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# Vaporization properties of $SrUO_3$ and $BaUO_3$ in atmospheres simulating accident conditions

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## Abstract

Effects of various environments on vaporization characteristics of $BaUO_3$ and $SrUO_3$ have been studied by means of the Knudsen effusion mass spectrometry. Three kinds of Knudsen cells were employed for simulating different accident atmospheres over temperature ranges from 1470 to 1920 K. The vapor pressures obtained in a platinum Knudsen cell were used as the standard values, with which those obtained in other conditions were compared. A graphite Knudsen cell was utilized to simulate the graphite environment of high temperature gas-cooled reactors (HTGR). On the other hand, a specially designed Knudsen cell with a gas inlet system attached to its bottom was employed in order to introduce reactive gases such as $D_2(g)$ or $D_2O(g)$ from the outside of the mass spectrometer into the cell. In this way, the effects of hydrogen or water vapor on the vaporization of fission products barium and strontium were examined. © 1997 Elsevier Science B.V.

## 1. Introduction

The thermochemical data for reactor materials and fission products have been provided for a wide variety of radioactive elements and their compounds by many researchers, for instance by Cordfunke and Konings in 1990 [1]. Many scientists are, however, still making approaches either to measure the absent data of the compounds of interest or to estimate by using various computer codes, since at least 25 elements and their many compounds are of importance for the reactor safety analyses. The so called 'gray phase' like (Ba, Sr, Cs)(Zr, U, Pu)$O_{3+x}$ is one example that has attracted much attention recently [2–5] because their properties are essential to interpret phenomena in high burnup uranium based fuels. While the vaporization properties of $BaUO_3$ and $SrUO_3$ in normal conditions have been investigated before [6,7], this paper is focused on their properties in case of a failed pin or a severe accident that may occur in LWR or HTGR. In an event of failures these compounds may be leaked from the nuclear fuel pins or coated particles to react with the coolant substance, then transported to the environment eventually. The test will provide some fundamental data for an experimental program, 'VEGA' initiated at JAERI to study phenomena associated with the fission product release and transport in severe accident conditions, e.g., fuel dissolution and chemistry. From this standpoint, platinum and graphite Knudsen cells were utilized in the measurements. The latter served as a graphite environment simulating the graphite coating layers of the Triso-coated particles as well as the graphite block in the core of HTGR. A gas inlet system was designed to introduce reactive sweep gases such as $D_2(g)$ or $D_2O(g)$ from the outside of mass spectrometer into the Knudsen cell. That has enabled us to investigate the influence of hydrogen or water vapor on the vaporization of the testing materials.

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## 2. Experimental

The samples were prepared by means of the hydrogen reduction of $BaUO_4(s)$ and $SrUO_4(s)$, as described in detail previously [6]. The main process can be expressed briefly as the following,

$$UO_3(s) + (\text{Ba or Sr})CO_3(s) = (\text{Ba or Sr})UO_4(s) + CO_2(g) \quad (1053\ \text{K}, 8\ \text{h}), \tag{1}$$

$$(\text{Ba or Sr})UO_4(s) + H_2(g) = (\text{Ba or Sr})UO_3(s) + H_2O(g) \quad (1673\ \text{K}, 8\ \text{h}). \tag{2}$$

Formation of the pure phase of $BaUO_3$ was confirmed by X-ray diffraction analysis. Since it was difficult to obtain pure $SrUO_3$, a mixture of $SrUO_3$ + 23mass%$UO_2$ was prepared for the present study. The modified Nuclide 12-90-HT type magnetic focusing 90° sector mass spectrometer employed in this study was described previously [8]. At first, a platinum Knudsen cell with an orifice of 0.5 mm in diameter was used. Then similar experiments were repeated by using a graphite cell with an orifice of 0.5 mm in diameter held in a tantalum susceptor. The gas inlet system made it possible that a molecular flow of $D_2(g)$ or $D_2O(g)$ be introduced from the outside of mass spectrometer into the Knudsen cell and so as to establish an equilibrium easily [9]. The absolute vapor pressure was calibrated by using silver as the standard reference material. The temperature in the Knudsen cell was also calibrated by measuring the melting point of silver.

## 3. Results and discussion

### 3.1. The effects of graphite environment

The dominant vapor species in graphite cell was Ba(g) over $BaUO_3$ as shown in Fig. 1. The vapor pressure of BaO(g) in graphite cell was lower than about $10^{-4}$ Pa. No CO(g) and $CO_2(g)$ were detected either. The following reactions were assumed to occur:

$$BaUO_3(s) = BaO(g) + UO_2(s), \tag{3}$$

$$BaO(g) = Ba(g) + 0.5O_2(g), \tag{4}$$

$$SrUO_3(s) = Sr(g) + UO_2(s) + 0.5O_2(g), \tag{5}$$

$$Sr(g) + 0.5O_2(g) = SrO(g), \tag{6}$$

$$C(s) + 0.5O_2(g) = CO(g), \tag{7}$$

$$C(s) + O_2(g) = CO_2(g), \tag{8}$$

$$UO_2(s) = UO_2(g). \tag{9}$$

By comparing with the vaporization features in platinum Knudsen cell as reference, it is obvious that the partial pressure of Ba(g) in graphite cell remarkably increased up to about three orders of magnitude higher than the whole vapor pressure of Ba-containing species in Pt cell.

Because the ratio of $P_{Ba}/P_{BaO}$ is found larger than $10^5$, the oxygen pressure in the graphite cell estimated from Eq. (4) could not be higher than about $10^{-23}$ Pa at 1500 K, then the partial pressures of CO(g), $CO_2(g)$ were calculated from Eqs. (7) and (8) as about $10^{-3}$ and $10^{-10}$ Pa, respectively, which were hard to be detected by our mass spectrometer. As for possibility of formation of carbides in graphite cell, the possible reaction such as $Ba(g) + 2C(s) = BaC_2(s)$ was considered. At 1500 K, calculated equilibrium pressure of Ba(g) from the above reaction is as high as 1800 Pa that is much higher than the experiment value of about 1 Pa. This indicates the barium carbide would not be formed in our test conditions. After the mass spectrometric test, X-ray diffraction showed no evidence of any carbides either.

As for $SrUO_3$, the dominant vapor species over $SrUO_3$ in graphite cell was Sr(g) as shown in Fig. 2. An increase of vapor pressure of Sr(g) was also found, but it was only 2 times higher than that in the Pt cell, a much smaller increment compared to $BaUO_3$. Compared to the $SrUO_3$ + $UO_2$ mixture, the reducing effect of graphite cell was much more significant in the vaporization of $BaUO_3$.

In the vaporization of both $BaUO_3$ and $SrUO_3$, graphite acted to decrease the oxygen potential in the cell so that the partial vapor pressures of Ba(g) and Sr(g) increased in the graphite cell while those of the oxide species decreased. The difference in the effect of graphite cell between $SrUO_3$ and $BaUO_3$ seems to be attributed to the different ratio of the vapor pressures of oxide-form and metallic-form vapor species. Since the Gibbs energy of formation of BaO(g) at high temperature is more negative (−213 kJ/mol at 1700 K) than that of SrO(g) (−95 kJ/mol at 1700 K), in Pt cell the abundance of BaO(g) becomes much higher than SrO(g), while that of Sr(g) is much higher than Ba(g). As a result, the effect of graphite cell on the increment in Sr(g) vapor pressure was not as much high as that for Ba(g).

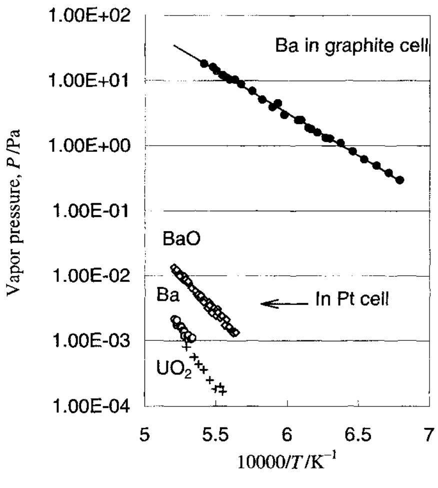

Fig. 1. Comparison of vaporization of $BaUO_3$ in Pt cell and in graphite cell.

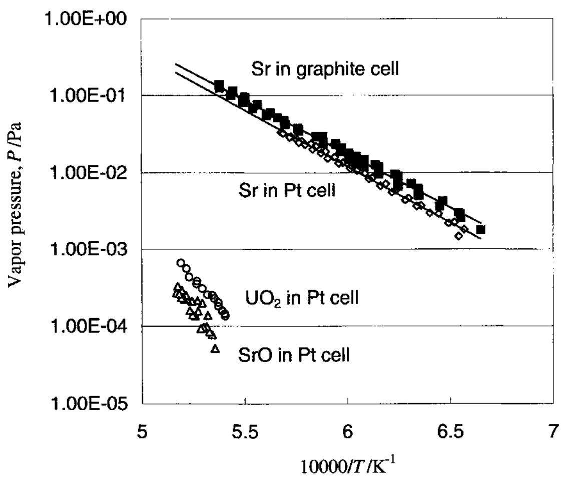

Fig. 2. Comparison of vaporization of $SrUO_3 + UO_2$ in Pt cell and in graphite cell.

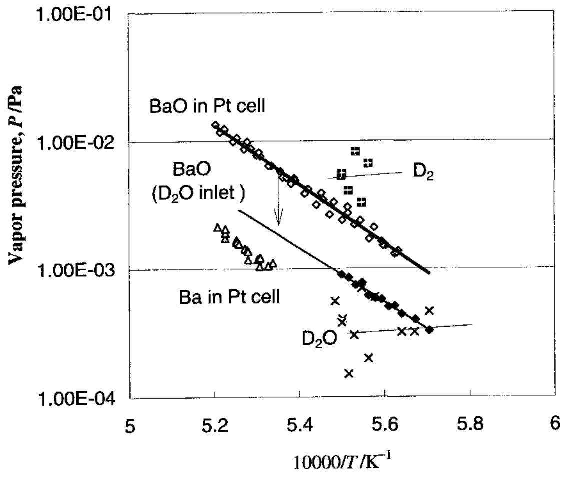

Fig. 3. Effect of $D_2O(g)$ admission on vaporization of $BaUO_3$ in Pt cell.

To estimate vapor pressures of fission products in real reactor cores, it is important to determine the oxygen potential inside the Knudsen cell and compare the values with the actual oxygen potentials in reactor cores. For the case of the $SrUO_3 + UO_2$ mixture, the oxygen potential in the Pt cell from 1700 to 1900 K was in the range from −474 to −392 kJ/mol calculated from Eq. (6). While that for $BaUO_3$ in Pt cell in the same temperature range was from −407 to −393 kJ/mol. Both of them fell in the actual oxygen potential range of −500 to −375 kJ/mol in the coated particles of HTGR as reported by Lindemer and Nordwall [10]. That means the conditions in Pt cell seem to be close to the real case of reactor core in normal operation state. On the other hand, the oxygen potential in the graphite Knudsen cell was roughly calculated to be below about −800 kJ/mol for both the samples. Such a low oxygen potential may be realized in the graphite region in case of failures of the coated layers. Accordingly, the simulation with the graphite cell in this study is important in assessing the fission products behavior both in normal and accident conditions in HTGR.

### 3.2. The vaporization characteristics in water vapor environment

The $D_2O(g)$ gas was selected to simulate water vapor environment, since it is a convenient way in the mass spectrometry to avoid any disturbance coming from the background $H_2O(g)$. When $D_2O(g)$ was introduced into the Knudsen cell from the outside, the partial vapor pressures of Sr(g) and SrO(g) over $SrUO_3 + UO_2$, as well as those of BaO(g) and Ba(g) over $BaUO_3$ all decreased compared to those in a Pt cell, as shown in Figs. 3 and 4.

X-ray diffraction analysis was made after the mass spectrometric test in $D_2O(g)$ environment. By means of X-ray diffraction analysis, two phases of $SrUO_{3.597}$ and $SrUO_3$ were identified in the central part of the $SrUO_3$ sample. Their diffraction patterns were consistent with the data given by ASTM/JCPDS files. The lattice constant of the $BaUO_3$ sample was also found to have decreased from 0.441609 to 0.438254 nm. It suggested the change from $BaUO_3$ toward $BaUO_{3.3}$. So both $BaUO_3$ and $SrUO_3$ in $D_2O(g)$ environment were oxidized to possess a higher oxygen content as follows:

$$BaUO_3(s) + xD_2O(g) = BaUO_{3+x}(s) + xD_2(g), \quad (10)$$

$$SrUO_3(s) + 0.597D_2O(g)$$
$$= SrUO_{3.597}(s) + 0.597D_2(g). \quad (11)$$

So the decreasing of vapor pressures of the main species in water vapor environment suggests that these two compounds have lower vapor pressures with higher oxygen content in their composition.

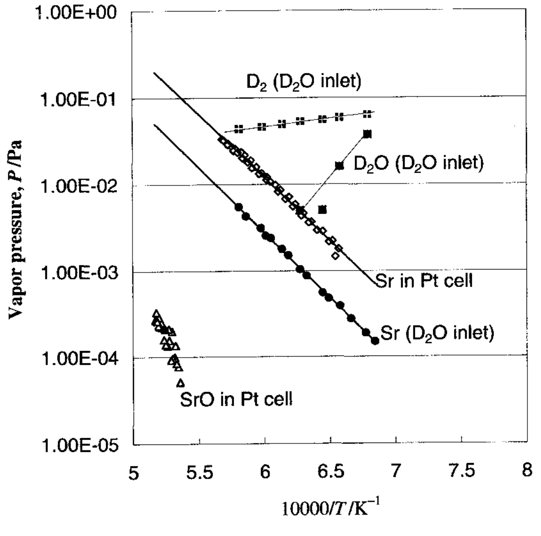

Fig. 4. Effect of $D_2O(g)$ admission on vaporization of $SrUO_3 + UO_2$ in Pt cell.

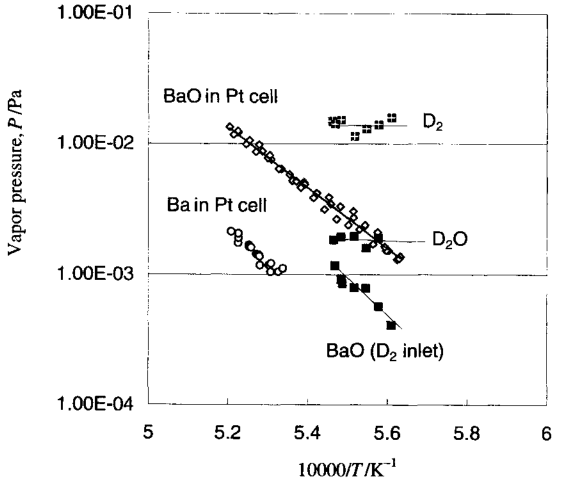

Fig. 5. Effect of $D_2(g)$ admission on vaporization of $BaUO_3$ in Pt cell.

It should also be noticed that there was no evidence of other vapor species such as BaOD and SrOD. Considering the following reactions,

$$Ba(g) + 2D_2O(g) = Ba(OD)_2 + D_2(g), \qquad (12)$$

$$Sr(g) + 2D_2O(g) = Sr(OD)_2 + D_2(g). \qquad (13)$$

Partial pressures of $Ba(OD)_2$ and $Sr(OD)_2$ at 1600 K are calculated to be around $10^{-7}$ Pa which is far below the detection limit of the mass spectrometer.

### 3.3. The vaporization characteristics in hydrogen environment

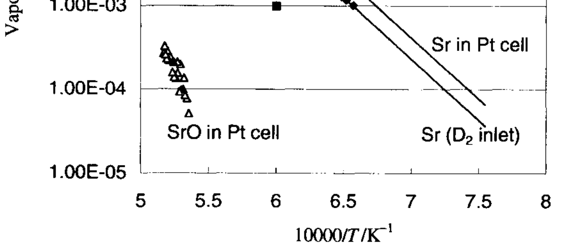

Fig. 6. Effect of $D_2(g)$ admission on vaporization of $SrUO_3 + UO_2$ in Pt cell.

Table 1
Oxygen potentials in different environments

| $RT \ln P_{O_2}$ (kJ/mol) | $BaUO_3$ at 1800 K | $SrUO_3 + UO_2$ at 1500 K |
|---|---|---|
| In graphite | −800 | −800 |
| In Pt | −415 | −510 |
| In $D_2$ environment | −355 | −410 |
| In $D_2O$ environment | −310 | −350 |

From the same reason as above, $D_2(g)$ instead of $H_2(g)$ was used to simulate hydrogen environment in the present study. When $D_2(g)$ was introduced into the Knudsen cell, the partial pressures of the main vapor species, that is, BaO(g) and Ba(g) over $BaUO_3$ and Sr(g) and SrO(g) over $SrUO_3 + UO_2$, decreased a little as shown in Figs. 5 and 6, respectively.

It should be noticed that no large difference of vaporization properties was found regardless of whether $D_2(g)$ or $D_2O(g)$ was introduced. In the temperature range of measurement, the partial pressure of $D_2(g)$ was always larger than that of $D_2O(g)$ in both cases. So the results in the $D_2(g)$ environment appeared to be very similar to those in the $D_2O(g)$ environment. From the ratios of $D_2(g)/D_2O(g)$, Ba(g)/BaO(g) and Sr(g)/SrO(g), the oxygen potentials in different environments were calculated and listed in Table 1:

$$RT \ln P_{O_2} \text{ (in graphite)} < RT \ln P_{O_2} \text{ (in Pt)}$$
$$< RT \ln P_{O_2} \text{ (in } D_2) < RT \ln P_{O_2} \text{ (in } D_2O).$$

According to the estimated phase diagram given by Cordfunke, the $BaUO_3$ or $SrUO_3$ can exist only in a very low oxygen potential [1]. They were found to be unstable in a Pt cell at high temperature during the mass spectrometric test. X-ray diffraction analysis indicated that both of them were oxidized toward a high oxygen content of $BaUO_{3.12}$ and $SrUO_{3.1}$ after a mass spectrometric test in the Pt cell [6,7]. Even when some amount of $D_2(g)$ was introduced into the cell, the $BaUO_3$ and $SrUO_3$ samples were still oxidized a little toward $BaUO_{3+x}$ and $SrUO_{3+x}$. If the pressure of input hydrogen was high enough to reduce these compounds according to Eq. (2), these two compounds could remain as the stoichiometric composition. Unfortunately, the amount of inlet gas in our case was limited because the gas flow into the cell should be maintained in the molecular flow region otherwise the equilibrium inside the cell would be destroyed.

## 4. Conclusion

As part of the efforts to clarify the chemical states of fission products and their compounds in accident conditions, the vaporization properties of $SrUO_3$ and $BaUO_3$ at high temperature have been studied by the Knudsen effusion mass spectrometry. A graphite Knudsen cell was employed to simulate the graphite environment of high temperature gas-cooled reactors. It had such a strong effect on the vaporization of $BaUO_3$ that the partial pressure of Ba(g) increased up to three orders of magnitude higher than the whole vapor pressure of Ba-containing species in a platinum cell. While it did not show such a strong influence on the vaporization of $SrUO_3$. A specially designed Knudsen cell with a gas inlet tube attached through its bottom was also utilized to investigate the influence of hydrogen or moisture atmosphere by introducing $D_2(g)$ or $D_2O(g)$ from the outside of mass spectrometer into the Knudsen cell. However, vapor pressures of all the main species, i.e., elemental and monoxide species, over these two compounds decreased in water vapor atmosphere. In hydrogen atmosphere, the vapor pressures of these main vapor species will also decrease as long as the pressure of hydrogen is not too high. It further suggested that hyperstoichiometric compounds $SrUO_{3+x}$ and $BaUO_{3+x}$ have lower vapor pressures compared with their stoichiometric compounds.

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