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Solid-state phase equilibria in the Co–Pt–Tb ternary system at 1173 K

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ABSTRACT

The solid-state phase equilibria in the Co–Pt–Tb ternary system at 1173 K (Tb ≤ 70%) were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) techniques. The 1173 K isothermal section consists of 14 single-phase regions, 25 two-phase regions and 12 three-phase regions. At 1173 K, we have observed that the maximum solubility of Tb in α-(Co, Pt) is below 1.5 at.%Tb, with the maximum solid solubility of Pt in the compounds $Co_{17}Tb_2$, Co_7Tb_2, Co_3Tb and Co_2Tb being below 1 at.%Pt, 2 at.%Pt, 3.5 at.%Pt and 2 at.%Pt, respectively. Furthermore, the maximum solid solubility of Co in the compounds Pt_5Tb, Pt_3Tb, Pt_4Tb_3, PtTb, Pt_4Tb_5, Pt_3Tb_5, $PtTb_2$ and $PtTb_3$ is below 1 at.%Co, whereas in Pt_2Tb it reaches 17 at.%Co. With the introduction of Co, the Pt_4Tb_3 phase gradually decomposes into the two neighboring compounds PtTb and Pt_2Tb, while with the Co content exceeded 9 at.%Co, the Pt_4Tb_3 phase disappears. No new ternary compounds or Co_5Tb were observed in our study.

1. Introduction

The Co–Pt, Pt–Tb, Co–Tb binary systems that bounds the Co–Pt–Tb ternary system have been widely investigated. It has been reported that cobalt and platinum form a continuous solid solution in the Co–Pt binary system at 1173 K [1]. The Co–Tb binary system phase equilibria had also been well studied [2–4], with the formation of five binary compounds $Co_{17}Tb_2$ ($Zn_{17}Th_2$ structure type), Co_5Tb ($CaCu_5$ structure type), Co_7Tb_2 (Co_7Er_2 structure type), Co_3Tb (Ni_3Pu structure type) and Co_2Tb (Cu_2Mg structure type) having been discovered. Specific research about the Co_5Tb compound showed it to be present after annealing at 1273 K for 100 h [5], however, its eutectoid decomposition reaction would take place at around 1083 K [6]. Thus, ones proposed it to be a high temperature phase or a metastable phase at low temperature [6,7]. Furthermore, nine binary compounds, Pt_5Tb (Pt_5Sm structure type), Pt_3Tb ($AuCu_3$ structure type), Pt_2Tb ($MgCu_2$ structure type), Pt_4Tb_3 (Pd_4Pu_3 structure type), PtTb (BFe structure type), Pt_4Tb_5 (Pu_5Rh_4 structure type), Pt_3Tb_5 (Mn_5Si_3 structure type), $PtTb_2$ (Co_2Si structure type) and $PtTb_3$ (CFe_3 structure type) have been reported in the Pt–Tb binary system [3,8–16]. Crystallographic data for these binary compounds of the Co–Tb and Pt–Tb systems are collected in Table 1.

However, the study about the Co–Pt–Tb ternary system itself has been comparatively scarce up to now. We present here a systematically experimental investigation of the isothermal section of this system at 1173 K so as to reveal their phase equilibria relationship.

2. Experimental

All samples were prepared by raw materials (terbium, cobalt, and platinum) with the purity above 99.9%. In order to build the solid-state phase equilibria in the Co–Pt–Tb system at 1173 K, 68 alloy buttons have been prepared by arc melting on a water-cooled copper hearth under argon atmosphere. These buttons were melted and turned at least four times to ensure homogeneity. The mass losses after the melting process were less than 0.5 wt%. After melting, the samples were sealed in quartz tubes pre-evacuated and refilled with purified argon, along with being annealed at 1173 K for 15 days followed by quenching in water. The brittle samples were ground to powders in a carnelian mortar for X-ray diffraction. A few tough samples were first pressed into slices (7 mm × 3 mm × 1 mm) and sealed in quartz tubes, then annealed under the protection of purified argon at 1173 K for 15 days to ensure homogeneity and eliminate the stress, further with quenching in ice-water for X-ray diffraction. The samples in the Co-rich region were crumbled to particles in a stainless steel mortar, and then ground to powders in a carnelian mortar, which were finally annealed under the protection of purified argon at 1173 K for several hours to eliminate the stress and quenched in ice-water for X-ray diffraction. X-ray diffraction (Cu Kα radiation), scanning electron microscopy and energy dispersion spectroscopy techniques were used in the phase analysis investigation. Samples for X-ray diffraction analysis were analyzed on a D8 advance diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. Phase analysis

3.1.1. The Pt–Tb binary system

The Pt_4Tb_3 compound (Pd_4Pu_3 type) exists up to 300 °C in the Pt–Tb binary system [12]. As for the binary system, our result also showed that the Pt_4Tb_3 exists at 900 °C (Fig. 1(a)), but with

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Table 1
Crystallographic data of the binary compounds of the Co–Tb, Pt–Tb systems.

Compounds	Structure type	Space group	Lattice parameters (nm)			References
			a	*b*	*c*	
$Co_{17}Tb_2$	Th_2Zn_{17}	$R\bar{3}m$	0.8344	–	1.219	[2,3]
Co_5Tb	$CaCu_5$	*P6/mmm*	0.49608	–	0.3981	[2,3]
$C0_7Tb_2$	Co_7Er_2	$R\bar{3}m$	0.5002	–	3.6211	[2,3]
Co_3Tb	Ni_3Pu	$R\bar{3}m$	0.502	–	2.445	[2,4]
Co_2Tb	Cu_2Mg	$Fd\bar{3}m$	0.7209	–	–	[2,3]
Pt_5Tb	Pt_5Sm	–	0.5248	0.9092	2.644	[8,9]
Pt_3Tb	$AuCu_3$	$Pm\bar{3}m$	0.40839	–	–	[3,10]
Pt_2Tb	$MgCu_2$	$Fd\bar{3}m$	0.7618	–	–	[3,11]
Pt_4Tb_3	Pd_4Pu_3	$R\bar{3}$	1.3163	–	0.5689	[3,12]
PtTb	BFe	*Pnma*	0.7013	0.449	0.5564	[3,13]
Pt_4Tb_5	Pu_5Rh_4	*Pnma*	0.7495	1.4602	0.7565	[3,14]
Pt_3Tb_5	Mn_5Si_3	$P6_3/mcm$	0.8415	–	0.6230	[3,15]
Pt Tb_2	Co_2Si	*Pnma*	0.7147	0.4772	0.8763	[3,15]
Pt Tb_3	CFe_3	*Pnma*	0.7077	0.9541	0.6444	[3,16]

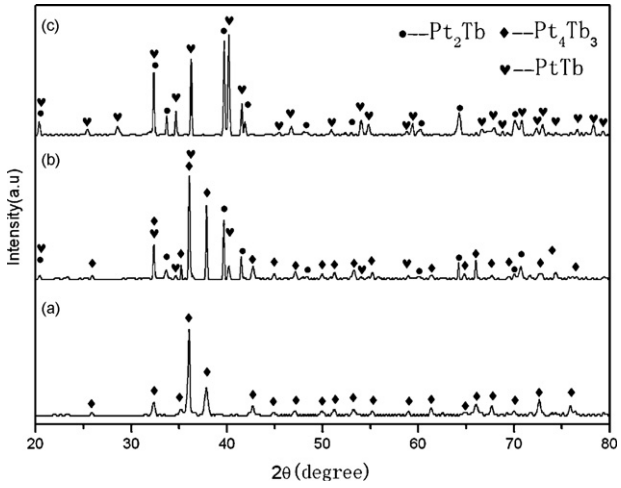

Fig. 1. Observed XRD patterns of the Pt_4Tb_3 (a), $Co_4Pt_{53}Tb_{43}$ (b) and $Co_9Pt_{48}Tb_{43}$ (c) compounds annealed at 1173 K for 15 days.

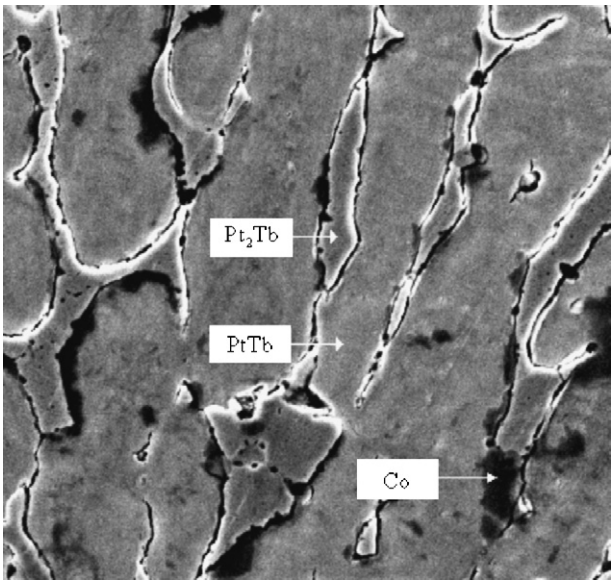

Fig. 2. SEM image of $Co_9Pt_{48}Tb_{43}$ sample annealed at 1173 K for 15 days.

the introduction of Co, it was found that the compound decomposed gradually into PtTb (BFe type) and Pt_2Tb ($MgCu_2$ type) (Fig. 1(b)). Further evidence is given by the XRD pattern and SEM image of the $Co_9Pt_{48}Tb_{43}$ sample, which is presented in Fig. 1(c) and Fig. 2, respectively. From XRD data, it was found that two phases PtTb and Pt_2Tb are present in $Co_9Pt_{48}Tb_{43}$, while from the SEM image, together with EDS analysis, it can be identified that it is a three-phase sample, which includes Co, Pt_2Tb and PtTb (although Co can not be detected in the XRD pattern). This suggested that Co addition destabilizes the Pt_4Tb_3 compound, leading to Pt_4Tb_3 complete decomposition in $Co_9Pt_{48}Tb_{43}$. The similar decomposition cases were also observed in Pr_3Pt_4 [17] and Nd_3Pt_4 [18].

Previous research has shown that the Pt_3Tb phase in the Pt–Tb binary system possesses the C15-type structure under the "as-crushed", arc-melted condition [10], but other experiments also revealed that if it was annealed at 1173 K for two hours, this alloy would adopt the L_{12}-type ($AuCu_3$ type) structure [19]. We prepared some samples between the Pt_3Tb and Pt_2Tb phase in the Pt–Tb binary system. From XRD patterns showed in Fig. 3, one can clearly visualize that the sample $Pt_{83}Tb_{27}$ consists of both Pt_3Tb with $AuCu_3$-type structure and Pt_2Tb with $MgCu_2$-type structure. This means that the phase Pt_3Tb with $AuCu_3$ structure type exists under our presently experimental condition. This conclusion is in good agreement with that reported in Ref. [2].

3.1.2. *The Co–Tb binary system*

The Co_5Tb compound ($CaCu_5$–type structure) was proved to be a high temperature phase with eutectoid decomposition temperature at about 1083 K in the series of Co_5R binary system [20], and it was also reported that the Co_5Tb compound would not

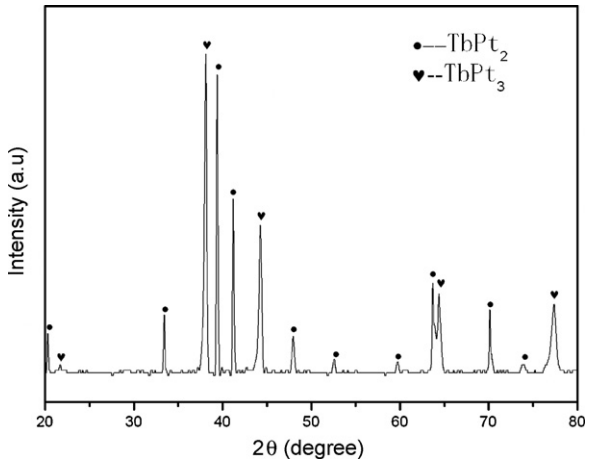

Fig. 3. Observed XRD pattern of the $Pt_{83}Tb_{27}$ sample annealed at 1173 K for 15 days.