A Re-Examination of Thermodynamic Modelling of U-Ru Binary Phase Diagram

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Abstract

Ruthenium (Ru) is one of the more abundant fission products (FPs) both in fast breeder reactors and thermal reactors. Post irradiation examinations (PIE) showthat both “the white metallic phase” (Mo-Tc-Ru-Rh-Pd) and "the other metallic phase" ($U(Pd\text{-}Rh\text{-}Ru)_3$) are present in spent nuclear fuels. Todescribe this quaternary system, binary subsystems of uranium (U) with Pd, Rh, and Ru are necessary. Presently, only the U-Ru system has been thermodynamically described but with some problems. As part of research on U-Ru-Rh-Pd quaternary system, an improved consistent thermodynamic model describing the U-Ru binary phase diagram has been obtained.

1. Introduction

FPs generated in nuclear power production not only shorten the useful life of the fuel, but may also cause other problems, *e.g.*, chemical interaction with cladding, physical deformation of the fuel rods (including sheath ballooning and element sagging) and fission gas release. These phenomena may lead to reactor trips or even accidents[1]**.**During the past decades, metallic fission products had been widely explored both by experimental studies and thermodynamic modelling. Kaye *et al*. thermodynamically described the so-called "the white metallic phase" which is mainly composed of Mo-Tc-Ru-Rh-Pd based on experimental phase diagrams and some calculated phase diagrams by other authors [2]**.** To include the effect of uranium, an extensive study on U-Ru-Rh-Pd quaternary system is in development, for which evaluations of the six subsystems (*i.e.*, Ru-Rh, Ru-Pd, Rh-Pd, U-Ru, U-Rh, and U-Pd) are necessary. The first three systems (*i.e.*, those of Pd-Rh-Ru)were calculated in[2]; the U-Ru system has been thermodynamically evaluated by Berche *et al*.[3], but is inconsistent with the models developed for Pd-Rh-Ru binary systems; and the U-Rh and U-Pd phase diagramshave been calculated and optimized thermodynamically and will be presented in another paper by the current authors.

Because a different lattice stability of *bcc Ru* (a metastable phase) had been used in the Ru-Rh and Ru-Pd systems evaluated by Kaye *et al*.[2] from the*bcc Ru*in the U-Ru system evaluated by Berche *et al*. [3], a choice had to be made as to which value for the lattice stability would be used in this work. For consistency with the earlier work by Kaye *et al*. [2] the lattice stability of of *bcc Ru* was selected from it. Therefore, it was necessary to readjust the interaction parameters of related phases, *i.e.*, those of bcc (γ-U) and β-U phases from the work of Berche *et al*. [3]. In addition, the hcp phase is missing in Berche *et al*. model, which might be due to missing *hcp U* (another metastable phase needed in calculation) data in SGTE database. Although the area of the field is small (the solubility of U in Ru is about 1.5 at%), it is very important in thermodynamic calculation. For example, in the Berche *et al*. model, the hcp-liquid phase boundary is at equilibrium with *hcp* Ru(pure Ru) above the eutectic temperature, and it does not appear in the metastable solution phase diagram. This will affect extrapolationsto higher order phase diagrams. Finally, the enthalpy of formation of URh_3 is calculated and compared with other experimental results and model predictions. More detailed discussion on this aspect will be done in the paper about U-Rh system modelling.

2. Thermodynamic modelling

The Gibbs energy equations used in this work are the same used in the Berche *et al*. model. However, these authors prefer a Köhler formalism, which has been adopted here, over the Redlich Kister formalism. Therefore, the interaction parameters of solution phases are transformed accordingly (Table 1).This has been done to maintain consistency with the extrapolation scheme used in the pre-established subsystems (*i.e.*, Köhler formalismwas used by Kaye *et al*. [2]). The excess Gibbs energy expressions of the two formalisms are given below.

Redlich Kister formalism:

$$G^E = X_A X_B\left[(A_0 + B_0 T) + (A_1 + B_1 T)(X_A - X_B) + (A_2 + B_2 T)(X_A - X_B)^2 + \cdots\right] \quad (1)$$

Köhler formalism:

$$G^E = X_A X_B\left[(a_0 + b_0 T) + (a_1 + b_1 T)X_B + (a_2 + b_2 T){X_B}^2 + \cdots\right] \quad (2)$$

Table 1

Transformation of interaction parameters of solution phases (J/mol)

Phase	Redlich Kister formalism (Berche *et al.*)			Köhler formalism		
	A_0	B_0	A_1	a_0	b_0	a_1
Liquid	-173587	10.82	-63720	-237307	10.82	127440
γ-U (bcc)	-164020	43.68	-19280	-183300	43.68	38560
β-U	-105000	0	0	-105000	0	0

For different stable states of the pure elements, it appears that Berche *et al.* used data from the SGTE database [4], but without listing them. This makes for some difficulties forduplicating the calculationsand different lattice stabilities for metastable structures used for an element necessitate readjustment of the interaction parameters of some solution phases, which, in turn, affect the values of thermodynmice properties, such as enthalpy of formation and entropy of the compounds. Therefore, the interaction parameters of γ-U and β-U solution phases transformed from Redlich Kister formalism (Table 1) had to be readjusted.

For systems involving U, many thermodynamic experimental data are not available, especially for metastable states. Efforts have been made to get calculated data by the *ab initio* method. Although first principle methods are under rapid development, uncertainties for calculated values vary in great magnitude upon understanding of targeted systems and methodologies. At present, there are no calculated data available for some phases in the U-Ru system; therefore, simplification or isotypic data have to be used, *e.g.*, Berche *et al.* used *ab initio* calculated value for σ phase ($D8_b$, prototype CrFe) as that of β-U phase. Because no

Gibbs energy value for *hcp*phase is available, they used the value for *fcc* phase as a reference value. To be strict, by using the *fcc* value, the Gibbs energy relative to *hcp* phase can be derived:

$$G_{Ru}^{\beta-U} - G_{Ru}^{fcc} = 18800 \text{ (From Berche \textit{et al.}[3])} \tag{3}$$

$$\left(G_{Ru}^{L} - G_{Ru}^{hcp}\right) - \left(G_{Ru}^{L} - G_{Ru}^{fcc}\right) = \left(G_{Ru}^{fcc} - G_{Ru}^{hcp}\right) \tag{4}$$

where L stands for liquid phase. Using SGTE element phase transition data[4], the Gibbs energy difference can be calculated:

$$\left(G_{Ru}^{fcc} - G_{Ru}^{hcp}\right) = (38589 - 14.80T) - (21019 - 8.94T) = 17570 - 5.86T \tag{5}$$

Similarly, combining with Equation (3),

$$\left(G_{Ru}^{\beta-U} - G_{Ru}^{fcc}\right) + \left(G_{Ru}^{fcc} - G_{Ru}^{hcp}\right) = G_{Ru}^{\beta-U} - G_{Ru}^{hcp} \tag{6}$$

$$G_{Ru}^{\beta-U} - G_{Ru}^{hcp} = 18800 + 17570 - 5.86T = 36370 - 5.86T \tag{7}$$

Of course, this will cause readjustment of all the interaction parameters of the system and is not included in this work.

Two other hypothetical structures are involved in this system: for element Ru, *bcc* structure is hypothetical; for element U, *hcp* structure is hypothetical. These solid structures do not exist for the pure elements, but they are needed in thermodynamic calculations of the phase diagram, *i.e.*, the *bcc* (γ-U) and hcp solid solutions. The former can be calculated from other stable Gibbs energy relative to that of melting point of U, but the latter cannot. In the assessment of Kaye *et al*. [2], the lattice stability of *bcc* Ru is different from that of Berche *et al*. [3]. In order to incorporate the U-Ru subsystem into existing Ru-Rh and Ru-Pd subsystems, the same lattice stability derived on the basis of Rand and Potter [5]is used in this work:

$$G_{Ru}^{hcp} - G_{Ru}^{bcc} = 8169 - 2.29T \tag{8}$$

As a regular solution model, the enthalpy of a structure of the elements is temperature independent; therefore, ΔH_{298} of *bcc* Ru is 8169 J/mol whereas S_{298} of *bcc* Ru is 30.82 J/mol·K. Table 2 lists lattice stabilities and referencing data of U-Ru system used in this model. Ru solubility in α-U is supposed to be zero[3]; therefore, no need for a hypothetical state of such structure in Ru. In the case of G (Added) is used, it means that a Gibbs energy difference is set relative to the stable state of the element at 1 atm, 298K.

Table 2
Lattice stability and referencing

Phase	U			Ru		
	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	38589	43.33	0
γ (bcc)	3231.08	47.98	0	8169.00	30.82	0
β (tetragonal_U)	2790.73	53.25	0	0	28.53	18800
α (orthorhombic_A20)	0	50.29	0	-	-	0
hcp	0	50.29	11659.50	0	28.53	0

After the necessary adjustments, new interaction parameters of liquid phase, solid solution phases, and compounds are listed in Tables 3 and 4.

Table 3
Excess Gibbs energy expressions

System	Excess Gibbs energy functions in Köhler formalism (J/mol)	Reference
Liquid	$\Delta G^{E}_{Liquid} = X_{Ru}X_{U}[(-237307+10.82T)+127440X_{U}]$	[3]
bcc (γ-U)	$\Delta \mathrm{G}^{\mathrm{E}}_{\mathrm{bcc}} = \mathrm{X}_{\mathrm{Ru}}\mathrm{X}_{\mathrm{U}}[(-168500+43.68\mathrm{T})+38560\mathrm{X}_{\mathrm{U}}](hypothetical)$	This work
Tetragonal (β-U)	$\Delta G^{E}_{\beta-U} = X_{Ru}X_{U}[-90000]$	This work
hcp	$\Delta G^{E}_{hcp} = X_{Ru}X_{U}[-100000]\ (hypothetical)$	This work

Table 4
Gibbs energy expressions of intermetallic compounds (J/mol)

Compound	Gibbs energy expression (J/mol)
URu_3	$G^{URu_3} = -177240+540.77T-101.224T\ln T-0.00923014T^{2}+235907T^{-1}$
U_3Ru_4	$G^{U_3Ru_4}-3G^{\alpha-U}_{U}-4G^{hcp}_{Ru} = -375879+68.8T$
U_3Ru_5	$G^{U_3Ru_5}-3G^{\alpha-U}_{U}-5G^{hcp}_{Ru} = -389217+51.8T$
URu-L	$G^{URu-L}-0.52G^{\alpha-U}_{U}-0.48G^{hcp}_{Ru} = -59766.5+14.68T$
URu-H	$G^{URu-H}-G^{URu-L} = -3.108-0.00057T$
U_2Ru	$G^{U_2Ru}-2G^{\alpha-U}_{U}-G^{hcp}_{Ru} = -123773+25.58T$

In Table 4, the Gibbs energy expression of URu_3 is different from others in form because in the U-Ru system its heat capacity is the only one which has been obtained from experiments. Therefore, the form of the Gibbs energy expression is similar to that of elements. Others without experimental heat capacity data are calculated using the Copp-Neumann rule (Table 5). Heat capacity data of condensed forms of elements involved in this work are from FACT database[6]

Table 5 Heat capacity calculated by Copp-Newmann rule ($C_p = \mathrm{a}+\mathrm{bT}+\mathrm{c}T^{-2}+dT^{2}$)

Compound	a	bx10^3	c	dx10^5	T_{min} (K)	T_{max} (K)
URu-L	24.996	2.598	-94233	1.332	298	1060
URu-H	24.996	2.598	-94233	1.332	1061	1414
URu_3	101.224	18.460	-471814	0	298	3000
U_2Ru	76.751	3.119	-267026	5.205	298	3000
U_3Ru_4	172.412	24.991	-682424	7.544	298	3000
U3Ru$_5$	195.326	33.116	-795178	7.438	298	3000

3. A summary of previous studies

The earliest studyofthe U-Ru phase diagram was published in 1958 [7], in which only a partial phase diagram was included. It can be seen that temperature measurement above 1000°C was difficult for this system.

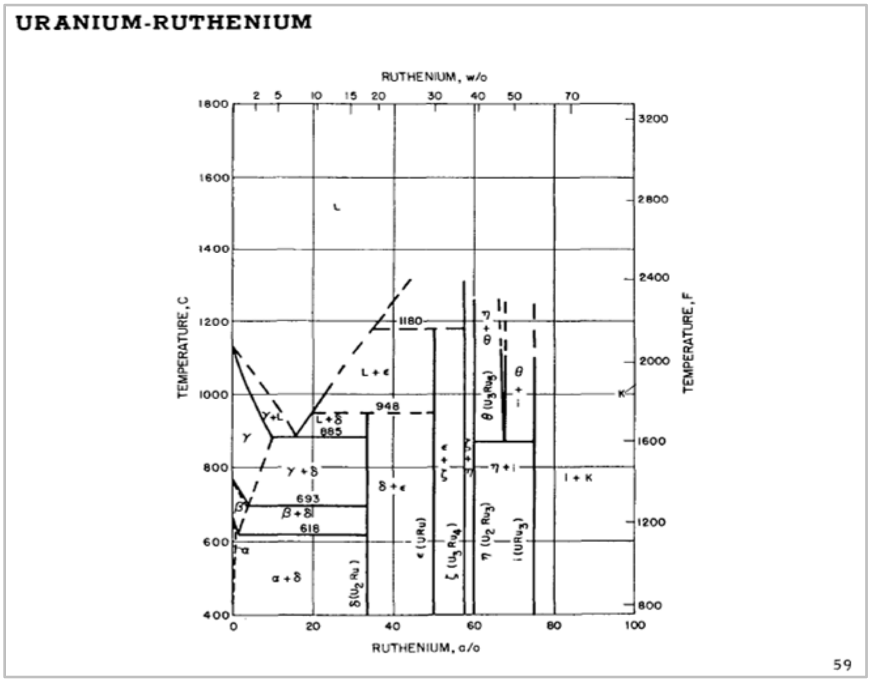


Figure 1 A partial U-Ru phase diagram (1958)[7].

The first complete U-Ru phase diagram was obtained experimentally by J.J. Park together with a U-Rh phase diagram in his PhD dissertation[8]. Three years later, the results were published as two separate papers[9].

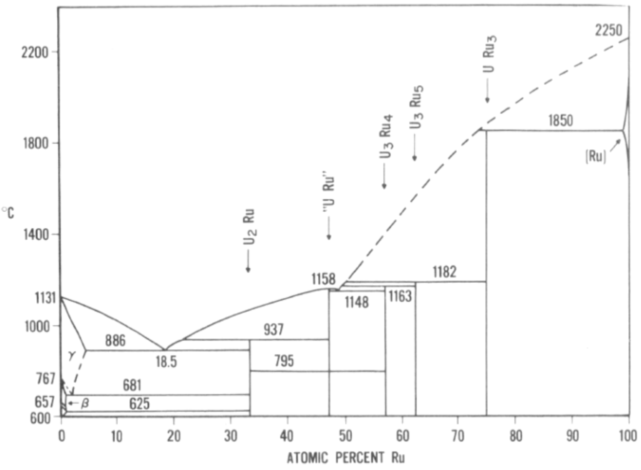


Figure 2The first complete U-Ru experimental phase diagram by J.J. Park(1965) [8].

More than two decades later, Mason and El-Genk re-examined the high temperature region (composition range over 50-100 at% Ru) of the system. They found that the reaction of URu_3 is not peritectic, but eutectic with a eutectic isotherm of 1861±20K and eutectic composition of 77.5±1 at%Ru[10].Their experiments show difficulties in the high temperature measurements combined with chemical interactions between samples and crucibles.In fact, it was so difficult to distinguish the liquidus that they gave two possible liquidus curves on the diagram.

The first thermodynamic assessment of U-Ru system was published in 2011 by Berche *et al*. [3], in which major changes had been made on the Ru-rich side: they changed the peritectic reaction to aeutectic reaction in accordance (but not exactly same) with the experiments of Mason and El-Genk but the *hcp* phase was missing.

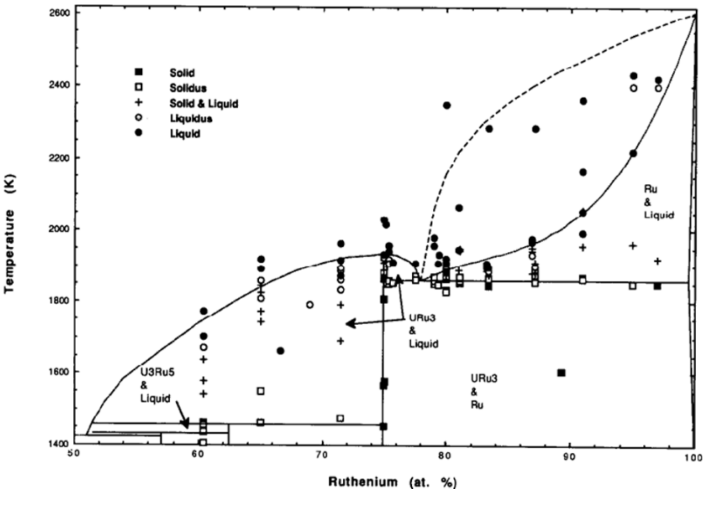
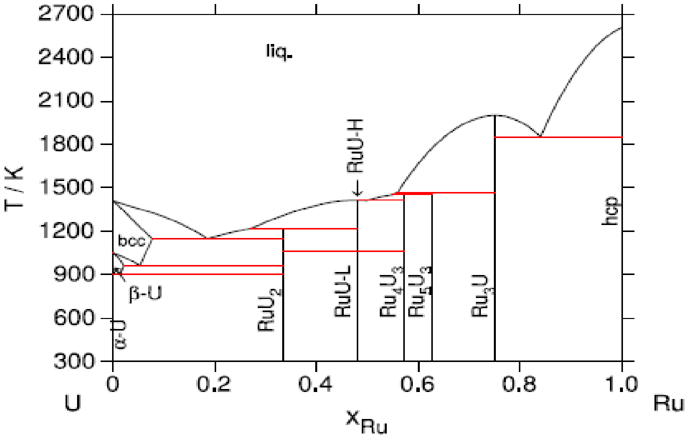


Figure 3 Re-examination of Ru-rich part of U-Ru system by Mason and El-Genk[10].



(a) Calculated phase diagram.

Figure 4 A thermodynamic description by Berche *et al.*[3].

4. Results

From the phase diagrams shown above, it can be seen that the different features of the high temperature measurements in different phase diagrams are non-negligible. For example, the calculated eutectic temperature is 1849 that is 274K lower than result from Park and 12K lower than experimental result of Mason and El-Genk. In the diagram proposed by Mason and El-Genk, although the two possible L/hcp liquidus separate as far as a maximum of about 230K at 87 at% Ru, the eutectic isotherm is well defined by experimental data. The eutectic composition (77.5 at% Ru) is supported by metallurgical analysis and observations by Edwards *et al.* [10]. The calculated eutectic composition is 83.8 at% Ru, which is 6.3 at% higher than the experimental data. The reason is not provided by Berche *et al.* and this will be part of future work of this study.

The temperatures of the two reaction types (peritectic and eutectic) affect the position of the *hcp* phase field. This phase was confirmed by Park without experimental data. Figure 5 shows the U-Ru phase diagram with hypotheticaland metastable solution phases (Note that the *hcp* phase is missing). This diagram shows several abnormal phenomena even as a metastable phase diagram: first, the bcc + liquid phase liquidus in Ru-rich region does not reflect true liquidus; second, the bcc + liquid region is separated from the β-U +bcc region; third, the minimum point of the bcc + liquid region does not have any physical meaning, *e.g.*, it is not an eutectic point; finally, the eutectic isotherms of α/β and β/γ transformation is now shown. All these mean that the metastable phase diagram is not a reasonable one.

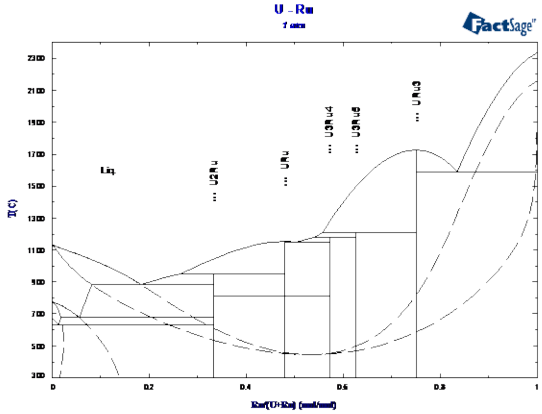


Figure 5 Re-calculated phase diagram with metastable solution phases without hcp phase (Referencing for *bcc* Ru see Table 2).

When the *hcp* phase is added (Figure 6), the liquidus in the new metastable solution phase diagram represents the calculated liquidus of the phase diagram with five compounds added above the eutectic isotherms. However, in Figure 6, the β-U + γ-U region is still standing alone in the metastable phase diagram. An isotherm appears as a three phase equilibrium at the Pd-rich side. According to our experience in dealing with the U-Rh and U-Pd systems, the isotherms should appear at the U-rich side and form an integrated and four closely related solution-phase metastable phase diagram. To realize this, a new set of interaction parameters has to be calculated. Although the area of the*hcp* phase is small, its effect on higher order phase diagrams might be non-negligible [11].

The re-assessed enthalpy of formation (ΔH_{298}) of URu_3 is -144700 J/mol, close to experimental results from Wijbenga *et al*. (-153200 J/mol[12]) and Jung and Kleppa (-124000 J/mol[13]). In the model of energy effects of alloys, the value is -152000 J/mol. Closer assessment of enthalpy of formation of URu_3 is significant in estimating enthalpy values of other compounds in this system.

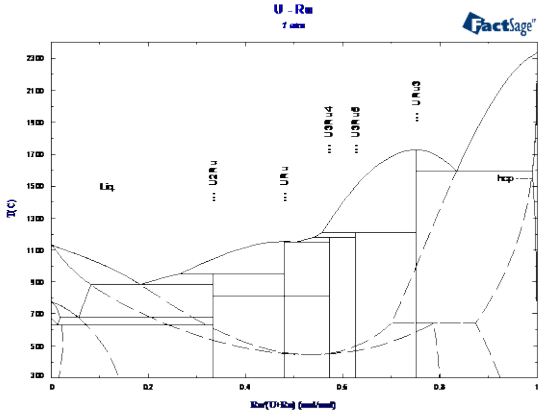


Figure 6 U-Ru phase diagram with metastable solution phases when *hcp* phase is added.

Figure 7 illustrates the recalculated phase diagram with published experimental data from Park and Mason and El-Genk. The most important phenomenon to be discussed here is the data from Mason and El-Genk around URu_3. This work is based on the pioneering work of Berche *et al.* and the liquid phase interaction parameter, which calculated the melting point of URu_3 as 1998K, while the eutectic isotherm at 1849 K and eutectic composition at 83.8 at% Ru, remained unchanged. As mentioned before, the results from Mason and El-Genk for the eutectic composition is supported by metallurgical examination and conformsto some otherresults (*e.g.*,[14]), and thus is a better source to base the thermodynamic modelling. By adopting their data, the liquidus of the liquid-URu_3 part meet naturally with the melting point of URu_3(1936K) and the eutectic composition (77.5 at% Ru).

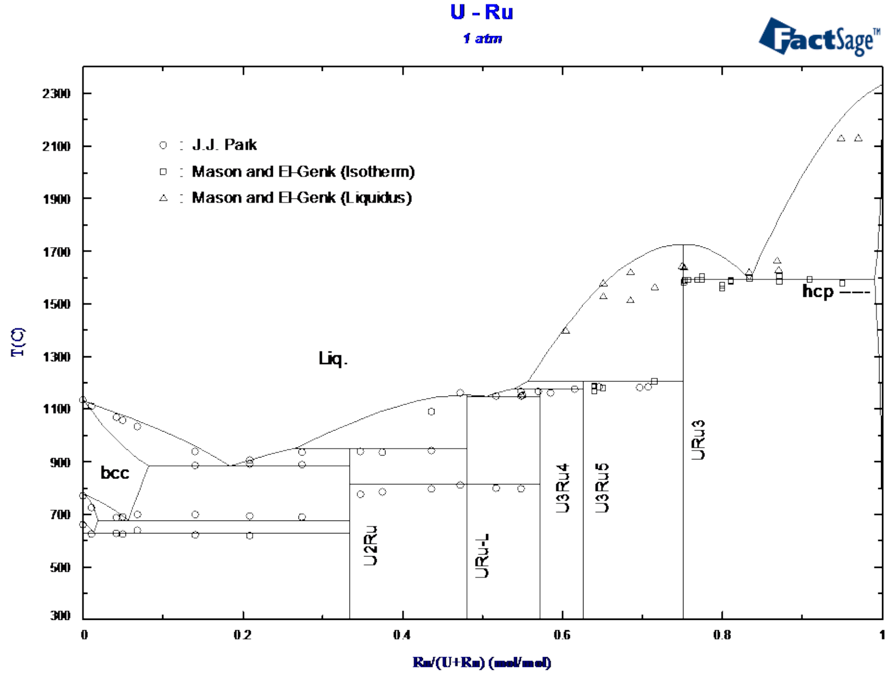


Figure 7Re-calculated phase diagram with published experimental data.

5. Conclusion

As part of work of U-Pd-Ru-Rh quaternary system, the U-Ru subsystem has been adapted to previous models that have different referencing for*bcc* Ru. Further the hcp phase missing in the previous model has been added. Some more reasonable improvements of the model are suggested, *e.g.*, improvements on $G_{Ru}^{\beta-U} - G_{Ru}^{hcp}$ value liquid phase interaction parametersand metastable phase relations for future work.

6. References

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