Characterization of phases in $Nd_{17}Fe_{75-x}Ti_xB_8$ $(0 < x \le 1.89)$ compounds

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Abstract

The microstructure of $Nd_{17}Fe_{75-x}Ti_xB_8$ $(0 < x \le 1.89)$ compound was investigated by using scanning electron microscopy and Mössbauer spectroscopy. It was shown that the Ti addition participates in three processes: (i) solubility in hard magnetic $Nd_2Fe_{14}B$-phase with a strong preference of the substitution of the $8j_2$ Fe sites, (ii) formation of Ti_2B-phase and (iii) formation of Fe containing X-phase (but not FeTi and Fe_2Ti phases). Ti substitution decreases the magnetic hyperfine field and increases the width of the absorption line at the Fe sites in the $Nd_2Fe_{14}B$ phase.

Key words: intermetallic, microstructure, Mössbauer spectroscopy

1. Introduction

The present problems are connected with sintered Nd-Fe-B type permanent magnets: insufficient thermal stability, corrosion resistance and mechanical properties force manufacturers to search for ways of their improvement. One basic way of achieving this is a conventional technique of adding of further elements to alloys. These additives can change the magnetic properties by substituting Fe or Nd in the hard magnetic $Nd_2Fe_{14}B$ (ϕ) phase and/or influence the alloy microstructure, e.g. due to formation of new intergranular and/or ingranular phases [1]. If the addition is less than approximately 1 wt.%, the elements are mostly homogenously distributed in all phases, and possibly influence the magnetic properties [2].

Partial substituting of Fe by Ti is very effective not only in enhancing the coercivity [3, 4], but also in improving the thermal stability [5] and corrosion resistance [6, 7] of sintered Nd-Fe-B type permanent magnets. Ti additives also have an undesirable property of decreasing the intrinsic properties, such as saturation magnetization, Curie temperature and magnetocrystalline anisotropy [3]. It is to be supposed that the changes of those features are caused by intrinsic properties of the hard magnetic (ϕ)-phase as well as by the microstructure of the permanent magnets. It is suggested [1] that the coercivity and corrosion resistance of Ti-doped Nd-Fe-B type permanent magnets are increased due to the presence of non-magnetic Ti_2B or Ti_2FeB phases in the intergranular region, that lead to an improved separation and decoupling of the hard magnetic grains. In addition an enhancement of the corrosion resistance should be expected, provided that the new intergranular phases are less sensitive to corrosion attack than Nd. The added Ti element also has to show a low solubility in hard magnetic ϕ phase and has led to the deterioration of intrinsic properties, through substitution of Fe atom. Savchenko et al. [8] suggested that Ti does not replace Fe sites in the ϕ phase but only creates Ti_2B phase. It should be pointed out that Nd-Fe-B compounds with Ti additives are expected to contain intermetallic FeTi and Fe_2Ti phases [9, 10]. Until now, there has been no information on the mechanism of changes of the intrinsic properties of the hard magnetic ϕ phase and of the phases relation of Nd-Fe-Ti-B compounds. In this report these problems are investigated and discussed.

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2. Experimental

The $Nd_{17}Fe_{75-x}Ti_xB_8$ compounds ($0 < x \leq 1.89$ at.%) were prepared by the induction melting of high purity (99.9 % or better) constituents in a water-cooled copper boat under argon atmosphere. The compounds were re-melted four times. Heat treatment under vacuum was applied to the samples at the temperature of 1240 K for 72 hours, which were then quenched in water.

The microstructure of all the alloys was determined by using scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission Mössbauer spectroscopy (TMS) at room temperature. XRD analysis was performed on powdered samples using a high resolution Guinier type diffractometer with Co(Kα) radiation. TMS was performed using a ^{57}Co source in Cr matrix with an activity of a 0.5 GBq. The velocity scale was calibrated using an α-Fe absorber. The spectra obtained were computer fitted, using the least squares iteration procedure. It was also assumed that the lines were Lorentzian ones.

With the purpose of identification of FeTi and Fe_2Ti phases with the Mössbauer spectroscopy, the alloys with the composition close to stoichiometric composition were melted in the argon-arc furnace. As the result of the conducted research it was found that Fe_2Ti is doublet with small quadruple splitting (0.411 ± 0.002 mm/s) and the phase FeTi is single line, as has been observed earlier [9].

The composition and quantity of phases of the alloys were determined on the basis of Mössbauer spectra analysis by the method described in [10, 11]. The quantitative contents of $Nd_{95}Fe_5$ (n) and Ti_2B phases are obtained on the basis of the conducted chemical analysis; the condition of $Nd_{95}Fe_5$ phase is connected with the fact that Nd can exist in the form of a solid solution, as well as in the form of Nd_2O_3 oxide.

3. Results and discussion

Figure 1, as an example, gives representative backscattered electron SEM micrographs of non-doped (Fig. 1a) and 1.47 at.% Ti-doped (Fig. 1b) $Nd_{17}Fe_{75}B_8$ compounds. Columnar grain structures and four phases are distinguished by brightness in accordance with their mean atomic number of the phases. Their composition, except the boron contents, analysed by EDX are: the hard magnetic matrix $Nd_2Fe_{14}B$ phase (ϕ-phase; grey area), the solid solution $Nd_{95}Fe_5$ phase (n-phase; the white area), the boron-rich $Nd_{1.1}Fe_4B_4$ phase (η-phase; the dark area) and one additional Ti_2B phase (T-phase; the black area) in Ti > 0.21 at.% doped compounds. The occurrence of the above phase in the compounds under SEM and EDX investigations was confirmed by the XRD pattern obtained by the authors. These observations are confirmed by Mössbauer analysis as well.

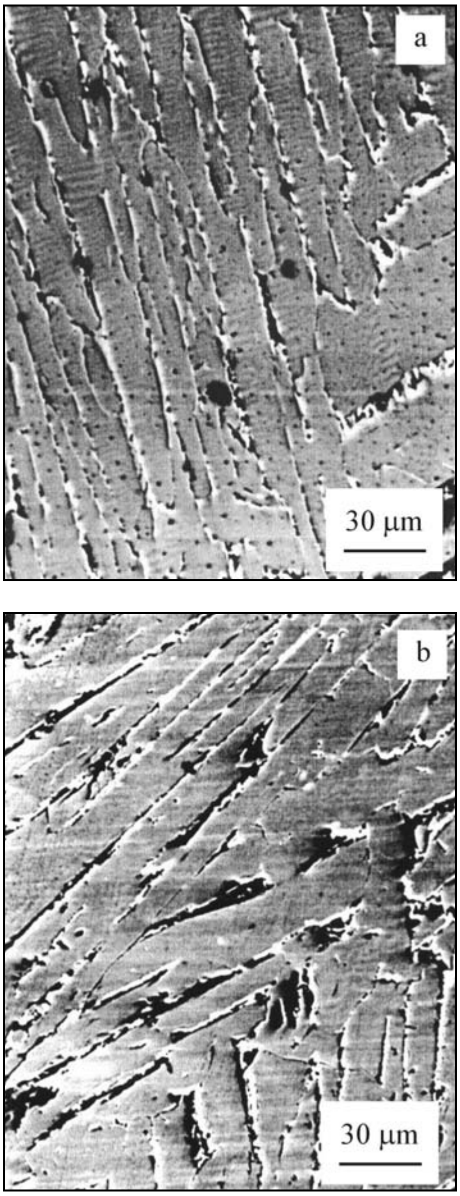

Fig. 1. Scanning electron micrographs of the $Nd_{17}Fe_{75-x}$-Ti_xB_8 compounds for $x = 0$ (a) and 1.47 at.% (b). The different observed regions are summarized in the text.

The Mössbauer spectra obtained for compounds investigated here are in good agreement with those in literature [12, 13]. They show the presence of the spectrum of ϕ-phase – sextet which contains six sub-sextets from six ($16k_1$, $16k_2$, $8j_1$, $8j_2$, 4e and 4c) crystallographically equivalent positions of Fe atoms in the elementary cell, of η-phase – central doublet with one line at −0.4 mm/s, $TiFe_2$ phase – doublet with small quadruple splitting at +4.11 ±0.02 mm/s, which is in good agreement with one obtained by Liou et al. [9]. The n-phase cannot by observed because it contains very little iron, and moreover it is present in small

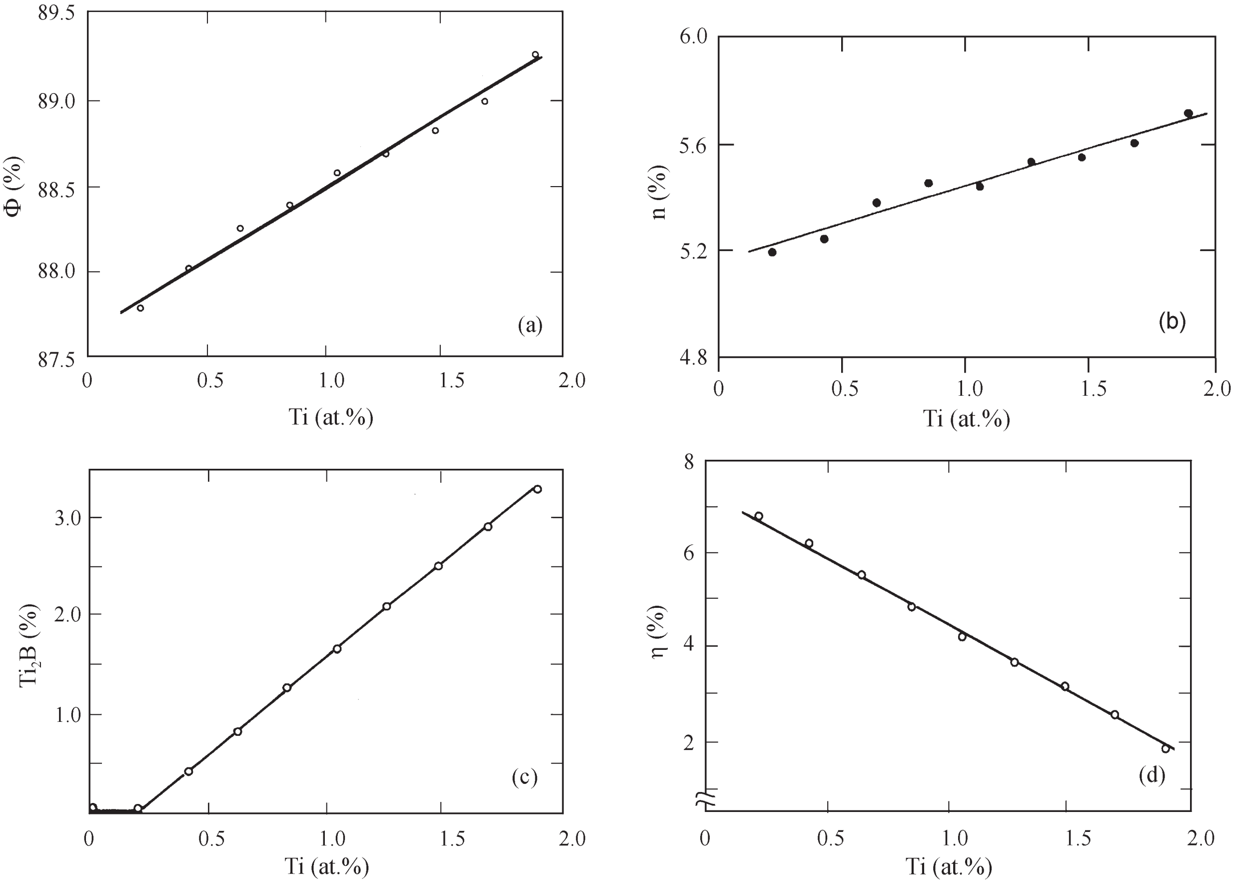

Fig. 2. Variation of the phases: a – $Nd_2Fe_{14}B$ (ϕ), b – Nd-rich (n), c – Ti_2B and d – $Nd_{1.1}Fe_4B_4$ (η) with Ti content (x) in the $Nd_{17}Fe_{75-x}Ti_xB_8$ compounds.

quantity in each of the compounds [13].

Another fact worth recalling is that of the left lines of central doublet from η-phase with one line step forward at −0.1 mm/s. It may be assumed that the observed little peak belongs to the X-phase, which could not be identified with the SEM, the EDX and XRD analysis. It is likely that the X-phase is a paramagnetic one (doublet) because the spectrum as whole does not show noticeable changes.

The quantitative contents of phases of $Nd_{17}Fe_{75-x}$-Ti_xB_8 ($0 < x \leq 1.89$ at.%) compounds are shown in Fig. 2. It can be seen that the amount of the ϕ-phase (Fig. 2a), n-phase (Fig. 2b) and Ti_2B-phase (Fig. 2c) increases, but the η-phase (Fig. 2d) decreases with an increasing concentration of Ti in the compound. The given results allow for the assumption that a part of Ti was dissolved in the main phases and the remaining part could attack either one or two B atoms. This last effect can be controlled by P parameter, which indicates the degree of fluctuation of B content in the compound sample from its "real" amount and which is given by the following

$$P_{1,2} = \frac{B_{\mathrm{ch}}}{B_{\mathrm{MS}}}100 - 100\%, \qquad (1)$$

where B_{ch} and B_{MS} denote the content of B (in at.%) in the alloy sample determined by a chemical analysis and Mössbauer fits based on ratios of the areas under spectra of the main phases (ϕ and η) and their stereochemical coefficient, respectively; P_1 and P_2 are the parameters of the alloy with and without Ti_2B phase, respectively. From Eq. (1) it follows that when $B_{\mathrm{ch}} = B_{\mathrm{MS}}$, parameter $P = 0$, which means the ideal case, which enables the absolute correlation between chemical and "Mössbauer" analysis of B content in the compounds. The value of parameters P_1 and P_2 of the compounds shows varied contents of Ti_2B-phase, see Fig. 3. It can be seen that the first parameter P_1 increases together with an increasing content of Ti in the compound, which indicates the changes of B content in the alloy sample, whereas the second parameter P_2 was practically constant and near to zero. It should be noticed that the increase of the parameter P_1 value along with the increase of Ti content in the alloy points to the increase of the Ti_2-phase in the alloy as well.

As is generally known (e.g. [12]), the magnetic hyperfine field, B_{hf}, in the $Nd_2Fe_{14}B$-phase decreases in the following sequence

$$8j_2 > 16k_2 > 4c > 16k_1 > 8j_1 > 4e. \qquad (2)$$

T a b l e 1. Fit parameters for room-temperature spectra measured by the ^{57}Fe Mössbauer effect for the $Nd_{17}Fe_{75-x}Ti_xB_8$ compounds ($0 < x \leq 1.89$). The parameters given are: δ, the isomer shift, B_{hf}, the hyperfine magnetic field, QS, the quadruple splitting, and G, the width of absorption line.

Mössbauer parameters	Fe sites	x (at. %)									
		0	**0.21**	**0.42**	**0.63**	**0.84**	**1.05**	**1.26**	**1.47**	**1.68**	**1.89**
The isomer shift δ (mm/s)	$16k_1$	-0.06±0.01	-0.06±0.01	-0.06±0.01	-0.07±0.01	-0.06±0.01	-0.06±0.01	-0.06±0.01	-0.06±0.01	-0.07±0.01	-0.06±0.01
	$16k_2$	-0.12±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01	-0.11±0.01
	$8j_1$	-0.19±0.02	-0.18±0.02	-0.18±0.02	-0.19±0.02	-0.18±0.02	-0.17±0.02	-0.16±0.02	-0.18±0.02	-0.16±0.02	-0.19±0.02
	$8j_2$	0.08±0.02	0.09±0.02	0.08±0.02	0.08±0.02	0.08±0.02	0.08±0.02	0.09±0.02	0.08±0.02	0.08±0. 2	0.09±0.02
	4e	0.07±0.04	0.08±0.04	0.06±0.04	0.06±0.04	0.04±0.04	0.04±0.04	0.04±0.04	0.04±0.04	0.03±0.04	0.05±0.04
	4c	-0.15±004	-0.16±0.04	-0.13±0.04	-0.16±0.04	-0.15±0.04	-0.16±0.04	-0.17±0.04	-0.16±0.04	-0.17±0.04	-0.14±0.04
The magnetic hyperfine field B_{hf} (T)	$16k_1$	28.72±0.02	28.64±0.02	28.57±0.02	28.46±0.03	28.40±0.02	28.34±0.02	28.23±0.02	28.23±0.02	28.23±0.02	28.21±0.03
	$16k_2$	30.69±0.02	30.56±0.02	30.47±0.02	30.34±0.04	30.33±0.04	30.30±0.04	30.29±0.04	30.28±0.04	30.28±0.05	30.27±0.06
	$8j_1$	26.41±0.05	26.31±0.06	26.17±0.05	26.08±0.06	26.04±0.06	26.00±0.06	25.94±0.06	25.71±0.06	25.70 ±0.08	25.71±0.06
	$8j_2$	34.50±0.05	34.48±0.06	34.38±0.06	34.27±0.06	34.24±0.07	34.19±0.07	34.13±0.04	34.13±0.07	34.15±0.08	34.12±0.06
	4e	26.29±0.10	26.08±0.11	25.76±0.10	25.57±0.11	25.52±0.11	25.43±0.11	25.40±0.11	25.40±0.12	25.38±0.13	26.40±0.11
	4c	31.12±0.20	31.07±0.20	31.01±0.17	31.01±0.20	30.89±0.21	30.87±0.21	30.85±0.22	30.86±0.22	30.88±0.22	30.88±0.22
The quardupole splitting QS (mm/s)	$16k_1$	0.24±0.02	0.24±0.02	0.25±0.02	0.23±0.02	0.23±0.02	0.23±0.02	0.22±0.02	0.23±0.02	0.22±0.02	0.22±0.02
	$16k_2$	0.10±0.02	0.10±0.02	0.10±0.02	0.11±0.02	0.10±0.02	0.11±0.02	0.12±0.02	0.11±0.02	0.12±0.02	0.11±0.02
	$8j_1$	0.06±0.04	0.06±0.04	0.07±0.04	0.07±0.04	0.07±0.04	0.08±0.04	0.10±0.04	0.06±0.04	0.10±0.04	0.07±0.04
	$8j_2$	0.64±0.04	0.64±0.04	0.64±0.03	0.65±0.03	0.65±0.03	0.65±0.04	0.65±0.04	0.65±0.04	0.65±0.04	0.65±0.04
	4e	0.12±0.06	0.12±0.06	0.10±0.05	0.13±0.06	0.14±0.05	0.13±0.05	0.17±0.05	0.14±0.06	0.14±0.06	0.14±0.06
	4c	0.24±0.06	0.24±0.06	0.25±0.06	0.23±0.06	0.22±0.05	0.21±0.05	0.20±0.06	0.21±0.06	0.23±0.06	0.22±0.06
The width of absorption line G (mm/s)	$16k_1$	0.335±0.010	0.375±0.010	0.342±0.011	0.355±0.011	0.354±0.011	0.374±0.011	0.374±0.011	0.375±0.012	0.374±0.012	0.374±0.012
	$16k_2$	0.338±0.011	0.338±0.011	0.343±0.011	0.350±0.012	0.357±0.015	0.354±0.012	0.363±0.012	0.364±0.012	0.363±0.012	0.363±0.012
	$8j_1$	0.345±0.014	0.345±0.014	0.351±0.014	0.363±0.014	0.380±0.014	0.386±0.014	0.400±0.014	0.401±0.015	0.400±0.015	0.400±0.015
	$8j_2$	0.326±0.013	0.326±0.013	0.329±0.013	0.337±0.014	0.349±0.014	0.353±0.014	0.360±0.014	0.361±0.015	0.362±0.015	0.362±0.015
	4e	0.343±0.017	0.343±0.017	0.348±0.017	0.363±0.017	0.373±0.017	0.376±0.017	0.378±0.018	0.376±0.018	0.371±0.018	0.378±0.018
	4c	0.336±0.012	0.357±0.012	0.341±0.012	0.351±0.012	0.359±0.012	0.366±0.012	0.374±0.012	0.376±0.012	0.376±0.013	0.371±0.013

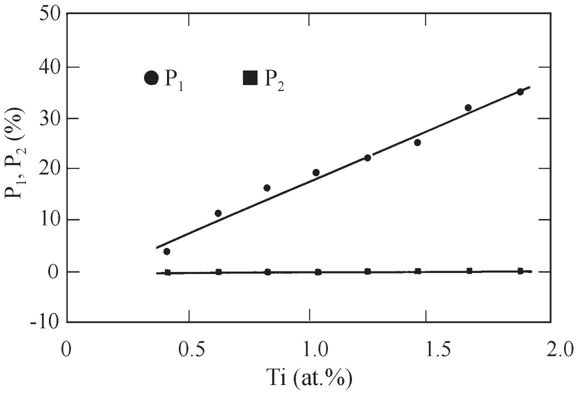

Fig. 3. The dependence of a degree of deviation of B content in the $Nd_{17}Fe_{75-x}Ti_xB_8$ compounds on Ti concentration. P_1 and P_2 are the parameters of the compounds with and without Ti_2B phase, respectively.

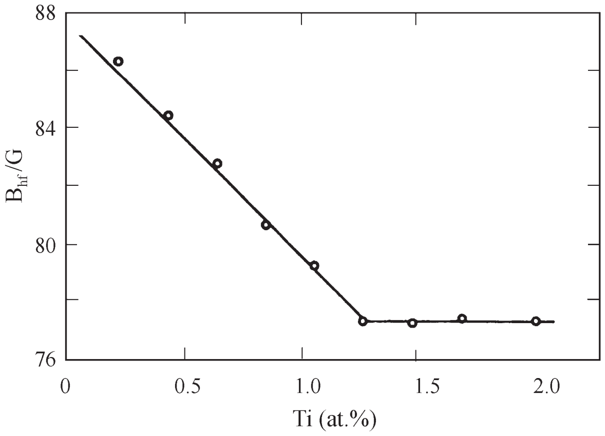

Fig. 4. The dependence of the ratio of the magnetic hyperfine field (B_{hf}) and the width of the absorption line (G) of the $Nd_{17}Fe_{75-x}Ti_xB_8$ compounds on Ti concentration.

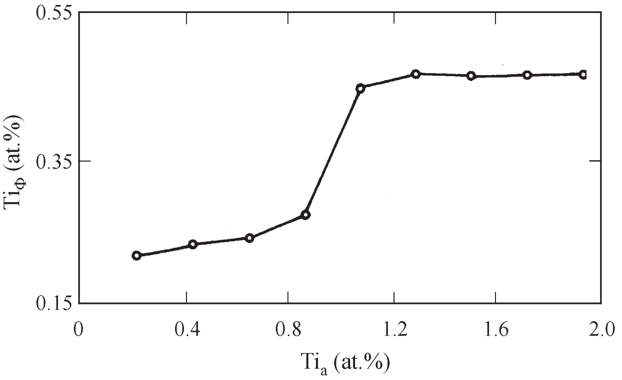

Fig. 5. Solubility of Ti in the $Nd_2Fe_{14}B$-phase (Ti_{ϕ}) as a function of overall $Ti_{(a)}$ concentration in the $Nd_{17}Fe_{75-x}$-Ti_xB_8 compounds.

In the $Nd_{17}Fe_{17-x}Ti_xB_8$ compounds the B_{hf} value always decreases along with the increase of Ti concentration at all Fe sites, as seen in Table 1. The decrease in the B_{hf} value is very well observed for the 4c, $8j_1$, $16k_2$ and 4e Fe sites and less so in the case of the $8j_2$ site. This shows that Ti has a strong preference for the $8j_2$ site. This fact was additionally confirmed by the changes in the relative intensity of the six sextets; with Ti concentration increasing up to 1.26 at.% the sensitivity for $8j_2$ site decreases while simultaneously increasing for other sites.

The analysis of the line width value (see Table 1) points to an increase in the lines width along with the increase of Ti content in the $Nd_2Fe_{14}B$ phase. Looking at the relation between the values B_{hf} and G, we conclude that the increase of substitution of Ti decreases the value of B_{hf}; substitution of Fe atoms for Ti ones leads to the reducing of the magnetic moment as Ti has non-magnetic atoms [14]. We also noticed that along with the increased Ti content in ϕ-phase the ratio of B_{hf}/G can be determined according to the following equation:

$$\left\langle \frac{B_{\mathrm{hf}}}{G} \right\rangle_{\mathrm{i}} = \frac{(B_{\mathrm{hf,k1}} + B_{\mathrm{hf,k2}} + B_{\mathrm{hf,j1}} + B_{\mathrm{hf,j2}} + B_{\mathrm{hf,c}} + B_{\mathrm{hf,e}})}{(G_{\mathrm{k_1}} + G_{\mathrm{k_2}} + G_{\mathrm{j_1}} + G_{\mathrm{j_2}} + G_{\mathrm{c}} + G_{\mathrm{e}})}, \tag{3}$$

where in numerator and in denominator is the sum of B_{hf} and G for six conditions of Fe sites of i-sample alloy, respectively. As shown in Fig. 4, with the increase of Ti content in ϕ-phase the ratio of B_{hf}/G is decreasing proportionally up to $x = 1.26$ at.%. Knowing the minimum (for $x = 1.26$ at.%) and maximum (for $x = 0$) values of the ratio of B_{hf}/G and the content of Ti in ϕ-phase with $x = 1.26$ at.%, it is possible to determine the Ti content in ϕ-phase with other values of x. The content of Ti in ϕ-phase as a function of overall Ti content in the alloy is presented in Fig. 5. It can be seen that up to $x = 1.26$ at.% the solubility of Ti in ϕ-phase increases, however, at the $x > 1.26$ at.% it remains practically unchanged. The presence of content of Ti in ϕ-phase in Fig. 5 is based on the simultaneous changes of the values B_{hf} and G. It should be noted, however, that Ti added to an alloy does not dissolve completely in ϕ-phase. The remaining part of Ti which does not participate either in the Ti_2B-phase formation (which is called "excessive" titanium) is active in X-phase formation and dissolves in the intergranular region [15]; our calculation shows that in the $Nd_{17}Fe_{75-x}Ti_xB_8$ alloys for $x = 1.47$, 1.68 and 1.89 at.% the amount of "excessive" Ti equals 0.105, 0.120 and 0.135 at.%, respectively.

4. Conclusion

The analysis of our experimental data concerning the microstructure of the $Nd_{17}Fe_{75-x}Ti_xB_8$ compounds allows for giving some conclusions:

1. The presence of four metallographic phases in compounds, namely of hard magnetic $Nd_2Fe_{14}B$, Nd-rich, $Nd_{1.1}Fe_4B_4$ and, for Ti > 0.21 at.%, additional Ti_2B-phase.

2. With the increasing of Ti concentration of the amount of the $Nd_2Fe_{14}B$ in the compound, Nd-rich and Ti_2B phases increase, while the $Nd_{1.1}Fe_4B_4$ phase decreases.

3. Ti atoms prefer $8j_2$ sites in the $Nd_2Fe_{14}B$ phase similarly to Al [13, 16], Nb [16] and Cr [17].

4. Partial substitution Fe by Ti atoms reduces the value of the magnetic hyperfine fields and increases the value of width of the absorption line at all Fe sites in the $Nd_2Fe_{14}B$-phase.

5. Ti atoms participate in three simultaneous processes: (i) solubility in $Nd_2Fe_{14}B$ phase, (ii) formation of Ti_2B phase, (iii) formation of additional X-phase (but not FeTi and Fe_2Ti phases).

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