DOUBLE SINTERING IN MANUFACTURING THERMOSTABLE Pr-Dy-Fe-Co-B-Cu-Al PERMANENT MAGNETS

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Abstract

The use of double sintering and rare-earth metal hydride additions allows us to substantially increase the hysteretic parameters of sintered permanent magnets having the composition (wt.%): Pr-14.7, Dy-16.9, Co-24.4, B-1.2, Al-0.3, Cu-0.15, Fe balance. The following magnetic characteristics were reached: B_r = 0.95 T, $_jH_c$ = 1640kA/m, H_k =1370kA/m, BH_{max} = 176 kJ/m^3, temperature coefficient of induction $|\alpha|< 0.01$ (T=-60°C to+100 °C). The found weak dependence of structure-sensitive parameters, such as $_jH_c$ and H_k on the cooling rate from the low-temperature heat-treatment temperature (500 °C) is discussed in connection with the invar and magnetostrictive behavior of the principal magnetic phase $(Pr,Dy)_2(Fe, Co)_{14}B$ at temperatures below the Curie temperature, which were used for the low-temperature treatment. Measurements of temperature dependences of the electrical resistivity of the magnets allowed us to demonstrate the presence and absence of the electrical-resistivity anomaly corresponding to the Curie temperature for magnets free from cobalt and with high cobalt content, respectively.

Keywords: Thermostable magnets (Pr,Dy)-(Fe,Co)-B, invar behavior, double sintering, low-temperature treatment, hysteretic parameters

1. INTRODUCTION

Sintered magnets based on $R_2Fe_{14}B$ (with R = rare-earth metal) intermetallic compounds are widely used in technology owing to their high both maximum energy product (BH_{max}), remanence (B_r), and magnetization coercive force ($_jH_c$) [1]. To increase the $_jH_c$ parameter that is responsible for the temperature and time stability of sintered magnets, the base composition ($Nd_{14-15}Fe_{ост.}B_{6-8}$) is alloyed with a number of elements, such as Pr, Dy and Tb (to increase the anisotropy field H_a), Ti, V, Mo and Nb (to prevent the grain growth during sintering and realize the 2-14-1 phase structuring), Al, Ga, and Cu (to improve the structure of boundary phases. To form the optimum structure and decrease the grain size, the following technological processes are used: strip-casting, hydrogen decrepitation and mechanical alloying that can be performed using binary mixtures (mixture of base $R_2Fe_{14}B$-based powder and REM or REM compounds additions) [2, 3]. The application of binary mixtures allows one to improve the structure of boundary phases and grain boundaries of the main magnetic phase and to realize the diffusion of required component of alloy directly through boundaries. Thus, the gradient distribution of the component within a grain can be formed. This effect reached by the binary-mixture technology is similar to that produced by the diffuse saturation of magnet surface with rare-earth metals and their compounds [4, 5]. However, in the last case, the diffusion of a component is realized within a magnet no

more than 4x4x4 mm in size, whereas, in the case of binary mixtures, the sizes of magnet are unlimited. Heat treatments at 800÷ 900°C and multistage heat treatments of magnets at temperatures of 475 ÷ 1000 °C [1], which are performed after sintering, are used to reach the required hysteretic properties of magnets. To decrease the reversible coefficient of magnetic induction (**α**), which determines the magnetic induction stability in a temperature range of -60 °C÷ +100°C, the Nd-Fe-B compositions are alloyed simultaneously with Dy, Tb, Pr (to 20 wt. %) and Co (to 25 wt. %) [6-10].

To realize the high-coercivity state in Nd-Fe-B magnets, the following three stages are of importance: (1) the formation of the state via sintering and low-temperature treatment (LTT) (at 500÷ 600 °C), (2) it fixation after LTT (usually via quenching at a rate of 10÷ 100 °C/s), and (3) retention of the state during operation.

The present work is aimed at the study of peculiarities of the formation of the high coercivity state of sintered Pr-Dy-Fe-Co-Al-Cu-B magnets in using double sintering [11] and different cooling rates (from 100 °C/s to 25 °C/h) from the LTT temperature.

2. EXPERIMENTAL

Starting alloys were prepared by induction melting in a high-purity argon atmosphere using pure charge components (Pr and Dy 99.8 wt.% purity, Armco iron, K0 cobalt, aluminum and copper 99.99 wt.% purity, crystalline boron no less than 99.99 wt.% purity) and subsequently were cast into a water-cooled copper slot (20 mm) mould. The chemical (charge) composition (wt.%) of the alloy is Pr-14.7, Dy-16.9, Co-24.4, B-1.2, Al-0.3, Cu-0.15, Fe-42.35 (was checked by atomic emission spectroscopy). The alloy was subjected to hydrogen decrepitation at 100 °C for 1 h in a dry hydrogen flow and subsequent fine milling for 50 min to a particle size of ~3 μm using a vibrating mill and an isopropyl-alcohol medium. After pressing and preliminary sintering at 1060 °C for 2 h, the sintered blank was subjected to repeated hydrogen decrepitation and fine milling with 2-wt% PrH_2 addition. After pressing in a transverse magnetic field and sintering at 1100 °C for 2, magnets were subjected to heat treatment in a vacuum at 900 °C for 2 h, slow cooling to 500 °C, and holding at this temperature for 1 h (magnet PM1) and 20 h (magnet PM2). The magnets were cooled to room temperature by either furnace cooling (for 2 h) or by quenching (for no more than 1 min). Reference magnets of the same composition were prepared using single sintering at 1060 °C for 2 h. After mechanical grinding of the magnets with a diamond tool and magnetization to technical saturation, their magnetic properties were measured at room temperature in fields of 3 T using a hysteresisgraph and closed magnetic circuit. The $|\alpha|$ coefficient was measured at temperatures of -60°C - +100 °C using a vibrating-sample magnetometer and with a magnetic circuit as well. The microstructure of magnets, which were subjected to electrolytic etching in a solution of chromium anhydride in orthophosphoric acid, was studied by atomic force microscopy (AFM). The domain structure (DS) of samples was studied by optical and scanning-probe microscopy using Neophot-30 and Axiovert 200MAT optical and Solver P47 scanning-probe microscopes. The electrical resistivity of permanent magnets was measured to an accuracy of 2.5% using a four-probe wilding technique and samples 2x2x15 mm^3 in size.

3. RESULTS AND DISCUSSION

The magnetic hysteresis properties (B_r, ${}_jH_c$, H_k, BH_{max}, $|\alpha|$) of magnets prepared by double sintering and reference magnet are given in **Table 1** and **Figure 1**. The magnetization (from thermally demagnetizing state) curves of them and dependences of ${}_jH_c$ and B_r on the magnetizing field are typical of magnets, the magnetization-reversal mechanism of which is due to the delayed growth of reverse magnetization nuclei [1].

It should be noted that the coercive force (${}_jH_c$) of PM2, which was held at 500 °C for 20 h, is higher substantially than that of PM1 and almost coincides with that of the magnet prepared by single sintering, which demonstrates the significantly lower B_r and BH_{max} magnitudes. In this case, the structure sensitive parameters, such as ${}_jH_c$ and H_k of the magnet prepared by singe sintering were independent on the holding time in a range of 1÷ 20 h.

Table 1 Magnetic properties of magnets prepared by double sintering with PrH_2 and at different holding at 500 °C, which are given in comparison with those of the reference magnet prepared by single sintering

Parameter	PM1 (1 h)	PM2 (20 h)	Reference magnet (single sintering)
B_r (T)	0.95	0.95	0.90
${}_jH_c$ (kA/m)	800	1600	1608
H_k (kA/m)	573	1353	1300
$(BH)_{max}$ (kJ/m^3)	164	176	153
$\lvert\alpha\rvert$(T=-60 to +100 °C) (%/K)	<0.01	<0.01	<0.01

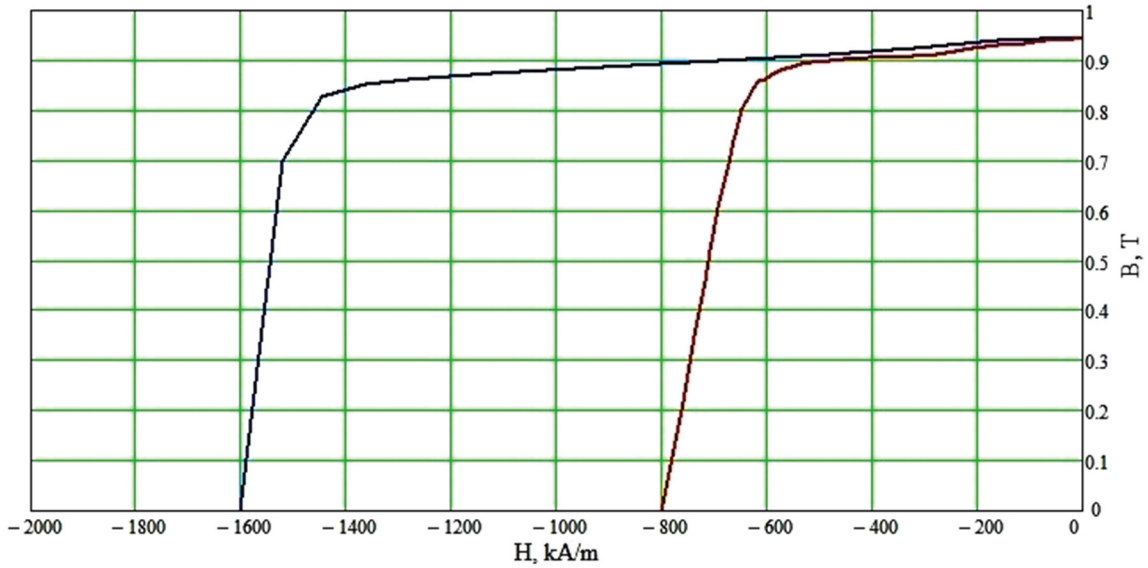

Figure 1 Magnetization reversal curves for permanent magnets (red curve) PM1 and (blue curve) PM2

The higher remanence of magnets prepared by double sintering is likely to be related to the possible increase in the content of main magnetic 2-14-1 phase (and, therefore, B_r and $(BH)_{max} = B_r^2$) at the expense of improvement of the structure and removing the ballast R_2O_3, RM_2 and R_{rich} phases (owing to their higher brittleness and faster milling as compared to those of the 2-14-1 magnetic phase) together with the milling medium (isopropyl alcohol) separated from the powder. The increase in the content of main magnetic phase is likely to be the cause for the higher coercive force of the magnet prepared by double sintering followed by subsequent prolonged holding (20 h) at 500 °C.

Studies of the dependence of hysteretic properties of magnets prepared by double sintering on the cooling rate after LTT showed that the ${}_jH_c$ parameter is almost unchanged over a wide cooling-rate range. This fact allows one to obtain the equivalent magnetic parameters for large magnets and in using massive charges of magnets during LTT, when the high cooling rate is difficult to be realized.

Optical-microscopic studies of the microstructure of magnets indicated no substantial differences in the structure of PM1 and PM2 samples. The average grain size was 20-25 μm.

Figure 2 shows the domain structure of the pole (basis) surface of PM2 (which was determined by AFM (**Figure 2a**) and magnetooptical Kerr effect (**Figure 2b**). The character of the domain structure is typical of hysteresis-free crystals and indicates the adequate texture of the magnets. This fact correlates with the high H_k magnitude, which characterizes the squareness of magnetization-reversal hysteresis loop. The domain structure of PM1 was observed to be analogous to that given in **Figure 2**.

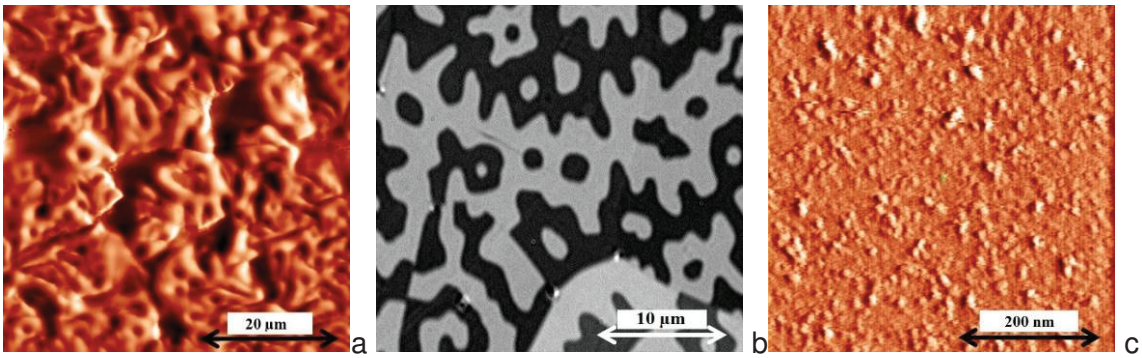

Figure 2 Domain structure on the pole surface of PM2 magnet: (a) magnetic AFM and (b) magnetooptic Kerr effect; (c) AFM image of the pole surface of PM2 magnet after electrochemical etching

Figure 3 shows temperature dependences of the electrical resistivity (ρ) measured for two sintered magnets. As is seen, the dependence for magnet PM2 (as well for PM1) demonstrates the monotonic increase in ρ in contrast to the dependence measured for the magnet low-alloyed with both dysprosium and cobalt, the composition (wt.%) of which is Nd-25.0, Pr-6.0, Dy-2.0, B-1.0, Al-0.4, Cu-0.2, and Fe - balance [12]. This magnet used as a model sample demonstrates the anomaly, i.e., the minimum in the temperature dependence of the electrical resistivity near 300 °C. The observed anomaly is the typical of the $Nd_2Fe_{14}B$ phase [13]. The authors assume, that the formation of the anomaly is related to the existence of, along with the disordered-spin scattering, other electron-magnon and electron-phonon interactions near the Curie temperature. The Curie temperature of the alloy with the high cobalt content is above 600 °C; this is confirmed by the absence of the anomaly in the temperature dependence of the electrical resistivity of the magnet with the high cobalt content (**Figure 3**). It is likely just the fact that the magnetic phase transformation is absent in the temperature range corresponding to the low-temperature treatment range explains the independence of the magnetization coercive force ${}_jH_c$ on the cooling rate from the LTT temperature. We consider the observed phenomenon from the viewpoint of the invar behavior of the main $(Pr,Dy)_2(Fe,Co)_{14}B$ magnetic phase at temperatures below the Curie temperature.

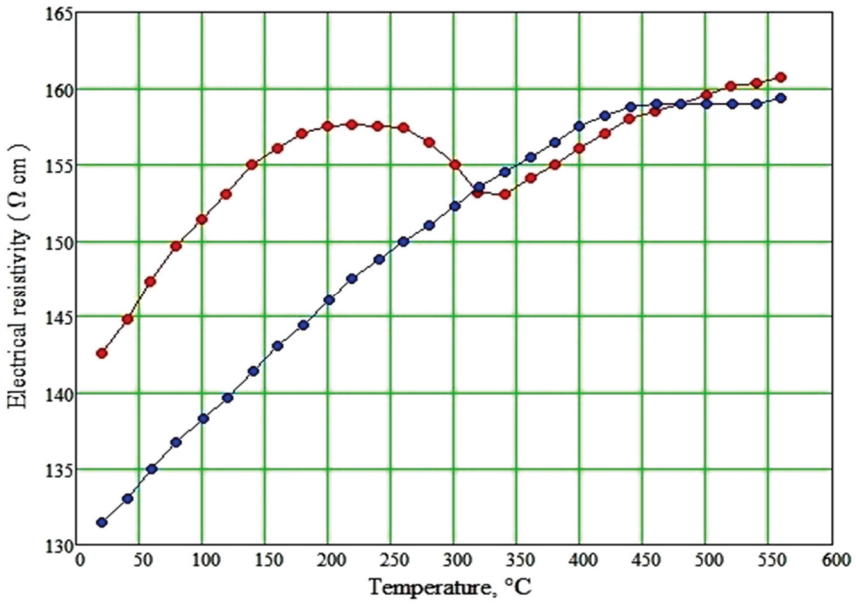

Figure 3 Temperature dependences of the electrical resistivity for magnet PM2 (blue curve) and reference cobalt-free magnet (red curve)

It is known that a number of ferromagnetic compounds of rare-earths with transition metals undergo the lattice compression and expansion during heating and cooling (which are related to the spontaneous volume magnetostriction) in passing through the Curie temperature, respectively [14-16]. The lattice expansion during cooling of the Nd-Fe-B-based alloy near the Curie temperature leads to the compression of grain-boundary phase, decrease in its amount and loss in its nonmagnetic-insulating properties, which determine the high-coercivity state. The absence of magnetic phase transformation in the temperature range of LTT leads to the absence of anomalous lattice expansion of the 2-14-1 magnetic phase during cooling, which already do not disturb the continuity of grain-boundary phase.

The magnetostriction aspect of the invar behavior of the cobalt-alloyed 2-14-1-phase lattice is noteworthy and should be considered individually. It should be noted that the maximum contribution to the invar behavior of the 2-14-1 phase is made by 3*d* metal sublattice and Fe-Fe bonds containing one of Fe atoms in the j_2 position [14]. Projections of the bonds dominate in the basal plane. The cobalt substitution for iron in the $R_2(Fe_{14-x}Co_x)B$ compound leads to, along with the increase in the Curie temperature, disappearance of invar effect (at $x = 0.3$) [17, 18] and decrease in the spontaneous volume magnetostriction with increasing cobalt content at the expense of decrease in the average magnetic moment of the 3*d*-metal sublattice. Cobalt atoms substitute for iron atoms in Fe(*16k*$_2$) [19] positions, which directly are related to j_2 positions, and ensure the lattice "rigidity".

Thus, the effect of main cobalt-containing magnetic phase on the grain-boundary phase during cooling of magnets decreases at the expense of increase in the cobalt-containing 2-14-1-lattice rigidity. This leads to the independence (or slight dependence) of the coercive force on the cooling rate of magnet from the LTT temperature (for traditional Nd-Fe-B magnets, the coercive force decreases in using slow cooling).

The increase in the "rigidity" of the main magnetic phase is possible at the expense of formed compositional nano-heterogeneity, which also can resist the spontaneous magnetostriction of the phase.

The electrochemical etching in the saturate solution of chromium anhydride in orthophosphoric acid and scanning atomic force microscopy allowed us to reveal the micro- and nano-scale relief on the surface of magnet. **Figure 2c** shows AFM image of the pole surface of the studied magnets. The found peculiarity of the studied sample is regular spherical precipitates 10-15 nm in size, which are observed on the etched surface of grain-matrix surface.

It is known that structural materials, in particular, Ti- and Ni-based alloys demonstrate a nonmonotonic dependence of a structure-sensitive parameter, such as the strength on the content of crystal-lattice defects. The increase in the strength characteristics of the alloys is reached also at the expense of both solid-solution hardening and formed heterogeneous structure within main-phase grains, in particular, coherent Ti_3Al or Ni_3Al precipitates. The heterogeneity of the main magnetic phase in hard-magnetic rare-earth materials also can lead to the increase in structure-sensitive parameters, such as (H_k, $_jH_c$) in, for example, $GdCo_4Cu$ and $Sm(Co_{0.8}Cu_{0.2})_{5.2}$ intermetallic compounds and as well sintered magnets based on $(Sm,Gd)Co_5$, $Sm(Co,Ni)_5$ and Nd-Fe-Ti(Mo,Nb,V)-B compositions [1]. In this case, the magnetization-reversal mechanism due to the delayed growth of reverse magnetization nuclei remains. It is likely that the existence of nano-heterogeneous structure (formed also at the expense of the applied REM hydrides) in 2-14-1 magnetic phase grains explains the high H_k magnitudes and unusual increase in $_jH_c$ (that is out of proportion to the H_a magnitude) of sintered magnets alloyed with heavy rare-earth metals (in particular, dysprosium) even in the absence of a gradient of these elements near grain boundaries. The size, shape, and chemical composition of precipitates, i.e., areas enriched in heavy rare-earth elements, which are likely to be due to both the chemical composition of magnet and manufacturing processes, affect substantially the $_jH_c$ magnitude. The nano-heterogeneous structure is formed during milling (mechanical alloying) and sintering. The role of LTT is likely to consist in the improvement of grain-boundary phases at the expense of diffusion of, in total case, light REMs (in our case, Pr) from 2-14-1 phase grains into R_{rich} grain-boundary phases [1, 20-21].

4. CONCLUSION

The use of double sintering and application of REM hydride additions allowed us to substantially improve the energy parameters of $(Pr,Dy)_2(Fe, Co)_{14}B$ magnets. The following characteristics were reached: B_r = 0.95 T, ${}_jH_c$ = 1640 kA/m, H_k = 1370 kA/m, BH_{max} = 176 kJ/m^3, $|\alpha| < 0.01$ (T = -60 ÷ +100 °C).The found weak dependence (and even the absence of the dependence) of the structure sensitive parameters, such as ${}_jH_c$ and H_k on the cooling rate from the LTT temperature for the magnets with the high cobalt content is related to the absence of invar effect for the main $(Pr, Dy)_2(Fe, Co)_{14}B$ magnetic phase at used LTT temperatures (below the Curie temperature).

The double-sintering technology and use of REM hydride additions can be applied for recovery of waste ends of large sintered magnets.

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