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Magnetic and structural properties of $TbFe_{10.8-x}Co_xW_{1.2}$ alloys

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Abstract

A series of new alloys of composition $TbFe_{10.8-x}Co_xW_{1.2}$ ($0 \leqslant x \leqslant 10.8$) has been synthesized and studied for their hard magnetic properties over the temperature range 4.2–1200 K. It is found that all compounds with $x \leqslant 5$ crystallize in a tetragonal structure of the $ThMn_{12}$ type. At higher cobalt content, *i.e.* $x > 5$, a considerable amount of an extraneous phase of the rhombohedral Th_2Zn_{17} structure is observed. These compounds exhibit planar anisotropy for $x \leqslant 5$ at room temperature. Above room temperature the plane-to-cone-type spin reorientation is found for this system. The Curie temperature (T_c) of these materials is considerably enhanced by cobalt substitution and ranges from 560 K ($TbFe_{10.8}W_{1.2}$) to 1003 K ($TbFe_{5.8}Co_5W_{1.2}$). The effect of cobalt substitution on the anisotropic behaviour in the Tb (Fe, Co)$_{10.8}W_{1.2}$ system is analysed.

1. Introduction

The iron-rich rare earth intermetallic compounds of the type $RFe_{12-x}T_x$ have recently attracted much attention because of their potential as permanent magnets [1–4]. These materials crystallize in the b.c.t. $ThMn_{12}$ structure. The thorium site is occupied by a rare earth atom while the manganese sites are occupied mainly by iron atoms. Binary alloys of RFe_{12} do not exist; however, Buschow and his coworkers have recently discovered that the $ThMn_{12}$-structured alloys are formed when R and iron are combined with small amounts of T ≡ Ti, V, Cr, Mo, W or Si [1–3, 5]. Jurczyk has recently reported the discovery of a new member of this class of compounds with rhenium (with $x = 1.2$) as the stabilizing element [6, 7].

Among these new 1:12-type materials, $SmFe_{11}Ti$ and $SmFe_{10}V_2$ have been found to be potentially suitable for fabricating permanent magnets [1–4]. Unfortunately, the saturation magnetization in these compounds is somewhat lower than that of the $Nd_2Fe_{14}B$ phase [8]. The way to increase the magnetic moment of the 3d atoms is to substitute iron for cobalt. For example, increasing the cobalt content in $YFe_{10.8-x}Co_xW_{1.2}$ leads initially to an increase in moment M_s, giving a maximum at $x = 2$ [7].

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Several of these compounds have been found to exhibit intrinsic magnetic spin reorientation at finite temperatures, which therefore limits their potential applicability to specific temperature ranges. In contrast to the 2:14:1 phase, where an easy magnetization direction along the c axis is expected for R elements having a negative second-order factor ($\alpha_J < 0$), the magnetization in the $ThMn_{12}$ type prefers the c axis when $\alpha_J > 0$. This is due to the nature of the coordination of the rare earth ions. In the R–3d intermetallics the temperature dependences of the rare earth and transition metal sublattice anisotropies are completely different. It is known that wherever the 4f sublattice and 3d anisotropies favour different directions, spin reorientation is likely to occur. There are many reports of spin reorientation phenomena in $RFe_{12-x}T_x$ ($R \equiv Nd$, Tb, Dy, Ho; $T \equiv Ti$, V) [9–13]. For example, $TbFe_{11}Ti$ exhibits a direct plane-to-axis (referred to increasing temperature) transition at about 330 K [14].

In our previous papers [11–13, 15] we have determined the phase diagrams for the spin arrangements in $R(Fe, Co)_{10}V_2$ systems where $R \equiv Nd$, Tb, Dy. Generally, it is found that all the vanadium compounds studied (for $x = 0$) possess uniaxial anisotropy at room temperature.

The purpose of the present study is to investigate the magnetic and structural properties of the $TbFe_{10.8-x}Co_xW_{1.2}$ system. We also discuss the effect of cobalt substitution on the anisotropic behaviour in $Tb(Fe, Co)_{10.8}W_{1.2}$ alloys.

2. Experimental details

The $TbFe_{10.8-x}Co_xW_{1.2}$ samples ($x = 0, 1, 2, 3, 5, 7.8, 10.8$) were prepared by induction melting of stoichiometric amounts of the constituent elements (purity 99.9% or better) in a water-cooled copper boat under an atmosphere of argon. As-cast ingots were heat treated at 870 °C for 2 weeks and then rapidly cooled to room temperature. X-ray diffraction (XRD) and magnetothermogravimetric (MTG) studies were employed to analyse the materials for their single-phase character. To determine the crystal structure and the easy direction of magnetization, XRD analyses were performed at room temperature on randomly oriented and aligned (in magnetic fields up to 10 kOe) powdered samples. MTG studies were performed by recording magnetization M *vs.* T curves under the influence of a non-homogeneous weak magnetic field ($H_{ext} \approx 0.4$ Oe) in an argon atmosphere with the use of a Perkin–Elmer thermogravimetric balance. These studies covered a temperature range of 300–1200 K. The Curie temperatures T_c were determined from these MTG data.

The spin reorientation phenomenon was studied using two different experimental techniques: a.c. susceptibility and magnetothermogravimetry. The a.c. susceptibility of the samples was measured during warming runs in the temperature range 4.2–320 K in a magnetic field $H_{rms} \approx 1$ Oe and at a frequency $f = 100$ Hz using a conventional mutual impedance method and a two-phase PAR 5206 lock-in amplifier to determine both the in-phase and out-of-phase components at various temperatures. As has been demonstrated earlier, a.c. susceptibility and magnetothermogravimetry constitute a good method to detect spin reorientation phenomenon [12, 13, 16].

3. Results and discussion

The XRD patterns of the annealed $TbFe_{10.8-x}Co_xW_{1.2}$ alloys ($x=0$, 1, 2, 3, 5) were indexed on the basis of the tetragonal $ThMn_{12}$-type structure. Replacement of iron by cobalt in this system beyond $x=5$ caused the appearance of extraneous phases, of which the rhombohedral Th_2Zn_{17} was the predominant one. However, X-ray studies of $TbFe_{10.8}W_{1.2}$ revealed the presence of small amount of α-Fe (see Fig. 1(a)) and for $TbCo_{10.8}W_{1.2}$ the major phase occurred in the Th_2Zn_{17}-type structure (see Fig. 1(b)). This was confirmed by metallographic analyses as well as identifying multiple Curie temperatures from low field thermomagnetic measurements. With increasing cobalt substitution the lattice parameters a and c were found to decrease monotonically (Table 1). This same trend has been reported recently for the $Y(Fe, Co)_{10.8}W_{1.2}$ system [7].

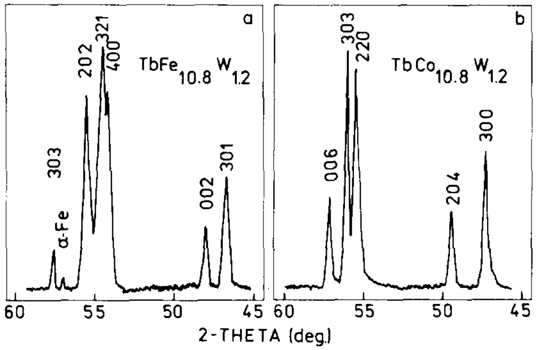

Fig. 1. XRD patterns of the $TbFe_{10.8-x}Co_xW_{1.2}$ alloys (Fe Kα radiation): (a) $x=0$, tetragonal $ThMn_{12}$-type structure; (b) $x=10.8$, rhombohedral Th_2Zn_{17}-type structure.

TABLE 1

Crystallographic data obtained for the $TbFe_{10.8-x}Co_xW_{1.2}$ alloys at room temperature

Composition x	Lattice parameters		V (Å^3)	DOM[a]
	a (Å)	c (Å)		
0	8.541	4.780	348.7	Planar
1	8.538	4.780	348.5	Planar
2	8.513	4.765	345.3	Planar
3	8.505	4.760	344.3	Planar
5	8.478	4.752	341.6	Planar

[a] DOM, direction of easy magnetization.

XRD patterns of random and magnetically aligned powders indicate that the $TbFe_{10.8-x}Co_xW_{1.2}$ alloys ($0 \leqslant x \leqslant 5$) possess planar anisotropy at room temperature (Table 1).

In the $ThMn_{12}$ structure terbium atoms prefer a planar magnetization ($\alpha_J < 0$). Furthermore, the rare earth anisotropy is a strong function of temperature and dominates at low temperatures. The 3d sublattice anisotropy is weakly temperature dependent and dominates at high temperatures [9].

For all $Tb(Fe, Co)_{10.8}W_{1.2}$ alloys ($0 \leqslant x \leqslant 5$) a.c. susceptibility measurements have been performed in the temperature range 4.2–320 K. We have not observed any anomalous behaviour in either the elastic, χ' (T), or viscous, χ'' (T), component. This means that at cryogenic temperatures these materials do not undergo spin reorientation.

In the $TbFe_{10.8-x}Co_xW_{1.2}$ alloys ($0 \leqslant x \leqslant 5$), however, we observe anomalies (a shoulder at temperatures below T_c; see Fig. 2). These may be ascribed to a spin reorientation, representing a change in magnetization, from planar to conical with increasing temperature, owing to the competing anisotropies of the iron and cobalt sublattices. The spin reorientation temperatures T_{SR} for the $Tb(Fe, Co)_{10.8}W_{1.2}$ materials are presented in Table 2. T_{SR} appears

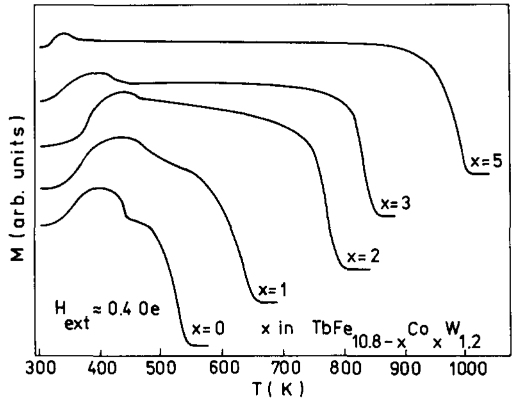

Fig. 2. Low field thermomagnetic curves recorded using a thermomagnetic balance for $TbFe_{10.8-x}Co_xW_{1.2}$ ($x=0$, 1, 2, 3, 5); $H_{ext} \approx 0.4$ Oe.

TABLE 2

Curie and spin reorientation temperatures for the $TbFe_{10.8-x}Co_xW_{1.2}$ system

Composition x	Curie temperature T_c (K)	Spin reorientation temperature T_{SR} (K)
0	560	440
1	663	488
2	778	460
3	852	420
5	1003	370

first to increase on substitution of iron with cobalt in Tb(Fe, Co)$_{10.8}$W$_{1.2}$ and then to decrease for alloys with $x > 1$.

From the composition dependence of the Curie temperature T_c of the TbFe$_{10.8-x}$Co$_x$W$_{1.2}$ alloys given in Table 2 it can be noticed that replacement of iron by cobalt produces an average increase in T_c of approximately 90 K per cobalt atom in the range $x \leqslant 5$. This suggests that cobalt atoms substitute preferentially at the iron sites involved with a negative exchange interaction in the ThMn$_{12}$ structure. Such a preferential site occupation has been demonstrated from neutron diffraction studies on the Y(Fe, Co)$_{11}$Ti system [17]. Yang *et al.* [17] have concluded that in the ThMn$_{12}$-type structure the 8*f* site has a strong preference for cobalt. The interatomic distances between 8*f* sites is the shortest among the various sites. The occupation of the 8*f* sites by cobalt will reduce a negative exchange of Fe–Fe and thus increase T_c.

Based on room temperature XRD as well as thermomagnetic results the phase diagram for the Tb(Fe, Co)$_{10.8}$W$_{1.2}$ system is shown in Fig. 3. It is interesting to observe that the phase diagram for the spin arrangement in Tb(Fe, Co)$_{10.8}$W$_{1.2}$ is in contrast to that observed in Tb(Fe, Co)$_{11}$Ti [14, 18]. The TbFe$_{11}$Ti alloy exhibits a direct plane-to-axis transition at about 330 K (with reference to increasing temperature) [14]. The magnetic structure of TbFe$_{11-x}$Co$_x$Ti ($0 \leqslant x \leqslant 5$) is not the same at all temperatures [18]. In this system, at cryogenic temperatures, two spin reorientations are observed, one which appears to be of the plane-to-cone variety and the other which appears to be of the cone-to-axis type (with reference to increasing temperature). Generally, for $x < 5$, T_{SR} decreases with increasing cobalt concentration in Tb(Fe, Co)$_{11}$Ti [18].

Finally, we conclude that in the TbFe$_{10.8-x}$Co$_x$W$_{1.2}$ system, which crystallizes in the ThMn$_{12}$ structure, cobalt readily substitutes for iron in the concentration range $0 \leqslant x \leqslant 5$. The plane-to-cone type of spin reorientation is found above room temperature.

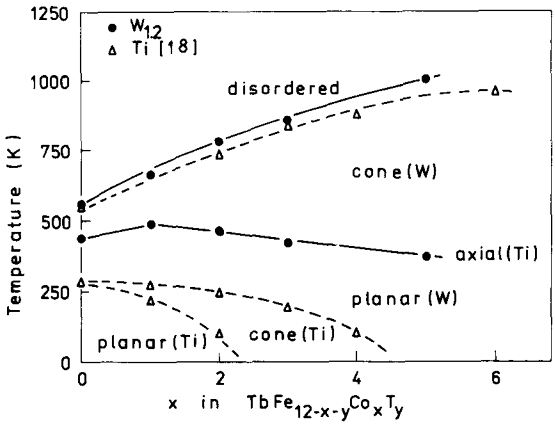

Fig. 3. Diagram of spin configuration types observed in the TbFe$_{10-x}$Co$_x$W$_{1.2}$ system.

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