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Research Article

Improvement of Thermal Stability of Nd-Tb-Fe-Co-B Sintered Magnets by Additions of Pr, Ho, Al, and Cu

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The present work investigates the influence of Pr, Al, Cu, B and Ho which were introduced into the Co-containing sintered magnets of Nd-Dy-Tb-Fe-Co-B type on the magnetic parameters (α, ${}_iH_c$, B_r, $BH_{\max}$). The effect of heat treatment parameters on magnetic properties was also studied. It was revealed that the essential alloying of NdFeB magnets by such elements as Dy, Tb, Ho, Co as well as by boron-forming elements, for example, by titanium, may lead to reducing of F-phase quantity, and, as a consequence, to decreasing of magnetic parameters. It was also shown that additional doping of such alloys by Pr, B, Al and Cu leads to a significant increase of the quantity of F-phase in magnets as well as solubility of the Dy, Tb, Ho and Co in it. This promotes the increase of magnetic parameters. It was possible to attain the following properties for the magnets $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ (at. %) after optimal thermal treatment {1175 K (3,6–7,2 ks) with slow (12–16 ks) cooling to 675 K and subsequently remaining at $T = 775$ K for 3,6 ks—hardening}: $B_r = 0,88$ T, ${}_iH_c = 1760$ kA/m, $BH_{\max} = 144$ kJ/m^3, $\alpha < |0,01|$%/K in the temperature interval 223–323 K.

1. Introduction

High-energy (the maximum energy product, $BH_{\max} > 400$ kJ/m^3) and high-coercive (intrinsic coercivity, ${}_iH_c > 2400$ kA/m) sintered permanent magnets can be produced now on the base of $Nd_2Fe_{14}B$ compound [1]. However, these magnets are significantly inferior to such materials as alnico, $Sm_2(Co,Fe,Cu,Zr)_{17}$, and $SmCo_5$ in reversible magnetic losses, which are characterized by remanence temperature reversible coefficient $\{\alpha = (\Delta B_r/B_r \cdot \Delta T) \cdot 100\%/K$, where is B_r—remanence$\}$.

Some improvement of this parameter is possible to achieve when replacing some Fe atoms by Co and some Nd ones by Dy (Tb). For example, $\alpha = -0.06\%$/K in the temperature interval 295–375 K was attained on the sintered magnets of $\{Nd_{0,8}(Dy,Tb)_{0,2}\}_{15\text{-}16}(Fe_{0,8}Co_{0,2})_{bal}\cdot B_{6\text{-}8}$ type after heat treatment {remaining at $T = 1175$ K for 7.2 kilosecond (ks) followed by the cooling with the rate of 0.01-0.02 K/s down to 575–705 K and duration at this temperature for 3.6 ks} [2–5].

Experimental saturation magnetization temperature dependences for single-phase compound of $(Nd_{1\text{-}x}R^*_x)_2(Fe_{1\text{-}y}Co_y)_{14}B$, where R*—Dy, Tb, Gd, and Ho are available [6–8]. It follows from these dependencies that for attaining near-zero α coefficient values in the operation temperature interval (295–375 K, in some case 225–425 K), it is necessary that x and y values should be 0.4-0.5 and 0.2-0.3 correspondingly.

However, if the content of R* and Co is more than 7,5 at.% ($x > 0,2$) and 15 at.% ($y > 0,2$) in the alloy of $(Nd_{1\text{-}x}R^*_x)_{15\text{-}16}(Fe_{1-y}Co_y)_{bal}\cdot B_{6\text{-}8}$ type, regularities observed for the single-phase compound no further hold true: while α coefficient shows no further changes, B_r and ${}_iH_c$ decrease with the speed higher than that observed for the single-phase compound. This makes impossible to achieve near-zero α coefficient value and optimal B_r and ${}_iH_c$ parameters [2]. It was explained [2] by phase equilibrium shifting resulting in new additional phases of $(Nd,R^*)(Fe,Co,B)_2$, $(Nd,R^*)(Fe,Co)_4B$ and other types [9–11] formation and decreasing of $(Nd,R^*)_2(Fe,Co)_{14}B$ phase quantity when the alloy is doped by R* and Co.

On the other hand, similar regularity of $Nd_2Fe_{14}B$ phase quantity decreasing and no further $_iH_c$ rising at the increasing of dysprosium (terbium) in the alloy were observed in $\{Nd_{0,8}(Dy,Tb)_{0,2}\}_{15\text{-}16}(Fe,Ti,Nb)_{bal} \cdot B_{6\text{-}7}$ type alloys. It was shown that doping of these alloys by Pr, Al, Cu as well as increasing of the boron content up to 8-9 at.% makes it possible to overcome this negative effect [2].

That is why the purpose of the present work was to investigate the influence of Pr, Al, Cu, B, and Ho introducing into the Co-containing sintered magnets of Nd-Dy-Tb-Fe-Co-B type on the magnetic parameters (α, $_iH_c$, B_r, BH_{max}). The effect of heat treatment parameters on magnetic properties was also studied.

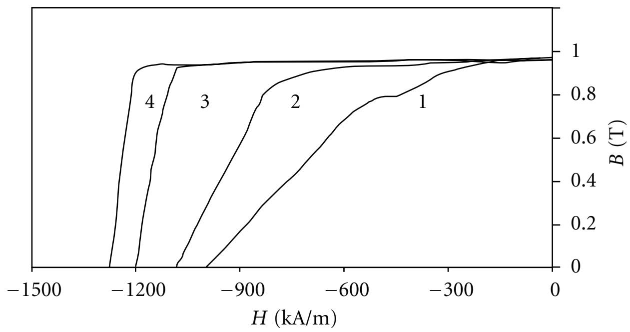

Figure 1: Demagnetizing parts of hysteresis loops of the magnets: $(Nd_{0,3}Pr_{0,5}Dy_{0,2})_{15}(Fe_{0,8}Co_{0,2})_{bal}\cdot Al_{0,2}B_z$, where z is 5,3 (1, $_iH_c$ = 980 kA/m), 6,3 (2, $_iH_c$ = 1070 kA/m), 7,3 (3, $_iH_c$ = 1190 kA/m), 8,3 (4, $_iH_c$ = 1250 kA/m).

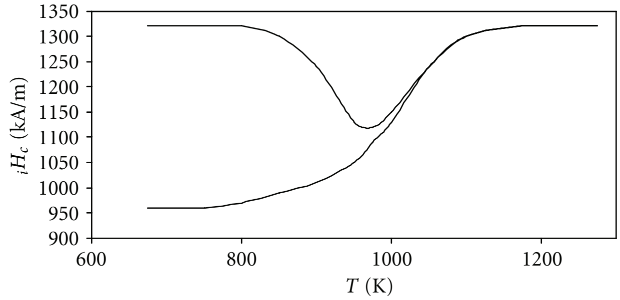

Figure 2: Dependences of $_iH_c$ of $(Nd_{0.25}Pr_{0.4}Dy_{0,35})_{15}(Fe_{0,72}Co_{0,28})_{bal}\cdot Al_{0,2}B_{7,5}$ magnets on the heat treatment temperature for the single (upper curve) and multistep heat treatment in the temperature 1275 K–675 K interval.

2. Experimental Procedure

Alloys of the $(Nd,Pr,Tb,Dy,Ho)_{12,5\text{-}17,0}(Fe,Co,Al,Nb,Ti,Cu)_{bal}\cdot B_{5,5\text{-}8,5}$ (at.%) type were prepared by vacuum-induction melting. Magnets were prepared using a conventional pattern [2]. Heat treatments in the 500–1275 K temperature interval were implemented for the selecting of the optimum schedule for the certain chemical composition alloy.

Investigations of remagnetization processes and magnetic properties evaluations were implemented with the help of hysteresisgraph and vibrating magnetometer. Chemical and phase composition of the alloys were controlled by a plasma emission spectrum method, local X-ray spectrum analysis, X-ray diffraction analysis, and Mössbauer's effect analysis according to procedures described in [2].

3. Experimental Results and Discussion

Figure 1 demonstrates demagnetizing parts of hysteresis loops of sintered magnets with the following chemical compositions: $(Nd_{0,3}Pr_{0,5}Dy_{0,2})_{15}(Fe_{0,8}Co_{0,2})_{bal}\cdot Al_{0,2}B_z$, where z is 5,3 (1, $_iH_c$= 980 kA/m), 6,3 (2, $_iH_c$ = 1070 kA/m), 7,3 (3, $_iH_c$ = 1190 kA/m), 8,3 (4, $_iH_c$ = 1250 kA/m) at room temperature. The optimal heat treatment schedules for these magnets were the following: 1175–1275 $\mathcal{K}$, 3,6 ks with subsequent quenching in inert gas (z = 5,3–7,3) and 1175 K, 3,6 ks + slow cooling (10–12 ks) + 900 K, 3,6 ks with subsequent quenching in inert gas (z = 8,3). Significant $_iH_c$ increasing is observed with the z raising from 5,3 up to 8,3. At the same time quadratility H_k (demagnetization field that reduces the intrinsic magnetization by 10%) of the curve was also improving.

Figure 2 demonstrates the dependences of $_iH_c$ on the heat treatment temperature for the $(Nd_{0,25}Pr_{0,4}Dy_{0,35})_{15}(Fe_{0,72}Co_{0,28})_{bal}\cdot Al_{0,2}B_{7,5}$ chemical composition. The upper curve reflects the results of the experiments when the samples were exposed to teat treatment only at some given temperature in the 675–1275 K interval with a 50 K step. Lower curve demonstrates the case when each sample was exposed to multistep heat treatment starting from 1275 K for 3,6 ks with the sequential reducing of the temperature down to 675 K (interval between stages was 50 K; endurance on the each stage was 3,6 ks). The value of $_iH_c$ was measured after the each stage. As can be seen from Figure 2, minimum of $_iH_c$ on upper curve corresponds to 975 K, while for the lower curve monotonous decreasing of $_iH_c$ from 1320 kA/m (1275 K) down to 960 kA/m (675 K) is observed. Analogous regularities are observed for chemical compositions $\{(Nd_{0,35}Pr_{0,65})_{1\text{-}x}Dy_x)\}_{15}(Fe_{1-y}Co_y)_{bal}\cdot Al_{0,2}B_{7,5}$ (at.%), x = 0,3-0,4, y = 0,22–0,30.

Higher level of magnetic properties (B_r = 0,88 T, $_iH_c$ = 1760 kA/m, magnetic field energy BH_{max} = 144 kJ/m^3, $\alpha < |0,01|$%/K in temperature interval 223–323 K) was obtained on sintered magnets with chemical composition $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ after the optimal heat treatment: 1175 K (3,6–7,2 ks) with slow (12–16 ks) cooling to 675 K and subsequently remaining at T = 775 K for 3,6 ks—hardening. Demagnetizing curves at various temperatures (from 293 K to 423 K) and the temperature $_iH_c$ dependence for the multistep heat treatment starting from 1175 K to 675 K with 3,6 ks endurance on the each stage are presented on Figures 3 and 4, respectively. The other part of the samples was continuously cooled from 1175 K to 675 K. Time of cooling was equal to the total endurance time during multistep heat treatment.

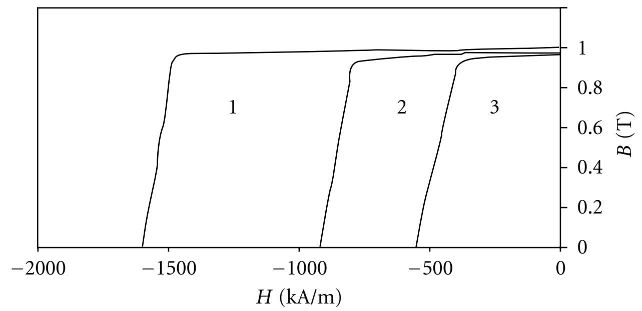

Figure 3: Demagnetizing parts of hysteresis loops of the magnets $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ at the temperatures 293 K (1, $_iH_c$ = 1600 kA/m), 373 K (2, $_iH_c$ = 920 kA/m), 423 K (3, $_iH_c$ = 550 kA/m).

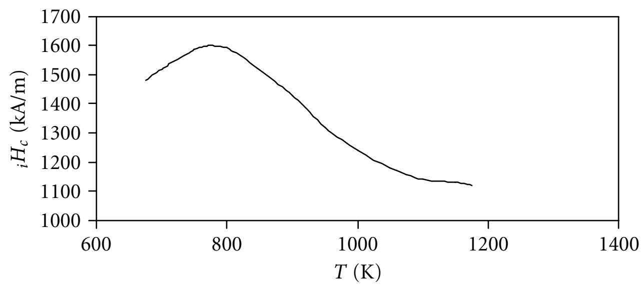

Figure 4: Temperature $_iH_c$ dependence of $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ magnets after multistep heat treatment (1175 K to 675 K).

It was noted that there is no significant difference in $_iH_c$ values between continuous and multistep changing of the temperature during heat treatment. Only total endurance time in the studied temperature interval is important. As a rule, it should be not less than 10 ks. Significant reduction of $_iH_c$ by 20–30% from the optimal value is observed at the rapid cooling (e.g., at the quenching in inert gas).

On the next stage we investigated the properties of the magnets additionally doped by titanium as it is known that this element increases $_iH_c$ in $Nd_{15}Fe_{bal}\cdot B_8$ magnets [2]. For the magnets $(Nd_{0.15}Pr_{0.35}Tb_{0.25}Ho_{0.25})_{15}(Fe_{0.71}Co_{0.29})_{bal}\cdot Al_{0,9}Cu_{0.1}Ti_{0.7\text{-}1.4}B_{8.5}$, the reduction of $_iH_c$ down to 1280–1360 kA/m occurs. The optimal heat treatment was revealed to be the high temperature at 1275 K with subsequent quenching down to the room temperature. Similar regularities were also observed for the alloy doped by Nb.

Significant $_iH_c$ increasing (up to 2100 kA/m) was observed in the sintered magnets, produced by the blending of the powders of the two alloys which had the extreme content of such elements as Tb, Ho, and Co (96 and 4 mass.% resp.): $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ and $(Nd_{0,2}Pr_{0,4}Tb_{0,4})_{15}(Fe_{0,8}Co_{0,2})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$. It might be explained by the chemical composition gradient in the near-boundary regions of the grains (higher Tb content and lower Co content).

It is known [2, 7, 8] that in order to increase thermal stability of $Nd_2Fe_{14}B$ compounds, such elements as Tb, Dy, Ho, and Co are introduced into the alloys. However if their content exceeds the critical level in the magnets, as is the case for instance for the magnet compositions $Nd_{0,8\text{-}x}(Tb,Dy,Ho)_x(Fe_{0,8\text{-}y}Co_y)_{bal}\cdot B_8$), where $x > 0{,}2$, $y > 0{,}2$, plummeting of the main magnetic parameters (B_r, $_iH_c$, BH_{max}) occurs. However, it was revealed that if the alloy beside these elements additionally doped by Pr, Al, and Cu, and the content of B is increased, simultaneous improving of all magnetic parameters (B_r, $_iH_c$, BH_{max}, α) is observed while x = 0,3-0,4 and y = 0,2-0,3. The optimal chemical composition was found to be $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ which provides the best combination of all investigated magnetic parameters including thermal stability. As follows from X-ray spectrum and Mössbauer effect analysis, this might be explained by the fact that alloying by Pr, Al, Cu, and B results in the simultaneous increasing both of F-phase content in magnets and the content of Dy, Tb, Ho, and Co in F-phase.

Parameters of optimal heat treatment for this composition are the following: 1175 K (3,6–7,2 ks) with subsequent (continuous or step) slow (10–12 ks) cooling to optimal temperature (775 K) and endurance at this temperature for 3,6 ks. It might be assumed that the improving of the main magnetic parameters after this treatment schedule is caused by the better isolation of the F-phase grains due to the Nd (or Nd and Pr) diffusion from F-phase into the grains boundaries [2, 12]. The temperature and endurance of the optimal thermal treatment depend on the F-phase homogeneity (in Nd or rare-earth element) region, which is determined by the chemical composition of the alloy and its production technology. Homogeneity region of F-phase is widened by such elements as Pr, Ga, and hydrogen and narrowed by Gd, Dy, Tb, Ho, Co, and Ni.

We assume to use these new compositions for recording heads for high coercivity media [13] and for GMFG {giant magnetic field gradient} devices for separation of dia-, para-, and weak magnetic materials [14].

4. Conclusion

Significant doping of NdFeB magnets by such elements as Dy, Tb, Ho, Co, Ti, and Nb might lead to the reducing of F-phase quantity and, as a consequence, to decrease of the main magnetic parameters. It was shown that additional alloying by Pr, Al, Cu and increasing of B content results in significant increase of F-phase the content in magnets as well as quantity of Dy, Tb, Ho, and Co in it. This promotes the increase of magnetic parameters.

It was possible to attain the following properties for the magnets $(Nd_{0,15}Pr_{0,35}Tb_{0,25}Ho_{0,25})_{15}$ $(Fe_{0,71}Co_{0,29})_{bal}\cdot Al_{0,9}Cu_{0,1}B_{8,5}$ (at.%) after the optimal thermal treatment {1175 K (3,6–7,2 ks) with slow (12–16 ks) cooling to 675 K and subsequent endurance at T = 775 K for 3,6 ks—hardening}: B_r = 0,88 T, $_iH_c$ = 1760 kA/m, BH_{max} = 144 kJ/m^3, $\alpha < |0,01|$%/K in the temperature interval 223–323 K.

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