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A computer assessment of the Ru–Rh and Ru–Pd systems

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Abstract

Optimized phase diagrams of the Ru–Rh and Ru–Pd systems were calculated using thermodynamic coefficients derived by the assessment of available experimental phase diagram and thermodynamic data. The excess Gibbs free energies of the phases are described employing the ordinary polynomial expressions in regular or subregular models. The temperatures of various transitions and the composition limits of the phases are reproduced closely.

1. Introduction

The assessment of the Ru–Rh and Ru–Pd systems are of importance to the nuclear industry since the elements ruthenium, rhodium and palladium are found together with molybdenum, and technetium as single- or two-phase metallic inclusions in irradiated UO_2 and (U, Pu)O_2 nuclear fuels.

Computer assessments of several binary systems of these five elements have been made and the resulted binary Gibbs excess free-energy coefficients have been used successfully in multiphase diagram calculations of the elements [1–4]. In the case of the Ru–Rh and Ru–Pd systems, there are no calculated Gibbs excess free-energy coefficients available and therefore the present assessments were undertaken using the available experimental phase diagram and thermodynamic data to provide the best of coefficients for use in higher order system constructions. The optimization program of Lukas *et al.* [5] was utilized in obtaining the best set of coefficients describing the phase diagrams.

2. Experimental phase diagram and thermodynamic data

2.1. The Ru–Rh system

Experimental study of the Ru–Rh system is very limited. Lattice parameter measurements in the ϵ-Ru(Rh) solid solution range have been reported [6]. A rather comprehensive constitutional investigation was made recently by Paschoal *et al.* [7]. They studied the system between 900 and 2300 °C and reported that the system is of the simple peritectic type (ϵ-Ru(Rh) + liquid = α-Rh(Ru)) with a peritectic temperature of 2090 °C (Fig. 1(a)). Peritectic compositions of Ru(Rh), Rh(Ru) and the liquid are about 60 at.% Rh, 65.5 at.% Rh and 70 at.% Rh. It was reported that only the solidus and peritectic lines could be measured by differential thermal analysis and liquidus lines of ϵ + liquidus and α + liquidus equilibria were not observed because of their very narrow ranges. The liquidus lines are shown in the diagram by broken lines. The solid region is characterized with broad solid solutions ϵ-Ru(Rh) and α-Rh(Ru) and a rather narrow $\epsilon + \alpha$ two-phase field. The solid solubility limits of the phases are not changed with decreasing temperature. No intermediate phases were observed.

No experimental thermodynamic data are available. Kaufman and Bernstein [8] made a computer calculation of the system on the basis of the regular solution model and estimated interaction parameters. It was suggested that the system is of the simple eutectic type.

2.2. The Ru–Pd system

The phase diagram (Fig. 2(a)) is based mainly on the studies of Darling and Yorke [9], Obrowski and Zwingmann [10] and Kleykamp [11]. They all agree that the system is a simple peritectic type (liquid + h.c.p. Ru(Pd) = f.c.c. Pd(Ru)) with no intermediate phases. This general form was also found by Rudnitskii and Polyakova [12], but they suggested that an intermediate

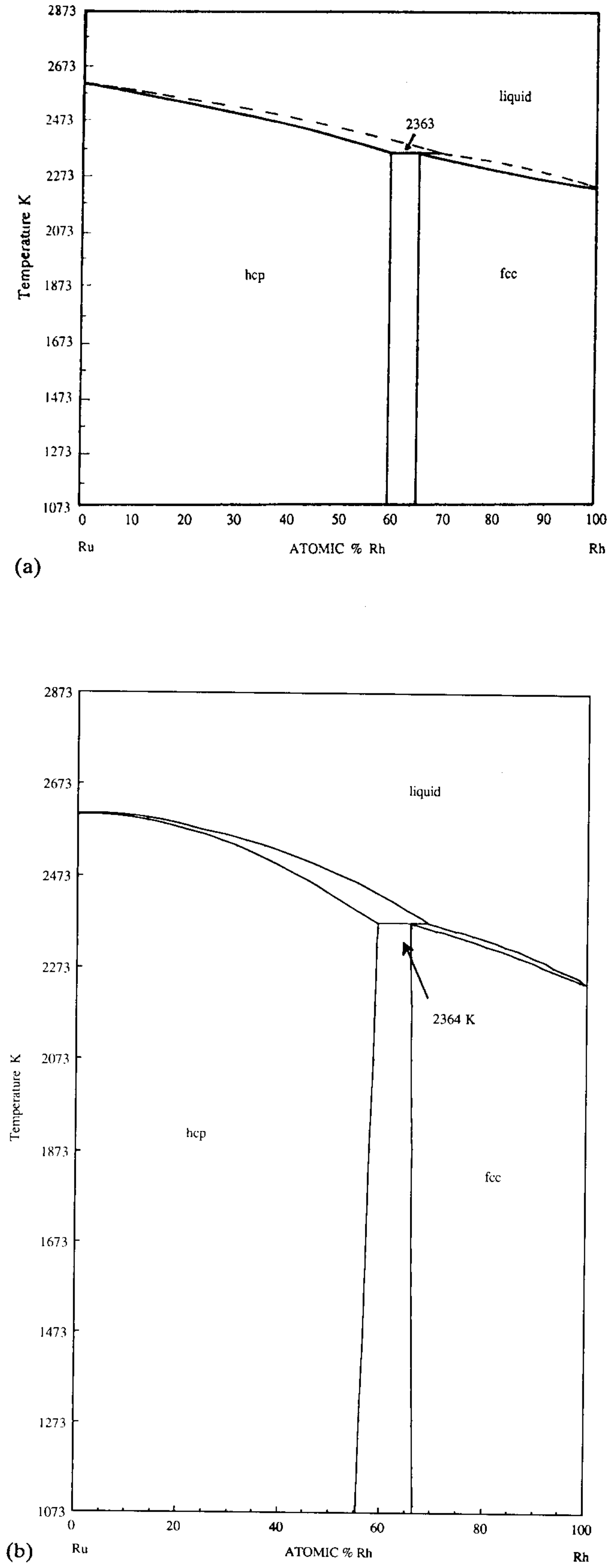

Fig. 1. Comparison of the Ru-Rh system. (a) The experimentally established Ru-Rh phase diagram. (b) The calculated Ru-Rh phase diagram.

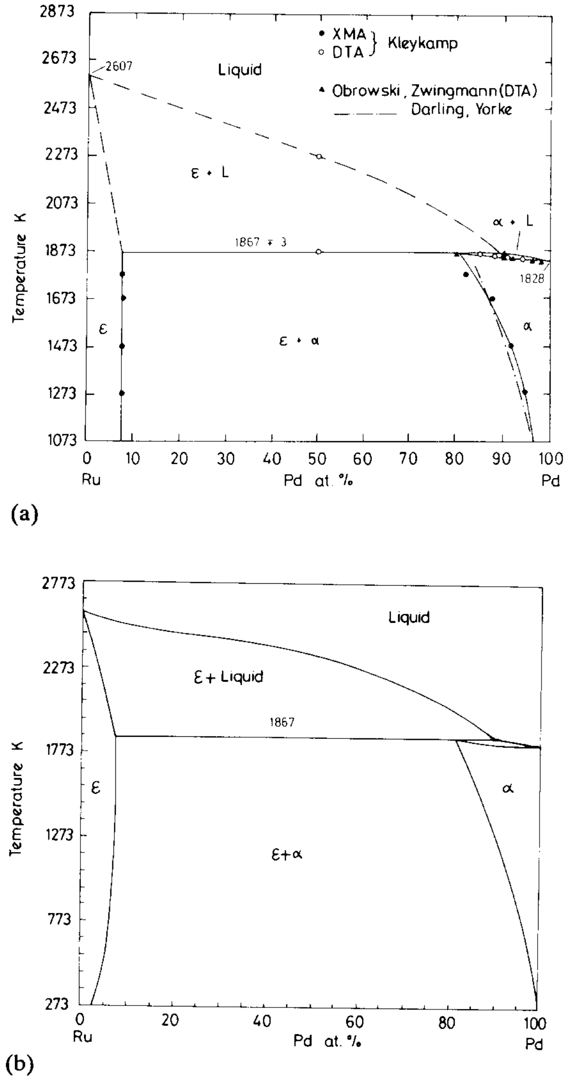

Fig. 2. Comparison of the Ru-Pd system. (a) The experimentally established Ru-Pd phase diagram. (b) The calculated Ru-Pd phase diagram.

phase (β) formed peritectoidally at 1575 °C, dissociating eutectoidally at 740 °C. Novikova [13] has reported a eutectic type between the above phases, at 1520 °C and 12 at.% Ru. However, no other investigators have confirmed the existence of the intermediate phase or the eutectic reaction.

The temperature of the peritectic reaction has been determined at slightly different temperatures ranging from 1580 to 1594 ± 3 °C [9–11]. The composition of the liquid phase and Pd(Rh) solid solution phase at the peritectic horizontal has been reported to contain between 88–91 at.% Pd and 81–84 at.% Pd [9–11]. The solubility of palladium in ruthenium was determined to be 7.7 ± 0.3 at.% Pd at the peritectic temperature and to be temperature independent, whereas the solubility of ruthenium in palladium decreases with decreasing temperature [9, 11].

Kleykamp [11] has measured the liquidus temperature as 1990 °C using an alloy with 50 at.% Pd and made an extrapolation in order to estimate the (ϵ-Ru(Pd) + liquid) region liquidus boundary employing the measured value, the peritectic liquid composition and the melting point of pure ruthenium. The ϵ-Ru(Pd) phase solidus above the peritectic temperature up to the melting point of pure ruthenium was again estimated by extrapolation. These are shown in the diagram as broken lines (Fig. 2(a)).

There are no experimental thermodynamic data apart from Kleykamp's [11] work. He measured the partial free energy of ruthenium using a calcia–zirconia solid electrolyte e.m.f. technique over the temperature range 1100–1200 K. The galvanic cell was operated using a two-phase Ru–50 at.%Pd alloy and partial free energies of ruthenium were derived directly as -5760 J mol^{-1} at 1100 K and -6260 J mol^{-1} at 1200 K.

Computer assessment of the system was attempted by Rand and Potter [2] but they do not report the calculated Gibbs excess free-energy coefficients.

3. Thermodynamic modelling

In the program of Lukas *et al.* the lattice stabilities of the pure elements are described by the equation

$$^0G = A - BT + CT(1 - \ln T) - \tfrac{1}{2}DT^2 - \tfrac{1}{2}ET^{-1} - \tfrac{1}{6}FT^3$$

In the present calculation the equations limited to the first two terms and lattice stability values of the pure elements ruthenium, rhodium and palladium are given in Table 1 [2, 14].

All the phases concerned were described using the regular or subregular models. The ordinary polynomial expression was employed for the composition dependence of the phases and the Gibbs energies are given by the following expression:

$$G_m = (1-x)_{Ru}\,{}^0G_{Ru} + x_{Pd}\,{}^0G_{Pd} + RT \times \{(1-x)_{Ru} \ln[(1-x)_{Ru}] + x_{Pd} \ln x_{Pd}\} + E_{G_m}$$

where the excess free energy is described as

$$E_{G_m} = (1-x)_{Ru} x_{Pd} (A_0 + A_1 x_{Pd})$$

$1-x$ and x are the mole fraction of individual components, ^0G_i are the lattice stability values of pure elements and A_i are the binary polynomial coefficients which are temperature dependent.

TABLE 1. Gibbs energies of transformations of elements

Element	Stable solid phase ϕ	$G^{liq} - G^{\phi}$ (J mol^{-1})	$G^{f.c.c.} - G^{\phi}$ (J mol^{-1})	$G^{h.c.p.} - G^{\phi}$ (J mol^{-1})
Pd	F.c.c.	$16480 - 9.02T$	0	$4180 + 5.86T$
Rh	F.c.c.	$26568 - 1188T$	0	$628 + 0.63T$
Ru	H.c.p.	$38589 - 14.802T$	$17570 - 5.86T$	0

4. Optimization

For the Ru–Rh system, only experimental phase diagram data points extending from 1173 to 2573 K including estimated solidus + liquidus data were used for input to the program data set. No additional estimated thermodynamic information was included.

The Ru–Pd phase diagram data points based mainly on the studies of Darling and Yorke [9], Obrowski and Zwingmann [10] and Kleykamp [11] have been utilized in the assessment of the system above 1073 K. The temperatures reported which are slightly different for the peritectic reaction together with slightly varied phase compositions were added to the data set. The suggested intermediate phase and the eutectic reaction information were not included. The estimations made by Kleykamp above the peritectic temperature were also input so as to guide the program of Lukas *et al.* to obtain reasonable Gibbs free-energy coefficients of the liquid phase.

The partial free energies for ruthenium of between 1100 and 1200 reported by Kleykamp were the only experimental thermodynamic data in the optimization. No estimated thermodynamic information was used.

The lattice stabilities for the elements combined with the phase diagram and thermodynamic data for each system were utilized in the program of Lukas *et al.* and following some attempts the best of coefficients producing the phase diagrams for Ru–Rh and Ru–Pd were obtained. The coefficients are shown in Table 2.

TABLE 2. The assessed Gibbs excess free-energy coefficients of the phases in binary Ru–Rh and Ru–Pd systems

Phase	Temperature dependence	Composition dependence
Ru–Rh system		
Liquid	$-35739.32 + 16.369T$	$(1-x)_{Ru} x_{Rh}$
F.c.c.	$-53477.07 + 21.738T$	$(1-x)_{Ru} x_{Rh}$
H.c.p.	$-26440.004 + 10.445T$	$(1-x)_{Ru} x_{Rh}$
Ru–Pd system		
Liquid	$187564.062 - 63.661T$	$(1-x)_{Ru} x_{Pd}$
	$-62169.281 + 6.64T$	$(1-x)_{Ru} x_{Pd} (x_{Pd})$
F.c.c.	$-5049.035 + 17.59T$	$(1-x)_{Ru} x_{Pd}$
H.c.p.	$-1524.818 + 14.933T$	$(1-x)_{Ru} x_{Pd}$

5. Results and discussion

5.1. *The Ru–Rh system*

A comparison of the experimental and calculated diagrams are shown in Figs. 1(a) and 1(b) respectively. It is clearly seen that the fitting of the experimental data is quite good although no thermodynamic data were utilized. The peritectic region and $\alpha+\epsilon$ two-phase fields are reproduced nicely. The peritectic temperature was calculated as 2364 K which is only 1 K above the value found experimentally [7]. The estimated liquidus lines are reasonably well established and they would be better if some experimental data were available. The calculated Gibbs energy curves for the phases are shown in Fig. 3. These results suggest that interaction between atoms of the system is not very strong and use of the regular model is adequate to reestablish the diagram.

5.2. *The Ru–Pd system*

The optimized diagram is compared with the experimental diagram in Figs. 2(a) and 2(b). As can be seen, agreement with the experimental diagram is very satisfactory. The peritectic temperature was found to be the same with the value established experimentally (1867 K). Rand and Potter reported [2] this temperature as 1910 K which is rather high and might be the consequence of the estimated thermodynamic data used. The temperature dependence of the h.c.p. Ru(Pd) and f.c.c. Pd(Ru) phase limits are calculated quite well.

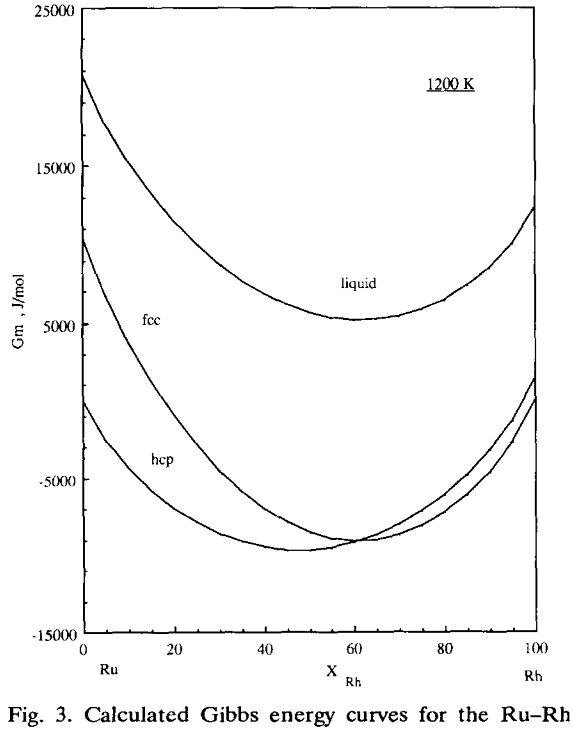

Fig. 3. Calculated Gibbs energy curves for the Ru–Rh system at 1200 K.

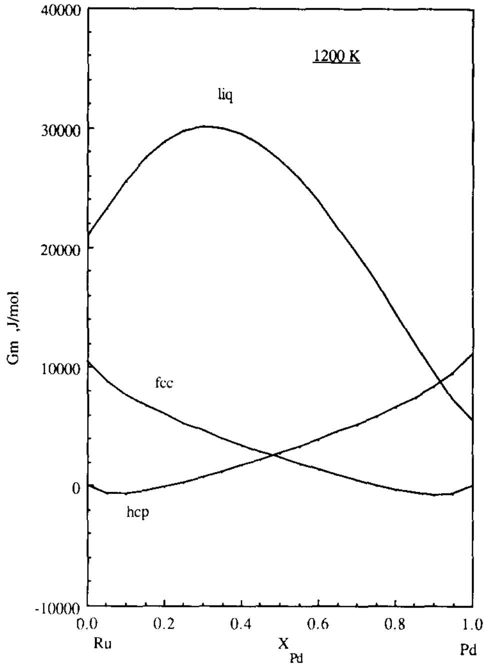

Fig. 4. Calculated Gibbs energy curves for the Ru–Pd system at 1200 K.

The equilibria involving the liquid phase + h.c.p. Ru(Pd) and the liquid phase + f.c.c. Pd(Ru) were also reproduced nicely although no thermodynamic data were available. These regions could be further improved if some experimental thermodynamic data were available. The Gibbs energy curves calculated using the regular or subregular models are shown in Fig. 4. The closeness of the calculated composition limits of the phases and their temperature variations show that the regular and subregular models were applied successfully to reproduce the Ru–Pd diagram. These results very clearly demonstrate that the coefficients thus obtained are very suitable for use in the relevant ternary phase diagram calculation.

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