Bi – Pd (Bismuth – Palladium)

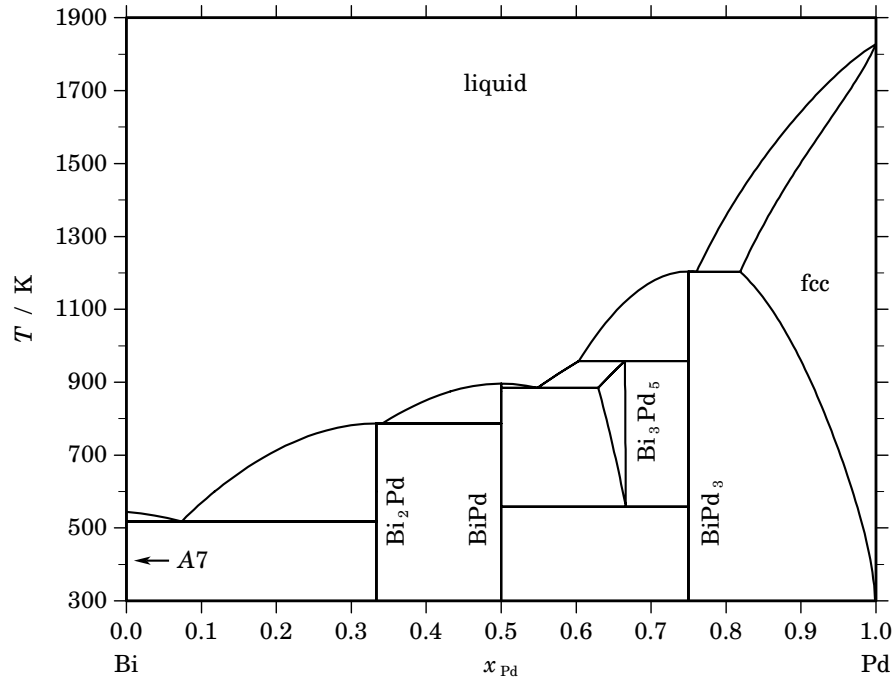

Fig. 1. Calculated phase diagram for the system Bi-Pd.

This system was assessed by Vřešťál *et al.* [2006Vre], from the available experimental information, and ab-initio calculations of the total energies of BiPd and Bi_2Pd. Bismuth is an important component both as a solvent of uranium in nuclear metallurgy, and also in lead-free solder materials, the substrates of which often containing palladium. The phase diagram is based on the experimental work of Zhuravlev and Zhdanov[1953], Zhuravlev [1957Zhu], Brasier and Hume-Rothery [1959Bra], using cooling curve analysis, Schweitzer and Weeks [1961Sch] who analysed the liquidus after equilibrating annealing. The experimental Bi-Pd phase diagram was assessed by Okamoto [1994Oka]. It presents three solution phases, the liquid with a complete miscibility range, the palladium rich terminal solid solution (fcc), and the intermediate solution phase Bi_3Pd_5 (62-71 at.%Pd). The following intermediate compounds have been identified with a very narrow non-stoichiometry range and two allotropic forms, αBi_2Pd, βBi_2Pd (1.5 at.%, 653 K), αBiPd, βBiPd (1 at.%, 483 K), $\alpha BiPd_3$, $\beta BiPd_3$ (1073 K). The structures of the intermetallic phases were experimentally studied by Schubert *et al.* [1953Sch], Zhuravlev and Zhdanov [1953Zhu], Kheiker *et al.* [1953Khe], Levin *et al.* [1953Lev], Zhdanov [1954Zhd], Zhuravlev [1958Zhu] and Bhatt and Schubert [1979Bat]. Two other compounds, Bi_2Pd_5 and $Bi_{12}Pd_{31}$, were put in evidence by Sarah and Schubert [1979Sar], the second one in a very limited temperature range (823 K - 878 K). However, in diffusion couple experiments using BiPd and pure Pd [2001Obe] only the formation of $BiPd_3$ and Bi_3Pd_5 has been observed but neither Bi_2Pd_5 nor $Bi_{12}Pd_{31}$ have been detected. Therefore, only three stoichiometric compounds, Bi_2Pd, BiPd and $BiPd_3$ without structural transformation were modelled by the assessor [2006Vre]. There is no reported solubility of palladium in rhombohedral bismuth. In addition, the solubility of bismuth in palladium at lower temperature has been determined [2001Obe] and the integral enthalpy of mixing of liquid Bi-Pd alloys has been measured by high temperature solution calorimetry in the range of 0-50 at.% Pd at 1028 K.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Bi,Pd)_1$
$A7$	$A7$	αAs	$hR2$	$R\overline{3}m$	RHOMBOHEDRAL_A7	$(Bi,Pd)_1$
αBi_2Pd	⋯	⋯	$mC12$	$C2/m$	A_BI2PD	Bi_2Pd_1
βBi_2Pd	$C11_b$	$MoSi_2$	$tI6$	$I4/mmm$	B_BI2PD	Bi_2Pd_1
αBiPd	⋯	⋯	$mP32$	$P2_1$	A_BIPD	Bi_1Pd_1
βBiPd	⋯	⋯	$oC32$	$Cmc2_1$	B_BIPD	Bi_1Pd_1
Bi_3Pd_5	⋯	⋯	$hP16$	⋯	BI3PD5	$(Bi,Pd)_1$
Bi_2Pd_5	⋯	⋯	$mC28$	$C2/m$	⋯	⋯
$Bi_{12}Pd_{31}$	⋯	⋯	$hR44$	$R3$	⋯	⋯
$\alpha BiPd_3$	⋯	⋯	$oP16$	$Pmma$	A_BIPD3	Bi_1Pd_3
$\beta BiPd_3$	⋯	⋯	⋯	⋯	B_BIPD3	Bi_1Pd_3
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Bi,Pd)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Pd}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ $BiPd_3$	congruent	1204.6	0.750	0.750		−13032
liquid $\rightleftharpoons$ $BiPd_3$ + fcc	eutectic	1203.1	0.761	0.750	0.819	−11662
liquid + $BiPd_3$ $\rightleftharpoons$ Bi_3Pd_5	peritectic	958.1	0.604	0.750	0.665	−6996
liquid $\rightleftharpoons$ BiPd	congruent	895.9	0.500	0.500		−18429
liquid $\rightleftharpoons$ BiPd + Bi_3Pd_5	eutectic	884.1	0.548	0.500	0.629	−15299
liquid $\rightleftharpoons$ Bi_2Pd	congruent	787.0	0.333	0.333		−14229
liquid $\rightleftharpoons$ Bi_2Pd + BiPd	eutectic	786.7	0.342	0.333	0.500	−14308
Bi_3Pd_5 $\rightleftharpoons$ BiPd + $BiPd_3$	eutectoid	558.5	0.666	0.500	0.750	−1146
liquid $\rightleftharpoons$ A7 + Bi_2Pd	eutectic	518.1	0.074	0.000	0.333	−10706

Table IIIa. Integral quantities for the liquid phase at 1828 K.

x_{Pd}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−9182	−8190	0.543	−4242	−2.160	0.000
0.200	−15786	−15200	0.321	−8180	−3.840	0.000
0.300	−20861	−20790	0.039	−11577	−5.040	0.000
0.400	−24420	−24720	−0.164	−14191	−5.760	0.000
0.500	−26317	−26750	−0.237	−15782	−6.000	0.000
0.600	−26340	−26640	−0.164	−16111	−5.760	0.000
0.700	−24221	−24150	0.039	−14937	−5.040	0.000
0.800	−19626	−19040	0.321	−12021	−3.840	0.000
0.900	−12062	−11070	0.543	−7122	−2.160	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Bi(liquid), Pd(liquid)

Table IIIb. Partial quantities for Bi in the liquid phase at 1828 K.

x_{Bi}	ΔG_{Bi} [J/mol]	ΔH_{Bi} [J/mol]	ΔS_{Bi} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Bi}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Bi}}$ [J/(mol·K)]	a_{Bi}	γ_{Bi}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1713	−550	0.636	−111	−0.240	0.893	0.993
0.800	−4157	−2520	0.895	−765	−0.960	0.761	0.951
0.700	−7863	−6390	0.806	−2442	−2.160	0.596	0.852
0.600	−13385	−12640	0.407	−5620	−3.840	0.415	0.691
0.500	−21317	−21750	−0.237	−10782	−6.000	0.246	0.492
0.400	−32333	−34200	−1.021	−18406	−8.640	0.119	0.298
0.300	−47272	−50470	−1.750	−28973	−11.760	0.045	0.149
0.200	−67424	−71040	−1.978	−42962	−15.360	0.012	0.059
0.100	−95851	−96390	−0.295	−60854	−19.440	0.002	0.018
0.000	−∞	−127000	∞	−83128	−24.000	0.000	0.004

Reference state: Bi(liquid)

Table IIIc. Partial quantities for Pd in the liquid phase at 1828 K.

x_{Pd}	ΔG_{Pd} [J/mol]	ΔH_{Pd} [J/mol]	ΔS_{Pd} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Pd}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Pd}}$ [J/(mol·K)]	a_{Pd}	γ_{Pd}
0.000	−∞	−87000	∞	−43128	−24.000	0.000	0.059
0.100	−76411	−76950	−0.295	−41414	−19.440	0.007	0.066
0.200	−62304	−65920	−1.978	−37842	−15.360	0.017	0.083
0.300	−51192	−54390	−1.750	−32893	−11.760	0.034	0.115
0.400	−40973	−42840	−1.021	−27046	−8.640	0.067	0.169
0.500	−31317	−31750	−0.237	−20782	−6.000	0.127	0.255
0.600	−22345	−21600	0.407	−14581	−3.840	0.230	0.383
0.700	−14343	−12870	0.806	−8922	−2.160	0.389	0.556
0.800	−7677	−6040	0.895	−4285	−0.960	0.603	0.754
0.900	−2753	−1590	0.636	−1151	−0.240	0.834	0.927
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Pd(liquid)

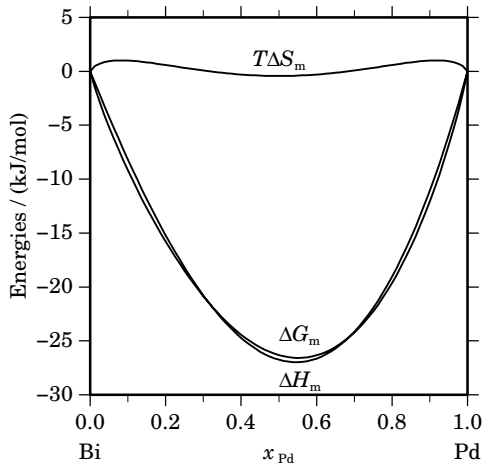

Fig. 2. Integral quantities of the liquid phase at T=1828 K.

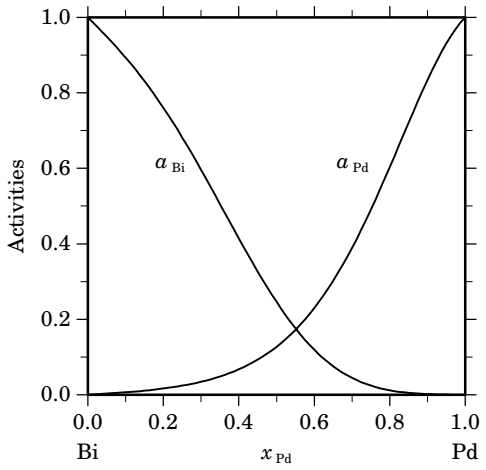

Fig. 3. Activities in the liquid phase at T=1828 K.

Table IVa. Integral quantities for the stable phases at 1028 K.

Phase	x_{Pd}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
liquid	0.000	0	0	0.000	0	0.000	0.000
	0.100	−8134	−6964	1.139	−5356	−1.564	0.405
	0.200	−14302	−12747	1.513	−10025	−2.648	0.809
	0.300	−18989	−17111	1.827	−13768	−3.252	1.214
	0.400	−22097	−19814	2.220	−16344	−3.375	1.619
	0.500	−23438	−20618	2.744	−17514	−3.019	2.024
	0.600	−22789	−19281	3.413	−17037	−2.183	2.428
	0.626	−22253	−18539	3.613	−16605	−1.881	2.535
$BiPd_3$	0.750	−19375	−25134	−5.603			0.000
fcc	0.882	−10260	−8275	1.931	−7162	−1.083	0.000
	0.900	−8995	−7164	1.782	−6217	−0.921	0.000
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Bi(liquid), Pd(fcc)

Table IVb. Partial quantities for Bi in the stable phases at 1028 K.

Phase	x_{Bi}	ΔG_{Bi} [J/mol]	ΔH_{Bi} [J/mol]	ΔS_{Bi} [J/(mol·K)]	$G_{\mathrm{Bi}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Bi}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Bi}	γ_{Bi}
liquid	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−1204	−550	0.636	−303	−0.240	0.869	0.965
	0.800	−3440	−2520	0.895	−1533	−0.960	0.669	0.836
	0.700	−7218	−6390	0.806	−4170	−2.160	0.430	0.614
	0.600	−13059	−12640	0.407	−8692	−3.840	0.217	0.362
	0.500	−21507	−21750	−0.237	−15582	−6.000	0.081	0.162
	0.400	−33150	−34200	−1.021	−25318	−8.640	0.021	0.052
	0.374	−36850	−38115	−1.231	−28432	−9.419	0.013	0.036
$BiPd_3$	0.250	−36850	14909	50.349			0.013	
	0.250	−71081	−120776	−48.342			0.000	
fcc	0.118	−71081	−62143	8.695	−52799	−9.089	0.000	0.002
	0.100	−74921	−64616	10.025	−55241	−9.120	0.000	0.002
	0.000	$-\infty$	−79436	∞	−69865	−9.310	0.000	0.000

Reference state: Bi(liquid)

Table IVc. Partial quantities for Pd in the stable phases at 1028 K.

Phase	x_{Pd}	ΔG_{Pd} [J/mol]	ΔH_{Pd} [J/mol]	ΔS_{Pd} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Pd}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Pd}}$ [J/(mol·K)]	a_{Pd}	γ_{Pd}
liquid	0.000	$-\infty$	−74735	∞	−56192	−18.038	0.000	0.001
	0.100	−70510	−64685	5.666	−50829	−13.478	0.000	0.003
	0.200	−57750	−53655	3.983	−43994	−9.398	0.001	0.006
	0.300	−46455	−42125	4.212	−36164	−5.798	0.004	0.015
	0.400	−35654	−30575	4.940	−27822	−2.678	0.015	0.039
	0.500	−25370	−19485	5.725	−19446	−0.038	0.051	0.103
	0.600	−15882	−9335	6.369	−11516	2.122	0.156	0.260
	0.626	−13550	−6866	6.501	−9552	2.613	0.205	0.327
$BiPd_3$	0.750	−13550	−38482	−24.253			0.205	
	0.750	−2139	6747	8.644			0.779	
fcc	0.882	−2139	−1082	1.028	−1068	−0.014	0.779	0.883
	0.900	−1670	−780	0.866	−770	−0.010	0.822	0.914
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Pd(fcc)

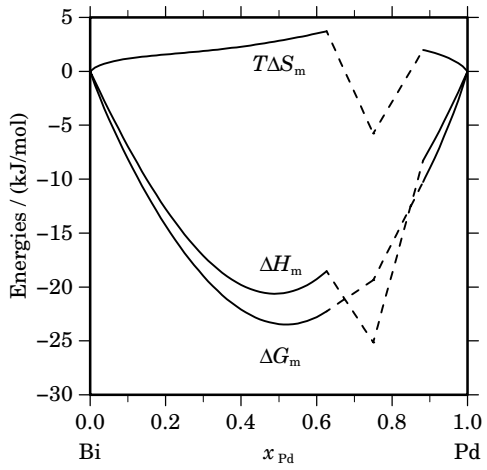

Fig. 4. Integral quantities of the stable phases at T=1028 K.

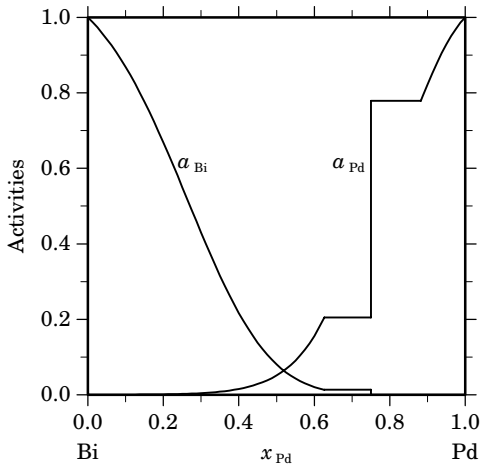

Fig. 5. Activities in the stable phases at T=1028 K.

Table V. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Pd}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C^{\circ}_{P}$ / (J/(mol·K))
Bi_2Pd_1	0.333	−24355	−25100	−2.500	0.000
Bi_1Pd_1	0.500	−31319	−33600	−7.650	0.000
Bi_1Pd_3	0.750	−22181	−22300	−0.400	0.000

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