In – Pd (Indium – Palladium)

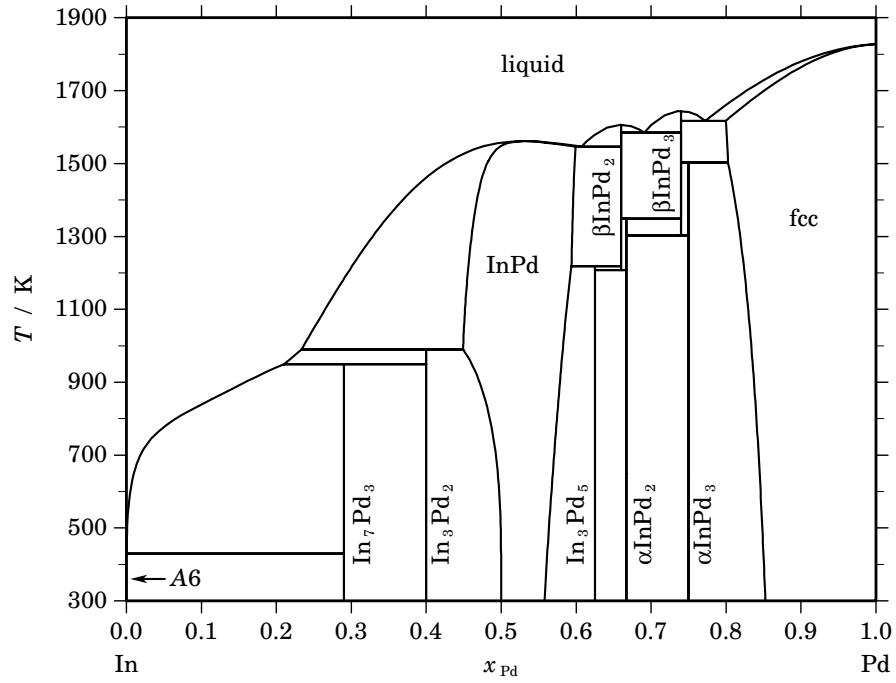

Fig. 1. Calculated phase diagram for the system In-Pd.

Palladium alloys with small amounts of indium are used for certain dental applications where In lowers the melting point of the alloys and causes the formation of an oxide layer which promotes the bonding between the alloy and ceramic materials. Furthermore, the In-Pd is of interest for the manufacturing of certain semiconductor devices when Pd-containing contacts are used on In-containing semiconductors, such as InSb or InP. The In-Pd system has been reviewed in [1992Oka] but since then new experimental work required a revision in the In-rich part. An updated review including an optimised thermodynamic dataset has been given by [2002Jia] which is presented here. The phase diagram has been determined by [1959Kni] and it has been modified later in the Pd-rich part [1988Sch] and recently in the In-rich part [2002Fla]. The enthalpy of mixing has been investigated for the melt in the range 0-65 at.% Pd at several temperatures and it has been found to be independent of temperature [1995ElA]. Enthalpies of formation for the solid phases have been determined in several investigations across the whole composition range and they are well represented by the calculation [2002Jia] within the deviations among the different datasets. Activities of In across the whole composition range have been reported from 873 K [1975Bir] up to 1273 K [1978Sch]. The heat capacities of the intermetallic compounds have been measured up to about 1000 K by [1975, 2001Per]. The dataset should not be used at too high temperatures because an artificial inverse miscibility gap opens in the liquid above 3100 K.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(In,Pd)_1$
$A6$	$A6$	In	$tI2$	$I4/mmm$	TETRAGONAL_A6	In_1
In_7Pd_3	$D8_f$	Ir_3Ge_7	$cI40$	$Im\overline{3}m$	IN7PD3	In_7Pd_3
In_3Pd_2	$D5_{13}$	Al_3Ni_2	$hP5$	$P\overline{3}m1$	IN3PD2	In_3Pd_2
InPd	$B2$	CsCl	$cP2$	$Pm\overline{3}m$	INPD	$(In,Pd)_1(Pd,\Box)_1$
In_3Pd_5	···	Ge_3Rh_5	$oP16$	$Pbam$	IN3PD5	In_3Pd_5
$\alpha InPd_2$	$C23$	Co_2Si	$oP12$	$Pnma$	INPD2_A	In_1Pd_2
$\beta InPd_2$	···	···	···	···	INPD2_B	$In_{17}Pd_{33}$
$\beta InPd_3$	···	···	···	···	INPD3_B	$In_{13}Pd_{37}$
$\alpha InPd_3$	$D0_{22}$	Al_3Ti	$tI8$	$I4/mmm$	INPD3_A	$InPd_3$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}\overline{3}m$	FCC_A1	$(In,Pd)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Pd}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons \beta InPd_3$	congruent	1644.5	0.740	0.740		−12565
liquid $\rightleftharpoons \beta InPd_3$ + fcc	eutectic	1617.2	0.772	0.740	0.800	−11246
liquid $\rightleftharpoons \beta InPd_2$	congruent	1606.4	0.660	0.660		−12665
liquid $\rightleftharpoons \beta InPd_2$ + $\beta InPd_3$	eutectic	1584.7	0.691	0.660	0.740	−11949
liquid $\rightleftharpoons$ InPd	congruent	1561.5	0.530	0.530		−15642
liquid $\rightleftharpoons$ InPd + $\beta InPd_2$	eutectic	1546.0	0.607	0.599	0.660	−12739
$\beta InPd_3$ + fcc $\rightleftharpoons \alpha InPd_3$	peritectoid	1502.3	0.740	0.803	0.750	−2892
$\beta InPd_2$ + $\beta InPd_3$ $\rightleftharpoons \alpha InPd_2$	peritectoid	1348.8	0.660	0.740	0.667	−2044
$\beta InPd_3$ $\rightleftharpoons \alpha InPd_2$ + $\alpha InPd_3$	eutectoid	1302.1	0.740	0.667	0.750	−2134
InPd + $\beta InPd_2$ $\rightleftharpoons In_3Pd_5$	peritectoid	1218.5	0.594	0.660	0.625	−767
$\beta InPd_2$ $\rightleftharpoons In_3Pd_5$ + $\alpha InPd_2$	eutectoid	1207.5	0.660	0.625	0.667	−1588
liquid + InPd $\rightleftharpoons In_3Pd_2$	peritectic	989.7	0.234	0.449	0.400	−6750
liquid + In_3Pd_2 $\rightleftharpoons In_7Pd_3$	peritectic	949.2	0.210	0.400	0.290	−5932
liquid $\rightleftharpoons A6$ + In_7Pd_3	eutectic	429.6	0.000	0.000	0.290	−3289

Table IIIa. Integral quantities for the liquid phase at 1900 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	−10269	−12872	−1.370	−5134	−4.073	0.000
0.200	−18251	−25809	−3.978	−10346	−8.138	0.000
0.300	−24684	−37886	−6.948	−15034	−12.027	0.000
0.400	−29309	−48080	−9.879	−18677	−15.475	0.000
0.500	−31790	−55270	−12.358	−20840	−18.121	0.000
0.600	−31800	−58235	−13.913	−21168	−19.509	0.000
0.700	−29043	−55658	−14.008	−19393	−19.087	0.000
0.800	−23233	−46120	−12.046	−15328	−16.207	0.000
0.900	−14005	−28106	−7.421	−8870	−10.124	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for In in the liquid phase at 1900 K.

x_{In}	ΔG_{In} [J/mol]	ΔH_{In} [J/mol]	ΔS_{In} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{In}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{In}}$ [J/(mol·K)]	a_{In}	γ_{In}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1517	178	0.892	147	0.016	0.908	1.009
0.800	−3783	−471	1.744	−258	−0.112	0.787	0.984
0.700	−7932	−3943	2.100	−2298	−0.866	0.605	0.865
0.600	−14872	−12531	1.232	−6802	−3.015	0.390	0.650
0.500	−25304	−28823	−1.852	−14354	−7.615	0.202	0.403
0.400	−39757	−55703	−8.393	−25282	−16.011	0.081	0.202
0.300	−58687	−96351	−19.823	−39667	−29.834	0.024	0.081
0.200	−82764	−154243	−37.620	−57339	−51.002	0.005	0.027
0.100	−114252	−233150	−62.578	−77877	−81.723	0.001	0.007
0.000	−∞	−337140	∞	−100611	−124.489	0.000	0.002

Reference state: In(liquid)

Table IIIc. Partial quantities for Pd in the liquid phase at 1900 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	−∞	−125562	∞	−48720	−40.443	0.000	0.046
0.100	−89034	−130323	−21.731	−52658	−40.876	0.004	0.036
0.200	−76122	−127161	−26.862	−50697	−40.244	0.008	0.040
0.300	−63772	−117085	−28.060	−44752	−38.070	0.018	0.059
0.400	−50965	−101403	−26.546	−36490	−34.165	0.040	0.099
0.500	−38276	−81717	−22.864	−27326	−28.627	0.089	0.177
0.600	−26496	−59924	−17.594	−18426	−21.841	0.187	0.311
0.700	−16339	−38218	−11.516	−10704	−14.481	0.355	0.508
0.800	−8350	−19089	−5.652	−4825	−7.508	0.589	0.737
0.900	−2867	−5323	−1.293	−1202	−2.169	0.834	0.927
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Pd(liquid)

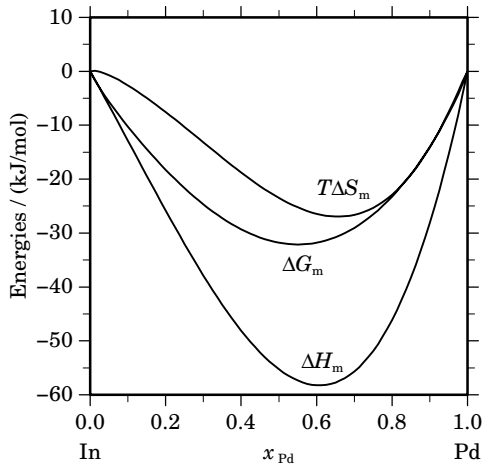

Fig. 2. Integral quantities of the liquid phase at T=1900 K.

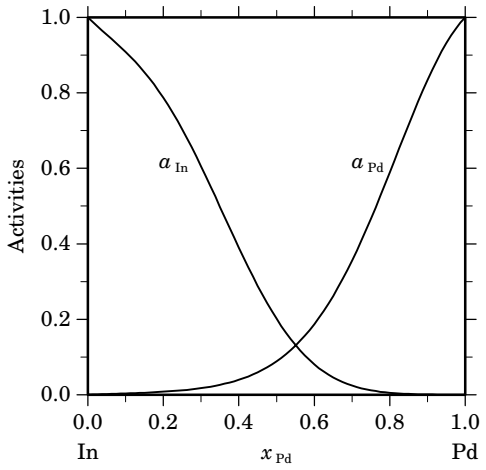

Fig. 3. Activities in the liquid phase at T=1900 K.

Table IV. 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))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
In_7Pd_3	0.290	−38518	−41122	−8.733	−1.067
In_3Pd_2	0.400	−52041	−56456	−14.811	−2.415
In_3Pd_5	0.625	−56502	−60537	−13.534	−1.768
$\beta InPd_2$	0.660	−54590	−58730	−13.885	0.000
$\alpha InPd_2$	0.667	−55055	−58941	−13.032	−1.677
$\beta InPd_3$	0.740	−48986	−52801	−12.796	0.000
$\alpha InPd_3$	0.750	−49942	−54212	−14.320	0.000

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