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U-Ru-Rh-Pd QUATERNARY SYSTEM: THERMODYNAMIC CALCULATIONS AND EXPERIMENTAL EXPLORATIONS

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Abstract

Fission products (FPs) in burned up nuclear fuels form a very complex system. In simulating the behavior of the FPs, multicomponent phase equilibrium data are needed in some thermodynamic and dynamic codes used in nuclear industry. Typically,an inclusion consisting of URu_3, URh_3 and UPd_3 were found in post irradiation examinations and it was called “the other intermetallic inclusion” to distinguish with the “white inclusion”, which is consisted of Mo, Ru, Rh, Pd and Tc. A few attempts in obtaining important isothermal sections involving these compounds were conducted experimentally during the 1990s, nonetheless, no further justification were conducted. In this work, by means of establishing the quaternary thermodynamic model, the validation of these experimental results becomes feasible. The paper is an introduction to the calculated URu_3-URh_3-UPd_3 quasi-phase diagram, U-Rh-Pd isothermal section and a comparison of them with their experimental counterparts. The results show that the model can predict phase equilibria at conditions that no experimental data are available and can identify some experimental fallacies.

1 Introduction

Nuclear energy is considered one of the cleanest energy forms. While CO_2 emission is minimized in the process, fission products are generated as the fissile nuclides split and radioactive fission products decay. The fission products are present in different phases depending on the fuel used, operation temperature, and heat transformation configurations, including gases, liquids, and solids.This change in fuel chemistry may change the volume or the shape of the fuel pellets andheat transfer efficiency that are crucial to operating conditions. Over time, serious deformation, corrosion,or even breach of claddings may occur and the consequences can be fatal. The existence of minor actinides and other radioactive components in the used fuel make the waste disposal very complicated. Solid fission products in UO_2 fuel contribute to deformation of the fuel pellets, including swelling and/or sagging of the pellets caused by heterogeneous change of physical properties in different locations. As a result, the “bambooing” and “hourglassing” of the pellets may exert stress and/or strain to zirconium cladding, which may lead to its breach [1].

Since the 1940s, many phase diagrams involving uranium have been constructed, first for the needs in developing nuclear weapons and after the war for the peaceful harnessing of nuclear fission for energy production. Because the process involves radioactive elements and many transitional elements, which are sometimes referred to as noble metals or even refractory metals, the processes are usually costly, time consuming and with risk of irradiation.

In investigating the behaviors of fission products, phase diagrams of related elements are helpful. For this purpose, however, the experimental phase diagrams have to be evaluated and described thermodynamically and a multicomponent model has to be established. For many systems, high

temperature measurements become one of the obstacles in precisely determining the liquidus of the refractory element-rich part of the diagram. For instance, the elevated melting point of Ru is 2334 °C(2607K). Thus for determining the Ru-rich liquidus in an alloy system involving Ru (*e.g.*, Ru–U), finding suitable metals or alloys to make a perfect thermocouple becomes a challenge in itself. Pyrometers, often a good alternative for these purposes, can also be problematic. For example, in their work on the Ru-U system, Mason and El-Genk had to use their eyes (the so-called"spot method") as the instrument failed to judge the liquidus boundary automatically [2]. Finally, in any determination, a container for samples is needed. For some refractory elements, it is difficult to eliminate the possibility of reactions of constituents in the sample with a crucible (in other words the crucible becomes part of a more complicated system). All these factors have led to discrepancies of experimental data from different authors and deteriorated the credibility of "experimental data".

Studies of the U-Ru-Rh-Pd quaternary system exhibit all these problems, and it should be noted that this is especially true of the U-Pd system. Another possible reason for the complexity of these systems is that all the platinum metals are effective catalysts for various processes, and Pd is the best candidate for nanoparticle catalysts [3]. Nonetheless, it is at such circumstances the importance of thermodynamic evaluation reveals.

2 Thermodynamic principles

The core of computational thermodynamics is the principle of Gibbs energy minimization, *i.e.*, at constant pressure and temperature a system drives toward a configuration at which it is at the lowest Gibbs energy (*G*) at equilibrium:

$$G^{\varphi} = \sum_{i=1}^{k} n_i G_i^{\varphi} = minimum \quad (1)$$

In the above equation, φ stands for a specific phase; *n* represents the number of moles; i represents a constituent in the phase, and *k*represents the total number of constituents in the phase. The principle is used in determining a phase boundary or an invariant equilibrium point in a phase diagram.

The molar Gibbs energy, G, of a solution can be expressed as:

$$G = G^{ideal} + G^{Excess} \quad (2)$$

where G^{ideal} represents the molar Gibbs energy that the solution would have if it were ideal, and G^{Excess} represents the excess Gibbs energy or in other words the difference between ideal behavior and actual behavior.

The G^{ideal}term can be split into two parts as shown in Equation 3 (taking an A-B binary system as an example) for a binary system.

$$G = \left(X_A G_A^{\circ} + X_B G_B^{\circ}\right) + \Delta G^{M,ideal} + G^{Excess} \quad (3)$$

where X_A and X_B represent the mole fractions of A and B (note $X_A + X_B = 1$), G_A° and $G_B^{\circ}$the Gibbs energy of components A and B, respectively,and$\Delta G^{M,ideal}$ represents the ideal Gibbs energy of mixing of A and B.

$\Delta G^{M,ideal}$, the ideal Gibbs energy of mixing, can be represented as a function of the mole fractions of A and B, multiplied by the gas constant *R* and *T*, the temperature, as shown in Equation 4.

$$G = \left(X_A G_A^\circ + X_B G_B^\circ\right) + RT(X_A lnX_A + X_B lnX_B) + G^{Excess} \quad (4)$$

The CALPHAD method use empirical expressions of thermodynamic properties, such as Gibbs energy, enthalpy, entropy, and heat capacity of the constituents or a collection of them. The equations used in this research are the same as those used by Berche *et al*. [4], but the Margules Power Series Formalism[5] is preferred instead of the Redlich-Kister Expansion[6] to describe the excess properties. For ternary systems, Kohler/Toop formalism is used in FactSage.

3 Results

The establishment of U-Ru-Rh-Pd quaternary system involves six subsystems: Pd-Rh, Pd-Ru, Rh-Ru, U-Pd, U-Rh, and U-Ru, in which thermodynamic models of Pd-Rh, Pd-Ru and Rh-Ru systems had been given by Kaye, Lewis and Thompson [7, 8]and U-Ru system had been thermodynamically described by Berche *et al*. in 2011[4].

Basic thermodynamic data for the elements Ru, Rh, Pd, and U have been well described in the literature and those related to this work are listed in Table 1.

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

Element	ΔH_{298}°	S_{298}°	$C_P = a + bT + cT^{-2} + dT^2$ $(J/mol \cdot K)$				T_{min}	T_{max}
	(*J/mol*)	**(*J/mol·K*)**	***a***	***b* x 10^3**	***c***	***d* x 10^6**	**(*K*)**	**(*K*)**
U-α	0	50.29	26.919	-2.5020	-76985	0.26558	298	942
U-β	2790.73	53.25	26.919	-2.5020	-76985	0.26558	942	1049
U-γ	3231.08	47.97	42.928	0	0	0	1049	1405
U-liq.	4375.22	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	46.84	25.028	5.4404	-67548	0	298	3000
Rh-fcc	0	31.51	20.811	13.400	33942	-2.2679	298	3000
Rh-liq.	26568	43.39	20.811	13.400	33942	-2.2679	298	3000
Ru-cph	0	28.53	22.236	4.1437	40607	1.6015	298	3000
Ru-liq.	38589	43.34	22.236	4.1437	40607	1.6015	298	3000

By establishing related compound databases and solution databases and optimization, the used thermodynamic properties and optimized unknown parameters are listed below:

3.1 **Thermodynamic properties (U-Ru binary system)**

The results and discussions on this system was published in the proceedings of CNS2015 [9] and therefore, omitted in this paper.

3.2 **Thermodynamic properties (U-Rh binary system)**

Table 2Lattice stability and referencing

Phase	U			Rh		
	ΔH_{298}° (J/mol)	S_{298}° (J/mol·K)	G(Added) (J/mol)	ΔH_{298}° (J/mol)	S_{298}° (J/mol·K)	G(Added) (J/mol)
Liquid	4375.22	44.24	0	26568	43.39	0
γ (bcc)	3231.08	47.98	0	6904	27.12	0
β (tetragonal_U)	2790.73	53.25	0	0	31.51	23400
α (orthorhombic_A20)	0	50.29	0	0	31.51	28400
Fcc	0	50.29	5000	0	31.51	0

Table 3Interaction parameters of solution phases

System	Excess Gibbs energy functions in Margules formalism (J/mol)	Reference
Liquid	$\Delta G_{Liquid}^{E} = X_{Rh}X_{U}[(-255000 + 5.00T) + 140000X_{U}]$	This work
bcc (γ-U)	$\Delta G_{bcc}^{E} = X_{Ru}X_{U}[(-168500 + 43.68T) + 38560X_{U}]$	This work
Tetragonal (β-U)	$\Delta G_{\beta-U}^{E} = X_{Rh}X_{U}[-114000]$ $(hypothetical)$	This work
Orthorhombic (α-U)	$\Delta G_{\alpha-U}^{E} = X_{Rh}X_{U}[-110000]$	This work
fcc	$\Delta G_{hcp}^{E} = X_{Rh}X_{U}[(-160000 + 5.00T) + 15000X_{U}]$ $(hypothetical)$	This work

Table 4Gibbs energy expressions of compounds

Compound	Gibbs energy expression (J/mol)
URh_3	$G^{URh_3} = -228000 + 555.00T - 104.445T\ln T - 0.00910274T^2 + 305016.5T^{-1}$
U_3Rh_4	$G^{U_3Rh_4} - 3G_U^{\alpha-U} - 4G_{Rh}^{fcc} = -485581 + 702.05T$
U_3Rh_5	$G^{U_3Rh_5} - 3G_U^{\alpha-U} - 5G_{Rh}^{fcc} = -539033 + 858.53T$
U_4Rh_3-L	$G^{U4Rh3-L} - 4G_U^{\alpha-U} - 3G_{Rh}^{fcc} = -461330 + 569.68T$
U_4Rh_3-H	$G^{U4Rh3-H} - G^{U4Rh3-L} = -557.763 - 1.12T$

3.3 **Thermodynamic properties (U-Pd binary system)**

Table 5Lattice stability and referencing

Phase	U			Pd		
	ΔH_{298}° (J/mol)	S_{298}° (J/mol·K)	G(Added) (J/mol)	ΔH_{298}° (J/mol)	S_{298}° (J/mol·K)	G(Added) (J/mol)
Liquid	4375.22	44.24	0	16480	46.84	0
γ (bcc)	3231.08	47.98	0	4180	34.47	0
β (tetragonal_U)	2790.73	53.25	0	0	37.82	5000
α (orthorhombic_A20)	0	50.29	0	0	37.82	3000
Fcc	0	50.29	5000	0	37.82	0

Table 6Interaction parameters of solution phases

System	Excess Gibbs energy functions in Margules formalism (J/mol)	Reference
Liquid	$\Delta G^{E}_{Liquid} = X_{Pd}X_{U}[(-268000 + 9.60T) + 165000X_{U}]$	This work
bcc (γ-U)	$\Delta G^{E}_{bcc} = X_{Pd}X_{U}[(-160000 + 40.00T) + 18000X_{U}]$	This work
Tetragonal (β-U)	$\Delta G^{E}_{\beta-U} = X_{Pd}X_{U}[-101000]\ (hypothetical)$	This work
Orthorhombic (α-U)	$\Delta G^{E}_{\alpha-U} = X_{Pd}X_{U}[-85000]$	This work
fcc	$\Delta G^{E}_{hcp} = X_{Pd}X_{U}[(-285000 + 6.00T + 3.00T\ln T) + 15200X_{U}]\ (hypothetical)$	This work

Table 7Gibbs energy expressions of compounds

Compound	Gibbs energy expression (J/mol)
UPd_3	$G^{UPd_3} = -240430.96 + 488.02T - 98.69T\ln T - 0.00923014T^2$
UPd	$G^{UPd} - G^{\alpha-U}_{U} - G^{fcc}_{Pd} = -165500 + 48.57T$
UPd_4	$G^{UPd_4} - G^{\alpha-U}_{U} - 4G^{fcc}_{Pd} = -236200 + 9.50T$
UPd_8	$G^{UPd_8} - 8G^{fcc}_{Pd} = -407700 + 152.78T$
U_5Pd_6	$G^{U_5Pd_6} - 5G^{\alpha-U}_{U} - 6G^{fcc}_{Pd} = -1110000 + 392.94T$

3.4 **Ternary system thermodynamic properties**

Table 8Ternary interaction parameters

Phase	**Interaction**	**i***	**j**	**k**	**A**	**B**	**Reference**
Liquid	Pd Ru Rh	1	1	1	-525000	0	[7]
	U Rh Pd	1	1	1	-234000	0	This work
	U Rh Ru	1	1	1	-124000	0	This work
	U Ru Pd	1	1	1	-300000	0	This work
fcc	Pd Ru Rh	1	1	1	-40000	0	[7]
	U Rh Pd	1	1	1	-223000	0	This work
cph	Pd Ru Rh	1	1	1	-90000	0	[7]

*i, j, and k are index of the interaction constituents used in the excess Gibbs energy expression

4 Discussion

4.1 **U-Ru binary system**

As mentioned above, the discussion on this system can be found in [9].

4.2 **U-Rh binary system**

4.2.1 A Summary of PreviousStudies

Park presented the U-Rh system phase diagram simultaneously in his PhD thesis with the U-Ru binary system and later published two separate papers in 1968 [10, 11]. This phase diagram subjects to no change to date, although there is inconsistence and disagreement about the existence of some of the compounds. For example, Chiswik *et al*. [12]indicated in 1958 that instead of U_4Rh_3, there are two additional compounds at about 33.3 at % Rh and 50 at % Rh (U_2Rh and URh, respectively). In 1974, based on work by Chiswik *et al.*, Naraine and Bell [13] re-examined the compounds by the electron probe micro-analysis and concluded that there are five compounds (instead of the four shown by Park) in the system, namely: URh_3, U_3Rh_5, URh_4, URh, and U_2Rh. If this is true, the U-Rh phase diagram will be more similar to that of U-Ru phase diagram. Nevertheless, because they did not measure the phase transition temperatures of the compounds, no changeswere made on the phase diagram. The thermodynamic model for this system does not support this configuration.

4.2.2 Discussion

In contrast to U-Ru system in which different experimental approaches had been carried out on the Ru-rich side and high temperature part of the phase diagram, disputes are focused on the U-rich side of the U-Rh phase diagram. These different results need to be judged by a thermodynamic evaluation or somefurther experimental explorations to eliminate discrepancies shown inTable 9:

Table 9 Main discrepancies in U-Rh binary system.

Author(s)	**Eutectic composition (at%)**	**U-rich side compounds**	**Year**	**Reference**
Chiswik *et al*.	~18	U_2Rh + URh	1958	[11]
Park	24.5	α-U_4Rh_3 + β-U_4Rh_3	1965	[11]
Naraine and Bell	--	U_2Rh + URh	1974	[13]
Kaye and Wang	17.5	α-U_4Rh_3 + β-U_4Rh_3	2014	This work

The lattice parameters, referencing, interaction parameters for solution phases and Gibbs energy expressions of compounds are listed in section3.2. The calculated U-Rh phase diagram with metastable extrapolation curves is shown inFigure 1.

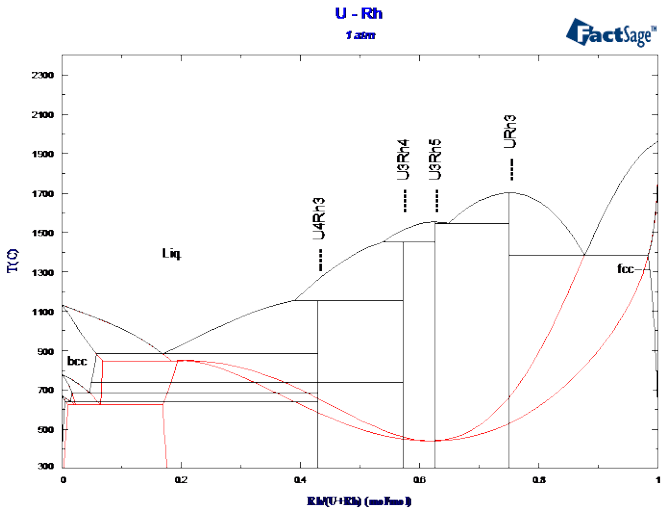

Figure 1Calculated U-Rh phase diagram with four compounds

The phase diagram from Park [11]is taken as the blueprint of this model. However, thermodynamic calculations indicate that it is impossible to set the U-rich eutectic composition to 24.5 at% in this assessment. The calculated value is 17.5 at% Rh, which is very close to the value given in [11]. The difference between these two values is caused by an incorrect interpretation of a datum close to the eutectic composition, which will be elaborated hereafter. Figure 2is a comparison with data of Park.

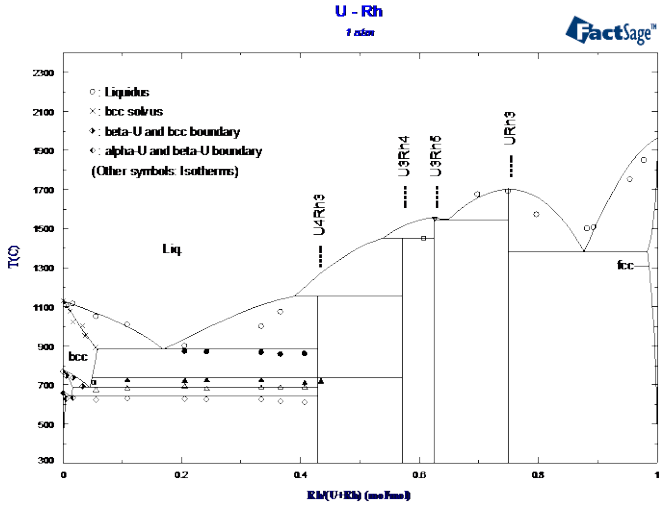

Figure 2 A comparison of calculated curves with experimental data of Park

In the thesis and papers by Park, the point (20.5 at% Rh, 897 ˚C) is listed together withall the other "fusion" (liquidus) points obtained by thermal analysis. This treatment led to a concave liquidus that seems thermodynamically improbable under the constrains of present lattice stabilities because to obtain such a liquidus the interaction parameters must be much less negative or even positive and relations to neighboring phases will be changed greatly. In addition, the thermodynamic properties, *e.g.*, enthalpy of formation and entropy of the compounds will not be comparable to the experimental data and the interaction parameters of liquid, bcc, and fcc solution phases will be completely incomparable with those of U-Ru and U-Pd systems. Practically, for this important

point, effective phase identification experiments should be carried out to decide which side of the eutectic point it should be attributed. Unfortunately, these kinds of evidence was missing in both the thesis and the paper. According to experimental assessments of U-Pd system, there may be intrinsic difficulties in phase identification in the U-rich region as well because of contamination problems, *i.e.*, the presence of unexpected compounds. Based on the thermodynamic evaluation, the eutectic composition should not be as high as 24.5 at% because this unreasonable value was probably caused by wrongly putting the disputed point (20.5 at% Rh, 897 °C) on the left side of the eutectic point on their phase diagram, whereas this point should be actually on the right side of the eutectic point. As a result, the disputed point had shifted the eutectic point far to the Rh-rich side (+7 at% Rh). This overestimated eutectic point, in turn, misled the determination of U-rich side eutectic point on the experimental U-Pd phase diagrams that will be discussed later.

Regarding the different configuration of the compounds in this system, the five-compound configuration by Naraine and Bell[13], a thermodynamic evaluation is carried out which proved that this configuration is not thermodynamically reasonable. Therefore, the five-compound configuration has been rejected in this work.

4.3 **U-Pd binary system**

4.3.1 A Summary of Previous Studies

In 1956 the first U-Pd phase diagram with whole composition range was proposed by Catterall *et al.*[14] but with great uncertainty from 75 to 100 at% Pd. In addition, the eutectic composition in U-rich part is up to 37.4 at% Pd (21 wt% Pd). In the same year, Park and Buzzard presented a report [15] at a Metallurgy Information Meeting sponsored by the United States Atomic Energy Commission, in which the progress in developing phase diagrams of uranium with all six platinum elements (Ru, Rh, Pd, Os, Ir, and Pt) were included, of which the diagram for U-Pd has distinctive features:The bcc eutectic composition is much lower than the one detected by Catterall *et al.* (13.7 wt% Pd[15]< 21 wt% Pd[14]); the two compounds detected by Catterall *et al.* was not detected at all within 30-35 wt% Pd and only a few features on the right part of the phase diagram were mentioned in the report; no solid phase boundaries were shown above 75 at% Pd.In 1963, Park, Fickle, and Mullen submitted a complete report concerning their research on the U-Pd system without publishing it [16]. For this reason, the research had been omitted thereafter.The compounds and liquidus within 75 to 100 at % Pd were experimentally investigated by Pells [17] in 1963. In this partial phase diagram, the following compounds are specified: UPd_3, UPd_4, UPd_5, U_2Pd_{11}, and U_2Pd_{17}. In 1968, a group of Soviet scientists re-examined this part of the phase diagram [18]. They denied the existence of U_2Pd_{11} and U_2Pd_{17},and declared the existence of UPd_8. By the same experimental methods, they obtained a very neatly shaped phase diagram, especially at high temperature range. Comparing with other author's efforts and results, the very small experimental errors seem to be a miracle. In 1986, a tentative phase diagram was obtained by combining U-rich part of the phase diagram from Catterall *et al.*[14]and the Pd-rich part of the phase diagram from Pells [17]and published in the ASM Handbook [19].In 1991, Kleykamp and Kang [20] rechecked experimentally on a few locations and combined the U-rich part of Catterall *et al.*[14]and the Pd-rich part of Terekhov *et al.*[18]diagrams into the extensively accepted U-Pd phase diagram.

When this phase diagram was compiled into the "Phase Diagram Updates" section in Journal of Phase Equilibrium in 1993 [21], the editor made three important comments: the liquidus about UPd_3 is too asymmetric; the liquidus and solidus of L + fcc region seems to cross one another when

extrapolated into U-rich side; regarding UPd_8, atomic ratio of 1:8 is rare for binary compounds.In other words, some phase boundaries on this diagram are thermodynamically improbable. The U-Pd phase diagram can also be found in *ASM Handbook*[19].

4.3.2 Discussion

During the 1950's and 1960's, among the three U-Me subsystems, the U-Pd system was the most frequently explored and yet it is the most controversial one. It is controversial not only in phase diagram data, but also in thermodynamic property measurements, *e.g.*, the enthalpy of formation of UPd_3 which will be discussed elsewhere. In spite of the instruments and methods used by different authors, *e.g.*, thermal analysis, differential thermal analysis, X-Ray diffraction, metallography, electron probe microanalysis *etc.*, the discrepancies are far beyond the ranges of random error and/or system error of the instruments. Contamination of samples by materials from the containers had been reported in U-Pd phase diagram determinations [14, 16]. The worst scenario might be the co-existence of contaminants and a catalyst, *e.g.*, when a BeO or ZrO crucible and platinum elements are coexisting in U-Me phase diagram determinations.

The purpose of thermodynamic evaluation is not just to imitate the experimental phase diagram but also to validate it and this might be the right time that thermodynamics speaks—as long as the parameters used are reliable, the databases are well established and all the unknown parameters and coefficients are properly assessed. No one can perform a measurement without a suitable container for the sample, but a reliable thermodynamic model can predict the result without interference of contaminants. This is why thermodynamic evaluations help in such complicated systems.

Figure 3shows the calculated U-Pd phase diagram with extrapolated solution phases. Although the phase diagram has all the phases and compounds that the "accepted" phase diagram has, there are some problems to be elaborated.

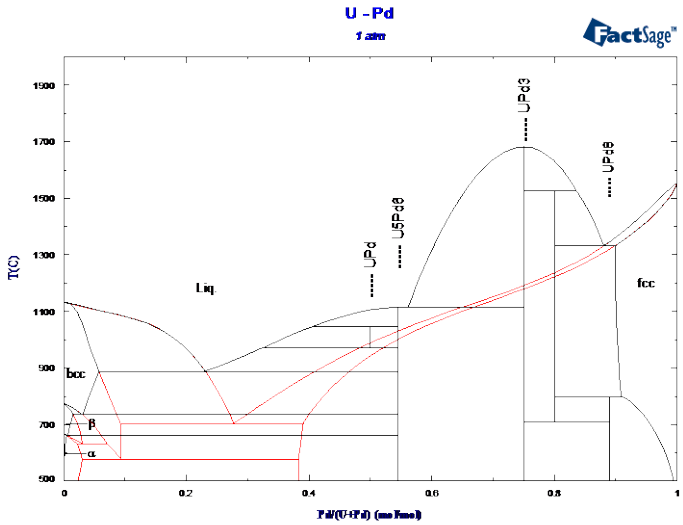

Figure 3 Calculated U-Pd phase diagram with extrapolated solution phases

4.3.2.1 The liquidus

Liquidus data were provided either partially or in full range of the composition by the four groups of scientists but with significant differences. The U-rich part will be discussed in the section about the eutectic point. Park *et al.* data are higher than that of Catterall *et al.* in range of 50 – 75 at% Pd, but about the same beyond 75 at%. In the range of 75-100 at% Pd, Terekhov *et al.* data are relatively high and unreliable because parts of the liquidus are so asymmetrical that thermodynamic calculations show that they do not form eutectic liquidus but peritectic, which are agreeable with the result of Pells.

The calculated liquidus is between that of Park *et al.* and Catterall *et al.* at Pd-rich side (Figure 4).

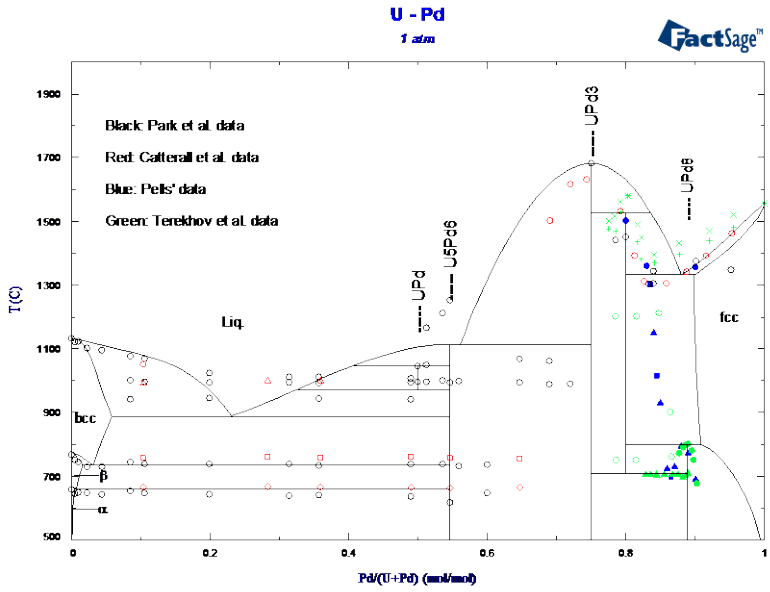

Figure 4 Calculated U-Pd phase diagram with experimental data from different authors

From Figure 3 it is seen that the fcc + liquid liquidus and solidus do not cross each other as they extrapolate into U-rich side in this model.

4.3.2.2 Solubility limit of U in Pd (fcc phase)

The fcc phase plays a very important role in U-Pd system, as well as in U-Rh-Pd ternary system. Unlike the fcc phase in U-Rh system and the cph phase in U-Ru system, in which the solubility of U in Rh or Ru are less than 2 at%, the solubility of U in Pd in U-Pd system were determined to be 22 at% (by Catterall *et al.*[14]), 15 at% (by Pells [17]) and 11 at% (by Park *et al.*[16]), respectively. The thermodynamic modelling shows that the limit is about 10 at% U. The unacceptable value by Catterall *et al.* was obviously caused by failing to identify the existence of intermetallic alloys or compounds. During the thermodynamic assessment, even the medium values by Pells and Terekhov *et al.* (about 15 at% Pd) could not be achieved, no matter how the coefficients of the Gibbs energy functions were changed. Because the minimum difference between calculated value and the experimental counterparts is about 5 at% Pd, great efforts were made in finding new experimental sources that support the thermodynamically calculated value. Finally the long omitted report by Park *et al.*[16] was obtained from the National Archives of U.S.A. with the direct help of NIST and the National Archive librarians. Among the institutions who worked on the U-Pd experimental

phase diagram, the U.S.A. group was the most experienced one because they worked out many U related binary phase diagrams, including that of U-Pt, U-Be, U-Ru, U-Rh, U-Pd etc. The report by Park *et al*. provides not only the closest experimental U solubility in Pd, but also some important clues of an experimental fallacy in the U-rich side eutectic determination (See 4.3.2.3). In addition, this report is the newest experimental investigation over the whole composition range of U-Pd system.

4.3.2.3 U-rich side eutectic composition and temperatures

For convenience of comparison, the differences of measured eutectic properties are listed in Table 10.

Table 10 Different results in eutectic property measurements

Author(s)	Composition (at%)	Temperature (°C)	Reference	Year
Catterall *et al.*	37.4	998	[14]	1956
Park and Buzzard	25.0	996	[15]	1956
Park, Fickle, and Mullen	23.5	1008	[16]	1963
Calculated value	23.1	888	This work	2014

The maximum difference of eutectic composition from experiments is 13.9 at%. A similar problem occurred in U-Rh system, but not as much as this. Both Park *et al*. and Catterall *et al*. had mentioned the contamination of BeO and ZrO crucibles. Although some compromising measures had been adopted, the effect persists. By a comparison of phase diagrams of nine U-Platinum-metals (Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt), a conclusion can be drawn that U reacts with Be and a compound with high melting point (UBe_{13}) is formed with Pd as a catalyst. This has greatly increased the difficulty in phase identification and makes the U-Pd (U-Rh as well) not a true binary system.

4.3.2.4 The Compounds

The contamination is not limited in eutectic determinations and fcc boundary determinations. It exerts great influence in all range of composition of this system. Therefore, the mystery is no less in compound identification than any other endeavors in the study of this system.

Park and Buzzard did not detect the existence of these two compounds in 1956[15]. Park pointed out clearly in their 1963 report that "the contamination present in the metallographic specimens interfered with the collection of reliable X-ray data [16]." Although they confirmed the existence of the two compounds, but "with some mental reservations," Catterall *et al.* acknowledged that the existence of these two compounds was established by microscopy because the unsatisfactory nature of the samples defies phase identification as well as X-ray analysis [14, p. 66]. The structures remain unknown on the list of summary by Okamoto in 1993 [21]. In 1994, to measure the magnetic properties of these compounds, Nishioka *et al.* attempted to prepare the samples in laboratory, and they declared failure in preparation of UPd [22]. On the other hand, they successfully obtained "a single phase of U_5Pd_6" and carried out measurements of magnetic susceptibility, magnetization, electricity resistivity and heat capacity of U_5Pd_6 at very low

temperatures, *e.g.*, for high-field magnetization isotherms within 4.2-14 K. This is agreeable with the calculated result. However, the calculated enthalpy of U_5Pd_6 in this work is unexpectedly higher than all the other compounds existing in this system (Table 11).

Table 11 Calculated thermodynamic properties of U-Pd system

	UPd	**U_5Pd_6**	**UPd_3**	**UPd_4**	**UPd_8**
$\Delta H^0_{298K}(J/mol)$	-165,500	-1,110,000	-210,500	-236,200	-407,700
$S^0_{298K}(J/mol\ K)$	39.45	85.00	176.35	192.50	200.00

There is no doubt about the existence of UPd_3. However, the experimental enthalpy of formation of it is controversial. Thermodynamic evaluation of this value is lower than all the existing data but still reasonable comparing with that of URu_3 and URh_3. Table 12 summarizes experimental data by Jung and Kleppa and the values calculated during the process of thermodynamic modelling of U-Me systems. The great magnitude of deviations in experimental data may be also caused by crucible contaminations. It is notable that the closest set of data (by de Boer *et al*. [23]) to that of this work is also calculated data by a model considering many atomic properties of the constituent elements (Model of Energy Effects in Alloys).

Table 12A summary of standard enthalpy of formation values from different authors

Authors	$\Delta_f H^0\ (kJ \cdot mol^{-1})$			**Reference**
	URu_3	**URh_3**	**UPd_3**	
Jung and Kleppa	-124.0	-278.8	-294.7	[24]
Wijbenga	-153.2	-301.2	-524.0	[25]
Lorenelli and Marcon			260.0	[26]
de Boer *et al*.	-152.0	-192.0	244.0	[23]
Holleck and Kleykamp	-224.9	-256.7		[27]
Edwards *et al*.	-195.0			[28]
Wang and Kaye	-144.7	-194.0	-210.5	This work

In the accepted phase diagram, UPd_4 has a broad range of homogeneity. However, Park, Fickle and Mullen treat it as a stoichiometric compound considering the uncertainty of phase boundaries at Pd-rich side of the diagram. Based on this and for the sake of a clear illustration of phase relationships, it is treated as a stoichiometric compound. There have been no arguments on its existence; however, in this calculated phase diagram it is shown that it is not stable at low temperatures.

UPd_8 was first detected by Pells[17] and later confirmed by Terekhov *et al.*[18] but it had never appeared in phase diagrams by Park *et al.*,neither in [15] nor in [16]. Because of its position (high Pd content and low phase transition temperature), it is calculated without any known thermodynamic properties. However, the calculated values may serve as a guide for future studies.

4.4 **The quaternary system**

The significance of establishing binary thermodynamic models lies not only in obtaining a digital description of the experimental phase diagrams, but also in calculating some unknown

thermodynamic properties, examining the experimental performances and making possibility of extrapolation to higher order systems. The establishment of a quaternary U-Ru-Rh-Pd thermodynamic model enables calculation of ternary isothermal sections in the quaternary system and estimate quasi- or pseudo-phase diagrams, *e.g.*, U-Rh-Pd, U-Ru-Pd, U-Ru-Rh, URu_3-URh_3, URu_3-UPd_3, URh_3-UPd_3, and URu_3-URh_3-UPd_3*etc*. The construction of these isotherm sections and quasi-phase diagrams experimentally are very costly and time consuming and it is impossible to get ternary isotherm sections at all different temperatures. Thermodynamic modelling, however, has this advantage. In this work, the U-Ru-Rh-Pd quaternary thermodynamic model has been successfully established and tested with the only set of existing experimental ternary data: the U-Pd-Rh system at 1050 ˚C. The consequence is that the model cannot only "describe" the isotherm diagram, but can be used to modify some of misuse of the data and can predict reasonably the feature of the "closed region" discovered in the experiments ofKleykamp and Kang [20].

4.4.1 U-Pd-Rh system at 1050 ˚C

4.4.1.1 A summary of previous studies

Of the U-Rh-Ru, U-Pd-Ru, and U-Pd-Rh ternary systems that are of interest, only the last one was investigated experimentally and at only one temperature (1050˚C). Kleykamp and Kang[20] prepared 74 samples and each of them was annealed at this temperature for at least 3 to 6 weeks. They discovered that although the single fcc phase of Rh and Pd solution exists at 1050 ˚C in Rh-Pd binary phase diagram, in the ternary phase diagram with U an isolated "island" or, as they named it, a "closed region" was identified at low U content region. In contrast with their acceptance of existence of U_5Pd_6 (stable between 980-1110 ˚C) as they combined U-Pd phase diagram from two sources, the compound is missing on their ternary isothermal section. They tried to validate the existence of the "closed region" by estimating the binary interaction parameters and simplifying the symmetric equation, and calculated some spinodal curves at different U-Pd interaction parameters. However, these approaches are proved unreasonable by thermodynamic modelling thatonly one U-Pd interaction parameter is valid. In this ternary system, even if the approach does work, the spinodal curves should be related to U-Rh interaction parameter as well. With these problems, the demarcation of other nearby "two-phase" regions is susceptible. The authors tried to validate the "closed region" by estimating binary interaction parameters in a ternary regular solution model but these parameters are self-consistent in a ternary system, *i.e.*, in such a thermodynamic model, each binary Gibbs energy function must be re-assessed or optimized, and they cannot be independent variables themselves. The miscibility gap should be a function of temperature instead of the binary interaction parameters. As a matter of fact, in such a ternary system, the miscibility gap is defined not only in terms of the binary interaction parameters of U-Pd solution phases, but also in terms of the U-Rh solution parameters. In addition, in the process of validation, their simplification of Equation (12) [20] is found to be not adequate because that α_{12} matters.

By means of reactions of $UN+3(Ru_x+Pd_{1-x})$ at 1400 ˚C (1673K) under vacuum condition, Kurosaki and Uno proved the formation of UPd_3, URu_3, and URh_3 and a tentative ternary quasi-phase diagram is obtained [29, 30, 31]. The diagram has only 13 experimental points and, therefore, further investigationis needed. Because UMe_3 solidify at very high temperatures which makes the observation of phase equilibrium very difficult, no liquid phase is shown at 1400 ˚C (1673 K).

4.4.1.2 Calculated U-Rh-Pd phase diagram at 1050 °C and comparison with experimental data

Figure 5 shows the calculated ternary isotherm section with experimental data from Kleykamp and Kang [20], which is the only available ternary experimental data related to the quaternary system. The phase relationship in this phase diagram is much simpler because of the adoption of simpler compound model in the cases of the controversial and unsophisticated binary experimental results. The design of the experiments was reasonable, however, the authors were not fully aware of the difficulty in phase identification of compounds by means of X-ray diffraction and the contamination and the catalysis effect of Pd in U-Pd system. Therefore, there were many samples that should be in three-phase regions were attributed to two-phase regions. As a result, the isothermal section is over complicated and with many disputable phase boundary demarcations. For example, the fcc phase at 1050 °C should be a two-phase equilibrium, that is, there is a miscibility gap between fcc and fcc#2. Nevertheless, in the hand drawn phase diagram there are three phases: α1, α2 and α (fcc), which is obviously violate the phase rule. The authors accepted the existence of the compound U_5Pd_6 in the binary phase diagram, but failed to detect it in their own experiment. This affected the determination of the liquidus in the ternary isotherm section. Another major difference of the experimental phase diagram from the calculated phase diagram is the area of the miscibility gap of the fcc phase region. The former is too large because of the insufficient annealing time of the samples. Detailed analysis of the interdiffusion of Rh and Pd will be provided elsewhere.

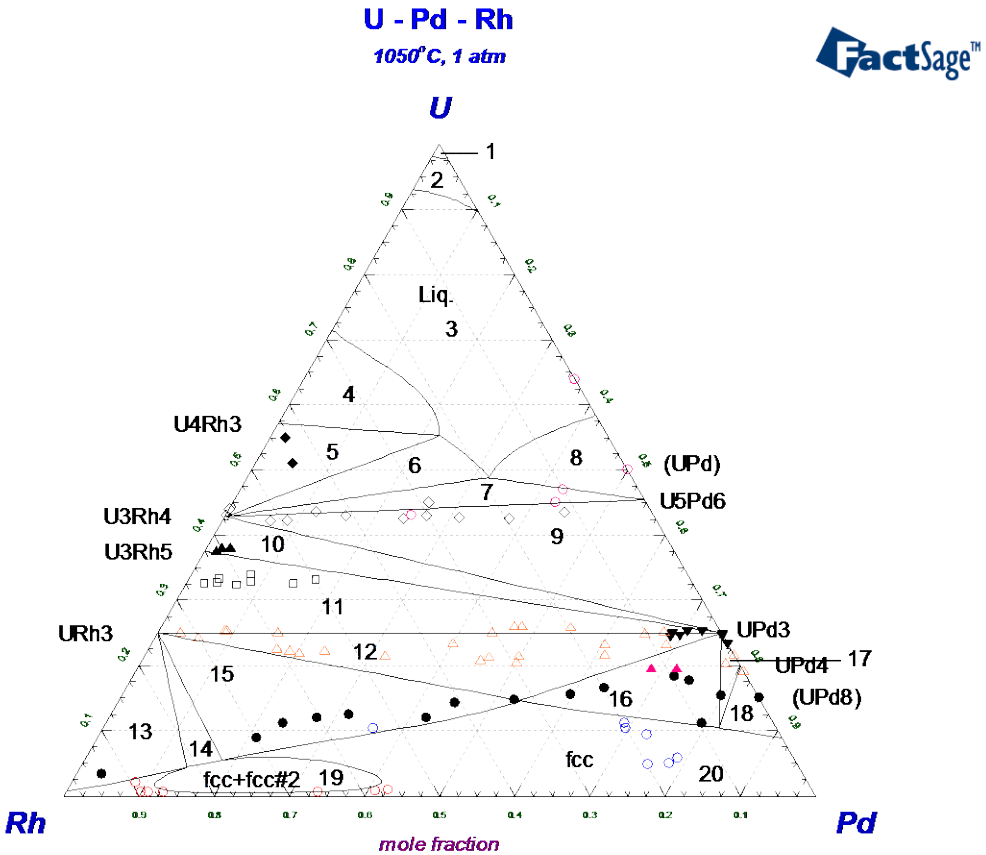

Figure 5. Calculated phased diagram with experimental nominal data from [20]

Because of the complexity of the phase boundaries and types of experimental data, the number of the phase regions and types of experimental data are summarized inTable 13.

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Table 13 Phase field classification and experimental symbols used inFigure 5

No. of phase field	Name(s) of phase(s) in the field	Total phases in the field	Types of experimental data by Kleykamp and Kang (K&K) in the phase field
1	bcc	1	None
2	bcc + liquid	2	None
3	liquid	1	○: Liquidus data
4	U_4Rh_3 + liquid	2	None
5	U_4Rh_3 + U_3Rh_4 + liquid	3	♦: U_4M_3 (M = Rh, Pd)
6	U_3Rh_4 + liquid	2	None
7	U_3Rh_4 + U_5Pd_6 + liquid	3	◊: U_3M_4; ○: Liquidus data
8	U_5Pd_6 + liquid	2	○: Liquidus data (K&K failed to identify U_5Pd_6)
9	U_5Pd_6 + U_3Rh_4 + UPd_3	3	◊: U_3M_4; ○: Liquidus data
10	U_3Rh_4 + U_3Rh_5 + UPd_3	3	▲: U_3M_5;▼: UPd_3 (ε)
11	U_3Rh_5 + URh_3 + UPd_3	3	□: UM_2; Δ: URh_3 (γ)
12	URh_3 + UPd_3 + fcc	3	Δ: URh_3; ▼: UPd_3 (ε)
13	URh_3 + fcc	2	●: fcc (α)
14	URh_3 + fcc + fcc#2	3	None
15	URh_3 + fcc	2	●: fcc (α); ○: fcc
16	UPd_3 + fcc	2	▲: γ (+α) ; fcc (α)
17	UPd_3 + UPd_4 + fcc	3	Δ: URh_3; ●: fcc (α)
18	UPd_4 + fcc	2	●: fcc (α)
19	fcc + fcc#2	2	○: fcc#2
20	fcc	1	○: fcc#2; ○: fcc

4.4.2 Predictions of some interested isopleths and isothermal sections

The U-Ru-Rh-Pd quaternary thermodynamic model can be used in calculating isothermal sections at any temperature and isopleths at any composition or compositions of the constituents. For example, except for U-Pd-Rh ternary isothermal section at 1050 °C, U-Rh-Ru and U-Pd-Ru ternary isotherms can also be obtained although they have not yet been obtained experimentally. These calculated phase diagrams are very useful for future experimental explorations because the model has been validated by U-Pd-Rh experimental data and developed on the basis of optimization of six

subsystem experimental data. As specific examples, quasi-phase diagrams involving UPd_3, URh_3 and URu_3 are illustrated here.

4.4.2.1 UPd_3-URh_3, UPd_3-URu_3 and URh_3-URu_3 quasi-phase diagrams

At present, no experimental phase diagrams of these ternary systems as well as the binary systems are available. The reasons arethe difficulty in obtaining large amount of pure compound materials, in high temperature measurements (their melting points are very high), and in handling of the samples, *e.g.*, their brittleness, hardness and impurities in them. In section 4.4.1.1, an attempt to establish UPd_3-URh_3-URu_3 phase diagram without binary phase diagrams has been introduced [30]. The result is tentative and it is not an equilibrium phase diagram. By means of the quaternary thermodynamic model, the binary quasi-phase diagrams can be easily calculated. All of the three calculated binary quasiphase diagrams show simple eutectic reactions (Table 14).

Table 14Calculated eutectic compositions and temperatures of binary UMe_3 phase diagrams

System		**Melting point of compounds (°C)**		**Eutectic properties**	
A	B	A	B	X_A	T_{eu} (°C)
URu_3	UPd_3	1725	1680	0.340	1354
URu_3	URh_3	1725	1700	0.504	1217
URh_3	UPd_3	1700	1680	0.485	1227

4.4.2.2 Calculated equilibrium UPd_3-URh_3-URu_3 phase diagram (1400 °C)

As a self-consistent quaternary treatment, it gives equilibrium isothermal sections at any temperature within the range of 0-2000 °C. For instance, in comparison with the experimental UPd_3-URh_3-URu_3 diagram constituted by Kurosaki and Uno[30], a calculated equilibrium isothermal section at 1400 °C (1673 K) is illustrated in Figure 6. In this phase diagram, liquid phase region is reasonably predicted which is missing in the above mentioned experimental phase diagram due to the failure in observing phase equilibrium at high temperatures.

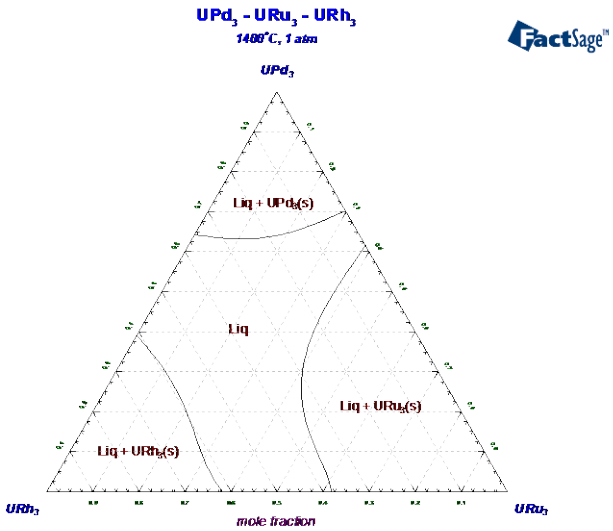

Figure 6Calculate UPd_3-URh_3-UPd_3 isothermal section at 1400˚C

A calculated liquidus projection is shown in Figure 7, in which, the contraction or expansion of the liquidus can be examined at different temperatures.

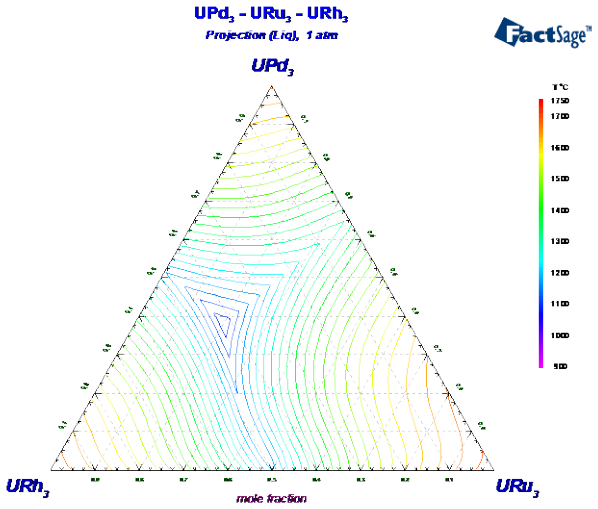

Figure 7Calculated liquidus projection of the UMe_3 ternary isothermal section between 900-1750˚C

4.4.2.3 The liquidus projection

By means of this quaternary thermodynamic model, liquidus projections of all ternary systems can be obtained. In Figure 8, liquidus projections for the U-Pd-Rh system are given.

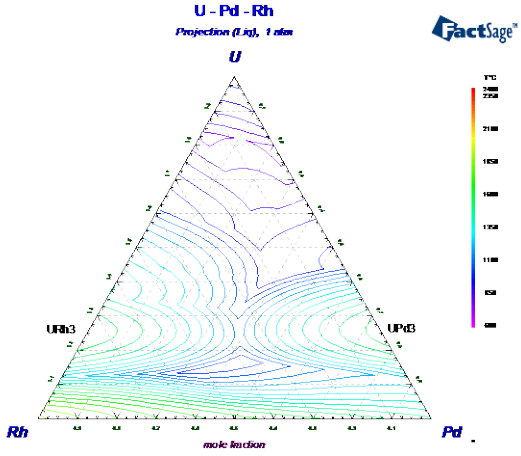

Figure 8Calculated U-Rh-Pd liquidus projections from 600-400˚C

These liquidus projections show that at low temperatures (800-900 ˚C), liquid phases form at U-rich side along the U-Rh and U-Pd axes (begin from the bcc-side eutectic temperatures). As temperature increases, one integrated liquid phase forms at a narrow temperature range of the eutectic points of the two systems and then, due to the formation of different compounds, the isotherm

separates.Finally, at temperatures above the highest melting points of the compounds the isotherms emerge again. The liquidus projections of U-Ru-Rh and U-Ru-Pd can also be calculated.

5 Conclusion

Starting from thermodynamic description of U-Ru system based on Berche *et al*. work, U-Rh and U-Pd binary systems have been described thermodynamically for the first time. In this process, difficult choices had been made due to the disagreements upon some important experimental data from different groups of scientists. The thermodynamic model has been shown to be useful in compromising the differences, especially in case of possible and inevitable contaminations by materials of sample containers. The self-consistent quaternary thermodynamic model successfully calculated the fcc miscibility gap found by Kleykamp and Kang and some misinterpretation of their data have been identified and analysed. The three dimensional features of the miscibility gap found only at 1050 °C isothermal section are presented and the critical temperature of the ternary miscibility gap is estimated to be 1146 °C. Quasi-phase diagrams of URu_3, URh_3, and UPd_3 are calculated as well as an equilibrium ternary section of URu_3-URh_3-UPd_3 at 1673K (1400 °C) in comparison with the experimental data by Kurosaki and Uno. The parameters and thermodynamic properties established or calculated in this work can be used in the previously established nuclear fuel model by the RMCC group under Thompson and Lewis for more accurate calculation of nuclear fission products at different burnups [32].

6 References

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