

STRUCTURE AND PHASE COMPOSITION OF Tb₃Co_{0.6}Cu_{0.4} ALLOYS FOR EFFICIENT ADDITIONS TO Nd-Fe-B SINTERED MAGNETS

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Abstract

Currently, many attempts have been taken to enhance the coercivity and reduce the heavy rare-earth consumption of Nd-Fe-B sintered magnets simultaneously. Some progresses have been made in efforts to introduce Dy and/or Tb in many forms, namely, oxides, fluorides, hydrides, intermetallic compounds and alloys. The Tb₃Co_{0.6}Cu_{0.4} composition was suggested to apply it as the efficient addition in manufacturing sintered Nd-Fe-B-based magnets. The alloy was prepared by arc melting in purified argon atmosphere, annealed at 600 °C for 90 h and subsequently subjected to hydrogenation. The phase composition and structure of the initial and hydrogenated alloy were studied by electron microscopy, electron microprobe and X-ray diffraction analyses. The in part substitution of copper for cobalt does not change the orthorhombic Fe₃C-type structure (space group *Pnma*) of the Tb₃Co compound. The copper solubility in the Tb₃Co and Tb₁₂Co₇ compounds was determined and the lattice parameters of the compositions were estimated. During hydrogenation, the Tb₃Co_{0.6}Cu_{0.4} composition was shown to decompose into TbH₂₋₃ hydride and fine dispersed (Co, Cu) mixture. Additions of the hydrogenated compound to Nd-Fe-B-based sintered magnets (the initial composition (wt.%) is Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Fe-balance was prepared by strip-casting technique and subjected to hydrogen decrepitation) allow us to manufacture magnets with $B_r = 1.35$ T and $jH_c = 1336$ kA/m.

Keywords: Co-Cu-Tb intermetallics, microstructure, hydrogenation, Nd-Fe-B magnets

1. INTRODUCTION

Currently, many attempts have been taken to enhance the coercivity and reduce the heavy rare-earth consumption of Nd-Fe-B sintered magnets simultaneously. Some progresses have been made in efforts to introduce Dy and/or Tb in many forms, namely, oxides, fluorides, hydrides, intermetallic compounds and alloys. In using many of the additions to powder mixtures for Nd-Fe-B sintered magnets, approaches named as grain boundary diffusion [1-3] and grain boundary restructuring [4-6] are realized. 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. It has been demonstrated that through controlling the process time and temperature in GBDP, the coercivity of the magnet can be greatly enhanced without sacrificing of remanence.

The alloying of the basic Nd-Fe-B composition with rare-earth metals added in the form of hydrides, which allows the improvement of hysteretic properties to be reached, was reported in [7-10]. It was shown previously that the used Tb and Dy hydride additions allow us to increase both the coercive force without sacrificing of remanence [9] and increase the stability of properties of magnets during low-temperature annealing [10].

The grain boundary restructuring with rare-earth-rich low-melting compounds added to base low-alloyed Nd-Fe-B-based compositions in the course of technological processing was realized in [4] with (Pr,Nd)₆Fe₁₃Cu, [5] with Dy_{32.5}Fe₆₂Cu_{5.5}, [6] with Dy₆₉Ni₃₁, [11] with Dy₈₈Mn₁₂ (wt.%) composition, [12] with Pr_{34.4}Co_{65.6} (wt.%), and [13] with Dy_{82.3}Co_{17.7} (wt.%) that is the low-melting eutectic composition. It was shown that intrinsic coercivity increases obviously with the addition of Dy_{82.3}Co_{17.7} and the maximum intrinsic coercivity is obtained when the content of Dy_{82.3}Co_{17.7} was 2 wt.%. At the same time, the remanence and maximum energy product decrease slightly with the increase of Dy_{82.3}Co_{17.7}. By adding a small amount of Dy_{82.3}Co_{17.7}, the coercivity is improved greatly, and the irreversible loss is decreased sharply. The increase of Curie temperature suggests that Co atoms have entered into the 2:14:1 main phase. Microstructural analysis indicates that a well-developed core-shell structure was formed in the magnets with the addition of Dy_{82.3}Co_{17.7}. In all cases in using compositions with a heavy rare-earth metal, it was enriched in the outer region of the Nd₂Fe₁₄B matrix grains during the sintering process, which favored to substitute for Nd in matrix grains to form the (Nd,Dy)₂Fe₁₄B core-shell phase.

The aim of this paper is to study the structure and phase composition of Tb₃Co_{0.6}Cu_{0.4} alloys, which can be used as additions to Nd-Fe-B sintered magnets and allow their magnetic properties to be increased.

2. EXPERIMENTAL

The base alloy having the composition (wt.%) Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Fe-balance was prepared by strip-casting technique and subjected to hydrogen decrepitation during heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h holding at this temperature [9]. The Tb₃Co_{0.6}Cu_{0.4} alloy was prepared by arc melting of starting components in an argon atmosphere on a water-cold copper bottom using a nonconsumable tungsten electrode. The ingot was subjected to homogenizing annealing at 600 °C for 90 h (the analogous annealing conditions were used in [14]). After that, the ingot was subjected to hydrogenation in two regimes: (regime 1) conditions applied for the strip-casting alloy, namely, the heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h holding at this temperature, and (regime 2) stepped heating in hydrogen atmosphere and holding at 200 °C and 500 °C (**Figure 1**) in a glass Sieverts-type apparatus were used. In the case of stepped heating, the hydrogenation up to the Tb₃Co_{0.6}Cu_{0.4}H_x composition with x = 7.65 was realized. We assume that such an hydrogen content corresponds to the complete hydrogenation of terbium to a terbium hydride.

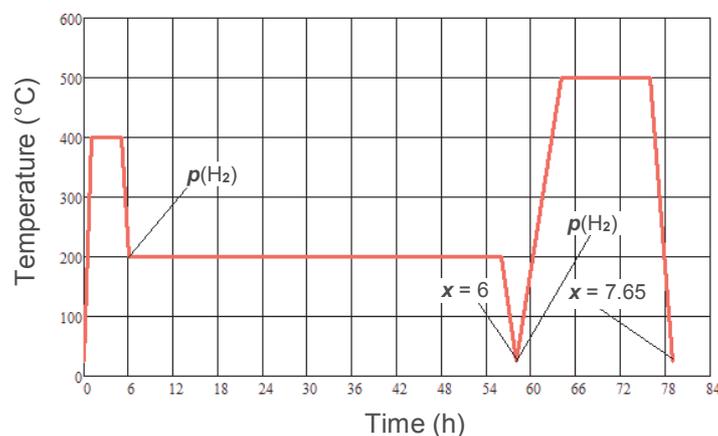


Figure 1 Schedule of hydrogenation of Tb₃Co_{0.6}Cu_{0.4} alloy

The mixture of the hydrogen-decrepitated strip-casting alloy and Tb₃Co_{0.6}Cu_{0.4} alloy hydrogenated under the conditions used for the strip-casting was subjected to fine milling for 40 min to an average particle size of 3 μm using a vibratory mill and isopropyl alcohol medium. After wet compaction of the pulp in a transverse magnetic field of 1500 kA/m, blanks of magnets were sintered at $T = 1080\text{ °C}$ for 2 h and subjected to optimum heat treatment at 500 °C for 2 h. The following subsequent low-temperature stepped heat treatments were used (LHT): 900 °C --- 400 °C; 500 °C --- 400 °C, 20 °C → (40 min) → 500 °C (20 min) → (6 h) → 400 °C (10 h).

Magnetic properties of magnets were studied at room temperature in magnetic fields of to 240 kA/m using a MN-50 hysteresigraph and a closed magnetic circuit.

The structure and phase composition of the annealed and hydrogenated Tb₃Co_{0.6}Cu_{0.4} alloy were studied by X-ray diffraction (XRD) analysis using a Ultima IV (Rigaku), Japan) diffractometer equipped with a "D/teX" detector, CuK_α radiation, and $2\theta = 3\text{-}70^\circ$ angular range; the scanning step is 0.001°. The structure and chemical composition of phases formed in the annealed Tb₃Co_{0.6}Cu_{0.4} alloy were studied by optical microscopy using AxioLabA1 (Carl Zeiss) microscope and the high-resolution field emission gun-scanning electron microscope QUANTA 450 FEG equipped with an EDX APOLLO X microprobe.

3. RESULTS AND DISCUSSION

Figure 2 shows results of metallographic analysis (unetched section) of the Tb₃Co_{0.6}Cu_{0.4} alloy subjected to homogenizing annealing. As is seen, the structure of the alloy is two-phase; the second phase is represented by regular inclusions.

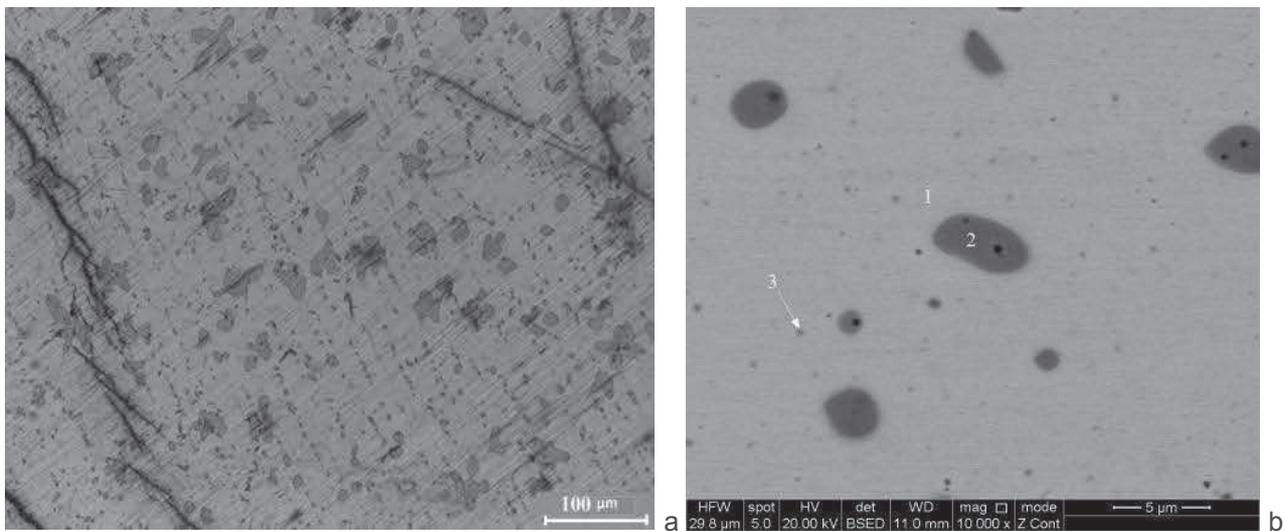


Figure 2 Microstructure of the Tb₃Co_{0.6}Cu_{0.4} alloy subjected to homogenizing annealing:
(a) optical microscopy and (b) SEM: 1 - Tb₃(Co,Cu), 2 - Tb(Co,Cu), 3 - Tb₁₂(Co,Cu)₇

According to X-ray diffraction data of the Tb₃Co_{0.6}Cu_{0.4} alloy (**Figure 3**), the matrix phase is the Tb₃Co-based composition. As is seen, the in part substitution of copper for cobalt does not change the orthorhombic Fe₃C-type structure (space group *Pnma*) of the Tb₃Co compound. The presence of Tb(Cu,Co) was also confirmed by the X-ray diffraction data.

The orthorhombic Fe₃C-type structure of Tb₃Co_{0.6}Cu_{0.4} alloy means that Tb atoms occupy sites of Fe atoms in the crystal lattice. Tb atoms form octahedral with Co atom located at their center. The in part substitution of copper for cobalt does not change the orthorhombic Fe₃C-type structure (space group *Pnma*) of the Tb₃Co compound, but changes its lattice parameters. The lattice parameters of the Tb₃Co compound are $a = 0.6978$

nm, $b = 0.9397$ nm, $c = 0.6272$ nm [15]. The lattice parameters of the $Tb_3Co_{0.6}Cu_{0.4}$ composition were estimated by X-ray diffraction; they are varied $a = 0.6929 - 0.6962$ nm $b = 0.946 - 0.9658$ nm, and $c = 0.6296 - 0.6320$ nm. As is seen, the substitution of Cu for Co changes the lattice parameters: the lattice parameters b and c increase because the radius of Cu atoms (0.128 nm) is higher than that of Co atoms (0.125 nm). However, the decrease of the lattice parameter a takes place. This is likely to be due to the fact that copper atoms substitute for cobalt atoms only in certain positions.

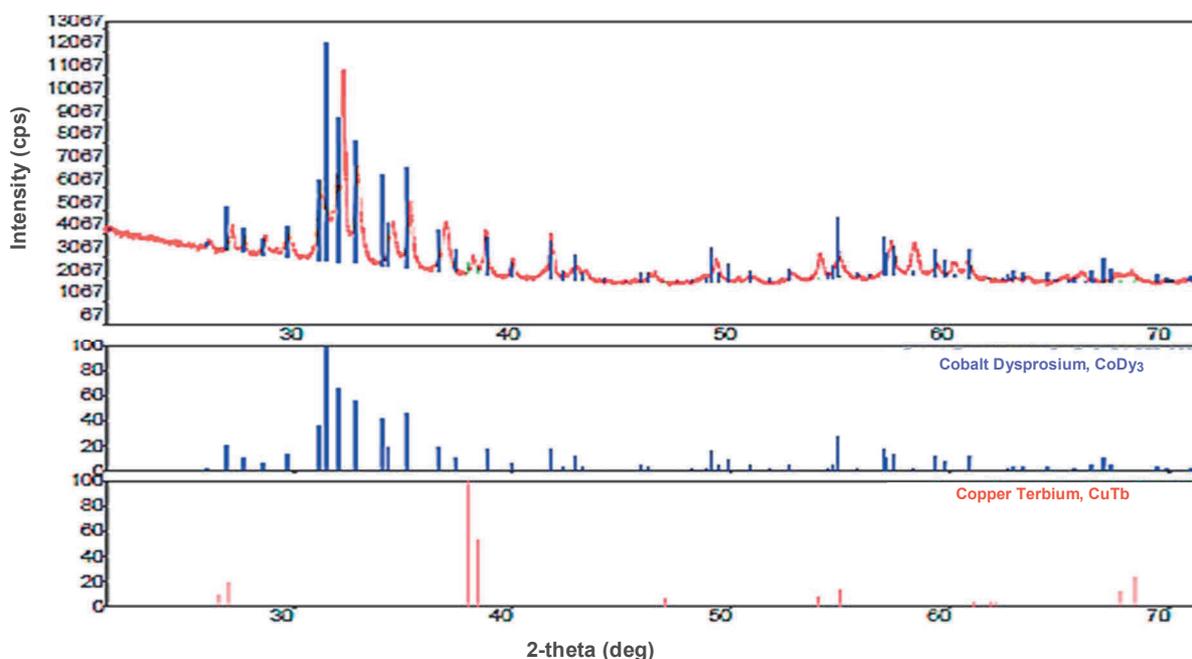


Figure 3 X-ray diffraction patterns for the $Tb_3Co_{0.6}Cu_{0.4}$ alloy after homogenizing annealing; bar diagrams for identified phases are shown (bottom)

The microstructure of the $Tb_3Co_{0.6}Cu_{0.4}$ alloy and chemical composition of found phases were studied by SEM and EDX microprobe analysis (**Figure 2**). The following phases were found: $Tb_3(Co,Cu)$ matrix (point 1), $Tb(Cu,Co)$ inclusions (point 2), and $Tb_{12}(Co,Cu)_7$ fine inclusions (point 3). The content of the latter phase is very low (it cannot be found by X-ray diffraction analysis). According to the electron microprobe analysis data, the composition of the matrix phase is variable $Tb_3(Co_{1-x}Cu_x)$ with $x = 0.25-0.4$; the composition of regular grey inclusions correspond to the $Tb(Cu_{1-y}Co_y)$ composition with $y = 0.05-0.2$. The $Tb_{12}(Co,Cu)_7$ was found can contain copper up to the composition $Tb_{12}(Co_{1-z}Cu_z)$ with $z = 0.4$. Variations of the composition of the matrix Tb_3Co -based phase correspond to the observed variations of the lattice parameters of the phase.

The formation of the 3:1 and 12:7 phase corresponds to the binary Co-Tb system phase diagram, whereas the 1:1 phase corresponds to the binary Cu-Tb phase diagram [16]. We assume that the solidification of the alloy occurs via the primary formation of Tb_3Co -based phase by peritectic reaction; the $TbCu$ -based compound is the secondary phase. According to the Co-Tb phase diagram, the solidification path can include the formation of the $Tb_{12}Co_7$ -based compound by peritectic reaction.

Figure 4 shows the X-ray diffraction pattern for the $Tb_3Co_{0.6}Cu_{0.4}$ compound hydrogenated in regime 1. As is seen, after hydrogenation, the TbH_2 and TbH_3 hydrides are the main phases, i.e. the hydrogenolysis takes place. A small amount of the $Tb_3Co_{0.6}Cu_{0.4}$ matrix phase also is present. However, reflections corresponding to cobalt and copper are not distinguishable. Probably, an ultrafine-grained (Co+Cu) mixture is formed.

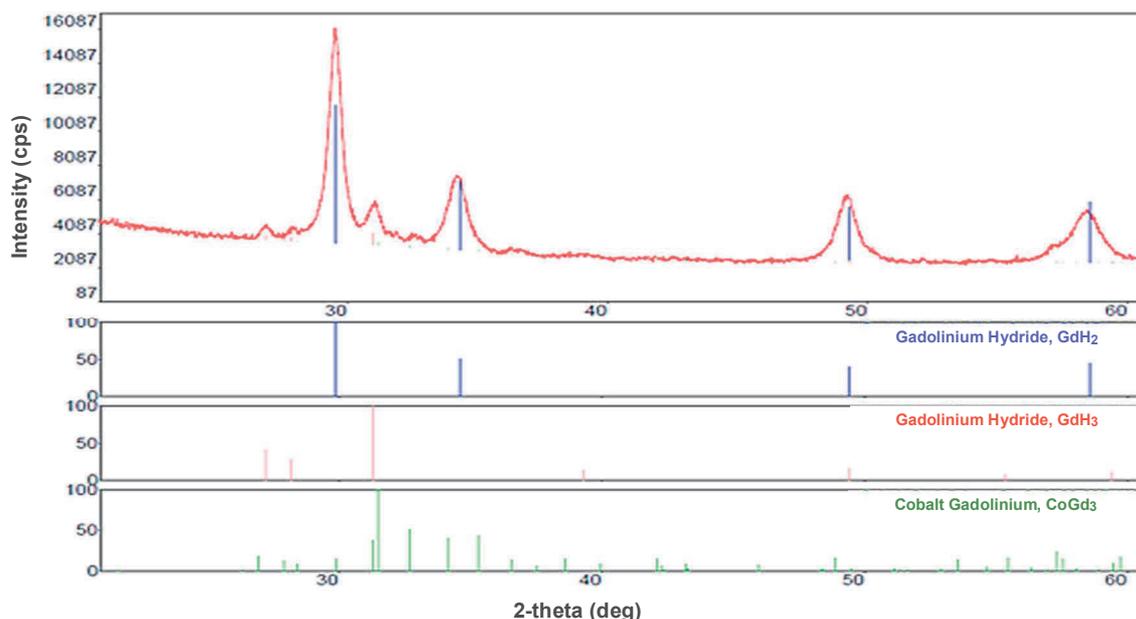


Figure 4 X-ray diffraction patterns for the $Tb_3Co_{0.6}Cu_{0.4}$ alloy after hydrogenation in regime 1; bar diagrams for identified phases are shown (bottom)

Figures 5 a, b shows results of stepped hydrogenation of $Tb_3Co_{0.6}Cu_{0.4}$ in regime 2. After stepped heating in hydrogen atmosphere and prolonged holding at 200 °C and 500 °C, we observed the presence of only the TbH_2 and TbH_3 hydrides. The detailed examination of the X-ray pattern allowed us to find the presence of broadened reflections of cobalt and copper (**Figure 5b**), which can be present in the form of fine-grained mixture. It should be noted that only the most intense reflections of Co and Cu are resolved (Co: $2\theta = 47.44^\circ$, (101); Cu: $2\theta = 43.30^\circ$, (111)).

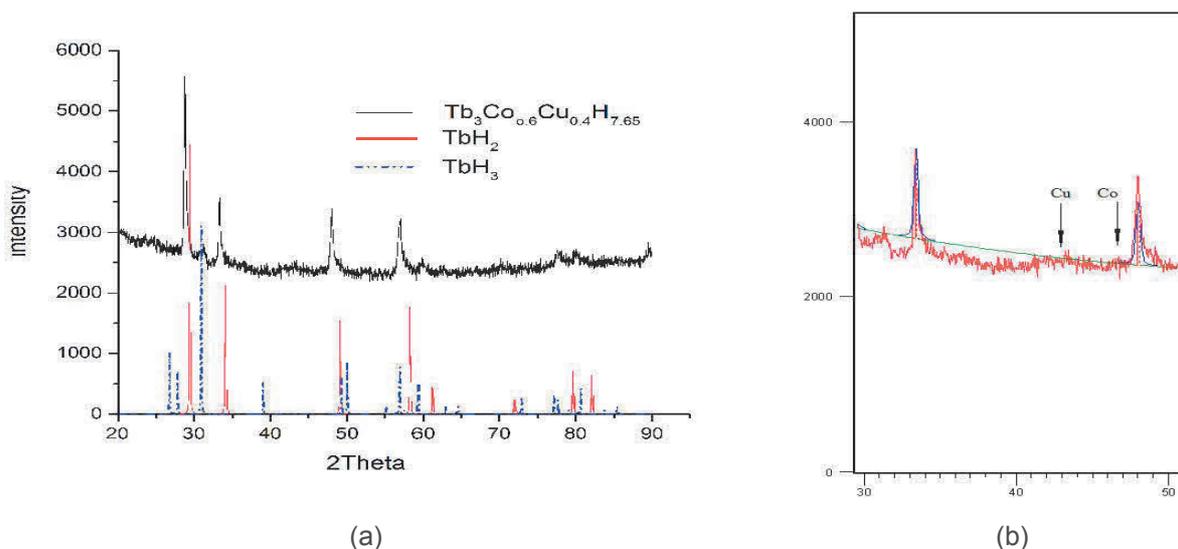


Figure 5 (a) X-ray pattern of the $Tb_3Co_{0.6}Cu_{0.4}$ alloy hydrogenated in regime 2 and (b) a portion of the X-ray diffraction pattern for the angular range $2\theta = 30-50^\circ$

The possibility of disproportionation or hydrogenolysis process in the Co-Pr system for the $Pr(Co,Cu)_5$ composition was demonstrated in [17]. The formation of PrH_{2-3} hydride and Co+Cu mixture (identified based

on clear reflections of Co and Cu) was observed. It was noted that no hydrogen-induced amorphization was found in this system.

Table 1 shows data on magnetic properties of sintered magnets prepared with 2 wt.% hydrogenated addition $Tb_3Co_{0.6}Cu_{0.4}$, which are compared with those obtained for sintered magnets prepared with 2 wt.% TbH_2 [9]. It should be noted that the magnetic properties of the magnets prepared with the hydrogenated $Tb_3Co_{0.6}Cu_{0.4}$ addition are higher than those in the case of TbH_2 [9]. One of possible causes for the increase is the less oxidated state of additions in the case of intermetallic compound. The other possible cause is the improve wettability of $Nd_2Fe_{14}B$ -phase grains with grain-boundary phases alloyed with cobalt and copper.

Table 1 Magnetic properties of sintered magnets prepared with 2 wt.% $Tb_3Co_{0.6}Cu_{0.4}H_x$ (with $x = \sim 2$) and subjected to optimum heat treatment at 500 °C for 2 h and subsequent low-temperature treatment 900 °C --- 400 °C; 500 °C --- 400 °C, 20 °C → (40 min) → 500 °C (20 min) → (6 h) → 400 °C (10 h)

Addition / Annealing conditions	B_r (T)	jH_c (kA/m)	H_k (kA/m)	BH_{max} (kJ/m ³)
$Tb_3Co_{0.6}Cu_{0.4}H_x$ \ optimum	1.35	1336	1200	360
TbH_2 / optimum	1.30	1520	1440	332
$Tb_3Co_{0.6}Cu_{0.4}H_x$ / optimum + low-temperature	1.35	1480		

Studies of the stability of structure-sensitive parameter of sintered magnets, namely, the coercive force jH_c to the low-temperature heat treatments (annealing at temperatures below the optimum heat-treatment temperature (500 °C), such studies are performed in estimating the time and temperature stability of magnets during their operation) show the increase in the coercive force (**Table 1**) up to 1480 kA/m in the case of hydrogenated $Tb_3Co_{0.6}Cu_{0.4}$ addition. This fact is not typical of sintered NdFeB magnets, which usually demonstrates the drop (or constancy) of the coercive force after low-temperature heat treatments at 350-450 °C.

4. CONCLUSION

The phase composition of the $Tb_3Co_{0.6}Cu_{0.4}$ alloy in the initial homogenized and hydrogenated states was studied. The alloy in the homogenized state contains $Tb_3(Co,Cu)$ matrix phase, $Tb(Cu,Co)$ inclusions, and $Tb_{12}(Co,Cu)_7$ fine inclusions. During hydrogenation of the three-phase alloy, the disproportionation or hydrogenolysis process takes place, which, whatever the three-phase composition of initial alloy, results in the formation of TbH_{2-3} hydride and fine (Co+Cu) mixture. The use of the hydrogenated $Tb_3Co_{0.6}Cu_{0.4}H_x$ addition to the powder mixture for manufacturing of sintered permanent magnets allows us to increase their magnetic characteristics. The increase in the hysteretic properties of magnets is related to the combined grain-boundary diffusion and grain-boundary restructuring effect realized with the hydrogenated $Tb_3Co_{0.6}Cu_{0.4}$ alloy addition.

ACKNOWLEDGEMENTS

The research was supported by the NCBR (Poland) within the project "ERA.Net RUS Plus: No. 146-MAGNES" financed by the EU 7th FP, grant no 609556, and Russian Academy of Sciences, project no. III.5.6. This paper was created within the project No. LO1203 „Regional Materials Science and Technology Centre - Feasibility Program" funded by the Ministry of Education, Youth and Sports of Czech Republic and the specific research projects No. SP2017/77 and No. SP2017/58.

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