Characterization of nanostructured Nd–Fe–Al permanent magnets

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ABSTRACT

Rapidly solidified $Nd_{60}Fe_{30}Al_{10}$ alloys produced in the form or ribbons or 1 and 5 mm diameter rods were examined using transmission electron microscopy (TEM), XRD, magnetic measurements, and Mössbauer spectroscopy. Strong dependence of the structure and magnetic properties on cooling rate was proved. The present work concerns the microstructure on the nanometric level (HRTEM) of the $Nd_{60}Fe_{30}Al_{10}$ alloy.

The specimens were in a form of 1 and 5 mm diameter rods and a rapidly solidified ribbons, prepared at a roll speed of 30 m/s. The high-resolution images shown large regions where the crystalline phase is present. The size of the crystallites depends on the quenching rate, which also influences the composition of the amorphous phase. In both, ribbon and rod samples, well defined boundaries of nanoscale grains of similar crystallographic orientations were observed. Basing on the observations in the dark field, we can say that the precipitates often form agglomerates whose components maintain the same crystallographic orientations. The studies revealed that the crystalline grains are frequently separated by a narrow layer of an intermediate phase.

The EDS examinations reveal that the individual crystallites differ in their chemical composition, but in all nano-regions examined, all the components of the alloy occur simultaneously, in the proportions varying around the average composition of the alloy.

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1. Introduction

The Nd–Fe–Al alloys, firstly described by Inoue et al. [1] in 1996, are inferior to Nd–Fe–B magnets as far as the magnetic properties are concerned, but their great advantage is that they do not need additional annealing after melt-spinning to achieve usable magnetic properties. In general, the properties of the magnets produced by casting from the liquid state are considered to depend on the cooling rate which, in turn, is defined by the casting method and the size of the component being cast. In the case of magnetically hard Nd–Fe–Al alloys [2], which do not require high cooling rates, it is possible to employ many casting methods depending on the desired size of the sample. Although, the Nd–Fe–Al alloys have been examined for more than 10 years, their structure has not yet been described unequivocally. This is because of the two reasons: (1) irrespective of whether it is examined on the micrometric, sub-micrometric or nanometric scale, the microstructure of these alloys appears to be varied and (2) examinations on the level of single nanometers are very difficult in technical terms and in addition one cannot be sure whether the results obtained in nano-regions are sufficiently representative of the entire material.

The microstructure of the Nd–Fe–Al alloys has been described in many literature reports [3,4], but only some of them take into account the effect of the crystallite size level assessed in the examinations [5]. When observing the material on the nanometric level, Sun et al. [5] found two phases called A1α and A1β which differed in their chemical compositions but they were not described in detail by the authors. It is only by analogy to the binary Nd–Fe system that we can suppose that the compositions of these phases are close to $Nd_{20}Fe_{80}$ and $Nd_{40}Fe_{60}$, respectively. On the sub-micrometric level, the mixture of these two phases, called A1, appears to be mixed with the Nd phase of a hexagonal structure. The components of this mixture have sizes of several tens of nanometers. On this size level, a well-marked texture was observed, which results in magnetic anisotropy of the material [3]. It has been demonstrated that even in rapidly solidified ribbons, which appear amorphous in X-ray examinations, the Nd phase precipitated along very well-marked directions is present. Observations conducted on the micrometric level also show the existence of various structural components [5].
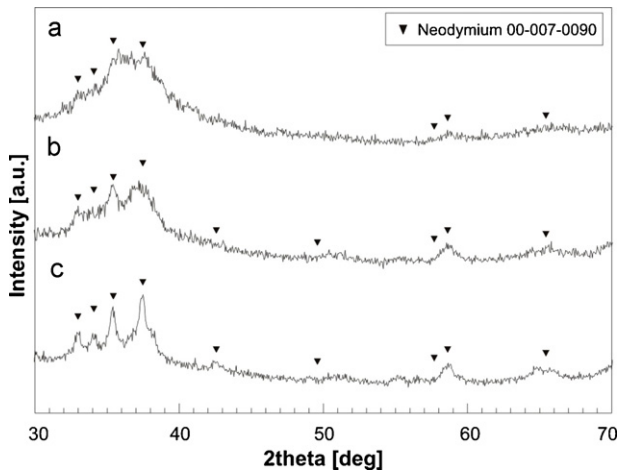
The present study was aimed at verifying the existing concepts of describing the microstructure of the Nd–Fe–Al alloys on various size levels using electron-microscopy.

2. Experimental

The $Nd_{60}Fe_{30}Al_{10}$ (at.%) alloy was prepared from elemental Nd, Fe, and Al with a purity of 99.9%, using arc melting in a titanium-guttered argon atmosphere. The

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Fig. 1. XRD patterns of (a) rapidly cooled ribbon, (b) 1 mm and (c) 5 mm diameter rods.

Fig. 2. SEM image of the microstructure of the rod-shaped sample 1 mm in diameter with marked (a) dark and (b) light areas.

samples in the form of ribbons were produced by melt-spinning at a copper roll having surface speed of 30 m/s. The cylinder-shaped 1 mm and 5 mm diameter rods were prepared by casting the material into a copper die. In both cases the casting temperature was 1100 °C. The alloys were melted in a quartz crucible by induction and pushed into the wheel/die by argon overpressure.
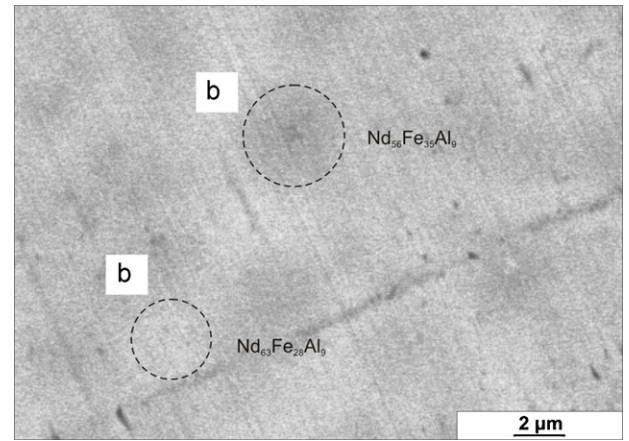
Magnetic measurements were performed using a Lake Shore vibrating sample magnetometer. The adopted cooling conditions permitted achieving good magnetic properties (H_c = 290 kA/m, B_r = 12.8 emu/g) of the 1 mm diameter rod, whereas the 5 mm diameter rod appeared to be cooled too slow (H_c = 227 kA/m, B_r = 8.75 emu/g). On the other hand, a ribbon appeared to be cooled too fast (H_c = 74 kA/m, B_r = 8.4 emu/g). The ribbon and the 5 mm diameter rod were examined for comparative purposes only.

Diffraction examinations were conducted in a Philips PW 1140 diffractometer using a cathodic lamp with Co-Kα radiation.

Mössbauer examinations were performed at room temperature in a Mössbauer spectrometer operating in the transmission configuration at a constant acceleration of the Mössbauer 57Co source in the Rh matrix, with a source activity of 50 mCi. The microstructure studies ware performed using a LEO 1530 scanning electron microscope and a JEM 3010 (300 kV) Jeol transmission electron microscope. The samples for transmission electron microscopy were prepared by double side grinding followed by ion beam milling.

3. Results and discussion

The X-ray diffraction pattern (Fig. 1) of investigated ribbon obtained by melt-spinning at a cooper roll speed of 30 m/s shows

typical halo characteristic of amorphous structure. In samples cooled at a lower rate (in our experiments the 1 and 5 mm diameter rods), the X-ray records contain peaks from Nd precipitates with a hexagonal structure.

Observations of rapidly solidified Nd–Fe–Al materials in a scanning electron microscope revealed diversity of structures within regions of micrometric size (Fig. 2). The smaller the size of these regions, the faster the sample is cooled. The EDS examinations of the 1 mm rod have shown that, on average, the chemical compositions of the dark areas (a in Fig. 2) and the light areas (b in Fig. 2) are $Nd_{56}Fe_{35}Al_9$ and $Nd_{63}Fe_{28}Al_9$, respectively. However, the results were widely spread. The light areas correspond to the grains described in Ref. [5], whereas the dark areas differ chemically and morphologically from those described by the authors of Ref. [5].

The Mössbauer spectra examinations (Fig. 3) showed that in the case of the ribbon cooled at a rate of 30 m/s, two nonequivalent surroundings of Fe atoms are present, an amorphous ferromagnetic phase (A in Fig. 3) and the Nd-rich nanocrystalline paramagnetic phase (B in Fig. 3), also observed using high resolution transmission electron microscopy. The Mössbauer spectrum obtained for the bulk samples indicated some differences in the phase constitution. Except for the paramagnetic component, a continuous line described by hyperfine field distribution (also observed in
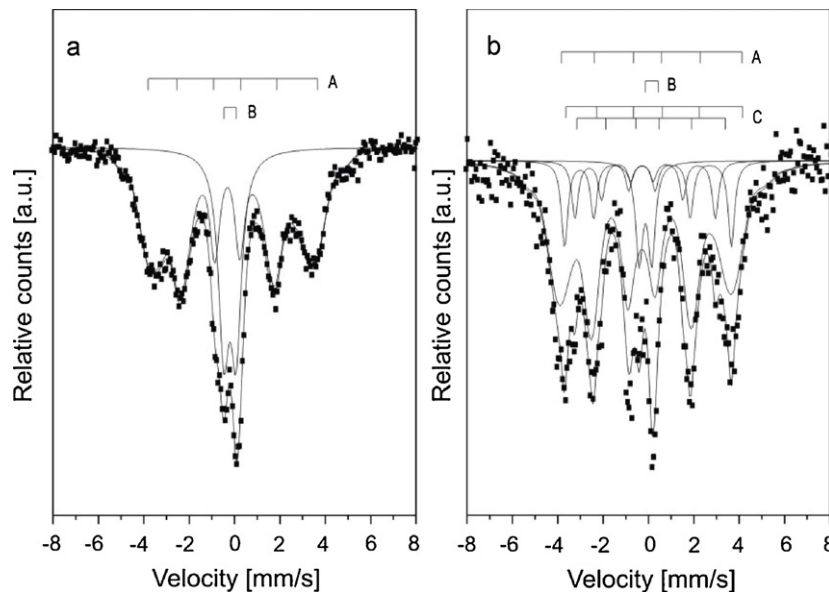
Fig. 3. Mössbauer spectrum obtained for (a) rapidly cooled ribbon and (b) 1 mm diameter rod.
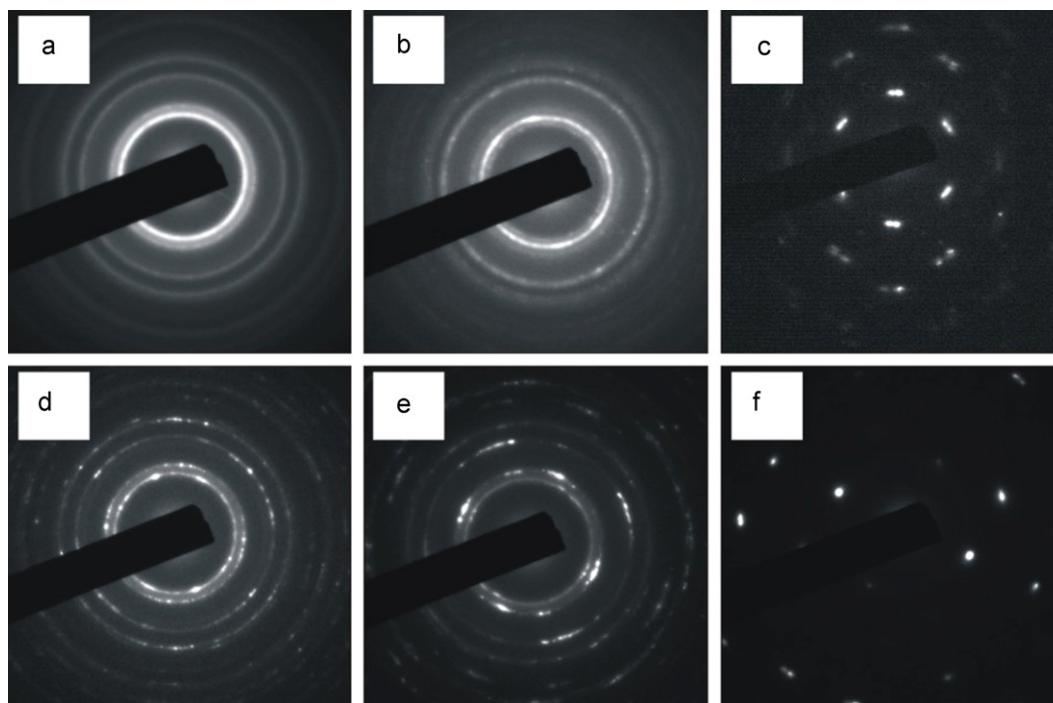
Fig. 4. Electron diffraction in (a) rapidly cooled ribbon, (b and c) 1 mm diameter rod (various regions) and (d–f) 5 mm diameter rod (various regions).

the ribbon samples), and additional two discrete sextet lines were detected (C in Fig. 3).

These two sextets may correspond to two ferromagnetic crystalline phases or to a single ferromagnetic phase with two magnetically nonequivalent positions of Fe atoms. The intensity of the doublet related to the paramagnetic component is considerably smaller in the rods (which were cooled at a lower rate than the ribbons). Moreover, in the hyperfine field distribution corresponding to the amorphous ferromagnetic phase, one can distinguish low- and high-field components that match various chemical surroundings of the iron atoms. These components indicate that the chemical composition of the amorphous phase, in the rod-shaped samples, differs from that present in the ribbons.

The electron diffraction patterns obtained for the rapidly cooled ribbon, 1 mm and 5 mm rods are shown in Fig. 4. The diffractions obtained for the ribbon in its various regions were similar and confirm the presence of an amorphous phase with nanocrystallites (Fig. 4a). Selected diffraction patterns for the 1 mm diameter rod consist of continuous rings characteristic of nanocrystalline material (Fig. 4b). Locally, a spot pattern is observed for higher size of the crystallites (Fig. 4c) with similar orientation.

In the case of the 5 mm diameter rod wide variation in the microstructure occurred. In most studied areas, the electron diffractions consist of continuous rings typical of nanocrystalline material (Fig. 4d), similar to those obtained for the sample with a diameter of 1 mm. In some areas, there are local enhancements in the diffraction rings indicating the presence of texture (Fig. 4e). Moreover, in various areas, for large crystallites only, a spot pattern is observed (Fig. 4f).

The transmission electron microscopy (TEM) of rapidly quenched ribbon shows that the volume fraction of the crystalline phase is high (Fig. 5). Percentage area of the doublet component of the Mössbauer line ∼27%, corresponding to the crystalline phase present in the phase constitution of the ribbon samples, confirms the TEM results.

On the basis of the observations in the dark field mode, we can say that the precipitates often form agglomerates whose components maintain the same crystallographic orientations. We have also observed a large group of grains whose orientation slightly departs from those that satisfy the Bragg law. In the dark field, the image of the microstructure of the 1 mm rod (Fig. 5d) does not differ much from the image obtained for the ribbon (Fig. 5a).

Dark field observations reveal a strong deformation of crystallites in the 5 mm diameter rod (Fig. 5g). It can be concluded that for slower cooling rates, the share of crystalline phase increases.

The high-resolution images (Fig. 5b, c, e, f, h, and i) show large regions where the crystalline phase is present. In the ribbon and rod samples, well defined boundaries of nanoscale grains of similar crystallographic orientations were observed. In general we can state that the rapidly cooled ribbon samples contain nanocrystalline precipitates of 2–5 nm diameter, distributed within an amorphous matrix. The high-resolution images confirm that the larger nanocrystals (10–20 nm), observed in the dark field, are agglomerates of several smaller crystals of similar orientations. The photographs clearly show crystalline regions with sizes that exceed the sample thickness. They may also occur in places where no ordering is visible.

The 1 mm rod contains nanocrystallites 5–30 nm in size, disoriented toward one another (larger of them are divided into fragments). The EDS examinations reveal that the individual crystallites differ in their chemical composition, but in all nano-regions examined, all the components of the alloy occur simultaneously, in the proportions varying around the average composition of the alloy. No precipitates of pure neodymium were found. The crystallites rich in Nd had elongated or oval shapes. In the rod-shaped sample, the crystalline phase predominates, whereas amorphous regions only occur within the boundary zone of the crystalline regions.

The HRTEM observation revealed that the microstructure of the 5 mm rod is very similar to that observed for the 1 mm diameter rod. The 5 mm rod contains disoriented nanocrystals 5–50 nm in size. In addition, larger crystallites with sizes of 100–200 nm are present.
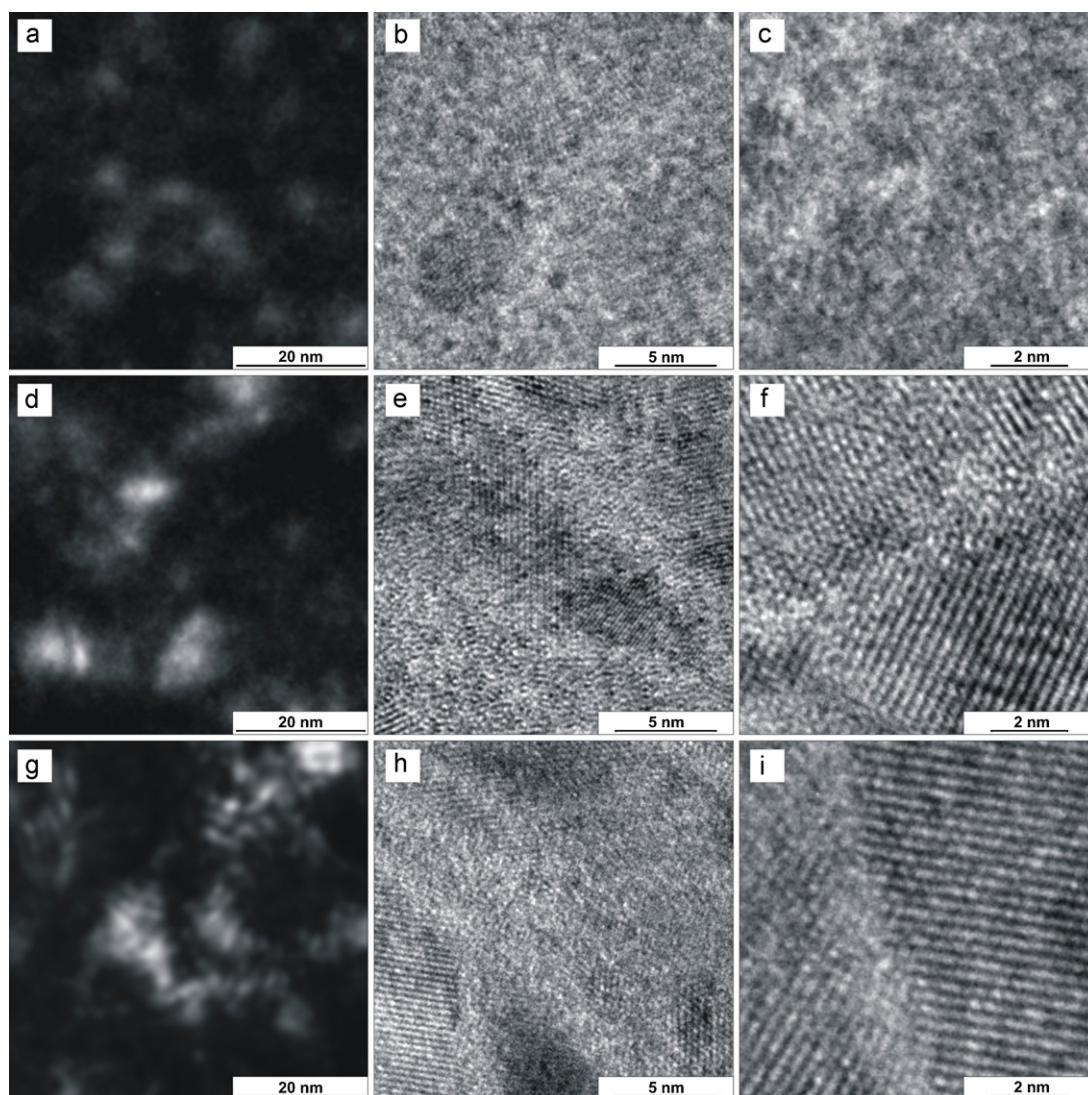
Fig. 5. Microstructure of (a–c) rapidly cooled ribbon, (d–f) the 1 mm rod and (g–i) the 5 mm rod; (a, d, g) images obtained in the dark field taken from the first electron diffraction ring.

The structural heterogeneities were observed in the form of bands (furrows) 2–3 nm wide at the crystallite borders and, in the images in the bright field, they appear lighter (Fig. 5e, f, h, and i). The high resolution image shows ordering of these bands. They are located in the border regions between the neighboring grains, within which the crystalline lattice is deformed and the atoms are rearranged. This is a characteristic feature of the microstructure of the rod-shaped sample. The fact that there are no such bands in the rapidly cooled ribbon sample suggests that they only form at the appropriate cooling rate. TEM examinations of the $Nd_{60}Fe_{30}Al_{10}$ alloys, on the nanometric level, revealed that the microstructure differs from that suggested in Ref. [5].

4. Conclusions

After being cooled at a high rate (ribbon-shaped sample cooled at 30 m/s) the $Nd_{60}Fe_{30}Al_{10}$ alloy contains amorphous ferromagnetic and Nd-rich crystalline precipitates of paramagnetic phases which exhibit texture. After slower cooling (rod-shaped samples), the share of the paramagnetic phase decreases and the chemical composition of the ferromagnetic phase alters. Moreover, the crystalline phase (or two crystalline phases) containing Fe appears. Electron-microscopic examinations confirmed the occurrence of texture in all samples. The crystalline phase occurs abundantly – it predominates in 1 mm and 5 mm rod samples. A characteristic feature of these samples is the existence of band-shaped transition regions, 2–3 nm wide, between the grains of the crystalline phase. In these regions, the crystalline lattice is strongly deformed due to the presence of a coherent boundary. Since these bands do not occur in the rapidly cooled ribbon, it can be supposed that they only form when an appropriate cooling rate is applied.

References

[1] A. Inoue, T. Zhang, W. Zhang, A. Takeuchi, Materials Transactions JIM 37 (2) (1996) 99.
[2] A. Inoue, T. Zhang, A. Takeuchi, IEEE Transactions on Magnetics 5 (1997) 3814.
[3] Y. Li, J. Ding, S.C. Ng, X.Z. Wang, Journal of Magnetism and Magnetic Materials 187 (1998) L273.
[4] R.W. McCallum, L.H. Lewis, M.J. Kramer, K.W. Denis, Journal of Magnetism and Magnetic Materials 299 (2006) 265.
[5] Z.G. Sun, W. Loser, J. Eckert, K.-H. Muller, L. Schultz, Journal of Magnetism and Magnetic Materials 261 (2003) 122.