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Letter

The phase diagram of Pd–Pr below 50 at.% Pr

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Abstract

The region containing 0–50 at.% Pr in the Pd–Pr phase diagram has been studied with X-ray diffraction, differential thermal analysis and microscopic techniques. It has been found that there are six intermetallic compounds with the presence of three eutectic reactions and three peritectic reactions in the region.

1. Introduction

A variety of Pd–RE alloys (where RE denotes a rare earth) have been applied in industry in recent years. Most of the phase diagrams of Pd–RE alloy systems have been studied [1–6]. Until now, however, the phase diagram of the Pd–Pr binary system has not been reported.

In this work, the Pd–Pr binary system was studied and the phase diagram (for praseodymium contents of 50 at.% or less) was established by means of X-ray diffraction, differential thermal analysis (DTA) and microscopic techniques.

2. Experiments

Palladium and praseodymium as 99.9% pure metal were used. For degassing, the palladium was refined in a high-frequency induction furnace filled with argon; then the obtained palladium ingots were rolled into foils. The calculated amounts of praseodymium were clad in palladium foils and melted in a boron nitride crucible with an argon atmosphere. Each alloy was fast cooled after being remelted twice. The samples obtained were sealed in silica tubes filled with argon and homogenized at 800 °C for 200 h, then slowly cooled to room temperature in 5 days.

The results of chemical analysis showed that palladium and praseodymium in the alloys were lost a little during melting and heat treatment. Usually the loss of praseodymium is relatively higher than that of palladium, so the

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composition of the alloys was shifted to the palladium-rich side. However, the maximum shift was less than 1 at.% and the experimental data were modified accordingly.

The X-ray diffraction experiments were performed in a Rigaku RV-200 diffractometer with Cu Kα radiation ($\lambda = 0.15405$ nm), where silicon powder was used as an internal standard.

Thermal analysis experiments were carried out on a Perkin–Elmer DTA-1700 differential thermal analyser. Samples were protected by flowing argon at a rate of 20 ml min^{-1}, at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. 0–22 at.% Pr region

The specimens were quenched after heat treatment at 650 °C for 150 h, 800 °C for 100 h and 950 °C for 50 h respectively. The solid solubility of praseodymium in palladium was determined to be about 6.9 at.%, 7.4 at.% and 8.0 at.% at 650 °C, 800 °C and 950 °C respectively by the lattice parameter method. Figure 1 shows a plot of the lattice parameter *vs.* composition.

It has been reported that there are AB_5-type intermetallic compounds in some Pd–RE systems [3–8]. In this work, the sample with 16.7 at.% Pr was analysed with X-ray diffraction and found to be essentially of a single-phase structure. The X-ray diffraction pattern of $PrPd_5$ is similar to those of $SmPd_5$ [8] and $SmPt_5$ [9], which shows it has an $SmPt_5$-type orthorhombic structure with the lattice parameters $a = 0.5278$ nm, $b = 0.9239$ nm and

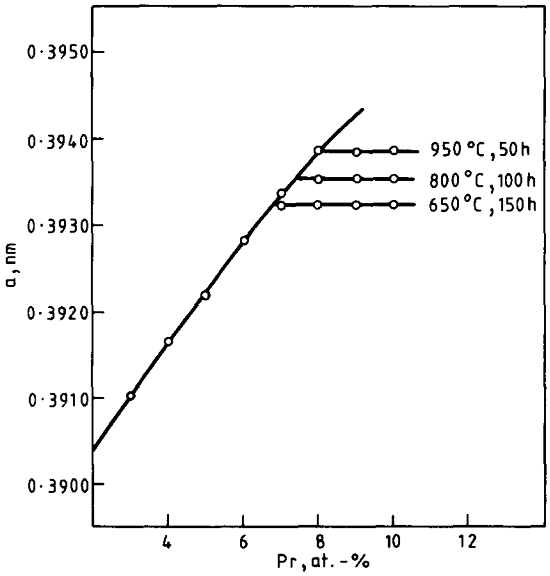

Fig. 1. The changes in lattice parameter *a vs.* composition.

$c = 2.575$ nm. X-ray diffraction data may be obtained from the authors. $PrPd_5$ forms at 1123 ± 4 °C as a product of the peritectic reaction $L + PrPd_3 \rightleftharpoons PrPd_5$. There also exists a eutectic reaction $L \rightleftharpoons PrPd_5 + (Pd)$ at 1041 ± 4 °C, and the eutectic point is at 11.5 at.% Pr.

3.2. 22–45 at.% Pr region

Results of X-ray diffraction, microscopic techniques and DTA showed that samples containing 25 at.% Pr, 33 at.% Pr, 40 at.% Pr and 45 at.% Pr are single-phase structures with the chemical formulae $PrPd_3$, $PrPd_2$, Pr_2Pd_3 and Pr_4Pd_5 respectively (Fig. 2). This is similar to the Pd–Y, Pd–Gd, Pd–Dy, Pd–Ho and Pd–Er systems reported by Loebich and Raub [1].

It has been shown experimentally that $PrPd_3$ is a solid–liquid congruently melting compound with a melting point of 1175 ± 4 °C, and an $AuCu_3$-type crystal structure. The sample, which contains 25 at.% Pr, has a lattice parameter $a = 0.4146$ nm. The homogeneous regions of $PrPd_3$ at 800 °C and 950 °C were determined by the disappearing-phase method to be about 23.5–25.5 at.% Pr and 23–25.5 at.% Pr respectively. In this region, the lattice parameter a changes from 0.4135 to 0.4155 nm.

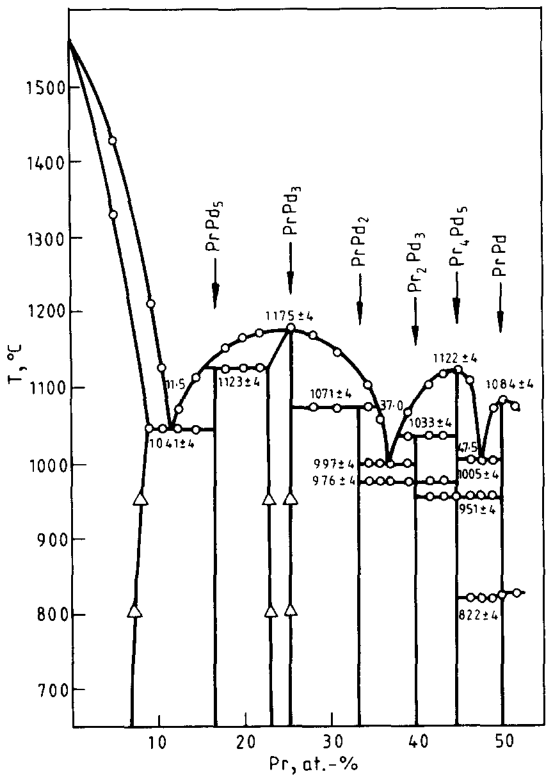

Fig. 2. The phase diagram of the Pd–Pr system (50 at.% Pr or less): O, DTA method; △, lattice parameter method or phase-disappearance method.

TABLE 1

X-ray diffraction data for PrPd (orthorhombic lattice)

hkl	I/I_1	d_{obs} (nm)	d_{calc} (nm)
020	12	0.5490	0.5446
110	8	0.3634	0.3655
021	5	0.3521	0.3501
111	100	0.2860	0.2855
040	40	0.2726	0.2723
130	35	0.2658	0.2651
041	80	0.2342	0.2339
131 002	95	0.2295	0.2293 0.2285
022	20	0.2100	0.2107
200	15	0.1943	0.1940
150	5	0.1904	0.1900
220 060	20	0.1822	0.1828 0.1815
042	25	0.1747	0.1751
132	16	0.1731	0.1731
221 061	12	0.1692	0.1697 0.1687
240	13	0.1576	0.1580
241	20	0.1488	0.1493
202	30	0.1482	0.1479
152	18	0.1464	0.1461
170	15	0.1441	0.1444
222 062	15	0.1423	0.1427 0.1421
113	10	0.1408	0.1406
171	14	0.1369	0.1377
043	16	0.1329	0.1330
260 133	25	0.1324	0.1326 0.1321
242	18	0.1301	0.1300
261	10	0.1276	0.1273
311	12	0.1238	0.1236
172	20	0.1224	0.1221
330	10	0.1218	0.1218
331	12	0.1178	0.1177
223	8	0.1170	0.1170

$PrPd_2$ and Pr_2Pd_3 form at 1071 ± 4 °C and 1033 ± 4 °C by the peritectic reactions $PrPd_3 + L \rightleftharpoons PrPd_2$ and $Pr_4Pd_5 + L \rightleftharpoons Pr_2Pd_3$ respectively. A eutectic reaction $L \rightleftharpoons PrPd_2 + Pr_2Pd_3$ occurs at 997 ± 4 °C and the eutectic point is at 37.0 at.% Pr. Pr_2Pd_3 has an isomeric transformation at about 976 °C.

Pr_4Pd_5 is a congruent-melting compound with a melting point of 1122 ± 4 °C and shows an isomeric transformation at about 951 °C. The crystal structures of $PrPd_2$, Pr_2Pd_3 and Pr_4Pd_5 have not been determined yet.

TABLE 2

Lattice parameters of some intermetallic phases in the Pd–Pr system

Phase	Structural type	Lattice parameters				Ref.
		a (nm)	b (nm)	c (nm)	V (nm^3)	
$PrPd_5$	Orthorhombic $SmPt_5$	0.5278	0.9239	2.575	1.256	Present work
$PrPd_3$	Cubic $AuCu_3$	0.4138			0.0709	[10]
		0.4146			0.0713	Present work
PrPd	Orthorhombic CrB	0.3850	1.0826	0.4614	0.1923	[10]
		0.3880	1.089	0.4571	0.1931	Present work

3.3. 45–50 at.% Pr region

There is a congruent-melting compound with a melting point of 1084 ± 4 °C at 50 at.% Pr. It has an isomeric transformation at about 822 ± 4 °C. Below this temperature it has a CrB-type orthorhombic structure with the lattice parameters $a = 0.3880$ nm, $b = 1.089$ nm and $c = 0.4571$ nm. Table 1 lists the X-ray diffraction data of PrPd. A eutectic reaction $L \rightleftharpoons Pr_4Pd_5 + PrPd$ takes place at 1005 ± 4 °C, and the eutectic point is at 47.5 at.% Pr.

Table 2 lists the lattice parameters of PrPd, $PrPd_3$ and $PrPd_5$ that have been reported.

4. Conclusion

The phase diagram of Pr–Pd was determined at up to 50 at.% Pr. Its basic form is similar to the Nd–Pd phase diagram [6]. There are six intermetallic compounds ($PrPd_5$, $PrPd_3$, $PrPd_2$, Pr_2Pd_3, Pr_4Pd_5 and PrPd), three peritectic reactions ($L + PrPd_3 \rightleftharpoons PrPd_5$, $L + PrPd_3 \rightleftharpoons PrPd_2$ and $L + Pr_4Pd_5 \rightleftharpoons Pr_2Pd_3$) and three eutectic reactions ($L \rightleftharpoons (Pd) + PrPd_5$, $L \rightleftharpoons PrPd_2 + Pr_2Pd_3$ and $L \rightleftharpoons Pr_4Pd_5 + PrPd$). In addition, it was determined that $PrPd_5$ has an $SmPt_5$-type structure with $a = 0.5278$ nm, $b = 0.9239$ nm and $c = 2.575$ nm, that $PrPd_3$ is of the $AuCu_3$-type structure with $a = 0.4146$ nm and that PrPd (below 822 ± 4 °C) crystallizes in a CrB-type structure with $a = 0.3880$ nm, $b = 1.089$ nm and $c = 0.4571$ nm.

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