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Vaporization properties of $Cs_2U_4O_{12}$ in LWR severe accident simulating conditions

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Abstract

Vaporization behaviors of $Cs_2U_4O_{12}$ were studied by using the Knudsen effusion mass spectrometric method at temperatures from 1273 to 1573 K. To clarify vaporization properties of $Cs_2U_4O_{12}$ in case of severe accident conditions of light water reactors, partial pressure measurements were made in D_2O/D_2 mixtures. The D_2O/D_2 environments were established in the Knudsen cell by introducing $D_2(g)$ or $D_2(g) + O_2(g)$ gas into the cell through a fine platinum tube attached to the bottom of the cell. Cesium vapor Cs(g) was found as the dominant vapor species over the compound either in vacuum or in the simulated atmospheres. In this study, the average temperature applied was 1423 K, the pressure of Cs(g) over the specimen in vacuum was 1.97 Pa while the oxygen potential measured was −148.2 kJ/mol. The pressure of Cs(g) increased moderately to 2.26 Pa after the introduction of the $D_2(g)$, and it decreased slightly to 1.56 Pa with the admission of $D_2(g)+O_2(g)$.

1. Introduction

Among the cesium uranates that could be produced in nuclear oxide fuel during irradiation, the existence of $Cs_2U_4O_{12}$ was once reported by Kleykamp [1]. It was considered that its formation in normal operation conditions could be due to local high oxygen potentials in the fuel. Recent research by Ugajin et al. [2] further concluded that its formation could be possible at intermediate oxygen potentials. With the current trend of effective usage of high burnup oxide fuels in LWRs, the behaviors of $Cs_2U_4O_{12}$ in accident conditions are of importance for nuclear reactor safety analysis. Although the thermodynamic data of $Cs_2U_4O_{12}$ at high temperatures were obtained using calorimetry [3,4], the data on the vaporization properties of this compound are limited.

In this study, the Knudsen-effusion mass spectrometry was employed to study the vaporization properties of $Cs_2U_4O_{12}$. A gas inlet system was attached to the Knudsen cell to investigate the vaporization of $Cs_2U_4O_{12}$ in oxidizing or reducing atmosphere. The gas flow rate of inlet gas $D_2(g)$ or $D_2(g) + O_2(g)$ was limited to less than 10^{-5} m^3 Pa/s in order to eliminate disturbances to the molecular equilibrium inside the Knudsen cell. Absolute partial vapor pressures of $D_2(g)$ or $D_2O(g)$ inside the Knudsen cell were determined from the gas inlet flow rates and the reactions products observed. In the temperature range from 1273 to 1573 K of the present study, partial pressures of $D_2O(g)$ were found less than 5 Pa both in $D_2(g)$ inlet and in $D_2(g) + O_2(g)$ inlet conditions.

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2. Experimental

2.1. Sample preparation

$Cs_2U_4O_{13}$, a precursor of $Cs_2U_4O_{12}$, was prepared by mixing UO_3 and Cs_2CO_3 (with mole ratio of 4:1) at 600°C in air for 16 h. $Cs_2U_4O_{13}$ obtained was later heated in Ar at 950°C for at least 6 h to yield $Cs_2U_4O_{12}$ by decomposition:

$$Cs_2U_4O_{13}(s) \rightarrow Cs_2U_4O_{12}(s) + 0.5O_2(g). \qquad (1)$$

The sample was identified as a single-phase $Cs_2U_4O_{12}$ by an X-ray powder diffraction analysis. The diffraction pattern of the sample was very close to the ASTM/JSPDS file No. 29-432. Since the total impurities of starting materials UO_3 and $CsCO_3$ were about 30 ppm, the impurity concentration in $Cs_2U_4O_{12}$ obtained was estimated to be less than 100 ppm.

2.2. Mass spectrometer with a gas inlet system

The HT-12-90 high temperature mass spectrometer of the authors' laboratory was described elsewhere [5]. In the present analysis, the gas inlet system has been improved to allow the introduction of $D_2O(g)$, $D_2(g)$, and a mixture of $D_2(g)/O_2(g)$ into the Knudsen cell, as shown in Fig. 1.

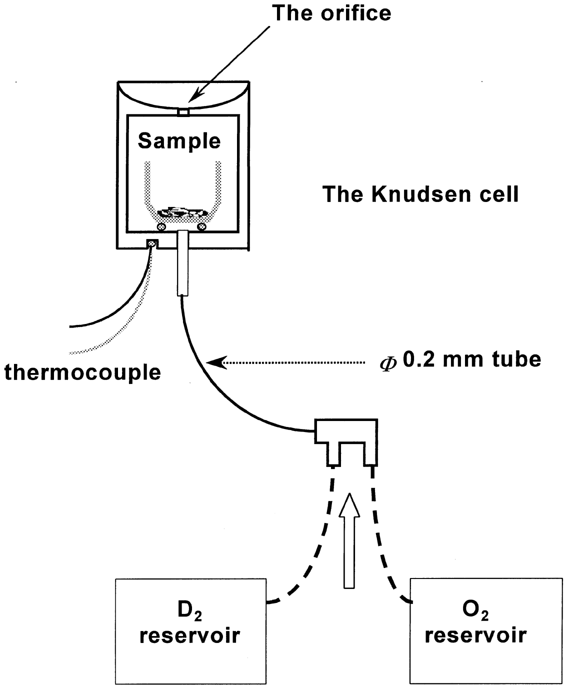

Fig. 1. Schematic diagram of the gas mixture inlet system.

For analyzing any possible fragmentation, the ionization efficiency curve (I.E.C.) of Cs^+ was measured. The I.E.C. of Cs^+ of $Cs_2U_4O_{12}$ in vacuum was found close to standard ionization curve. The influence of any possible fragmentation from CsO^+ or Cs_2O^+ is negligible since Cs^+ has been observed to be the dominant vapor species. One typical I.E.C curve was plotted in Fig. 2. Consistent results were obtained in vacuum and in the $D_2(g)$ admission. In addition, the I.E.C of Cs^+ obtained is the same with or without the presence of CsOD(g). This suggests that fragmentation of $CsOD^+$ does not occur when the electron impact energy is less than 20 eV. Therefore, an electron impact energy of 20 eV was chosen for the measurements of Cs^+, $CsOD^+$, D_2O^+ and O_2^+. However, a 30 eV was used for UO_3^+ in order to obtain higher intensity. Values of partial vapor pressures of each vapor species were calculated using the method described in Ref. [6]

3. Results

3.1. Vaporization behavior of $Cs_2U_4O_{12}$ in vacuum, $1273 < T < 1573$ K

In vacuum, the main vapor species over $Cs_2U_4O_{12}$ found were Cs(g), $O_2(g)$ and $UO_3(g)$ while neither CsO(g) nor $Cs_2O(g)$ was detected. UO_2^+ signals observed were believed to have resulted from the fragmentation of parent $UO_3(g)$ based on thermodynamic calculation. The pressure–temperature dependences of these vapor species, plotted in Fig. 3, are also given in Table 1.

The sample was cooled down to room temperature before an X-ray powder diffraction analysis was performed. The results are shown in Fig. 4. A mixture of UO_2 and U_4O_9 phases were detected on the upper part of the sample. The lattice constants of UO_2 and U_4O_9 measured (0.5474 and 0.5451 nm) are close to those of the ASTM data (0.5471 and 0.5440 nm, respectively).

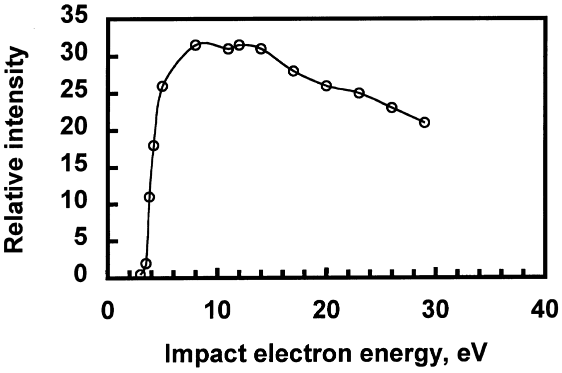

Fig. 2. I.E.C. of Cs^+ over Cs_2UO_4.

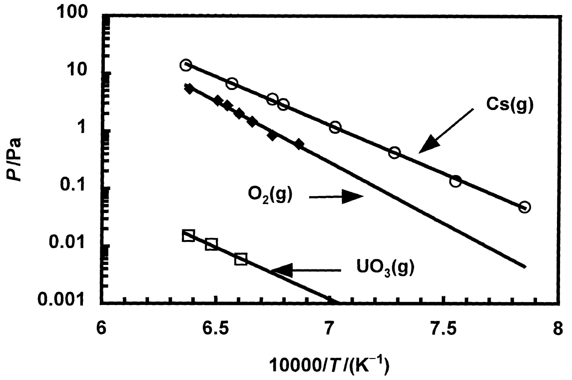

Fig. 3. Vapor pressures over $Cs_2U_4O_{12}$ in vacuum.

This implies that the hyperstoichiometric UO_{2+x} was formed according to the U–O phase diagram [3]. This result is consistent with the experimental database by Ugajin et al. [2]. They found that UO_{2+x} coexisted with $Cs_2U_4O_{12}$ if oxygen potentials at 1073 K were in the range of −209 to −260 kJ/mol. In this study, the oxygen partial pressures were measured directly by the mass spectrometer. The background pressure in the vacuum chamber outside the Knudsen cell was maintained as about $2–4 \times 10^{-5}$ Pa. Using the oxygen pressures obtained in $1273 < T < 1573$ K shown in Table 1, the oxygen potential at 1073 K is extrapolated to be about −215 kJ/mol. Thus, the following decomposition reaction was proposed to occur:

$$Cs_2U_4O_{12}(s) = 4UO_{2+x}(s) + 2(1-x)O_2(g) + 2Cs(g). \tag{2}$$

3.2. *Effects of $D_2(g)$ or $D_2(g)$ + $O_2(g)$ admission on the vaporization of $Cs_2U_4O_{12}$*

When $D_2(g)$ with flow rate of 9.2×10^{-6} m^3 Pa/s was introduced into the cell, the partial pressure of D_2O reached above 1 Pa due to $D_2(g) + 0.5O_2(g) = D_2O(g)$ reaction. Under this condition, the main vapor species detected were Cs(g), $O_2(g)$, $D_2O(g)$, CsOD(g) and a small amount of $UO_3(g)$, as shown in Fig. 5. The results are also given in Table 1. The partial pressure of $D_2(g)$ could not be detected because it decreased to less than the detection limit of the mass spectrometer. The equilibrium pressure of $D_2(g)$ at 1500 K obtained (10^{-3} Pa) from the thermodynamic calculation of the reaction $D_2(g) + 0.5O_2(g) = D_2O(g)$ agrees with the measurement result. In a separate experiment, $O_2(g)$ and $D_2(g)$ were added simultaneously to the Knudsen cell. The gas flow rates for both of the inlet gases were 5×10^{-6} m^3 Pa/s and the oxygen and deuteron ratio was maintained close to unity at the inlet of the Knudsen cell.

The $O_2(g)$ and $D_2(g)$ inside the Knudsen cell were measured. In this condition, the main vapor species remained the same as the case of $D_2(g)$ admission, while the absolute partial vapor pressures changed only slightly, as shown in Fig. 6.

A comparison of Cs(g) pressure under different experimental conditions was shown in Fig. 7. The effects of inlet gases were checked by measuring the intensity of Cs^+ simultaneously with gas introduction. For example, a 23% decrease in the intensity of Cs^+ was observed at 1273 K as soon as the $D_2(g)$ + $O_2(g)$ was introduced. On the other hand, it increased about 120% compared with that in vacuum when $D_2(g)$ was introduced. These changes, however, became smaller at higher temperatures. Measurements on oxygen pressures showed that the introduction of $D_2(g)$ + $O_2(g)$ into the Knudsen cell increased the oxygen potential in equilibrium with the specimen while introduction of $D_2(g)$ caused reducing atmosphere, as shown in Table 2. Furthermore, we found that the change of Cs(g) pressure in different environments was comparatively small compared to the substantial variation of Cs(g) pressure over Cs_2UO_4 observed previously [7] in either hydrogen or water vapor environment. The evaluation of this discrepancy is further discussed in the following section.

Table 1

Pressure–temperature relationships under various atmospheric conditions in the form of $\ln P/\mathrm{Pa} = a + b/T$ of $Cs_2U_4O_{12}$

Vapor species	In vacuum $\ln P/\mathrm{Pa} = a + b/T$	$D_2(g)$ admission $\ln P/\mathrm{Pa} = a + b/T$	D_2+O_2 admission $\ln P/\mathrm{Pa} = a + b/T$
Cs	$a = 28.05 \pm 0.33$	$a = 23.41 \pm 0.40$	$a = 28.08 \pm 0.17$
	$b = -39691.7 \pm 474.9$	$b = -32762.3 \pm 579$	$b = -40069.7 \pm 251$
O_2	$a = 32.74 \pm 1.55$	$a = 32.74 \pm 1.60$	$a = 22.46 \pm 0.90$
	$b = -48586.9 \pm 2300$	$b = -49147.7 \pm 2410$	$b = -32701 \pm 1339$
CsOD	Not available	$a = 11.32 \pm 0.91$	$a = 10.02 \pm 0.63$
		$b = -20780.5 \pm 1346$	$b = -19575 \pm 920$
D_2O	Not available	$a = -3.19 \pm 0.69$	$a = -5.61 \pm 0.96$
		$b = 5990 \pm 1029$	$b = 8603 \pm 1439$
UO_3	$a = 22.09 \pm 2.10$	$a = 40.34 \pm 2.10$	$a = 21.73 \pm 4.40$
	$b = -41161.3 \pm 3244$	$b = -69533 \pm 3247$	$b = -40456 \pm 6802$

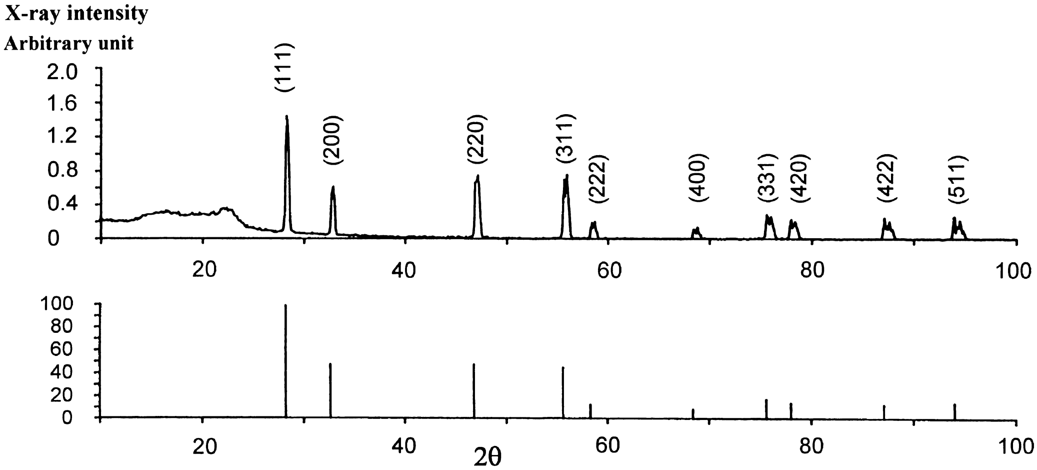

Fig. 4. X-ray diffraction pattern of the sample after mass spectrometry (top) as compared to ASTM/JSPDS reference of UO_2(s) (bottom).

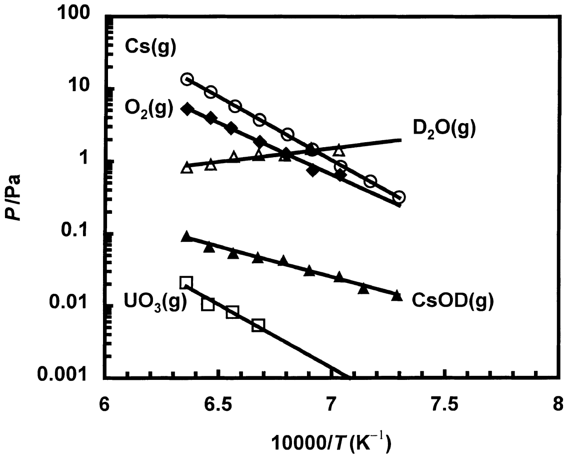

Fig. 5. Vapor pressures over $Cs_2U_4O_{12}$ with D_2(g) admission.

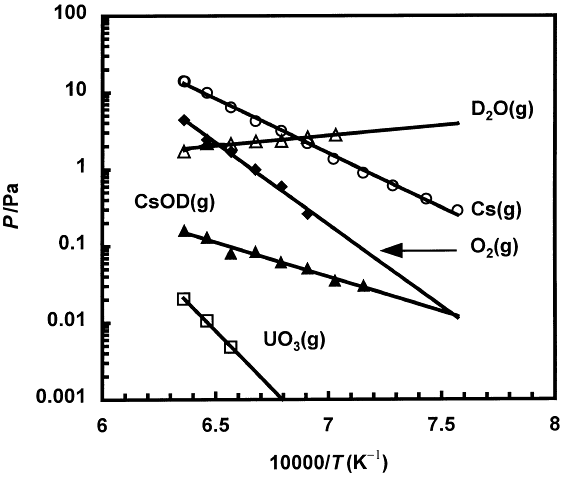

Fig. 6. Vapor pressures over $Cs_2U_4O_{12}$ with $D_2(g)/O_2(g) = 1$ admission.

4. Discussion: possible buffer effect by hyperstoichiometric UO_{2+x}

As mentioned in the previous section, the influence of $D_2(g)/O_2(g)$ admission on the vaporization of $Cs_2U_4O_{12}$ was much less significant compared to that on Cs_2UO_4. There are two possible explanations. First, the amount of inlet gas was too small to render significant change on the environmental condition. Secondly, it could be due to the coexistence of $Cs_2U_4O_{12}$ and UO_{2+x}. In fact, x in UO_{2+x} has a fairly wide range at high temperatures, for example $0 < x < 0.23$ at 1400 K. Using oxygen potential calculation model reported by Blackburn [8], the composition change of uranium dioxide from stoichiometric UO_2 to hyperstoichiometric $UO_{2.1}$ at 1473 K can cause a large increase in oxygen pressure from about 10^{-15} Pa to about 10^{-1} Pa. (however, the change from $UO_{2.05}$ to $UO_{2.1}$ is small). The large decrease of Cs^+ intensity with time observed in the initial phase of vaporization was probably resulted from the oxidation of UO_2 to UO_{2+x}. As a result, the influence of introduction of D_2(g) or $D_2(g) + O_2(g)$ on oxygen potentials inside the Knudsen cell was small. No significant effects of $D_2(g)/D_2O(g)$ introduction were obtained on changes in partial pressures of Cs(g), CsOD(g) and UO_3(g). Under these simulated conditions, Cs(g) together with CsOD(g) is still the main chemical form of cesium in the gas state over $Cs_2U_4O_{12}$. The substantial

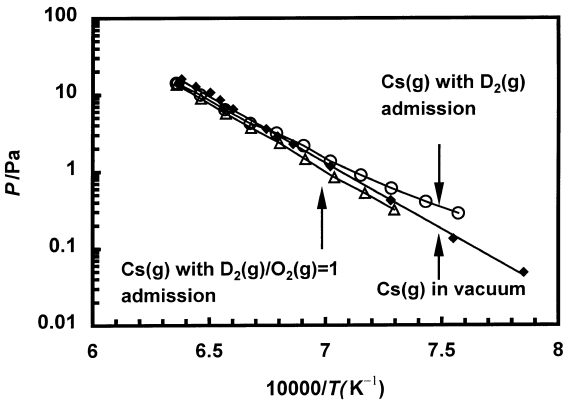

Fig. 7. Comparison of change in Cs pressure in different environments.

increase of the pressure of Cs(g) may occur only if the oxygen potential on the occasion of a real reactor accident is sufficiently low.

Assuming that UO_2 + α-U_4O_9 found at room temperature on the specimen resulted from the cooling of high temperature phase of UO_{2+x}, the hyperstoichiometric composition of UO_{2+x} could be estimated. A value of $x = 0.11$ was obtained from the X-ray powder diffraction analysis. By the Blackburn's model, a value of $x = 0.15$ could be calculated from the measured oxygen pressures in the present study. The discrepancy may be resulted from the oxygen pressure measurements. The oxygen potential evaluation will be revealed in the future work.

Using $\Delta_f H^\circ(UO_{2.10})$ reported by Ugajin et al. [9] and Cordfunke's thermodynamic table, the enthalpy change for reaction (2) at the averaged temperature of the experiment can be calculated:

$$\begin{aligned}&\Sigma\Delta_f H^\circ(1450\ \mathrm{K})\\&\quad = 4\times\Delta_f H^\circ(1450\ \mathrm{K})|_{UO_{2+x}} - \Delta_f H^\circ(1450\ \mathrm{K})|_{Cs_2U_4O_{12}}\\&\quad = 1272\ \mathrm{kJ/mol}.\end{aligned}$$

While, the reaction enthalpy change obtained for this study at 1450 K is

$$\begin{aligned}\Sigma\Delta_f H^\circ(1450\ \mathrm{K}) &= -2R(b_{Cs}+b_{O_2}) + x\times 2Rb_{O_2}\\&= (1280\pm 46)\ \mathrm{kJ/mol},\end{aligned}$$

where b is the corresponding slope of the pressure–temperature curve listed in Table 1.From the discussion above, it is concluded that the current experimental data are consistent with the value calculated from the published data.

5. Conclusions

1. Vaporization behaviors of $Cs_2U_4O_{12}$ were investigated both in vacuum and in $D_2(g)/O_2(g)$ mixture gas environments in a temperature range from 1273 to 1573 K. Cs(g) was found to be the dominant vapor species of $Cs_2U_4O_{12}$ in vacuum condition, which is the same as the case of Cs_2UO_4. When the sample was cooled down to room temperature, a mixture of UO_2 and U_4O_9 were observed on the upper part of the specimen. It suggested the decomposition of $Cs_2U_4O_{12}$ into UO_{2+x} during the vaporization process at high temperatures.
2. Cs(g), CsOD(g), $D_2O(g)$ and $O_2(g)$ are the main vapor species if $D_2(g)$ or D_2 + $O_2(g)$ is introduced into the Knudsen cell. Compared to the vaporization in vacuum, Cs(g) pressure increased only slightly when $D_2(g)$ was introduced into the cell. In $D_2O(g)$ environment, however, partial pressure of Cs(g) was slightly lower than that in vacuum.
3. The influence of $D_2(g)$ or $D_2(g)$ + $O_2(g)$ environment examined in the simulation did not show significant effect on the vaporization of $Cs_2U_4O_{12}$ compared to that of Cs_2UO_4. If the oxygen potential in a reactor accident is decreased sufficiently low by hydrogen reduction atmosphere, large increase of Cs(g) pressure from $Cs_2U_4O_{12}$ will be expected.

Acknowledgements

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Table 2
Comparison of environmental conditions at 1500 K

Environment condition	$D_2(g)$ inlet	In vacuum	$D_2(g)/O_2(g) = 1$ inlet
Oxygen pressures (Pa)	0.98	1.34	1.73
Oxygen potentials (kJ/mol)	−144	−140	−137
Cesium pressures (Pa)	3.76	3.70	3.12

References

[1] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.
[2] M. Ugajin et al., J. Nucl. Mater. 230 (1996) 195.
[3] E.H.P. Cordfunke, R.J.M. Konings, in: Thermochemical Data for Reactor Materials and Fission Products, Elsevier, Amsterdam, 1990.
[4] V. Venugopal et al., J. Nucl. Mater. 199 (1992) 29.
[5] M.Yamawaki et al., J. Nucl. Mater. 223 (1995) 80.
[6] A. Suzuki et al., J. Nucl. Mater. 248 (1997) 111.
[7] J. Huang et al., J. Alloys Compounds 271–273 (1998) 625 .
[8] P.E. Blackburn, J. Nucl. Mater. 46 (1973) 244.
[9] M. Ugajin et al., J. Nucl. Mater. 116 (1983) 175.