

Palladium – Rhodium – Uranium

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Introduction

The only phase diagram investigation of this system has been carried out by [1991Kle]. They studied the isothermal section at 1050°C. Alloys were prepared by using Rh and Pd powders (99.7 and 99.9 mass% pure, respectively) and U filings containing 120 ppm oxygen and 120 ppm nitrogen as impurities. U was cleaned for superficial oxide by nitric acid. Pellets of the component powders and filings were arc-melted under reduced argon pressure, crushed and pressed again, and finally annealed at 1050°C for 500 h under static Ar atmosphere. Samples were analyzed by metallography, electron probe microanalysis, X-ray diffraction and DTA (the last one only on selected binary Pd-U alloys).

Binary Systems

Rh-U binary subsystem is accepted after [Mas2]. The phase diagram Pd-Rh is taken from [1994Tri]. As for Pd-U it is here preferred the phase diagram reported by [1991Kle], shown in Fig. 1, which is in agreement with [Mas2] in the range 0-75 at.% Pd and different at higher Pd concentration. In particular, with respect to [Mas2], the existence of the UPd₅ and U₂Pd₁₁ phases is not confirmed, while the Pd richest phase at about 88 at.% Pd is reported as UPd₈ instead of U₂Pd₁₇. Moreover, the UPd₄ phase, previously considered as peritectic forming, is reported by [1991Kle] as congruent melting at 1585°C.

Solid Phases

The Pd-Rh-U solid phases are reported in Table 1. It may be observed that one ternary line compound U(Rh_{1-x}Pd_x)₂ with the MgZn₂ Laves structure is formed and several binary phases show more or less extended ternary solutions. For the fcc and AuCu₃ solid solutions, isoparametric curves according to [1991Kle] are reported in Fig. 2.

Isothermal Sections

The isothermal section at 1050°C investigated by [1991Kle] is reported in Fig. 3. Main features of this section are the following: the continuous (Pd-Rh) based fcc solid solution, extending up to about 18 at.% U (with 9.5 at.% Rh and 72 at.% Pd), includes a large miscibility gap; isostructural URh₃ and UPd₄ AuCu₃ type phases form a continuous solid solution crossing the composition triangle; the U(Rh_{1-x}Pd_x)₂ ternary line compound extends between $x = 0.04$ and $x = 0.25$; the binary-based U₃(Rh_{1-x}Pd_x)₄ solution extends up to $x = 0.47$; most of the U rich part of the section, not investigated, is occupied by the liquid phase.

It may be observed that, according to the accepted binary, U₅Pd₆ should appear in the section: it has been added in Fig. 3 and related equilibria are tentatively indicated by interrupted lines.

Thermodynamics

According to [1991Kle], the fcc region at 1050°C splits into two conjugate solid solutions when more than 0.6 at.% U is dissolved in binary Pd-Rh solution. In other words the critical temperature of the fcc miscibility gap, which is about 915±5°C in the Pd-Rh binary, is steeply raised by U additions. The closed region of immiscibility within the fcc solid solution range was evaluated by use of binary interaction parameters in a ternary regular solution model. The isothermal spinodal curves at 1050°C and the critical temperature were calculated using different values of the interaction parameters (α_{M-M}). The results, taken from [1991Kle], are shown in Fig. 4. From these calculations relative partial molar Gibbs energies of U in Rh and Pd at infinite dilution were evaluated as -290 and -390 kJ·mol⁻¹, respectively.

The heat capacities of U(Rh_xPd_{1-x})₃ at $x = 0$ and $x = 0.15$ were measured by [1997Ari] over the 290-1500 K temperature range by direct heating pulse calorimetry and reported in small graphs in the original paper.

The heat capacity of UPd₃ measured by [1997Ari] was smaller than the literature data up to 900 K. The heat capacity of U(Rh_{0.15}Pd_{0.85})₃ was a little larger than that of UPd₃, with a similar temperature dependence. On the basis of the measured heat capacities and the literature data concerning enthalpy and entropy of formation of the binary UPd₃ phase, the Gibbs energy of the U(Rh_{0.15}Pd_{0.85})₃ solution was calculated by [1997Ari] as $\Delta_f G^\circ = -497.6 + 3.01 \cdot 10^{-3} \cdot T$ (with $\Delta_f G^\circ$ in kJ·mol⁻¹ and T in K).

Miscellaneous

Electronic structure of the U(Rh_xPd_{1-x})₃ phase has been studied by [1988Eri], while X-ray photoelectron spectroscopy studies on the same phase have been carried out by [1998Fuj].

References

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γU) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	[Mas2]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	$a = 1075.9$ $c = 565.6$	[Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2]
α, (Rh _x Pd _{1-x})	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu		0 < x < 1 dissolves up to 18 at.% U at 9.5 at.% Rh see Fig. 2 for the variation of the lattice parameters inside the solid solution
(Pd) < 1555		$a = 389.03$	at 25°C [Mas2]
(Rh) < 1963		$a = 380.32$	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ , (URh ₃ ,UPd ₄)	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃		$0 < x < 1$ see Fig. 2 for the variation of the lattice parameters inside the solid solution
URh ₃ < 1700		$a = 399.2$	[1991Kle]
UPd ₄ < 1585		$a = 407.4$ $a = 404.7$	defective structure at 1050°C and UPd _{3.6} at 1050°C and UPd _{4.3} [1991Kle]
U(Rh _x Pd _{1-x}) ₃	<i>hP16</i> <i>P6₃/mmc</i> TiNi ₃	$a = 578.8 \pm 0.3$ $c = 954.7 \pm 1.4$	$0 < x < 0.09$ at $x = 0.09$ (max Rh solubility, U rich side) [1991Kle]
UPd ₃ < 1640		$a = 577.5 \pm 0.1$ $c = 965.4 \pm 0.3$	at $x = 0$, U rich side [1991Kle]
		$a = 576.3 \pm 0.2$ $c = 954.1 \pm 0.9$	at $x = 0$, Pd rich side [1991Kle]
U ₅ Pd ₆ 1110 - 980	-	-	54.54 at.% Pd [1991Kle]
UPd 1047 - 970	-	-	50 at.% Pd [1991Kle]
U ₃ (Rh _{1-x} Pd _x) ₅ < 1550	-	-	$0 < x < 0.05$ [1991Kle]
U ₃ (Rh _{1-x} Pd _x) ₄ < 1450	-	-	$0 < x < 0.47$ [1991Kle]
β U ₄ Rh ₃ 1155 - 720	-	-	at 43 at.% Rh [Mas2]
α U ₄ Rh ₃ < 720	-	-	at 43 at.% Rh [Mas2]
* τ_1 , U(Rh _{1-x} Pd _x) ₂	<i>hP12</i> <i>P6₃/mmc</i> MgZn ₂	$a = 534.3 \pm 0.5$ $c = 869.4 \pm 2.7$	$0.04 < x < 0.25$ [1991Kle] at $x = 0.04$

Fig. 1: Pd-Rh-U.
The accepted Pd-U
phase diagram

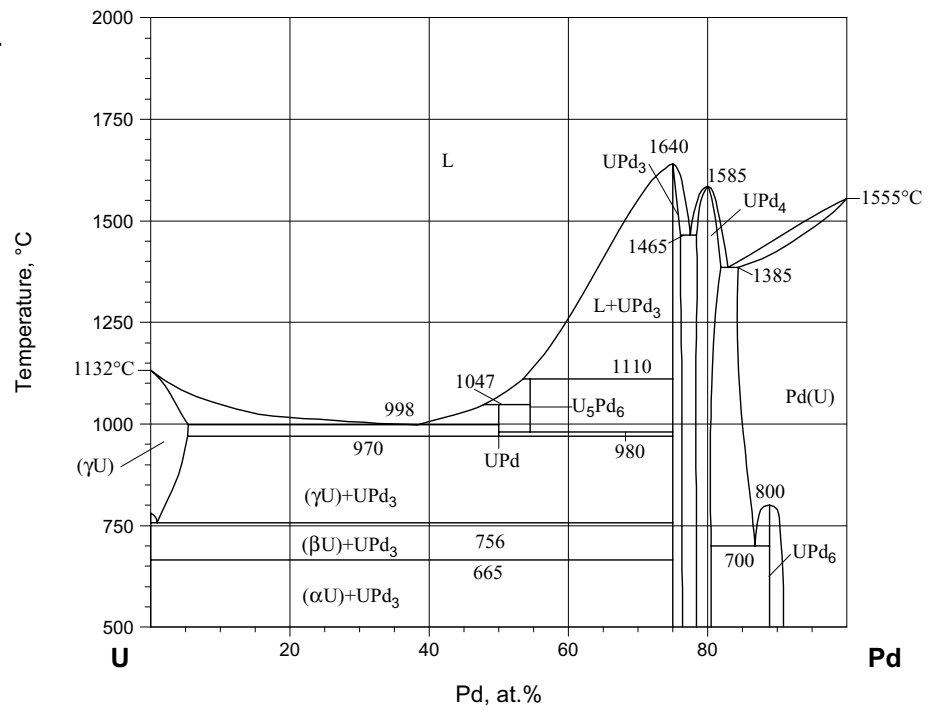


Fig. 2: Pd-Rh-U.
Isoparametric curves showing the variation of the lattice parameter a in α and γ solid solutions

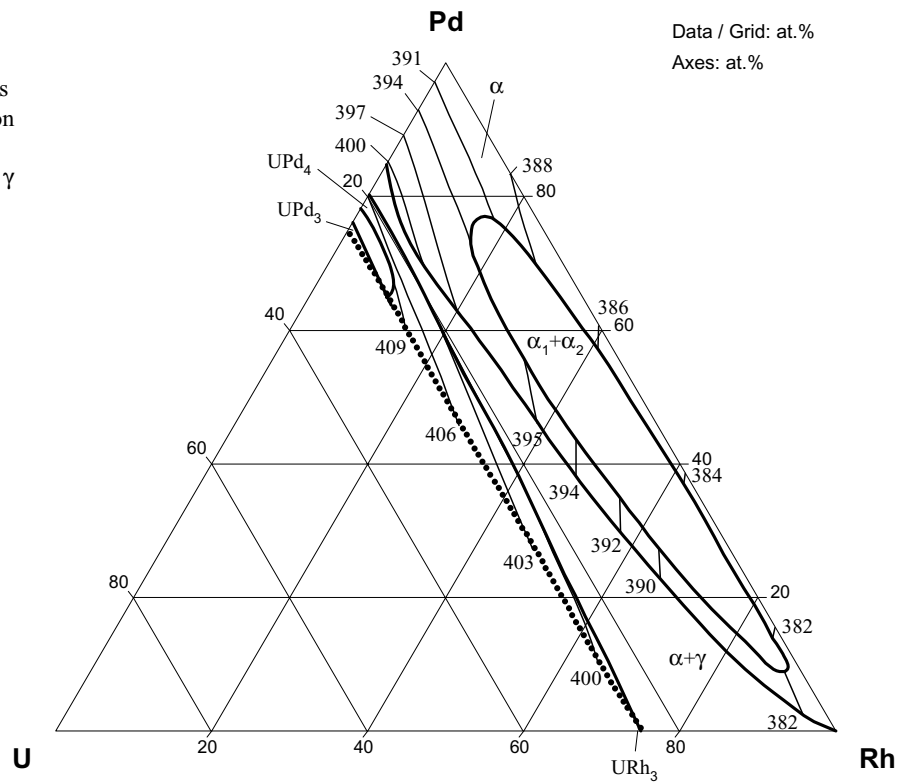


Fig. 3: Pd-Rh-U.
Isothermal section at
1050°C

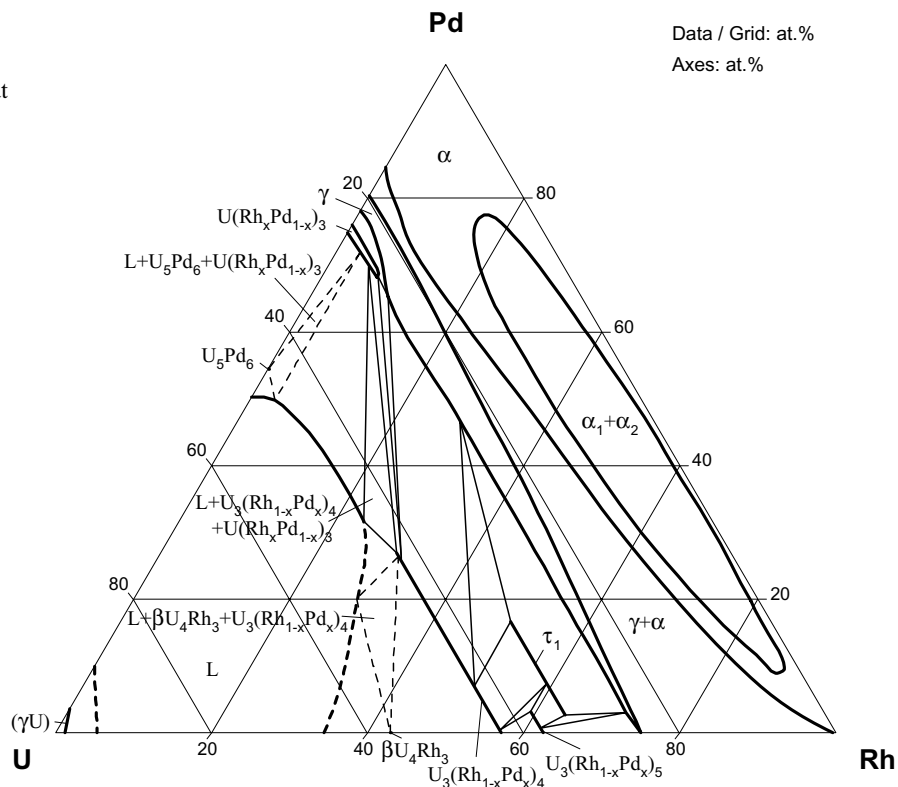


Fig. 4: Pd-Rh-U.
Calculated spinodal
curves in the fcc
immiscibility region
at 1050°C

