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The magnetocaloric effect in (Dy,Tb)Co_2 alloys

Kunming Gu, Junqin Li *, Weiqin Ao, Yongxi Jian, Jiaoning Tang

School of Materials, Shenzhen University, Shenzhen Key Laboratory of Special Functional Materials, Shenzhen 518060, PR China

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Abstract

Series of $Tb_xDy_{1-x}Co_2$ alloys (x = 0.1, 0.3, 0.5, 0.7, 0.9) were prepared by arc-melting method. All the alloys were found to be the pure Laves phase, indicating the continuous solid (Dy,Tb)Co_2 solution formed from $DyCo_2$ and $TbCo_2$. The maximal change of entropy ΔS_M decreases from 8.86 to 2.64 J/kg K under magnetic field change of 0–1.5 T as Tb content increases from 0.1 to 0.9, due to the change of transition type from first-order to second-order. The results of Arrott plots and Inoue-Shimizu model confirmed the transition type changes from first-order to second-order occurs with Tb content x between 0.1 and 0.3.

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Keywords: $Tb_xDy_{1-x}Co_2$ alloys; Magnetocaloric effect; Phase transition

1. Introduction

The intermetallic rare-earth compounds RCo_2 (R rare earth) have attracted much attention in recent years because of the first-order metamagnetic transition in some of the compounds, which could lead to large magnetocaloric effect (MCE) [1–3]. The Co 3d-electrons were thought instability in RCo_2 compounds and could perform a field-induced transition under a relative low magnetic field especially in case R ions have a local moment. The transition is called metamagnetic transition and is first-order when R is Dy, Ho and Er, while second-order for the others [4].

The important of first-order on large magnetocaloric effect has been widely recognized by researchers [5,6]. For RCo_2 compounds, $TbCo_2$ and $DyCo_2$ are the neighbours with the opposite transition types. Moreover, $TbCo_2$ and $DyCo_2$ have the very similar lattice parameters. Thus, it was expected that change of transition type from first- to second-order would occur when the Dy is substituted by a certain Tb in $DyCo_2$ alloys without causing serious aberration of lattice parameters. Although the magnetic entropy was expected to decrease with increasing of Tb content, the peak of ΔS_M was expected to shift to higher temperature because $TbCo_2$ has a relative higher Curie temperature. It must be interesting to investigate the details of the change of transition and the investigation might bring out some intrinsic information for the two type of transitions and the transform of them.

2. Experiment

Series of $Tb_xD_{1-x}Co_2$ alloys (x = 0.1, 0.3, 0.5, 0.7, 0.9) were prepared by arc-melting the stoichiometric mixtures of high purity Dy (99.99%), Tb (99.9%) and Co (99.9%) in argon atmosphere in a water-cooled copper container. The as-prepared samples were annealed at 900 °C for 2 weeks in a sealed quartz tube with vacuum of 6×10^{-3} Pa.

The structure of the sample was characterized by X-ray diffraction (XRD) method using Co Kα radiation, wavelength of 1.78901 Å. The Materials Data Inc. software Jade 5.0 [7] and a powder diffraction file (PDF release 2003) were used to analyze the XRD patterns of the samples. The magnetic properties were measured using vibrating sample magnetometer (VSM) with magnetic field up to 1.5 T.

3. Results and discussion

The XRD patterns of the $Tb_xD_{1-x}Co_2$ alloys are shown in Fig. 1.

The XRD analysis confirmed that all the annealed samples were of pure single phase with the cubic $MgCu_2$ structure, indicating a continuous solid solution (Dy,Tb)Co_2 formed from $TbCo_2$ and $DyCo_2$. The lattice parameters obtained from the XRD patterns by Jade 5.0 software are listed in Table 1. It shows

* Corresponding author. Tel.: +86 755 26538537; fax: +86 755 26536239.
E-mail address: kmgu@szu.edu.cn (K.M. Gu).

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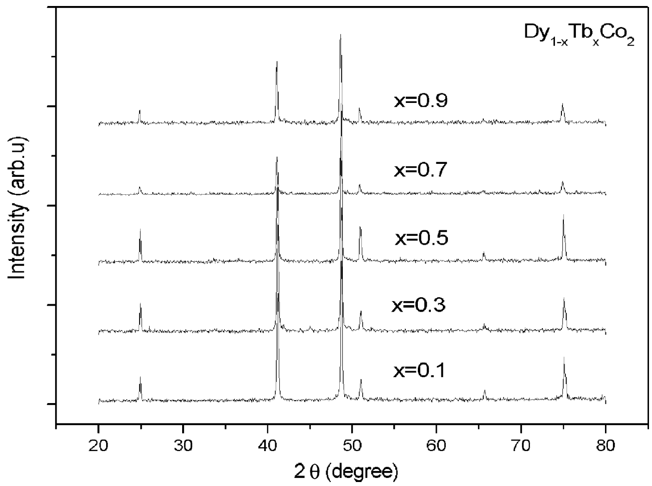

Fig. 1. XRD pattern of $Dy_{1-x}Tb_xCo_2$ alloys.

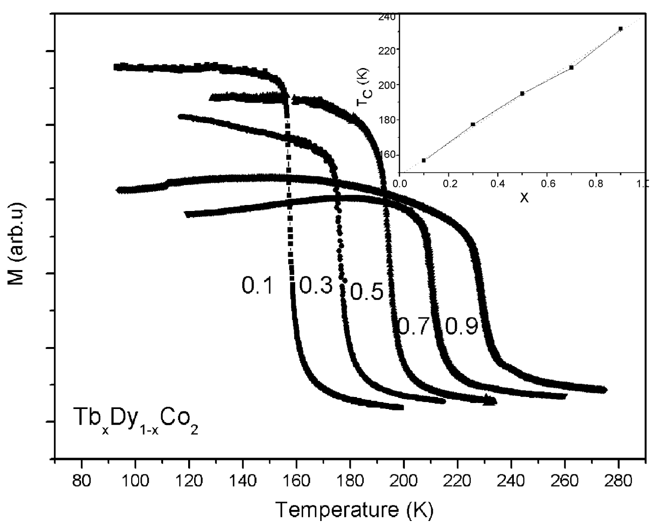

Fig. 2. Temperature dependence of magnetization of $(Tb_xDy_{1-x})Co_2$ alloys, inlet: Curie temperature vs. Tb content x.

that the lattice constant increases with increasing the Tb content x due to the substitution of larger Tb for Dy in $DyCo_2$.

Fig. 2 shows the temperature dependence of magnetization (M–T curves) of Tb_xCo_2 under an applied magnetic field of 0.1 T. The Curie temperature T_C for each sample determined by the peak point of $|dM/dT|$ from its M–T curve was also listed in Table 1. As Tb content x increases from $x = 0.1$ to 0.9, the Curie temperature of $Dy_{1-x}Tb_xCo_2$ increases from 157.5 to 228 K near linearly. In the past research, some compounds, such as $(Er_{1-x}, Gd_x)Co_2$ [8], $(Gd_{1-x}, Tb_x)Co_2$ [9] display nonlinear phenomenon and was attribute to the different f–d exchange

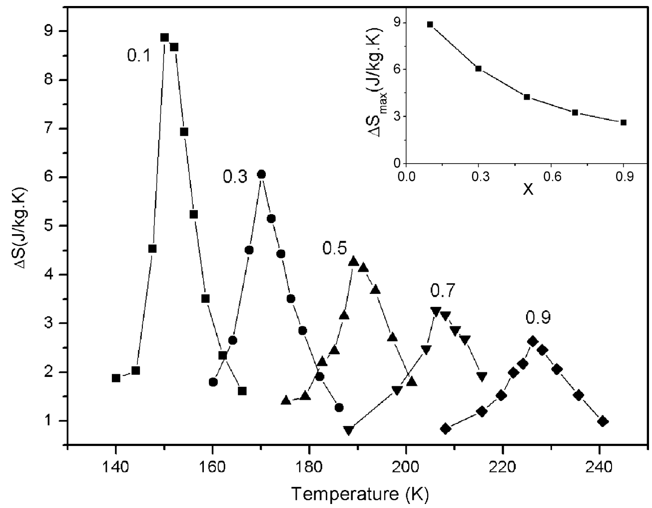

Fig. 3. ΔS_M vs. T of $Tb_{1-x}Dy_xCo_2$, inlet: $\Delta S_{M.max}$ vs. Tb content x, the maximal magnetic field is up to 1.5 T.

interaction with changing of x content. In our work, the degree of nonlinear is much smaller than that of those compounds. It might result from the smaller difference of the lattice constant between $TbCo_2$ and $DyCo_2$.

Based on the magnetization isotherms measured near Curie temperature, the change in entropy of each sample near their ordering temperature was calculated using the integrated Maxwell relation [10]:

$$\Delta S_M(T_{av}, H) = \int_0^H \left(\frac{\partial M_{T_{av}}}{\partial T}\right)_H dH \approx \frac{1}{\Delta T}\int_0^H [M(T_{i+1}, H) - M(T_i, H)]dH$$

where $T_{av} = (T_{i+1} - T_i)/2$ means an average temperature and $\Delta T = T_{i+1} - T_i$ is the temperature difference between the two magnetization isotherms measured at T_{i+1} and T_i with the magnetic field changing from 0 to H. The results are shown in Fig. 3.

Because the Curie temperature increases with increasing Tb content x, the peak of ΔS_M shifts notably to higher temperature. Moreover, the half-peak width increases markedly. However, the maximal change of entropy ΔS_M decreases rapidly from 8.86 to 2.64 J/kg K under magnetic field change of 0–1.5 T as the substitution of Tb for Dy in $DyCo_2$. The decreasing of ΔS_M is an expected result because $DyCo_2$ undergoes first-order transition and $TbCo_2$ undergoes a second-order transition while materials with large magnetic entropy often undergoes a first-order transition. The substitution of Dy by Tb would drives the magnetic transition from a first-order to a second-order, thus result in decrease magnetic entropy change. The question is: when

Table 1
Lattice parameters, Curie temperature and c_1 peak temperature of (Tb_xDy_{1-x}) Co_2, the figures in the brackets showed the error of the last effective digit of each datum

x	0.1	0.3	0.5	0.7	0.9
a (Å)	7.192 (2)	7.196 (2)	7.199 (1)	7.2067 (4)	7.2068 (8)
T_C (K)	157.5 (2)	176.7 (2)	194.1 (2)	210.0 (2)	228.5 (2)
T'_C (K)	149.0 (2)	169.0 (2)	188.0 (2)	206.0 (2)	224.0 (2)