Effect of Annealing of a Pr−Dy−Fe−Co−B Alloy on Its Phase Composition and the Properties of Related Sintered Magnets

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Abstract—The effect of annealing of a $(Pr_{0.41}Ce_{0.12}Dy_{0.47})_{13.46}(Fe_{0.64}Co_{0.36})_{80.3}B_{6.24}$ alloy at 1000°C on its microstructure and the properties of sintered magnets made of it has been studied. In the annealed state, the composition of the main magnetic phase $(Pr,Dy)_2(Fe,Co)_{14}B$ changes sharply (dysprosium content changes), the residual induction of the sintered magnets made of the annealed alloy increases by 6%, and the coercive force determined from magnetization increases by 8.5%. The volume content of the main magnetic phase $R_2(Fe,Co)_{14}B$ in sintered magnets $(Nb,Dy)−(Fe,Co)−B$ and $(Pr,Dy)−(Fe,Co)−B$ is found. The content of this phase in neodymium-based magnets is approximately half as much.

INTRODUCTION

The influence of the phase composition of an alloy on the properties of sintered magnets made of it is undeniably a deciding factor, particularly, in the case of a multiphase alloy belonging to the R−Co−B system (R is rare-earth metal or metals (REM)). The R−Co−B [1−4] and R−(Fe,Co)−B [5−8] systems are enriched in intermetallic compounds as compared to the R−Fe−B system [9]. In particular, the region of the Nd−Fe−B phase diagrams, to which the compositions of fabricated sintered Nd−Fe−B magnets correspond, contains only three phases, namely, $Nd_2Fe_{14}B$, $NdFe_4B_4$, and an intercrystalline phase consisting of neodymium with impurities of iron and boron with an approximate composition 95 at % Nd, 3−5 at % Fe, and traces of B [10]. The same is also true of Pr−Fe−B [9]. It is the phase consisting of neodymium (or praseodymium) that provides liquid-phase sintering of Nd(Pr)−Fe−B magnets. Sintered $(Pr,Dy)−(Fe_{1-y}Co_y)−B$ materials with $y > 0.2$ do not contain a pure praseodymium phase, and the sintered magnet corresponds to the Pr−Co−B phase diagram [11]. The phase composition of the magnet is only determined by the cobalt content and is independent of dysprosium alloying [12]. In [12], it was shown that the sintering of $(Pr,Dy)−(Fe_{1-y}Co_y)−B$ materials is liquid-phase over

the entire cobalt content region. It was supposed that the main components forming a liquid phase are the following compounds: $(Pr,Dy)(Fe,Co)_2$, $(Pr,Dy)(Fe,Co)_2B_2$, $(Pr,Dy)(Fe,Co)_4B$, $(Pr,Dy)(Fe,Co)_3B_2$, and $(Pr,Dy)(Fe,Co)_3$. However, this conclusion is based on the phase compositions of sintered magnets rather than alloy ingots [12]. It is natural to expect that the phase composition of an ingot and magnets can be different. The phase compositions of the as-cast metals were not studied in [12].

The materials alloyed with cobalt and heavy REMs were studied in a number of works [13, 14]. For example, the study of $(Nd_{21}Pr_{0.23}Dy_{0.43}Tb_{0.06}Gd_{0.07})_{13.9}(Fe_{0.80}Co_{20})_{78.49}Cu_{0.03}Al_{0.2}B_{7.38}$ materials in [13] showed that the magnetization of the sintered material significantly increased as the cobalt content decreased quite sharply. It is related to that the cobalt ion in the intermetallic $(Pr,Dy)_2(Fe,Co)_{14}B$ compound has a magnetic moment 1.4 μB, unlike the magnetic moment of the iron ion (2.2 μB) [15]. The $(Pr_{0.50}Dy_{0.50})_{13.84}(Fe_{0.65}Co_{0.35})_{77.88}Al_{0.74}Cu_{0.16}B_{7.38}$ material was studied in [14]. It should be noted that the temperature coefficients of induction (TCI) of the material were given in [13, 14]; however, it is known that the temperature dependences of the magnetization of the materials of the noted compositions are
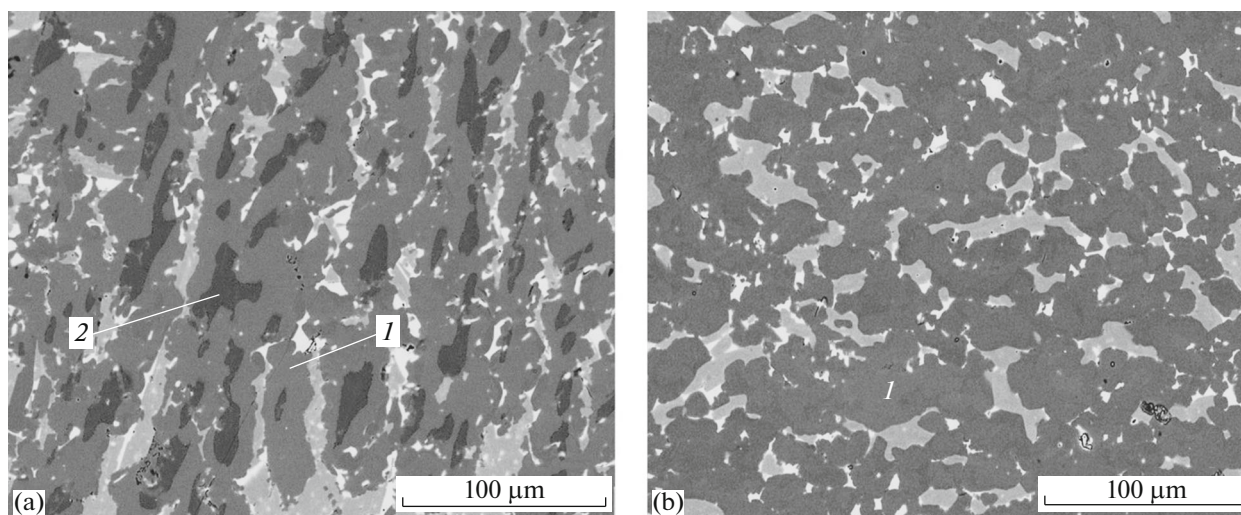
Fig. 1. Microstructures the $(Pr_{0.41}Ce_{0.12}Dy_{0.47})_{13.46}(Fe_{0.64}Co_{0.36})_{80.3}B_{6.24}$ alloy ingot in (a) as-cast state and (b) after annealing at 1000°C for 10 h. (*1*) $(Pr,Dy)_2(Fe,Co)_{14}B$ phase and (*2*) $(Pr,Dy)_2(Fe,Co)_{14}B$ phase of a changed composition.

always characterized by a maximum in the temperature range 0−40°C and the maximum is dependent on the cobalt content. Because of this, it is incorrect to characterize it using only TCI [16]. According to [17], copper exactly replaces iron in the intermetallic compound $(Pr,Dy)_2(Fe,Co)_{14}B$ alloyed with copper; i.e., the cobalt content in it increases. As is shown in [16] for samples with different copper contents and an unchanged cobalt content, the maximum in the temperature dependence of magnetization decreases as the copper content increases. It means that the thermal stability of the material increases.

In this work, we studied the phase composition of the as-cast metal before and after annealing in a vacuum furnace and the properties of sintered magnets made of it.

EXPERIMENTAL

$(Nd,Dy)−(Fe,Co)−B$ and $(Pr,Dy)−(Fe,Co)−B$ alloys with different cobalt contents were prepared in a vacuum induction furnace in an argon atmosphere. Alloy ingots were milled into particles <630 μm in size in a cone inertial crusher with nitrogen blowing, and the particles were then fragmented in a centrifugal planetary mill in a Solkane 141b CN cooling medium. Prismatic magnet preforms were fabricated by pressing in a magnetic field 800 kA/m applied perpendicular to the pressing force. Sintering was carried out at 1100−1140°C (1 h) in an SNVE 1.3.1/16I3 vacuum furnace. Magnets were fabricated from both the initial alloy ingots and the annealed ingots. The contents of the main magnetic phase $R_2(Fe,Co)_{14}B$ were determine in all magnets. The phase compositions of the as-cast ingot of the $(Pr_{0.41}Ce_{0.12}Dy_{0.47})_{13.46}(Fe_{0.64}Co_{0.36})_{80.3}B_{6.24}$ alloy and the ingot annealed at 1000°C (10 h) in an SNVE 1.3.1/16I3 vacuum furnace were comprehen-

sively studied. Electron-probe microanalysis (EPMA) was carried out using a Karl Zeiss EVO MA10 scanning electron microscope equipped with an SDD (silicon-drift) energy-dispersive detector (X-MAX Oxford Instruments) for EPMA with an active crystal area of 80 mm² and with the AZTEC Energy software. The analysis locality was 1 μm² and the analysis depth was 1 μm. Micrographs were taken in the backscattered electron mode, where contrast is determined by the mean atomic number of the phase. The larger the mean atomic number of the phase, the brighter this phase in a photograph. It should be noted that phases can hardly be distinguished in contrast (particularly, when the content of one of them is low); nevertheless, their compositions can be quantitatively determined. The magnetic characteristics of the magnets made of the as-cast alloy ingot and the annealed ingot were measured on a PERMAGRAPH C300 hysteresisgraph.

RESULTS

Figures 1a and 1b show the microstructures of the ingots of the $(Pr_{0.41}Ce_{0.12}Dy_{0.47})_{13.46}(Fe_{0.64}Co_{0.36})_{80.3}B_{6.24}$ alloy in the as-cast and annealed states. It follows that the main magnetic phase $R_2F_{14}B$ (F = Fe + Co) of the initial ingot is heterogeneous and consists of two phases with different compositions (see Fig. 1a). In Fig. 1b, these phase are slightly different in contrast; because of this, we failed to determine the volume content of the inclusion ($R_2F_{14}B$ phase of a changed composition). According to the interpretation of the phase compositions of the ingots (Table 1), the dysprosium contents in the $R_2F_{14}B$ phase and in the inclusion in the as-cast alloy ingot are higher than those in the annealed alloy. In addition, in the as-cast

Table 1. EPMA results of the $(Pr_{0.41}Ce_{0.12}Dy_{0.47})_{13.46}(Fe_{0.64}Co_{0.36})_{80.3}B_{6.24}$ alloy ingot

Ingot	Phase*	Phase content, vol %	Phase composition, atomic fraction
As-cast	$R_2F_{14}B$	64.8	$(Pr_{0.50}Dy_{0.50})_2(Fe_{0.68}Co_{0.32})_{14}B$
	Inclusion $R_2F_{14}B$	14.1	$(Pr_{0.38}Dy_{0.62})_2(Fe_{0.70}Co_{0.30})_{14}B$
	RF_4B	15.9	$(Pr_{0.48}Ce_{0.02}Dy_{0.50})(Fe_{0.54}Co_{0.46})_4B$
	RF_3B_2	3.3	$(Pr_{0.46}Ce_{0.03}Dy_{0.50})(Fe_{0.49}Co_{0.51})_3B_2$
	RF_2	2.4	$(Pr_{0.80}Ce_{0.03}Dy_{0.18})(Fe_{0.41}Co_{0.59})_2$
After annealing	$R_2F_{14}B$	77.6	$(Pr_{0.53}Ce_{0.05}Dy_{0.42})_2(Fe_{0.65}Co_{0.35})_{14}B$
	Inclusion $R_2F_{14}B$	**	$(Pr_{0.61}Ce_{0.07}Dy_{0.32})_2(Fe_{0.66}Co_{0.34})_{14}B$
	RF_4B	17.7	$(Pr_{0.46}Ce_{0.13}Dy_{0.41})(Fe_{0.49}Co_{0.51})_4B$
	RF_2	3	$(Pr_{0.72}Ce_{0.15}Dy_{0.13})(Fe_{0.43}Co_{0.57})_2$

* In the phase composition, F = Fe + Co, R = Pr + Dy + Ce.
** We failed to determine the phase content because of insufficient contrast.

Table 2. Properties of the magnets fabricated of the $(Pr_{0.41}Ce_{0.12}Dy_{0.47})_{13.46}(Fe_{0.64}Co_{0.36})_{80.3}B_{6.24}$ alloy in (numerator) as-cast and (denominator) annealed (at 1000°C for 10 h) states

ρ, g/cm^3	B_r, T	H_{cJ}, kA/m
7.83	0.90	936
7.84	0.95	1016

In the initial alloy, the $R_2F_{14}B$ phase composition is enriched in dysprosium almost by 20% as compared to that in the annealed alloy. In addition, as is seen from Table 1, the dysprosium content in the as-cast alloy inclusion is almost twice as high as that in the annealed alloy inclusion. Thus, the increase in B_r in the magnets fabricated of the annealed alloy (Table 2) can be quite well explained: despite a decrease in the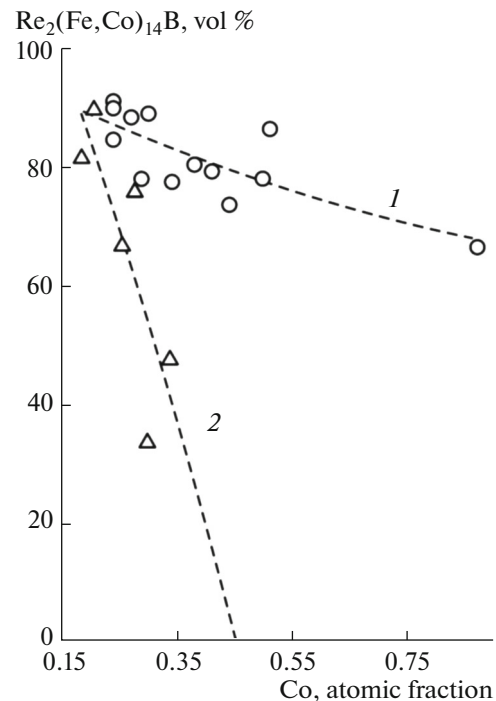 alloy, the inclusion of the $R_2F_{14}B$ phase of a changed composition has a higher dysprosium content than in the main $R_2F_{14}B$ phase and a lower dysprosium content than in the annealed alloy. Attention is drawn to the fact that, in the as-cast alloy, the $R_2F_{14}B$ phase does not contain cerium, but the annealed alloy contains cerium and the cerium content in other phases is significantly higher.

Table 2 gives the properties of the magnets fabricated of the as-cast and annealed alloys. It is seen that the characteristics of the magnets fabricated of the annealed alloy are higher in residual induction B_r (by 6%) and in coercive force H_{cJ} (by 8.5%). Figure 2 shows the dependence of the volume content of the $R_2(Fe,Co)_{14}B$ phase in the sintered materials on the cobalt content for the (Pr,Dy)–(Fe,Co)–B and (Nd,Dy)–(Fe,Co)–B compositions. Figure 3 shows the calculated data for the temperature dependence of the magnetization calculated in a molecular-field approximation by the procedure described in [19].

DISCUSSION

It is known that cerium in the $R_2F_{14}B$ compound is in the ionic Ce^{4+} state and has a zero magnetic moment [9], and dysprosium and praseodymium are in the Dy^{3+} and Pr^{3+} states, respectively, and have magnetic moments of 10 and 3.1 μB, respectively [9].

Fig. 2. Volume content of the $R_2(Fe,Co)_{14}B$ phase in the sintered materials ((*1*) (Pr,Dy)–(Fe$_{1-y}$Co$_y$)–B, (*2*) (Pr,Dy)–(Fe$_{1-y}$Co$_y$)–B) as a function of the cobalt content.
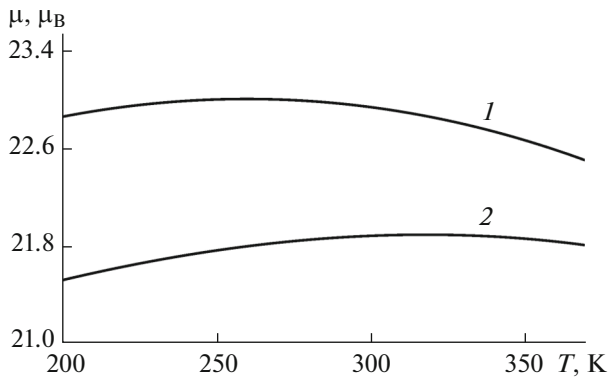
Fig. 3. Temperature dependence of the saturation magnetization of sintered magnets (*I*) $(Pr_{0.52}Dy_{0.48})_{13.56}(Fe_{0.80}Co_{0.20})_{79.55}B_{6.89}$ and (*2*) $(Pr_{0.52}Dy_{0.48})_{13.56}(Fe_{0.65}Co_{0.35})_{79.55}B_{6.89}$. Magnetization μ is given per the formula unit of the $(Pr,Dy)_2(Fe,Co)_{14}B$ phase in Bohr magnetons.

content of the main magnetic phase $R_2F_{14}B$, its composition is significantly depleted of dysprosium, whose magnetic moment is directed antiferromagnetically with respect to the magnetic moments of praseodymium, iron, and cobalt. It should be underlined that we failed to determine the amount of the magnetic phase−inclusion because of weak contrast. The surprising thing is the absence of cerium in the $R_2F_{14}B$ phase of the as-cast alloy and its significantly lower contents in all the phases as compared to the annealed alloy. In this case, the amount of the cerium-containing phases increases. It can be supposed that, in the initial alloy, cerium is nonuniformly distributed in the ingot, which was not detected by EPMA. The cause is not clear up to now. It seems likely that it is the low dysprosium content in the $R_2F_{14}B$ phase that leads to an increase in residual induction B_r of the magnets fabricated of it. This is likely to be related to the segregation inhomogeneity of the ingot. The Ce^{4+} ion has the smallest ionic radius; because of this, it initially substitutes for Dy^{3+} ions, the radius of which is smaller than the Pr^{3+} radius [20]. Thus, when the $R_2F_{14}B$ phase is alloyed with nonmagnetic Ce^{4+} ions, magnetic Dy^{3+} and Pr^{3+} ions occupy certain rather than arbitrary sites; in this case, the exchange interaction in the lattice is changed. As is seen from Table 1, a liquid phase forms during sintering mainly from two phases RF_4B and RF_2, from which RF_4B is main. In Fig. 2, the curves demonstrate a sharp difference between the volume contents of the $R_2(Fe,Co)_{14}B$ phase in the neodymium- and praseodymium-based materials. The content of the $R_2(Fe,Co)_{14}B$ phase in the neodymium-based magnets is lower by a factor of almost two at a Co content of 0.35 atomic fractions. This makes the (Nd,Dy)−(Fe,Co)−B magnets unpromising because of a low residual induction.

CONCLUSIONS

(1) We determined the volume content of the main magnetic $R_2(Fe,Co)_{14}B$ phase in sintered magnets (Nd,Dy)−(Fe,Co)−B and (Pr,Dy)−(Fe,Co)−B (R = Nd, Pr, Dy). This phase content in the neodymium-based magnets is lower by a factor of almost two.

(2) Annealing of the ingot at a temperature of 1000°C for 10 h leads to a decrease in the dysprosium content in the main magnetic phase $(Pr,Dy)_2(Fe,Co)_{14}B$. The cobalt content is changed insignificantly. The magnetic characteristics of the magnets fabricated of the annealed alloy are higher in residual induction (by 6%) and coercive force determined from magnetization (by 8.5%) as compared to those of the initial alloy.

(3) Two phases, RF_4B and RF_2 (F = (Fe + Co)), where the first phase is main, take part in the formation of a liquid phase in sintering.

(4) The main magnetic $R_2F_{14}B$ phase in the initial ingot is inhomogeneous and consists of two phases with different dysprosium contents.

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