

Phase composition investigations of the Nd-Fe alloys processed by various methods

Katarzyna Pawlik,
Jerzy J. Wysocki,
Jacek Olszewski,
Oksana I. Bodak,
Piotr Pawlik

Abstract In the paper, the phase composition changes for the series of $\text{Nd}_{10+x}\text{Fe}_{90-x}$ ($x = 0; 0.5; 1; 1.5; 2; 2.5; 3; 3.5; 4$) binary alloys, produced by long time annealing and rapid solidification methods were investigated. X-ray diffractometry and Mössbauer spectroscopy were used to determine the phase composition of the alloys. These structural investigations revealed the existence of two crystalline phases in the long time annealed samples: bcc α -Fe and rhombohedral $\text{Nd}_2\text{Fe}_{17}$ of the $\text{Th}_2\text{Zn}_{17}$ -type structure. Furthermore, the single phase region was observed for the Nd concentration above 12 at.%. For the rapidly solidified ribbon samples, a low volume fraction of the α -Fe and the crystalline phase of hexagonal symmetry were detected.

Key words Nd-Fe binary system • intermetallic compounds • Mössbauer spectroscopy • phase composition

Introduction

According to the commonly accepted Nd-Fe binary phase diagram [7] the only stable crystalline binary phase is the $\text{Th}_2\text{Zn}_{17}$ -type (space group $R\bar{3}m$) [2] rhombohedral intermetallic $\text{Nd}_2\text{Fe}_{17}$ compound. In Fig. 1a, the unit cell of this phase is depicted. The rare earth (Nd) atoms occupy the single crystallographic site – 6c in the unit cell, while there are four crystallographically inequivalent positions for Fe atoms: 6c, 9d, 18f, 18h. The 6c site, for Fe atoms (“dumbbell site”) plays an important role in determining the magnetic properties of $\text{RE}_2\text{Fe}_{17}$ compounds (RE – rare earth element). The short bond between such 6c-iron atoms is responsible for low Curie temperatures of these compounds [3]. According to above mentioned Nd-Fe binary phase diagram, the single phase alloy can be produced only for the stoichiometric alloy composition that corresponds to 10.5 at.% of Nd. However, in case of some RE-T (T – 3d transition metal element) binary systems, in a certain range of elements concentration, the single phase structure was observed [1]. Inside such homogeneity region, the lattice constants are subjected to some variations due to changes in the occupation of atomic positions. Mössbauer spectroscopy allows determining the Fe sites for which the greatest changes of the hyperfine interactions are detected. That is the result of the Fe nuclei surrounding changes. Our recent X-ray diffraction studies of Nd-Fe system, revealed existence of similar homogeneity region in this binary system [4]. Therefore, the aim of this work is the investigation of Nd content effect on the phase composition and Mössbauer spectra parameters.

As was shown for Sm-Fe alloys, the inequilibrium condition processing (i.e. rapid solidification methods, mechanical alloying) resulted in improvement of the magnetic properties, especially in increase of the coercivity

K. Pawlik[✉], J. J. Wysocki, J. Olszewski, P. Pawlik
Department of Materials Processing
Technology and Applied Physics,
Institute of Physics,
Częstochowa University of Technology,
19 Armii Krajowej Ave., 42-200 Częstochowa, Poland,
Tel./Fax: +48 34/ 325 07 95,
e-mail: pawlik@mim.pcz.czyst.pl

O. I. Bodak
Institute of Chemistry and Environment Protection,
Pedagogical University of Częstochowa,
13/15 Armii Krajowej Ave., 42-200 Częstochowa, Poland
and Department of Inorganic Chemistry,
Lviv State University,
290005 Lviv, Ukraine

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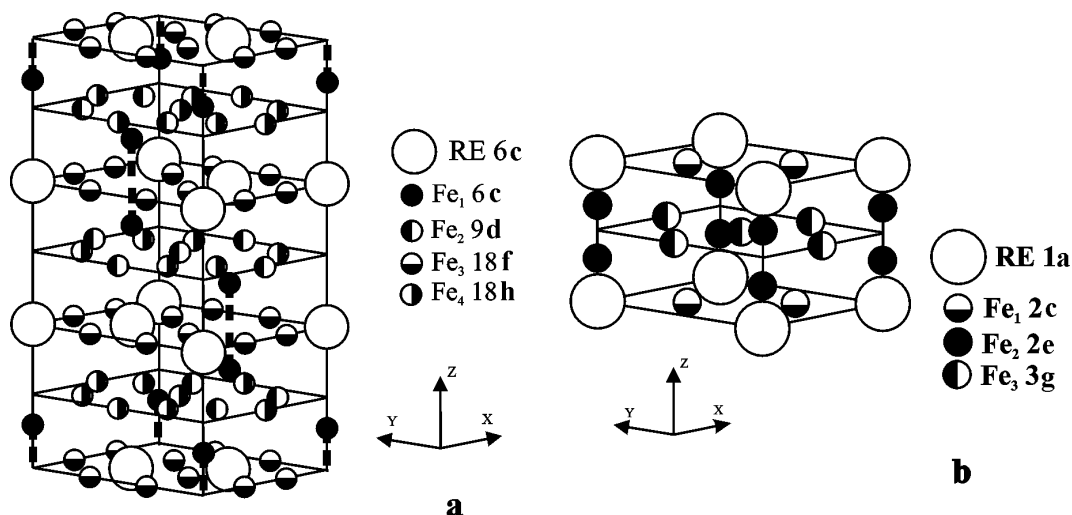


Fig. 1. Schematic unit cells of: (a) stable $\text{RE}_2\text{Fe}_{17}$ phase [2] (the vertical dashed lines represent the shortest interatomic distances between Fe dumbbell atoms) and (b) metastable REFe_7 phase [4].

and Curie temperature [8]. The formation of a modified TbCu_7 -type ($P6/mmm$ space group) metastable phase is one of the sources of this behaviour. Further annealing of such structure resulted in transition to the $\text{Th}_2\text{Zn}_{17}$ -type stable structure [8]. The Fe atoms occupy: 2c, 2e, and 3g positions in the unit cell of REFe_7 , while RE atoms enter the 1a sites (Fig. 1b). Dumbbell Fe atoms that occupy 2e positions are randomly distributed without long range order.

Investigations of the magnetic properties of Nd-Fe alloy melt spun ribbon samples revealed enhancement of the saturation magnetization $\mu_0 M_s$ and remanence $\mu_0 M_r$ values in respect to the long time annealed alloys [4]. Therefore, the second aim of the work is to find out if there exists the TbCu_7 -type metastable phase in the investigated ribbons.

Experimental

The phase composition changes for the series of $\text{Nd}_{10+x}\text{Fe}_{90-x}$ ($x = 0; 0.5; 1; 1.5; 2; 2.5; 3; 3.5; 4$) binary alloys, were investigated. The ingot samples were produced by arc-melting of high purity components under Ar atmosphere and then re-melted several times to obtain the homogeneity. Subsequently, the ribbon samples were produced by controlled atmosphere melt spinning at the copper roller velocity ~ 40 m/s for all compositions investigated. The ingot samples of the same compositions were sealed off to the quartz tubes under Ar atmosphere and annealed at 873 K/168 h. By this route, two kinds of samples of the same composition: the long time annealed (LTA) alloys and rapidly solidified ribbons (RSR) were produced. The X-ray diffractometry and Mössbauer spectroscopy were used to determine phase composition of the samples. The XRD patterns were measured using a Philips diffractometer with $\text{Co K}\alpha$ radiation. Transmission Mössbauer spectra were obtained at 295 K on a constant acceleration spectrometer which utilized a rhodium matrix Co^{57} source and was calibrated at room temperature with an α -Fe foil. The Mössbauer spectra analysis was carried out using the Normos software. The estimated errors of the hyperfine parameters were at most ± 0.01 mm/s for the isomer shifts, ± 0.02 mm/s for the quadrupole splittings and ± 0.1 T for the hyperfine fields.

Results and discussion

The qualitative dependence of the phase composition on the Nd contents for both types of samples was determined from X-ray diffractometry. The selected XRD patterns for the LTA and the RSR samples are presented in Fig. 2 for 10, 11.5 and 13 at.% Nd content. For all LTA samples, the existence of the $\text{Nd}_2\text{Fe}_{17}$ phase was observed. Furthermore, for the samples up to 11.5 at.% of Nd, an additional α -Fe phase was detected. However, with increasing Nd concentration, the α -Fe peak intensities decreased and for the Nd content higher than 12 at.%, the single phase structure was observed. These results suggest different phase composition of the Nd-Fe alloys than that reported in paper [7], where no homogeneity region was observed. The phase identification for the RSR samples indicated a possibility of formation of the NdFe_7 metastable crystalline phase having the TbCu_7 -type structure [5]. Furthermore, the α -Fe peaks were observed for the ribbon samples with Nd content lower than 11 at.%. For higher Nd concentration alloy ribbons, the α -Fe peak intensities are too small to

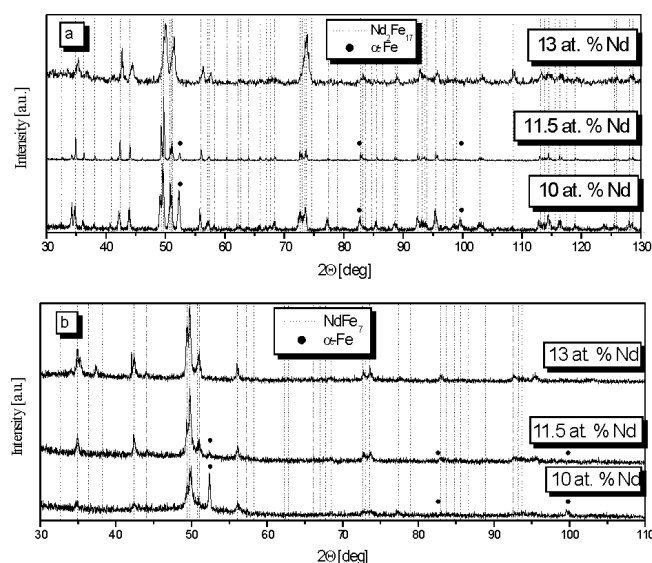


Fig. 2. XRD patterns for the long time annealed (LTA) (a), and the rapidly solidified ribbon (RSR) (b) samples of the Nd-Fe alloys with various Nd contents.

distinguish them from the background. For 12 at.% of Nd ribbons, some additional low intensity peaks were detected, which indicate a change of the symmetry from hexagonal ($P6/mmm$) to rhombohedral ($R\bar{3}m$).

Mössbauer spectra analysis performed with Normos software, allowed determining the isomer shift (IS), the hyperfine field (B) and the quadrupole splitting (QS) for a given component sextet. For the $\text{Nd}_2\text{Fe}_{17}$ unit cell, the iron atoms occupy four inequivalent crystallographic positions: 6c, 9d, 18f, 18h, for which some specific chemical surroundings exist that determine four different values of isomer shift. However, in the magnetically ordered state, the number of constituent sextets depends further on the direction of the easy axis of magnetization, which in the case of $\text{Nd}_2\text{Fe}_{17}$ phase lies in the basal plane of the unit cell [3]. Therefore, as in paper [3], the investigated spectra were fitted with seven sextets corresponding to the magnetically inequivalent Fe positions: 6c, 9d₆, 9d₃, 18f₁₂, 18f₆, 18h₁₂, 18h₆ with relative intensities of 6:6:3:12:6:12:6. In Fig. 3, some selected transmission Mössbauer spectra obtained for the LTA samples, of $\text{Nd}_{10+x}\text{Fe}_{90-x}$ ($x = 1.5; 2$) alloys are presented. For all analyzed LTA samples the hyperfine parameters are collected in Table 1. It should be noticed that this set of parameters was the best possible fit with correct physical meaning of their values for iron based alloys. For 11.5 at.% of Nd sample, the additional eighth sextet with hyperfine parameters characteristic of the α -Fe was present. For higher Nd concentrations, the α -Fe was no longer detected and their spectra were satisfactorily fitted with the seven above mentioned sextets that confirms the single phase structure of those alloys. The easiest position to assign the appropriate Zeeman sextet in the $\text{Th}_2\text{Zn}_{17}$ -type structure is the 6c site that is occupied by dumbbell Fe atom pair with its axis parallel to the c -axis of the unit cell. The Fe atoms in this position are surrounded by 13 other nearest neighbour Fe atoms. Additionally, in the dumbbell pair the interatomic distance (2.41 Å) is

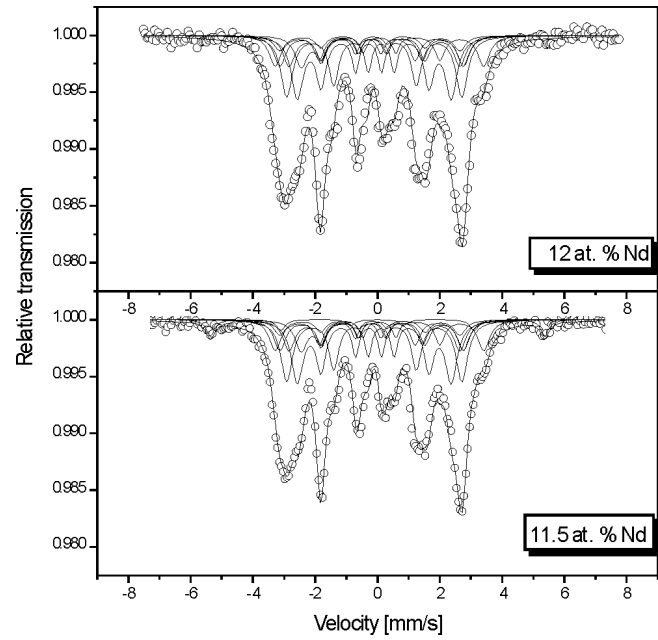


Fig. 3. Transmission Mössbauer spectra and their constituent sextets obtained for the long time annealed samples (LTA) of Nd-Fe alloys with 11.5 and 12 at.% of Nd.

shorter than the interatomic distances of all the other Fe sublattices in this crystal as well as in the metallic iron (2.51 Å) [6]. The largest hyperfine field sextet was therefore assigned to the Fe nuclei in this site. As in [3], six other sextets were assigned based on the values of their isomer shifts with the following sequence: $\text{IS}(6c) > \text{IS}(18h) > \text{IS}(18f) > \text{IS}(9d)$. In Fig. 4 changes of the hyperfine field B , the isomer shift IS and the quadrupole splitting QS values vs. the Nd concentration for each of the magnetically inequivalent Fe positions are presented. The hyperfine field changes are approximately similar for all seven constituent

Table 1. The hyperfine parameters of the Mössbauer spectra measured for long time annealed Nd-Fe alloys of various Nd contents.

Nd content [at.%]	Phase Iron atoms positions Hyperfine parameters	$\text{Nd}_2\text{Fe}_{17}$							α -Fe
		6c	9d ₆	9d ₃	18f ₁₂	18f ₆	18h ₁₂	18h ₆	
11.5	B_f [T]	20.8	17.9	17.9	16.4	17.4	16.4	16.1	33.3
	IS [mm/s]	0.06	-0.19	-0.19	-0.11	-0.11	-0.07	-0.07	0
	QS [mm/s]	0.00	-0.09	-0.09	0.35	0.15	-0.39	0.45	0
12	B_f [T]	20.8	18.0	18.0	16.5	17.5	16.6	16.3	
	IS [mm/s]	0.05	-0.20	-0.20	-0.11	-0.11	-0.10	-0.10	
	QS [mm/s]	-0.06	-0.06	-0.06	0.36	0.13	-0.38	0.45	
13	B_f [T]	19.8	16.9	16.5	15.5	16.1	15.7	15.4	
	IS [mm/s]	0.06	-0.18	-0.18	-0.12	-0.12	-0.08	-0.08	
	QS [mm/s]	-0.04	-0.09	-0.02	0.36	0.09	-0.44	0.45	
13.5	B_f [T]	20.2	17.4	17.5	15.9	16.8	16.1	15.5	
	IS [mm/s]	0.05	-0.24	-0.24	-0.10	-0.10	-0.10	-0.10	
	QS [mm/s]	-0.02	-0.13	0.55	0.32	-0.08	-0.41	0.45	
14	B_f [T]	20.9	17.8	17.8	16.5	17.2	16.6	16.2	
	IS [mm/s]	0.06	-0.19	-0.19	-0.11	-0.11	-0.08	-0.08	
	QS [mm/s]	-0.02	-0.11	-0.11	0.38	0.13	-0.39	0.45	

sxtets, reaching minimum for 13 at.% of Nd. The largest differences of the hyperfine fields between crystallographically equivalent positions were observed for $18f_{12}$ and $18f_6$ sites. For Fe atoms in $9d_6$ and $9d_3$ positions, no significant differences were detected. Furthermore, with increasing Nd concentration, the isomeric shift IS remains constant for 6c, 18f and 18h positions (within the experimental errors values), while for 9d site deviation of IS for 13.5 at.% of Nd, larger than the experimental error, was observed. The largest variations of the QS values, with increasing Nd concentration, are visible for $9d_3$ position. Those results indicate some modifications of the 9d Fe atoms surroundings. Additional Nd atoms present for the Nd contents that exceed the stoichiometry of Nd_2Fe_{17} phase could be present in those surroundings.

The Mössbauer spectra analysis carried out on the RSR samples revealed low volume fractions of the crystalline α -Fe phase: 3% and 2.5%, respectively for 11.5 at.% and 12 at.% of Nd. For the Nd contents of 11.5 at.% and 12 at.%, this phase was not detected by XRD due to its low volume fraction. In Fig. 5a, the transmission Mössbauer spectrum measured for the 12 at.% of Nd ribbon sample is presented. The broadening effect of the spectral lines related to the presence of metastable nanocrystalline structure was observed. The presence of the nanocrystalline

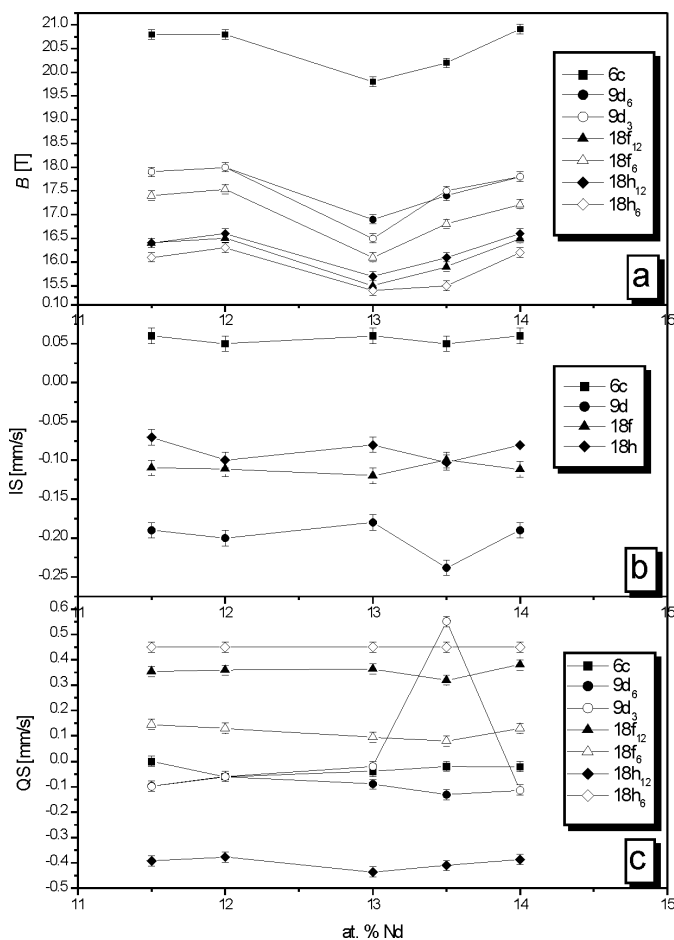


Fig. 4. The dependence of the hyperfine field B (a), the isomeric shift IS (b) and the quadrupole splitting QS (c) values on the Nd concentration for each of the magnetically inequivalent Fe positions.

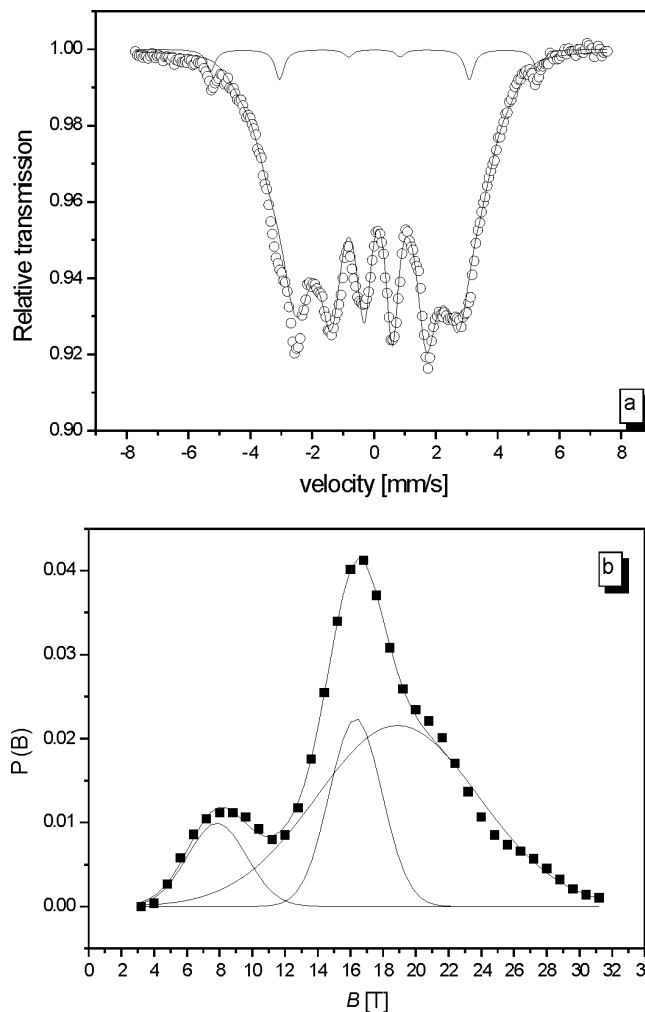


Fig. 5. A transmission Mössbauer spectrum for 12 at.% of Nd ribbon sample with marked Zeeman sextet corresponding to the α -Fe phase and the continuous spectra component (a) and the hyperfine field distribution of the continuous component (b).

structure was confirmed by calculations of the mean crystallite size (~ 30 nm) from the broadening of XRD peaks measured for the RSR samples. However, further investigations of the crystalline structure by the TEM method are required. The decomposition of the spectrum into a discrete component related to the α -Fe phase and a continuous one allowed to extract the hyperfine magnetic field distribution of this continuous part (Fig. 5b). Subsequent deconvolution of the hyperfine field distribution into three Gaussian distributions, allowed to find three peaks corresponding to hyperfine fields of 19, 16 and 8 T. These values can be assigned to three inequivalent Fe atom positions in the $TbCu_7$ -type unit cell (Fig. 1b). Significant linewidths of Gaussian curves for this phase are the result of a variation in the number of the nearest neighbours of a given Fe atom crystallographic position that is the effect of the processing method. Similar Mössbauer spectra and the hyperfine field distributions were obtained for other RSR sample compositions up to 12 at.% of Nd. For higher Nd concentrations similar wide hyperfine field distributions were extracted from the spectra, but no α -Fe spectrum component was present.

Conclusions

X-ray diffraction and Mössbauer spectroscopy revealed the presence of the α -Fe phase for the long time annealed samples with Nd contents up to 11.5 at.%. Above this concentration, the long time annealed samples are of a single phase structure. The hyperfine parameter changes revealed the largest structural modifications corresponding to the surrounding of Fe atoms in the 9d site. This indicates that the additional Nd atoms for the Nd contents, exceeding the stoichiometry of $\text{Nd}_2\text{Fe}_{17}$ phase, could be present in those surroundings.

For rapidly solidified Nd-Fe alloys with Nd concentrations up to 12 at.%, the coexistence of the α -Fe phase and a strongly deformed nanocrystalline phase (possibly TbCu_7 -type structure) were observed.

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