Thermodynamic Calculation on the Vaporization of Fission-Produced Noble Metal System in Vacuum and Oxidative Atmosphere at High Temperatures

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The vaporization behavior of fission-produced noble metal system (Mo-Ru-Pd, Mo-Ru-Rh and Mo-Tc-Pd) in vacuum and oxidative atmosphere at high temperatures was investigated by the thermodynamic calculation on the basis of the regular solution model and the available experimental data. The palladium and rhodium in the alloys, and molybdenum and ruthenium in the alloys vaporize preferentially at high temperature in vacuum and in air, respectively. At low temperature below 385 K in air, ruthenium and technetium in the alloys vaporize predominantly by oxidation.

KEYWORDS: thermodynamic calculation, thermodynamic properties, vaporization, vapors, fission-produced noble metal system, vacuum, oxidative atmosphere, high temperature, ruthenium, technetium, palladium, rhodium, alloys, oxidation

I. INTRODUCTION

It is well known that fission-produced noble metals (Ru, Rh and Pd) form fine metallic inclusions in the fuel together with Mo and Tc, and the chemical states of these noble metals in the fuel depend on temperature, oxygen potential, burnup etc.(1)

These three noble metals Pd, Rh and Ru are valuable and their natural resources are rather limited, and hence they can be recognized as an alternative resource to meet a part of the increasing need of noble metals. The methods for separating these noble metals from other fission products reported so far are the separation from alkaline Purex waste solution(2)(3), that from fission product oxide mixture obtained by calcining the high level liquid waste(4) and that from insoluble residue in the dissolution of spent fuel(5)(6). The present authors have demonstrated a possible method for the recovery of Mo, Ru and Pd metals from the insoluble residue produced in dissolver solution of spent fuel by means of lead extraction(6). Recently the present authors have also shown that the separation of Mo and/or Ru from the simulated fission-produced alloy (Mo-Ru-Pd alloy) can be done by the preferential vaporization during oxidation(7).

The thermodynamic studies on Mo-Ru-Pd alloys have been carried out by several investigators(8)~(11). Yamawaki et al.(8) determined the thermodynamic activity of Mo in the s-phase of Mo-Ru-Pd alloys in the temperature range of 1,200~1,300 K by measuring the EMF (electro-motive-force) values using the solid galvanic cell. Kleykamp(11) also measured the thermodynamic activity of Mo in the \( \alpha + \beta + s \) three-phase region in the phase diagram between 1,150 and 1,250 K with the solid galvanic cell. Present authors(9)(10) made the vapor pressure measurements on the \( \varepsilon \)-phase of Mo-Ru-Pd alloys in the temperature range of 1,200~1,300 K by measuring the EMF (electro-motive-force) values using the solid galvanic cell. Present authors(9)(10) also measured the thermodynamic activity of Mo in the \( \alpha + \beta + s \) three-phase region in the phase diagram between 1,150 and 1,250 K with the solid galvanic cell. Present authors(9)(10) made the vapor pressure measurements on the \( \varepsilon \)-phase of Mo-Ru-Pd alloys with different compositions by mass-spectrometry in the temperature range between 1,536 and 1,791 K, from which the thermodynamic activity of Pd in the alloys was determined.

In the present study, three kinds of thermodynamic calculation were done. At first the equilibrium vapor pressures over pure metals (Mo, Ru, Pd, Rh and Tc) and those over the...
\( \varepsilon \)-phase of the alloys (Mo-Ru-Pd, Mo-Ru-Rh and Mo-Tc-Pd) in vacuum are calculated as a function of temperature based on the regular solution model \(^{(23)}\)\(^{(24)}\) together with the experimental data \(^{(8)}\)\(^{(10)}\)\(^{(12)}\)\(^{(22)}\). Secondly the equilibrium oxygen partial pressures for the oxidation of pure metals and those for the alloys are calculated in the same way. Finally the vapor pressures of the gaseous species during oxidative vaporization of the metal and alloys are estimated as a function of oxygen partial pressure. It is noted that three ternary alloys of Mo-Ru-Pd, Mo-Ru-Rh and Mo-Tc-Pd are used for the present thermodynamic calculation instead of the Mo-Tc-Ru-Rh-Pd alloy, since Tc and Rh form completely solid solutions with Ru and Pd, respectively, and that two kinds of typical compositions of the alloy, one is that of 45:45:10 \( \% \) i.e. Mo\(_{0.46}\)Ru\(_{0.46}\)Pd\(_{0.10}\) (we designate as alloy 1 in this paper), Mo\(_{0.45}\)Ru\(_{0.45}\)Rh\(_{0.10}\) (designated as alloy 1') and Mo\(_{0.45}\)Tc\(_{0.45}\)Pd\(_{0.10}\) (designated as alloy 1''), and the other is that of 20:60:20 \( \% \) i.e. Mo\(_{0.29}\)Ru\(_{0.46}\)Pd\(_{0.25}\) (designated as alloy 2), Mo\(_{0.29}\)Ru\(_{0.49}\)Rh\(_{0.20}\) (designated as alloy 2') and Mo\(_{0.25}\)Tc\(_{0.49}\)Pd\(_{0.20}\) (designated as alloy 2''), are selected for the calculation. The former is in the compositional region of the fission-produced noble metals observed in LWR fuel and the latter is that in FBR fuel in general \(^{(13)}\).

II. EQUILIBRIUM VAPOR PRESSURES IN VACUUM

The vapor pressures over pure metals Mo\(^{(12)}\), Ru\(^{(13)}\), Pd\(^{(3)}\), Rh\(^{(14)}\) and Tc\(^{(15)}\) are shown in Fig. 1 as a function of temperature. The vapor pressure of Pd(g) over Pd(s) is highest and those of Mo(g) over Mo(s), Tc(g) over Tc(s) and Ru(g) over Ru(s) are appreciably low in comparison with that of Pd(g).

The temperature dependence of the vapor pressure of Pd(g), which is a predominant gas species, over Mo-Ru-Pd alloys has been measured previously by the present authors \(^{(9)}\)\(^{(10)}\) and the result are shown in Fig. 2 together
with that over pure Pd metal. It is seen from Fig. 2 that (1) the vapor pressures of Pd(g) over Mo-Ru-Pd alloys are lower than that over pure Pd metal, as was expected, and (2) the vapor pressures of Pd(g) do not simply vary with the concentrations of Pd in the Mo-Ru-Pd alloys.

The thermodynamic activities of Mo, Ru and Rh in Mo-Ru-Pd(Rh) alloys can be calculated based on the regular solution model using the Kaufman & Bernstein's interaction parameters, but for that of Tc in Mo-Tc-Pd alloy, the interaction parameters proposed by Haines...
et al. was used due to the lack of data in Kaufman & Bernstein's parameter. From the thermodynamic activities, thus calculated, the vapor pressures of Mo(g) and Ru(g) over alloys 1 and 2, Rh(g) over alloys 1' and 2' and Tc(g) over alloys 1'' and 2'' were calculated and shown in Fig. 3 in comparison with those of Mo(g) and Pd(g) obtained experimentally. The vapor pressures of Mo(g) over Mo$_{0.200}$Ru$_{0.580}$Pd$_{0.220}$ and Mo$_{0.500}$Ru$_{0.963}$Pd$_{0.137}$ were estimated by the present authors from the E.M.F. data experimentally obtained by Yamawaki et al. in the temperature range of 1,200~1,300 K, and extrapolated to the high temperatures as shown in Fig. 3. It is seen from Fig. 3 that the vapor pressures of Pd(g) experimentally obtained over alloys 1 and 2 are close to those over these alloys calculated from the regular solution model and that the vapor pressures of Mo(g) estimated from the E.M.F. data over Mo$_{0.200}$Ru$_{0.580}$Pd$_{0.220}$ and Mo$_{0.500}$Ru$_{0.963}$Pd$_{0.137}$ are also in good agreement with those over alloys 1 and 2, respectively, calculated from the regular solution model. The orders of magnitude of the vapor pressures of Pd(g) and Mo(g) over alloys 1 and 2 indicated by the experiment are also in accord with those predicted from the regular solution model. Therefore the regular solution model is considered to be appropriate for the thermodynamic calculation of these alloys, as a first approximation. It may be concluded that the vapor pressure of Pd(g) over the alloys is much higher than that of Rh(g), Ru(g), Mo(g) and Tc(g), indicating preferential loss of Pd from the alloys in vacuum.

### Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>Solid or liquid oxides</th>
<th>Gaseous species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>MoO$_2$, MoO$_4$</td>
<td>Mo, MoO$_2$, MoO$_3$, (MoO$_4$)$_2$, (MoO$_5$)$_3$</td>
</tr>
<tr>
<td>Ru</td>
<td>RuO$_{2.5}$, (RuO$_4$)$_2$, RuO$_4$</td>
<td>Ru, RuO, RuO$_3$, RuO$_5$</td>
</tr>
<tr>
<td>Pd</td>
<td>PdO</td>
<td>Pd, PdO</td>
</tr>
<tr>
<td>Rh</td>
<td>(RhO$_2$, RhO)$_2$, RhO$_4$</td>
<td>Rh, RhO, RhO$_5$</td>
</tr>
<tr>
<td>Tc</td>
<td>TcO$_2$, TcO$_3$, TcO$_4$, TcO$<em>5$, TcO$</em>{10}$</td>
<td>Rc, TcO, TcO$_3$</td>
</tr>
</tbody>
</table>

† Not well determined

In the oxidative atmosphere, the vapor pressure of gaseous oxide species over solid oxides is generally higher than that of metal. The vapor pressures of various gaseous species over the alloys and those over the relevant oxides at 1,000 and 1,500 K were calculated as a function of oxygen partial pressure by assuming that (1) the composition of the relevant alloys can be kept until the formation of solid oxide of the constituent, and (2) the effect of the nonstoichiometry of the oxide upon the value of the vapor pressures is negligibly small.

The vapor pressures of Mo(g), MoO$_2$(g), MoO$_3$(g), MoO$_4$(g), MoO$_5$(g), (MoO$_4$)$_2$(g) and (MoO$_5$)$_3$(g)
Fig. 4 Oxygen partial pressure for oxidation of Mo, Ru and Pd in Mo–Ru–Pd alloys, Rh in Mo–Ru–Rh alloys and Tc in Mo–Tc–Pd alloys

The vapor pressures of Ru(g), RuO(g), RuO\(_2\)(g) and RuO\(_3\)(g) over alloy 1 and RuO\(_2\)(s) at 1,000 and 1,500 K were also calculated from the thermodynamic activity of Ru in the alloy and the data of the free energy of formation of Ru(g)\(^{113}\), RuO(g)\(^{113}\), RuO\(_2\)(g)\(^{113}\), RuO\(_3\)(g)\(^{113}\), RuO\(_2\)(s)\(^{16}\), RuO\(_3\)(s)\(^{12}\), MoO\(_3\)(s, l)\(^{12}\), and the results are shown in Fig. 6 as a function of oxygen partial pressure. It is seen from the figure that at high oxygen partial pressures close to air, the vapor pressures of (MoO\(_3\))\(_n\)(g) (n=1~3) become high.

over alloy 1, MoO\(_3\)(s) and MoO\(_3\)(s, l) at 1,000 and 1,500 K were calculated from the thermodynamic activity of Mo in the alloy and the data of the free energy of formation of Mo(g)\(^{113}\), MoO(g)\(^{113}\), MoO\(_2\)(g)\(^{113}\), MoO\(_3\)(g)\(^{113}\), (MoO\(_3\))\(_2\)(g)\(^{119}\), (MoO\(_3\))\(_3\)(g)\(^{119}\), MoO\(_3\)(s)\(^{12}\), MoO\(_3\)(s, l)\(^{12}\), and the results are shown in Fig. 5 as a function of oxygen partial pressure.
Fig. 5 Vapor pressures of various gaseous species containing Mo over Mo$_{0.450}$Ru$_{0.450}$Pd$_{0.100}$ (alloy 1), MoO$_2$(s) and MoO$_3$(s,l) as a function of oxygen partial pressure at 1,000 and 1,500 K.

The vapor pressures of Pd(g) and PdO(g) over alloy 1 and PdO(s) at 1,000 and 1,500 K were calculated from the thermodynamic activity of Pd in the alloy and the data of the free energy of formation of Pd(g)$^{(9)}$, PdO(g)$^{(21)}$ and PdO(s)$^{(17)}$, and the results are shown in Fig. 7, where the free energy of formation of PdO(g) was calculated by the present authors from the data by Olivei$^{(21)}$. It is noted that Pd in the alloy 1 is not oxidized to PdO(s) and the vapor pressure of Pd(g) is higher than that of PdO(g) at 1,000 and 1,500 K in air.

The vapor pressures of Rh(g) and RhO(g) over alloy 1' and Rh$_2$O$_3$(s) at 1,000 and 1,500 K were calculated from the thermodynamic activity of Rh in the alloy and the data of the free energy of formation of Rh(g)$^{(14)}$, RhO(g)$^{(22)}$ and Rh$_2$O$_3$(s)$^{(1)}$, and the results are shown in Fig. 8. The vapor pressure of RhO(g) could not be calculated due to the lack of the thermodynamic data. The vapor pressure of RhO(g) is higher than that of Rh(g), though the magnitude of the vapor pressure of RhO(g) is not so high in comparison with those of (MoO$_3$)$_n$(g), RuO$_4$(g) and RuO$_3$(g) as
Fig. 6 Vapor pressures of various gaseous species containing Ru over Mo_{0.450}Ru_{0.450}Pd_{0.100} (alloy 1) and RuO_2(s) as a function of oxygen partial pressure at 1,000 and 1,500 K.

Fig. 7 Vapor pressures of various gaseous species containing Pd over Mo_{0.450}Ru_{0.430}Pd_{0.100} (alloy 1) and PdO(s) as a function of oxygen partial pressure at 1,000 and 1,500 K.

The vapor pressures of Tc(g), TcO(g) and Tc_2O_7(g) over alloy 1, TcO_2(s) and TcO_3(s) at 1,000 and 1,500 K were calculated from the thermodynamic activity of Tc in the alloy and the data of the free energy of formation of Tc(g)\(^{15}\), TcO(g)\(^{18}\), Tc_2O_7(g)\(^{18}\), TcO_2(s)\(^{18}\) and TcO_3(s)\(^{18}\), and the results are shown in Fig. 9. The vapor pressure of Tc_2O_7(g) is the highest in the oxygen partial pressure near air. Among the oxides in the Mo-O, Ru-O, Pd-O, Rh-O and Tc-O systems, the solid oxides of Ru and Tc with the highest valency i.e. RuO_4(s) and Tc_2O_7(s) have the highest vapor pressure of RuO_4(g) and Tc_2O_7(g) at low temperature below 385 K and the lowest melting point of 299 K\(^{18}\) and 393 K\(^{18}\), respectively. The temperature dependence of the vapor pressures of RuO_4(g) over RuO_4(l) and that of Tc_2O_7(g) over Tc_2O_7(s, l) are shown in Fig. 10. The boiling points of RuO_4(l) and Tc_2O_7(l) are 385 K\(^{18}\) and 584 K\(^{18}\), respectively.

The vapor pressures of various gaseous species over MoO_3(s, l), Ru(s), RuO_2(s), Pd(s), PdO(s), Rh(s), Rh_2O_3(s), TcO_2(s), TcO_3(s) in air, thus calculated, are shown as a function of temperature in Fig. 11. With increasing temperature in air, some of the solid oxides such as RuO_4(s), PdO(s) and Rh_2O_3(s) are reduced to the metals. As seen in the figure, the vapor pressures of (MoO_3)_n(g) (n=1~3), RuO_3(g) and RuO_4(g) are higher than the other gaseous oxides formed from the elements of the alloys in air at temperature above 400 K. It may be concluded that the e-phase of the Mo-Ru-Pd, Mo-Ru-Rh and Mo-Tc-Pd alloys vaporizes incongruently with preferential loss of Mo and Ru in the oxidative atmosphere.
Fig. 8 Vapor pressures of various gaseous species containing Rh over Mo_{0.450}Ru_{0.450}Rh_{0.100} (alloy 1') and RhO_{3}(s) as a function of oxygen partial pressure at 1,000 and 1,500 K

Fig. 9 Vapor pressures of various gaseous species containing Tc over Mo_{0.450}Tc_{0.450}Rh_{0.100} (alloy 1''), TcO_{2}(s) and TcO_{3}(s) as a function of oxygen partial pressure at 1,000 and 1,500 K

Fig. 10 Temperature dependence of vapor pressures over RuO_{4}(l) and TcO_{3}(s,l) at low temperatures

IV. CONCLUSION

From the thermodynamic calculation based on the regular solution model, the following conclusion on the vaporization of the fission-produced alloy system was obtained:

1. In vacuum, the magnitude of the vapor pressure of Pd(g), Rh(g), Ru(g), Mo(g) and Tc(g) are found to be in order of decreasing over the ε-phase of the Mo-Ru-Pd (alloys 1 and 2), Mo-Ru-Rh (alloys 1' and 2') and Mo-Tc-Pd (alloys 1'' and 2''). The Pd and Rh can be separated from other constituents of the alloy by preferential vaporization in vacuum.

2. In the oxidative atmosphere at high temperature, the vapor pressures of gaseous oxide species, (MoO_{3})_{n}(g) (n=1~3), MoO_{2}(g), RuO_{4}(g), RuO_{3}(g), PdO(g), RhO_{2}(g) and TcO(g) are higher than those of the relevant metal gas species except the case for Pd where the vapor pressure of Pd(g) is higher than that of PdO(g) in air. Since
the vapor pressures of the gaseous oxide species containing Mo and Ru are higher than that of other gaseous species, Mo and Ru in the alloy can be separated from other constituents of the alloy by preferential vaporization in the oxidative atmosphere such as air.

(3) In the oxidative atmosphere at low temperature below 385 K, the vapor pressure of RuO₄(g) over RuO₄(s, l) and that of Tc₂O₇(g) over Tc₂O₇(s, l) are very high. The Ru and Tc in the alloy can be separated from other constituents of the alloy by preferential vaporization by oxidation in air at low temperature, if the oxidation rates of Ru and Tc in the alloy are enough high.

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