ELSEVIER

Journal of Nuclear Materials 280 (2000) 111–115

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Letter to the Editors

Volatile molecule PuO_3 observed from subliming plutonium dioxide

C. Ronchi *, F. Capone, J.Y. Colle, J.P. Hiernaut

Institute for Transuranium Elements, European Commission, Joint Research Centre, 76125 Karlsruhe, Germany

Received 15 November 1999; accepted 11 April 2000

Abstract

Mass spectrometric measurements of effusing vapours over PuO_2 and (U, Pu)O_2 indicate the presence of volatile PuO_3 (g) molecules. The formation of plutonium trioxide vapour is due to a chemical process involving oxygen adsorbed during oxidation of the sample. Although in the examined samples, the fraction of trioxide effusing in vacuo was of the order of 0.02 ppm of the plutonium content, under steady-state oxidation conditions it has been shown that the process can have a relevant effect on the sublimation rate of the dioxide. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

This paper reports experimental evidence that, under certain conditions, PuO_3 (g) is formed by sublimation of PuO_2. The finding is interesting since this vapour species is not considered in the current models of the Pu–O system, which, in this respect, is believed to be essentially different from the U–O system.

Actually, although plutonium can assume a hexavalent form in halides (e.g., fluorides and plutonylchlorides) or oxo-compounds (e.g., plutonates) most specialists are of an opinion that, in the explored Pu–O condensed phase diagram, $PuO_{2.00}$ (s) represents the highest oxide form, and its equilibrium vapour is effectively composed of PuO_2 (g), PuO (g), Pu (g) and oxygen. Treatments of PuO_2 near 2000 K under 40 bar oxygen [1] aimed at producing a higher oxide did not produce the expected result. A variety of endeavours to activate chemical reactions between PuO_2 and the various oxidising agents led to the same negative conclusion.

Actually, in 1950s, during the first preparations of plutonium dioxide from sulphates or nitrates, some experimenters [2] observed that the effective oxygen stoichiometry (O/Pu) of the product was higher than two (of the order 2.04–2.08). This effect was later confirmed by a number of similar tests. However, the maximum *hyperstoichiometry* eventually attained was found to depend on the morphology of the sample used (usually a powder). Hence, it was inferred that extra oxygen in the dioxide samples was present in the form of adsorbed atoms. A direct proof of oxygen adsorption came indeed a few years later from two works [3,4], where this effect was observed, at low temperatures, both in stoichiometric and *hypostoichiometric* PuO_2. In these experiments, very high surface concentrations of oxygen were attained (of the order of several cm^3 per gram solid), depending on the crystallographic orientation of the external surface. For instance, up to one oxygen atom per primitive cell can be adsorbed for (1 0 0) orientations.

On the other hand, however, the possibility that the interstitial oxygen can be dissolved in the cubic dioxide phase was definitively excluded in the context of the first thermodynamic studies of the Pu–O system [5]. Thus, by the end of 1960s any systematic quest of plutonium oxides higher than PuO_2 was practically abandoned. More recently, this question emerged again, when hazards due to off-gases from nuclear waste incineration and oxidation processors were considered with increasing concern. In fact, in this scenario, if a sufficiently high oxygen pressure is present to produce or maintain UO_{2+x} (s), then the oxide volatility increases by orders of magnitude above that of the stoichiometric dioxide, due

---

* Corresponding author.

0022-3115/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S 0 0 2 2 - 3 1 1 5 (0 0) 0 0 0 5 8 - 1

to the formation of UO_3 (g). Fortunately, under the same conditions, plutonium undergoes much lower vaporisation rates, thanks to its apparent inability to form higher oxides than PuO_2. These predictions have been repeatedly checked in transpiration experiments, where hot PuO_2 samples are exposed to a flow of gas and the swept vapours are collected and analysed. Now, the results of some of these tests seem not to be in agreement with the established thermodynamic properties of the Pu–O system. In fact, by analysing the data measured in their transpiration experiments on plutonium oxide, Krikorian et al. [6] found that the dependence of the transpiration rate of plutonium on oxygen pressure could only be explained by the presence of a trioxide molecule in the vapour. These authors assumed a complete analogy between the volatility behaviour of plutonium and uranium, and, by postulating the existence of PuO_3, they proceeded to deduce from the measured transpiration data the partial pressure of this vapour species. Although they have no definitive evidence for the formation of this molecule, they point out that the vaporisation rate of plutonia in oxygen-rich gas flow exhibits features, which cannot be understood in terms of the current thermodynamic model.

More recently, in an independent work by Domanov et al. [7], formation of higher plutonium oxides was again considered as an essential feature under certain transpiration conditions. In this work, a PuO_2 sample was heated in a stream of helium/oxygen, and the volatile species in trace amounts were investigated by thermochromatographic techniques; the condensation of plutonium in a tube downstream was analysed by α-detection, along a temperature gradient. The interpretation of the experimental results suggested that the sweeping gas was carrying molecules of type PuO_n with $n > 2$. Yet, even in this case, no direct proof of the existence of these oxides could be produced.

Finally, a few words here are in order concerning a very recent paper by Haschke et al. [8]. Based on a previous work [9], these authors reiterated their claim to have observed, by combined XPS and XRD analysis, a solid phase PuO_{2+x} as a reaction product of metallic plutonium with water, whereby this oxide should be formed at 523 K and ‘decompose to PuO_2 upon heating in a vacuum’. The existence of stable PuO_{2+x} (s), which cannot be easily made consistent with other corroborated properties of the Pu–O system, might be allied with the results reported in this paper. Therefore, though this short note is not intended to contribute to this controversy, we thought it right to emphasise that, under our experimental conditions, no evidence in favour of the possibility of dissolving extra oxygen in solid PuO_2 at high temperatures could be found. We are, however, of the opinion that some of the established views on the oxidation behaviour of plutonium should perhaps be reconsidered.

2. Experimental results

During Knudsen effusion experiments on MOX (uranium–plutonium mixed oxide nuclear fuel), presently in progress at JRC-ITU, mass spectrometry (MS) analysis frequently revealed the presence of mass 287 in the effusing vapours, with concentrations clearly above the levels of customary impurity or memory effects. If this mass had to be attributed to an oxide, then PuO_3 was the most likely candidate. Actually, MS identification of Pu is often disturbed by the presence of uranium hydrides. In our case, compounds of type $UO_2(OH)$ were then considered, but their formation could be excluded from the absence of the respective mass peak due the isotope ^{235}U, whose concentration was high enough in some of the examined samples. Under oxidation conditions, tungsten oxides up to WO_3 were observed when a tungsten cell was used. The masses of these oxides do not interfere with our measurements. The mass peak 287 is only weakly affected by $Ca^{183}WO_4$ (Ca is a fabrication impurity of W). This compound can be recognised from the characteristic peak sequence of the four major tungsten stable isotopes. The identification of this mass with PuO_3 was, therefore, hardly questionable.

However, as the purity grade of the MOX samples was rather low, tests were carried out with a well-characterised sintered PuO_2, fabricated form Oak Ridge high purity plutonium. Chemical and isotopic analysis were repeated shortly before the experiments; the data are reported in Table 1.

2.1. Test 1

The PuO_2 specimens were oxidised in air at 1500 K, and then annealed in vacuum at high temperature in a

Table 1
Metal analysis of the PuO_2 sample

Species/ nuclide	Concentration	Isotope fraction
^{238}Pu	99.334%	119 ± 1.4 ppm
^{239}Pu		91.951 ± 0.016%
^{240}Pu		7.8539 ± 0.0052%
^{241}Pu		0.14654 ± 0.00014%
^{242}Pu		370.9 ± 0.6 ppm
^{234}U	19.8 ± 0.2 ppm	1.92 ± 0.02%
^{235}U	638 ± 7 ppm	62.07 ± 0.68%
^{236}U	170 ± 3 ppm	16.54 ± 0.3%
^{238}U	200 ± 3 ppm	19.46 ± 0.3%
^{237}Np	122 ± 2 ppm	–
^{241}Am	5513 ± 15 ppm	–

Knudsen cell (different cells were used made of tungsten, thoria or alumina). The results confirm a number of unintentional, previous observations: above approximately 1800–1900 K, temperature at which the vaporisation rate of PuO_2 becomes measurable by MS, an effusing species identifiable with PuO_3 (g) was found.

The employed instrument is a quadrupole mass analyser, operated with a Faraday cage and a secondary electron multiplier. Three turbo-molecular pumps and an oil-free 'Dryvac' rotary pump evacuate the system. A large trap with circulating liquid nitrogen surrounds the ion source. Vessel and TM pumps are located in a glove box filled with a nitrogen atmosphere (water content < 100 ppm). The heavy ($M > 200$) hydrocarbon rest gases have concentrations below the detection limit.

Fig. 1 shows the MS signals corresponding to the pertinent mass windows. One can see that the starting *total* effusion rate remains, for a short time, of the order of a few tens of seconds, more than one order of magnitude *higher* than in $PuO_{2.00}$ under steady-state effusion regime. Furthermore, the observed vapour composition is different from that of the equilibrium vapour over $PuO_{2.00}$.

In addition, evidence in favour of the identification of ^{287}M with plutonium trioxide was obtained as a second peak at ^{288}M, whose height relative to that of ^{287}M, is close to the isotopic fraction $^{239}Pu/^{240}Pu$ reported in Table 1. Fig. 2 shows a mass scan (analogue output) recorded during a few minutes after the appearance of mass 287.

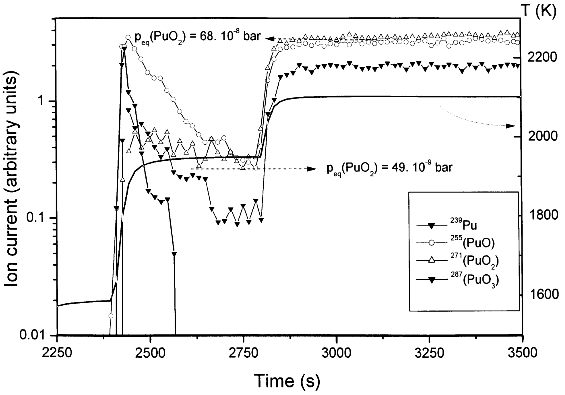

Fig. 1. Main effusion components from PuO_2 oxidised in air.

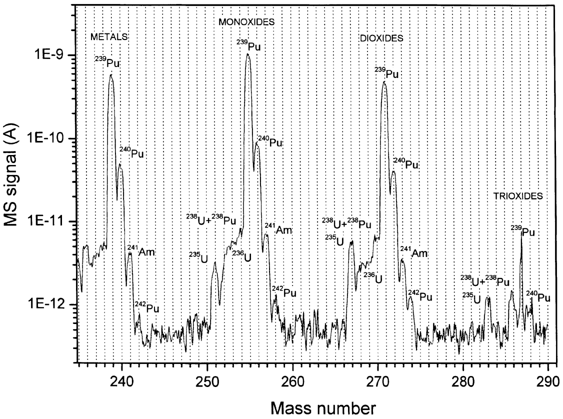

Fig. 2. Conditions as in Fig. 1. Mass spectrum showing the actinide oxide peaks.

Due to the lack of data on the ionisation and fragmentation cross-section of the PuO_3 molecule, a conversion of the mass spectrometer signals into concentrations was tentatively made. For this purpose, the parameters of UO_3 were applied [10] to estimate the partial effusion rates from the respective ion currents. This calculation is, however, not straightforward. In fact, UO_3 has a high ionisation energy ($E_i = 10.8$ eV) that is just below the first fragmentation energy ($E_{fi} = 11.3$ eV, for $\rightarrow UO_2^+ + O$). As a consequence, at the used MS ionising electron energies (40–70 eV), fragmentation of UO_3 occurs with production of UO_2^+, UO^+ and U^+, in that order. Calibration experiments show that only $\approx 36\%$ of the inelastic electron collisions with UO_3 produce one ion UO_3^+, while the others lead to various dissociation processes. Now, since PuO_2 has a much higher ionisation energy ($E_i = 10.1$ eV) than UO_2 ($E_i = 5.4$ eV), and since that of PuO_3 is likely larger, the fragmentation of the latter molecule should lead to a preferential formation of PuO^+ ($E_i = 6.6$ eV) and molecular oxygen. This can be the reason why the MS signal of PuO^+, measured during vaporisation of PuO_3, is higher than that normally measured over stoichiometric PuO_2 at the same effusion temperature. Although these considerations are merely speculative, and the individual vaporisation rates of the various oxides remain uncertain in our case, the values concerning the total effusion rate of the plutonium-bearing species are nevertheless sufficiently indicative for a marked deviation from the equilibrium vaporisation conditions. Actually, as time elapses at constant temperature, the measured concentration of the trioxide in the vapour decreases, whilst that of PuO_2 increases in relative weight, so that when PuO_3 effectively disappears, the dioxide becomes the major species. At this stage, a reliable calculation of the ionisation/fragmentation processes can be carried out, and the measured effusion rates are in agreement with the values of the equilibrium partial pressures calculated from the standard thermodynamic data. This agreement is also maintained during the subsequent annealing steps, produced after disappearance of PuO_3.

Of particular interest is the fraction of plutonium mass vaporised during the stage, where enhanced sample volatility was observed due to the presence of PuO_3.

A reasonably precise evaluation of this fraction (2×10^{-2} ppm of the initial plutonium atoms) could be obtained in the case of the sintered sample oxidised in air. From the sample geometry, one can estimate that 5–10% of the surface area exposed to oxygen contribute to form PuO_3.

2.2. Test 2

Experiments were also carried out with hypostoichiometric PuO_{2-x}, previously submitted to oxygen adsorption at low temperature (400 K). After this treatment, the bulk of the sample was still hypostoichiometric. Even in this case, however, the trioxide was observed in vapour under the same temperature conditions as for the stoichiometric oxide, but at much lower concentrations.

2.3. Test 3

A third experiment was finally carried out under ‘in situ’ oxidation conditions. A sample of slightly hypostoichiometric PuO_2 ($O/M \simeq 1.98$) was heated in the Knudsen cell at 1990 K under ultra-high vacuo ($<10^{-11}$ bar). The electronically controlled gas inlet valve was then completely opened, letting CO_2 flow through a capillary into the cell, at the maximum rate compatible with the differential pumping system of the device (the use of CO_2 instead of oxygen is recommended for safety reasons in glove boxes): during circa 20 s, the vacuum in the MS ion source could be stabilised just below 10^{-8} bar, whilst in the furnace vessel the estimated pressure was of the order of 10^{-2}–10^{-1} bar.

The MS measurements of the effusing vapours are plotted in Figs. 3 and 4. One can see that the current of *all* PuO_x ions increases by a factor of ≈ 50. The change of all the species by approximately the same factor is in disagreement with the predictions for equilibrium conditions, according to which the variation of the pressure of PuO_x is an exponential function of x. Also a marked change in the sample stoichiometry cannot explain this effect, for the total pressure of Pu-bearing species over Pu_2O_3 and PuO_2 at this temperature is almost the same. Therefore, the increase in the sublimation rate is due to formation of PuO_3 on the surface, whilst the other detected oxides are ionisation fragments of the trioxide. On the contrary to the case of Fig. 1, the PuO_2 component is here larger than PuO. This is likely due to oxidation of PuO (g) in the gas phase, for the bulk sample had no time to oxidise and remained hypostoichiometric, as demonstrated by the vapour composition after the closure of the gas inlet valve. The oxidation conditions were, therefore, far from thermodynamic equilibrium.

An additional proof that only surface atoms of plutonium are involved in the detected sublimation ‘burst’ is furnished by the signal of UO_3 (g) that is *evidently almost unaffected* by the applied transient conditions. Actually, uranium was present as an impurity in the sample, but, for a sufficiently high oxygen potential, UO_3 (g) is by orders of magnitude the most volatile species in the U–Pu–O system, so that non-congruent vaporisation conditions are established. These are apparently governed by the bulk stoichiometry of the sample, which was little affected by the short pressure transient.

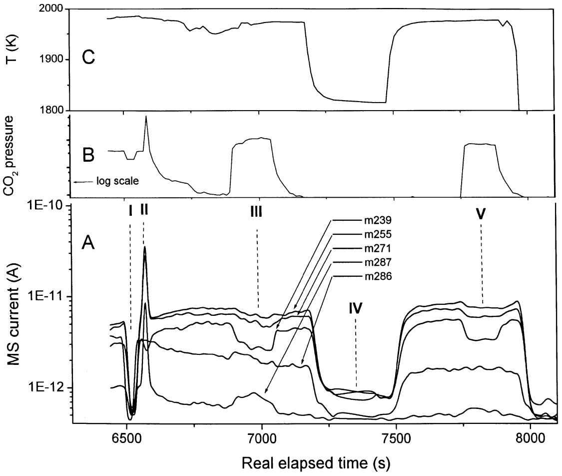

Fig. 3. Vaporisation of PuO_3 in a flux of CO_2. Oxygen potential during the transient test: $\Delta G(O_2) \sim -127$ kJ/mol. (A) Mass spectrometer signals recorded during the full transient test with gas pressure. *Legend*: (I) Chopper inserted; (II) short, full opening of the gas inlet valve; (III) partial, longer opening of the valve, entailing a decrease of temperature inside the cell; (IV) cooling down; (V) idem as in (III). (B) Estimated gas pressure evolution in the Knudsen-cell. The first tick label of the ordinate (logarithmic scale) corresponds to approximately 10^{-4} bar. (C) External temperature of the cell.

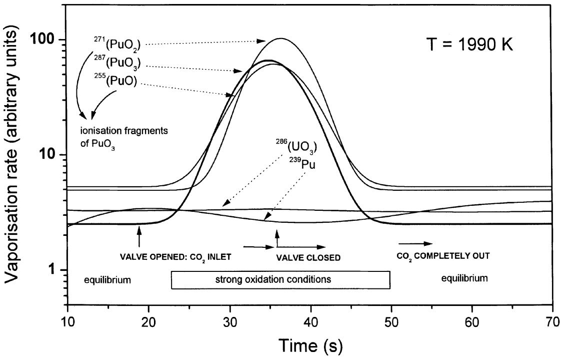

Fig. 4. Vaporisation rates during stage II of Fig. 3. The ionisation cross-section of PuO_3 was assumed to be equal to that of UO_3.

3. Discussion and conclusion

Knudsen-effusion experiments combined with MS reveal that plutonium dioxide exposed to oxygen emits vapours with mass numbers of 287 and 288, which can be attributed to PuO_3 (g). From the reported experimental data, the following independent arguments concur to make this attribution very likely:

1. First, the fact that whenever the supposed trioxide is present in large concentrations, the masses of PuO_2, PuO and Pu are also detected by the mass spectrometer with concentrations exceeding the values predicted by thermodynamic equilibrium. Hence these latter can only represent ionisation fragments of the trioxide.
2. The smaller peak corresponding to mass 288 has a height corresponding to the fraction of ^{240}Pu present in the sample.
3. The supposed trioxide appears only when the sample is exposed to oxygen.

The molecule PuO_3 (g) is not formed from a gas–gas reaction of PuO_2 (g) with oxygen or carbon dioxide, since in some cases the measured absolute effusion rate of the trioxide from the cell is markedly higher than that of the dioxide under equilibrium conditions. The experiment, and especially the third test reported in this paper, shows that plutonium trioxide is not an equilibrium species over PuO_2 (s), but rather the product of a reaction of gaseous oxygen with the surface of the solid.

Some questions concerning the oxidation process of solid PuO_x are raised by these results. The experiment shows that, though stable PuO_3 (g) was formed by sublimation from free surfaces exposed to oxygen, this atom did not diffuse, after adsorption, into the dioxide lattice to form a hypothetical solid solution PuO_{2+x} or higher oxides. The reason of this property may or may not be regarded as directly pertinent to the reported observations; however, the fact that excess oxygen is retained on the solid surface up to temperatures of the order of 2000 K implies that oxygen must undergo a reaction with a much larger free-energy gain than the few hundreds of joules per mole involved in the adsorption process [3,4]. Formation of surface configurations can be conjectured, e.g., as clusters on surface ledges, which can preferentially sublime in the form of PuO_3 (g), yet, their nature and concentration under steady-state conditions – as, for instance, in transpiration experiments – remain unknown.

These results may disclose new aspects of the oxidation limits of PuO_x, as well as mechanisms entailing, for particular conditions, a more cautious assessment of the effective volatility of this actinide.

References

[1] B. Riley, Sci. Ceram. 5 (1970) 83.
[2] J.L. Drummond, G.A. Welsh, J. Chem. Soc. (1957) 4781.
[3] J.L. Stakebake, J. Nucl. Mater. 23 (1967) 154.
[4] J.L. Stakebake, M.R. Dringman, J. Nucl. Mater. 23 (1967) 1349.
[5] E.E. Jackson, M.H. Rand, UKAEA Harwell Report AERE-3636, 1963.
[6] O.H. Krikorian, A.S. Fontes, B.B. Ebbinghaus, M.G. Adamson, J. Nucl. Mater. 247 (1997) 161.
[7] V.P. Domanov, G.V. Buklanov, Y.V. Lobanov, in: C.E.A. Palmer (Ed.), Abstract Book of the Seventh International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Lake Tahoe, CA, 1999, p. 164.
[8] J.M. Haschke, T.H. Allen, L.A. Morales, Science 287 (2000) 285.
[9] J.L. Stakebake, D.T. Larson, J.M. Haschke, J. Alloys Comp. 202 (1993) 251.
[10] F. Capone, Y. Colle, J.P. Hiernaut, C. Ronchi, J. Phys. Chem. A 103 (50) (1999) 10899.