Journal of Alloys and Compounds 509 (2011) 258–261

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Isothermal section of the Y–Co–V ternary system at 500 °C

X.X. Wei [a], J.L. Yan [a,*], H.W. Du [a], C.L. Wu [a], K.W. Zhou [a], Y.H. Zhuang [a], J.Q. Li [b]

[a] College of Materials Science and Engineering, Guangxi University and Key Laboratory of Nonferrous Metal Materials and New Processing Technology, Ministry of Education, Guangxi University, Nanning, Guangxi 530004, PR China

[b] College of Materials Science and Engineering, Shenzhen University and Shenzhen Key Laboratory of Special Functional Materials, Shenzhen 518060, PR China

ARTICLE INFO

Article history:
Received 26 July 2010
Received in revised form 5 September 2010
Accepted 8 September 2010
Available online 22 September 2010

Keywords:
Rare earth alloys and compounds
Phase diagrams
X-ray diffraction
SEM

ABSTRACT

The isothermal section of the Y–Co–V system at 500 °C has been investigated by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. Only one ternary compound YV_xCo_{12-x} with a homogeneity range of $1.30 \le x \le 3.64$ was found in this system. The maximum solid solubilities of V in Y_2Co_{17}, Y_2Co_7, YCo_3, YCo_2 and Y_3Co are about 10.0, 1.0, 3.0, 4.0 and 4.0 at.% V, respectively. The compounds VCo and VCo_3 have a homogeneity range of 46–66 at.% V and 22–30 at.% V, respectively. The maximum solid solubility of Y in VCo is about 2.0 at.% Y.

1. Introduction

In the past decades the search for novel permanent magnet materials with the addition of a third element to the R–Co system (where R is the rare earth) has led to the discovery of the ternary compounds, such as $R(Co, M)_{12}$ (type 1:12) and $R_3(Co, M)_{29}$ (type 3:29) (where M is Ti, V, Cr, Mn, Nb, Mo, etc.), which show outstanding magnetic properties. Phase relationships and solubility limits of the compounds in the R–Co–M ternary systems are valuable for material development and thus have attracted research interest [1–3]. For the R–Co–V systems, the phase diagrams for R = Er at 600 °C [1], Gd [2] and Dy [3] at 500 °C have been reported, respectively. In this paper the isothermal section of the Y–Co–V system at 500 °C is presented.

The binary phase diagram of the Y–Co system was firstly investigated by Pelleg and Carlson [4] and Strnat et al. [5], and then by Buschow [6] and Ray [7]. The existence of nine intermetallic compounds, i.e. Y_3Co, Y_3Co_2, YCo, Y_2Co_3, YCo_2, YCo_3, YCo_4, YCo_5 and Y_2Co_{17} in the Y–Co system was reported by Pelleg and Carlson [4]. Strnat et al. [5] proposed that the phase YCo_4 was actually Y_2Co_7 and later the phase Y_2Co_7 was generally accepted by the researchers [6,7]. The partial phase diagram of this system was studied by Khan [8] for 66–100 at.% Co and Grover et al. [9] for 25–50 at.% Co. Recently, the Y–Co system was reinvestigated by Wu et al. [10], and the existence of 12 compounds, namely Y_3Co, Y_8Co_5, Y_3Co_2, Y_9Co_7, YCo, Y_6Co_7, Y_2Co_3, YCo_2, YCo_3, Y_2Co_7, YCo_5 and Y_2Co_{17} was confirmed. The compound Y_9Co_7 was modified to be Y_4Co_3 by Okamoto [11] based on the crystallographic data determined by Berthet-Colominas et al. [12]. Thermodynamic assessment of the Y-Co system was recently reported by Du et al. [13] and the stoichiometries of Y_4Co_3 and Y_6Co_7 were accepted. The phase diagram of the V–Co system was reported with three intermetallic compounds, i.e. VCo_3, VCo and V_3Co [14–16]. No binary compound is formed in the Y–V system [17]. One ternary compound YV_2Co_{10} with tetragonal $ThMn_{12}$-type structure was reported [18] and the magnetic properties of the solid solution YV_xCo_{12-x} was studied [19]. Crystallographic data for the phases in the Y–Co–V system are listed in Table 1.

2. Experimental

Co (99.9 wt.%), Y (99.9 wt.%) and V (99.9 wt.%) were used as the starting materials. Alloy samples of 2 g each were prepared by arc melting the constituent elements under high purity argon atmosphere on a water-cooled copper hearth. Each sample button was turned over and re-melted several times to ensure homogeneity. The weight loss during arc melting was less than 1 wt.%. The Samples in the Co-rich corner (>66.7 at.%Co) were annealed in an evacuated quartz tube at 800 °C for 30 days, and subsequently cooled to 500 °C and kept for 10–40 days. The other alloys were annealed in an evacuated quartz tub at 600 °C or 500 °C for 40–67 days. All the alloy samples were then quenched in liquid nitrogen.

Powder X-ray diffraction (XRD) data were collected at room temperature on a Rigaku D/Max 2500 V diffractometer with CuKα and graphite monochromator operated at 40 kV, 200 mA. The experimental XRD patterns were analyzed using JADE5 software [20] by comparing them with the powder diffraction files and the calculated ones obtained by using the PowderCell program [21]. Microstructures of selected samples were examined by scanning electron microscope (SEM) using backscatter electron (BSE) imaging after standard metallographic preparation. SEM investigation was carried out using Hitachi S-3400N SEM equipped with energy dispersive X-ray spectroscopy (EDS) for phase identification and composition determination.

---

* Corresponding author. Tel.: +86 771 3233530; fax: +86 771 3233530.
E-mail address: yjl@gxu.edu.cn (J.L. Yan).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.09.071

3. Results and discussion

By analyzing the XRD patterns of all the alloy samples and based on the results of SEM/EDS, the existence of 12 binary compounds in the Y–Co system, i.e. Y_3Co, Y_8Co_5, Y_3Co_2, Y_4Co_3, YCo, Y_6Co_7, Y_2Co_3, YCo_2, YCo_3, Y_2Co_7, YCo_5 and Y_2Co_{17}, and three binary compounds in the V–Co system, i.e. VCo_3, VCo and V_3Co was confirmed. Our results showed that the compounds Y_2Co_{17} and YCo_3 are rhombohedral Th_2Zn_{17}-type and rhombohedral Be_3Nb-type structures, respectively, which are in agreement with the results of Wu et al. [10]. No crystallographic data for the compounds Y_2Co_3 and Y_6Co_7 were found in literature. Pelleg and Carison [4] reported that the compound Y_2Co_3 was cubic. However, Wu et al. [10] considered that the phase of Y_2Co_3 was not cubic, though they did not solve its crystal structure. We have determined the structure of the compound Y_2Co_3 in our previous work on phase diagram study of the Y–Co–Nb system. Y_2Co_3 crystallizes in the orthorhombic La_2Ni_3-type structure (space group *Cmca*) with lattice parameters $a = 0.5316(2)$ nm, $b = 0.9472(4)$ nm and $c = 0.7083(3)$ nm [22]. The calculated diffraction pattern of Y_2Co_3 based on this structure matches well with the observed diffraction pattern of relevant alloys. About the phase of Y_6Co_7, its crystal structure is yet to be established. However some of its main reflections have been figured out in this work. Fig. 1 shows the XRD pattern of the alloy with nominal Y_6Co_7 composition (Alloy #2 in Fig. 2). XRD analysis indicated that it has some unidentified reflection peaks except for the phases of YCo_2 and Y_2Co_3. The unidentified reflection peaks were considered to be corresponding to the Y_6Co_7 phase. The 2-theta positions are marked in Fig. 1, they are 30.92, 31.26, 34.12, 34.92, 36.32, 41.84, 44.04, 44.80 (°2θ). Both or either one of the Y_8Co_5 and Y_3Co_2 phases were observed in alloy samples which have been annealed at 600 °C or 500 °C. Some of these samples were re-annealed at about 730 °C for 7 days and then kept at 500 °C for 5 days before XRD experiments. XRD analysis of these samples revealed the disappearing of the Y_8Co_5 phase and the enhancement or the presence of the Y_3Co_2 phase. This indicates that the Y_3Co_2 phase is a metastable phase existing in the as-cast alloys and in alloys annealed at or above 600 °C.

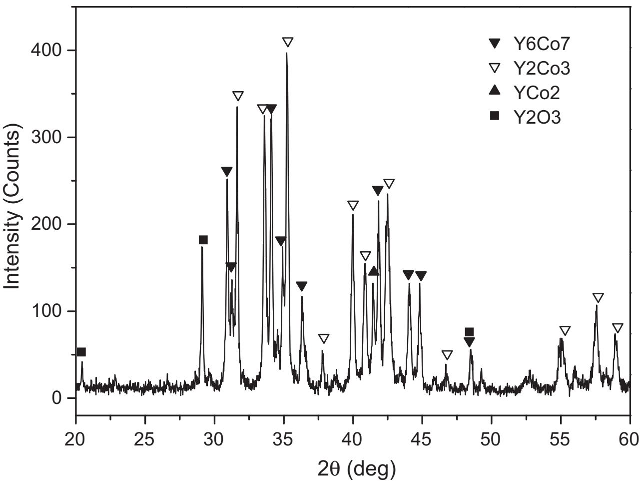

Fig. 1. XRD pattern of the alloy with nominal Y_6Co_7 composition (Alloy #2 in Fig. 2) annealed at 600 °C for 50 days and then at 500 °C for 15 days. Peaks attributed to Y_2Co_3, YCo_2 and Y_2O_3 are identified.

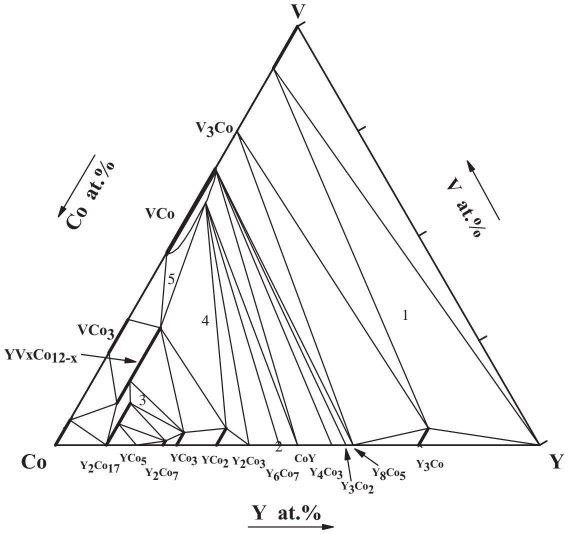

Fig. 2. Isothermal section of the Y–Co–V ternary system at 500 °C.

Table 1
Crystallographic data for the compounds in the Y–Co–V system.

Phase	Space group	Structure type	Lattice parameters (nm)			β(o)	Ref.
			a	b	c		
Y_2Co_{17}	*P6₃/mmm*	Th_2Ni_{17}	0.8355		0.8128		[18]
Y_2Co_{17}	*R-3m*	Th_2Zn_{17}	0.8356		1.220		[18]
YCo_5	*P6/mmm*	$CaCu_5$	0.4951		0.3975		[18]
Y_2Co_7	*R-3m*	Er_2Co_7	0.5000		3.615		[18]
YCo_3	*R-3m*	Be_3Nb	0.5020(5)		2.440(3)		[18]
YCo_3	*P6₃/mmc*	$CeNi_3$	0.5015		1.628		[18]
YCo_2	*Fd-3m*	Cu_2Mg	0.7218				[18]
Y_2Co_3	*Cmca*	La_2Ni_3	0.5316(2)	0.9472(4)	0.7083(3)		[22]
$Y_{\sim6}Co_{\sim7}$		Unknown					
YCo	*Cmcm*	BCr	0.4106(1)	1.0358(5)	0.3906(1)		[18]
Y_4Co_3	*P6₃/m*	Ho_4Co_3	1.1528(5)		0.4051(2)		[18]
Y_3Co_2	*Pnnm*	Y_3Co_2	1.2248(5)	0.9389(6)	0.3975(3)		[18]
Y_8Co_5	*P2₁/c*	Y_8Co_5	0.7058(2)	0.7286(2)	2.4277(8)	102.11	[18]
Y_3Co	*Pnma*	CFe_3	0.7052	0.9450	0.6338		[18]
VCo_3	*P-6m2*	VCo_3	0.5032		1.227		[18]
VCo	*P4₂/mnm*	$CaCu_5$	8.800		4.552		[18]
V_3Co	*Pm-3n*	Cr_3Si	0.4676				[18]
YV_2Co_{10}	*I4/mmm*	$ThMn_{12}$	0.83566		0.46975		[18]

Ternary compound YV_2Co_{10} with tetragonal $ThMn_{12}$-type structure was confirmed to exist in the Y–Co–V system, no other ternary compound was found. The compound YV_2Co_{10} exhibits a linear homogeneity range along the line of 7.7 at.% Y. To determine the solubility range of YV_xCo_{12-x}, we prepared alloy samples along the iso-concentration line of 7.7 at.% Y with the concentration of V

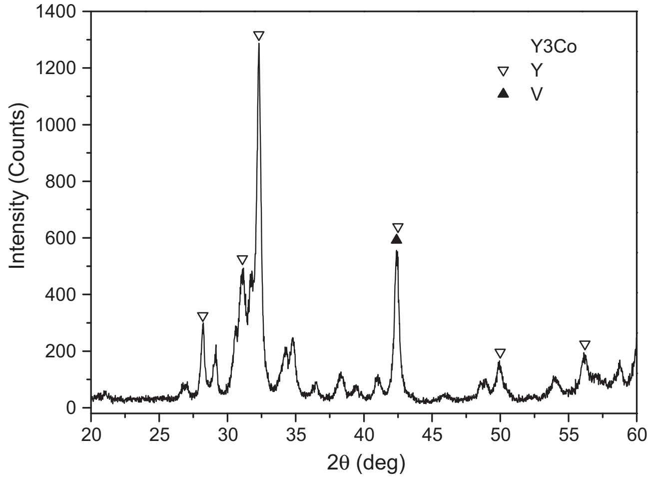

Fig. 3. XRD pattern of alloy Y57V31Co12 (Alloy #1 in Fig. 2) annealed at 500 °C for 62 days: three-phase region of Y + Y_3Co + V. Peaks attributed to Y and V are marked, all the other peaks are attributed to Y_3Co.

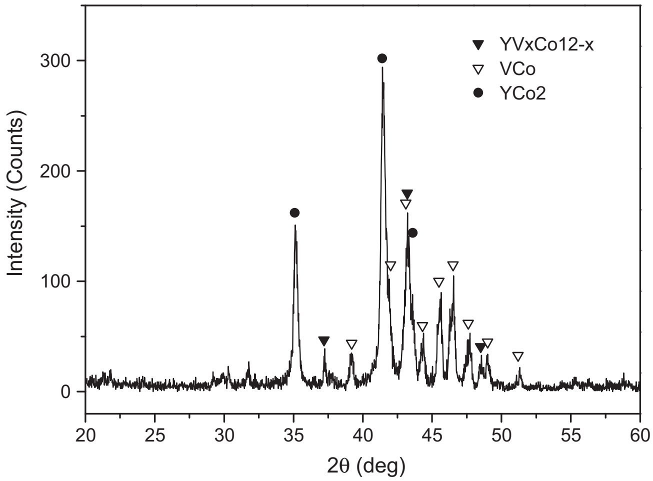

Fig. 5. XRD pattern of alloy Y16V30Co54 (Alloy #4 in Fig. 2) annealed at 500 °C for 67 days: three-phase region of YV_xCo_{12-x} + YCo_2 + VCo.

varying from 6 to 36 at.% based on the reported homogeneity range of phase RV_xCo_{12-x} for R = Y [19], Er [1], Gd [2] and Dy [3]. In this work the homogeneity of compound YV_xCo_{12-x} was found to be $1.30 \leq x \leq 3.64$, i.e. 10–28 at.% V.

By analyzing the XRD patterns of the samples and identifying the phases in each sample, together with SEM/EDS results for selected samples, we constructed the isothermal section of the ternary Y–Co–V system at 500 °C (Fig. 2), The XRD pattern for alloy Y57V31Co12 (Alloy #1 in Fig. 2) in the Y-rich corner is presented in Fig. 3. XRD analysis of this alloy indicated that it is located in the three-phase region of Y_3Co, V and Y. To fully determine the three-phase region of (YV_xCo_{12-x} + Y_2Co_{17} + YCo_3), SEM/EDS investigation was also carried out. Fig. 4 presents the XRD pattern and the BSE image of alloy Y12.5V11Co76.5 (measured composition Y13.2V11.1Co75.7) (Alloy #3 in Fig. 2). Both results of phase identification and composition determination by XRD and SEM/EDS have indicated that alloy Y12.5V11Co76.5 contains three phase, the dark grey phase with measured composition of Y9.1V15.6Co75.3 is YV_xCo_{12-x}, the matrix phase with measured composition of Y11.6V10.0Co78.4 is Y_2Co_{17} and the light grey phase with measured composition of Y25.0V1.2Co73.8 is YCo_3. The homogeneity ranges of some binary compounds were determined by using the phase-disappearing method on the analysis of XRD patterns. The maximum solid solubilities of V in the compounds Y_2Co_{17}, Y_2Co_7, YCo_3, YCo_2 and Y_3Co are about 10, 1.0, 3.0, 4.0 and 4.0 at.% V, respectively. The compounds VCo_3 and VCo have a narrow homogeneity range of 22–30 and 46–66 at.% V, respectively. The maximum solu-

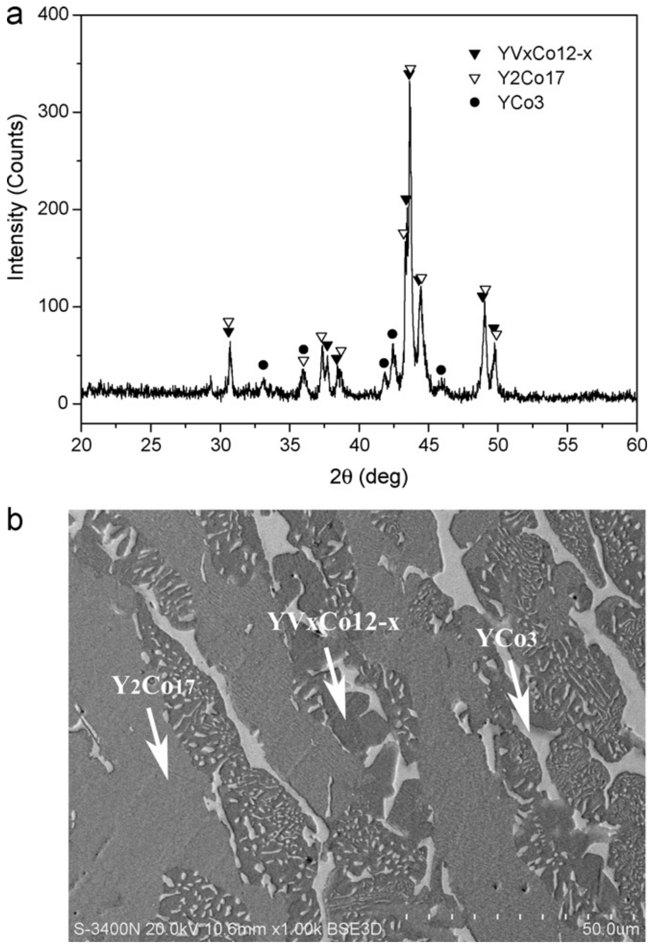

Fig. 4. XRD pattern (a) and microstructure (b) of Y12.5V11Co76.5 (Alloy #3 in Fig. 2) annealed at 800 °C for 30 days and then at 500 °C for 13 days. The dark grey phase is YV_xCo_{12-x}, the light grey phase is YCo_3, and the matrix phase is Y_2Co_{17}.

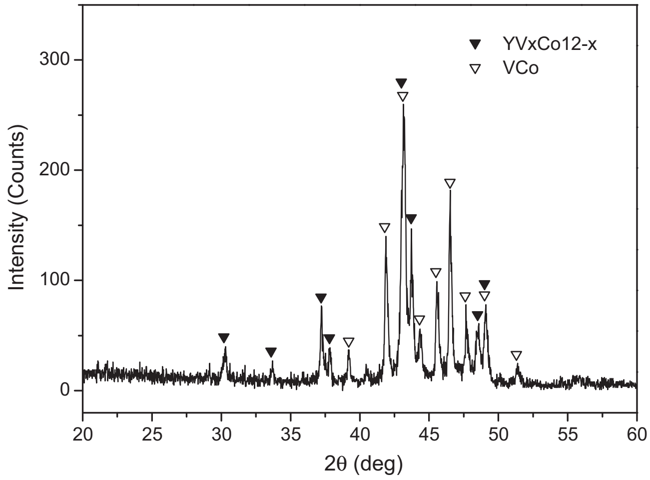

Fig. 6. XRD pattern of alloy Y4V40Co56 (Alloy #5 in Fig. 2) annealed at 800 °C for 30 days and then at 500 °C for 13 days: two-phase region of YV_xCo_{12-x} + VCo.

bility of Y in VCo is 2.0 at.%. No noticeable solubility was found for other compounds.

The isothermal sections of the R–Co–V systems for R = Gd at 500 °C [2], R = Dy at 500 °C [3] and R = Er at 600 °C [1] have been studied, and a large two-phase region of (RCo_2 + VCo) were reported to exist in these systems. However in our work no such a two-phase region was observed, instead a two-phase region of (YV_xCo_{12-x} + VCo) was found. Fig. 5 presents the XRD pattern of the alloy Y16V30Co54 (Alloy #4 in Fig. 2). XRD analysis indicated that the alloy Y16V30Co54 contains three phase YV_xCo_{12-x}, YCo_2 and VCo. In addition, the XRD pattern of alloy Y4V40Co56 (Alloy #5 in Fig. 2) contains only two phases of YV_xCo_{12-x} and VCo (Fig. 6). Based the XRD results of the alloys prepared around these regions, the phase boundaries of the three-phase region of (YV_xCo_{12-x} + YCo_2 + VCo) and the two-phase region of (YV_xCo_{12-x} + VCo) were determined.

4. Conclusions

The isothermal section of the Y–Co–V system at 500 °C has been determined by means of XRD and SEM/EDS techniques. Only one ternary compound YV_xCo_{12-x} was found in this system and it exhibits a linear homogeneity range for $1.30 \leq x \leq 3.64$. The existence of 15 binary compounds, i.e. Y_3Co, Y_8Co_5, Y_4Co_3, Y_3Co_2, YCo, Y_2Co_3, Y_6Co_7, YCo_2, YCo_3, Y_2Co_7, YCo_5, Y_2Co_{17}, VCo_3, VCo and V_3Co was confirmed. The maximum solid solubilities of V substitution for Co in the compounds Y_2Co_{17}, Y_2Co_7, YCo_3, YCo_2 and Y_3Co are about 10, 1.0, 3.0, 4.0 and 4.0 at.%, respectively. The compounds VCo_3 and VCo have a narrow homogeneity range of 22–30 and 46–66 at.% V, respectively. The maximum solubility of Y in VCo phase is about 2.0 at.%.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Nos. 50861004, 50871070).

References

[1] B. Kotur, O. Myakush, I. Zavaliy, J. Alloys Compd. 442 (2007) 17–21.
[2] W. He, X. Xia, J. Huang, H. Zhong, J. Yang, W. Zheng, L. Zeng, J. Alloys Compd. 470 (2009) 218–221.
[3] H. Wang, H. Zhou, Q. Yao, X. Hu, S. Pan, Z. Wang, J. Alloys Compd. 479 (2009) 180–183.
[4] J. Pelleg, O.N. Carlson, J. Less-Common Met. 9 (1965) 281–288.
[5] K.J. Strnat, W. Ostertag, N.J. Adams, J.C. Olson, Proc. 5th Rare Earth F Res. Conf. Vol. 5, Ames, Iowa, 1965, pp. 67–76.
[6] K.H.J. Buschow, Philips Res. Rep. 26 (1971) 49–64.
[7] A.E. Ray, Cobalt 1 (1974) 13.
[8] Y. Khan, Z. Metallkd. 65 (1974) 489–495.
[9] A.K. Grover, B.R. Coles, B.V.B. Sarkissian, H.E.N. Stone, J. Less-Common Met. 86 (1982) 29–36.
[10] C.H. Wu, Y.C. Chuang, X.P. Su, Z. Metallkd. 82 (1991) 73–79.
[11] H. Okamoto, J. Phase Equilib. 13 (1992) 326–328.
[12] C. Berthet-Colominas, J. Laforest, R. Lemaire, R. Pauthenet, J. Sohweizer, Cobalt 39 (1968) 97–101.
[13] Z. Du, D. Lu, J. Alloys Compd. 373 (2004) 171–178.
[14] W. Koster, H. Schimd, Z. Metallkd. 46 (1955) 195–197.
[15] J.F. Smith, J. Phase Equilib. 12 (1991) 324–331.
[16] L.J. Nagel, B. Fultz, L. Robertson, J. Phase Equilib. 18 (1997) 21–23.
[17] T.B. Massalski, P.R. Subramanian, H. Okamoto, L. Kacprzak (Eds.), Binary Alloy Phase Diagrams, vols. 1–3, 2nd ed., ASM International, Materials Park, OH, 1990.
[18] P. Villars (Ed.), Pearson's Handbook: Crystallographic Data for Intermetallic Phases, desk ed., ASM International, Materials Park, OH, 1997.
[19] M. Jurczyk, J. Magn. Magn. Mater. 87 (1990) 1–4.
[20] Materials Data JADE Release 5, XRD pattern processing, Materials Data Inc., Livermore, CA, 1999.
[21] W. Kraus, G. Nolze, J. Appl. Crystallogr. 29 (1996) 301–303.
[22] J.L. Yan, C. Gao, C. Liu, X.X. Wei, Y.H. Zhuang, J.Q. Li, J. Alloys Compd., under review.