Crystallographic model of microstructure formation in Nd2Fe14B type compounds with titanium

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Abstract. The magnetic properties of permanent magnets of the Nd-Fe-B type alloyed with titanium, depending on the chemical composition and heat treatment, are studied. Crystallographic model of formation of a microstructure in compounds of the Nd2Fe14B type with titanium is proposed. Analysis of the experimental data provides an opportunity to suggest that to explain the dependence of the intrinsic coercive force on the parameters of heat treatment for various chemical compositions, it is necessary to take into account the change of state of the main and boundary phases due to diffusion processes and phase transfers.

1. Introduction

In well-known publications, authors explained differently causes of the growth of the intrinsic coercive force (iHc) under heat treatments for sintered magnets such as Nd3Fe14B. Based on electron microscopic study of Nd13Fe7B8 magnets before and after heat treatment at 870K, Sagawa et al. [1] connect iHc growth with stress decrease at the grain boundaries of the Nd3Fe14B main phase due to their greater smoothness in comparison with the initial state. In [2-4], the iHc growth at T = 935-1025 K in sintered Nd13(Fe0.1Co0.9Ni0.1)17Ti0.17B8 magnets is explained by the formation of the main hard-magnetic phase Nd3(Fe,Co,Ni,Ti)14B in grains and finely dispersed borides of the TiB2 type in the grain boundaries. Tarasov et al. [5], investigating magnets of the Nd-Fe-B type with different boron content, conclude that the optimum processing temperature (775-875 K) is associated with the diffusion of boron from the main hard-magnetic phase of Nd3Fe14B to the grain boundaries.

However, a number of experimental facts did not find a logical explanation [6], in particular: iHc breakdown in the temperature range 625-725 K, the nonmonotonic dependence of iHc on the temperature and soak time, the appointment of preliminary high-temperature treatment at 1175 K. One of the alloying chemical elements that lead to an iHc growth and a temperature stability of the properties of magnets is titanium. Herewith iHc is quite sensitive to the chemical composition of the alloy, in particular, to changes in the content of titanium and boron [7]. As follows from this work, titanium alloying of such alloy as Nd17Fe75.5Ti8B4 leads to the occurrence of borides TiB2, complex eutectic (Nd-Fe-Ti-B), and titanium replace iron atoms in the lattice of the Nd3Fe14B phase at position 8j2. The highest solubility of titanium in the Nd3(Fe,Ti)14B phase (0.34 wt. % and 0.48 at%) and the maximum intrinsic coercive force is in the composition of the alloy Nd17Fe73.7Ti1.28B8.

Research results of the effect of boron additives and heat treatment parameters on the magnetic properties and phase composition of the Nd-Fe-Ti-B permanent magnets are shown below. Crystallographic model of formation of a microstructure in compounds of the Nd3Fe14B type with titanium is also proposed.
2. Methods
Magnets with composition (wt. %) Nd – 34.60, Fe – 63.95, B – 1.35 (check alloy) and Nd – 34.60, Ti – 0.96, B – 1.10, Fe – 63.34 (base alloy 1) were made by the conventional powder metallurgy method. The ingots were crushed to a coarse powder and then were ground in a vibration ball mill. Alloying of the titanium-containing alloy was carried out by admixing of amorphous boron to the powder of the base alloy 1 before the fine grinding operation in an amount of 0.10; 0.15; 0.20; 0.30 wt. % for samples 2, 3, 4, 5, respectively. The powder was aligned in a field of 1.5 T transverse to the pressing direction and was compacted with 100 MPa. The green compacts were sintered at 1350-1410K for 2 h. The final annealing was at 600-1200K for 1 h. The magnetic properties were determined with a hysteresigraph at room temperature. A chemical analysis of structural components were performed by the use of the Comebax radiospectrum micro-analyzer. Microstructure and domain structure were studied in the samples with the help of the Neophot-30 microscope. Crystallographic models were developed in programs Atoms V6.0 and Diamond ver. 3.1b.

![Graphs](image)

**Figure 1.** $H_c$ dependence of the sequentially increasing in temperature from 525 to 1175K heat treatment by duration 3,6 ks for Nd-Fe-Ti-B magnets. The letters mean the dependences of various initial conditions: 1175K, 3,6 ks + 1025K, 3,6 ks (a); 1175K, 3,6 ks + 1025K, 3,6 ks + 675K, 36 ks
3. Results and discussions
Figure 1 shows the graphs of connection between the $H_r$ of the magnets (1-5) and the sequentially increased temperature of annealing by duration 3.6 ks for the various initial condition. Fall in $H_r$ (line a) or its growth (line b) happens at magnification of temperature of an annealing from 525 K up to 675-825 K in an association from the initial condition. This difference of $H_r$ behaviour in an association from the initial condition is eliminated at higher temperatures of heat treatment. Optimum temperatures of the annealing of the 1-3 samples are 1025-1050 K. At further increasing of a content of the boron (samples 4 and 5), the graphs have at the beginning "plateau" in the interval of temperatures 775-1075 K(sample 4), corresponding maximum value ($B_i$), then - a second maximum $H_r$ in the interval 825-875 K(sample 5). Increasing of heat treatment temperature up to 1175 K leads to the $H_r$ falling.

Microstructures and domain structure studies of same samples have shown that between them is not observed essential difference, in spite of the profound difference of values. Excluding can be a fact "flaking-destroying" of boundary phases of low-coerctive samples during preparation of the microsections, it can point to the stress condition of boundaries. By means of the scanning electron microscopy and local X-ray analysis, a phase composition and sharing the elements in phase forming magnets were researched. Magnets consisted of $\Phi$-phase with the contents of titanium not more 0.48 at.%, borides (TiB$_2$ and Nd$_6$Fe$_{51}$B$_{24}$) of complex eutectic, in which enters titanium in the form of boride component (Nd-3.9, Fe-5.0, Ti-66.9, B-24.2 wt. %), RE - rich phase, including neodymium oxides.

An analysis of the magnetization curve from the thermally-demagnetized state and the shape of the domain structure of sintered magnets with titanium, indicates that they are implementing a magnetization reversal mechanism due to a delay in the nucleation of the reverse domains.

For the check alloy (Nd-34.60, Fe-63.95, B-1.35), which does not contain titanium, pattern of $H_r$ change depending on the heat treatment temperature, which are characteristic for ternary alloys based on Nd-Fe-B [1], are preserved, namely, the presence of one $H_r$ peak at temperature 775-875 K (in this case, at 825 K). Depending on the initial state, a different behavior of $H_r$ is observed at low annealing temperatures (475-775 K).

The $H_r$ dependency graphs on the temperature and duration of low-temperature annealing of the magnets with composition (wt.%) Nd – 34.60, Fe – 63.24, Ti – 0.96, B – 1.20 (sample 2) are shown in Figure 2. At the first stage (graphs 1-3), the series of samples was subjected to various temperature effects in the interval 475-1175 K with successively increasing soaking times from 0.4 to 57.6 ks. As can be seen from Figure 2, the graphs are nonmonotonic. The temperature corresponding to the minimum of $H_r$ decreases with an increase summary soaking time from 825 to 725 K. After soaking at 725 K for 57.6 ks, $H_r$ decreases from 1056 kA/m (state after sintering) to 520 kA/m, i.e. more than twice. A less deep minimum is also observed in the temperature range of 875-975 K, and with an increase in the soaking time, this minimum shifts also toward lower temperatures. At temperatures of 925 K and 975 K, with an increasing soaking time, $H_r$ fall is replaced by its growth. It should be noted that nature of the variation of iHc in the temperature range 625-675 K is nonmonotonic. The fact that there are no $H_r$ changes at T = 825 K and soaking time of more than 3.6 ks indicates the presence of various causes forming a high-coerctive state. The maximum $H_r$ corresponds to a heat treatment temperature of 1025-1050 K, and the growth process practically ending after 0.4 ks. A further $H_r$ increase is achieved after additional heat treatment: 1175 K, 3.6 ks + 1025 K, 3.6 ks.

As it follows from Figure 2 (graphs 7-11) with a consistent increase in soaking time of all samples at 725 K to 57.6 ks, the nature of the $H_r$ change is qualitatively preserved, the absolute value of $H_r$, in all cases decreases. During subsequent treatment (Figure 2, upper part of the right graph) at T = 1025 K, 7.2 ks, the values of iHc increase sharply for all magnets in the series. Additional heat treatment (1175 K, 3.6 ks + 1025 K, 7.2 ks) leads to an iHc increase in some samples and decrease in other samples of the series (Figure 2, graph 13).

It is found that in the sintered permanent magnets in which the maximum values of iHc are realized, a reversible cyclic change of this parameter is observed for various heat treatments: at T = 1025 K (maximum) and at T = 1175 K (minimum).
Figure 2. Graphs of $H_c$ dependence of the magnets of Nd-34.6, Fe-bal, Ti-0.96, B-1.20 (wt. %) composition on the temperature and duration of low-temperature annealings. Digits 1 – 7 mean total duration (ks) of the annealing. Digits 8 – 11 duration (ks) of the subsequent annealing at 725K: 8 – 7.2; 9 – 14.4; 10 – 28.8; 11 – 57.6. Digits 12 and 13 indicate the regimes of subsequent heat treatments respectively: 1025K, 7.2 ks and 1175K, 3.6 ks + 1025K, 7.2 ks

In Figure 3 and Figure 4 graphically presented: a flat and a 3-dimensional crystallographic model, showing the optimal phase conjugation of Nd$_2$Fe$_{14}$B and TiB$_2$. The error of conjugation is less than 4%, which is significantly less than the difference in the Nd$_2$Fe$_{14}$B$_{12}$ and TiB$_2$ phases [3-4].

Analysis of the experimental data provides an opportunity to suggest that to explain the dependence of the intrinsic coercive force on the parameters of heat treatment for various chemical compositions, it is necessary to take into account the change of state of the main and boundary phases due to diffusion processes and phase transfers. Magnets with titanium, but without cobalt and nickel, have a higher $H_c$ than that of permanent magnets Nd$_{15}$Fe$_{77}$B$_8$ and Nd$_{15}$(Fe$_{0.6}$Co$_{0.3}$Ni$_{0.1}$Ti$_{0.01}$)$_{77}$B$_8$, and also sufficiently high (800 kA/m) magnetic properties are observed immediately after sintering, in contrast to magnets of the type Nd$_{15}$Fe$_{77}$B$_8$ (400-480 kA/m) [1].

4. Conclusions
Heat treatment at T = 1025 K increases $H_c$ to 960-1040 kA/m. This can be attributed to two reasons: the difficulty of the grains growth of the main Nd$_3$Fe$_4$Bp hase during sintering due to the presence of TiB$_2$ borides in the intergranular space, and due to the stabilization of the Nd$_3$Fe$_4$B phase grains by nanodispersed TiB$_2$ borides within this phase and by dissolved titanium. During heat treatment at 1025 K, titanium, which occur in a solid solution, presumably diffuses to the nanoprecipitation of TiB$_2$, thereby improving the conjugation of the Nd$_3$Fe$_4$B and TiB$_2$ lattices. The consequence of this is an increase in $H_c$. Such an explanation does not contradict the experimental data [8], the absence of a homogeneity region in boron in the compound Nd$_3$Fe$_4$B.
5. References

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