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The Other Metallic Phase in Spent Nuclear Fuel ~A Complete Thermodynamic Evaluation of the U-Pd-Rh-Ru System~

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ABSTRACT – During burnup of nuclear fuel, fission products accumulate. Post-irradiation examination of burned up nuclear fuel has revealed the presence of several phases, namely: the fuel matrix of UO_2, with dissolved oxides present; a white metallic phase consisting of the so-called "noble metals" (*i.e.*, Mo-Ru-Pd-Rh-Tc); a grey oxide phase consisting of alkali or alkaline earth oxides (*e.g.*, $BaZrO_3$ or Cs_2UO_4); and a second metallic phase containing an alloy of UPd_3-URh_3-URu_3, which tends to coat grains of UO_2. Understanding how these phases behave becomes especially important from a safety perspective, if one considers a potential accident scenario. The quaternary system U-Pd-Rh-Ru has been evaluated and a thermodynamic model has been developed by first considering the six binary sub-systems, and the four ternary sub-systems. A critical examination of the U-Pd, U-Rh, and U-Ru experimental phase diagrams has been made, with attention placed on both the solution phases, generally present on the uranium side of the diagrams and the UPd_3-URh_3-URu_3 compounds. Finally the implications of this new model and its potential refinements of the Royal Military College of Canada nuclear fuel treatment developed by previous authors (notably the RMC group under Thompson and Lewis) will be explored.

Introduction

Understanding and predicting the chemical changes that occur in nuclear fuel as a result of irradiation has been a problem for many years. Early research by Olander [1] and Cubicciotti [2-5], provided a reasonable understanding. Figure 1 depicts a conceptual representation of irradiated fuel, which illustrates some of the dominant phases.

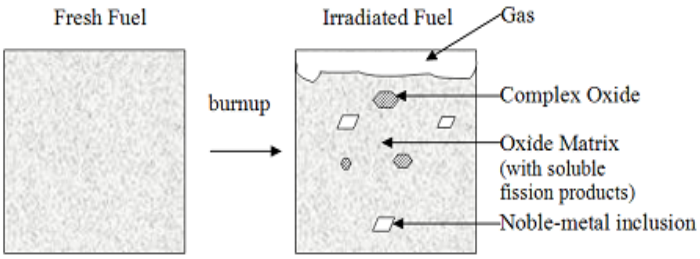

Figure 1. Simplified representation of irradiating UO_2 nuclear fuel, after Olander [1].

Previous modelling, especially that done at the Royal Military College of Canada (RMCC) in collaboration with other groups, has recently been documented [6]. The treatment developed at the RMCC, known as the RMCC Nuclear Fuel Thermochemical Treatment (RNFTT), has thermochemical models† that predict the behaviour of the phases shown in Figure

† In this paper, the convention adopted in [**Error! Bookmark not defined.**] will be followed that the term "model" will be used to represent a particular phase, and "treatment" will be used to refer to a collection of models that together represent a system. So, a model is a subset of a treatment.

1. However, work by Bramman *et al*. [7], Kleykamp [8], Uno *et al.* [9], and Kurosaki and Uno [10,11] identified another metallic phase of UPd_3-URh_3-URu_3. In the RNFTT, this phase termed the "other metallic" phase, not shown in the representation of Figure 1, is modelled as a simple ideal mixture of the three compounds.

A potential improvement to the RNFTT, is to model the U-Pd-Rh-Ru quaternary system. To accomplish this, self-consistent thermochemical evaluations of each of the six binary systems is required. Previous work by Kaye *et al*. [12,13], as part of the modelling of the Noble metal inclusions (*i.e.*, Mo-Pd-Rh-Ru-Tc), has provided a complete evaluation of the Pd-Rh-Ru ternary. But while this represents half of the binary systems in the U-Pd-Rh-Ru quaternary, the previous models also provide constraints on the thermodynamic modelling, which will be explained in the next section.

Experimental investigations of the three binary systems involving uranium can be summarized as follows: for U-Pd [14-19]; for U-Rh [20-23]; and for U-Ru [20,21,24,25]. Also, there is considerable work concerning the principle compounds in these three systems, namely: UPd_3 [26-33]; URh_3 [29-31,33-36]; and URu_3 [29-31,33-37]. Further, there has been a recently published thermochemical evaluation of the U-Ru binary system [38], but unfortunately this evaluation is not consistent with Kaye *et al*. [12,13].

1. Thermodynamic Modelling

This section will outline the modelling of the Pd-Rh-Ru-U quaternary, beginning with the thermodynamic data selected for the elements, proceeding to the six binary systems, and finally extrapolating these binary evaluations to the complete Pd-Rh-Ru-U quaternary.

1.1 The Elements: Pd, Rh, Ru, and U

Basic thermodynamic data for the elements Pd, Rh, Ru, and U have been well described in the literature and the enthalpies of formation at 298 K, standard entropies at 298 K, and heat capacities of elements related to this work are listed in Table 1.

Table 1. Thermodynamic data of U, Pd, Rh, and Ru.

Element	ΔH°_{298}	S°_{298}	$c_P = a + bT + cT^{-2} + dT^2$ $(J \cdot mol^{-1} \cdot K^{-1})$				T_{min}	T_{max}
	$J{\cdot}mol^{-1}$	$J{\cdot}mol^{-1}{\cdot}K^{-1}$	a	b x 10^3	c	d x 10^6	(K)	(K)
U-α	0	50.29	26.919	-2.5020	-76985	0.2656	298	942
U-β	2790.7	53.25	26.919	-2.5020	-76985	0.2656	942	1049
U-γ	3231.1	47.97	42.928	0	0	0	1049	1405
U-liq.	4375.2	44.24	48.660	0	0	0	1405	4407
Pd-*fcc*	0	37.82	25.028	5.4404	-67548	0	298	3000
Pd-liq.	16480.0	46.84	25.028	5.4404	-67548	0	298	3000
Rh-*fcc*	0	31.51	20.811	13.4000	33942	-2.2679	298	3000
Rh-liq.	26568.0	43.39	20.811	13.4000	33942	-2.2679	298	3000
Ru-*cph*	0	28.53	22.236	4.1437	40607	1.6015	298	3000
Ru-liq.	38589.0	43.34	22.236	4.1437	40607	1.6015	298	3000

Table 1 shows that U has three allotropic crystal structures. α-U has crystal structure of orthorhombic_A20, which transforms to β-U (tetragonal crystal structure) at 942 K (669 ºC). β-U is the stable crystal structure for only 107 ºC, before transforming at 1049 K (776 ºC) to γ-U

with a *bcc* crystal structure, which then melts at 1405 K (1132 ºC). The other three elements have only one stable crystal structure: *fcc*-Pd, *fcc*-Rh, and *cph*-Ru, respectively.

The data presented in **Error! Reference source not found.** provides the lattice stabilities for the stable crystal structures of the four elements of the Pd-Rh-Ru-U quaternary system. However, the information presented in **Error! Reference source not found.** is not sufficient for the purposes of a thermodynamic evaluation. It is also necessary to consider hypothetical lattice stabilities (*e.g.*, Pd as a *cph* or a *bcc* crystal structure) for these elements as well. Because this evaluation is to be self-consistent with the existing RNFTT, the lattice stabilities developed in Kaye *et al.* [12,13] were used here. It should be noted that there is some discrepancy between these values and those of Dinsdale [39]. The Gibbs energy expressions for the elements in each phase (real or hypothetical) are given as the energy required to transition from the particular phase into the liquid (reference) state (*i.e.*, they can be considered as expressions for the Gibbs energies of melting, regardless of the phase). The results are summarised in Table 2.

Table 2. Lattice stabilities for the components referenced to the liquid phase.

Phase	Gibbs energy ($J\ mol^{-1}$)	Comment
Pd *(liquid)*	0	Reference phase
Pd *(bcc)*	-12300 + 12.37T	Hypothetical
Pd *(cph)*	-12300 + 14.88T	Hypothetical
Pd *(fcc)*	-16480 + 9.02T	Stable
Pd *(ortho)*	-13495 + 9.04T	Hypothetical
Pd *(tetra)*	-6780 + 9.02T	Hypothetical
Rh *(liquid)*	0	Reference phase
Rh *(bcc)*	-19664 + 16.27T	Hypothetical
Rh *(cph)*	-25910 + 12.51T	Hypothetical
Rh *(fcc)*	-26568 + 11.88T	Stable
Rh *(ortho)*	1834 + 11.88T	Hypothetical
Rh *(tetra)*	-3166 + 11.88T	Hypothetical
Ru *(liquid)*	0	Reference phase
Ru *(bcc)*	-30420 + 12.51T	Hypothetical
Ru *(cph)*	-38589 + 14.80T	Stable
Ru *(fcc)*	-21019 + 8.94T	Hypothetical
Ru *(ortho)*	Solution not present	Hypothetical
Ru *(tetra)*	-19792 + 14.81T	Hypothetical
U *(liquid)*	0	Reference Phase
α-U *(ortho)*	-13252 + 11.24T	Stable < 942 K
β-U *(tetra)*	-10704 + 8.52T	942 K < stable <1049 K
γ-U *(bcc)*	-5941 + 3.98T	1049K < Stable < 1405 K
U *(fcc)*	-8252 + 11.24T	Hypothetical
U *(cph)*	-1592 + 11.24T	Hypothetical

1.2 Previous Model of the Pd-Rh-Ru Ternary System

Previous work by Kaye *et al*. [12,13], developed a model for the Pd-Rh-Ru ternary system, using the lattice parameters presented in Table 2, and the Gibbs Excess Mixing parameters given in Table 3.

Table 3. Excess Gibbs Energy of Mixing parameters for the Pd-Rh-Ru ternary [12,13].

Phase	Subsystem	Expression for the excess Gibbs energy (ΔG^E) ($J\ mol^{-1}$)
Liquid	Pd-Rh	$X_{Pd}X_{Rh}[20027 - 2260X_{Rh} - (2.74 - 0.56X_{Rh})T]$
bcc	Pd-Rh	$X_{Pd}X_{Rh}[20920]$ (hypothetical)
cph	Pd-Rh	$X_{Pd}X_{Rh}[20920]$ (hypothetical)
fcc	Pd-Rh	$X_{Pd}X_{Rh}[21247 + 2199X_{Rh} - (2.74 - 0.56X_{Rh})T]$
Liquid	Pd-Ru	$X_{Pd}X_{Ru}[187564.062 - 62169.281X_{Pd} - (63.661 - 6.64X_{Pd})T]$
bcc	Pd-Ru	$X_{Pd}X_{Ru}[20000]$ (hypothetical)
cph	Pd-Ru	$X_{Pd}X_{Ru}[-1524.818 + 14.933T]$
fcc	Pd-Ru	$X_{Pd}X_{Ru}[-5049.035 + 17.59T]$
Liquid	Rh-Ru	$X_{Rh}X_{Ru}[-35739.32 + 16.369T]$
bcc	Rh-Ru	0 (hypothetical)
cph	Rh-Ru	$X_{Rh}X_{Ru}[-26440.004 + 10.445T]$
fcc	Rh-Ru	$X_{Rh}X_{Ru}[-53477.07 + 21.738T]$
Liquid	Pd-Rh-Ru	$X_{Pd}X_{Rh}X_{Ru}(-52500)$
cph	Pd-Rh-Ru	$X_{Pd}X_{Rh}X_{Ru}(-90000)$
fcc	Pd-Rh-Ru	$X_{Pd}X_{Rh}X_{Ru}(-40000)$

As discussed in Kaye *et al*. [12,13], ternary excess terms were necessary. A representative ternary isothermal section at 1973 K for the Pd-Rh-Ru system is shown in Figure 2. Note that there is agreement between the model and the experimental data reported by Paschoal *et al*. [40].

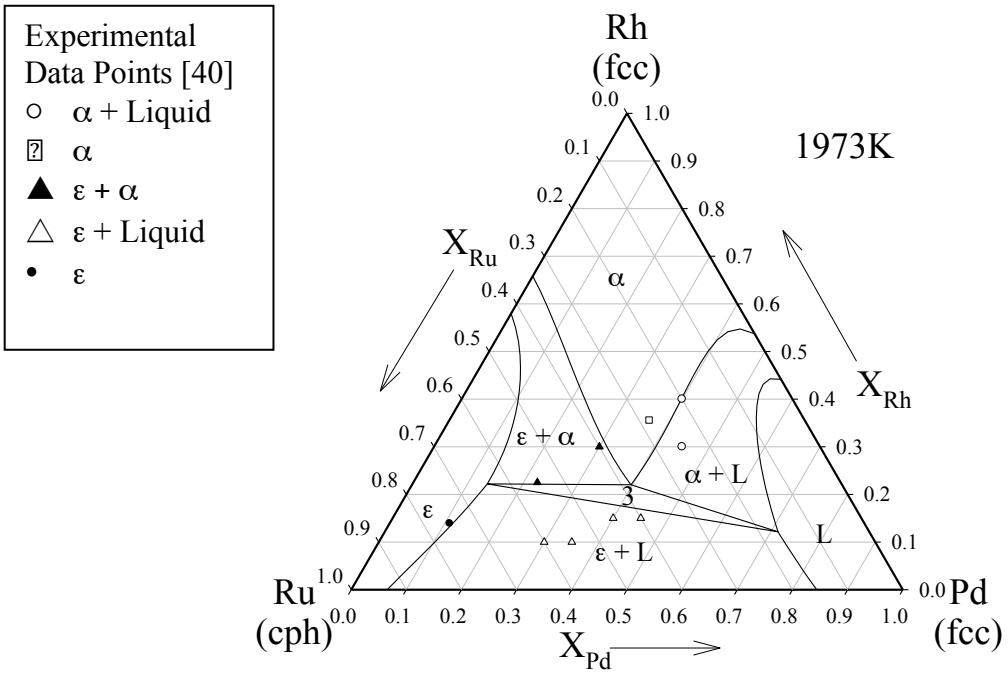

Figure 2. Pd-Rh-Ru ternary section at 1973 K as modelled by Kaye *et al*. [12,13] compared to the data of Paschoal *et al*. [40].

1.3 Expanding the Model to Include Uranium

The three binary systems that involve uranium differ from the binary systems involving only Pd, Rh, and Ru, since the Pd-U, Rh-U, and Ru-U diagrams have compounds with fairly

exact stoichiometries. The Gibbs Excess Mixing parameters for the Pd-U, Rh-U, and Ru-U binary models and the extrapolated ternary systems are presented in Table 4. These parameters can be used in conjunction with the lattice stabilities from Table 2, to develop Gibbs Energy of Mixing curves for the different solution phases. It should be noted that the compounds present in each of these binary systems have been modelled as compounds with exact stoichiometric proportions. The presence and data for each of these compounds will be presented in the sections concerning the evaluation of each specific binary system.

Table 4. The Gibbs Excess Mixing parameters for the Pd-U, Rh-U, and Ru-U systems.

Phase	Subsystem	Expression for the excess Gibbs energy (ΔG^E) ($J\ mol^{-1}$)
Liquid	Pd-U	$X_{Pd}X_U[-268000 + 165000X_U + (9.60 + 0X_U)T]$
bcc	Pd-U	$X_{Pd}X_U[-160000 + 18000X_U + (40.00 + 0X_U)T]$
cph	Pd-U	0 (hypothetical)
fcc	Pd-U	$X_{Pd}X_U[-285000 + 15200X_U - (6.00 + 0X_U)T + 3T\ln T]$
orthorhombic	Pd-U	$X_{Pd}X_U[-85000]$
tetragonal	Pd-U	$X_{Pd}X_U[-101000]$
Liquid	Rh-U	$X_{Rh}X_U[-255000 + 140000X_U + (5.00 + 0X_U)T]$
bcc	Rh-U	$X_{Rh}X_U[-168000 + 17000X_U + (38.00 + 0X_U)T]$
cph	Rh-U	0 (hypothetical)
fcc	Rh-U	$X_{Rh}X_U[-160000 + 15000X_U + (5.00 + 0X_U)T]$
orthorhombic	Rh-U	$X_{Rh}X_U[-110000]$
tetragonal	Rh-U	$X_{Rh}X_U[-114000]$
Liquid	Ru-U	$X_{Ru}X_U[-255000 + 140000X_U + (5.00 + 0X_U)T]$
bcc	Ru-U	$X_{Ru}X_U[-168500 + 38560X_U + (43.68 + 0X_U)T]$
cph	Ru-U	$X_{Ru}X_U[-100000]$
fcc	Ru-U	0 (hypothetical)
orthorhombic	Ru-U	0
tetragonal	Ru-U	$X_{Ru}X_U[-90000]$
Liquid	U-Pd-Rh	$X_UX_{Pd}X_{Rh}(-234000)$
Liquid	U-Pd-Ru	$X_UX_{Pd}X_{Ru}(-300000)$
Liquid	U-Rh-Ru	$X_UX_{Rh}X_{Ru}(-124000)$
fcc	U-Pd-Rh	$X_UX_{Pd}X_{Rh}(-223000)$

1.4 The Pd-U System

The palladium-uranium system is characterized by three solid uranium-rich solutions of limited palladium solubility on the uranium side of the diagram, a *fcc*-solid solution of reasonable uranium solubility on the palladium side, and five stoichiometric compounds in between. This evaluation accepts the presence of the following compounds: UPd, U_5Pd_6, UPd_3, UPd_4, and UPd_8. The evaluated thermodynamic properties for these compounds are given in Table 5. Note that the heat capacity for UPd_3 is valid up to its congruent melting temperature of 1973 K.

Table 5. Thermodynamic properties of palladium-uranium compounds.

	$\Delta H^\circ_{298.15\,K}$	$S^\circ_{298.15\,K}$	$c_p = a + bT + cT^{-2} + dT^2$ ($J\cdot mol^{-1}\cdot K^{-1}$)			
Compound	($J\cdot mol^{-1}$)	($J\cdot mol^{-1}\cdot K^{-1}$)	***a***	***b x 10³***	***c***	***d x 10⁶***
UPd	-165,500	39.45	52.13	-16.75	-414510	38.08
U_5Pd_6	-1,110,000	85.00	327.86	-97.97	-2409924	201.90
UPd_3	-210,500	176.35	98.69	11.41	0	0

UPd_4	-236,200	192.50	155.76	-59.47	-1426632	72.66
UPd_8	-407,700	200.00	284.61	-11.64	-2776128	118.74

Combining the compound data presented in Table 5, the lattice stability data from Table 2, and the excess Gibbs energy data for the various solution phases from Table 4, an evaluation of the Pd-U phase diagram can be determined, as shown in Figure 3.

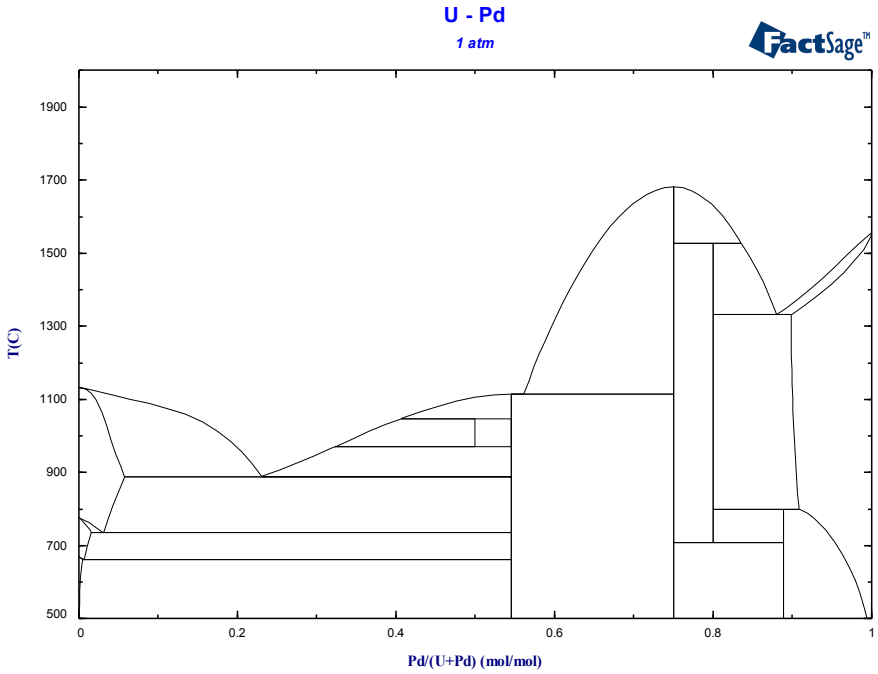

Figure 3. The evaluated phase diagram for Pd-U.

1.5 The Rh-U System

The rhodium-uranium system is also characterized by three solid uranium-rich solutions of limited rhodium solubility on the uranium side of the diagram, a *fcc*-solid solution of limited uranium solubility on the rhodium side, and four stoichiometric compounds in between. This evaluation accepts the presence of the following compounds: U_4Rh_3, U_3Rh_4, U_3Rh_5, and URh_3. Of these compounds, U_4Rh_3 has two isotropic forms: the low temperature form, α-U_4Rh_3 ($T < 993$ K); and the higher temperature form, β-U_4Rh_3 ($993 \text{ K} < T < 1428$ K). It should also be noted that the heat capacity data for U_3Rh_4, U_3Rh_5, and URh_3 are valid up to either their congruent melting points (*i.e.*, 1823 K for U_3Rh_5 and 2013 K for URh_3) or the peritectic reaction (*i.e.*, 1723 K for U_3Rh_4). The evaluated thermodynamic properties for these compounds are given in Table 6.

Table 6. Thermodynamic properties of rhodium-uranium compounds.

	$\Delta H^{\circ}_{298.15\,K}$	$S^{\circ}_{298.15\,K}$	$c_p = a + bT + cT^{-2} + dT^2$ *(J·mol^{-1}·K^{-1})*			
Compound	*(J·mol^{-1})*	*(J·mol^{-1}·K^{-1})*	***a***	***b x 10^3***	***c***	***d x 10^6***
α-U_4Rh_3	-442,740	190.75	252.80	-67.99	-643620	109.25
β-U_4Rh_3	-442,740	190.69	252.80	-67.99	-643620	109.25
U_3Rh_4	-461,180	196.10	274.26	-84.82	-678176	83.70
U_3Rh_5	-508,540	226.60	322.64	-104.14	-789868	84.71
URh_3	-194,000	153.40	104.45	18.21	-610033	0

An evaluation of the Rh-U phase diagram, shown in Figure 4, was made by combining the compound data from Table 6, the lattice stability data from Table 2, and the excess Gibbs energy data for the solution phases from Table 4.

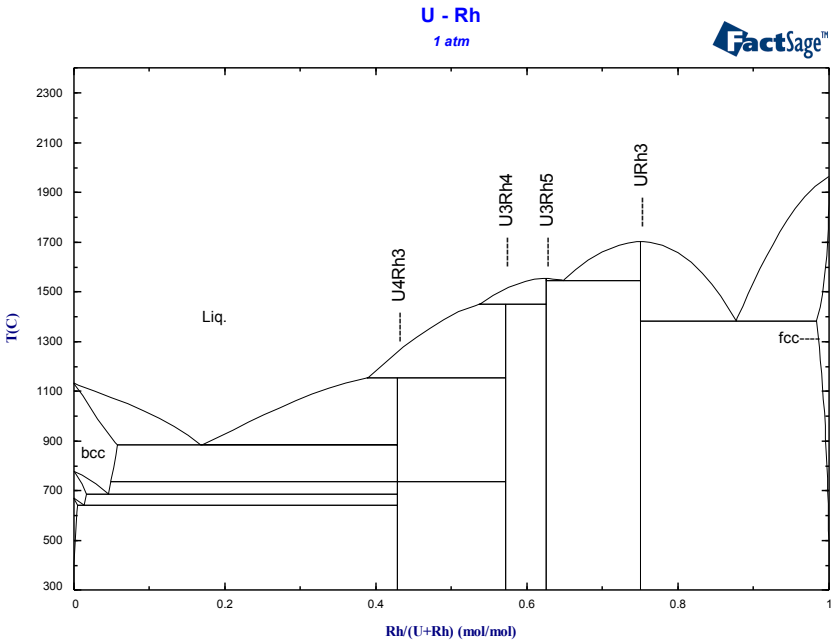

Figure 4. The evaluated phase diagram for Rh-U.

1.6 The Ru-U System

The ruthenium-uranium system is characterized by two solid uranium-rich solutions of limited ruthenium solubility on the uranium side of the diagram (in contrast to the Pd-U and Rh-U systems there is not an orthorhombic solution phase since at low temperatures there is negligible solubility of Ru in α-U), a fcc-solid solution of limited uranium solubility on the ruthenium side, and five stoichiometric compounds in between. This evaluation accepts the presence of the following compounds: U_2Ru, URu, U_3Ru_4, U_3Ru_5, and URu_3. Of these compounds, URu has two isotropic forms: the low temperature form, α-URu (T < 1060 K); and the higher temperature form, β-URu (1060 K < T < 1414 K). The thermodynamic properties for these compounds are given in Table 7.

Table 7. Thermodynamic properties of ruthenium-uranium compounds.

	$\Delta H^{\circ}_{298.15\,K}$	$S^{\circ}_{298.15\,K}$	$c_p = a + bT + cT^{-2} + dT^2$ $(J{\cdot}mol^{-1}{\cdot}K^{-1})$			
Compound	$(J{\cdot}mol^{-1})$	$(J{\cdot}mol^{-1}{\cdot}K^{-1})$	***a***	***b x 10³***	***c***	***d x 10⁶***
U_2Ru	-123,770	103.40	76.75	3.12	-267026	52.05
α-URu (low)	-597,660	25.16	25.00	2.60	-94233	13.32
β-URu (high)	-597,700	25.16	25.00	2.60	-94233	13.32
U_3Ru_4	-375,880	196.30	172.41	24.99	-682424	75.44
U_3Ru_5	-389,220	241.90	195.33	33.12	-795178	74.38
URu_3	-144,700	145.30	101.22	18.46	-471814	0

An evaluation of the Ru-U phase diagram, shown in Figure 5, was made by combining the compound data from Table 7, the lattice stability data from Table 2, and the excess Gibbs energy data for the solution phases from Table 4.

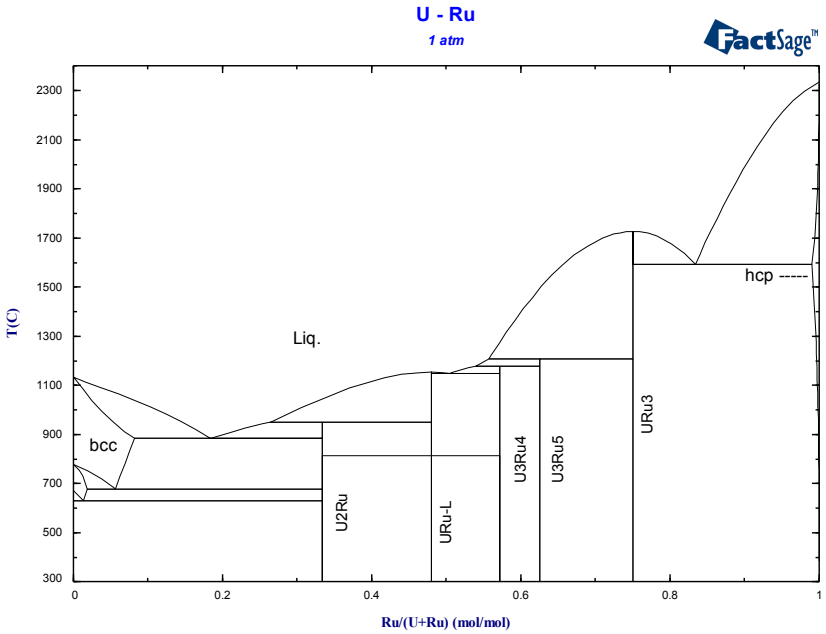

Figure 5. The evaluated phase diagram for Rh-U.

1.7 Ternary Sections in the Quaternary

While it is difficult to depict a three dimensional model on a two dimensional surface, and thus accurately illustrate the four component (*i.e.*, Pd-Rh-Ru-U system), ternary sections at various temperatures can be computed and easily displayed.

Figure 6 shows a calculated Pd-Rh-U ternary isothermal section (T = 1050 ºC). The regions in the interior of the diagram are labelled 1 through 20, and their constituents are given in Table 8.

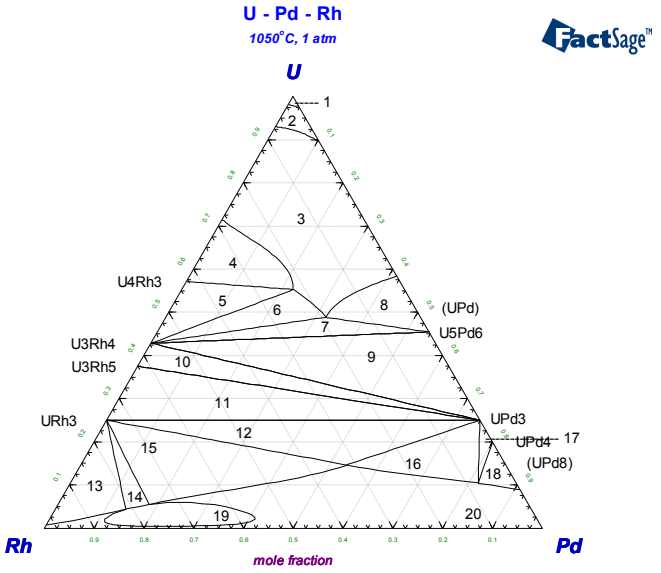

Figure 6. The evaluated ternary phase diagram for Pd-Rh-U at 1050 ºC.

Table 8. The region numbers and corresponding phases shown in Figure 6 (and Figure 11).

Region Number	Phase(s) present	Region Number	Phase(s) present
1	bcc	11	$U_3Rh_5 + URh_3 + UPd_3$
2	*bcc* + liquid	12	$URh_3 + UPd_3$ + fcc
3	liquid	13	URh_3 + *fcc*
4	U_4Rh_3 + liquid	14	URh_3 + *fcc* + *fcc*#2
5	$U_4Rh_3 + U_3Rh_4$ + liquid	15	URh_3 + *fcc*
6	U_3Rh_4 + liquid	16	UPd_3 + *fcc*
7	$U_3Rh_4 + U_5Pd_6$ + liquid	17	$UPd_3 + UPd_4$ + *fcc*
8	U_5Pd_6 + liquid	18	UPd_4 + *fcc*
9	$U_5Pd_6 + U_3Rh_4 + UPd_3$	19	fcc + fcc#2
10	$U_3Rh_4 + U_3Rh_5 + UPd_3$	20	fcc

A second ternary isothermal section at 1400 ºC is shown in Figure 7. In this case the diagram illustrates a very specific plane in the Pd-Rh-Ru-U quaternary system, where the ratio of fission products to uranium is 3:1.

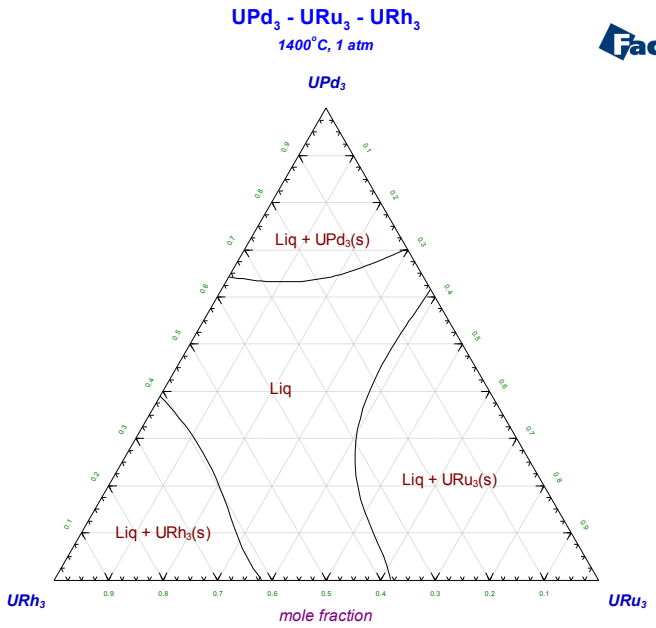

Figure 7. The evaluated ternary phase diagram for UPd_3-URh_3-URu_3 at 1400 ºC.

2. Discussion

In this section, each binary evaluation involving uranium, as presented above, will be compared to available experimental data. Note that in many instances, the experimental data are not in agreement, thus necessitating a choice to prefer one set of data over another.

2.1 Pd-U

A comparison of the evaluated phase diagram from this work for the Pd-U system, with experimental data from others [14,16-18] is presented in Figure 8. It can be seen that two regions of the calculated diagram differ from the experimental data, namely the placement of the eutectic temperature and composition on the uranium rich side of the diagram (*i.e.*, at $X_{Pd} \approx 0.24$) and the placement of the liquidus and maximum solubility of uranium in the *fcc* solid phase on the palladium rich side of the diagram (*i.e.*, at $X_{Pd} > 0.75$).

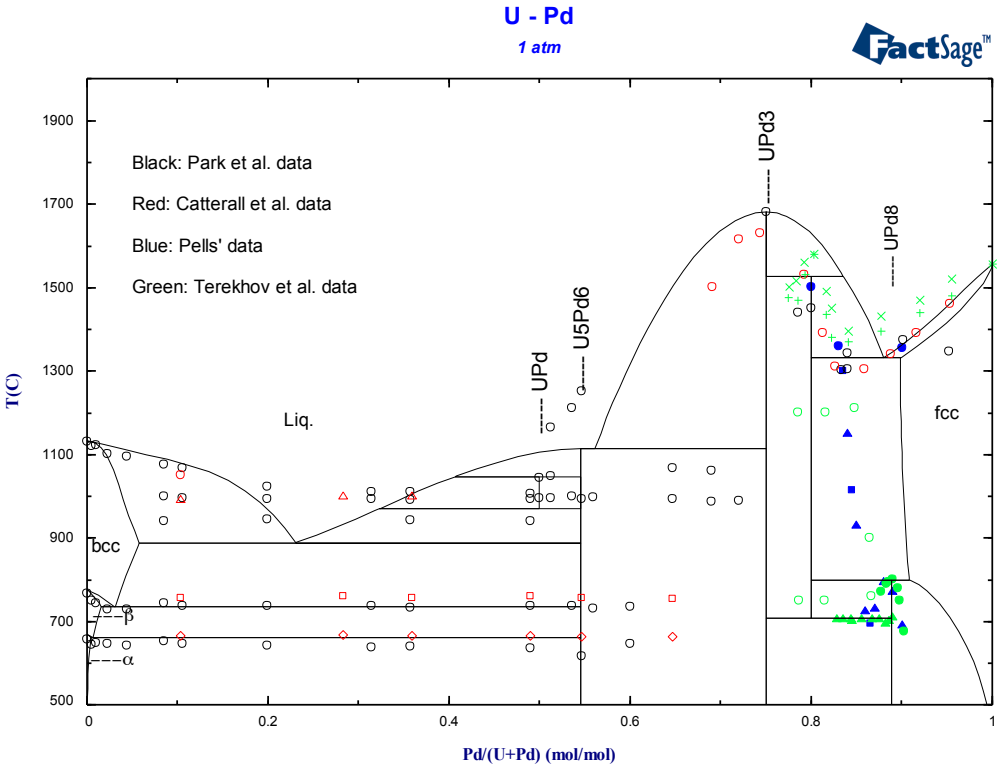

Figure 8. Comparison of experimental data [14,16-18], with the current evaluation of the Pd-U binary system.

On the palladium side of the diagram it is impossible to reconcile the conflicting data, without making choices as to whom to find more credible. For example in the work of Catterall *et al*. [14], it is suggested that single phase alloys exist from 78 at.% Pd upwards. However, they also do not detect the existence of UPd_4 or UPd_8, which were detected by Pells [17] and confirmed by Terekhov *et al*. [18].

Part of the difficulty in this region of the diagram also involves what happens at the higher temperatures. Park *et al*. [16] suggested that UPd_4 is formed in a peritectic reaction from UPd_3 and the liquid. They also suggested that the solubility of uranium in palladium was about 11 at.%, and they did not detect UPd_8 (although in fairness, they may not have looked for the compound). Kleykamp and Kang [19] suggested a congruent melting reaction for UPd_4, and a greater solubility of uranium in palladium. Their diagram was published in the *Journal of Phase Equilibria* [41]. However, Okamoto noted that there were concerns around the liquidus at UPd_3 (too symmetrical), that the shape of the *Liquid + fcc* two phase region would not extrapolate well to the opposite side of the diagram, and that compounds such as UPd_8 are rare. The current evaluation does extrapolate well to the opposite side of the diagram, keeps the original peritectic reaction as the formation of UPd_4, and accepts the existence of UPd_8.

The second problematic region in terms of reconciling the data, centres on the eutectic reaction on the uranium rich side of the diagram. The various liquidus data from Park [16] and Catterall *et al*. [14] suggest a temperature for the eutectic about 110 ºC higher than the temperature proposed here. Part of the difficulty is that there is a lack of consensus for the eutectic composition. Catterall *et al*. [14] place the eutectic reaction at 37.4 at.% Pd, while Park

and Buzzard [15] and Park *et al*. [16] give the eutectic at 25.0 at.% and 23.5 at.%, respectively. Further, in the diagram proposed by Kleykamp and Kang [19], the shape of the liquidus seems improbable.

In this evaluation a lower eutectic temperature has been proposed. The various experiments are known to have been conducted using beryllium oxide crucibles and the compound UBe_{13} should form in these situations, especially in the presence of Pd acting as a catalyst. If this were the case, the reported temperature values would be inflated.

2.2 Rh-U

A comparison of the evaluated phase diagram from this work for the Rh-U system, with experimental data from others [20,21] is presented in Figure 9.

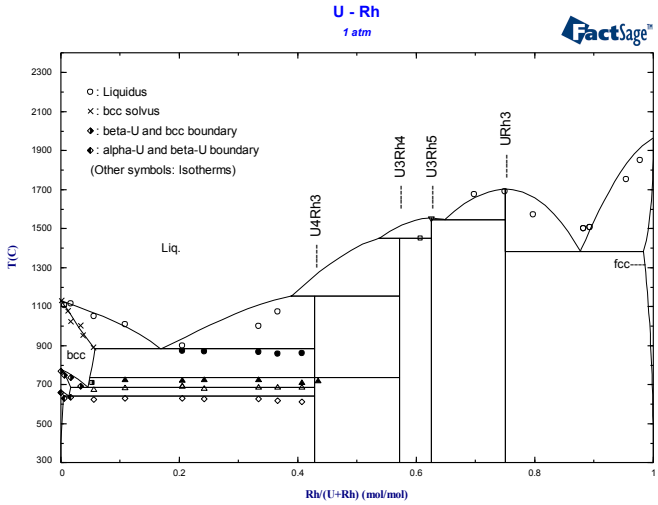

Figure 9. Comparison of experimental data from the work of Park [20,21], with the current evaluation of the Rh-U binary system.

In the work of Chiswik *et al*. [22] and Naraine and Bell [23], the compound U_2Rh is proposed. While the presence of this compound might make the diagram look more like the Ru-U diagram (since U_2Ru exists), this would mean that experimental work by Park would be in error. This paper rejects the formation of U_2Rh.

In resolving the eutectic temperature and composition on the uranium-rich side of the diagram, this evaluation believes that the liquidus point reported to be just above 20 at.% Rh, is on the right side of the eutectic composition and not the left as suggested by Park [20,21]. The point in question was derived from metallographic examination and is open to interpretation. Further the eutectic composition proposed in this evaluation is in keeping with that given by Chiswik *et al*. [22].

2.3 Ru-U

A comparison of the evaluated phase diagram from this work for the Rh-U system, with experimental data from others [20,21] is presented in Figure 10.

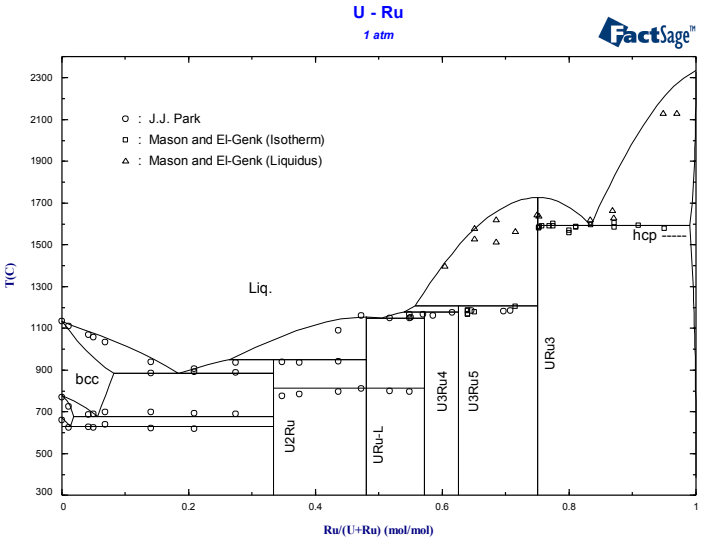

Figure 10. Comparison of experimental data from Park [20,21]and Mason and El-Genk [25], with the current evaluation of the Ru-U binary system.

It is important to note that this evaluation differs from the evaluation of Berche *et al*. [38] in that it treats Ru as a closed-packed hexagonal solid capable of dissolving some uranium (in other words there is a closed-packed hexagonal solution present).

2.4 The Pd-Rh-U Ternary Section at 1050 ºC

The evaluated phase diagram from this work for the Pd-Rh-U ternary system at 1050 ºC is compared with experimental data from Kleykamp and Kang [19] in Figure 11.

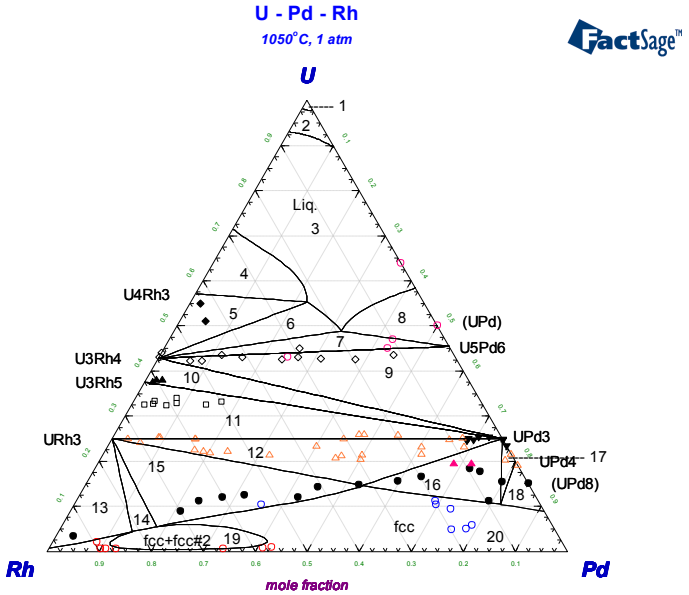

Figure 11. Comparison of experimental data from Kleykamp and Kang [19] at 1050 ºC with the evaluated diagram. The labelling of the phase regions was given in Table 8.

Figure 11 suggests that there is more than reasonable agreement between the proposed thermodynamic model and the limited experimental data available from the literature.

3. Impact on the RMC Nuclear Fuel Thermochemical Treatment

The full implications of this new treatment of the Pd-Rh-Ru-U quaternary system have yet to be explored in the Nuclear Fuel Thermochemical Treatment developed at the Royal Military College of Canada. However, it is important to note that the current treatment (*i.e.*, treating UPd_3-URh_3-URu_3 as an ideal solution) is only a first approximation. Thus implementation of these models into the RNFTT will provide a more realistic representation of the behaviour of these three fission products (*i.e.*, Pd, Rh, and Ru) as they interact with the rest of the fuel.

4. Conclusions

The proposed thermodynamic model for the Pd-Rh-Ru-U quaternary system represents a thorough examination of available experimental data for the binary sub-systems, the ternary sub-systems, and compounds. Resolutions of conflicting data have been made such that where there is a contradiction, a reasonable compromise has been selected. Rationale has also been given as to the underlying reasons for these choices. Finally, the authors believe that when implemented into the RMC Nuclear Fuel Thermochemical Treatment, the proposed model will generate an improvement in the fidelity of the RNFTT.

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