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Section 2. Vaporization

High-temperature, Knudsen cell-mass spectroscopic studies on lanthanum oxide/uranium dioxide solid solutions

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Abstract

Knudsen cell-mass spectroscopic experiments were carried out with lanthanum oxide/uranium oxide solid solutions (1%, 2% and 5% (metal at.% basis)) to assess the volatilization characteristics of rare earths present in irradiated nuclear fuel. The oxidation state of each sample used was conditioned to the 'uranium dioxide stage' by heating in the Knudsen cell under an atmosphere of 10% CO_2 in CO. The mass spectra were analyzed to obtain the vapour pressures of the lanthanum and uranium species. It was found that the vapour pressure of lanthanum oxide follows Henry's law, i.e., its value is directly proportional to its concentration in the solid phase. Also, the vapour pressure of lanthanum oxide over the solid solution, after correction for its concentration in the solid phase, is similar to that of uranium dioxide. © 2001 Published by Elsevier Science B.V.

1. Introduction

Under some postulated reactor accident conditions, the fuel can reach high temperatures and the release of fission products and actinides present in the fuel can become important for safety considerations. Rare-earth elements form a significant fraction of the fission products produced during nuclear fission [1]. High-temperature Knudsen cell-mass spectroscopic experiments, with lanthanum doped-uranium oxide, were carried out to understand the volatilization of rare earths present in the used fuel. Lanthanum can be considered representative of the majority of rare-earth elements [2]. These experiments provide data needed for the validation of computer codes used to model fission-product release from fuel and transport in the reactor coolant system for reactor safety analysis.

2. Experimental

Samples of La_2O_3/UO_2 were prepared with three different concentrations of lanthanum in UO_2 (1%, 2%, and 5% (metal at.% basis), i.e., $La/(La + U) = 0.01$, 0.02 and 0.05). A known amount of La_2O_3 powder was dissolved in concentrated nitric acid and the resulting solution was diluted to 50 ml using distilled water. The lanthanum nitrate–nitric acid solution was mixed with a solution of uranyl nitrate (20.0 g of $UO_2(NO_3)_2 \cdot 6H_2O$ in 50 ml of distilled water). Ammonium hydroxide (concentration 25% NH_4OH, volume 30 ml) was added to the uranium–lanthanum solution to precipitate ammonium diuranate along with co-precipitated lanthanum. The resulting slurry was simmered for 1 h, cooled, centrifuged and the liquid was decanted. Dilute ammonium hydroxide was added to the precipitate to reslurry it, followed by centrifugation. The precipitate-washing procedure was repeated five times. The resulting precipitate was air-dried at 105°C for 1 h, and then converted to lanthanum-doped U_3O_8 by heating in air at 900°C for ~20 h. This solid was reduced to lanthanum-doped UO_2 by heating in a flowing H_2/Ar mixture (3% H_2) for 3–4 h at ~850°C [3]. The homogeneity of the resulting $(La,U)O_y$ (where y has a value close to 2) was verified by X-ray diffraction. The XRD patterns of the samples were dominated by the fluorite lattice peaks

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Table 1
Ionization cross-sections used to calculate pressures

Parent species	Ionization process	Ionization cross-sections[a]	Source
O	$O + e^- \rightarrow O^+ + 2e^-$	0.9	Margreiter et al. [14]
U	$U + e^- \rightarrow U^+ + 2e^-$	4.6	Halle et al. [15]
La	$La + e^- \rightarrow La^+ + 2e^-$	11.96	Mann [16]
LaO	$LaO + e^- \rightarrow LaO^+ + 2e^-$	9.7	[b]
UO	$UO + e^- \rightarrow UO^+ + 2e^-$	3.29	[b]
UO_2	$UO_2 + e^- \rightarrow UO_2^+ + 2e^-$	1.21	[b]
UO_3	$UO_3 + e^- \rightarrow UO_3^+ + 2e^-$	0.31	[b]

[a] Ionization cross-section units are 10^{-16} cm^2.
[b] This work – see text for the procedure used to arrive at the value.

indicating that the lanthanum was present as a solid solution in the UO_2 lattice. [1] The radii of the U^{4+} and La^{3+} ions are close enough to favour the formation of the solid solutions of their oxides [5–8]. It has been shown in several reports that UO_2 and La_2O_3 can form a continuous series of solid solutions [9,10].

The Knudsen cell-mass spectrometer system used in this work has been described in detail elsewhere [11,12]. Tantalum was used as the cell material. A tantalum capillary, from a vacuum feed through, brought the flow of reactive gases into the Knudsen cell [11]. The cell was inductively heated.

Solid $(La,U)O_y$ was placed in the Knudsen cell and pumped for more than 2 h to establish the working vacuum in the Knudsen cell-mass spectrometer system. A gas flow of 10% CO_2 in CO (2 ml/min) was introduced into the cell and the cell was heated to 1130°C. This step ensured that the uranium in the solid sample was primarily U(IV). [2] The heating and the gas flow were stopped after 1 h and the sample was cooled to room temperature. After an interval of about 1 h, the cell was heated to the target temperature (2120°C or 2000°C) under vacuum and the mass spectra of the gases effusing from the Knudsen cell were recorded as a function of time. Volatile species effusing from the cell orifice and entering the mass spectrometer were ionized by electron bombardment (at 30 eV) to produce positive ions which were analyzed using the mass spectrometer. Before and after each experiment, the sensitivity of the mass spectrometer was determined using a calibrated leak of perfluorotributylamine (FC43).

3. Results and discussion

3.1. Calculation of vapour pressure

The peaks seen at mass 139 (La^+), 155 (LaO^+), 238 (U^+), 254 (UO^+), 270 (UO_2^+) and 286 (UO_3^+) in the mass spectra were analyzed to obtain the vapour pressures of the corresponding lanthanum and uranium species. The vapor pressure, p_i, of a species i in the effusing gas from the Knudsen cell was calculated [12] using the equation

$$P_i = I_i T / (\sigma_i \ \gamma_i \eta_i k_{Ag} f s), \tag{1}$$

where I_i is the signal intensity of the cation formed from the ionization of the species, T the temperature/K, σ_i the ionization cross-section of the precursor to the ion, γ_i the mass dependence of the quadrupole analyzer and electron multiplier efficiency for the mass of the ion, η_i the isotopic abundance, k_{Ag} the calibration constant, derived from a calibration experiment with the silver primary standard, f the correction for the area of the orifice of the cell (relative to that in the silver experiment), and s is the correction for the sensitivity of the instrument on the day of the experiment (FC43 secondary standard).

The accuracy of the vapour pressures determined using Knudsen cell-mass spectroscopy depends greatly on the chemical system being studied and the uncertainty in the values of the various terms in Eq. (1), particularly on the value of the ionization cross-section. The values for the ionization cross-sections used in this work are listed in Table 1. The value selected for the oxygen atom (σ_O) is from the paper by Margreiter et al. [14] for 30 eV electron energy. The value for the uranium atom (σ_U) is from the experimental results of Halle et al. [15] which are supported by the calculations of Margreiter et al. [14]. For the lanthanum atom ionization cross-section (σ_{La}), the lower of the two values calcu-

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[1] Analysis of the observed diffraction peaks of the fluorite lattice, with 20°<2θ<80°, gave value of unit-cell parameter $a = 5.501$, 5.498 and 5.501 Å for the samples with La content of 1%, 2% and 5%, respectively. (Error in the lattice parameter is estimated to be ±0.02 Å.) These values of the unit-cell parameter are slightly higher than the literature value of the unit-cell parameter for UO_2 (i.e., 5.4704 Å [4]).

[2] The oxygen potential of a CO/CO_2 atmosphere, with [CO]/[CO_2] = 10, at 1130°C, the temperature used to condition the samples prior to the Knudsen cell experiment, is ∼−376 kJ/mol according to the relationship given by Lindemer and Sutton [13]. Under such conditions UO_2 should be the stable phase [6,7] and this explains the absence of a UO_3 signal in most of the experiments.

Table 2
Apparent pressures calculated from ions seen in the Knudsen cell-mass spectra of La-doped urania samples

Exp.	Temp. (°C)	La (at.%)	Vapour pressure[a]					
Ion			139 La^+	155 LaO^+	238 U^+	254 UO^+	270 UO_2^+	286 UO_3^+
96H2	2120	5	1.95E−06	5.80E−06	1.41E−05	7.10E−05	1.46E−04	1.17E−06
96H2	2120	5	1.80E−06	5.25E−06	1.69E−05	7.99E−05	1.46E−04	
96H2	2120	5	1.70E−06	5.04E−06	1.74E−05	8.44E−05	1.46E−04	5.87E−07
96H3	2120	2	8.00E−07	2.00E−06	1.15E−05	5.77E−05	1.58E−04	
96H3	2120	2	7.00E−07	2.00E−06	1.15E−05	6.22E−05	1.46E−04	
96H3	2120	2	5.90E−07	1.80E−06	1.32E−05	6.66E−05	1.46E−04	
96H4	2120	1	2.60E−07	1.50E−06	1.19E−05	8.88E−05	1.34E−04	
96H4	2120	1	2.80E−07	1.80E−06	1.35E−05	1.07E−04	1.46E−04	
96H4	2120	1	3.00E−07	1.90E−06	1.52E−05	1.11E−04	1.34E−04	
96H7	2000	2	2.00E−07	2.00E−06	3.47E−06	1.69E−05	6.09E−05	
96H7	2000	2	1.80E−07	1.50E−06	2.60E−06	1.47E−05	5.84E−05	4.30E−07
96H7	2000	2	2.10E−07	2.00E−06	2.60E−06	1.55E−05	5.72E−05	3.52E−07

[a] Vapour pressure values (in atm) are for the parent species of the ion. Read 1.95E−06 as 1.95×10^{-6}.

lated by Mann is selected [16,17]. The value for σ_{LaO} is calculated using the formula of Kordis and Gingerich [18] for calculating the ionization cross-section of diatomic species from those of the atoms, i.e.,

$$\sigma_{Lao} = 0.75(\sigma_{La} + \sigma_{O}). \qquad (2)$$

Calculation of the ionization cross-sections of different uranium oxides is more problematic [19–21]. We used the relative values of the product of the multiplier yield and the relative ionization cross-sections given by Blackburn and Danielson [20] to calculate the ionization cross-sections for different uranium oxides from the experimentally determined value of the ionization cross-section for the U atom (Table 1). The error introduced by assuming a constant value for the multiplier yield (for the mass range 238–286 amu) is acceptable considering the other sources of error in the method. [3]

3.2. Vapour pressures

Mass spectra of the gases effusing from the Knudsen cell were recorded as a function of time after the cell had reached the desired temperature. Generally 8–12 spectra were recorded for every experiment, over a period of about 2 h. For each experiment, the vapour pressure values of each species, obtained using Eq. (1), were plotted as a function of heating time. The time dependence of the LaO^+ and UO_2^+ ion peaks were very similar and suggest that the lanthanum oxide was being volatilized along with the uranium dioxide matrix. Three values near the maximum of the vapour pressure–time plot (generally in the early part of the experiment) were selected to represent the vapour pressure under the experimental conditions and such values are listed in Table 2. The significant figures in these results are only to the first decimal place. Following the practice in the thermodynamic literature, extra (non-significant) figures are shown in Table 2 to preclude rounding errors.

Fig. 1 shows the 'total vapour pressure' of the lanthanum species as a function of lanthanum metal concentration in the solid phase. The total vapour pressure of lanthanum species is assumed to be the sum of the vapour pressures of LaO and La calculated from the intensities of the La^+ (139) and LaO^+ (155) ions, re-

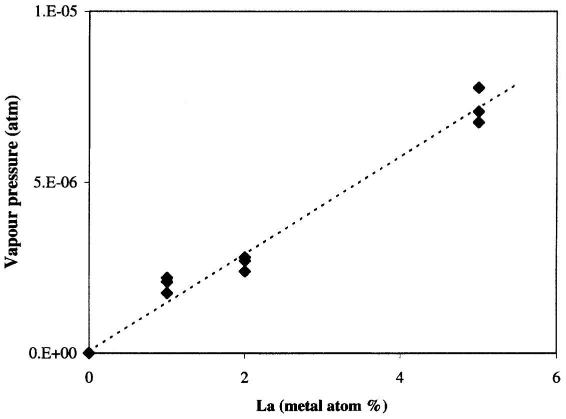

Fig. 1. Total vapour pressure of lanthanum species as a function of lanthanum concentration in La-doped urania at 2120°C. The dashed line shows a linear fit to the observed data. (Read 1.E−05 as 1×10^{-5}.)

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[3] If a different set of values of the ionization cross-sections than those used here becomes accepted, one can calculate the pressure results for the new values of the ionization cross-sections from the detailed results listed in Table 2.

spectively. The La^+ ions were most probably formed by the cracking of LaO during ionization by the electrons [22], i.e.,

$$\mathrm{Lao} + e^- \rightarrow La^+ + 2e^- + O \qquad (3)$$

The much higher intensity observed for LaO^+ relative to that of La^+ (Table 2) suggests that the majority of the LaO species do not undergo cracking under the experimental conditions used here. The plot of total vapour pressure of La species vs. La concentration in the solid shows a linear relationship in agreement with Henry's law [23].

Fig. 2 shows a plot of the total vapour pressure of the uranium species as a function of lanthanum metal concentration in the solid phase. The total vapour pressure value of uranium species shown in this figure is the sum of the pressures of U, UO, UO_2 and UO_3 calculated, using Eq. (1), from the intensities of U^+ (238), UO^+ (254), UO_2^+ (270) and UO_3^+ (286) ions, respectively. The values calculated for UO_3 are much smaller than those for UO_2 (Table 2) and the inclusion of UO_3 pressure in calculating the total vapour pressure of uranium species makes little difference in the value of the total pressure. The UO_3^+ signal was seen only in a few experiments (Table 2) and it was transient. This observation, about the transient nature of the UO_3^+ signal from UO_{2+x} samples, is in agreement with the work of others [11,20].

Fig. 2 also shows values of the vapour pressure of UO_2 (at 2000°C and at 2120°C – the two temperatures used in this work) as calculated using the relationships proposed by Wang et al. [24] and Ackermann et al. [25]. Our observed values are slightly higher than the calculated values for UO_2. The literature results shown in Fig. 2 give support to the approximate method used here to obtain vapour pressures from mass-spectroscopic data. The agreement between the vapour pressures of UO_2 obtained here with those in the literature validates the method used here to condition the sample of doped UO_{2+x} to the U(IV) stage.

Fig. 3(a) shows the ratios of the total vapour pressures of uranium and lanthanum species, i.e., (Σ pressures of uranium species)/(Σ pressures of lanthanum species) observed for different samples at 2120°C. As expected, the observed ratio of uranium to lanthanum

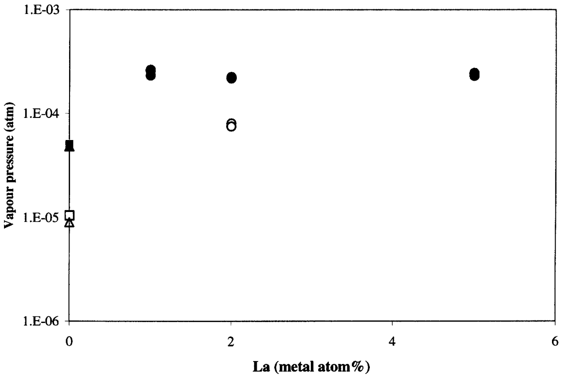

Fig. 2. Total vapour pressure of uranium species as a function of lanthanum concentration in La-doped urania: (a) ●, experiments at 2120°C; (b) ○, experiments at 2000°C; (c) ■, calculated value at 2120°C using relationship of Wang et al. [24]; (d) ▲, calculated value at 2120°C using relationship of Ackermann et al. [25]; (e) □, calculated value at 2000°C using relationship of Wang et al.; and (f) △, calculated value at 2000°C using relationship of Ackermann et al. (Read 1.E–03 as 1×10^{-3}.)

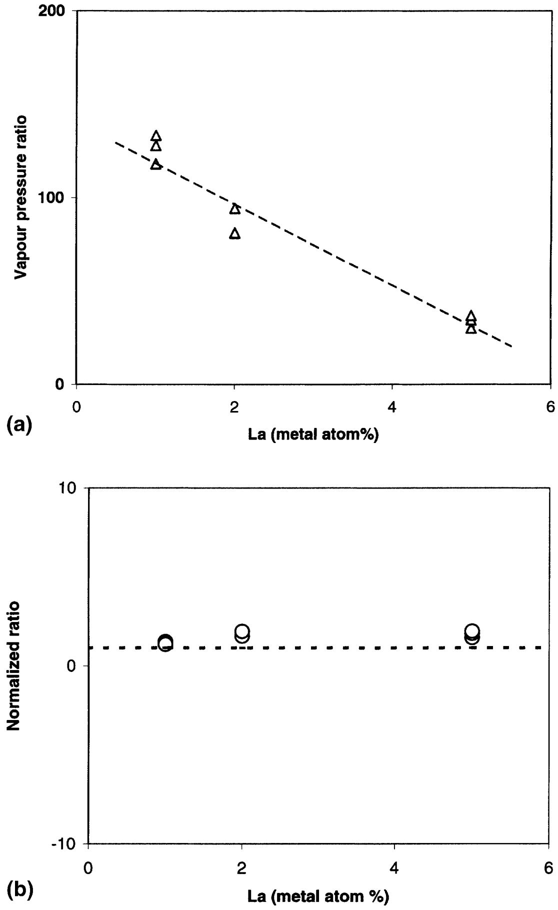

Fig. 3. (a) Ratio of total vapour pressure of the uranium species and total vapour pressure of the lanthanum species, at 2120°C, as a function of lanthanum concentration in the solid phase in La-doped urania. (b) Normalized ratio of total vapour pressure of the uranium species and total vapour pressure of the lanthanum species, at 2120°C, as a function of lanthanum concentration in the solid phase in La-doped urania. The ratio normalized for the metal atom concentrations in the solid phase. The horizontal dashed line shows normalized ratio value = 1.

vapour pressures increases as the lanthanum concentration decreases. However, when this ratio is corrected for the concentrations of the two metals in the solid phase, the value of the normalized ratio is nearly constant and is close to 1, Fig. 3(b). The results shown in Fig. 3(b) suggest that the rate of volatilization of lanthanum oxide is similar to that of uranium dioxide, in agreement with the conclusions of LeBlanc and McFarlane [11]. Alexander et al. also observed similarities in the normalized volatilization rates of uranium dioxide and lanthanum oxide for their solid solutions [26].

4. Summary and conclusions

High-temperature Knudsen cell-mass spectroscopy experiments were carried out on samples of solid solutions of lanthanum oxide and uranium dioxide, containing varying concentrations of lanthanum. There is good agreement between the vapour pressures of UO_2 calculated from the results obtained here and those calculated from the results given in the literature. The results thus validate the method described herein, in which a sample of doped UO_{2+x} is pre-conditioned with flowing CO/CO_2 to a known oxygen potential, and subsequently heated to measure the vapour pressure of rare-earth fission products.

The lanthanum oxide vapour pressure, in the solid solution of lanthanum oxide/uranium dioxide, follows Henry's law, i.e., its value is directly proportional to its concentration in the solid solution. At around 2100°C and in vacuum, the vapour pressure of lanthanum oxide over a lanthanum oxide/uranium dioxide solid solution is similar to that of uranium dioxide when their concentrations in the solid phase are taken into account.

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References

[1] J.C. Tait, I.C. Gauld, G.B. Wilkin, Derivation of intial radionuclide inventories for the safety assessment of the disposal of used CANDU® fuel, Atomic Energy of Canda Limited Report, AECL-9881, 1989.

[2] C.A. Alexander, J.S. Ogden, L. Chan, S.B. Burson, in: J.T. Rogers (Ed.), Fission Product Transport in Reactor Accidents, Hemisphere, New York, 1990, p. 127.

[3] J.C. Clayton, S. Aronson, J. Chem. Eng. Data 6 (1961) 43.

[4] I. Cohen, R.H. Berman, J. Nucl. Mater. 18 (1966) 77.

[5] W.B. Wilson, C.A. Alexander, A.F. Gerds, J. Inorg. Nucl. Chem. 20 (1961) 242.

[6] T. Matsui, K. Naito, J. Nucl. Mater. 138 (1986) 19.

[7] T. Fujino, J. Nucl. Mater. 154 (1988) 14.

[8] S. Sunder, N.H. Miller, W.H. Hocking, P.G. Lucuta, J. Alloys Comp. 213&214 (1994) 503.

[9] H.G. Diel, C. Keller, J. Solid State Chem. 3 (1971) 621.

[10] E. Stadlbauer, U. Wichmann, U. Lott, C. Keller, J. Solid State Chem. 10 (1974) 341.

[11] J.C. LeBlanc, J. McFarlane, Volatilization of fission products from SIMFUEL, CANDU owners group R&D report, COG-97-031-I (1997), available from Document Center, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada.

[12] J. McFarlane, J.C. LeBlanc, J. Nucl. Mater. 256 (1998) 145.

[13] T.B. Lindemer, A.L. Sutton Jr., J. Am. Ceram. Soc. 71 (1988) 553.

[14] D. Margreiter, H. Deutsch, T.D. Mark, Int. J. Mass Spectrosc. 139 (1994) 127.

[15] J.C. Halle, H.H. Lo, W.L. Fite, Phys. Rev. A 23 (1981) 1708.

[16] J.B. Mann, J. Chem. Phys. 46 (1967) 1646.

[17] J.B. Mann, in: R. Ogata, T. Hanakawa (Eds.), Recent Developments in Mass Spectroscopy, University Press, Tokyo, 1970, p. 814.

[18] J. Kordis, K.A. Gingerich, J. Chem. Phys. 58 (1973) 5141.

[19] A. Pattoret, J. Drowart, S. Smoes, Trans. Faraday Soc. 65 (1969) 98.

[20] P.E. Blackburn, P.M. Danielson, J. Chem. Phys. 56 (1972) 6156.

[21] F. Capone, Y. Colle, J.P. Hiernaut, C. Ronchi, J. Phys. Chem. A 103 (1999) 10899.

[22] C. Younes, L.D. Nguyen, A. Pattoret, High Temp. High Press. 13 (1981) 105.

[23] W.J. Moore, Physical Chemistry, 3rd Ed., Prentice-Hall, Englewood Cliffs, NJ, 1962, p. 103.

[24] W.-E. Wang, D.R. Olander, T.B. Lindemer, J. Nucl. Mater. 211 (1994) 85.

[25] R.J. Ackermann, E.G. Rauh, M.H. Rand, in: Thermodynamics of Nuclear Materials 1979, IAEA-SM-236/69, vol. I, IAEA, Vienna, 1980, p. 11.

[26] C.A. Alexander, J.S. Ogden, L. Chan, R.W. Wright, in: Fission Product Transport in Reactor Accidents, IAEA-SM-296/99, vol. 2, IAEA, Vienna, 1988, p. 179.