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The isothermal section of Dy–Co–Cr ternary system at 500 °C

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ABSTRACT

The isothermal section of the Dy–Co–Cr ternary system at 500 °C was investigated by X-ray powder diffraction (XRD), metallography and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The isothermal section consists of 11 single-phase regions, 20 two-phase regions and 10 three-phase regions. The only ternary compound $DyCo_{12-x}Cr_x$ (space group *I*4/*mmm*) with $ThMn_{12}$-type structure was confirmed in this system. The homogeneity range in $DyCO_{12-x}Cr_x$ was found to be about $x = 3.6–4.4$. The lattice parameters for $DyCO_{12-x}Cr_x$ with $3.6 \leq x \leq 4.4$ are $a = 0.8312–0.8334$ nm and $c = 0.4706–0.4722$ nm. The maximum solid solubilities of Cr in Dy_2Co_{17}, $DyCo_3$ and $DyCo_2$ are about 16.0, 5.0 and 17.0 at.%, respectively.

1. Introduction

As a potential candidate for permanent magnet applications, the rare earth-transition metal intermetallic compounds $R_x(T, M)_y$ (where R: rare earth, T: transition metal Fe or Co, M: Ti, V, Cr, Mn, Nb, Mo, etc.) of the type 1:12, 2:17 and 3:29 have been studied extensively in the last decades. A third element M is required to stabilize the 1:12 and 3:29 compounds [1,2]. And the properties of the compounds of the type 1:12, 2:17 and 3:29 have been studied intensively [3–8]. Those studies have been stimulated for the possibility of using some of these materials for high performance permanent magnet applications. Moreover, phase diagrams can provide important information for developing new materials. So, it is essential to have a detailed knowledge of the phase diagrams of RE–Co–M systems. The phase diagrams of Er–Co–V [9], Gd–Co–V [10], Dy–Co–Ti [11] and Dy–Co–V [12] ternary systems have been reported in the literatures. So far, no phase diagram of the Dy–Co–Cr ternary system is found. In this work, we studied the isothermal section of the Dy–Co–Cr ternary system at 500 °C.

A detail description of the binary Dy–Co, Co–Cr and Dy–Cr phase diagrams was given in Refs. [13,14], together with the available crystallographic data and stability temperature range of all the intermediate phases. There are seven compounds in the Dy–Co system, namely, Dy_2Co_{17} (Th_2Ni_{17}-type structure, space group $P6_3/mmc$), Dy_2Co_7 (Er_2Co_7-type structure, space group $R\bar{3}m$), $DyCo_3$ ($NbBe_3$-type structure, space group $R\bar{3}m$), $DyCo_2$ ($MgCu_2$-type structure, space group $Fd\bar{3}m$), Dy_4Co_3 (Ho_4Co_3-type structure, space group $P6_3/m$), $Dy_{12}Co_7$ ($Ho_{12}Co_7$-type structure, space group $P2_1/c$) and Dy_3Co (CFe_3-type structure, space group *Pnma*). The $DyCo_5$ ($HoCo_5$-type structure, space group $P6/mmm$) phase decomposes into Dy_2Co_{17} and Dy_2Co_7 at 1130 °C. Wu et al. [15] reinvestigated this system. They demonstrated that the compound Dy_4Co_3 is a metastable phase. Thermodynamic assessment of this system [16] agrees well with the experiments reported by Wu et al. [15]. There is one compound σ (CoCr) in the Co–Cr binary system. No intermetallic phase was found in the Dy–Cr binary system. One ternary compound $Dy(Co, T)_{12}$ has been reported in Refs. [1,2,17]. The compound Dy (Co, Cr)$_{12}$ crystallizes with $ThMn_{12}$-type structure (space group *I*4/*mmm*). Like the Th_2Ni_{17}-(2:17), the $ThMn_{12}$-type (1:12) can be derived from the $CaCu_5$-type structure by replacement of a fraction of the R sites in the $CaCu_5$ structure by pairs of Co atoms (dumb-bells).

2. Experimental

All alloys were synthesized through arc melting pieces Cr (99.95% purity), Co (99.9% purity), and Dy (99.9% purity) on a water-cooled copper hearth using a tungsten electrode in a partial argon atmosphere. The samples were melted several times in order to achieve a full homogenization. The samples with different compositions were prepared. Weight loss of the samples during arc melting is less than 1. Each sample was wrapped into tantalum foil, encapsulated in an evacuated quartz tube and annealed at 750 °C for more than 30 days, followed by lowering at a rate of 10 °C/h to 500 °C and keeping at the temperature for more than 15 days, then quenched into an ice-water mixture.

The samples for X-ray diffraction (XRD) analysis were powdered and investigated by X-ray diffraction on a Rigaku D/Max 2500 PC X-ray diffractometer (Cu, Ka, monochromator), using JADE 5.0 software [18] to analyze the angles, ranging

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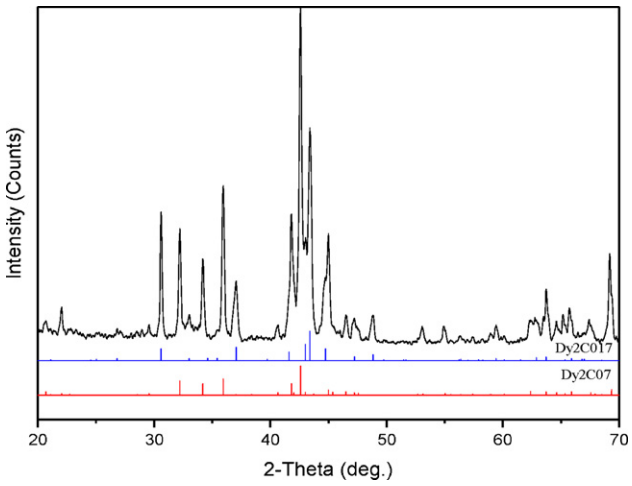

Fig. 1. X-ray diffraction (XRD) pattern of alloy $DyCo_5$.

from 2θ=20° to 80° at 40 kV, 25 mA. Some representative alloys were analyzed in a JSM-5610LV scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). From all these results, the phase relations in the Dy–Co–Cr system were determined.

3. Results and discussion

3.1. Phase analysis

By analyzing and comparing the X-ray diffraction patterns and metallographs of the samples, we have confirmed the existence of seven binary compounds: Dy_2Co_{17}, Dy_2Co_7, $DyCo_3$, $DyCo_2$, $Dy_{12}Co_7$, Dy_3Co and σ (CoCr) in the Dy–Co and Co–Cr systems at 500 °C. In Refs. [19,20], the authors have studied the R_4Co_3 (R = Gd, Tb, Dy) phase. The result shows the single-phase R_4Co_3 (R = Gd, Tb, Dy) are formed hardly even after annealed for a long time at low temperatures. Dy_4Co_3 phase cannot be found in its XRD pattern in our work as well, which is in good agreement with the result reported Ref. [11,12,21]. In Ref. [21], $DyCo_5$ is considered as a high temperature phase with an eutectoid decomposition temperature approximately at 1130 °C. In our work, Fig. 1 shows the XRD pattern of alloy $DyCo_5$. From the XRD patterns of $DyCo_5$, the compound $DyCo_5$ has been decomposed into Dy_2Co_{17} and Dy_2Co_7 at 500 °C. This is in good agreement with Ref. [21]. Thus, the compounds Dy_4Co_3 and $DyCo_5$ should not be presented in this isothermal section.

Liang and Yang et al. [1,2,17] reported the existence of two ternary compounds, namely $R_x(T,M)_y$ of the type 1:12 and 3:29. We prepared a series of samples with composition of $DyCo_{12-x}Cr_x$. Fig. 2 shows the XRD patterns of $DyCo_{12-x}Cr_x$ (x = 3.6, 4.0 and 4.4). The lattice parameters for $DyCO_{12-x}Cr_x$ with $3.6 \le x \le 4.4$ are a = 0.8312–0.8434 nm and c = 0.4706–0.4722 nm. The X-ray diffraction patterns of these samples are in agreement with the data on the calculated XRD pattern of $DyCo_{10}Cr_2$. Due to the compound of $Dy_3Co_{29-x}Cr_x$, we prepared some samples with composition of $Dy_3Co_{29-x}Cr_x$ ($0.6 \le x \le 4.0$). The results show that the XRD patterns of the alloy samples consist of two phases, i.e. Dy_2Co_{17} and Co. So the compound of Dy_3 (Co, Cr)$_{29}$ structure was not observed in our work.

3.2. Solid solubility

By comparing the movement of the diffraction patterns of the single phases and the disappearance of the phases, the solid solubilities of Cr in Dy_2Co_{17}, $DyCo_3$ and $DyCo_2$ were roughly obtained. The lattice parameters of compounds $Dy_2Co_{17-x}Cr_x$, $DyCo_{3-x}Cr_x$ and

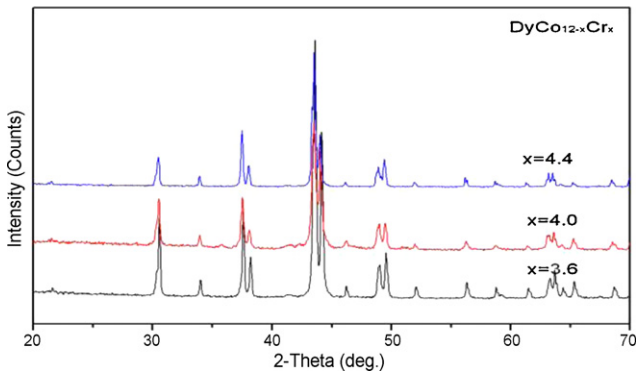

Fig. 2. XRD patterns of $DyCo_{12-x}Cr_x$ with different x (x = 3.6, 4.0, x = 4.4).

$DyCo_{2-x}Cr_x$ were also calculated and refined from X-ray diffraction patterns by using the computer Software Jade 5.0 and the least square method to determine the solubilities of Cr in these compounds. The solid solubilities of Cr in Dy_2Co_{17}, $DyCo_3$ and $DyCo_2$ were about 16.0, 5.0 and 17.0 at.% Cr, respectively. The solubility of Dy in σ (CoCr) was less than 2.0 at.%. The $DyCO_{12-x}Cr_x$ compound has a narrow homogeneity range of 27.7–33.9 at.% Cr.

3.3. Isothermal section at 500 °C

From the results of XRD analysis, metallography and SEM/EDS of all samples, we have identified the phase equilibria in the Dy–Co–Cr ternary system and constructed its isothermal section at 500 °C, as shown in Fig. 3. It consists of 11 single-phase regions, 20 two-phase regions and 10 three-phase regions. Phase identification and phase relationships by XRD for selected alloy are given in Fig. 4. The X-ray diffraction pattern for the sample with the composition of $Dy_{10}Co_{46}Cr_{44}$ located in the $DyCo_3 + DyCo_{12-x}Cr_x + CoCr$ three-phase regions. In order to determine the exact their phase relationships and phase composition, a SEM and EDS analysis are performed for the sample, shown in Fig. 5. The SEM image shows that the alloy consists of three-phase regions, the grey areas are the phase $DyCo_{12-x}Cr_x$, the dark areas are CoCr and the white areas are $DyCo_3$. XRD and SEM/EDS results of the sample $Ce_{10}Co_{46}Cr_{44}$ are presented in Table 1.

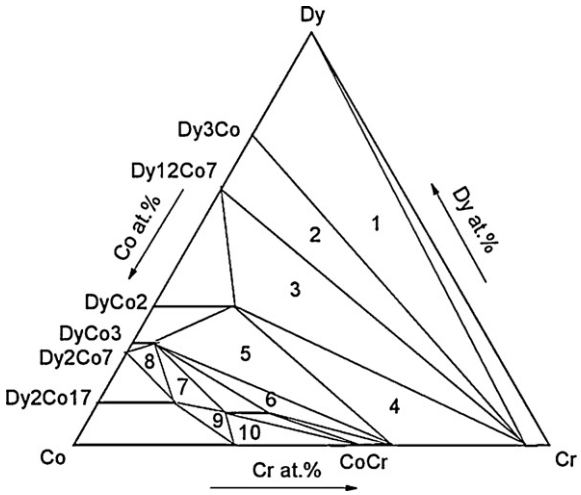

Fig. 3. Isothermal section of the Dy–Co–Cr system at 500 °C.

Table 1
XRD and SEM/EDS results of the sample $Dy_{10}Co_{46}Cr_{44}$.

Alloy	Alloy composition (at.%)			Phase identified by EDS (at.%)				Phase identified by XRD	Notes
	Dy	Co	Cr	Dy	Co	Cr	Phase		
$Dy_{10}Co_{46}Cr_{44}$	10	46	44	0.7	32.9	66.4	CoCr	CoCr	The dark areas in Fig. 5
				8.2	50.7	41.1	$DyCo_{12-x}Cr_x$	$DyCo_{12-x}Cr_x$	The grey areas in Fig. 5
				27.5	56.7	15.8	$DyCo_3$	$DyCo_3$	The white areas in Fig. 5

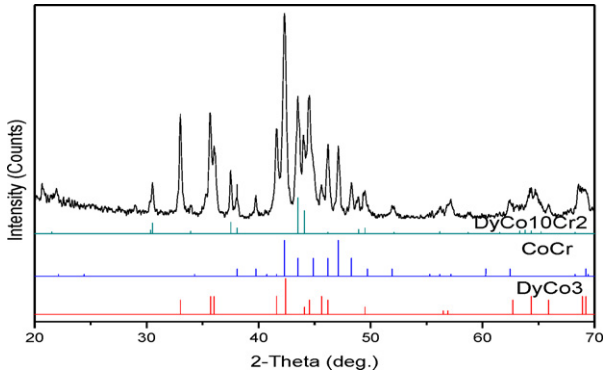

Fig. 4. X-ray diffraction (XRD) pattern of alloy $Dy_{10}Co_{46}Cr_{44}$ situated in the three-phase region no. 6.

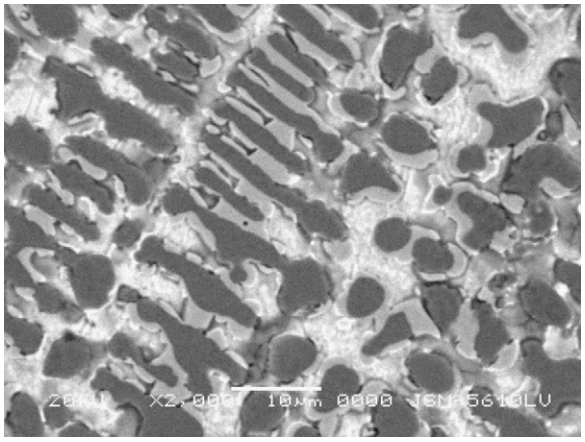

Fig. 5. Micrograph (2000×) of sample $Dy_{10}Co_{46}Cr_{44}$, the grey areas are the phase $DyCo_{12-x}Cr_x$, the dark areas are CoCr and the white areas are $DyCo_3$.

4. Conclusion

The phase equilibria of the Dy–Co–Cr system at 500 °C have been investigated by using XRD, metallography and SEM/EDS techniques. It consists of 11 single-phase regions, 20 two-phase regions and 10 three-phase regions. The ternary phase $DyCo_{12-x}Cr_x$ (space group *I*4/*mmm*) was confirmed in the Dy–Co–Cr ternary system. The variation of lattic parameters with the composition was studied for the ternary solid solution phase $DyCo_{12-x}Cr_x$ and the solubility limit was determined to be $DyCo_{12-x}Cr_x$ ($x = 3.6–4.4$). And the solid solubilities of Cr in Dy_2Co_{17}, $DyCo_3$ and $DyCo_2$ were about 16.0, 5.0 and 17.0 at.% Cr, respectively.

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