Journal of Alloys and Compounds, 191 (1993) 165–168
JALCOM 505

Computer assessment of the palladium–rhodium system

R. Gürler*, L. A. Cornish** and J. N. Pratt
School of Metallurgy and Materials, University of Birmingham, Birmingham (UK)

(Received September 9, 1992)

Abstract

An optimised phase diagram for the Pd–Rh binary system has been calculated using thermodynamic coefficients derived from published experimental phase equilibrium and thermodynamic data. Solid-state information was assessed by means of the Lukas optimisation program, and estimates were made of thermodynamic properties for the liquid phase using relationships between solid and liquid values established by Williams and by Kubaschewski. The presence of a solid-state immiscibility gap is confirmed; the critical temperature of 910 °C is higher than in previous phase diagrams but in agreement with decomposition temperatures indicated by more recent electrical resistivity studies.

1. Introduction

The present assessment of the Pd–Rh system was performed in the course of recent experimental and computer studies of phase equilibria in Mo–Pd–Rh ternary alloys. It was undertaken in order to resolve uncertainties in the location of the binary solid-state miscibility gap, to provide a more complete Pd–Rh binary diagram by the estimation of the unknown liquidus and solidus lines, and to establish binary thermodynamic coefficients for use in computations of the ternary phase diagram. Published experimental phase diagrams and thermodynamic data were used in the Lukas assessment program [1] to derive optimised thermodynamic coefficients for the Pd–Rh solid solutions. Corresponding values for the liquid phase were estimated from the assessed solid-state data using Williams' model [2]. The complete phase diagram was then computed by means of a standard free-energy minimisation procedure.

2. Previous studies

2.1. Phase diagram data

No information exists concerning the liquidus or solidus of the system since the highest temperature at which it has been investigated is 1300 °C, where Raub [3] established the existence of a continuous range of f.c.c. solid solutions. His X-ray measurements showed lattice parameters that decreased almost linearly with increasing Rh content, with only very slight positive deviations from Vegard's law. Metallographic investigations at lower temperatures (900–600 °C) by Raub *et al.* [4] have shown decomposition into two f.c.c. solid solutions to occur at temperatures below approximately 845 °C; their lattice parameter measurements on the two-phase alloys have established the limits of the miscibility gap and they have reported this to be as shown in Fig. 1. In this alloy system the approach to equilibrium is extremely slow and may not have been completely attained at the lowest temperature (600 °C) despite the very long annealing times (8736 h). The existence of a miscibility gap was also indicated by the work of Rudnitskii *et al.* [5] who detected sharp changes in the temperature dependence of the thermoelectric potentials of the alloys; however these were observed at temperatures ranging 100–300 °C higher than the boundary reported by Raub *et al.* [4]. More recently Shield and Williams [6] have re-examined the system by means of electrical resistivity measurements; these were made using both increasing and decreasing temperatures over ranges typically between 400 °C and 1400 °C. Their results also indicate that decomposition of the continuous solid solutions generally occurs at slightly higher temperatures than those given by Raub *et al.* [4], but the differences are much less than those suggested by the thermoelectric potential measurements. The decomposition temperatures reported by Shield and Williams are again plotted in Fig. 1, however their annealed samples did not provide additional two-

---

*Present address: Metallurgical Institute, Anadolu University, Turkey.

**Present address: Department of Metallurgy, University of Witwatersrand, South Africa.

0925-8388/93/$6.00

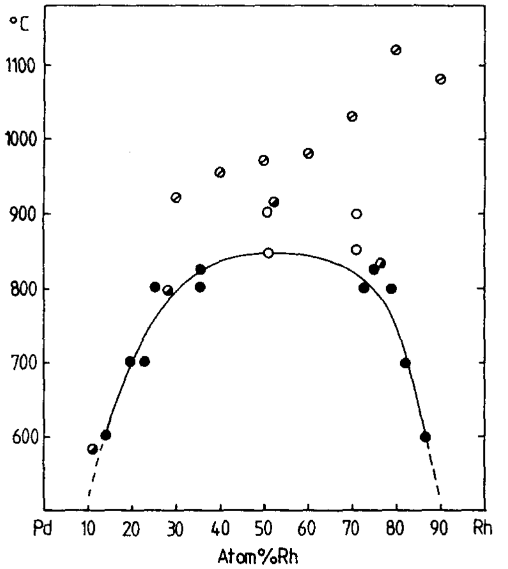

Fig. 1. Pd–Rh solid-state miscibility gap experimental data: ○–● – Raub *et al.* [4], X-ray and metallographic studies; ⊘ – Rudnitskii *et al.* [5], thermoelectric potential studies; ◑ – Shield and Williams [6], electrical resistivity studies.

phase tie-line information since X-ray diffraction patterns showed only single-phase lattice parameters and microprobe analysis did not detect any compositional variations. This was attributed to the fine scale (approximately 10 nm) of precipitation of the second phase.

2.2. *Thermodynamic data*

Thermodynamic studies of the Pd–Rh system are limited to a single investigation by Myles [7]. Using the torsion–effusion technique, the vapour pressure of palladium was measured over a wide range of solid solution compositions at temperatures between approximately 1515 K and 1665 K. The thermodynamic properties at 1575 K, which he derived from his vapour pressure data, are summarised in Table 1. The system is characterised by positive deviations from Raoultian behaviour, positive excess entropies and endothermic enthalpies of formation, and Myles concluded that a strong tendency towards phase separation must exist in the solid solutions. Budworth *et al.* [8] have made low temperature heat capacity measurements and derived Debye temperatures and electronic heat coefficients from these. The values are indicative of positive deviations from Neumann–Kopp behaviour at higher temperatures and are thus supportive of Myles' observation of positive excess entropies of formation.

3. Thermodynamic modelling

Thermodynamic coefficients for the solid solutions were derived using the Lukas program [1]. In optimising the data, the treatment was finally restricted to a form in which enthalpies and entropies were assumed to be independent of temperature, and the composition dependence of each excess property of the solution phase is described by only two coefficients, *i.e.* essentially of sub-regular form.

Lattice stability values for Rh were taken from Katz *et al.* [9], while those given by Potter and Rand [10] were used for Pd. Solid–solid equilibrium data points, taken from the miscibility gap boundary as reported by Raub *et al.* [4], and partial free energy and enthalpy of formation values at 1575 K, given by Myles [7] provided the experimental input data. Information from the studies of Shield and Williams [6] was not included in the optimisation since no independent tie-lines were defined by their observations. Results from Rudnitskii *et al.* [5] were similarly omitted for this reason and also because of their large deviation from most other work. High temperature C_p values, estimated from the low temperature electronic heat coefficients and Debye temperatures [8], although included initially, were omit-

TABLE 1. Experimental thermodynamic properties of Pd–Rh solid solutions at 1575 K. Reference states: Pd(f.c.c.) and Rh(f.c.c.) [7]

x_{Pd}	$\Delta\bar{G}_{Pd}$	$\Delta\bar{G}_{Rh}$ (J mol^{-1})	$\Delta\bar{H}_{Pd}$	$\Delta\bar{H}_{Rh}$	$\Delta\bar{S}_{Pd}$ (J K^{-1} mol^{-1})	$\Delta\bar{S}_{Rh}$	ΔS	ΔG (J mol^{-1})	ΔH
0.9	−1046	−14226	335	47614	0.88	39.25	4.73	−2395	5063
0.8	−1925	−8996	6067	15104	5.10	15.31	7.11	−3347	7869
0.7	−2971	−5899	4728	17573	4.90	14.90	7.91	−3849	8577
0.6	−3891	−4100	7488	13054	7.20	10.88	8.66	−3975	9665
0.5	−3975	−3975	9372	10795	8.45	9.37	8.91	−3975	10083
0.4	−4686	−3431	15230	5858	12.64	5.90	8.58	−3933	9581
0.3	−6109	−2678	17782	4519	15.19	4.56	7.74	−3682	8494
0.2	−8117	−2008	28577	837	23.26	1.78	6.11	−3222	6360
0.1	−13347	−1172	32635	42	29.20	0.7	3.60	−2385	3306

ted from the final optimisation as being too uncertain. The lattice stability values used for the elements, and the thermodynamic coefficients yielded by the optimisation program, are given in Table 2.

The liquid phase could not be included in the optimisation procedure since no relevant data were available except for the lattice stabilities and melting points of the pure components. However, estimates of the thermodynamic properties of the liquid alloys were made so as to permit a calculation of the solid–liquid phase equilibrium of the system.

Enthalpies of formation for the liquid alloys were derived from those of the solid solutions by means of Williams' model [2]. Using a simplified version of the Guggenheim model [11] the enthalpies of formation of solid solutions may be expressed as

$$\Delta H_s = x(1-x)W[1+2AWx(1-x)/T]$$

where W is an interaction energy as in the Guggenheim model, x is the mole fraction and A is an empirical parameter. From an examination of literature data for the enthalpies of formation of liquid and solid binary metallic solutions, Williams established a value for A of -0.0234 mol K J^{-1} and further concluded that the value of W for liquid alloys is, on average, 4.2 kJ mol^{-1} more negative than for the corresponding solids. Enthalpies of formation of liquid alloys may therefore be approximated as

$$\Delta H_l = x(1-x)(W-4.2)[1+2A(W-4.2)x(1-x)/T]$$

Using the above equations and the assessed heats of formation of the solid solutions, values for the enthalpies of formation were derived over the complete composition range. A nominal temperature of 2000 K was adopted for the purpose of the calculation. The resulting liquid values were fitted to a sub-regular approximation giving the enthalpy coefficients shown in Table 2.

TABLE 2. Element lattice stabilities and thermodynamic property coefficients for the phases of the Pd–Rh binary system. Reference states: Pd(f.c.c.), Rh(f.c.c.)

Elements	ΔH	ΔS	Composition dependence
Pd(f.c.c.)	0	0	$(1-x_{Rh})$
Pd(liq)	16480	9.02	$(1-x_{Rh})$
Rh(f.c.c.)	0	0	x_{Rh}
Rh(liq)	26568	11.88	x_{Rh}
Alloy phases	ΔH^{xs}	ΔS^{xs}	
Solid(f.c.c.)	21247	2.74	$x_{Rh}(1-x_{Rh})$
	2199	−0.56	$x_{Rh}^2(1-x_{Rh})$
Liquid[a]	20027	2.74	$x_{Rh}(1-x_{Rh})$
	2260	−0.56	$x_{Rh}^2(1-x_{Rh})$

[a] Estimated using Williams' model [2].

Kubaschewski [12, 13] has demonstrated that the entropies of fusion of completely disordered alloys may be calculated additively from the entropies of fusion of the component metals. Since, at temperatures well above the miscibility gap, the Pd–Rh solid solutions can be assumed to have become completely random, it follows that the excess entropies of formation of the liquid and solid solutions will have identical values at temperatures not too far removed from the melting range. The excess entropy coefficients for the liquid phase, given in Table 2, are therefore set equal to those of the solid phase.

4. Results and discussion

Integral thermodynamic properties indicated by the optimised coefficients are shown in Table 3, while calculated and original experimental activities of Pd at 1575 K are compared in Fig. 2. The computed and measured activity values are in satisfactory agreement,

TABLE 3. Integral thermodynamic properties of Pd–Rh solid solutions at 1575 K indicated by optimised coefficients

x_{Rh}	ΔS (J K^{-1} mol^{-1})	ΔH (J mol^{-1})	ΔG
0.9	2.90	2090	−2480
0.8	4.53	3680	−3450
0.7	5.57	4790	−3990
0.6	6.17	5420	−4310
0.5	6.38	5590	−4460
0.4	6.20	5310	−4450
0.3	5.60	4600	−4250
0.2	4.58	3470	−3750
0.1	2.94	1930	−2710

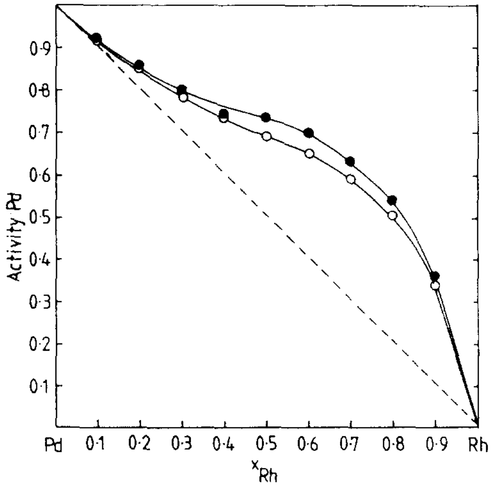

Fig. 2. Activities of palladium in Pd–Rh f.c.c. solid solutions, 1575 K: ● – Myles [7], vapour pressure studies; ○ – present work, computed values.

although the assessed integral free energies of formation at 1575 K are approximately 500 J more negative around the equiatomic composition than the reported experimental values. The coefficients arising from the mutual optimisation of the original thermodynamic and phase diagram information also imply that the enthalpies of formation of the solid solutions may be significantly less endothermic than reported by Myles [7] (see Table 1) and that the excess entropies of formation, while still positive, may also be smaller than his values.

Using the optimised coefficients, the excess free energies of formation of the solid and liquid phases are given by the respective expressions:

$$\Delta G^{xs}(\text{f.c.c.})$$

$$=x_{\mathrm{Rh}}(1-x_{\mathrm{Rh}})[21247+2199x_{\mathrm{Rh}}-T(2.74-0.56x_{\mathrm{Rh}})]$$

and

$$\Delta G^{xs}(\text{liq})$$

$$=x_{\mathrm{Rh}}(1-x_{\mathrm{Rh}})[20027-2260x_{\mathrm{Rh}}-T(2.74-0.56x_{\mathrm{Rh}})]$$

These, together with a free energy minimisation program, have been used to generate the binary-phase diagram for the Pd–Rh system presented in Fig. 3. As might be expected, the liquidus–solidus region is of simple form with a comparatively narrow freezing range at all compositions. However, the liquidus and solidus remain tentative since they are calculated without the benefit of any experimental thermodynamic data for the liquid phase, and are thus strongly dependent on the validity of the assumptions made in the treatment of this phase. Clearly, experimental investigation of this region of the diagram remains desirable.

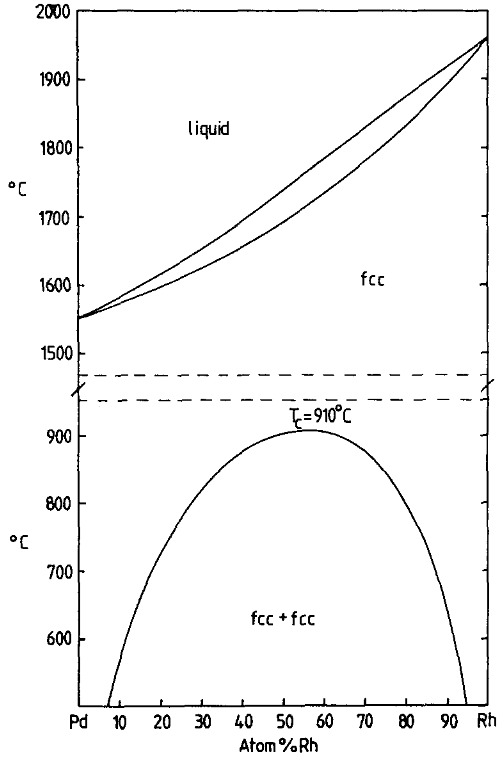

Fig. 3. The computed Pd–Rh phase diagram.

The calculated solid-state miscibility gap is in good agreement with that of Raub *et al.* [4] in the Pd-rich regions, but indicates the boundary to be at slightly higher temperatures at high Rh contents. The maximum temperature of phase separation, however, does appear to be significantly higher than the value of 845 °C suggested by Raub *et al.* The present computation has yielded a temperature of 910 °C in excellent agreement with that of 911 °C indicated by the results of Shield and Williams [6]. These closely similar values constitute independent evidence for the higher critical temperature since it should be recalled that results from the latter electrical resistivity studies were not used in the optimisation program. Shield and Williams' experimental observation of decomposition at these higher temperatures is attributable to their use of the electrical resistivity method that will be sensitive to the onset of precipitation on a very fine scale, while earlier studies will have required significantly more discontinuous separation of the two solid solutions before detection.

References

1 H. L. Lukas, E. Th. Henig and B. Zimmerman, *Calphad J.*, *1* (1977) 225–236.
2 R. O. Williams, *Calphad J.*, *8* (1984) 135–148.
3 E. Raub, *J. Less-Common Met.*, *1* (1959) 3–18.
4 E. Raub, H. Beeskow and D. Menzel, *Z. Metallk.*, *50* (1959) 428–431.
5 A. A. Rudnitskii, R. S. Polyakova and I. I. Tyvrin, *Izv. Sektora Platiny i Drug Blagorodn. Metal., Inst. Obsch. Neorgan. Khim., Akad. Nauk S.S.S.R.*, *29* (1955) 190–196.
6 J. E. Shield and R. K. Williams, *Scripta Metall.*, *21* (1987) 1475–1479.
7 K. M. Myles, *Trans. Metal. Soc. A.I.M.E.*, *242* (1968) 1523–1526.
8 D. W. Budworth, F. E. Hoare and J. Preston, *Proc. R. Soc. A*, *257* (1960) 250–262.
9 S. A. Katz, V. Ya. Chekhovskoi, N. B. Gorina, V. Polyakova and E. M. Savitskii, *V.S.E.V. I. Konif, Kalorif*, *2* (1977) 351–357.
10 M. H. Rand and P. E. Potter, *Physica*, *103B* (1981) 21–30.
11 E. A. Guggenheim, *Mixtures*, Oxford University Press, London, 1952.
12 O. Kubaschewski, *Z. Elektrochem.*, *47* (1941) 475–484.
13 O. Kubaschewski, *Z. Physik. Chem.*, *192* (1943) 292–308.