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VAPORIZATION STUDY ON FISSION-PRODUCED NOBLE METAL ALLOYS BY MASS-SPECTROMETRIC METHOD *

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ABSTRACT

The vapor pressures over the ϵ-phase of the $Mo_xRu_yPd_z$ alloys ($x = 0.20–0.45$, $y = 0.15–0.60$, $z = 0.20–0.40$) were measured by means of mass spectrometry in the temperature range 1536–1791 K. Palladium vapor was observed as the only gaseous species. The chemical activities of palladium in the alloys, determined from the vapor pressures of Pd(g), were compared with those calculated on the basis of the regular solution model using the Kaufman and Bernstein parameters. Applying a least-squares fit to the chemical activity of palladium obtained experimentally in this study, the interaction parameters and the free energy of formation were determined for the regular solution model and the Hillert model. The vapor pressures of Mo(g) and Ru(g) over the Mo–Ru–Pd alloys were calculated using the regular solution model. Thermodynamic quantities such as the partial molar free energy of mixing, the excess partial molar free energy of palladium and the partial molar enthalpy and entropy of Pd(g) over the Mo–Ru–Pd alloys were also calculated from the palladium vapor pressures.

INTRODUCTION

White metallic inclusions composed of noble metals (ruthenium, rhodium, palladium), technetium and molybdenum are known to exist mainly as the hexagonal ϵ-phase in irradiated nuclear fuels [1–3]. Thermodynamic data on these metallic inclusions are of importance, for example in the case of a severe accident involving the power reactor or in the case of dissolution in the reprocessing of spent fuel. Since technetium and rhodium form completely solid solutions with ruthenium and palladium, respectively, three-component alloys consisting of ruthenium, palladium and molybdenum are representative of these metallic inclusions.

A thermodynamic study of the Mo–Ru–Pd alloys has been carried out by Yamawaki et al. [4], who determined the activities of molybdenum in the

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honor of his contribution to calorimetry and thermal analysis.

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Mo–Ru–Pd alloys in the temperature range 1200–1300 K by measuring the e.m.f. values of galvanic cells using the solid electrolyte $ZrO_2(+CaO)$. Recently vapor pressure measurements over pure Pd, $Mo_{0.450}Ru_{0.450}Pd_{0.100}$ and $Mo_{0.225}Ru_{0.675}Pd_{0.100}$ were carried out by the present authors [5], and the chemical activity of palladium determined from the vapor pressure of Pd(g) was found to be lower than that calculated from the regular solution model with Kaufman and Bernstein's parameters [6].

In the present work, the vapor pressure measurements over Mo–Ru–Pd alloys of five different compositions in the single ϵ-phase region was carried out by mass spectrometry in the temperature range 1536–1791 K in an attempt to derive the chemical activity and thermodynamic quantity of palladium in the ϵ-phase of the Mo–Ru–Pd alloys as a function of composition and to compare them with those calculated on the basis of the regular solution model using the values of the Kaufman and Bernstein's parameter [6]. By applying a least-squares analysis to the chemical activities derived experimentally using the vapor pressures, values of the free energy and interaction parameter were determined for the regular solution model and for the Hillert model [7]. The vapor pressures of Ru(g) and Mo(g) over the Mo–Ru–Pd alloys were estimated as functions of temperature and composition using the regular solution model. Thermodynamic quantities such as the partial molar free energy of mixing, the excess partial molar free energy of palladium and the partial molar enthalpy and entropy of Pd(g) were also calculated from the palladium vapor pressures.

EXPERIMENTAL

Sample preparation

The alloys were prepared from molybdenum, ruthenium and palladium powders, each of which had a purity of 99.9%. Samples of about 0.5 g were prepared with different proportions of Mo, Ru and Pd powders and pressed into pellets, which were then placed in a tungsten Knudsen cell and heated in a high frequency induction furnace at 1723 K in vacuum (10^{-4}–10^{-5} Pa) for about 2 h. For all the samples the weight loss was observed to be < 1 mg. The weight loss is caused by the vaporization of Pd only, since the vapor pressure of Pd is much higher than that of Mo or Ru. Since the error in the nominal composition of Pd is very small ($< 2\%$ of Pd content), the nominal compositions of alloys were adopted as the compositions for the samples in the present study. The samples prepared in the present study were as follows: $Mo_{0.200}Ru_{0.600}Pd_{0.200}$, $Mo_{0.400}Ru_{0.400}Pd_{0.200}$, $Mo_{0.350}Ru_{0.350}Pd_{0.300}$, $Mo_{0.400}Ru_{0.200}Pd_{0.400}$ and $Mo_{0.450}Ru_{0.150}Pd_{0.400}$. For the vaporization studies the sample pellets were pulverized to a powder.

Apparatus and method for vapor pressure measurements

The vapor pressures were measured using a time-of-flight mass spectrometer (CVC model MA-2) equipped with an alumina Knudsen cell in a tungsten holder heated by electron bombardment. The electron energy used to ionize the palladium vapor was 14 eV. The absolute pressure was determined by comparing the intensity of the ionic current of the palladium vapor with that of silver vapor over silver metal. Atomic ionization cross-sections for Pd and Ag were taken from the table by Mann [8]. The relative multiplier gain was calculated by assuming inverse proportionality to the square root of the mass of the vaporizing species [9]. Temperature measurement was made with a Leeds and Northrup disappearing-filament optical pyrometer, for which the error was determined to be ± 5 K by comparison with the melting point of Pt metal and the e.m.f. values of a Pt–Pt–13% Rh thermocouple. Observation was made through an orifice in the Knudsen cell. To keep the compositional change of samples as small as possible during the vaporization experiments, all measurements reported in this study were carried out within 2 h. Before and after the vapor pressure measurements, X-ray diffraction analysis indicates that each powder sample was of single ϵ-phase with a h.c.p. structure.

RESULTS AND DISCUSSION

Vapor pressure

Only one gaseous species, Pd(g), was observed over the ϵ-phase of the Mo–Ru–Pd alloys. The temperature dependence of the vapor pressure of

TABLE 1

Parameters for equations for calculating the vapor pressures of Pd(g) [a]

Sample	A	B	Temp. range (K)	Ref.
Pd	1.9425	11.194	1200–1640	[1]
Pd	1.8655	10.868	1294–1488	[2]
Pd	1.963 ± 0.033	11.438 ± 0.200	1567–1758	[3]
$Mo_{0.450}Ru_{0.450}Pd_{0.100}$	1.925 ± 0.032	10.380 ± 0.190	1603–1775	[3]
$Mo_{0.225}Ru_{0.675}Pd_{0.100}$	1.928 ± 0.007	10.780 ± 0.139	1576–1757	[3]
$Mo_{0.200}Ru_{0.600}Pd_{0.200}$	1.947 ± 0.003	11.016 ± 0.097	1538–1791	This study
$Mo_{0.400}Ru_{0.400}Pd_{0.200}$	1.941 ± 0.006	10.732 ± 0.118	1546–1760	This study
$Mo_{0.350}Ru_{0.350}Pd_{0.300}$	1.933 ± 0.011	10.827 ± 0.211	1544–1753	This study
$Mo_{0.400}Ru_{0.200}Pd_{0.400}$	1.933 ± 0.013	10.757 ± 0.258	1558–1760	This study
$Mo_{0.450}Ru_{0.150}Pd_{0.400}$	1.941 ± 0.006	10.743 ± 0.123	1536–1761	This study

[a] $\text{Log}\,(p(\text{Pa}) \equiv -(A\times10^4)/(T+B)$.

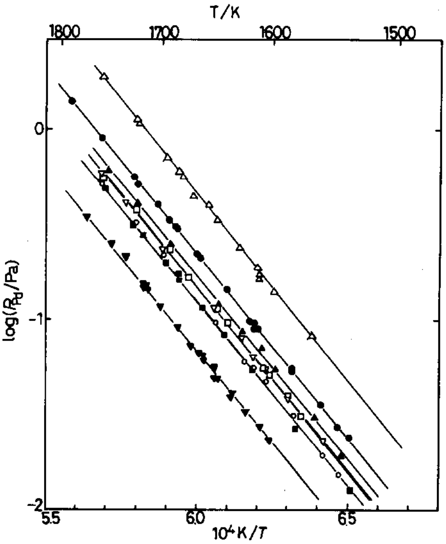

Fig. 1. Temperature dependences of the vapor pressures of Pd(g) over pure Pd and over Mo–Ru–Pd alloys: △, pure Pd [5]; ▼, $Mo_{0.450}Ru_{0.450}Pd_{0.100}$ [5]; □, $Mo_{0.225}Ru_{0.675}Pd_{0.100}$ [5]; ●, $Mo_{0.200}Ru_{0.600}Pd_{0.200}$; ▽, $Mo_{0.400}Ru_{0.200}Pd_{0.400}$; ■, $Mo_{0.450}Ru_{0.150}Pd_{0.400}$; ○, $Mo_{0.400}Ru_{0.400}Pd_{0.200}$; ▲, $Mo_{0.350}Ru_{0.350}Pd_{0.300}$.

Pd(g) over $Mo_{0.200}Ru_{0.600}Pd_{0.200}$, $Mo_{0.400}Ru_{0.400}Pd_{0.200}$, $Mo_{0.350}Ru_{0.350}Pd_{0.300}$, $Mo_{0.400}Ru_{0.200}Pd_{0.400}$ and $Mo_{0.450}Ru_{0.150}Pd_{0.400}$ obtained in this study is shown in Fig. 1, together with that over $Mo_{0.450}Ru_{0.450}Pd_{0.100}$, $Mo_{0.225}$-$Ru_{0.675}Pd_{0.100}$ and pure Pd metal previously reported by the present authors [5]. The vapor pressure equations obtained from a least-squares analysis are given in Table 1.

It may be seen from Fig. 1 that (1) the vapor pressures of Pd(g) over the Mo–Ru–Pd alloys are lower than that over pure palladium metal, as was expected, and (2) the vapor pressures of Pd(g) do not simply vary with the concentrations of palladium in the Mo–Ru–Pd alloys. Using the vapor pressure value of Pd(g) over pure palladium metal obtained experimentally by the present authors [5], the vapor pressures of Pd(g) over the $Mo_xRu_yPd_z$ alloys can be calculated from the chemical activity of palladium on the basis of the regular solution model using the Kaufman and Bernstein parameters (eqns. (1)–(5)) [6].

$$RT \ln a_{Pd} = G_{Pd} + RT \ln z + y^2E_1 + (1-z)^2E_2 - y(1-z)E_3 \tag{1}$$

$$G_{Pd} = 1046 + 1.255T \ (\mathrm{J\ mol^{-1}}) \tag{2}$$

$$E_1 = -30\,966 \ (\mathrm{J\ mol^{-1}}) \tag{3}$$

$$E_2 = -20\,175 \ (\mathrm{J\ mol^{-1}}) \tag{4}$$

and

$$E_3 = E_1 + E_2 - E_3' \ (\mathrm{J\ mol^{-1}}) \tag{5}$$

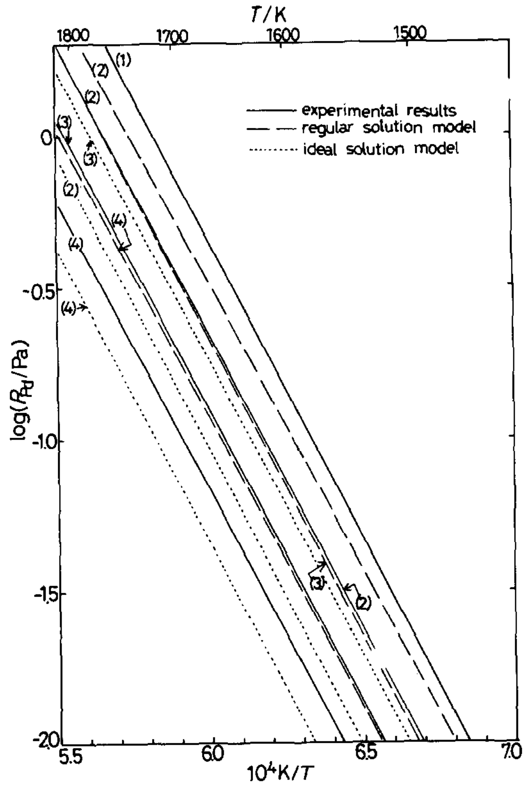

Fig. 2. Comparison of Pd(g) vapor pressures obtained experimentally with those calculated using the regular solution model and the ideal solution model: (1) Pd(g) over Pd(s); (2) Pd(g) over $Mo_{0.200}Ru_{0.600}Pd_{0.200}$(s); (3) Pd(g) over $Mo_{0.450}Ru_{0.150}Pd_{0.400}$(s); (4) Pd(g) over $Mo_{0.450}Ru_{0.450}Pd_{0.100}$(s).

where G_{Pd} is the difference in the free energy of formation between α(f.c.c.) and ϵ(h.c.p.) forms of palladium, E_1, the interaction parameter of the ϵ-phase for the binary Mo–Ru system, E_2, that of the binary Mo–Pd system, E_3', that of the binary Ru–Pd system and R the gas constant. The vapor pressures of Pd(g) over the $Mo_{0.200}Ru_{0.600}Pd_{0.200}$ and $Mo_{0.450}Ru_{0.150}Pd_{0.400}$ samples thus calculated are shown in Fig. 2, together with those over pure palladium metal and $Mo_{0.450}Ru_{0.450}Pd_{0.100}$ previously reported by the present authors [5], and those calculated from the ideal solution model. The vapor pressures of Pd(g) measured experimentally over these three Mo–Ru–Pd alloys are lower than those calculated from the regular solution model, but the vapor pressures of Pd(g) observed in the present experiment have an order of magnitude in accord with those predicted using the regular solution model. The vapor pressures of Pd(g) obtained experimentally over the $Mo_{0.200}Ru_{0.600}Pd_{0.200}$ and $Mo_{0.450}Ru_{0.450}Pd_{0.100}$ samples are higher than those calculated from the ideal solution model, but those experimental values over $Mo_{0.450}Ru_{0.150}Pd_{0.400}$ are

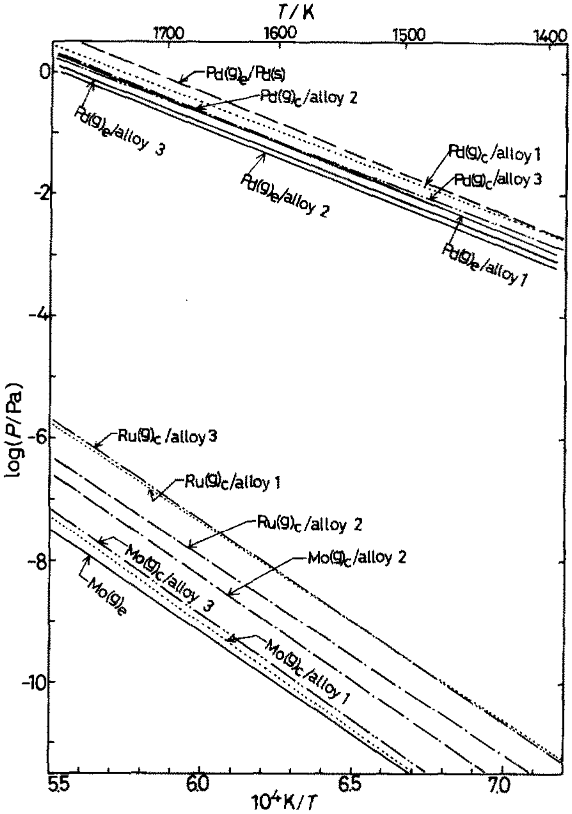

Fig. 3. Temperature dependences of the vapor pressures of Pd(g), Ru(g) and Mo(g) over $Mo_{0.200}Ru_{0.600}Pd_{0.200}$, $Mo_{0.450}Ru_{0.150}Pd_{0.400}$ and $Mo_{0.225}Ru_{0.675}Pd_{0.100}$: — — — $Pd(g)_e$, experimental values for pure Pd(s) in this study; ——— $Pd(g)_e$, experimental values for $Mo_{0.200}Ru_{0.600}Pd_{0.200}$ (alloy 1), for $Mo_{0.450}Ru_{0.150}Pd_{0.400}$ (alloy 2) and $Mo_{0.225}Ru_{0.675}Pd_{0.100}$ (alloy 3); ——— $Mo(g)_e$, extrapolated values for $Mo_{0.200}Ru_{0.580}Pd_{0.220}$ from the e.m.f. data obtained experimentally by Yamawaki et al. [4] in the range 1200–1300 K.

lower than those predicted by this model. This suggests that the Mo–Ru–Pd alloys exhibit positive or negative deviations from ideal behavior depending on the contents of molybdenum, ruthenium and palladium in the alloys.

The vapor pressures of Mo(g) and Ru(g) over Mo–Ru–Pd alloys can also be calculated using the regular solution model (similar equations of a_{Mo} to that of a_{Pd} in eqn. (1)) using the vapor pressure of Mo(g) over pure molybdenum metal [10] and that of Ru(g) over pure ruthenium metal [11], respectively. The vapor pressures of Mo(g) and Ru(g) over $Mo_{0.225}Ru_{0.675}$-$Pd_{0.100}$, $Mo_{0.200}Ru_{0.600}Pd_{0.200}$ and $Mo_{0.450}Ru_{0.150}Pd_{0.400}$ thus calculated are shown in Fig. 3 together with those of Pd(g). The vapor pressures of Mo(g) over $Mo_{0.20}Ru_{0.58}Pd_{0.22}$ at high temperatures were also estimated by the present authors from the e.m.f. data experimentally obtained by Yamawaki et al. [4] in the temperature range 1200–1300 K, and extrapolated to the high temperatures as shown in Fig. 3. As may be seen from this figure, the vapor pressures of Mo(g) and Ru(g) are extremely low compared with those of Pd(g). It may be concluded that the ϵ-phase of the Mo–Ru–Pd alloy vaporizes incongruently with preferential loss of palladium.

Chemical activity

The chemical activities and activity coefficients of the Mo–Ru–Pd alloys determined from the vapor pressures of Pd(g) are given in Table 2, including those at 1723 K calculated on the basis of the regular solution model using eqns. (1)–(5). Some activity coefficients of palladium are large at this temperature. A large activity coefficient is often attributed to the presence of a precipitated second phase, but the effect of such a phase need not be considered here because Mo–Ru–Pd alloy samples were chosen to be in the single ϵ-phase region according to the experimental phase diagram previously determined by the present authors [5]. In addition, X-ray diffraction analysis showed the presence of the single ϵ-phase only, before and after the vaporization experiments. The orders of magnitude of the vapor pressures of Pd(g) over Mo–Ru–Pd alloys indicated by the experiment are in accord with those predicted using the regular solution model with eqns. (1)–(5) (Fig. 2). Hence, the difference in the concentrations of molybdenum and ruthenium in the ϵ-phase is thought to affect significantly the activity of palladium.

The chemical activity values obtained experimentally at 1723 K for palladium (a_{Pd}) in the Mo–Ru–Pd alloys are plotted in Figs. 4–6 together with those calculated on the basis of the regular solution model using eqns. (1)–(5). In Fig. 4, the experimental values of a_{Pd} for Mo–Ru–Pd alloys with the concentration ratio $N_{Mo}/N_{Ru} = 1$ show positive deviation from ideal solution behavior. The values of a_{Pd} calculated using the regular solution model also show a positive deviation. The values of a_{Pd} and a_{Mo} for the

TABLE 2

Activity and activity coefficients of Pd in ϵ-phase of Mo–Ru–Pd alloys

Sample	Chemical activity log a_e	Temp. range (K)	Chemical activity ($T = 1723$ K)		Activity coefficient ($T = 1723$ K)		Activity ratio a_c/a_e
			a_e [a]	a_c [b]	γ_e [a]	γ_c [b]	
$Mo_{0.450}Ru_{0.450}Pd_{0.100}$	$380/T - 1.058$	1603–1775	0.145	0.252	1.45	2.52	1.74
$Mo_{0.225}Ru_{0.675}Pd_{0.100}$	$350/T - 0.700$	1576–1757	0.319	0.452	3.19	4.52	1.42
$Mo_{0.200}Ru_{0.600}Pd_{0.200}$	$160/T - 0.422$	1538–1791	0.469	0.693	2.35	3.47	1.48
$Mo_{0.400}Ru_{0.400}Pd_{0.200}$	$220/T - 0.710$	1546–1760	0.262	0.434	1.31	2.17	1.66
$Mo_{0.350}Ru_{0.350}Pd_{0.300}$	$300/T - 0.611$	1544–1753	0.366	0.572	1.22	1.91	1.57
$Mo_{0.400}Ru_{0.200}Pd_{0.400}$	$300/T - 0.681$	1558–1760	0.311	0.543	0.778	1.36	1.75
$Mo_{0.450}Ru_{0.150}Pd_{0.400}$	$220/T - 0.695$	1536–1761	0.271	0.476	0.677	1.19	1.76

[a] Experimental value. [b] Value calculated on the basis of the regular solution model.

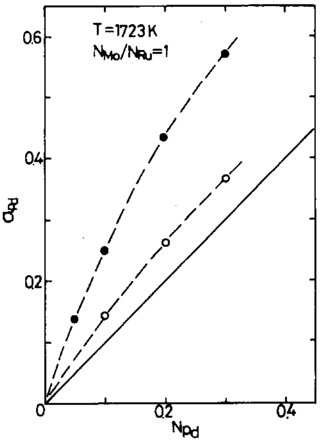

Fig. 4. Activities of palladium a_{Pd} versus atomic fractions of palladium N_{Pd}: ○ - - - - - - ○, experimental values; ● - - - - - - ●, values calculated by the regular solution model; ———, ideal solution model.

Mo–Ru–Pd alloys with $N_{Mo}/N_{Ru} = 1/3$ at 1723 K are shown in Fig. 5. The values of a_{Pd} exhibit a positive deviation while on the other hand, those of a_{Mo} exhibit a negative deviation. It may be seen from Figs. 4–6 that the values of a_{Pd} for the Mo–Ru–Pd alloys depend on the concentration ratio N_{Mo}/N_{Ru}, the a_{Pd} values decrease with increasing N_{Mo}/N_{Ru} ratio, and the experimental values of a_{Pd} are somewhat different from those estimated using the regular solution model with eqns. (1)–(5). Kaufman and Bernstein

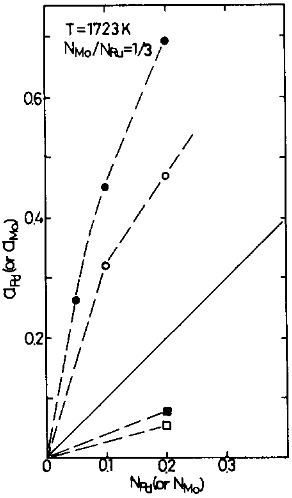

Fig. 5. Activities of palladium a_{Pd} and molybdenum a_{Mo} versus atomic fractions N_{Pd} and N_{Mo}: ○———○, experimental values of a_{Pd}; ●———●, values of a_{Pd} calculated by the regular solution model; □———□, experimental values of a_{Mo}; ■———■, values of a_{Mo} calculated by the regular solution model; ———, ideal solution model.

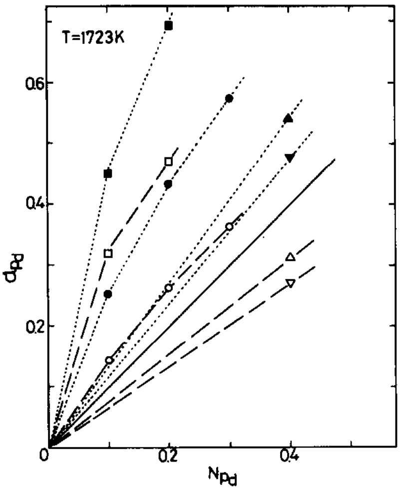

Fig. 6. Activities of palladium a_{Pd} versus atomic fractions of palladium N_{Pd} for Mo–Ru–Pd alloys with various ratios of N_{Pd}/N_{Ru}: ▽———▽, experimental values and ▼———▼, values calculated by the regular solution model for $N_{Mo}/N_{Ru} = 3$; △———△, experimental values and ▲———▲, calculated values for $N_{Mo}/N_{Ru} = 2$; ○———○, experimental values and ●———●, calculated values for $N_{Mo}/N_{Ru} = 1$; □———□, experimental values and ■———■, calculated values for $N_{Mo}/N_{Ru} = 1/3$; ———, ideal solution model.

assumed the values of E_1, E_2 and E_3 to be independent of temperature in eqn. (1) (RSM-I model). To improve the agreement between the calculated and observed activity values, two models were adopted by applying a least-square fit to the experimental a_{Pd} values of pure Pd and Mo–Ru–Pd alloys. One was the regular solution model (RSM-II) similar to eqn. (1) but the interaction parameters of E_1, E_2 and E_3 in eqn. (1) were assumed to be the linear functions of temperature. The other was the Hillert model [7] which includes the excess free energy (G^E) in the following form

$$G^E = xy[E_1 + (y-x)E_4] + yz[E_2 + (z-y)E_5] + zx[E_3 + (x-z)E_6] \tag{6}$$

and gives the chemical activity of palladium for $Mo_xRu_yPd_z$ alloys as

$$\begin{aligned} RT \ln a_{Pd} = {} & G_{Pd} + RT \ln z + y^2E_1 + (1-z)^2E_2 - y(1-z)E_3 \\ & + [2yx(x-y)]E_4 + [x(x-4zx-2yz)]E_5 \\ & + [2xyz + y^2(4z-1)]E_6 \end{aligned} \tag{7}$$

where E_4, E_5 and E_6 are the interaction parameters of the binary Mo–Ru, Mo–Pd and Ru–Pd systems, respectively. Using the Hillert model, two analyses were carried out. First the interaction parameters E_1, E_2 and E_3 were assumed to have constant values, as proposed by Kaufman and Bernstein, and E_4, E_5, E_6 and G_{Pd} were assumed to be linear functions of temperature (HLM-I model). Second, all interaction parameters E_1–E_6 and

TABLE 3

Parameters of the regular solution model and the Hillert model

Parameters	RSM-I [a]	This study ($J\ mol^{-1}$)		
		RSM-II [b]	HLM-I [b]	HLM-II [b]
E_1	-30966	$48909-68.674T$	-30966	$-70215-5.609T$
E_2	-20175	$35781-48.100T$	-20175	$-81194+48.303T$
E_3	-80513	$70905-123.470T$	-80513	$-214579+96.441T$
E_4	–	–	$95546-66.167T$	$264093-257.192T$
E_5	–	–	$-49828+33.849T$	$-44732+33.716T$
E_6	–	–	$-26995+19.721T$	$-41330+30.061T$
G_{Pd}	$1046+1.255T$	$-2387+1.255T$	$-5183+1.255T$	$61.732-0.033T$

[a] RSM-I: regular solution model by Kaufman and Bernstein [6].

[b] RSM-II, HLM-I, HLM-II: see the text in this study.

the free energy of formation G_{Pd} were assumed to be linear functions of temperature (HLM-II model). Interaction parameters and the free energy of formation obtained from a least-square fitting by RSM-II, HLM-I and HLM-II models are given in Table 3, together with those calculated using

TABLE 4

Chemical activities of palladium

Sample	T(K)	a_e [a]	a_c RSM-I [b]	a_c RSM-II [c]	a_c HLM-I [c]	a_c HLM-II [c]
$Mo_{0.450}Ru_{0.450}Pd_{0.100}$	1723	0.145	0.252	0.142	0.164	0.145
	1540	0.154	0.275	0.152	0.168	0.153
$Mo_{0.400}Ru_{0.200}Pd_{0.400}$	1723	0.311	0.543	0.326	0.320	0.311
	1540	0.326	0.553	0.337	0.332	0.326
$Mo_{0.450}Ru_{0.150}Pd_{0.400}$	1723	0.271	0.476	0.264	0.272	0.271
	1540	0.280	0.477	0.276	0.284	0.281
$Mo_{0.200}Ru_{0.600}Pd_{0.200}$	1723	0.469	0.693	0.487	0.490	0.468
	1540	0.481	0.788	0.504	0.501	0.481
$Mo_{0.225}Ru_{0.675}Pd_{0.100}$	1723	0.319	0.452	0.310	0.311	0.318
	1540	0.337	0.534	0.325	0.329	0.336
$Mo_{0.350}Ru_{0.350}Pd_{0.300}$	1723	0.366	0.572	0.369	0.367	0.365
	1540	0.384	0.607	0.381	0.376	0.379
$Mo_{0.400}Ru_{0.400}Pd_{0.200}$	1723	0.262	0.434	0.263	0.280	0.263
	1540	0.271	0.468	0.276	0.288	0.276

[a] Chemical activity of Pd obtained experimentally in this study.

[b] Chemical activity of Pd calculated on the basis of the regular solution model using Kaufman and Bernstein parameters.

[c] Chemical activity of Pd calculated from three models described in this paper.

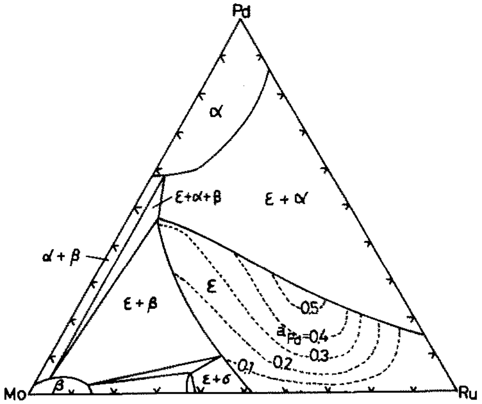

Fig. 7. Iso-activity curves at 1723 K calculated from the HLM-II model in this study.

the model proposed by Kaufman and Bernstein (RSM-I model). Imoto et al. [12] have recently published values of the temperature-dependent interaction parameters and the free energy of formation on the basis of the Hillert model using binary phase diagrams of Mo–Ru, Ru–Pd and Mo–Pd [13–15]. The chemical activities of palladium over Mo–Ru–Pd alloys of seven different compositions were calculated in this study from the parameters proposed by Imoto et al. Calculated values were higher than those obtained experimentally in this study in all cases. The chemical activities of palladium calculated on the basis of four models (RSM-I, RSM-II, HLM-I and HLM-II) are summarized in Table 4. As may be seen from this table, agreement between the chemical activities of palladium calculated from three models (RSM-II, HLM-I, HLM-II) and those obtained experimentally is fairly good in comparison with those based on the model by Kaufman and Bernstein (RSM-I). Although the difference between three of the models (RSM-II, HLM-I and HLM-II) in the present study seems to be small, the HLM-II model including the seven temperature-dependent parameters (E_1–E_6, G_{Pd}) may show best fit to represent the experimental result. The iso-activity curves calculated from the HLM-II model at 1723 K are shown in Fig. 7.

Thermodynamic quantities

Partial molar free energy of mixing $\Delta\overline{G}_i$ and the excess partial molar free energy $\Delta\overline{G}_i^{\mathrm{E}}$ of the component i can be calculated from the chemical activity, a_i and the molar fraction of the component i, N_i, in the alloy by the following equations

$$\Delta\overline{G}_i = RT\ \ln(a_i) \tag{12}$$

$$\Delta\overline{G}_i^{\mathrm{E}} = \Delta\overline{G}_i - RT\ \ln(N_i) \tag{13}$$

TABLE 5

Partial molar quantities of palladium for ϵ-phase of Mo–Ru–Pd alloy

Sample	Partial molar free energy of mixing of Pd $\Delta\overline{G}_{Pd}$(J mol^{-1})	Excess partial molar free energy of Pd $\Delta\overline{G}^E_{Pd}$(J mol^{-1})	Temp. range (K)	$\Delta\overline{G}^E_{Pd}$(1723 K) (J mol^{-1})
$Mo_{0.450}Ru_{0.450}Pd_{0.100}$	$\Delta\overline{G}_{Pd} = 7276 - 20.26T$	$\Delta\overline{G}^E_{Pd} = 7276 - 1.11T$	1603–1775	5363
$Mo_{0.225}Ru_{0.675}Pd_{0.100}$	$\Delta\overline{G}_{Pd} = 6701 - 13.40T$	$\Delta\overline{G}^E_{Pd} = 6701 + 5.75T$	1576–1757	16608
$Mo_{0.200}Ru_{0.600}Pd_{0.200}$	$\Delta\overline{G}_{Pd} = 3063 - 8.08T$	$\Delta\overline{G}^E_{Pd} = 3063 + 5.30T$	1538–1791	12195
$Mo_{0.400}Ru_{0.400}Pd_{0.200}$	$\Delta\overline{G}_{Pd} = 4212 - 13.59T$	$\Delta\overline{G}^E_{Pd} = 4212 - 0.174T$	1546–1760	3912
$Mo_{0.350}Ru_{0.350}Pd_{0.300}$	$\Delta\overline{G}_{Pd} = 5744 - 11.70T$	$\Delta\overline{G}^E_{Pd} = 5744 - 1.69T$	1544–1753	2832
$Mo_{0.400}Ru_{0.200}Pd_{0.400}$	$\Delta\overline{G}_{Pd} = 5744 - 13.04T$	$\Delta\overline{G}^E_{Pd} = 5744 - 5.42T$	1558–1760	−3595
$Mo_{0.450}Ru_{0.150}Pd_{0.400}$	$\Delta\overline{G}_{Pd} = 4212 - 13.31T$	$\Delta\overline{G}^E_{Pd} = 4212 - 5.69T$	1536–1761	−5592

TABLE 6

Partial molar enthalpies and entropies of Pd(g) of alloys at the average temperature over each range

Sample	Temp. range (K)	$\Delta\bar{H}$ (kJ mol^{-1})	$\Delta\bar{S}$ (J mol^{-1} K^{-1})
$Mo_{0.450}Ru_{0.450}Pd_{0.100}$	1603–1775	368.6 ± 6.1	198.7 ± 3.6
$Mo_{0.225}Ru_{0.675}Pd_{0.100}$	1576–1757	369.1 ± 1.3	205.6 ± 2.7
$Mo_{0.200}Ru_{0.600}Pd_{0.200}$	1538–1791	372.8 ± 0.6	210.9 ± 1.9
$Mo_{0.400}Ru_{0.400}Pd_{0.200}$	1546–1760	371.6 ± 1.1	205.5 ± 2.3
$Mo_{0.350}Ru_{0.350}Pd_{0.300}$	1544–1753	370.1 ± 2.1	207.3 ± 4.0
$Mo_{0.400}Ru_{0.200}Pd_{0.400}$	1558–1760	370.1 ± 2.5	206.0 ± 4.9
$Mo_{0.450}Ru_{0.150}Pd_{0.400}$	1536–1761	371.6 ± 1.1	205.7 ± 2.4

The values of $\Delta\bar{G}_{Pd}$ and $\Delta\bar{G}^{E}_{Pd}$ obtained in the present study are summarized in Table 5. The negative values of $\Delta\bar{G}^{E}_{Pd}$ for the Mo–Ru–Pd alloys with the concentration ratio $N_{Mo}/N_{Ru} > 2$ indicate the negative deviation of the chemical activities from Raoult's law. The partial molar enthalpies and entropies of Pd(g) over the alloys were also calculated from the palladium vapor pressure and are given in Table 6.

CONCLUSIONS

(1) The vapor pressures of Pd(g) over Mo–Ru–Pd alloys were measured as functions of composition and temperature by means of mass spectrometry. The vapor pressure of Pd(g) measured experimentally was much higher than that of Ru(g) and Mo(g) calculated using the regular solution model, indicating that the ϵ-phase of the Mo–Ru–Pd alloy vaporizes incongruently with the preferential loss of palladium.

(2) The chemical activities of palladium in the Mo–Ru–Pd alloys with constant N_{Mo}/N_{Ru} ratio increased with increasing atomic fraction of palladium (N_{Pd}).

(3) The chemical activities of palladium in the Mo–Ru–Pd alloys with constant N_{Pd} increased with decreasing ratio of N_{Mo}/N_{Ru}.

(4) The chemical activities of palladium in the Mo–Ru–Pd alloys obtained by the experiment were not in good agreement with those calculated from the regular solution model using Kaufman and Bernstein's parameters, but the order of magnitude of the experimental values was in accord with the expectation from the regular solution model.

(5) By applying a least-squares fitting, closer approximation was obtained using the revised regular solution model and Hillert's model than when using the regular solution model with Kaufman and Bernstein's parameters.

(6) Thermodynamic quantities such as the partial molar free energy of mixing of palladium, the excess partial molar free energy of palladium and the partial molar enthalpy and entropy of Pd(g) over the Mo–Ru–Pd alloys were also calculated from the palladium vapor pressures.

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