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The interaction of palladium with cobalt and erbium at 600°C

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Abstract

The interaction of the components in the Er–Co–Pd system at 600°C was investigated over the composition range 0–50 at% of erbium by X-ray powder, metallography, electron probe microanalysis (EPMA), DTA and SEM. The isothermal section at 600°C was determined based on these results.

Keywords: Phase equilibria; Ternary section; Rare earth

1. Introduction

The intermetallic compounds RE–Fe,Co,Ni (RE, rare earth) are known to exhibit unique magnetic properties (high saturation magnetization and Curie temperature). But the practical use of such materials is limited due to their high oxidizability and poor processibility. The addition of noble metals (NM) could solve the problem and improve their technological characteristics. Therefore, the study of ternary alloys RE–Fe(Co,Ni)–NM is of great interest. This report is devoted to the study of the phase equilibria in the Er–Co–Pd system at 600°C.

There is no data on the physical–chemical interactions of the elements in the Er–Co–Pd system in the literature. The three limiting binary systems Er–Pd, Er–Co and Co–Pd have been studied in detail [1–8]. Palladium and cobalt form a continuous series of solid solution [1,2]. The phase diagram of the Er–Pd system is characterized by a wide range of palladium-based solid solution and by the formation of the following intermetallic compounds (IMC): $ErPd_3$, $ErPd_2$, Er_2Pd_3, Er_3Pd_4, Er_4Pd_5, ErPd, Er_3Pd_2, Er_5Pd_2 [3–6]. The crystal structure of the IMC $ErPd_2$, Er_2Pd_3 and Er_4Pd_5 was not determined. At 565–548°C, the equiatomic phase ErPd undergoes polymorphic transformation CsCl(HT)→CrB(LT). Sacamoto et al. [5] assumed that the regulated $ErPd_7$ phase forms at 450°C. The binary phase diagram Er–Co was investigated previously [7,8]. There are five intermediate phases in the Co-rich (Co>50 at%) region in the Er–Co system: $ErCo_2$, $ErCo_3$, Er_2Co_7, $ErCo_5$, Er_2Co_{17}. The $ErCo_5$ decomposes into Er_2Co_7 and Er_2Co_{17} at 1240°C [7] or 1150°C [8].

2. Experimental details

The phase equilibria in the Er–Co–Pd system (Er<50 at%) have been determined by analyzing 70 samples having a mass of 2 g. The starting materials were palladium (purity: 99.9%), erbium (purity: 99.67%) and cobalt (purity: 99.9%). The samples were pressed and melted in an electric arc furnace in a purified argon atmosphere with a nonconsumable tungsten electrode and a water cooled copper hearth. Titanium was used as a getter during melting. The alloys were remelted twice in order to achieve complete fusion and homogeneity. After melting, the alloys having mass losses of <1.5% were sealed in evacuated double-walled quartz ampoules containing titanium chips as getters. Annealing was performed in a resistance furnace at 600°C for 2500 h with a subsequent quench in ice water.

Metallography, X-ray, electron probe microanalysis (EPMA), scanning electron microscopy (SEM) and differential thermal analysis (DTA) were used in the present investigation. Microstructures were examined with a Neophot 32 microscope at magnifications of 125–400× and a Camebax microanalyzer (400–2000×). Pd-rich samples were etched in a $Br_2+C_2H_5OH$ (1:4) solution; Co-rich samples were etched by HNO_3+CH_3COOH (1:2) mixture. A $HNO_3+C_2H_5OH$ (1:2) mixture was used for etching Er-rich alloys.

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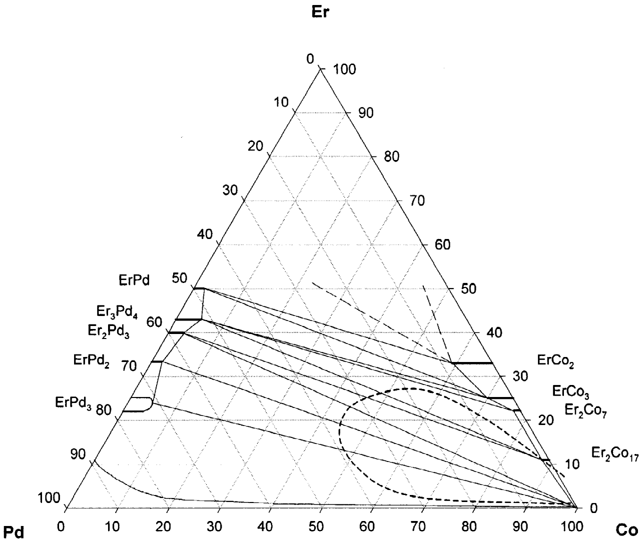

Fig. 1. Isothermal cross-section of the Er–Co–Pd system at 600°C.

X-ray phase analysis was performed on powder samples with a DRON-3.0 (Cu Kα monochromatizated radiation).

EPMA and SEM was carried out on a Camebax Microbeam analyser using K_β, L_α and L_β lines for Co, Pd and Er, respectively. Numerical evaluation of the results was performed using standard computer programs.

High temperature VDTA-8M2 equipment (W–W/Re thermocouples) was used for DTA experiments. Pure Fe, Cu and Pt metals were used as calibration standards.

The alloys composition control was carried out by control weighting, metallography, EPMA and spectrophotometry using SF-46 device.

3. Results and discussion

The results obtained enabled us to establish the isothermal section at 600°C of the Er–Co–Pd phase diagram over the composition range 0–50 at% of Er (Fig. 1). As expected, the ternary phases are absent in above system. We confirmed the existence of ErPd, Er_3Pd_4, Er_2Pd_3, $ErPd_2$, $ErPd_3$, Er_2Co_{17}, Er_2Co_7, $ErCo_3$ and $ErCo_2$ binary compounds (shown on the axes of the composition triangle). The crystal structure of Er_2Pd_3 and $ErPd_2$ intermetallides was not described previously. RE_2Pd_3 compounds are known only for Y, Gd, Er, Dy, Ho, and their crystal structure also were not determined. $REPd_2$ compounds exist in all RE–Pd systems, but the crystal structure was only determined for $EuPd_2$, $ScPd_2$ (Laves phases), $LuPd_2$ (tetragonal, $MoSi_2$ type) and $SmPd_2$ (monoclinic, unknown prototype) [3]. Suitable monocrystals could not be obtained, so no crystal structure determinations were performed. The phase corresponding to the composition Er_4Pd_5 was not detected in the as-cast or in the thermally treated (at 600°C) states (in agreement with Ref. [4]). The $ErPd_7$ ordered phase was supposed to form at 723 K peritectoidly: $\alpha\text{-Pd}+ErPd_3 \leftrightarrow ErPd_7$ by Sakamoto et al. [5]. We did not observe any ordering for above composition. The crystal structure of the equiatomic phase ErPd is bcc (CsCl type, $a=0.3453(5)$ nm), but is orthorhombic (CrB type, $a=0.3661(9)$, $b=1.0540(8)$, $c=0.4507(5)$ nm) in the Er44Pd56 composition alloy. In the palladium-rich alloys of the ternary system, the ErPd phase was identified as CrB type also. So the increase of the palladium content and addition of the third component seem to intensify the bcc lattice destabilization and increase the polymorphic transformation CsCl(HT)→CrB(LT) temperature.

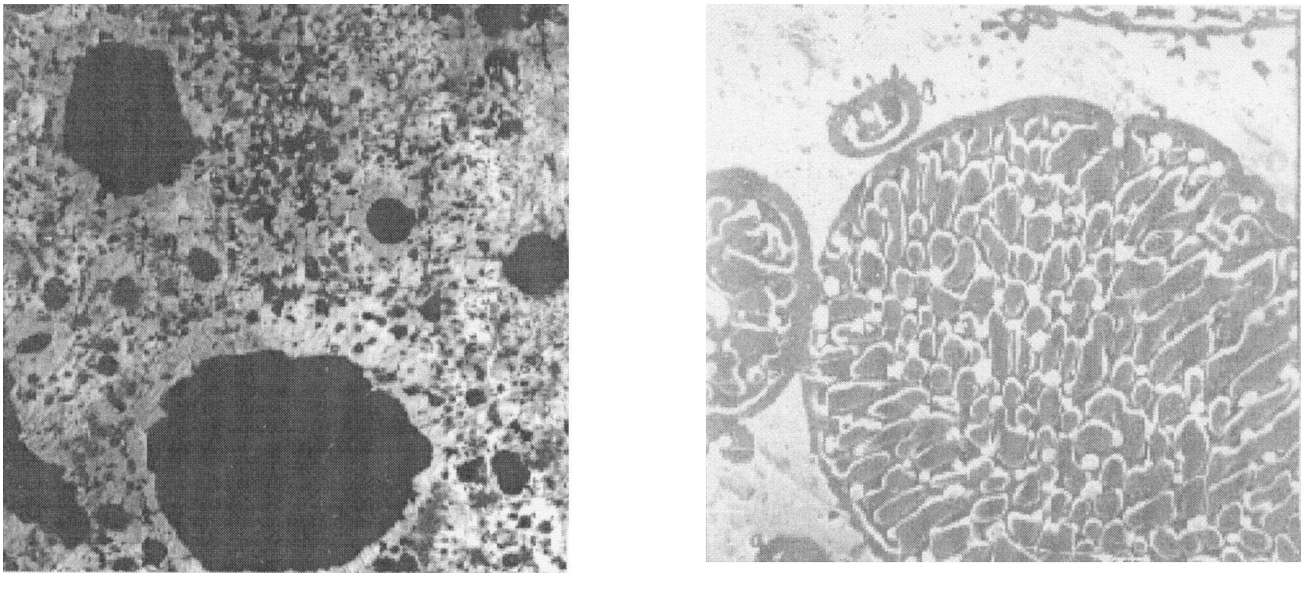

Fig. 2. Microstructure of $Er_{33}Co_{57}Pd_{10}$ (a) and $Er_{14}Co_{66}Pd_{20}$ (b).

Table 1
Data for the EPMA of some immiscible alloys of the Er–Co–Pd system

Alloy composition (at%)			Composition of phases (at%)						Phase
			Matrix			Inclusions			
Co	Er	Pd	Co	Er	Pd	Co	Er	Pd	
66	14	20	5.00	43.80	51.20				Er_3Pd_4
						99.93	0.00	0.07	Co
						0.00	59.8	40.20	Er_2Pd_3
69	11	20	99.96	0.00	0.04				Co
						3.10	3.27	64.20	$ErPd_2$
84	11	5	99.97	0.00	0.03				Co
						0.00	40.40	59.60	Er_2Pd_3
						0.00	42.90	57.10	Er_3Pd_4
55	25	20	0.00	42.20	57.80				Er_3Pd_4
						78.20	19.80	2.00	Er_2Co_7
						84.60	13.10	2.30	Er_2Co_{17}
81	14	5	85.10	12.70	2.20				Er_2Co_{17}
						0.00	43.00	57.00	Er_3Pd_4
95	2.5	2.5	98.30	0.00	1.70				Co
						87.40	9.60	3.00	Er_2Co_{17}

The isothermal section of the Er–Co–Pd system is characterized by the formation of ternary solid solution regions of different widths. All these regions are based on the initial binary compounds of Er–Pd and Er–Co systems and extend into the ternary system along the corresponding constant Er concentration lines. The palladium solubility in Er_2Co_{17}, Er_2Co_7 and $ErCo_3$ phases does not exceed 2–3 at%, but reaches 8 at% in Laves phase $ErCo_2$. An homogeneity region of 22–25 at% Er ($a=0.4055(1)$–$0.4051(1)$ nm) was defined for the $ErPd_3$ phase ($AuCu_3$ type), 5 at% of Co being dissolved. The other binary phases of the Er–Pd system dissolve <5 at% of Co. The most extended region is the ternary solid solution based on Co and Pd. The solid solubility of Er in Pd is 11 at% at the temperature under investigation.

The distinctive feature of this state diagram is the presence of a miscibility gap in the Co-rich region. The alloys from this region have a very distinctive microstructure (Fig. 2). The composition of solidified immiscible liquids correspond to one of the Co, Er_2Co_7, Er_2Co_{17} phases on one side and one of the intermediate phases in the Er–Pd system (Er_2Pd_3, Er_3Pd_4, $ErPd_2$) on the other side (Table 1). Using high pure metals, repeated remelting and long-time annealing does not eliminate the existence of immiscibility region. The DTA experiments confirm the melting temperatures of the miscibility gap to be much higher than 600°C, so melting the alloys by increasing the temperature is impossible.

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