Structural and magnetic properties of the as-cast Nd$_{10}$Fe$_{83}$Zr$_1$B$_6$ ribbons, studied by X-ray diffraction and Mössbauer spectroscopy

Abstract. The Nd$_{10}$Fe$_{83}$Zr$_1$B$_6$ alloy ribbons, prepared by melt-spinning technique, have been investigated by X-ray diffraction (XRD) and Mössbauer spectroscopy. Magnetic properties were studied by Faraday balance and vibrating sample magnetometry (VSM). The ribbon samples were produced at various surface velocities of the copper wheel from 10 m/s to 20 m/s. The XRD and Mössbauer spectra analysis have shown that the ribbons consist of the soft magnetic α-Fe, hard magnetic Nd$_2$Fe$_{14}$B and disordered phases. The results showed that a uniform Nd$_2$Fe$_{14}$B/α-Fe nanocomposite structure with fine α-Fe grains can be obtained at an optimum velocity of the copper roll of 20 m/s. The samples produced in these conditions had the best magnetic properties ($\mu_0 H_C = 0.84$ T, $\mu_0 M_R = 1.05$ T, $\mu_0 M_S = 1.36$ T, $(BH)_{max} = 160$ kJ/m$^3$) with strong exchange coupling between the hard magnetic Nd$_2$Fe$_{14}$B and soft magnetic α-Fe phases. The amorphous phase existing between grains causes an increase in the remanence and remanence ratio.

Key words: hard magnetic magnets • melt-spinning technique • Mössbauer spectroscopy • nanocomposites

Introduction

Hard magnets Nd-Fe-B, discovered in the 1980’s belong to the latest generation of magnets with best magnetic properties and have been intensively studied until now [2, 3]. In recent years a great interest is focused on the so-called nanocomposite magnets consisting of α-Fe/ Nd$_2$Fe$_{14}$B phases for which the grain diameters are lower than 40 nm. It is well known that the addition of Zr improve the energy product and squareness of the hysteresis loop in two-phase nanocomposite magnets. This is due to the fact that the admixture of Zr or Nb retards the growth of crystalline phases [7, 10]. The raw material for nanocomposite magnets are ribbons produced by the melt-spinning technique [1, 4, 8, 9]. The characteristic feature of nanocomposite magnets which distinguish them from magnets with larger grains, is the remanence enhancement due to the exchange interactions between the soft and hard magnetic grains. Majority of the previous studies were concentrated around to the remanence enhancement via the exchange coupling between neighboring α-Fe and Nd$_2$Fe$_{14}$B grains. But some authors suggest that the disordered intergranular phase existing at grain boundaries may improve the exchange coupling by reducing the effective anisotropy constant and thus increasing the exchange interaction length [5, 6, 11]. The volume fraction of the disordered phase can be modified by changes in rapid solidification processing conditions. Therefore, in the present work the influence of the phase constitution and volume fraction of constituent phases on the magnetic properties,
of the Nd₁₀Fe₈₃Zr₁B₆ alloy ribbons obtained at various surface velocities were studied.

**Experimental**

The Nd₁₀Fe₈₃Zr₁B₆ alloy ribbons of various thicknesses were prepared by arc-melting of the high-purity elements under an Ar atmosphere. The ingot sample was re-melted several times in order to ensure homogeneity of its structure. The ribbons of various thicknesses from 35 μm to 50 μm, were melt-spun at various surface velocities, from 10 m/s to 20 m/s. The pressure inside the chamber was 0.4*10⁵ Pa. The phase constitution was examined using a Bruker D8 Advance X-ray diffractometer equipped with a Lynx Eye semiconductor detector and CuKα radiation. The hysteresis loops were measured at room temperature using a LakeShore 7307 vibrating sample magnetometer at external magnetic fields up to 2 T. From the major hysteresis loops, the magnetic parameters, i.e.: coercivity μ₀Hₐ, remanence μ₀Mₜ, saturation magnetization μ₀Mₛ, and maximum magnetic energy product (BH)ₘₘₚ were determined. The thermomagnetic curves M(T) were obtained using the Faraday balance operating at a magnetic field of 0.87 T and temperature range from 300 K to 850 K with a heating rate of 10 K/min. The Mössbauer studies were performed using a Polon Mössbauer spectrometer with constant acceleration of a ⁵⁷Co source embedded within a Rh matrix and activity of 100 mCi. The spectra analysis was performed using WinNorms for the Igor 3.0 package.

**Results and discussion**

The X-ray diffraction patterns obtained for the Nd₁₀Fe₈₃Zr₁B₆ alloy ribbons in the as-cast state, melt-spun at various velocities of the copper wheel are presented in Fig. 1. It was shown that the increase of velocity of the copper wheel from 10 m/s to 20 m/s, resulted in an increase of intensities of peaks corresponding to the hard magnetic Nd₂Fe₁₄B phase. Fur-
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were incorporated. The one doublet corresponds to the presence of the paramagnetic Nd$_{10+}$Fe$_4$B$_4$ phase that was not detected by XRD. Due to the application of rapid solidification technique for preparation of the samples, the existence of some disordered phases in the investigated samples was also expected. Therefore, for complete fitting a broad component corresponding to the hyperfine field distribution was also used.

The Mössbauer spectra analysis allowed to determine weight fractions of constituent phases. These values are collected in Table 1.

<table>
<thead>
<tr>
<th>Sample (m/s)</th>
<th>Nd$<em>{10}$Fe$</em>{83}$B V (wt.%)</th>
<th>α-Fe V (wt.%)</th>
<th>Nd$_{10+}$Fe$_4$B$_4$ V (wt.%)</th>
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<tr>
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It was shown that for all investigated ribbons the major crystalline phase formed during rapid solidification is the hard magnetic Nd$_{2}$Fe$_{14}$B. In case of the ribbons melt-spun at velocities not higher than 18 m/s, a similar fractions of disordered phase (more than 30 wt.%) were determined, while α-Fe takes above 10 wt.%. The spectra analysis revealed also some traces of the paramagnetic Nd$_{1+}$Fe$_4$B$_4$ phase in the melt-spun ribbon. A significant change of the phase constitution was observed for the ribbon obtained at the velocity of 20 m/s, where only ~23 wt.% of the Nd$_{2}$Fe$_{14}$B phase, and more than 70 wt.% of the disordered phase was determined. Furthermore, the hyperfine field distributions corresponding to the disordered phase suggest significant changes of their chemical composition together with the velocity of the copper roll. The hyperfine field distributions for continuous component of the resolved spectra measured for ribbons produced at 10 m/s and 20 m/s are shown in Fig. 4. Similar distributions were incorporated. The one doublet corresponds to the presence of the paramagnetic Nd$_{10+}$Fe$_4$B$_4$ phase that was not detected by XRD. Due to the application of rapid solidification technique for preparation of the samples, the existence of some disordered phases in the investigated samples was also expected. Therefore, for complete fitting a broad component corresponding to the hyperfine field distribution was also used.

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Fig. 3. The Mössbauer spectra for ribbons produced at (a) 10 m/s, (b) 12 m/s, (c) 16 m/s, (d) 18 m/s, (e) 20 m/s.

Fig. 4. The hyperfine field distributions corresponding to the continuous components of the Mössbauer spectra representing disordered component of ribbons obtained at 10 m/s (a) and 20 m/s (b).
and corresponding continuous components were obtained for specimens produced at velocities lower than 18 m/s.

The distribution determined for ribbon produced at 20 m/s is broad and asymmetric with a maximum around 22 T. Such a distribution and fraction of disordered phase indicates that grains of crystalline phases are dilute within the amorphous matrix. In case of ribbons melt-spun at velocities lower than 18 m/s the hyperfine field distributions are narrow with its maximum around 27 T. According to suggestion reported in [8] the high field distributions are narrow with its maximum around 27 T. Such a distribution and fraction of disordered phase indicates that grains of crystalline phases are dilute within the amorphous matrix. In case of ribbons melt-spun at velocities lower than 18 m/s the hyperfine field distributions are narrow with its maximum around 27 T. According to suggestion reported in [8] the high field distributions are narrow with its maximum around 27 T. Such a distribution and fraction of disordered phase indicates that grains of crystalline phases are dilute within the amorphous matrix.

The demagnetization curves for the obtained ribbons from the existence of intergranular phases. The presence of such phases can cause the reduction of effective anisotropy constant $K_{\alpha}$ and increasing the exchange length $L_{ex} = \frac{\sqrt{J}}{(K)}$, where $J$ is the exchange constant. The demagnetization curves for the obtained ribbons are shown in Fig. 5.

The improved magnetic properties were obtained at a velocity between 18 m/s and 20 m/s ($\mu_0H_C = 0.84$ T, $\mu_0M_K = 1.05$ T, $\mu_0M_K = 1.36$ T, $(BH)_{max} = 160$ kJ/m$^3$). Application of lower velocities results in greater grain size of the nanocrystalline phase, which, in turn, allows easier demagnetization of the sample and weakens the exchange coupling between magnetically soft and magnetically hard grains. The effect is clear for samples produced at velocities 10 m/s, 12 m/s, 16 m/s where the demagnetization curve shape (clear kink) can indicate the lack of the exchange coupling characteristic of multiphase materials. The demagnetization curve for the remaining samples are smooth and single stage which indicates strong exchange coupling between magnetic hard and magnetic soft phases and have a high remanence ratio $M_r/M_s$ equal to 0.8. It is interesting to note that quite good magnetic properties ($\mu_0H_C = 0.84$ T, $\mu_0M_K = 1.05$ T) were obtained for only partially crystallized sample suggesting that the disordered intergranular phases can increase the exchange coupling.

**Conclusions**

- The Nd$_{10}$Fe$_{80}$Zr$_x$B$_{10}$ ribbons obtained at the wheel velocities from 10 m/s to 20 m/s in as-cast state are partially crystalline and consist of the hard Nd$_3$Fe$_{14}$B, soft $\alpha$-Fe and disordered phases.
- The calculated Mössbauer spectra fit well to the experimental ones if they were decomposed into six Lorentzian sextets corresponding to six magnetically non-equivalent position of the Fe atom in a unit cell of hard Nd$_3$Fe$_{14}$B phase, one sextet corresponding to $\alpha$-Fe, one component with hyperfine field distribution corresponding to the disordered NdFeB phase and one doublet corresponding to the paramagnetic Nd$_{1+\epsilon}$Fe$_{14}$B phase (for ribbons melt-spun at velocities not higher than 18 m/s).
- In case of the ribbons melt-spun at velocities not higher than 18 m/s, the disordered phase has a similar volume fraction (above 30 wt.%), while $\alpha$-Fe takes above 10 wt.%. The ribbons obtained at 20 m/s consist of more than 70 wt.% of disordered phase and have the best magnetic parameters, the remanence ratio and good hysteresis loop squareness.
- The remanence enhancement results not only from the direct exchange coupling between fine Nd$_3$Fe$_{14}$B and $\alpha$-Fe grains, but from exchange coupling via the layers of disordered phases surrounding the crystalline grains.

**References**