The Pd-Ru System (Palladium-Ruthenium)

S.N. Tripathi, S.R. Bharadwaj, and S.R. Dharwadkar
Bhabha Atomic Research Centre

Equilibrium Diagram

The assessed Pd-Ru phase diagram (Fig. 1) is based on the experimental results of [59Rud], [60Dar], [62Obr], and [89Kel]. The Pd-Ru phase diagram was investigated by [59Rud], [60Dar], [62Obr], [62Nov], and [89Kel] by X-ray microanalysis, XRD, DTA, thermo-electromotive force measurements, hardness measurements, electrical resistivity measurements and temperature coefficient of electrical resistance measurements, etc. The assessed phase diagram is a simple peritectic type without any intermediate phases or eutectoid transformation and *differs significantly* from those of [59Rud], [60Dar], [62Nov], [62Obr], [89Kel], and [Massalski1]. The equilibrium phases in this system are (1) the liquid, L; and (2) the two terminal solid solutions, (αPd) and (εRu).

The system was exhaustively investigated by [59Rud] over the entire composition range using twelve alloys with 5 to 90.5 at.% Ru in the temperature range of 100 to 1800 °C. The resulting phase diagram was characterized by two peritectic reactions: (1) (εRu) + L ↔ β at 1593 °C resulting in the formation of an intermediate β phase containing up to ~19 at.% Ru, and (2) β + L ↔ (αPd) at 1575 °C with terminal αPd containing ~13 at.% Ru.

[59Rud attributed the thermal effect observed consistently around ~724 °C at all compositions to eutectoid dissociation of the β phase. [60Dar] measured lattice parameters, hardness, and resistivity of Pd-rich alloys up to ~20 at.% Ru with microscopic analyses of the specimens just above and below the solidus. These data established the Pd-Ru phase diagram as a simple peritectic type with a peritectic temperature of 1580 °C and without any intermediate phase or eutectoid transforma-

Table 1 Pd-Ru Lattice Parameters

Composition, at.% Ru	Lattice parameters, nm a	b	c	Comment	References
0	0.388903	...	...	...	[Massalski2]
5.25	0.3878	...	...	Annealed	[59Rud]
5.60	0.3887 ,145 0.2	...	...	1000 °C/3 weeks	[89Kle]
6.0	0.3877	...	...	...	[62Obr]
8.0	0.3876	...	...	...	[62Obr]
8.4	0.3880 ± 0.2	...	...	1200 °C/5 days	[89Kle]
8.57	0.38789	...	...	Quenched from 1500 °C	[60Dar]
9.24	0.38784	...	...	Quenched from 1500 °C	[60Dar]
10.0	0.3874	...	...	...	[62Obr]
10.47	0.3879	...	...	Annealed	[59Rud]
12.40	0.3877 ± 0.1	...	...	1400 °C/2 days	[89Kle]
15.07	0.38747	...	...	Quenched from 1500 °C	[60Dar]
15.66	0.38825	...	...	Annealed	[59Rud]
16.93	0.38751	0.27030	0.42845	Quenched from 1500 °C	[60Dar]
17.90	0.3871 ± 0.2	...	...	1500 °C/1 day	[89Kle]
20.35	0.38764	0.27031	0.42836	Quenched from 1500 °C	[60Dar]
20.89	0.38785	...	...	Annealed	[59Rud]
31.08	0.38715	...	...	Annealed	[59Rud]
41.23	0.3880	...	...	Annealed	[59Rud]
51.28	0.3866	...	...	Annealed	[59Rud]
61.22	0.3865	0.2698	0.4274	Annealed	[59Rud]
71.06	0.3865	0.2682	0.4274	Annealed	[59Rud]
71.09	...	0.27030	0.42851	Quenched from 1500 °C	[60Dar]
80.81	0.3878	0.27010	0.42730	Annealed	[59Rud]
80.88	...	0.27026	0.42851	Quenched from 1500 °C	[60Dar]
90.5	...	0.27024	0.42845	Quenched from 1500 °C	[60Dar]
91.8	...	0.2703 ± 0.1	0.4288 ± 0.2	1400 °C/2 days	[89Kle]
92.6	...	0.2705 ± 0.1	0.4287 ± 0.2	1500 °C/1 day	[89Kle]
97.39	...	0.27067	0.42858	...	[54Hel]
97.48	...	0.27066	0.42856	...	[54Hel]
97.95	...	0.27064	0.42844	...	[54Hel]
98.04	...	0.27065	0.42847	...	[54Hel]
100	...	0.27058	0.42816	...	[Massalski2]

tion. [62Obr] investigated the Pd-rich region of the system (<20 at.% Ru) by thermal, microscopic, and X-ray methods and determined with high precision the solidus temperatures of the fcc αPd phase, the peritectic temperature of 1585 ± 5 °C, the peritectic composition of 9 at.% Ru, and a maximum solubility of Ru in (Pd) of 16 at.% Ru at the peritectic temperature. In sharp contradiction to earlier reports, [62Nov] concluded from their thermal and metallographic studies that the system was eutectic in nature with a eutectic temperature of 1520 °C and a eutectic composition of 12.5 at.% Ru. The system was reinvestigated recently by [89Kle] by X-ray microanalysis (XMA), XRD, and DTA of four Pd-rich alloys, one equiatomic and one Ru-rich, and was shown in concurrence with [60Dar] and [62Obr] to have a simple peritectic-type phase diagram

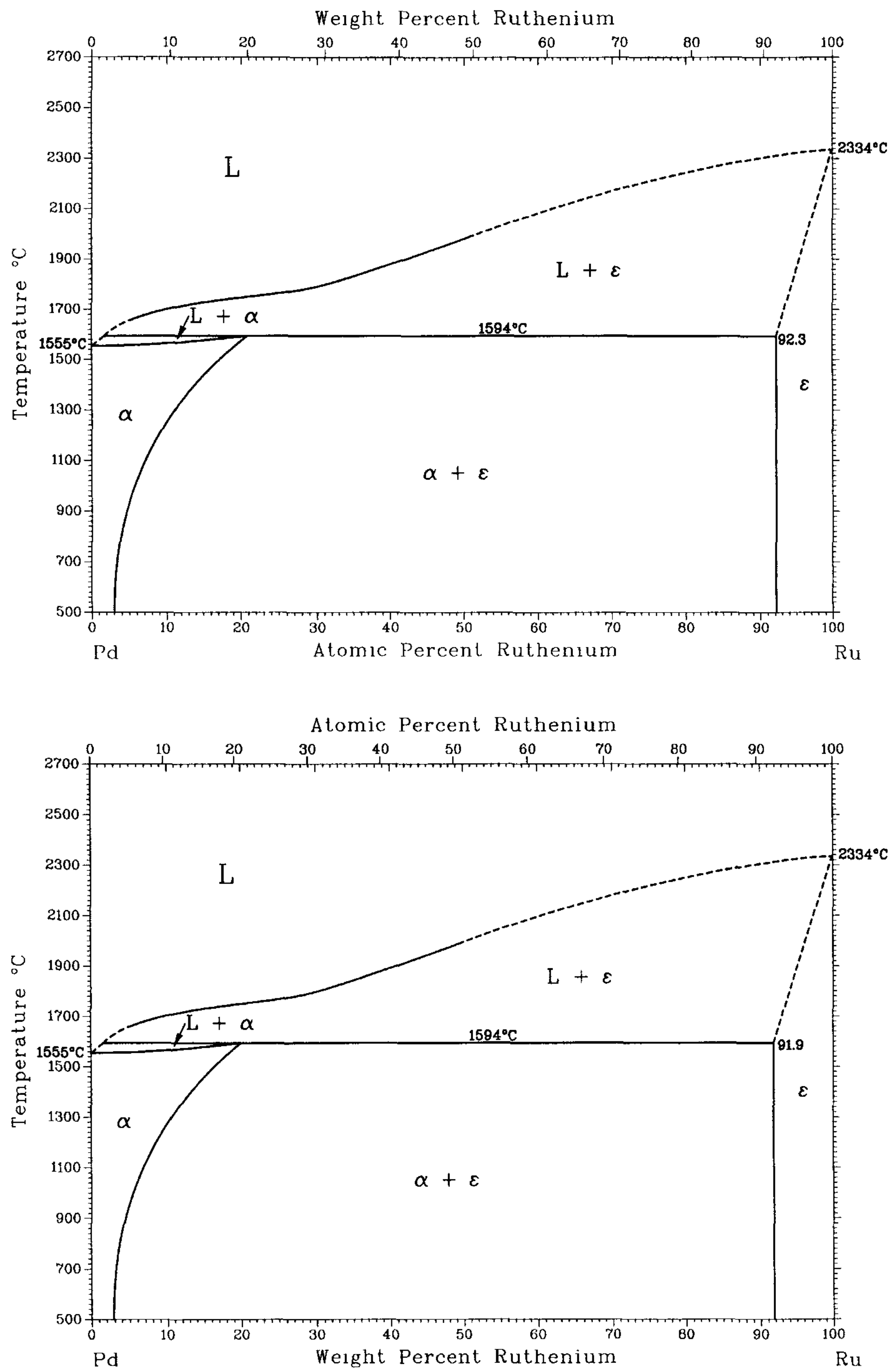


Fig. 1 Assessed Pd-Ru diagram.

with a peritectic temperature of 1594 ± 3 °C and a peritectic composition of ~12 at.% Ru.

The experimental results of various investigators are plotted in Fig. 2, and assessed phase boundaries are shown therein by solid and broken lines.

Liquidus and Solidus

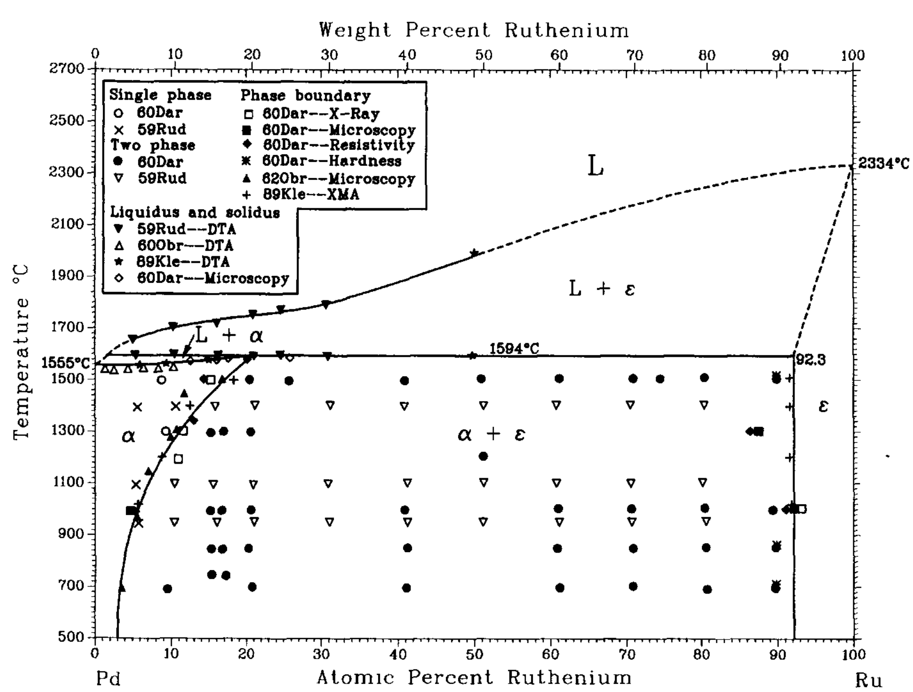
[59Rud] measured the liquidus temperatures on Pd-rich alloys in the range from ~5 to ~31 at.% Ru, and [89Kle] measured the liquidus at equiatomic composition. No experimental data exists for the liquidus below 5 at.% Ru and above 50 at.% Ru. The RuO_2 that was observed by [59Rud] in X-ray photographs of some of their alloys would decompose at 1 atm with $T \geq$ 1560 °C in oxygen [63Bel] and at lower temperatures in air, inert gases, and vacuum In the absence of any details on the environmental conditions of thermal analysis of [59Rud] and assuming that DTA was carried out in air with 21% O_2, it would be reasonable to consider that RuO_2 did not exist in the alloys at the melting point of Pd (1555 °C) and higher temperatures, *i.e.*, at the solidus temperatures and much more so at the liquidus lying above 1594 °C, the peritectic isotherm. Hence the liquidus and solidus temperatures of [59Rud] are those of RuO_2 free and pure alloys. Furthermore, since the thermocouples of [59Rud] were calibrated against the melting points of Au, Pd, and Pt (1063, 1552, and 1769 °C as against the latest ones, 1064.4, 1555, and 1769 °C), their temperatures can be assigned an accuracy within ± 3 °C. The close match between the peritectic temperature of 1593 °C by [59Rud] and that of 1594 °C by [89Kle], whose specimens were prepared from 99.9% pure metals (Heraeus) by arc-melting under reduced argon pressure and were homogenized under vacuum, further speaks of the reasonable purity of the [59Rud] alloys at solidus temperatures and above. Hence the liquidus data of [59Rud] are accepted and combined with the equiatomic liquidus point of [89Kle] to construct the liquidus line of the assessed diagram. The composition of the Pd-rich melt of the peritectic reaction, L + ε ↔ α, was estimated to be ~9 at.% Ru [62Obr] on the basis of microscopic examination of the quenched solid and 12 at.% Ru by [89Kel]. In view of the assessed accuracy and credibility of the solidus and liquidus determinations of [59Rud] and hence the consequent shape of the liquidus, the composition is estimated to be ~1.5 at.% Ru as shown in Fig. 1 and 2.

Solidus temperatures of the α phase are reported by [59Rud] (5 to 31 at.% Ru), [60Dar] (5.95 to 25.86 at.% Ru), [62Obr] (2 to 10 at.% Ru), and [89Kle] (6 to 15 at.% Ru). These results mostly agree well. Solidus temperatures up to 8 at.% Ru are negligibly different from the melting temperature of Pd. With further increase in Ru content, the solidus rises to the temperature of the peritectic reaction, *i.e.*, 1594 °C at ~21 at.% Ru.

In view of an excellent agreement between [59Rud] and [89Kle] on the peritectic temperature, the peritectic line at 1594 °C is accepted.

Primary Phases

αPd Phase. Ru dissolves in fcc Pd and forms a single-phase homogeneous solid solution only at temperatures >400 °C [84Gol]. The solubility of Ru in (Pd) increases with temperature and shows, according to the present assessment, a maximum of ~21 at.% Ru at the peritectic temperature in contrast to



~13.5 at.% Ru [59Rud], 16 at.% Ru [62Obr], 17 at.% Ru [60Dar,84Gol], and 19 at.% Ru [89Kel] and decreases to ~3 at.% Ru at 500 °C. The limiting composition of 21 at.% Ru at 1594 °C was derived by judiciously drawing a line through the phase boundary data of [60Dar], [62Obr], and [89Kle], and allowing it to intersect the peritectic isotherm. The solubility of Ru in (Pd) in a α phase was extensively studied by [60Dar], [62Obr], and [89Kle], and the phase boundary determinations are in fairly good agreement to delineate the α phase. The single-phase field is further characterized by a smooth and continuous variation of hardness and specific resistance over compositions up to ~10 at.% Ru.

εRu Phase. Pd dissolved in cph Ru and forms a solid solution having cph structure and represented as the ε phase. A consistent observation in XMA of 50 at.% alloy after heat-treatment at 1000, 1200, 1400, and 1500 °C for 3 weeks, 5, 2, and 1 day(s), respectively, confirming the ε phase at 7.7 ± 0.3 at.% Pd [89Kle] independent of temperatures <1594 °C delineates the ε-phase field. The 7.7 at.% isopleth is accepted as the solvus on the Ru-rich side.

Intermediate Phase?

Though [59Rud] reported the formation of an intermediate β phase (~$RuPd_4$) on the basis of microstructure, thermoelectromotive force of the couple formed by the alloys with platinum, and resistance measurements of alloys quenched from 1400, 1100, and 950 °C, no confirming evidence is found in later investigations. The phase distinct from α and ε in metallographs and the discontinuities in the plots of specific resistance the thermoelectromotive force, in Pd-rich alloy compositions attributed by [59Rud] to a β phase probably rose due to internal oxidation of Ru in the alloys.

Addendum

The Pd-Ru system has been computer assessed by [81Ran] and [93Gur]. [81Ran] assessed the peritectic temperature as 1910 K, which is high probably due to the use of estimated input data; but [93Gur] found the peritectic temperature to be exactly the same as that established experimentally (1867 K). The optimized diagram of [93Gur] is quite similar to that of [89Kle] except at lower temperatures below the peritectic line where the solubility of Pd in (εRu) decreases with decreasing temperature. Compared to the phase diagram of [89Kle], the phase boundaries of εRu(Pd), ε + L, and αPd + L and their temperature dependences are well reproduced in the diagram of [93Gur]. This is only because the estimations of [89Kle] about the above-stated phase fields have been input in the Lukas optimization program. The computer assessment of [93Gur] has completely ignored the highly accurate (±3 °C) liquidus and solidus data of [59Rud] (as argued earlier) on the phase boundaries of the ε + L field in the region adjacent to the α + L field. The diminishing solubility of Pd in (εRu) with a decrease in temperature as computed in the assessment of [93Gur] is reasonable as expected, but the experimental status of the (εRu) boundary below the peritectic line and of the α + L boundaries remain as shown in the present phase diagram.

Crystal Structure and Lattice Parameters

The constituent metals Pd and Ru belong to different crystal structures, so only a limited mutual solid solubility is observed. Pure Pd crystallizes with an fcc Cu-type structure and pure Ru as a cph Mg-type structure.

The lattice parameters of the coexisting phases in the Pd-Ru system were determined by [54Hel], [59Rud], [60Dar], [62Obr], and [89Kel] and are given along with their compositions in Table 1. The lattice parameters of [59Rud] are adjusted to the latest values: $a = 0.3890$nm for Pd, and $a = 0.27053$ nm and $c = 0.42814$ nm for Ru. Hence the numbers are different from [59Rud].

Thermodynamics

Except for equiatomic composition, there is no experimental thermodynamic information on the Pd-Ru system. The relative partial molar Gibbs energy of Ru, G_{Ru}, in 50 at.% alloy was determined [89Kle] by solid state galvanic cells of the following type at temperatures in the range $<1100 \leq T/K \leq 1200$.

(–)Pt/Ru,RuO_2/Zr(Ca)O_2/RuO_2,Ru-Pd alloy/Pt(+)

The emf measured was expressed as

$$E(\text{mv}) = 0.63 + 0.013T(\text{K})$$

and

$$G_{Ru}\,(1200\ \text{K}) = -6.26\ \text{kJ/mol}$$

[83Mie] and [83Nie] theoretically calculated the relative partial molar enthalpy of solution of Ru in Pd at infinite dilution and reported $H^{ex}_{Ru} = 21$ kJ/mol.

Suggested Future Experimental Work

The liquidus below 5 at.% Ru and above 50 at.% Ru and the solidus beyond 90 at.% Ru remain tentative and need experimental determination.

According to the present assessment, the composition of the Pd-rich peritectic melt is ~1.5 at.% Ru based on DTA results of [59Rud] compared to 9 at.% Ru based on [62Obr]. A careful microscopic scrutiny of specimens up to ~10 at.% Ru subjected to various heating and cooling rates and precision DTA measurements would be useful in resolving the controversy and to arrive at a unique composition.

Cited References

54Hel: A. Hellawall and W. Hume-Rothery, "The Lattice Spacings of Dilute Solid Solutions of Zr, Nb, Mo, Rh and Pd in Ru," *Philos. Mag.*, *45*, (367), 797-806 (1954). (Crys Structure; Experimental)

***59Rud:** A.A. Rudnitskii and R.S. Polyakova, "The Palladium-Ruthenium System," *Russ. J. Inorganic Chem.*, *4*(6), 631-636 (1959). (Equi Diagram, Crys Structure; Experimental; #)

60Dar: A.S. Darling and J.M. Yorke, "The Ruthenium-Palladium System," *Platinum Met. Rev.*, *4*(3), 104-110, (1960). (Equi Diagram. Crys Structure; Experimental; #)

62Nov: O.A. Novikova, "Palladium-Ruthenium Alloys," TR: Inst. Met. in A.A. Baikova, *Akad. Nauk SSSR*, (11), 155-163 (1962). (Equi Diagram; Experimental)

62Obr: W. Obrowski and G. Zwingmann, "Structure of Palladium-Ruthenium System and Properties of Palladium-Rich Alloys," *Z. Metallkd., 33*(7), 453-455 (1962). (Equi Diagram; Crys Structure; Experimental; #)

63Bel: W.E. Bell and M. Tagami, "High Temperature Chemistry of the Ruthenium-Oxygen System," *J. Phys. Chem., 67*(11), 2432-2436 (1963). (Equi Diagram; Experimental)

81Ran: M.H. Rand and P.E. Potter, "Thermodynamics and Phase Diagrams of Mo-Pd-Ru and Related Systems," *Physica, 103B*, 21-30 (1981). (Equi Diagram; Experimental)

83Mie: A.R. Miedema and A.K. Niessen, "The Enthalpy of Solution for Solid Binary Alloys of Two 4d Transition Metals," *Calphad, 7*(1), 27-36 (1983). (Thermo; Theory)

83Nie: A.K. Niessen and A.R. Miedema, "The Enthalpy Effect on Forming Diluted Solid Solutions of Two 4d and 5d Transition Metals," *Ber. Bunsenges. Phys. Chem., 87*(9), 717-724 (1983) (Thermo; Theory)

84Gol: N.N. Golikova, N.N. Syutkin, and V.K. Rudenko, "Influence of Ruthenium on the Structure of a Pd-Cu Alloy," *Phys. Met. Metallogr. (USSR), 58*(4), 183-186 (1984). (Equi Diagram; Experimental)

***89Kle:** H. Kleykamp, "Constitution and Thermodynamics of the Mo-Ru, Mo-Pd, Ru-Pd and Mo-Ru-Pd Systems," *J. Nucl. Mater., 167*, 49-63 (1989). (Equi Diagram; Crys Structure; Experimental; #)

93Gur: R. Gurler, "Computer Assessment of Ru-Rh and Ru-Pd," *J. Alloys Compd., 191*, 31-35 (1993). (Equi Diagram; Review)

*Indicates key paper.

#Indicates presence of a phase diagram.

Pd-Ru evaluation is contributed by **S.N. Tripathi, S.R. Bharadwaj,** and **S.R. Dharwadkar**, Applied Chemistry Division, Bhabha Atomic Research Centre, Bombay-400085, India. Bibliographic assistance was provided by ASM International. Literature searched through August 1991. Dr. S.N. Tripathi and Ms. S.R. Bharadwaj are the Alloy Phase Diagram Program Contributing Editors for platinum metals.