Formation of the High-Coercive State in Rare-Earth Magnets

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Abstract—The effect additives of $TbAl_3$ hydride have on the magnetic properties and structure of sintered permanent magnets based on Pr−Fe−Co−Cu−B alloy with increased temperature stability is studied. Such magnetic properties as $B_r = 1.07$ T, $BH_{max} = 216$ kJ m^{-3}, $_jH_c = 2000$ kA m^{-1}, $H_k = 1680$ kA m^{-1}, $H_k/_jH_c = 0.84$, and $\alpha = -0.030\%$ °C^{-1} (in the temperature range of 20−100°C) are achieved.

INTRODUCTION

There are currently two main groups of rare-earth sintered hard-magnetic materials (alloys of Nd−Fe−B and Sm−Co−Fe−Cu−Zr) in which such mechanisms of magnetization as the nucleation delay of reverse domains and the delay in the displacement of domain boundaries [1] are observed, respectively. The latter group of hard-magnetic materials has better temperature stability, due to its higher Curie temperatures, but requires more complex manufacturing technology [2]. The structural state of the $Nd_2Fe_{14}B$ phase plays an important role in the first group of hard-magnetic materials [3−5]. The structural state of the main phase can be altered substantially (e.g., to improve its stability, to create an elastic-stressed state inside it, or to create a nanoheterogeneous distribution of alloying elements), by doping the base alloy in particular, along with features of the technological processes (e.g., mechanical doping, hydride dispersion, and using additives of hydrides of rare-earth metals). This allows us to greatly enhance the technological and operational resistance of permanent magnets (PMs). PMs are doped with such elements as Dy, Tb, Pr, and Co to improve their temperature stability on the basis of $Nd_2Fe_{14}B$ intermetallic compound.

The aim of this work was to optimize the composition of Nd−Fe−B alloy and the process for reducing the reversible temperature coefficient of magnetic induction (α) to values that correspond to sintered magnets based on Sm−Co alloys (0.03% °C^{-1}).

EXPERIMENTAL

Our initial alloys with the chemical composition shown in Table 1 were smelted in a vacuum induction furnace from pure charge materials in a medium of especially pure argon. Their chemical composition was monitored via atomic emission spectroscopy. Magnets with the chemical composition of the C-alloy and the ratio of this alloy with the addition of $TbAl_3$ were chosen such that the resulting chemical composition of the magnet corresponded to that of magnet B. The base alloys (1−3) and the additive alloy of $TbAl_3$ were subjected to hydride dispersion in a dry hydrogen channel at 400°C for 1 h, and were then finely ground inside a vibration mill for 50 min in isopropyl alcohol to a mean particle size of 3 microns. Joint fine grinding with the addition of $TbAl_3$ (1.2 wt %) was done for C magnets. The magnets were pressed in a transverse magnetic field and sintered for 2 h at $T = 1100$°C, after which they were thermally treated in vacuum for 2 h at $T = 900$°C and then slowly cooled (1−2°C min^{-1}) to 500°C and kept at this temperature for 1 h. Magnetic measurements were made using a MH-50 hysteresig-

Table 1. Chemical composition of the alloys (wt %)

Magnet	Nd	Pr	Tb	Fe	Co	B	Cu	Al	$TbAl_3$
A	21.6	−	10.4	46.4	19.9	1.1	0.2	0.4	−
B	−	21.6	10.4	46.4	19.9	1.1	0.2	0.4	−
C	−	21.6	9.6	46.4	19.9	1.1	0.2	−	1.2

Table 2. Magnetic properties of the alloys at room temperature

Magnet	B_r, T	BH_{max}, kJ m^{-3}	$_jH_c$, kA m^{-1}	H_k, kA m^{-1}	$H_k/_jH_c$
A	1.110	240	1240	810	0.65
B	1.064	214	1680	1210	0.72
C	1.070	216	2000	1680	0.84

raph in a closed magnetic circuit. The reversible temperature coefficient of magnetic induction (α) was measured in the temperature range of 20–100°C on magnet samples using a vibration magnetometer, and in a magnetic circuit using a teslameter and a microwebermeter. The Curie temperature (T_C) was determined by measuring the temperature dependences of the initial magnetic permeability and magnetization. The microstructure of the magnets was investigated via optical and scanning microscopy (SEM) and local X-ray diffraction analysis (LXRDA). X-ray analysis of powders prepared from sintered magnets was done on a DRON-3M diffractometer using copper CuK_α radiation and a graphite monochromator.

RESULTS AND DISCUSSION

The data from magnetic measurements of PMs at room temperature using the MH-50 hysteresisgraph in a closed magnetic circuit are presented in Table 2. Coefficient α was measured in the temperature range of 20–100°C. It was 0.060, 0.030, and 0.030% °C^{-1} for magnets of types A, B, and C, respectively. Analysis of these measurements shows that such parameters as residual induction B_r, maximum energy product BH_{max}, and coefficient α (in absolute value) were greater in magnitude for magnet A than for B- and C-type magnets. However, the other parameters (coercive magnetization force $_jH_c$ and demagnetizing field intensity, at which the residual magnetization was 90% of H_k and $H_k/_jH_c$) are much lower. For B- and C-type magnets, such parameters as B_r, BH_{max}, and α almost coincide. Parameters $_jH_c$, H_k, and $H_k/_jH_c$ were greater in magnitude for C magnets than those of B magnets.

The results from measuring the magnetic properties of C-type magnets at elevated temperatures in the range of 20–100°C are presented in Table 3. These data allowed us to determine the temperature coefficient of the coercive magnetization force. It was 0.55% °C^{-1} in the temperature range of 20–100°C. Curie temperature T_C for the investigated magnets was found to be ~490, ~560, and ~570°C for magnets of the A, B, and C types, respectively.

SEM and LXRDA studies of microstructure showed that the chemical composition of the main phase in A-type magnets is expressed by the formula $(Nd_{0.8}Tb_{0.2})_2(Fe_{0.8}Co_{0.2})_{14}B$ (at %). In addition to the main phase, ones such as $(Nd,Tb)_3(Fe,Co)$,

$(Nd,Tb)_{rich}$, $(Nd)_{1.1}(Fe,Co)_4B_4$, $(Nd,Tb)(Fe,Co)_2$ were observed. The composition of the main phase for B- and C-type magnets was $(Pr_{0.7}Tb_{0.3})_2(Fe_{0.72}Co_{0.28})_{14}B$. In the latter case, there was a gradient distribution of terbium and aluminum in the grain (which was maximal at the grain boundaries). There was no boundary high-permeability Laves phase in B- and C-type magnets.

The lower structurally sensitive parameters ($_jH_c$, H_k, and $H_k/_jH_c$) for A-type magnets, relative to those of types B and C, can be explained by there being a lower terbium content in the main magnetic phase, and by the presence of high-permeability phase $(Nd,Tb)(Fe,Co)_2$. The data from magnetic measurements (i.e., the high values of such parameters as B_r and BH_{max} for A-type magnets) also testify to this phenomenon. This follows from the magnetic moment of terbium atoms being directed antiparallel to the magnetic moments of cobalt and iron atoms in a phase lattice of the $(Nd,Pr)_2Fe_{14}B$ type, while it has lower saturation magnetization and double the values of the anisotropy field (~21 T). For comparison, the anisotropy fields for the $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$ compounds were ~7 and ~9 T, respectively [1].

The more structurally sensitive parameters ($_jH_c$, H_k, and $H_k/_jH_c$) for C-type magnets compared to those of the B type are explained by the high content of terbium and aluminum in the boundary region of the main magnetic phase. A similar effect was observed earlier on sintered cobalt-free magnets of the $(Nd,Pr,Tb)_2Fe_{14}B$ type, i.e., an increase in $_jH_c$ when there was a gradient of terbium [3, 5] and/or aluminum [6].

Table 3. Magnetic properties of magnet C at elevated temperatures

T, °C	B_r, T	BH_{max}, kJ m^{-3}	$_jH_c$, kA m^{-1}
20	1.070	216	2000/25.1
50	1.062	212	1552/19.4
80	1.052	209	1230/15.4
100	1.045	205	1120/14.1

CONCLUSIONS

It was shown that praseodymium stabilizes the structure of intermetallic compounds of the $(Pr,Tb)_2(Fe,Co)_{14}B$ type with high contents of cobalt (up to 20 wt %). Adding $TbAl_3$ hydride during the manufacture of sintered magnets enhances the coercive magnetization force and improves the temperature stability of magnetic induction.

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