

Magnetic interactions in NdFeB bulk permanent magnets with additions

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NdFeB-based bulk nanocomposite permanent magnets (with Dy and Co partially substituting Nd and Fe, respectively) with additions of Early Transition Metals (ETM = Mo, Ti, Zr, Cu, Nb, V, W), in form of rods with diameters ranging from 0.5 to 0.8 mm, have been prepared by devitrification annealing of amorphous and partly-amorphous precursors produced by injection die casting. A fully amorphous structure was obtained for rods with the diameter as large as 0.6 mm. The as-cast rod samples are magnetically soft and the magnetic hardness develops as the samples are devitrified to the optimum nanostructure. The best-achieved hard magnetic properties have been obtained for the optimum devitrified (15 min at 630 °C) Nd₃Dy₁Fe₆₆Co₁₀B₂₀ samples of 0.6 mm in diameter: $H_c = 296$ kA/m, $\mu_0 M_r = 0.86$ T, $M_r/M_{max} = 0.65$ and $(BH)_{max} = 74$ kJ/m³. The Mössbauer spectra indicate the coexistence of 4 magnetic phases: 2:14:1, α -Fe, Fe₃B and a short-range ordered intermetallic Fe-B-type phase.

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1. Introduction

Bulk permanent magnets present the advantage that can be cast in different shapes with predefined dimensions, avoiding the dilution of magnetic phases during compaction by the polymer binder as in the case of bonded magnets. Rare-Earth – Transition Metal – Metalloid (RE-TM-M) alloys present a real potential for strong bulk miniature permanent magnets since nanocrystalline ribbons with thicknesses as large as 250 μ m can be obtained by devitrification of amorphous ribbon precursors prepared through methods involving quenching from the melt. Recently, it has been reported that using liquid quenching techniques, less than 1 mm in diameter RE-(Fe,Co)-B based bulk glassy alloys have been prepared, which lead further, upon devitrification annealing, to fully dense Fe₃B / Nd₂Fe₁₄B nanocomposite permanent magnets [1-4]. It is well known that the good permanent magnetic properties of RE-TM-M nanocomposite alloys are generated through the magnetic hardening of the iron-base soft magnetic phases (i.e. α -Fe, Fe₃B, and Fe₂₃B₆) by the RE₂TM₁₄B hard magnetic phase. This occurs when the structure is homogeneous and refined to the nanometer scale, thus ensuring effective magnetic coupling of the grains over short distances through exchange interactions [5].

This paper focuses on the possibility of direct casting miniature NdFeB-based bulk permanent magnets in different three-dimensional shapes for various applications, with amorphous structure followed by subsequent optimal annealing. The method represents a viable alternative to the methods used so far, methods

employing powder or flakes compaction. The investigation of the magnetic interactions in NdFeB-based bulk permanent magnets by means of Mössbauer spectroscopy is shedding light over the intrinsic mechanisms governing the macroscopic magnetic behavior of such materials and will further help designing various cast shaped bulk permanent magnets for specific applications.

2. Experimental procedure

Master alloys have been prepared from pure elements by arc-melting in an Ar atmosphere. Nd_{4-x}Dy_xFe_{66-y}Co₁₀ETM_yB₂₀ (ETM = Ti, Zr, Mo, Cu, Nb, V, W) ($x = 0 \div 1$) ($y = 0; 1; 3; 4$) bulk nanocomposite permanent magnets in form of rods with diameters ranging from 0.5 to 0.8 mm and length of up to 20 mm have been prepared by devitrification annealing of amorphous and partly-amorphous precursors produced by injection die-casting.

The samples structure in the as-cast state and after devitrification annealing was checked by X-ray diffraction (XRD) in 2 different geometries: (1) by reflection (or conventional XRD) using a DRON 2.0 diffractometer in the Bragg-Brentano configuration (Co-K α radiation) and (2) by transmission using the high energy synchrotron radiation (65 keV) from ID11 beam at ESRF Grenoble. A fully amorphous structure was obtained for rods with the diameter as large as 0.6 mm [4, 6]. In order to induce the nanocrystalline structure, the as-cast samples were devitrified by annealing for different durations (between 10 and 20 min.) at temperatures ranging between 610 °C

and 700°C. Particular annealing at higher temperatures has been done only for structure-related studies.

The phase transformation reactions observed on the DSC (differential scanning calorimetry) traces were used as a basis for choosing the devitrification annealing parameters to induce optimum nanocomposite structures associated in later investigations with good hard magnetic properties [4, 6]. The first exothermic maximum on the DSC curves corresponds to the separation of Fe₃B phase within the amorphous matrix, whilst the 2:14:1 phase appears at higher temperatures. At 660°C, the structure consists of a mixture of Fe₃B, Fe₂₃B₆ and Nd₂Fe₁₄B phases. Cu favors the formation of clusters within the amorphous matrix and leads to the early appearance of Fe₃B phase, whereas Nb stimulates the formation of Fe₂₃B₆ crystalline phase. The second exothermic maximum observed on the DSC curves is less pronounced and appears in the temperature range 700 – 900 °C, depending on the samples composition and dimensions. The increase of the heating rate from 20 to 40 K/sec results in the displacement of the phase transitions temperatures towards higher ones and increases also the amount of the energy released during the exothermic processes (e.g., the maximum corresponding to the primary crystallization is shifted with about 14°C for Nd₃Dy₁Fe₆₆Co₁₀B₂₀ bulk rod [6]).

The DSC results have been confirmed by the thermomagnetic measurements performed in the temperature range 300 – 1100 K using a Vibrating Sample Magnetometer (VSM) in a maximum applied field of 1.5 T. The same VSM has been used to measure the M-H curves of the investigated samples.

The Mössbauer spectroscopy has been used to determine the volumetric ratio and the magnetic phases distribution for the investigated samples. The Mössbauer spectra have been recorded at room temperature (300 K) in transmission geometry, using a ⁵⁷Co source in Rh matrix. The isomer shift at RT has been reported to the displacement of the metallic Fe isomer shift. Lorentz-type theoretic functions have been used to fit the absorption lines.

3. Results and discussion

The as-cast rod samples are magnetically soft and the magnetic hardness develops as the samples are devitrified to the optimum nanostructure, as shown in Fig. 1. It is worthwhile to note that for pre-defined thermal annealing conditions the addition of Mo, Ti, Zr, Cu, Nb or V are not necessarily enhance the hard magnetic behavior (Fig. 1). The best-achieved hard magnetic properties have been obtained for the optimum devitrified (15 min at 630°C) Nd₃Dy₁Fe₆₆Co₁₀B₂₀ samples of 0.6 mm in diameter, and are: $iH_c = 296 \text{ kA/m}$, $\mu_0 M_r = 0.86 \text{ T}$, $M_r/M_{\max} = 0.65 \text{ si}$ $(BH)_{\max} = 74 \text{ kJ/m}^3$. This sample exhibits a complex multiphase structure refined to tens of nanometers [4, 6] consisting of a mixture of nanograins of 2:14:1 hard magnetic phase and α -Fe + Fe₃B soft magnetic phases, as indicated by AFM measurements (Fig. 2) and Rietveld

analysis. Upon heating and maintenance at 610-630 °C, Fe₃B precipitates and subsequently Nd₂Fe₁₄B phase begins to appear. The formation of the 2:14:1 grains determines the large values of coercivity. According to the thermomagnetic investigations, the annealing at temperatures of about 840 °C leads to the formation, besides the above mentioned phases, of α -Fe (Fig. 2c).

The thermomagnetic curves presented in previous work [4, 6] indicated clearly ferromagnetic-paramagnetic transitions both in the as-cast state and after devitrification. The first ferromagnetic-paramagnetic transition appears at about 290 °C for Co-free samples and is ascribed to the initial amorphous phase existent in the as-cast state. During heating at higher temperatures, the Fe₃B phase precipitates and favors the formation of the Nd₂Fe₁₄B hard magnetic phase. The second heating allows determining the Curie temperatures of the new formed phases: 2:14:1 (~ 310°C) and Fe₃B (~ 525 °C). For the Co-containing samples the Curie temperatures of the new precipitated phases are with 50°C higher than for the Co-free samples.

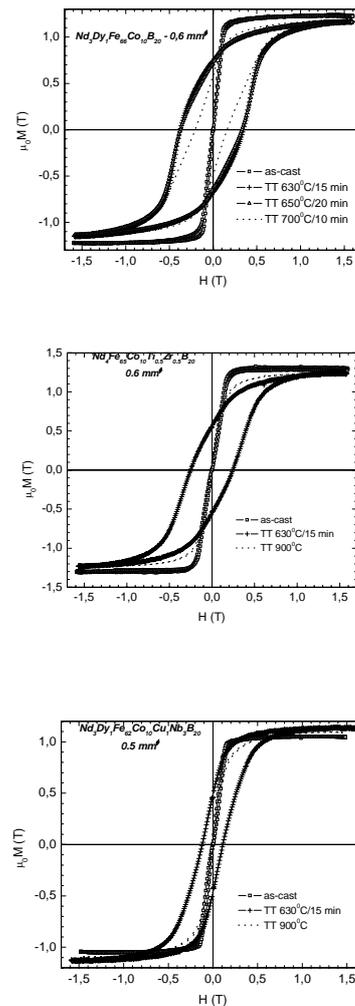


Fig. 1. M-H loops for Nd_{4-x}Dy_xFe_{66-y}Co₁₀ETM_yB₂₀ bulk samples in the as-cast state as well as after devitrification and crystallization.

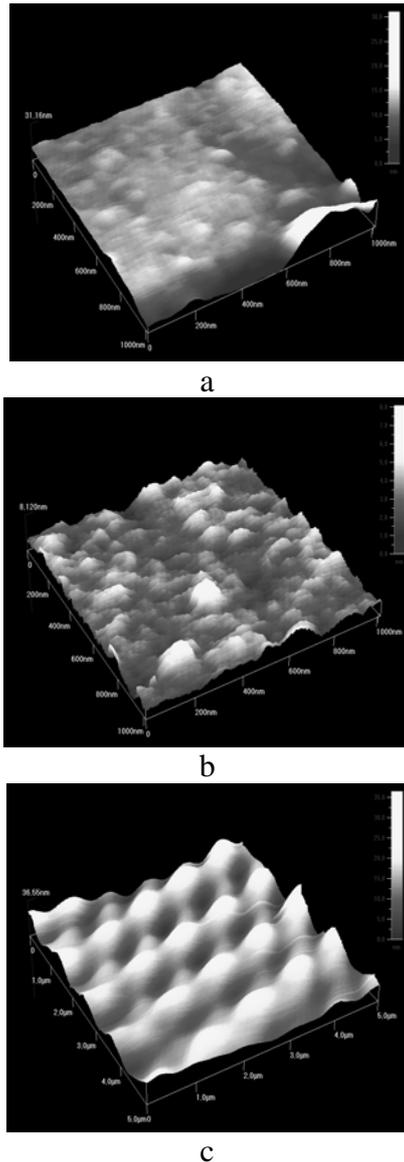


Fig. 2. AFM images obtained on the cross-section of $\text{Nd}_3\text{Dy}_1\text{Fe}_{66}\text{Co}_{10}\text{B}_{20}$ cast rods, 0.6 mm in diameter: (a) as-cast state (amorphous); (b) after annealing at 630°C for 15 min. (nanocrystalline optimum structure); (c) after annealing at 850°C for 10 min. (fully crystalline).

The Mössbauer spectra for $\text{Nd}_3\text{Dy}_1\text{Co}_{10}\text{Fe}_{66}\text{B}_{20}$ bulk samples in the as-cast state (a) and after annealing at 630°C for 15 min. (b) and at 700°C for 10 min. (c) are presented in Fig. 3. The spectrum of the as-cast sample (Fig. 3a) indicates the co-existence of 3 phases: (i) a B-rich Fe-B phase which might also contains other substitutions, having a hyperfine field of 5 T, (ii) a 2 sextets Fe-B phase containing a low content of B with $B_{\text{hf},1} = 21$ T and $B_{\text{hf},2} = 25$ T, which can be attributed to the Fe_2B phase (about 75 % from the total volume), and (iii) a Fe-rich phase with B substitutions with $B_{\text{hf}} = 32$ T (the relative area is about 22 %). The annealing leads to the appearance of 2:14:1 phase. In this case, the spectra have been fitted considering the 6 sextets corresponding to this

phase. The 6 sub-spectra corresponds to 6 distinct positions of Fe in the Wigner-Seitz cell, i.e. 16k1, 16k2, 8j1, 8j2, 4e and 4c. Additionally, 3 positions associated to B-rich Fe-B phase, Fe-rich phase and to a magnetic phase of intermediary hyperfine field ($B_{\text{hf}} = 21$ T) have been used during the fitting procedure. Both the intermediary hyperfine field phase and the Fe-rich phase indicate a high degree of substitution. The Fe-rich phase content is increasing from 7 % into the optimum annealed sample (630°C for 15 min.) (b) to 10 % into the partially crystallized sample (700°C for 10 min.) (c). If we consider that the Fe-B phase with $B_{\text{hf}} = 21$ T is magnetically soft, than the percentage of soft magnetic phases is 25 % into sample (b) and 40 % into sample (c). The difference of 75 % and 60 %, respectively, corresponds to the 2:14:1 hard magnetic phase, in agreement with the magnetic measurements in Fig. 1. However, the hyperfine field of the 2:14:1 phase is with 1-2 T smaller than the values already reported in the literature, but the other hyperfine parameters are in the same range compared with the $\text{Nd}_3\text{Dy}_1\text{Co}_{10}\text{Fe}_{63}\text{Cu}_1\text{Nb}_2\text{B}_{20}$ sample presented in Fig. 4. Additionally, for $\text{Nd}_3\text{Dy}_1\text{Co}_{10}\text{Fe}_{66}\text{B}_{20}$ bulk samples the lines width is less wide, indicating a more clear evidence of the 2:14:1 formation compared with the $\text{Nd}_3\text{Dy}_1\text{Co}_{10}\text{Fe}_{63}\text{Cu}_1\text{Nb}_2\text{B}_{20}$ bulk samples.

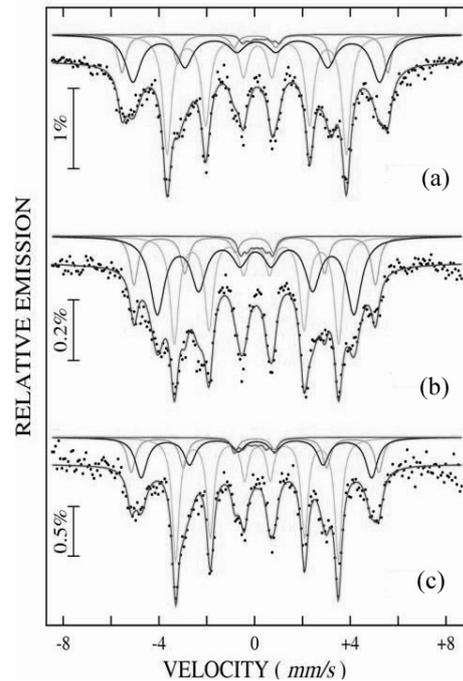


Fig. 3. Mössbauer spectra at RT for $\text{Nd}_3\text{Dy}_1\text{Co}_{10}\text{Fe}_{66}\text{B}_{20}$ bulk samples in the as-cast state (a) and after annealing: $630^\circ\text{C}/15$ min. (b); $700^\circ\text{C}/10$ min. (c).

Thus, we can conclude that $\text{Nd}_3\text{Dy}_1\text{Co}_{10}\text{Fe}_{66}\text{B}_{20}$ annealed samples consist in a mixture of soft and hard magnetic phases, and consequently the macroscopic magnetic behavior is typical for an “exchange-spring”-type permanent magnet. A further enhancement of the magnetic properties could be obtained either by the increase of the hard magnetic phase amount or by a better

selectivity of soft magnetic phases (a Fe-rich soft magnetic phase will be beneficial instead of the Fe-B phase with $B_{hf} = 21$ T). However, the Mössbauer spectra confirm the best hard magnetic behavior of this sample compared with the ones containing additions, as indicated by structural and magnetic measurements.

The spectra of the as-cast and annealed $Nd_3Dy_1Co_{10}Fe_{63}Cu_1Nb_2B_{20}$ samples are presented in Fig. 4. The as-cast sample spectrum suggests an amorphous material or a very disordered structurally one. The average hyperfine field is about 27 T, indicating a distribution of Fe neighbors close to the one observed for the amorphous $Fe_{80}B_{20}$ alloys, but depending strongly on the different substitutions. Despite of the monobar distribution, the hyperfine fields distribution is not regular but exhibiting a tendency of structuring on positions similar to the metallic Fe and Fe-B, respectively, as a consequence of the samples crystallization tendency. Indeed, after the devitrification annealing (b) the fitting with a distribution of hyperfine parameters specific to the amorphous alloys is not perfectly suitable for the present case, and thus a fitting consisting of a superposition of a few sextets has been used instead. We have used 6 sextets, with the order of the hyperfine fields being somehow similar to the one for the 2:14:1 hard magnetic phase. However, the hyperfine parameters values are not typical for a hard magnetic phase, because of the isomer shift and the quadrupolar splitting. Additionally, the lines widths are larger and the hyperfine fields are with 1-2 T smaller than the ones corresponding to the 2:14:1 phase. All these aspects indicate the presence of substitutions and eventually of a disordered hard magnetic phase. From the magnetic point of view, the annealed sample presents magnetic characteristics specific to a hard magnetic phase (larger intrinsic coercive field) compared with the as-cast state one. On the other hand, the annealed sample does not show clearly the presence of the soft magnetic phase, which means a reduced saturation magnetization (Fig. 1), not very convenient for a permanent magnet material.

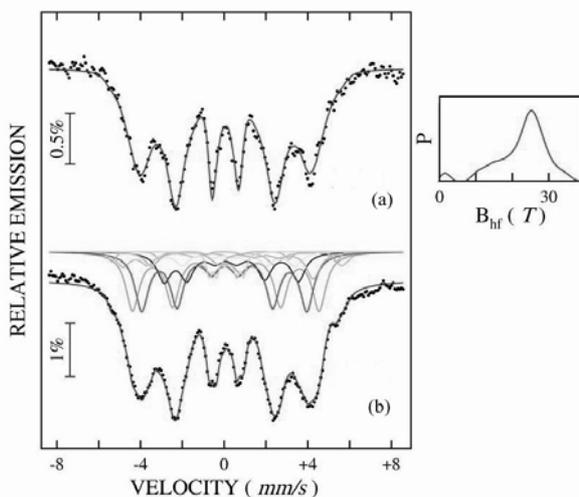


Fig. 4. The Mössbauer spectra at RT for $Nd_3Dy_1Co_{10}Fe_{63}Cu_1Nb_2B_{20}$ bulk samples in the as-cast state (a) and after annealing at $700^\circ C/10$ min. (b).

Fig. 5 shows the Mössbauer spectra at RT for $Nd_4Co_{10}Fe_{65}Ti_{0.5}Zr_{0.5}B_{20}$ bulk samples in the as-cast state and after devitrification annealing at 2 different temperatures.

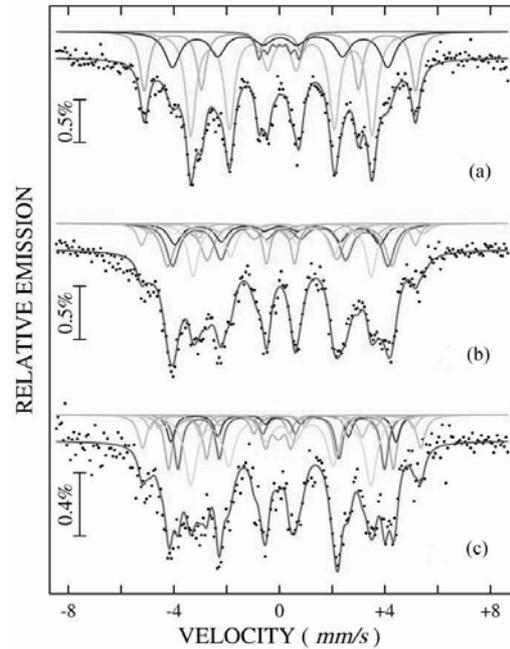


Fig. 5. RT Mössbauer spectra corresponding to $Nd_4Co_{10}Fe_{65}Ti_{0.5}Zr_{0.5}B_{20}$ bulk samples in the as-cast state (a) and after annealing at $650^\circ C/15$ min. (b) and $700^\circ C/10$ min. (c), respectively.

The spectra have been fitted with 4 magnetic sub-networks. Independent of the samples structure (in the as-cast state or after devitrification annealing), the most intense magnetic component (about 50 % from the relative area) exhibits a hyperfine field of about 23 T, and can be ascribed to a Fe-B phase (most probably Fe_2B). The less intense component (2-3 % of the relative area) has a very low hyperfine field (about 5 T), and can be associated with a disordered Fe-B phase, B-rich and containing substitutions. Finally, the magnetic phases with larger hyperfine fields exhibit a different behavior depending on the annealing temperature. In the as-cast sample, the coexistence of 2 magnetic phases with $B_{hf,1} = 34$ T and $B_{hf,2} = 32$ T, attributed to the α -Fe nanocrystals with different substitutions, was revealed (the substitutions are small enough and do not contribute essentially to the structure change, but can modify the hyperfine field). The optimally devitrified sample (b) exhibit a bcc α -Fe phase with substitutions and with $B_{hf} = 32$ T and a phase with a hyperfine field of 26 T which can be attributed to a Fe-B phase (most probably Fe_3B). In the sample annealed at $700^\circ C$ for 10 min., B from the magnetic phase with large hyperfine field (26 T) is mostly expelled, and the spectrum is similar to the one of the as-cast state sample, i.e. the coexistence of bcc α -Fe and bcc α -Fe with impurities. From the magnetic point of view, the presence of the above mentioned phases (Fe-B and metallic Fe with or without substitutions) suggests a soft magnetic behavior

(the coercive field is relatively small), with a saturation magnetization higher for the as-cast sample and the one treated at a higher temperature.

In conclusion, we should mention that the annealed samples, in which the hard magnetic phase formation is favored along with the disordered soft magnetic α -Fe and Fe-B, exhibit a good magnetic behavior. When the hard magnetic phase presents defects (which seems to favor the formation of Fe₃B), the magnetic performances of the samples are limited.

4. Conclusions

(Nd,Dy)-(Fe,Co)-B-based bulk nanocomposite permanent magnets with additions of Early Transition Metals (ETM = Mo, Ti, Zr, Cu, Nb, V, W) have been prepared by devitrification annealing of amorphous and partly-amorphous precursors produced by injection die casting. The as-cast rod samples are magnetically soft and the magnetic hardness develops as the samples are devitrified to the optimum nanostructure. The best-achieved hard magnetic properties have been obtained for the optimum devitrified (15 min at 630 °C) Nd₃Dy₁Fe₆₆Co₁₀B₂₀ samples of 0.6 mm in diameter: $H_c = 296$ kA/m, $\mu_0 M_r = 0.86$ T, $M_r/M_{max} = 0.65$ and $(BH)_{max} = 74$ kJ/m³. The Mössbauer spectra indicate the coexistence of 4 magnetic phases: 2:14:1, α -Fe, Fe₃B and a short-range ordered intermetallic Fe-B-type phase. The best magnetic behavior is achieved for annealed samples at 630 °C for 15 min., because of the better refinement of the 2:14:1 hard magnetic phase and the presence of soft magnetic α -Fe and Fe-B disordered phases. The presence of defects in the 2:14:1 hard magnetic phase, which favor the formation of Fe₃B phase, is steadily worsening the hard magnetic behavior of the investigated samples. The precipitation of different magnetic phases with specific

microstructures is strongly influenced by the presence of additives, samples diameters and thermal history.

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