EFFECT OF Al AND Fe SUBSTITUTION IN THE COBALT SUBLATTICE ON THE STRUCTURE AND MAGNETIC PROPERTIES OF (Tb,Dy,Ho)Co_2 ALLOYS

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Abstract

The effect of Al and Fe substitution in the cobalt sublattices on structural and magnetic properties of $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ compound has been studied. Surface topology features, element and phase compositions, temperature dependences of lattices parameters, magnetization, magnetocaloric effects and magnetostriction of these multicomponent alloys have been obtained and analyzed. The relationship between magnetic properties and micro- and nanoscale structural features of samples was established.

Keywords: Rare earth intermetallics, substitution, structure, magnetocaloric effect, magnetostriction

1. INTRODUCTION

The cubic Laves phases RCo_2 compounds (R = rare-earth metal) are characterized by instability of the Co-sublattice magnetic moments [1, 2] and, as a consequence, characterized by interesting effects that can be used in practice. In such compounds in the Curie temperature region, both significant magnetostriction and a large magnetocaloric effect (MCE) are observed [3-8]. Using various combinations of rare-earth metals and the partial substitution of some metals for Co, one can improve RCo_2 properties and to create new functional materials based on them [9-13]. The present study is focused on analyzing the surface layer morphology, the Curie temperature variations, the magnetocaloric effect, and the magnetostriction induced in RCo_2 Laves-phase samples by partial substitution of cobalt. Three compositions for investigation were chosen, namely, $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$, $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$ and $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Fe_{0.25}$. The reason for choosing these compounds is possibility to obtain an alloy with compensated magnetic anisotropy, and, consequently, to observe all the above-described effects in comparatively weak magnetic fields. Fe and Al were chosen to replace Co atoms, because such substitution can increase the Curie temperature of $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ and remove it toward to room temperature.

2. MATERIALS AND METHODS

Initial rare-earth components with a reduced concentration of metallic and gas-forming impurities were used for melting. For this purpose, terbium, dysprosium, and holmium were subjected to additional vacuum distillation [14]. Compounds were synthesized by direct alloying in an electric arc furnace (Leybold- Heraeus) in helium atmosphere at an excess pressure of 0.11 MPa in the chamber. Thus, impurity side effects were excluded. In order to obtain samples with a homogeneous composition, they were subjected to triple remelting with subsequent homogenizing annealing at a temperature of 900 °C for a one month.

The phase composition of synthesized compounds was monitored before and after annealing by X-ray diffraction analysis by Ultima IV (Rigaku) X-ray diffractometer at room temperature. The temperature dependent structural study was performed on an X-ray powder diffractometer Supernova (Agilent) using a Mo$K\alpha$ radiation. The temperature of the sample was controlled with non-liquid nitrogen Cobra cryostream from Oxford Cryosystems in the range of 120 - 300 K. Diffraction patterns were treated by the Rietveld method

using FullProf refinement package. The elemental compositions of the samples were controlled using a REAN table X-ray fluorescent energy dispersive analyzer (ZAO "Nauchnye Pribory," St. Petersburg). An analysis was carried out in air at the supply voltage of the X-ray tube of 20 kV using Ti-10 and Cu-40 filters. The surface topology of the synthesized RCo_2 Laves-phase samples was studied by atomic force microscopy (AFM) using a SMENA-A scanning probe microscope (Solver platform, ZAO NT-MDT, Russia) both in semicontact and contact modes at room temperature. The obtained AFM images were processed with Nova_1443 and Nova_Px 2.0 visualization and analysis software.

The magnetization was measured using a standard SQUID magnetometer in the temperature range of 4.2 - 400 K in a magnetic field up to 5 T. The magnetocaloric effect was measured in fields of up to 1.8 T by direct method using the MagEq MMS 901 setup (OOO Polimagnit, AMT&C Group, Russia) and indirectly based on the most common approach to the determination of the MCE amplitude applying the Maxwell's equations to field dependences of the sample magnetization measured at different temperatures. The magnetostriction in the polycrystalline samples was measured by the strain-gauge method in the temperature range 80 - 360 K in magnetic fields up to 1.2 T. An external magnetic field was applied along the direction of the measurement of the magnetostriction (longitudinal magnetostriction $\lambda_{\parallel}$) and perpendicularly to it (transverse magnetostriction $\lambda_{\perp}$).

3. RESULTS AND DISCUSSION

The phase composition of the synthesized compounds was investigated by X-ray phase analysis before and after annealing. Studies showed that before annealing, in addition to the main $MgCu_2$ type phase, the samples contained some amount of an impurity $PuNi_3$ type phase. As follows from the analysis of the phase diagram, this impurity phase is formed because of an incomplete peritectic reaction. X-ray analysis of the samples after annealing (**Figure 1a**) showed that the initial $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ compound and the $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$ compound with aluminum were single-phase, and the iron-containing $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Fe_{0.25}$ alloy contained 96% of the main phase. The lattice parameter and the unit cell volume were determined (**Table 1**). The elemental analysis performed shows that the composition of the samples prepared corresponds to the nominal composition within the error (e.g., **Figure 1b** shows the $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ compound X-ray diffraction spectrum with the specified weight percentages of each element).

Temperature-induced X-ray studies indicated that the cubic crystal structure of both compounds is rhombohedrically distorted when a transition to a magnetically ordered state occurs. Such distortions can correspond either to first or second order transitions [15, 16]. In RCo_2, the existence of structure distortion would cause a large anisotropic magnetostriction along the magnetization direction. The spontaneous volume magnetostriction appeared during the transition from magnetically disordered to the magnetically ordered state (near the Curie temperature) can be estimated using relation

$$\omega_s = [V_m(T) - V_p(T)] / V_p(T), \quad (1)$$

where V_m is the unit cell volume at given temperature, and V_p is the unit cell volume in the paramagnetic region.

Near the transition temperature is found that the spontaneous magnetostriction of the $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ alloy is ~ $4.5 \cdot 10^{-3}$, which is higher than in $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$ alloy ($\omega_S \approx 3.6 \cdot 10^{-3}$). The micro- and nanoscale analysis of 3D surface relief (**Figure 2**) provided information regarding the grain structure of the synthesized phase, its degree of dispersion, the morphology of individual grains, the phase composition homogeneity, defects of the crystal structure and is described in more detail in previously our paper [17]. The size and shape of grains were estimated both by analyzing the obtained 2D and 3D cross section profiles and with the Grain Analysis software component, which was in good agreement. The average grain size $<D>$ is given in **Table 1**. Spatial anisotropy of the structure was revealed in 3D spatial morphology studies. It should be noted, the alloy

with aluminum is stronger than others and prone to agglomeration. As particles with an average diameter of 143 nm and conglomerates with dimensions of 0.3 - 0.5 in width and up to microns in length is observed.

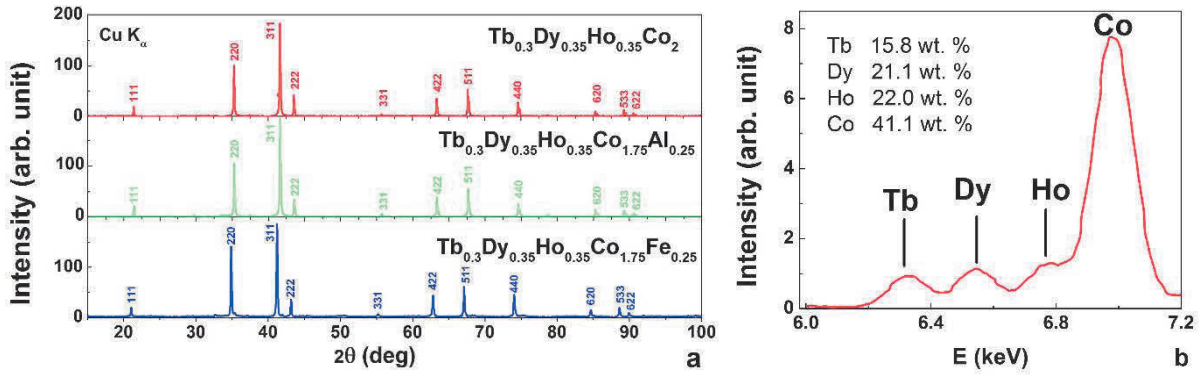

Figure 1 The room-temperature X-ray diffraction data of all compounds (a) and X-ray spectrum of the $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ compound (b)

Table 1 Lattice parameter (*a*), unit cell volume (*V*), average grain size <*D*>, spin-reorientation transition temperature (T_{SR}), Curie temperature (T_C), magnetic entropy change ($-\Delta S$) and adiabatic temperature change (ΔT_{ad}) at $T = T_C$ and $\Delta\mu_0 H = 1.8$ T for $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{2-x}T_x$ (T = Al, Fe; x = 0, 0.25) compounds

Alloy	*a* (nm)	*V* (nm^3)	<*D*> (nm)	T_{SR} (K)	T_C (K)	ΔT_C (K)	$-\Delta S$ (J/kg·K)	ΔT_{ad} (K)
$Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$	0.719	0.372	720	80	147	-	8.4	2.7
$Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$	0.7194	0.372	143	68	163	16	4.3	1.1
$Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Fe_{0.25}$	0.7211	0.375	77	55	354	207	1.0	0.9

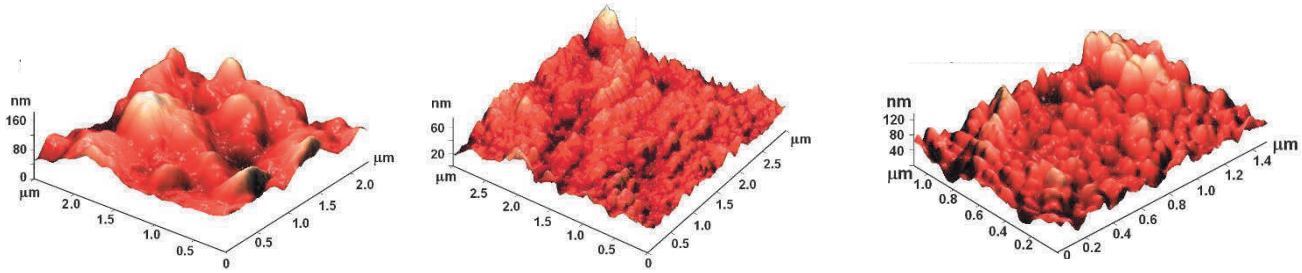

Figure 2 3D images of the synthesized RCo_2 - type compounds surface

The thermomagnetic analysis results in a 20 mT magnetic field confirmed that the samples were single-phase. In addition, these data allowed us to determine the Curie temperature (T_C) and spin-reorientation transition temperature (TSR) of the studied compounds as the extremum of the temperature dependence of magnetization d*M*/d*T* derivative (**Table 1**). The subsequent aluminum substitution for cobalt, the Curie temperature increases by just 16 K; in contrast, the iron substitution for cobalt leads to a substantial (207 K) increase in T_C. At the same time, with partial replacement of cobalt by aluminum and iron, the spin reorientation transition temperature decreases by 12 and 25 K, respectively.

The thermodynamic coefficients method was used to determine the order of the phase transition from a magnetically ordered state to a magnetically disordered one. It was found that the initial compound features a first-order transition. Following the partial substitution of cobalt with aluminum or iron, the transition turns into

a second-order transition. It is known that the RCo_2-type compounds can exhibit significant MCE in the Curie temperature region [18-22]. If a compound undergoes a first-order transition substantial heat release or absorption can be observed in the transition temperature region in a varying external magnetic field. This effect is manifested in a narrow temperature interval. The MCE magnitude at second-order magnetic phase transitions is lower, but the effect is observed in a wider temperature range. The MCE magnitude, the wide range of operating temperatures, the temperature at which the largest MCE is observed and the possibility of its variation are very important for the technical application of such materials.

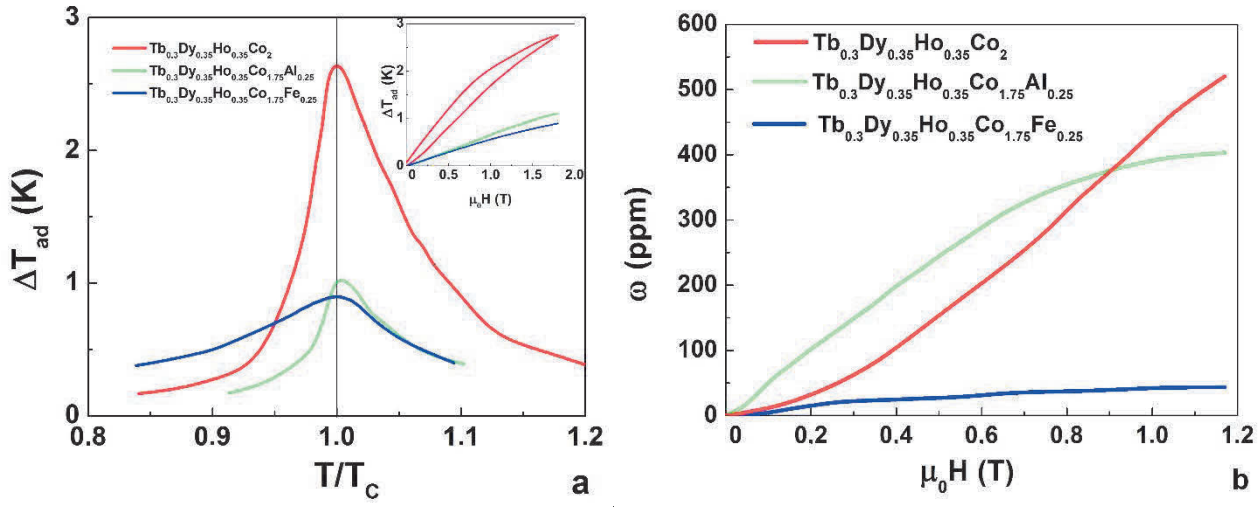

Figure 3 Temperature variation of MCE in $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{2-x}T_x$ (T = Al, Fe; x = 0, 0.25) compounds at 1.8 T (a). Field dependencies of MCE (Inset 3a) and volume magnetostriction (3b) in $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{2-x}T_x$ (T = Al, Fe; x = 0, 0.25) compounds at the Curie temperature

MCE of the investigated compounds were measured directly under adiabatic conditions, recording the initial and final temperatures (ΔT_{ad}) of samples placed in a magnetic field, and indirectly studied previously [6,17, 23-25]. **Figure 3(a)** shows the MCE vs. reduced temperature dependencies for $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$, $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$ and $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Fe_{0.25}$ compounds measured by a direct method at the magnetic field change from 0 to 1.8 T. The partial aluminum and iron substitution for cobalt leads to a significant decrease in the value of MCE, but the range of operating temperatures increases. The MCE values obtained by direct and indirect method at $T = T_C$ and $\Delta\mu_0 H$ = 1.8 T are given in the **Table 1**. The MCE field dependence of the $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ compound in contrast to compounds with aluminum and iron, demonstrates a small hysteresis (**Figure 3a**).

The longitudinal ($\lambda_{||}$) and transverse ($\lambda_{\perp}$) magnetostriction of the $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$, $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$ and $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Fe_{0.25}$ compounds as functions of temperature and applied external magnetic field was studied. The longitudinal magnetostriction of all samples under study is positive throughout the temperature range. The transverse magnetostriction is negative at low temperatures, its absolute value decreases with increasing temperature, changes sign and assumes a maximum positive value near the Curie temperature. The volume and anisotropic magnetostrictions of the studied polycrystalline samples were found by the formulas: $\omega = \lambda_{||} + 2\,\lambda_{\perp}$ and $\lambda_{anis} = 2/3(\lambda_{||} - \lambda_{\perp})$. The volume magnetostriction has a maximum at the Curie temperature. **Figure 3(b)** shows the field dependencies of volume magnetostriction in $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{2-x}T_x$ (T = Al, Fe; x = 0, 0.25) compounds at the Curie temperature. It can be seen that the volume magnetostriction magnitude of the initial sample and the sample with aluminum is almost an order of magnitude greater than in the sample with iron. The $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{1.75}Al_{0.25}$ compound has a maximum value of all up to 0.9 T and almost reaches saturation, while volume magnetostriction of $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$

continues to grow, reaching 1300 ppm at 8 T [24]. The investigated compounds in the region of the liquid nitrogen boiling point have similar values of anisotropic magnetostriction (~ 800 ppm in a magnetic field of 1.2 T). A giant anisotropy of magnetostriction is observed in these compounds at low temperatures not only as a result of localization of 4*f*-magnetic moment of rare-earth atoms, but also due to the existence of a localized part of the spin density of 3*d*-electrons in cobalt atoms.

4. CONCLUSION

The influence of partial substitution of cobalt by aluminum and iron on the structure, magnetic, magnetocaloric and magnetostrictive properties of rare-earth Laves phases is investigated in the work on the example of multicomponent compound $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_2$ with compensated magnetic anisotropy in the RE sublattice. Single-phase samples of $Tb_{0.3}Dy_{0.35}Ho_{0.35}Co_{2-x}T_x$ compounds (T = Al, Fe; x = 0, 0.25) were synthesized and studied in a complex manner. It was found that partial substitution (12.5 wt.%) in the 3d sublattice leads both to a change in the structure of the compounds and to a significant change in their functional properties, and the substitution of iron, in comparison with aluminum, exerts a stronger influence on all the investigated parameters. Both types of substitutions lead to an increase in the volume of the unit cell, while the rhombohedral distortions of the cubic structure present in the initial compound in the magnetically ordered state are conserved. The grain size of substituted compounds decreases. The grains of all compounds, and especially of the composition with aluminum, tend to agglomerate. Substitutions in the 3d sublattice lead to a decrease in the magnetocaloric effect and volume magnetostriction, but the temperatures of the maximum of the observed effects increase significantly, and the operating temperature range increases. These circumstances make compounds with partial replacement of cobalt by aluminum and iron promising, for example, for use as components of combined working bodies of magnetic refrigerators.

ACKNOWLEDGEMENTS

The work is supported by the RFBR and Moscow city Government according to the research project 15-33-70040 mol_a_mos.

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