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**Oxidation Behaviour of Noble-Metal  
Inclusions in Used UO<sub>2</sub> Nuclear Fuel**

**Tenue à l'oxydation des inclusions de  
métal noble dans le combustible nucléaire  
à UO<sub>2</sub> irradié**

Rod McEachern

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OXIDATION BEHAVIOUR OF NOBLE-METAL INCLUSIONS  
IN USED  $\text{UO}_2$  NUCLEAR FUEL

by

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Research Chemistry Branch  
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ABSTRACT

The literature on the chemistry of the noble-metal (Mo-Rh-Ru-Pd-Tc) inclusions found in used nuclear fuel has been reviewed. The Mo-Ru-Pd phase diagram is reasonably well understood, and the pseudoternary Mo-(Tc+Ru)-Rh+Pd system can be used to qualitatively understand the phase chemistry of the noble-metal inclusions. The kinetics of the oxidation reaction are not particularly well understood, but they are of limited applicability to understanding the properties of used fuel. In contrast, it is important to determine the thermodynamic activity of molybdenum in noble-metal inclusions, so that analysis of their molybdenum content can be used as a probe of the local oxygen potential of the used fuel.

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TENUE À L'OXYDATION DES INCLUSIONS DE MÉTAL NOBLE DANS LE  
COMBUSTIBLE NUCLÉAIRE À  $UO_2$  IRRADIÉ

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RÉSUMÉ

L'auteur a examiné la documentation sur la chimie des inclusions de métal noble (Mo-Rh-Ru-Pd-Tc) dans le combustible nucléaire irradié. La courbe des phases Mo-Ru-Pd est raisonnablement bien comprise, et on peut utiliser le réseau pseudoternaire Mo-(Tc+Ru)-Rh+Pd) pour comprendre qualitativement la chimie de phase des inclusions de métal noble. La cinétique de la réaction d'oxydation n'est pas particulièrement bien comprise, mais elle s'applique de façon limitée à la compréhension des propriétés du combustible irradié. Par contraste, il est important de déterminer l'activité thermodynamique du molybdène dans les inclusions de métal noble, de sorte que l'on puisse utiliser l'analyse de la teneur en molybdène comme échantillon du potentiel d'oxygène local du combustible irradié.

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## 1. INTRODUCTION

The “white inclusions” containing Mo, Tc, Ru, Rh and Pd, in used (U,Pu)O<sub>2</sub> fuel have been studied extensively over the past 30 years (Kleykamp 1985 and references therein). The composition and phase chemistry of these noble-metal particles has received considerable attention because the slow dissolution rate of these particles in nitric acid complicates reprocessing of used fuel (Kleykamp 1988a,b). Moreover, the nature of the noble-metal inclusions provides insight into the oxygen potential of the fuel since the Mo/MoO<sub>2</sub> equilibrium occurs at oxygen potentials that are similar to the oxygen potentials of slightly hyperstoichiometric UO<sub>2+x</sub> (Kleykamp 1985). Oxidized molybdenum enters the complex (Ba,Sr,Cs) (U,Pu,Zr,Mo,RE)O<sub>3</sub><sup>1</sup> oxide phase (Kleykamp 1985) according to the equilibrium



so that the concentration of molybdenum in the alloy can be used to determine the local oxygen potential of the used fuel (Kleykamp 1977,1985,1988a).

## 2. FISSION PRODUCT INVENTORY OF Mo, Tc, Ru, Rh AND Pd

The total inventory of fission-product Mo, Tc, Ru, Rh and Pd has been calculated for typical used LWR fuel (Guenther et al. 1988) for burnups ranging between 20 and 50 MWd/kg U. Corresponding fission-product inventories for typical used CANDU<sup>®</sup> fuel (burnup = 7.93 MWd/kg U) have been calculated by Tait et al. (1989). For simplicity, the data on the concentration of Mo, Tc, Ru, Rh and Pd in the used fuel have been calculated in terms of their relative abundance, in atom %, and the results are given in Table 1 and illustrated in Figure 1. Examination of Figure 1 shows that used CANDU fuel is enriched in ruthenium and depleted in molybdenum, relative to used LWR fuel. These differences between the data for CANDU fuel and the data of LWR fuel are partly due to the different cooling times in the 2 types of calculations (6 a for LWR, immediately after discharge for CANDU) and partly due to different nuclear reactions inherent in the 2 types of fuel.

<sup>1</sup> RE = rare-earth elements

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TABLE 1

RELATIVE ABUNDANCE OF FISSION-PRODUCT Mo, Tc, Ru, Rh AND Pd  
IN USED UO<sub>2</sub> FUEL, CALCULATED IN TERMS OF ATOM %  
OF THE TOTAL Mo-Tc-Ru-Rh-Pd CONTENT

Data are for used LWR fuel 6 a after discharge, as calculated by Guenther (1988), except as noted otherwise.

Burnup (MWd/kg U)	Tc	Ru	Rh	Pd	Mo	Tc + Ru	Rh + Pd
20	9.98	26.03	6.17	14.75	43.07	36.01	20.92
25	9.58	26.33	5.84	16.24	42.01	35.91	22.08
30	9.22	26.62	5.50	17.56	41.10	35.84	23.06
35	8.88	26.89	5.16	18.79	40.29	35.77	23.95
40	8.55	27.14	4.83	19.88	39.55	35.69	24.71
45	8.26	27.41	4.52	20.88	38.94	35.67	25.40
50	7.98	27.67	4.24	21.77	38.38	35.65	26.01
7.93*	10.81	32.71	5.59	12.01	38.87	43.52	17.60

\* Data for typical CANDU fuel immediately after discharge, calculated from results presented by Tait et al. (1989).

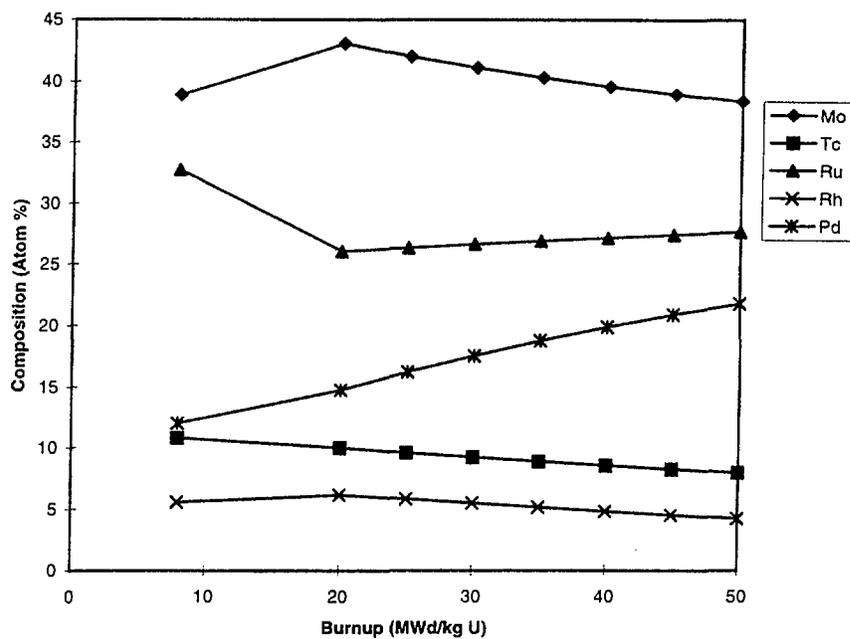


FIGURE 1: Composition of Mo-Tc-Rh-Ru-Pd Noble-Metal Inclusions in Used Fuel, as a Function of Burnup. Data are for used LWR fuel 6 a after discharge (Guenther et al. 1988) except for the points at 7.93 MWd/kg U, which are for freshly discharged used CANDU fuel (Tait et al. 1989).

### 3. RELEVANT PHASE DIAGRAMS

The 5-component Mo-Tc-Ru-Rh-Pd system is generally simplified by considering the ternary Mo-Ru-Pd system since the latter 3 are the most abundant elements in the noble-metal inclusions. Moreover, the Tc-Ru and Rh-Pd pairs are completely miscible (the latter only below 845°C) (Darby et al. 1962,1963; Paschoal 1983).

Kleykamp (1989) recently compiled data on the ternary Mo-Ru-Pd system in the temperature range 1133 to 1700°C and performed additional experiments to determine the ternary phase diagram at 1000°C (Figure 2). Examination of Figure 2 reveals that the ternary Mo-Ru-Pd system is dominated by the large solubility of molybdenum and palladium in the hexagonal-close-packed ruthenium lattice. The resulting solid solution Ru(Mo,Pd) is identified as the  $\epsilon$  phase in Figure 2. Solid solutions in the palladium and molybdenum lattices are identified as  $\alpha$  and  $\beta$  respectively in Figure 2. The intermediate phases  $\epsilon'$  ( $\text{Mo}_9\text{Pd}_{11}$ ) and  $\sigma$  ( $\text{Mo}_5\text{Ru}_3$ ) are stable only over the limited temperature ranges 1370 to 1720°C and 1143 to 1915°C respectively (Kleykamp 1989).

Kleykamp (1985,1988a,1989) surveyed available X-ray microanalysis and XRD powder diffraction (XRD) data of noble-metal particles in used (U,Pu) $\text{O}_2$  fuel and reported that they generally consist of the single Ru(Mo,Tc,Rh,Pd) hexagonal  $\epsilon$  phase. There are, however, many exceptions. Fuels with a high molybdenum content and low oxygen potential consist of two phases: below 1900°C high-power LWR fuel rods display the  $\epsilon$  and the  $\beta$  phases (Kleykamp 1979, Kleykamp et al. 1985), whereas above 1900°C, coated-high-temperature reactor (HTR) fuel particles display both the  $\epsilon$  and the  $\sigma$  phases (Forthmann et al. 1974, Kleykamp 1975). Also, the cold regions of fast breeder reactor (FBR) fuel have low molybdenum and high palladium contents; thus they can display a mixture of  $\epsilon$  and  $\alpha$  phases (Kleykamp 1985, Kleykamp et al. 1985). The data for used LWR, HTR and FBR fuels, presented by Kleykamp (1988a), are illustrated in Figure 3(a). The phase diagram shown in Figure 3(a) is the ternary Mo-Ru-Pd system (1700°C) upon which is projected the pseudoternary Mo-(Tc+Ru)-(Rh+Pd) data for the various used fuels.

The data of Kleykamp (1985,1988a,1989) display good agreement between the observed phases in the Mo-Tc-Ru-Rh-Pd system and the isothermal section of the ternary Mo-Ru-Pd phase diagram. We thus conclude that the Mo-Ru-Pd ternary phase diagram is an acceptable tool for description of the phase chemistry of the noble-metal inclusions. The composition data for used LWR and CANDU fuel, as shown in Table 1 are thus illustrated in Figure 3(b) with the pseudoternary Mo-(Tc+Ru)-(Rh+Pd) system at 1000°C.

Examination of Figure 3(b) shows that at 1000°C the composition of Mo-Tc-Ru-Rh-Pd inclusions in used CANDU fuel is in the  $\epsilon$  field, near the border with the two-phase ( $\epsilon+\beta$ ) field. We thus expect that noble-metal inclusions in used CANDU fuel will generally be only of the  $\epsilon$  phase. However, molybdenum-rich samples might display (in addition to the  $\epsilon$  phase) formation of some  $\sigma$  phase ( $\text{Mo}_5\text{Ru}_3$ ) if the sample were heated to very high temperatures (e.g. 1900°C) or formation of the  $\beta$  phase at lower temperatures. The  $\beta$  phase thus formed would subsequently react to form  $\text{MoO}_2$  and the multi-compound oxide phase (Kleykamp 1977, Paschoal et al. 1983).

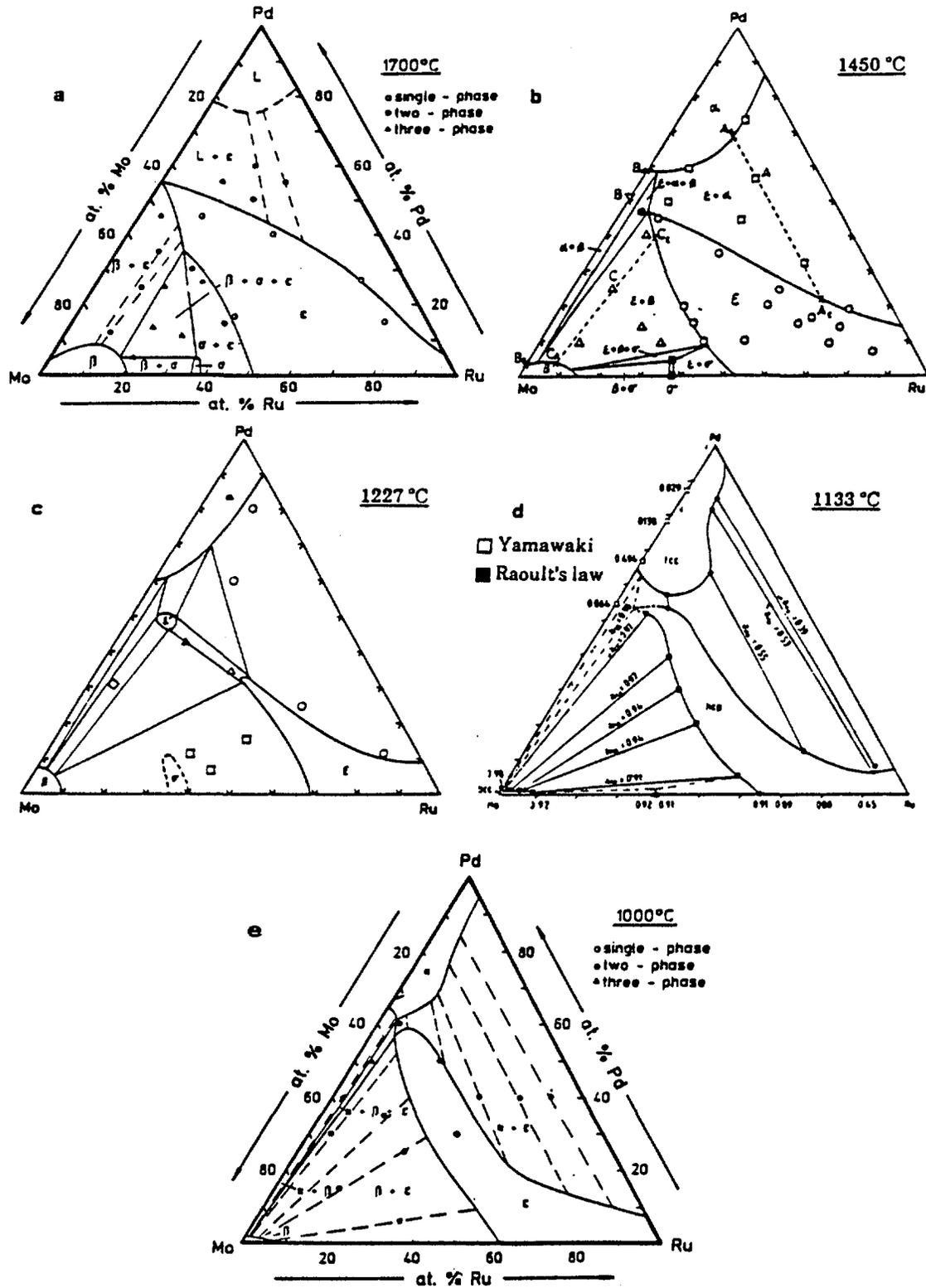


FIGURE 2: Isothermal Ternary Mo-Ru-Pd Phase Diagrams at a Temperature of (a) 1700°C (Paschoal et al. 1983), (b) 1450°C (Naito et al. 1988), (c) 1227°C (Fukuzawa et al. 1984), (d) 1133°C (Cornish and Pratt 1988) and (e) 1000°C (Kleykamp 1989) Adapted from the Figures Compiled and Presented by Kleykamp (1989).

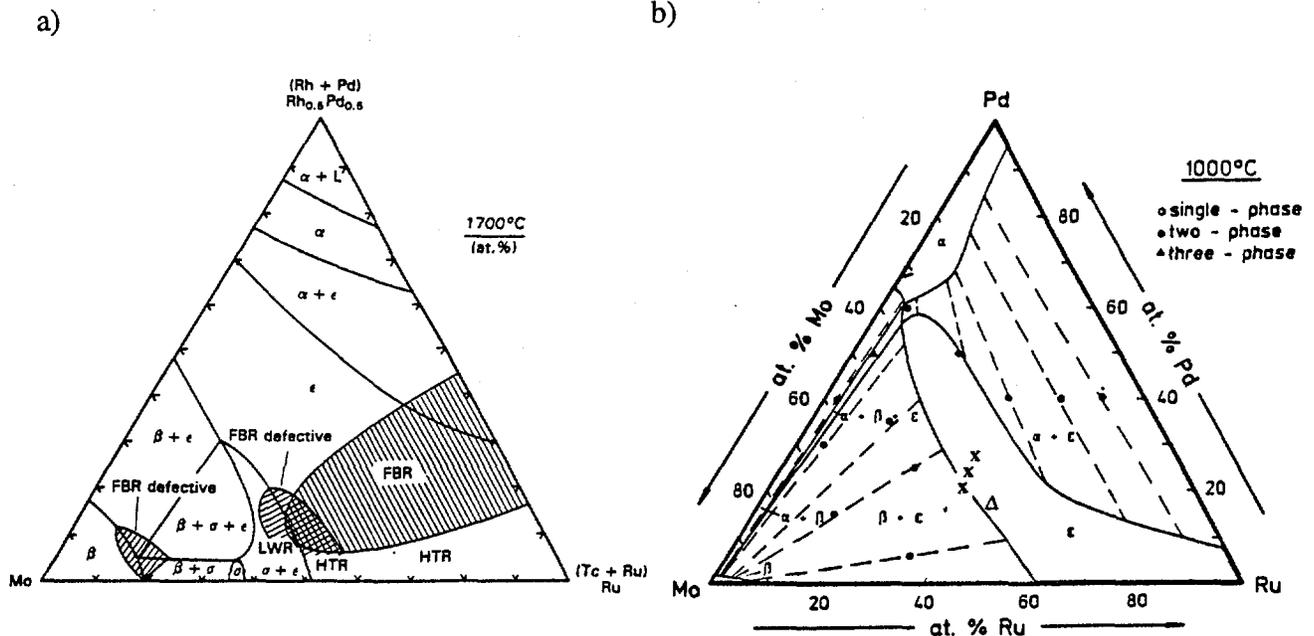


FIGURE 3: (a) Isothermal Ternary Mo-Ru-Pd Phase Diagram at 1700°C upon which is Superimposed the Pseudoternary Mo-(Tc+Ru)-(Rh+Pd) Phase Data for used LWR, HTR and FBR Fuels. This illustration is taken from Kleykamp (1988a) (b) Isothermal ternary Mo-Ru-Pd phase diagram at 1000°C (Kleykamp, 1989) upon which are superimposed the pseudoternary Mo-(Tc+Ru)-(Rh+Pd) compositions for used LWR fuel (x) for burnups ranging from 20 to 50 MWd/kg U as calculated by Guenther et al. (1988) and for used CANDU fuel ( $\Delta$ ) with a burnup of 7.93 MWd/kg U (Tait et al. 1989).

The oxygen potential of used fuel rises during the course of burnup, and it may become high enough that noble-metal inclusions will be depleted in molybdenum because of their oxidation and subsequent migration to the complex multi-component oxide phase of general composition (Ba,Sr,Cs)(U,Pu,Zr,Mo,RE)O<sub>3</sub>, or their complete release from the fuel matrix (Kleykamp 1985). The noble-metal inclusions in samples, which are palladium-rich and molybdenum-poor, may consist of the  $\epsilon$  and the  $\alpha$  phases (Paschoal et al. 1983, Naito et al. 1988). Clearly, analysis of the composition and phases in the noble-metal inclusions in used CANDU fuel can provide useful information on the nature and history of the fuel, but the results will need to be interpreted carefully.

#### 4. OXIDATION BEHAVIOUR

It is well known that molybdenum metal oxidizes at oxygen potentials similar to that of slightly hyperstoichiometric UO<sub>2+x</sub> (Kleykamp 1985). Oxidized molybdenum will leave the noble-metal

inclusions, and enter the (Ba,Sr,Cs)(U,Pu,Zr,Mo,RE)O<sub>3</sub> ceramic phase (Kleykamp 1985), or it will be volatilized from the fuel completely. Thus it has been proposed that the molybdenum content of the noble-metal inclusions is a measure of the local oxygen potential of the fuel (Kleykamp 1977). To obtain a detailed understanding of the oxidation behaviour of the noble-metal inclusions in used fuel, one must estimate the activity of the various components within the alloy.

Naito et al. (1988) recently studied the oxidation behaviour of Mo<sub>0.45</sub>Ru<sub>0.45</sub>Pd<sub>0.10</sub> by estimating the activity of the various metals in the alloy. The activity of palladium was determined for the range 1330 to 1485°C by vapour-pressure measurements (Naito et al. 1988, Matsui and Naito 1989a), and the activities of molybdenum and ruthenium were estimated using the regular solution model (Kaufman and Bernstein 1970). They then estimated the oxygen potentials associated with the equilibria (Naito et al. 1988):



where  $[\text{M}]_{\epsilon}$  (M = Mo, Ru, Pd) represents the individual constituent of the Mo-Ru-Pd alloy. The oxygen partial pressure associated with each of the above equilibria (for the pure elements) is plotted as a function of temperature in Figure 4.

Naito et al. (1988) compared their theoretical results with experimental data obtained at 1450°C. For this temperature, they calculated the oxygen potential required to oxidize the molybdenum in Mo-Ru-Pd alloys with compositions between 10.9 and 62.5 atom %. Each sample was then oxidized at 1450°C at 2 oxygen potentials: 1 above the calculated molybdenum-oxidation pressure, and 1 below. No reaction occurred at oxygen potentials below that associated with the  $[\text{Mo}]_{\epsilon}/\text{MoO}_2$  equilibrium. In contrast, those experiments with high oxygen potentials yielded a molybdenum oxide with composition  $\sim\text{MoO}_{1.8}$ <sup>2</sup>. Electron microprobe analysis (EMPA) of the oxidized material indicated that oxidation of the molybdenum causes it to segregate from the parent material. The composition and structure of the remaining molybdenum-depleted noble-metal phases were consistent with the Mo-Ru-Pd phase diagram at 1450°C. In 2 cases, the depletion of molybdenum was great enough that the noble-metal particles had composition associated with the 2-phase ( $\epsilon + \alpha$ ) region of the phase diagram; in these cases both the  $\epsilon$  and  $\alpha$  phases were indeed observed.

<sup>2</sup> With the exception that molybdenum oxide was not detected for that sample that had the lowest molybdenum content (10.9 atom %). Such an observation is perhaps due to volatilization of the small quantity of molybdenum oxide formed.

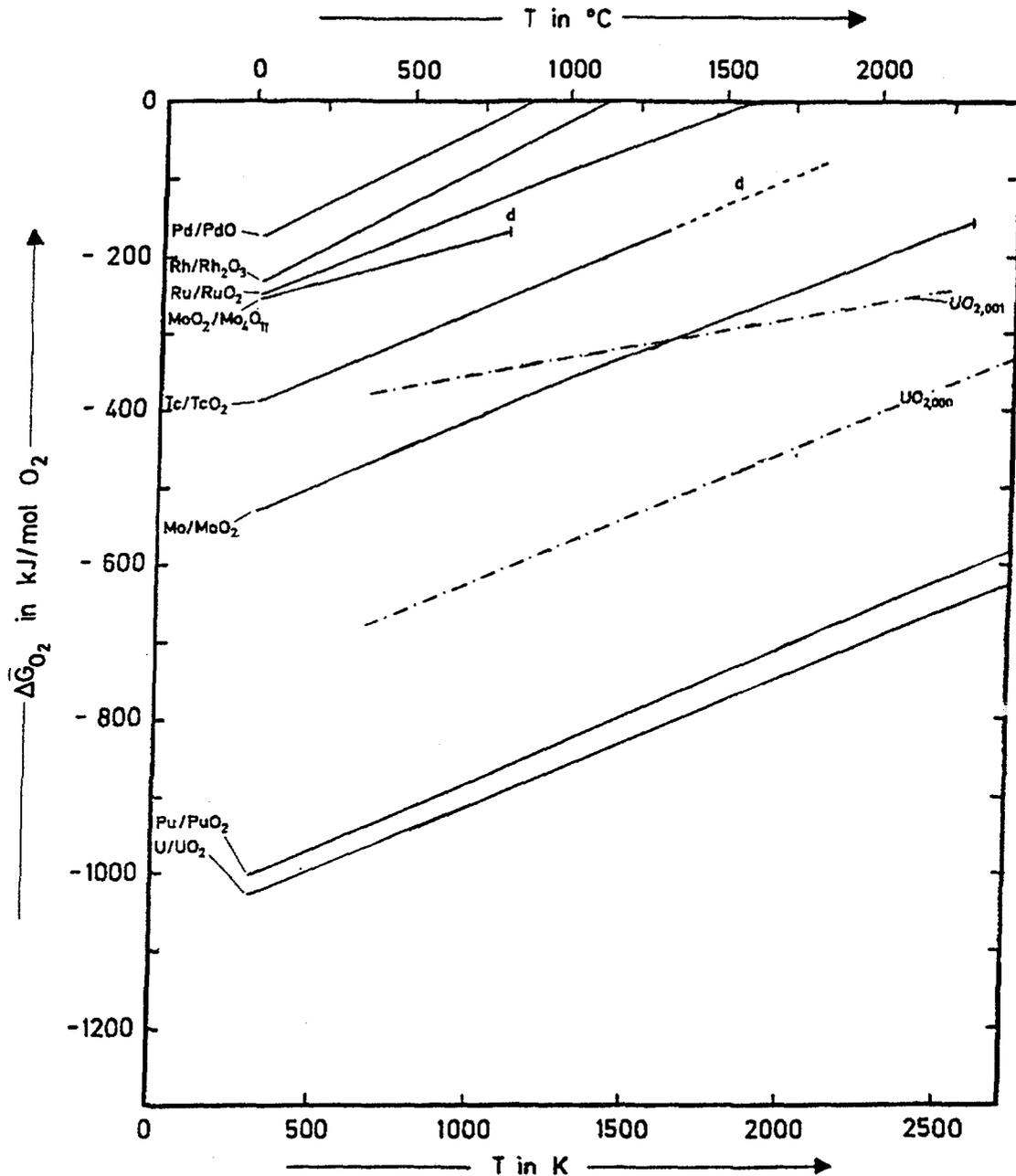


FIGURE 4: Oxygen Partial Pressure Associated with Oxidation Reactions (2) -(4). Adapted from Naito et al. (1988).

Matsui and Naito (1989b) extended the work of Naito et al.(1988) to include several alloys consisting of 3 of the 5 metals: Mo, Tc, Ru, Rh and Pd. As in the earlier study, the activity of palladium in the various alloys was estimated from the vapour-pressure measurements (Matsui and Naito 1989a), and the activity of each of the other constituents was calculated by the regular solution method (Kaufman and Bernstein 1970). Matsui and Naito (1989b) then calculated the oxygen partial pressure associated with the oxidation reaction for each metal; the results are

illustrated in Figure 5. Examination of Figure 5 suggests that the oxygen pressure associated with oxidation of the elements in noble-metal inclusions increases in the order Mo, Tc, Ru, Rh, and Pd. Moreover, oxidation of molybdenum to  $\text{MoO}_3$  will be complete prior to any oxidation of Ru, Rh or Pd. The equations describing the oxygen potentials illustrated in Figure 5 were not given in the work by Matsui and Naito (1989b). The expression for the oxygen pressure associated with oxidation of molybdenum in  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  was estimated from Figure 4 of Matsui and Naito (1989b) and found to be

$$\log(P_{\text{O}_2}/\text{Pa}) = -30,357 \cdot (T)^{-1} + 14.14 \quad (5)$$

The data illustrated in Figure 5 indicate that the oxidation behaviour of the metals Mo, Tc, Ru, Rh and Pd depends to some extent on the composition of the alloy. However, variations in oxidation behaviour associated with alloy composition are not great enough to change the overall sequence of oxidation.

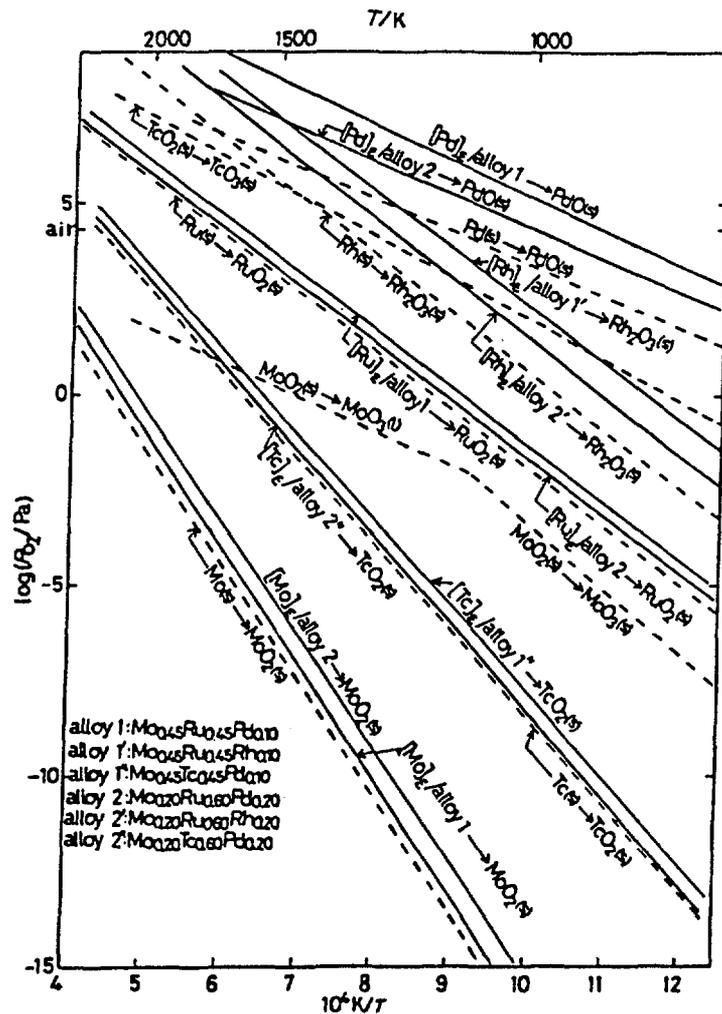


FIGURE 5: Partial Pressure of Oxygen Associated with the Oxidation Reactions for Mo, Tc, Ru, Rh and Pd in Ternary Alloys Composed from Three of These Metals. Taken from reference Matsui and Naito 1989a.

Ugajin and Shiba (1982) studied the effect of oxygen potential on the chemical state of simulated fission products in  $(\text{Th}_{0.81}\text{U}_{0.19})\text{O}_2$ . They heated such samples for 5 h at  $1500^\circ\text{C}$  at various oxygen potentials. They found that oxygen potentials of  $-327$  and  $-291 \text{ kJ mol}^{-1}$  did not result in oxidation of the ternary Mo-Ru-Pd alloy (composition, atom %, Mo 61.3/Ru 28.8/Pd 9.9). However, oxidation in the range  $-259$  to  $-127 \text{ kJ mol}^{-1}$  resulted in the formation of  $\text{BaMoO}_4$  and  $\text{Nd}_2\text{Zr}_2\text{O}_7$  through the reactions



Selective oxidation of molybdenum (and its depletion from the noble-metal inclusions) was confirmed by EMPA and lattice-parameter measurements following the heat treatment. Although the alloy compositions varied somewhat (so that exact comparison is not possible) the oxygen potentials required for molybdenum oxidation in the experiments reported by Ugajin and Shiba (1982) are comparable to those reported by Naito et al. (1988).

Ugajin and Shiba (1982) were able to model the oxidation process successfully. They claimed that oxidation of molybdenum from the alloy (reaction 2) is the key stage in the oxidation process (Ugajin and Shiba 1980) so that the oxygen potential in equilibrium with a noble-metal alloy system will be given by

$$\Delta G(\text{O}_2) = \Delta G_f^\circ(\text{MoO}_2) - RT \ln a_{\text{Mo}} \quad (8)$$

The activity of molybdenum in the alloy was estimated by the regular solution model (Kaufman and Bernstein, 1970), and thus the value of  $\Delta G(\text{O}_2)$  required for oxidation of molybdenum in the alloy was estimated to be  $-272 \text{ kJ mol}^{-1}$ . The calculated oxygen potential is consistent with the experimental observation that the noble-metal inclusions underwent oxidation at  $-259 \text{ kJ mol}^{-1}$  but not at  $-291 \text{ kJ mol}^{-1}$ .

In conclusion, the oxidation behaviour of noble-metal alloys can be estimated by calculation of the activity of each of the components. Some experimental data are available for these activities, and other data can be calculated using the regular solution method. The limited experimental data available are in reasonable agreement with such calculated oxygen potentials. The composition of noble-metal alloys has a significant impact on the calculated oxygen potentials, but the effect is not great enough to change the overall trend, which remains (in decreasing tendency to oxidize): Mo, Tc, Ru, Rh, Pd. Oxidation behaviour of noble-metal alloys is governed by the behaviour of molybdenum. To a first approximation, the oxygen potential for noble-metal inclusions in used fuel is given by Equation (5).

5. VAPOURIZATION OF Mo, Tc, Ru, Rh, Pd AND THEIR OXIDES

The vapour pressure of the various elements (and their oxides) in the noble-metal inclusions has been reasonably well studied because of the potential commercial value of Pd, Ru and Rh and also because of the implications of fission-product volatilization in a hypothetical reactor-accident scenario. Matsui and Naito (1989a) calculated the vapour pressure (1000 and 1500 K) as a function of oxygen potential for each of the relevant metal and metal-oxide species in equilibrium with alloys of composition similar to those observed in LWR and FBR used fuel. They performed such calculations by using the activity of palladium derived from experimentally determined vapour-pressure measurements (Matsui and Naito 1989a), along with the activity of molybdenum, technetium, rhodium and rhenium calculated by the regular solution model (Kaufman and Bernstein 1970) and known thermodynamic data for  $\text{MoO}_2(\text{s})$ ,  $\text{MoO}_3(\text{s,l})$ ,  $\text{RuO}_2(\text{s})$ ,  $\text{PdO}(\text{s})$ ,  $\text{Rh}_2\text{O}_3(\text{s})$ ,  $\text{TcO}_2(\text{s})$  and  $\text{TcO}_3(\text{s,l})$ . As an example of the calculations performed by Matsui and Naito (1989b), a plot of the vapour pressure of the molybdenum-containing species in equilibrium with  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  as a function of oxygen partial pressure is given in Figure 6.

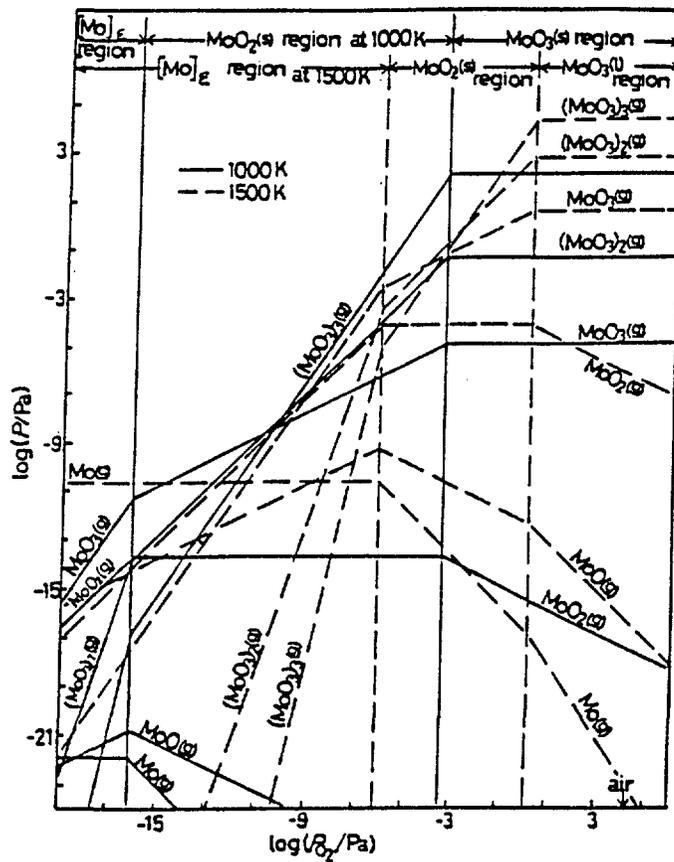


FIGURE 6: Vapour Pressure of Molybdenum and the Various Molybdenum Oxides in Equilibrium with  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  as a Function of Oxygen Pressure at 1000 and 1500 K. Taken from Matsui and Naito (1989b).

The results reported by Matsui and Naito (1989a,b) indicate that in vacuum the vapour pressure of the various metals follows the trend: Pd >> Rh > Ru > Mo > Tc. In oxidizing atmospheres, the vapour pressures of the various metal oxides are higher than are those of the metals (with the exception of palladium). The vapour pressure of gaseous oxides of molybdenum and ruthenium are significantly higher than are the rest of the metals, so that incongruent volatilization of Mo and Ru is expected when noble-metal inclusions are heated in an oxidizing atmosphere.

## 6. KINETIC DATA

The reaction mechanism and kinetics for the rate of oxidation of the noble-metal inclusions are not particularly well understood. Even for pure metals, such as molybdenum, the oxidation reaction is complicated because several reactions are involved in the process. For example, in the oxidation of molybdenum, Ong and Fassell (1962) identified, in general, three consecutive reactions:



Moreover, Reaction (9) is diffusion controlled (Ongard Fassell 1962), whereas Reaction (10) is not (Floquet and Bertrand 1991a,b) so that the overall oxidation/volatilization model is complex (Ongard Fassell 1962).

Thermodynamic considerations will have a major influence on the nature of the oxidation process. Below the Mo(s)→MoO<sub>2</sub>(s) line in Figure 5, molybdenum metal will be the stable phase, although some degree of surface oxidation likely still occurs (Fogel 1976). Between the Mo(s)→MoO<sub>2</sub>(s) and the MoO<sub>2</sub>(s)→MoO<sub>3</sub>(s,l) lines of Figure 5 bulk oxidation will proceed to MoO<sub>2</sub> while above the MoO<sub>2</sub>(s)→MoO<sub>3</sub>(s,l) line the stable phase will be either MoO<sub>3</sub>(s) or MoO<sub>3</sub>(l).

Experimental results are generally in agreement with the above discussion. For example, Figure 5 indicates that air oxidation at 10 to 100 kPa yields MoO<sub>3</sub> at any temperature below 2000 K, and experiments have consistently shown this to be the case (Floquet and Bertrand 1991a,b, Raynaud 1984, Braverman et al. 1974, Barr 1978, Volykhov and Chapaikin 1983, Gaulbransen 1970) with only the occasional dissenting voice (Zhizhin et al. 1982). In contrast, oxidation when P(O<sub>2</sub>) was 4 x 10<sup>-5</sup> Pa is expected to result in the formation of MoO<sub>2</sub>, which is consistent with experimental results reported by (Nozoye et al. 1976).

It has been suggested that the formation of MoO<sub>2</sub> follows diffusion-controlled kinetics (Ong and Fassell 1962) although reaction to form this compound has not been particularly well studied. The formation of MoO<sub>3</sub> has been studied more extensively than has the formation of MoO<sub>2</sub>, but the mechanism for MoO<sub>3</sub> formation is not yet agreed upon. Floquet and Bertrand (1991a,b)

suggested that the formation of  $\text{MoO}_3$  follows nucleation-and-growth kinetics, whereas Valyukhov and Chapaikin (1983) reported that it is diffusion-controlled, and Ong and Fassell (1962) stated that it is phase-boundary controlled. At elevated temperatures the vapour pressure of  $\text{MoO}_3$  is substantial; thus for example, the rate of volatilization determines the oxidation rate at 700 to 760°C (Braverman et al. 1974).

Examination by X-ray photoelectron spectroscopy (XPS) of the oxide film formed by air oxidation of molybdenum has also yielded ambiguous results. Barr (1978) reported that the oxide film formed by air oxidation is essentially pure  $\text{MoO}_3$ , whereas Valyukhov (1983) found that the oxide film has a layered structure, with  $\text{MoO}_3$  on the surface, and layers of successively decreasing amounts of oxygen, with a layer of  $\text{MoO}$  at the film-metal interface. This observation may be the result of sample reduction by the ion beam.

Oxidation of complex alloys representative of the noble-metal inclusions in used fuel has not been studied extensively. Matsui et al. (1990) air-oxidized Mo, Ru, Rh and Pd powders as well as the alloy  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  in the range 673 to 973 K. They reported that Mo, Ru and  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  oxidized according to parabolic kinetics but that Pd had cubic kinetics and Rh had linear kinetics. The parabolic rate constant for oxidation of  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  was intermediate between those for molybdenum and ruthenium. Examination by XRD of  $\text{Mo}_{0.45}\text{Ru}_{0.45}\text{Pd}_{0.10}$  after air oxidation displayed the presence of  $\text{MoO}_3$  and  $\text{RuO}_2$  on the surface, indicating that oxidation at 673 to 973 K probably proceeds by selective diffusion of these metals to the sample surface, followed by oxidation and subsequent volatilization. However, the results reported by Matsui et al. (1990) are only preliminary, and further study will be required.

## 7. SUMMARY AND SUGGESTIONS FOR FURTHER WORK

The ternary Mo-Ru-Pd phase diagram is reasonably well understood for the range 1000 to 1700°C, and it appears to be acceptable for modelling the pseudoternary Mo-(Tc+Ru)-(Rh+Pd) system. It would be useful to determine the Mo-Ru-Pd phase diagram at lower temperatures, but this is probably not practical because of the long equilibration times. Moreover, the noble-metal inclusions will generally be of the hexagonal  $\epsilon$  phase; the presence of any other phases can probably be interpreted qualitatively by the 1000°C phase diagram.

The oxidation kinetics and mechanism appear to be quite poorly understood for noble-metal alloys, and even for pure molybdenum. The high-temperature (e.g., 1450°C) studies have indicated that molybdenum diffuses to the surface and is then oxidized. This mechanism leaves the noble metal parent material depleted in molybdenum. However, the low-temperature (e.g., 600°C) bulk oxidation and the surface reaction near 200°C are not yet fully understood, and require further study. It is probably not practical for one to embark on a detailed study of the oxidation mechanism for the pure metals. Rather, a practical approach to the problem would be to perform isothermal tests on the oxidation of a typical noble-metal alloy. Subsequent analysis of the product by XPS or XRD or both (depending on the extent of oxidation) would then yield information on the reaction mechanism and the extent of surface enrichment of the various

metals. Moreover, if the samples were prepared so that they had a reasonably consistent particle size, then it should be possible to derive the relevant diffusion coefficients from the kinetic data.

Known thermodynamic parameters for the noble-metal oxides, along with the activity of the various metals in the alloy (experimental, where possible, or calculated by the regular solution method) can be used to predict the speciation in the solid phase and the vapour pressure in equilibrium with it. The limited experimental data available are in reasonably good agreement with such calculated results. It should be thus possible to develop a thermodynamic database so that a free-energy-minimization code (e.g., CHMWRK, FACT) can be used to predict the vapour pressure of the various metal and metal-oxide species. Moreover, such a database could be used to predict the composition of the alloy as a function of oxygen potential and temperature. Calculated results can be compared to experimental data obtained from Knudsen-cell experiments.

The following specific tests are proposed:

- Isothermal oxidation experiments on a typical Mo-Ru-Rh-Pd alloy, covering the range of oxygen potentials from  $-400 \text{ kJ mol}^{-1}$  to that of air. Temperatures will range from 200 to  $1000^\circ\text{C}$ . Data analysis should yield reaction mechanism and products, the extent of surface enrichment/depletion of Mo and Ru, as well as diffusion coefficients for these elements. Such kinetic experiments will ultimately be required to fully understand noble-metal alloys, however they are not of immediate concern like the following thermodynamic points.
- Determination of an accurate quaternary Mo-Rh-Pd-Ru phase diagram at relevant temperatures. This can, and will, be achieved by measurement of the vapour pressure of volatile elements as a function of temperature and composition. A free-energy minimization code such as FACT can then be used to optimize the phase diagram. This information can then be used to accurately predict the molybdenum speciation as a function of oxygen potential.

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