Pd – Sm (Palladium – Samarium)

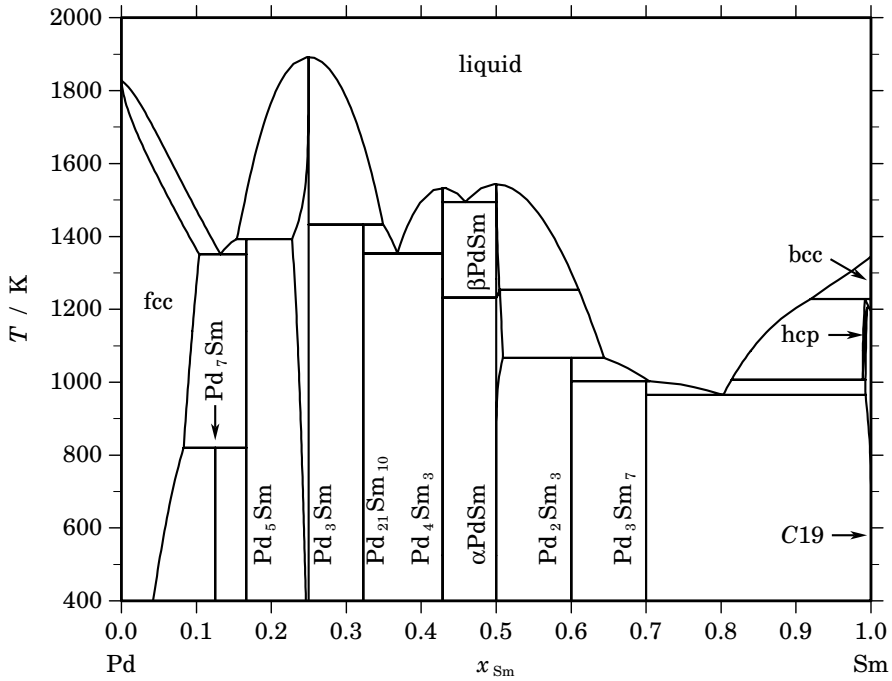

Fig. 1. Calculated phase diagram for the system Pd-Sm.

Intermetallic compounds of palladium with rare earth metals are of interest due to their potential use in hydrogen diffusion membranes for purification and isotope enrichment. A review on the Pd-Sm system and a thermodynamic assessment has been given by [2000Du]. The optimisation is based on the phase diagram data which have been reported in [1973Loe] across the whole composition range with additional investigations in Pd-rich alloys by [1989Sak]. Enthalpies of formation have been reported for PdSm [1975Pal, 1998Guo] and for Pd_3Sm and Pd_4Sm_3 [1998Guo]. Data for the other intermetallic compounds have been estimated. For the liquid no thermodynamic data have been available. From the dataset [2000Du] a rather unusual transformation behaviour is calculated for the Sm-phases having dissolved small amounts of Pd, as shown in the enlarged part of the phase diagram, Fig. 2. However, it should be noted that the only investigation in this region of the system [1973Loe] does not provide any quantitative data for the solubility of Pd in either of the phases of Sm. It has only been stated that the solubility of Pd in Sm is certainly below 1 at.% and that dissolution of Pd in Sm results in a peritectic reaction at 1228 K.

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[1975Pal] A. Palenzona, S. Cirafici: Thermochim. Acta **12** (1975) 267–275.
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[1998Guo] Q. Guo, O.J. Kleppa: Metall. Mater. Trans. B **29B** (1998) 815–820.
[2000Du] Z. Du, H. Yang: Z. Metallkd. **91** (2000) 455–459.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Pd,Sm)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Pd,Sm)_1$
Pd_7Sm	⋯	⋯	$c*^*$	⋯	PD7SM	Pd_7Sm_1
Pd_5Sm	⋯	⋯	$o*72$	⋯	PD5SM	Pd_5Sm_1
Pd_3Sm	$L1_2$	$AuCu_3$	$cP4$	$Pm\overline{3}m$	MPD3	$Pd_3(Pd,Sm)_1$
$Pd_{21}Sm_{10}$	⋯	⋯	$mC124$	$C2/m$	PD21SM10	$Pd_{21}Sm_{10}$
Pd_4Sm_3	⋯	⋯	$hR14$	$R\overline{3}$	PD4SM3	Pd_4Sm_3
βPdSm	⋯	⋯	⋯	⋯	MSM_B	$(Pd,Sm)_1Sm_1$
αPdSm	$B33$	CrB	$oC8$	$Cmcm$	MSM_A	$(Pd,Sm)_1Sm_1$
Pd_2Sm_3	⋯	⋯	⋯	⋯	PD2SM3	Pd_2Sm_3
Pd_3Sm_7	$D10_2$	Fe_3Th_7	$hP20$	$P6_3mc$	PD3SM7	Pd_3Sm_7
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Pd,Sm)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Pd,Sm)_1$
$C19$	$C19$	αSm	$hR3$	$R\overline{3}m$	RHOMB_C19	$(Pd,Sm)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Sm}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ Pd_3Sm	congruent	1892.6	0.250	0.250		−17371
liquid $\rightleftharpoons$ βPdSm	congruent	1543.4	0.500	0.500		−16078
liquid $\rightleftharpoons$ Pd_4Sm_3	congruent	1533.7	0.429	0.429		−11538
liquid $\rightleftharpoons$ Pd_4Sm_3 + βPdSm	eutectic	1494.4	0.459	0.429	0.500	−12868
Pd_3Sm + liquid $\rightleftharpoons$ $Pd_{21}Sm_{10}$	peritectic	1432.8	0.250	0.349	0.323	−6860
liquid + Pd_3Sm $\rightleftharpoons$ Pd_5Sm	peritectic	1392.8	0.154	0.228	0.167	−16571
liquid $\rightleftharpoons$ $Pd_{21}Sm_{10}$ + Pd_4Sm_3	eutectic	1353.5	0.368	0.323	0.429	−8983
liquid $\rightleftharpoons$ fcc + Pd_5Sm	eutectic	1350.8	0.132	0.104	0.167	−14236
βPdSm + liquid $\rightleftharpoons$ αPdSm	peritectic	1253.6	0.504	0.610	0.505	−373
βPdSm $\rightleftharpoons$ Pd_4Sm_3 + αPdSm	eutectoid	1231.8	0.500	0.429	0.500	−500
liquid + bcc $\rightleftharpoons$ hcp	peritectic	1228.0	0.920	0.999	0.992	−3329
hcp $\rightleftharpoons$ $C19$	congruent	1206.9	0.996	0.996		−83
αPdSm + liquid $\rightleftharpoons$ Pd_2Sm_3	peritectic	1067.0	0.509	0.644	0.600	−24025
hcp $\rightleftharpoons$ liquid + $C19$	metatectic	1007.0	0.989	0.814	0.993	−85
Pd_2Sm_3 + liquid $\rightleftharpoons$ Pd_3Sm_7	peritectic	1002.9	0.600	0.704	0.700	−33524
liquid $\rightleftharpoons$ Pd_3Sm_7 + $C19$	eutectic	965.0	0.803	0.700	0.993	−24810
fcc + Pd_5Sm $\rightleftharpoons$ Pd_7Sm	peritectoid	820.1	0.083	0.167	0.125	−4864

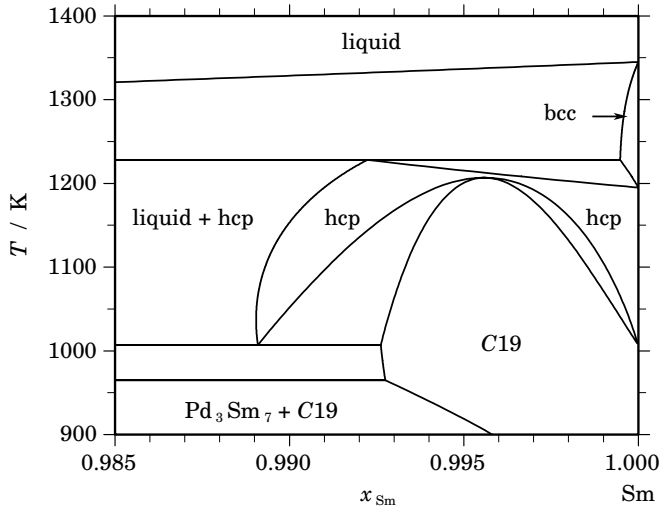

Fig. 2. Partial phase diagram for the system Pd-Sm.

Table IIIa. Integral quantities for the liquid phase at 1900 K.

x_{Sm}	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)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−33174	−40773	−3.999	−28038	−6.702	0.000
0.200	−54865	−67889	−6.855	−46960	−11.016	0.000
0.300	−67497	−83073	−8.198	−57847	−13.277	0.000
0.400	−72413	−88047	−8.228	−61782	−13.824	0.000
0.500	−70796	−84535	−7.231	−59846	−12.994	0.000
0.600	−63755	−74260	−5.529	−53123	−11.125	0.000
0.700	−52345	−58946	−3.474	−42695	−8.553	0.000
0.800	−37548	−40315	−1.456	−29643	−5.617	0.000
0.900	−20186	−20092	0.050	−15051	−2.653	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. 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)]	$G_{\mathrm{Pd}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Pd}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Pd}	γ_{Pd}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−6403	−7115	−0.375	−4739	−1.251	0.667	0.741
0.800	−21037	−26164	−2.698	−17512	−4.553	0.264	0.330
0.700	−41790	−53698	−6.267	−36156	−9.233	0.071	0.101
0.600	−66574	−86272	−10.367	−58504	−14.615	0.015	0.025
0.500	−93344	−120439	−14.260	−82394	−20.024	0.003	0.005
0.400	−120135	−152751	−17.166	−105660	−24.785	0.000	0.001
0.300	−145157	−179762	−18.213	−126137	−28.224	0.000	0.000
0.200	−167087	−198026	−16.284	−141662	−29.666	0.000	0.000
0.100	−186444	−204096	−9.290	−150069	−28.435	0.000	0.000
0.000	$-\infty$	−194524	∞	−149194	−23.858	0.000	0.000

Reference state: Pd(liquid)

Table IIIc. Partial quantities for Sm in the liquid phase at 1900 K.

x_{Sm}	ΔG_{Sm} [J/mol]	ΔH_{Sm} [J/mol]	ΔS_{Sm} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Sm}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Sm}}$ [J/(mol·K)]	a_{Sm}	γ_{Sm}
0.000	$-\infty$	−481754	∞	−329575	−80.094	0.000	0.000
0.100	−274109	−343689	−36.621	−237734	−55.766	0.000	0.000
0.200	−190176	−234792	−23.482	−164751	−36.864	0.000	0.000
0.300	−127480	−151614	−12.702	−108460	−22.713	0.000	0.001
0.400	−81172	−90709	−5.019	−66697	−12.638	0.006	0.015
0.500	−48249	−48631	−0.201	−37298	−5.964	0.047	0.094
0.600	−26169	−21933	2.230	−18099	−2.018	0.191	0.318
0.700	−12568	−7167	2.843	−6934	−0.123	0.451	0.645
0.800	−5164	−887	2.251	−1639	0.395	0.721	0.901
0.900	−1713	353	1.087	−49	0.211	0.897	0.997
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Sm(liquid)

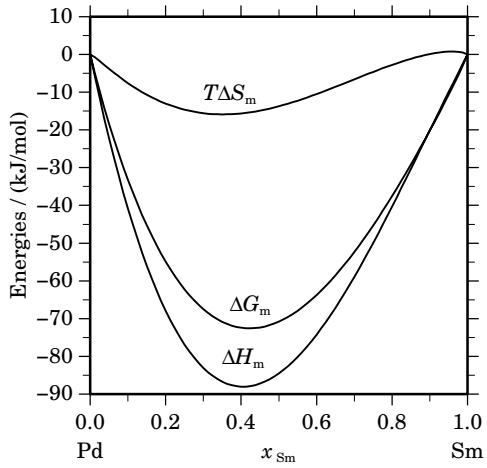

Fig. 3. Integral quantities of the liquid phase at T=1900 K.

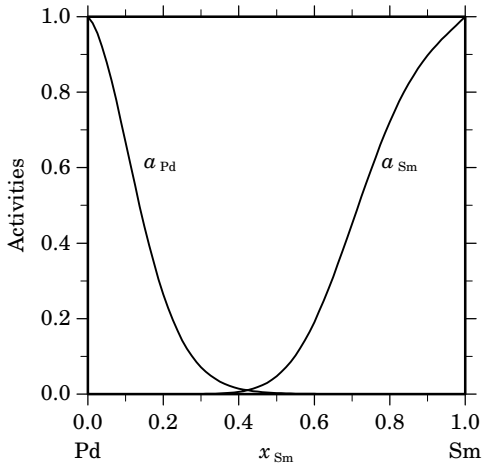

Fig. 4. Activities in the liquid phase at T=1900 K.

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

Compound	x_{Sm}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
Pd_7Sm_1	0.125	−50065	−54184	−13.816	0.000
Pd_5Sm_1	0.167	−61735	−65216	−11.673	0.000
Pd_3Sm	0.250	−76326	−78630	−7.730	0.000
$Pd_{21}Sm_{10}$	0.323	−79495	−81600	−7.059	0.000
Pd_4Sm_3	0.429	−83754	−85887	−7.153	0.000
αPdSm	0.500	−85011	−87873	−9.596	0.000
βPdSm	0.500	−84633	−87373	−9.191	0.000
Pd_2Sm_3	0.600	−83287	−90298	−23.516	0.000
Pd_3Sm_7	0.700	−73285	−82372	−30.477	0.000