original composition. For this purpose Mössbauer spectroscopy (MS) and X-ray diffracion (XRD) in combination with a measurement of thermomagnetic (TM) curves were used. Magnetic properties before and after thermomagnetic analysis was measured using the Superconducting Quantum Interference Device (SQUID) magnetometer. On the basis of this results magnetic behaviour of investigated magnetic materials was discussed.

EXPERIMENTAL

The composition of the parental material was Nd - 12 mass %, Pr - 0.2 mass %, B - 4.2 mass %, Al - 0.3 mass %, Fe - balance. Basic data concerning both powder samples are summarized in Table 1. Magnetic characteristics of the optimized materials were measured on a vibrating sample magnetometer.

Table 1. Origin and basic magnetic characteristics of materials studied

Code	Preparation	Treatment	Coercivity [MA/m]	Remanence [T]	*Energy product [J/m^3]*
B2	centrifugal atomization	660°C/5 min.	0.22	1.09	*85.1*
S2	*melt spinning*	*660°C/2 min.*	*0,27*	*1.18*	*95.5*

Both the materials, centrifugally atomized and melt-spun, were in the powder form that was directly suitable for the Mössbauer spectroscopy and X-ray diffraction.

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 [4]. 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 [5, 6, 7] was applied.

X-ray diffraction measurements were performed on an X'Pert PRO MPD multi-purpose X-ray diffraction system from PANanalytical using Co K_α radiation.

For TM measurements small cold-pressed tablets were prepared, having diameter of about 3 mm. The thermomagnetic curves were measured using an EG&G vibrating sample magnetometer in the field of intensity of 3.98 kA/m. The heating and cooling rate was kept at 4 K/min. After the TM measurement the MS and XRD experiments were repeated on the materials used. The subsequent measurements were done on a softly manually crumbled material of both tablets. Magnetic properties of samples before and after TM measurements were measured on the room temperature, on the SQUID magnetometer with magnetic field strength $\mu_0 H$ from -5T up to 5T.

RESULTS AND DISCUSSION

It is known that the phase composition of the studied material is not very simple [8, 9, 10]. As the every supposed phase is represented by several components in Mössbauer spectrum, the final model of each spectrum is rather complex, including possible

surface/interface components as well. Nevertheless, the prezence of supposed main phases was confirmed. Mössbauer spectra of both centrifugaly atomized and melt-spun material as taken before the TM measurement are presented in the Fig. 1.

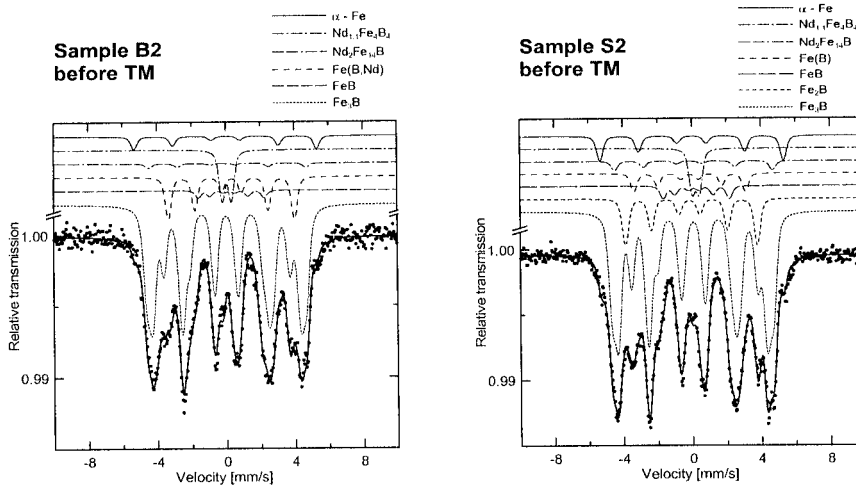

Fig. 1. Mössbauer spectra of the centrifugally atomized (left) and melt-spun material (right) in the as received state. Detected phases are extracted

To explain the constitution of some minor phases and to validate the others, X-ray diffraction was used. The diffraction spectra approved the complexity of both materials (see Fig. 2). Also in this case the main components agree with the supposed structure. The $Nd_{1.1}Fe_4B_4$ phase detected by the MS is what about its amount just on method sensitivity threshold and the existence of this phase is very questionable in both original materials in every case. The components of Mössbauer spectra labelled as Fe(Nd,B) and Fe(B) have very probably their origin on surfaces and/or interfaces of fine grains of individual phases. On the XRD curves atoms of such structures appear just in the form of an elevated background count.

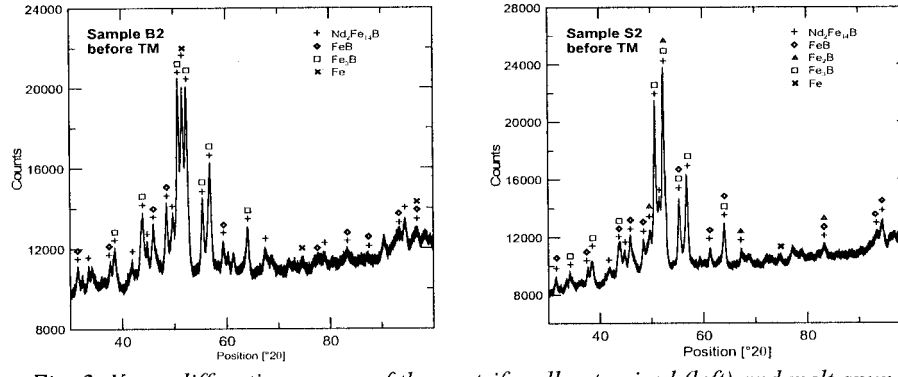

Fig. 2. X-ray diffraction curves of the centrifugally atomized (left) and melt-spun material (right) in the as received state. Detected phases are marked

Next method that brings us information about phase composition is the measurement of TM curves. The only differences between both materials there are in distribution of iron atoms between phases and the absence of Fe_2B phase in the centrifugally atomized

material (in agreement with MS and XRD results – see Fig. 3). The $Fe_{72}B_{28}$ phase [11] is to be understand more as a representative of Fe(Nd,B) and Fe(B) components as mentioned at Mössbauer spectra discussion.

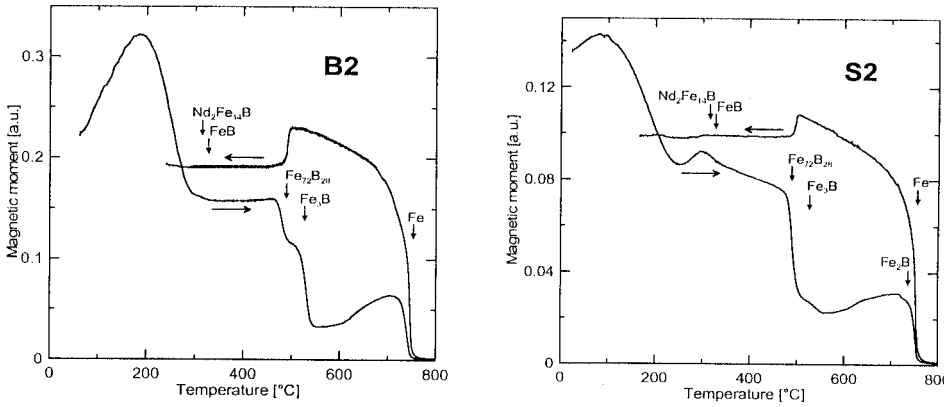

Fig. 3. Thermomagnetic curves of the centrifugally atomized (left) and melt-spun material (right). Detected Curie temperatures are marked

Combining the results of all three methods, the most pronounced differences can be seen in larger content of low-moment nonstoichiometric Fe(Nd,B) phases in the centrifugally atomized material originating in surface and/or interface atoms on the expense of stoichiometric Fe_2B and $Nd_2Fe_{14}B$ phases that are together with Fe_3B and α-Fe phases responsible for the magnetic qualities.

To judge the way and degree of thermal decomposition of both materials during the TM measurement the MS and XRD methods were applied once more. The resulting Mössbauer spectra are depicted in the Fig. 4.

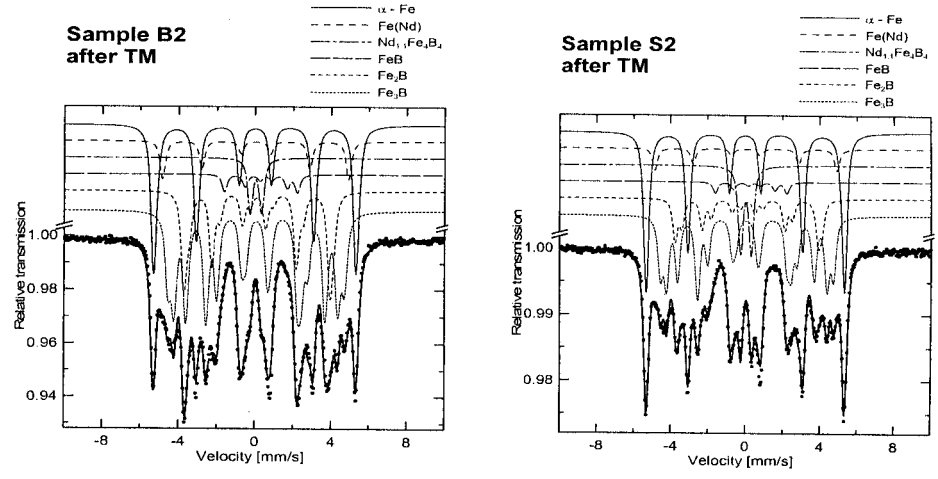

Fig. 4. Mössbauer spectra of the centrifugally atomized (left) and melt-spun material (right) after the thermomagnetic measurement. Detected phases are extracted

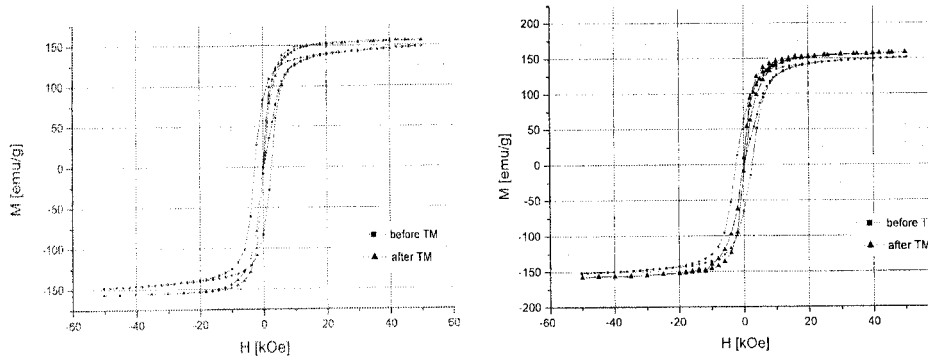

Fig. 5. SQUID hysteresis loops of the centrifugally atomized (left) and melt-spun material (right) before and after the thermomagnetic measurement

Magnetic behaviour of investigated magnetic materials before and after TM measurements is presented, with appropriate SQUID hysteresis loops, on Fig. 5. The shape of SQUID hysteresis loops illustrate the substantial difference between the state with optimized magnetic properties and the state after the decomposition induced by the TM measurements.

According to both MS and XRD results, the main decomposition product is the α-Fe, as could be supposed already from the TM curve. This phase is accompanied by a number of different Fe-B phases, predominantly of the tetragonal Fe_3B structure. The $Nd_2Fe_{14}B$ phase was decomposed completely, and all methods are in mutual agreement. Those phase transformations are in correspondence with change of magnetic behaviour which is clearly illustrated as the shape of SQUID hysteresis loops. The thermal decomposition will be the main reason for the quality loss of investigated hard magnetic materials. Comparing both the materials, the thermal decomposition is more pronounced on the melt-spun sample.

CONCLUSION

Obtained values of magnetic properties can be explained by the different phase composition of both materials. The centrifugally atomized material contains more nonstoichiometric "dirty" phases originating from surface and/or interface regions. In that regions iron atoms of reduced magnetic moments are present spoiling the magnetic qualities of the material. In addition, relative content of the $Nd_2Fe_{14}B$ phase as well as important Fe_3B and Fe_2B phases is lowered in the material discussed. The TM measurement decomposes both materials in a similar way. The main products of the decomposition process are α-Fe phase and Fe_2B.

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