PHASE FORMATION IN THE Tb-Co-Cu SYSTEM IN A RANGE OF $Tb_3(Co,Cu)$ COMPOUND

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Abstract

In recent years, the application of various additions (hydrides, oxides, intermetallic compounds, etc.) in powder mixtures for manufacturing Nd-Fe-B magnets shows promise as the method that allows one to increase the hysteretic characteristics of the magnets at the expense of realized grain-boundary diffusion and grain-boundary structuring processes. The processes allow one to introduce both the heavy rare-earth metals and copper that was shown also to favour the increase in the hysteretic parameter of Nd-Fe-B-based compositions. In the present work, we consider the alloys $Tb_3(Co_{1-x},Cu_x)$ with x = ~0.4 as additions to Nd-Fe-B-based powder mixtures. The alloys were prepared by arc melting in an argon atmosphere and subjected to homogenizing annealing at 600 °C for 90 h. The phase composition and phase equilibria in the system were studied by X-ray diffraction analysis, differential thermal analysis (DTA), optical and scanning electron microscopy, electron microprobe analysis, and low-temperature thermal magnetic analysis. The composition was shown to be three-phase, $Tb_3(Co,Cu)$, $Tb_{12}(Co,Cu)_7$, and Tb(Co,Cu) that is the primarily solidified phase in the system. The copper solubility in the Tb_3Co and $Tb_{12}Co_7$ compounds and cobalt solubility in the TbCu compound were determined. A portion of the isothermal section of the Tb-Co-Cu system with at 600 °C was constructed. The possibility of the hydrogenation of the $Tb_3(Co_{1-x},Cu_x)$ composition with x = ~0.4 with the formation of TbH_x, Co, Cu was demonstrated.

Keywords: Grain boundary diffusion, Nd-Fe-B magnets, Tb-Co-Cu system, phase equilibria

1. INTRODUCTION

Recently, the significant increase in the hysteretic properties of the sintered Nd-Fe-B-based magnets has been demonstrated in using additions of rare-earth metal (REM) compounds (hydrides, fluorides, oxides, intermetallides and low-melting eutectics). The increase is reached at the expense of grain-boundary diffusion of heavy REM with the formation of $(Nd, R)_2Fe_{14}B$ "shells" at grain boundaries of the main magnetic phase and subsequent grain boundary restructuring [1-10]. The use of R_3Co compounds (R = Nd, Dy) was realized in [11] by introducing them into permanent magnets through the gas phase and led to the increase in the hysteretic properties, namely, in the coercive force from 400 to 875 kA/m.

Earlier, we have showed the application of hydrogenated $R_3(Co, Cu)$ compounds as additions to Nd-Fe-B powder mixtures in order to increase the hysteretic properties of magnets [12]. The use of hydrogenated Cu-containing REM compounds is described in [13] and also demonstrated an extreme increase in the hysteretic characteristics of Dy-depleted magnets owing to the introduction of Cu. The use of compounds containing Co and Cu simultaneously can solve the problem of introducing these components into the magnet composition. It is known that the alloying with cobalt leads to an increase in the Curie temperature of compound $REM_2(Fe, Co)_{14}B$ [14], and also allows the temperature coefficient of induction to be regulated. Thus, the introduction of cobalt and copper into the alloy can favor the reaching of required level of hysteretic properties of magnets.

All REM-rich R_3Co compounds are formed by a peritectic reaction [15] and thus their preparation in a single-phase state is difficult. Phase equilibria in R-Co-Cu systems, in particular, with REM contents of 67-75 at. % have not yet been adequately studied [16]. The concentration limits of the existence of $R_{12}(Co, Cu)_7$, $R_3(Co, Cu)$ and R(Cu, Co) ternary phases [17] have not been determined. These data are of importance in understanding processes occurred during saturation of alloys with hydrogen in manufacturing of magnets. The R_3Co compounds have an orthorhombic structure of the Fe_3C type (the Pnma space group) [18].

The present work is devoted to the study of phase equilibria of the Tb-Co-Cu system in the concentration range of Tb 60-100 at.%. The interaction of the $Tb_3(Co_{1-x}Cu_x)$ alloy with hydrogen is also considered in order to predict the behavior of $Tb_3(Co_{1-x}Cu_x)$ additions in manufacturing of Nd-Fe-B-based permanent magnets.

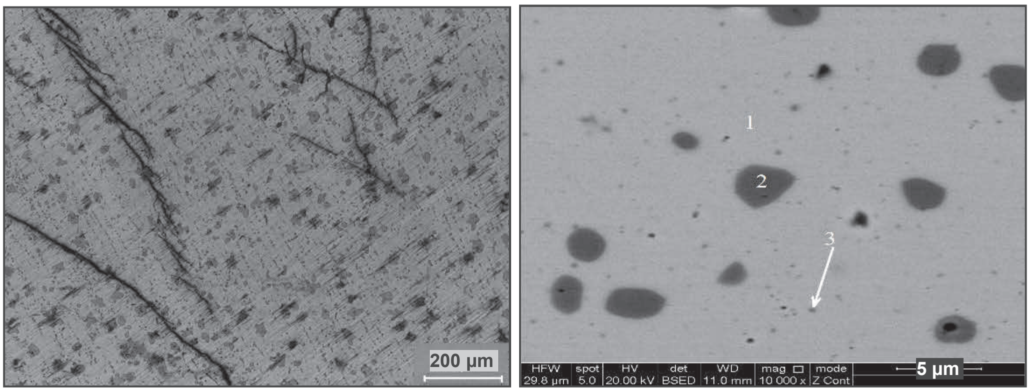
2. EXPERIMENTAL

The $Tb_3(Co_{1-x}Cu_x)$ alloy with x = 0.4 was prepared by arc melting of starting components (Tb-99.9 at.%, electrolytic Co K-1 grade, and oxygen-free copper) in an argon atmosphere using a water-cold copper mould and a nonconsumable tungsten electrode. The ingot was subjected to homogenizing annealing at 600 °C for 90 h followed by rapid cooling (20°C/min); thus fixed phase state corresponds to a temperature of 600 °C. The structure of the alloy was studied by optical and electron microscopy using an AxioLabA1 (Carl Zeiss) microscope and a QUANTA 450 FEG electron microscope equipped with an EDX APOLLO X microanalyzer, respectively; the back-scattered electron (BSE) mode image was used. The magnetic properties of the alloy were measured in the temperature range of 4.2-300 K in a magnetic field of 100 Oe using a vibrating-sample magnetometer and an NM-1 Oxford superconducting magnet. The differential thermal analysis of the alloy was carried out in an argon atmosphere at a heating/cooling rate of 15°C/min using a Setaram Setsys -1750 device. The Tb-Co-Cu alloy was saturated with hydrogen at 270°C in a hydrogen flow (at 0.1 MPa pressure) for 1 h. The phase composition of the alloy was studied by X-ray diffraction (XRD) analysis using a Ultima IV (Rigaku, Japan) diffractometer equipped with a "D/teX" detector, CuKα radiation; the scanning step is 0.001°). X-ray diffraction patterns were process and the phase composition of alloys was determined using PowderCell software. The data on the crystal structure type, lattice parameters, and crystallographic positions of atoms in the Tb-Co, Tb-Cu, and H-Tb system alloys were used to simulate theoretical XRD patterns [19-21].

3. RESULTS AND DISCUSSION

3.1. Microstructure and electron microprobe analysis of $Tb_3(Co,Cu)$ alloy

The microstructure of $Tb_3(Co,Cu)$ alloy subjected to prolonged homogenizing annealing is shown in **Figure 1**. As is seen, the structure is not single-phase and is characterized by the presence of rounded and petal-shaped inclusions. The element composition of the observed inclusions in the $Tb_3(Co,Cu)$ alloy was determined by SEM/EDX method (**Table 1**). According to EMA data, the compositions of inclusions correspond to $Tb_3(Co, Cu)$ (main phase); Tb(Cu, Co (large inclusions), and of $Tb_{12}(Co, Cu)_7$ (small inclusions) (see **Figure 1b**).



(a) (b)

Figure 1 (a) Microstructure of $Tb_3(Co,Cu)$ alloy after homogenizing annealing (optical microscopy) and (b) SEM (BSE) image of the structure: 1 - $Tb_3(Co,Cu)$, 2 - $Tb(Co,Cu)$, 3 - $Tb_{12}(Co,Cu)$

Thus, the alloy subjected to prolonged homogenizing annealing is multiphase. The determined limits of Co / Cu solubility in the found phases correspond to compositions $Tb_3(Co_{1-x}Cu_x)$ with x = 0.25-0.27; $Tb(Cu_{1-y}Co_y)$ with y = 0.05-0.19, and $Tb_{12}(Co_{1-z}Cu_z)$ with z = 0.4.

Table 1 Electron microprobe analysis data for the $Tb_3(Co,Cu)$ alloy (at.%)

Element/phase	**Tb**	**Co**	**Cu**
Phase_1	55.1	8.1	36.8
Phase_2	74.6	18.8	6.6
Phase_3	68.0	19.2	12.8

3.2. X-ray diffraction analysis

Figure 3 shows X-ray diffraction analysis of the alloy $Tb_3(Co,Cu)$ subjected to prolonged annealing in an argon atmosphere. To identify observed reflections, the X-ray diffraction pattern was processed using PowderCell software. Unmarked reflections (in **Figure 2**) belong to the main $Tb_3(Co,Cu)$ phase; marked reflections correspond to $Tb(Cu_{1-y}Co_y)$ and $Tb_{12}(Co_{1-z}Cu_z)$ phases. The analysis of crystal structures of the found compounds and construction of theoretical XRD patterns for the simulated structures allowed us to determine variations of lattice parameters of phases alloyed with Co (for $Tb(Cu_{1-y}Co_y)$ and Cu (for $Tb_3(Co_{1-x}Cu_x)$ and $Tb_{12}(Co_{1-z}Cu_z)$ (see **Table 2**). As is seen, the alloying of the binary compounds with Co and Cu does not change the crystal structure type of binary compounds. The phases present in the alloy are alloyed modifications of the binary compounds in accordance with their phase diagrams [15, 17].

Table 2 Crystallographic parameters of the Tb-Co-Cu phases for a composition range of Tb 60-75 at.%

№	**Compound**	**Space group**	**C**	**a (nm)**	**b (nm)**	**c (nm)**	**References**
1	Tb_3Co	Pnma	Fe_3C	0.6985	0.9380	0.6250	[18]
2	$Tb_3(Co_{1-x}Cu_x)$, x=0.25-0.27	Pnma	Fe_3C	0.69723	0.94343	0.62623	This work
3	$Tb_{12}Co_7$	$P2_1/c$	$Ho_{12}Co_7$	0.8390	0.1132	0.1397	[21]
4	$Tb_{12}(Co_{1-z}Cu)_7$ z=0.4	$P2_1/c$	$Ho_{12}Co_7$	0.829	0.1122	0.1387	This work
5	TbCu	Pm3m	CsCl	3.48	3.48	3.48	[20]
6	$Tb(Cu_{1-y}Co_y)$ y=0.05-0.19	Pm3m	CsCl	3.4791	3.4791	3.4791	This work

X-ray diffraction data confirmed the presence of the phase following phases found by EMA: Tb_3Co, $Tb_{12}Co_7$, TbCu. Analysis of variations of the lattice parameters indicates the alloying of the present phases with cobalt and copper with varying degrees of substitution of Cu for Co and of Co for Cu.

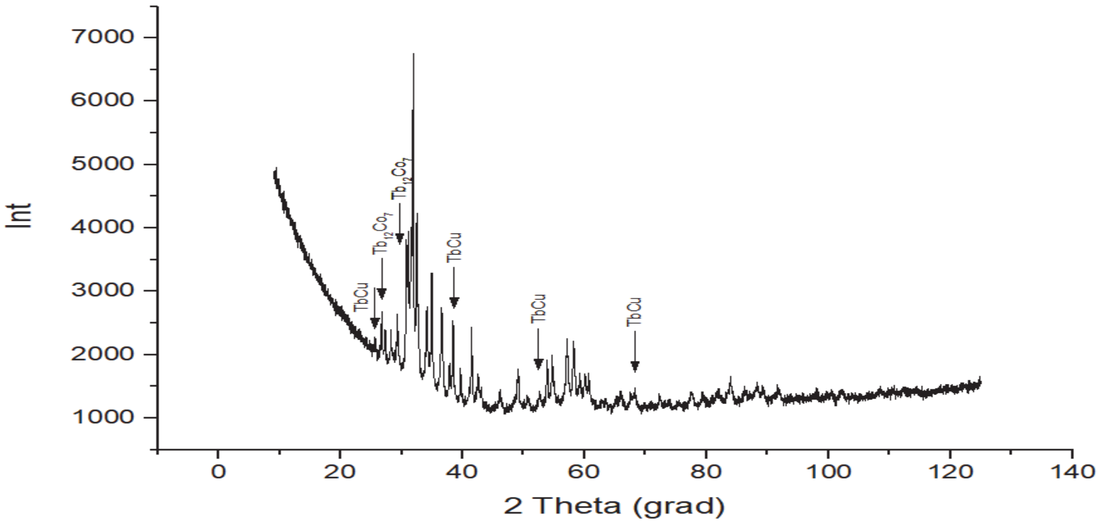


Figure 2 X-ray diffraction pattern of the $Tb_3(Co,Cu)$ alloy

3.3. Magnetic measurements

The temperature dependence of the magnetization of compound $Tb_3(Co,Cu)$ in a weak magnetic field in a temperature range 4.2-250 K (**Figure 3**) was measured and analyzed. It is known [18] that the compound Tb_3Co demonstrates the paramagnetic-antiferromagnet transformation at T_N = 82 K and a metamagnetic transformation at 72 K related to the incommensurability of the magnetic and crystal structures. These transformations are clearly observed in the dependence (anomalies 1 and 2, respectively).

The analysis of the measured curve given in **Figure 3** allows us to determine the temperatures of the phase transitions corresponding to change in the magnetic order of the compounds: Curie temperature of the $Tb_{12}(Co,Cu)_7$ compound is T_C = 100 K (3), the Neel temperature of the Tb(Co,Cu) compound is T_N = 115 K (4), and the Neel and Curie temperature of Tb equal to T_N = 218 K (5) and T_C = 230 K (6), respectively. The determined temperatures of the phase transitions agree adequately with data obtained by other investigators [22-24]. As discussed above, the alloy has the multiphase composition. Moreover, the magnetic measurements allowed us to identify the presence of pure Tb. Thus, we can conclude that the fixed state of the alloy $Tb_3(Co_{1-x}Cu_x)$ with x = 0.4 is nonequilibrium.

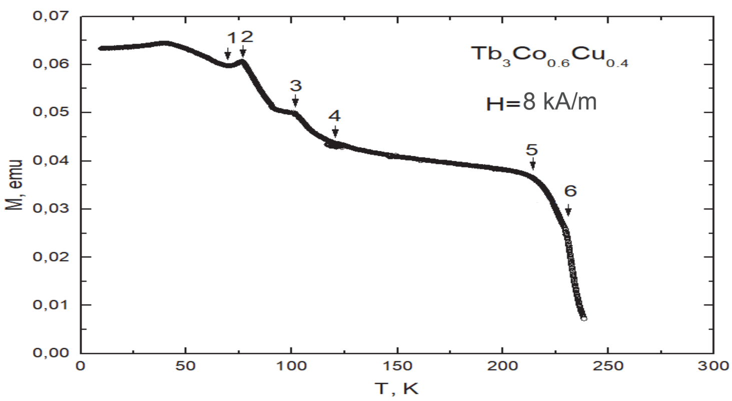


Figure 3 The temperature dependence of the magnetization of $Tb_3(Co_{1-x}Cu_x)$ alloy with x = 0.4 measured in a magnetic field of 8 kA/m

3.4. Phase equilibria in the Tb-Co-Cu system

The Tb_3(Co, Cu) alloy was studied by the DTA during heating and cooling. According to the DTA data (**Figure 4**), the solidification of the alloy begins with the precipitation of primary crystals of Tb(Co, Cu) compound at a temperature of temperature ~770 °C, corresponding to equilibrium L + Tb(Co,Cu)$_{primary}$ (solidus). At a temperature of ~732 °C, a peritectic reaction occurs with the formation of Tb_3(Co,Cu), equilibrium L + Tb(Co,Cu)$_{primary}$ + Tb_3(Co,Cu). At a temperature of ~663 °C, the Tb_{12}(Co, Cu)$_7$ phase is formed by the peritectic reaction; equilibrium L + Tb_3(Co,Cu) + Tb(Co,Cu)$_{primary}$+ Tb_{12}(Co,Cu)$_7$.

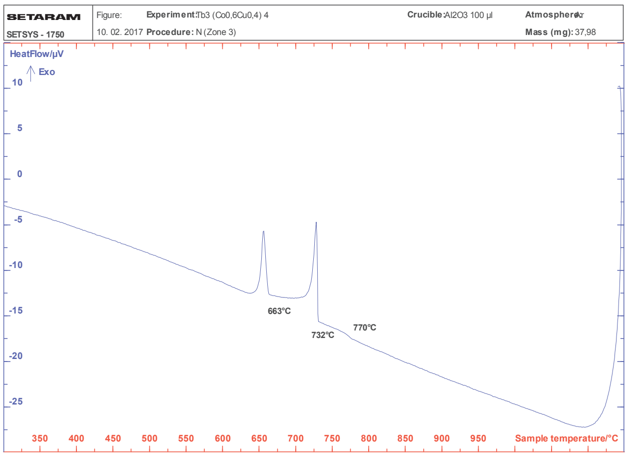


Figure 4 The temperature dependence of the magnetization of $Tb_3(Co_{1-x}Cu_x)$ alloy with x = 0.4 measured in a magnetic field of 8 kA/m

Based on the XRD and EMA data (SEM/EDX) and magnetic measurements, and DTA data, a portion of isothermal section of the Tb-Co-Cu ternary system at a temperature of 600 ° C was constructed for a composition range of Tb 60-100% (**Figure 5**) and a solidification scheme for the alloy was proposed. The alloy under study is marked by a "cross" in the region of existence of three-phase equilibrium: Tb + Tb_3Co + $Tb_{12}Co_7$.

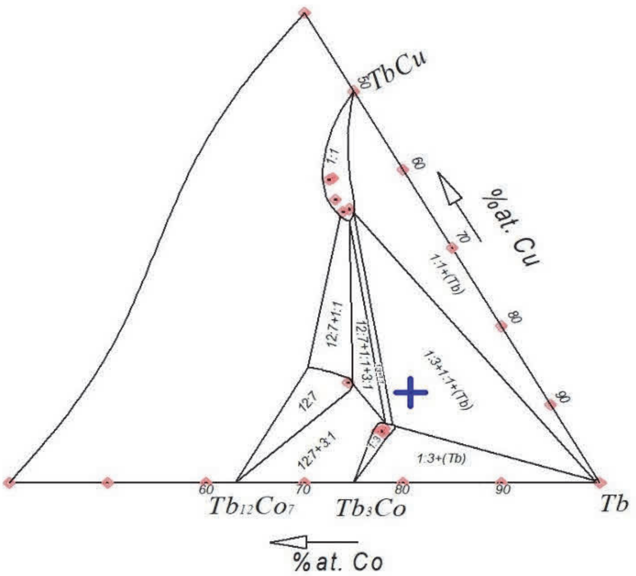


Figure 5 Isothermal section of the Tb-Co-Cu ternary system at 600 °C

3.5. Interaction of $Tb_3(Co_{1-x}Cu_x)$ alloy with hydrogen

Saturation of the alloy Tb_3(Co, Cu) with hydrogen led to the embrittlement of the alloy, preparation of a powder material suitable for the further introduction of the composition into the Nd-Fe-B magnetic alloy powder during cooperative mailing. After saturation with hydrogen, the alloy was studied by XRD (**Figure 6**, unmarked reflections correspond to TbH_2 hydride).

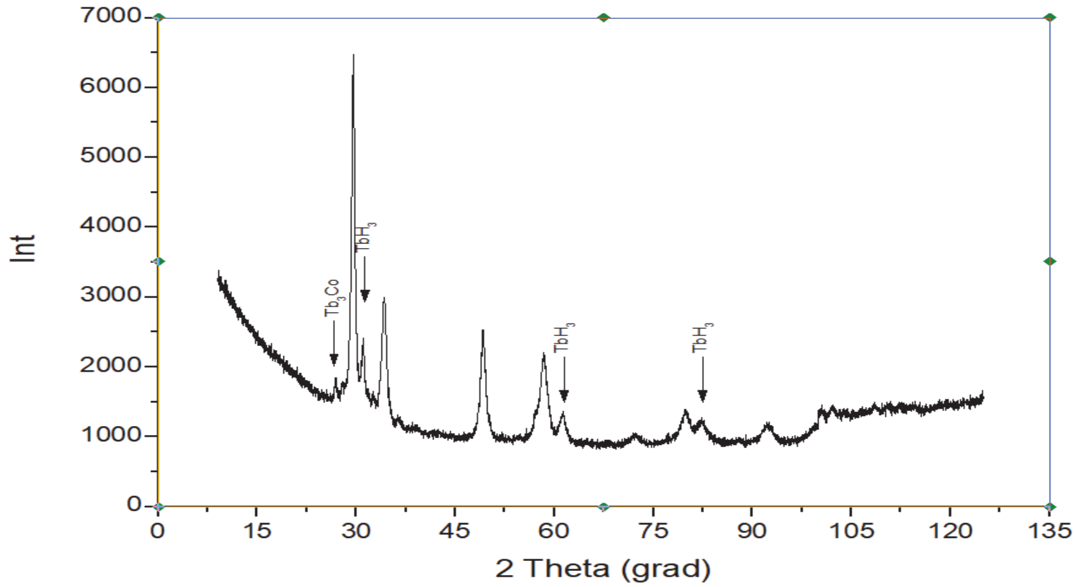


Figure 6 X-ray diffraction pattern of the alloy $Tb_3(Co,Cu)$ after saturation with hydrogen

As is seen, the saturation of the alloy with hydrogen leads to the formation of terbium hydrides TbH_2 and TbH_3, a small amount of the $Tb_3(Co,Cu)$ also is present. Simulation of X-ray diffraction patterns of Co, Cu and $Tb_{12}(Co,Cu)$ and Tb(Co,Cu) phases did not allowed us to find the presence of the phases in the hydrogenated alloy. We assume the presence of a finely dispersed mixture (Co, Cu) without the formation of a quasi-solid solution.

4. CONCLUSION

- The microstructure of the alloy $Tb_3(Co,Cu)$ was studied by optical and electron microscopy. The EMA allowed us to determine the compositions of the present phases. The concentration limits of Co / Cu solubilities in the phases are determined.
- X-ray diffraction analysis of the alloy carried out in using PowderCell software indicated the presence of the Tb_3(Co, Cu), Tb (Co, Cu) and Tb_{12}(Co, $Cu)_7$ phases and confirmed the existence of solubility of Cu and Cu corresponding phases.
- The temperature dependence of the magnetization of the $Tb_3(Co,Cu)$ alloy was studied in the temperature range 4.2-300 K. The magnetic measurements allowed us to find the presence of Tb in the alloy. The temperatures of magnetic transformations of the present phases were observed in the dependence.
- The isothermal section of the ternary Tb-Co-Cu system at 600 ° C was constructed. The solidification path of the studied alloy was described using DTA data.
- Saturation of the alloy with hydrogen leads to the embrittlement of composition with the formation of mainly TbH_2 TbH_3 hydrides; a small amount of residual Tb_3(Co, Cu) compound is observed.

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REFERENCES

[1] KIANVASH,A., MOTTRAM, R.S. and HARRIS, I.R. Densification of $Nd_{13}Fe_{78}NbCoB_7$-type sintered magnet by (Nd, Dy)-hydride additions using a powder blending technique. *Journal of alloys and Compounds.* 1999. vol. 287, pp. 206-214.

[2] KIM, T.-H., LEE, S.-R., KIM, H.-J., LEE, M.-W. and JANG, T.-S. Magnetic and microstructural modification of the Nd-Fe-B sintered magnet by mixed DyF_3/DyH_x powder doping. *Journal of Applied Physics.* 2014. vol. 115, no. 17, pp. 17A763.

[3] LÖEWE, K., BROMBACHER, C., KATTER, M. and GUTFLEISCH, O. Temperature-dependent Dy diffusion process in Nd-Fe-B permanent magnets. *Acta Materiala.* 2015. vol. 83, pp. 248-255.

[4] LIU, W. Q., SUN, H., YI, X. F., LIU, X. C., ZHANG, D. T., YUE, M. and ZHANG, J. X. Coercivity enhancement in Nd-Fe-B sintered permanent magnet by Dy nanoparticles doping. *Journal of Alloys and Compounds.* 2010. vol. 501, pp. 67-69.

[5] MASAHIRO, I., MASARU, I., MINORU, N., MASAKI, N. and HIROTOSHI, F. Microstructure analysis of High coercitivity PLD-made Nd-Fe-B thick-film improved by Tb-coating-diffusion treatment. *Materials Transactions.* 2010. vol. 51, pp. 1939-1943.

[6] LIANG, L., MAN, T., ZHANG, P., JIN, J. and YAN, M. Coercivity enhancement of NdFeB sintered magnets by low melting point $Dy_{32.5}Fe_{62}Cu_{5.5}$ alloy modification. *Journal of Magnetism and Magnetic Materials.* 2014. vol. 355, pp. 131-135.

[7] GUO, S., CHEN, R.J., DING, Y., YAN, G.H., LEE, D. and YAN, A.R. Effect of DyH_x addition on the magnetic properties and microstructure of $Nd_{14.1}Co_{1.34}Cu_{0.04}Fe_{bal.}B_{5.84}$ magnets. *Journal of Physics: Conference Series.* 2011. vol. 266, pp. 16-19.

[8] BURKHANOV, G.S., LUKIN, A.A., KOLCHUGINA, N.B., KOSHKID'KO, Yu.S., DORMIDONTOV, A.G., SKOTNICOVÁ, K., ZIVOTSKY, O., ČEGAN, T. and SITNOV, V.V. Effect of low-temperature annealing on the structure and hysteretic properties of Nd-Fe-B magnets prepared with hydride-containing mixtures. In *REPM 2014: 23rd International Workshop on Rare-Earth and Future Permanent Magnets and Their Applications.* Annapolis, USA, 2014. pp. 367-369.

[9] LUKIN, A., KOLCHUGINA, N.B., BURKHANOV, G.S., KLYUEVA, N.E. and SKOTNICOVA, K. Role of Terbium hydride additions in the formation of microstructure and magnetic properties of sintered Nd-Pr-Dy-Fe-B magnets. *Inorganic Materials. Applied Research.* 2013. vol. 4, pp. 256-259.

[10] BURKHANOV, G.S., KOLCHUGINA, N.B., LUKIN, A.A., KOSHKID`KO, Yu.S., CWIK, J., SKOTNICOVA, K. and SITNOV, V.V. Structure and magnetic properties of Nd-Fe-B magnets prepared from DyH_2-containing powder mixtures. *Inorganic Materials: Applied Research.* 2018. vol. 9, no. 3, pp. 509-516.

[11] TARASOV, E.N, MILYAEV, O.A., KUDREVATYH, N.V., BOGATKIN, A.N., ANDREEV, S.V. and BASHKOV Y.F. The effect of the chemical composition and aggregate state of additives on the magnetic properties of permanent magnets from Nd-Fe-B alloys, *Physics and chemistry of materials treatment.* 1999. no. 1, pp. 84-87.

[12] BURKHANOV, G.S., KOLCHUGINA, N.B., KOSHKID`KO, Yu.S., CWIK, J., SKOTNICOVA, K., CEGAN, T., PROKOF`EV, P.A., DRULIS, H. and HACKEMER, A. Structure and phase composition of $Tb_3Co_{0.6}Cu_{0.4}$ alloys for efficient additions to Nd-Fe-B sintered magnets, *METAL 2017: 26th International Conference on Metallurgy and Materials*. Ostrava: TANGER, 2017. pp. 1775-1781.

[13] ZHANG, Y., MA, T., LIU, X., LIU, P., JIN, J., ZOU, J. and YAN, M. Coercivity enhancement of Nd-Fe-B sintered magnets with intergranular adding (Pr, Dy, Cu)−Hx powders. *Journal of Magnetism and Magnetic Materials.* 2016. vol. 399, pp. 159-163.

[14] HERBST, J.F. Preferential site occupation and magnetic structure of $Nd_2(Co_xFe_{1-x})_{14}B$ systems. *J. Appl. Phys.* 1986, vol. 60, no. 12, pp. 4224-4229.

[15] *Binary Alloy Phase Diagram*. Ed. by T.B. MASSALSKI, H. OKAMOTO, P.R. SUBRAMANIAN, L. KACPRZAK , 2nd ed., Materials Park, Ohio: ASM International, 1990. 3589 p.

[16] KOLCHUGINA, N.B. and DOBATKINA, T. Co-Cu-Tb Ternary Phase Diagram Evaluation. *In MSI Eureka, Effenberg, G. (Ed.), MSI, Materials Science International, Stuttgart* (2017), Document ID: 10.36935.1.4 (Crys. Structure, Phase Diagram, Phase Relations, Assessment, 14)

[17] SUBRAMANIAN, P.R. and LAUGHLIN, D.E. *Binary Alloy Phase Diagrams*. Second Edition", vol. 2, T.B. MASSALSKI (editor-in-chief). The Materials Information Society. Materials Park, Ohio (1990).

[18] BARANOV, N. V., GUBKIN, A. F., VOKHMYANIN, A. P., PIROGOV, A. N., PODLESNYAK, A., KELLER, L., MUSHNIKOV, N. V. and BARTASHEVICH, M. I. High-field magnetization and magnetic structure of Tb_3Co. *Journal of Physics: Condensed Matter.* 2001. vol. 19, p. 326213 (14 pp.).

[19] BUSCHOW, K.H.J. and VAN DER GOOT, A.S. The crystal structure of rare-earth cobalt compounds of the type R3Co. *Journal of the Less Common Metals.* 1969. vol. 18, iss. 3, pp. 309-311.

[20] SUBRAMANIAN, P.R., “Cu (Copper)”, in “Phase Diagrams of Binary Copper Alloys”, P.R. Subramanian, D.J. Chakrabarti and D.E. Laughlin (Eds.*), ASM International, Materials Park*, OH, 1-3 (1994) (Equi. Diagram, Crys. Structure, Thermodyn., Review, 16)

[21] ADAMS, W., MOREAU, J.-M., PARTHÉ, E. and SCHWEIZER, J. $R_{12}Co_7$ compounds with R = Gd, Tb, Dy, Ho, Er. Acta Cryst. 1976. B32, 2697-2699.

[22] IBARRA, M.R., ALGARABEL, P.A. and PAVLOVIC, A.S. High-field magnetostriction of TbCu, DyCu and HoCu. *Journal of Applied Physics*. 1990. vol. 67, p. 4814.

[23] DENG, J.Q., ZHUANG, Y.H., LI, J.Q. and HUANG, J.L. Magnetic properties of $Tb_{12}Co_7$. *Physica B:Condensed Matter.* 2007. vol. 391, no. 2, pp. 331-334.

[24] KOEHLER, W. C., CHILD, H. R., WOLLAN, E. O. and CABLE, J. W. Some magnetic structure properties of terbium and of terbium-yttrium alloys. *Journal of Applied Physics.* 1963. vol. 34, p. 1335.