

Thermochemical Behavior of Gallium in Weapons-Material-Derived Mixed-Oxide Light Water Reactor (LWR) Fuel

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The use of weapons-derived plutonium in light water reactor (LWR) fuel must consider the effects of up to 1 mass% of gallium that is used in weapons plutonium alloy. The potential effects of this residual gallium have been examined for 5% PuO₂-95% UO₂ from a thermochemical standpoint. The state and effect of gallium in the fuel are predicted, based on the oxygen potential of the fuel and the effects of burn-up. The possibility of vapor-phase transport of gallium to the fuel clad and potential interaction with the clad also is assessed.

I. Introduction

TO FURTHER the efforts of reducing nuclear weapons stockpiles, the United States has established a dual-track policy for the disposition of surplus plutonium that has been manufactured for weapons use. The two approaches are (i) immobilization and disposal as radioactive waste and (ii) consumption as fuel in commercial light water reactors (LWRs). The fuel, which is termed mixed-oxide (MOX) fuel for the mixture of UO₂ and PuO₂ it contains, has broad commercial experience. Although very limited use has been made of MOX fuel in the United States, more than 300 000 LWR MOX fuel rods have been irradiated worldwide. That experience has been satisfactory, with no reported problems that are not common with UO₂ fuel.

Weapons-grade plutonium in the U.S. stockpile differs from commercial, recycled reactor plutonium in that the weapons material contains added quantities of elemental gallium (up to levels of 1 mass%). In metallic form, gallium readily interacts with most other metals and, thus, presents a potential problem for LWR MOX fuel. The small amount of gallium that remains in the fuel after fabrication may migrate to the zirconium alloy (Zircaloy) clad, possibly causing effects such as liquid-metal embrittlement (gallium is a liquid at temperatures >303 K). The concentration of fission-product gallium normally generated in LWR fuel is exceptionally small; therefore, irradiated LWR fuel performance cannot provide adequate guidance with regard to this issue. To partially address the potential problem of gallium-clad interactions, fuel-processing techniques are being evaluated for reducing the residual gallium content of the fuel to <100 ppm.

The chemistry of nuclear fuel during burn-up is complex; a large fraction of the periodic table is produced as products of fission, and these elements must be included in any assessment of fuel behavior. A particular issue is the oxidation

state of the metallic fission products that are generated. These products are dependent on the oxygen partial pressure (p_{O_2}) within the fuel, which can vary due to the release of oxygen from the actinide dioxide when it fissions, the extent of oxidation of the generated fission products (which is a function of p_{O_2}), and the increase in the oxygen-to-metal (O/M) ratio of the remaining fuel, which has a substantial homogeneity range. The complex interaction of all these effects results in the equilibrium state of the fuel and an equilibrium p_{O_2} value.

The purpose of this paper is to use thermochemical computational analysis to assess the state and effect of gallium in proposed LWR MOX fuel that contains 5 mass% PuO₂, both as-fabricated and during burn-up, and to determine species vapor pressures in the complex nuclear fuel system. The knowledge of the state of the gallium and the vapor pressures will provide important information with regard to the mechanisms and rates of transport in the fuel and the likelihood of interaction with the fuel cladding.

II. The Gallium-Oxygen System

Currently, no published gallium-oxygen phase diagram is available. The only condensed gallium oxide phase that is known with confidence is Ga₂O₃. Some evidence exists for a condensed Ga₂O suboxide phase, which decomposes at ~1075 K.¹ Limited thermochemical information in Samsonov² indicates that the phase sublimates at 923-973 K, has a melting point of 925 K, and has a boiling point of 1000 K. This contradictory information, as well as comments in the text noting that the existence of solid Ga₂O is not demonstrated, does not give much confidence in the stability of the phase. However, reliable data for the Ga₂O and GaO gaseous species are available in Barin.³

Given the scarcity and uncertainty of the information about the condensed suboxide phase, it has not been included in the following analysis; however, data can be added, should more-detailed information be developed. As a suboxide, it will form at a lower oxygen activity than does Ga₂O₃; therefore, neglecting its presence should be a conservative assumption in terms of the interaction of gallium metal with fuel cladding, because this results in the assumed presence of elemental gallium at possibly higher oxygen activities than would actually be the case. Thus, the only condensed gallium oxide phase considered is Ga₂O₃, and uncombined gallium will be present as the metal or the sesquioxide, depending on the oxygen potential. The thermodynamic data of Barin³ (Table I) contain the unique set of oxygen potential-temperature values at which both the metal and oxide coexist and which delineates the boundary that separates the formation of the stable oxide from elemental gallium. This boundary is plotted in Fig. 1; the figure shows that low oxygen potentials cause the metal to be stable and higher values result in the exclusive formation of the sesquioxide. Note that the oxygen potential is defined as $RT \ln p_{O_2}^*$, where R is the ideal gas law constant, T the absolute temperature, and $p_{O_2}^*$ the oxygen partial pressure normalized to the standard-state pressure of 0.101 MPa.

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Table I. Thermodynamic Values at 1000 K for the Gallium–Oxygen System[†]

Component	ΔH_f° (kJ/mol)	S° (J·(mol·K) ⁻¹)
Gallium liquid, Ga(l)		91.859
Oxygen gas, O ₂ (g)		243.578
Ga ₂ O ₃ (s)	-1091.208	220.136
Ga ₂ O(g)	-121.071	347.999
GaO(g)	133.973	279.381

[†]Thermodynamic data from Barin.³

III. Behavior in PuO₂

Depending on the fuel-preparation process, the PuO₂ may be atomically mixed with the UO₂, the PuO₂ may be present as second-phase agglomerates within the larger-volume UO₂, or some intermediate situation may prevail. To explore the extremes, both completely homogeneous and heterogeneous fuel will be considered. In the latter case, it is necessary to consider the fuel chemistry, assuming that gallium is locally present with essentially pure PuO₂.

(1) As-Fabricated Fuel

By considering the PuO₂ phase to be independent of the fission products and UO₂, the PuO₂ oxygen potential can be compared to that of the gallium/Ga₂O₃ boundary. PuO₂ has a wide homogeneity range, with oxygen potential values measured for x values in PuO_{2-x} as large as 0.3676.⁴ Thus, the dioxide phase can be substantially substoichiometric, with resultant oxygen potentials significantly lower than that of nominal PuO₂. A representation of the chemical thermodynamic behavior of PuO_{2-x} developed by Besmann and Lindemer⁵ can be used to determine the partial molar free energy of oxygen ($\Delta\bar{G}_{O_2}$) as a function of composition and temperature. However, the oxygen potential for stoichiometric PuO₂ is not uniquely definable, because, in accordance with the phase rule, this invariant composition can exist over a range of oxygen pressures. PuO₂ is, effectively, a limiting composition, because, unlike the uranium–oxygen system, there are no con-

densed plutonium oxide phases with an O/M ratio of >2. To assess the state of gallium in an agglomerate of PuO₂, it is assumed that the phase can be approximated by the behavior of PuO_{1.9999}, which is the highest oxygen-content composition for which oxygen potential data have been measured.⁵

The temperature–oxygen potential relationship for PuO₂ (PuO_{1.9999}) is given in Fig. 1, based on Besmann and Lindemer,⁵ who developed the formulation

$$\Delta\bar{G}_{O_2} = -821000 + 168.47T - 3RT \ln \frac{1.5x \left(1 - \frac{x}{2}\right)^{1/3}}{(1-2x)^{4/3}} - \frac{3x^2 - 12x + 3}{\left(1 - \frac{x}{2}\right)^2} (63470 - 49.36T) \quad (1)$$

Because the enthalpies and entropies are partial quantities, they can vary substantially with composition and result in the relatively steep slope that is observed in Fig. 1. At higher temperatures, the PuO₂ line in the figure lies at oxygen potentials that are more positive than those for the gallium–Ga₂O₃ equilibrium, thus assuring that gallium will be present as the oxide form with PuO₂. Yet, at temperatures below ~900 K, the opposite prevails; thus, it is possible to have elemental gallium in equilibrium with PuO₂. This observation suggests that, if the local oxygen potential is governed exclusively by the PuO₂ phase and if the dioxide was only very slightly substoichiometric, elemental gallium could be present at relatively low temperatures.

(2) During Burn-up

During burn-up, oxygen is released in proportion to the O/M ratio of the fuel, so that O/M oxygen atoms are released for every actinide atom that is fissioned. Because PuO₂ is already in its highest oxidation state and cannot accommodate more oxygen, and assuming the oxygen does not transport to the surrounding UO₂, only the fission products can react to form

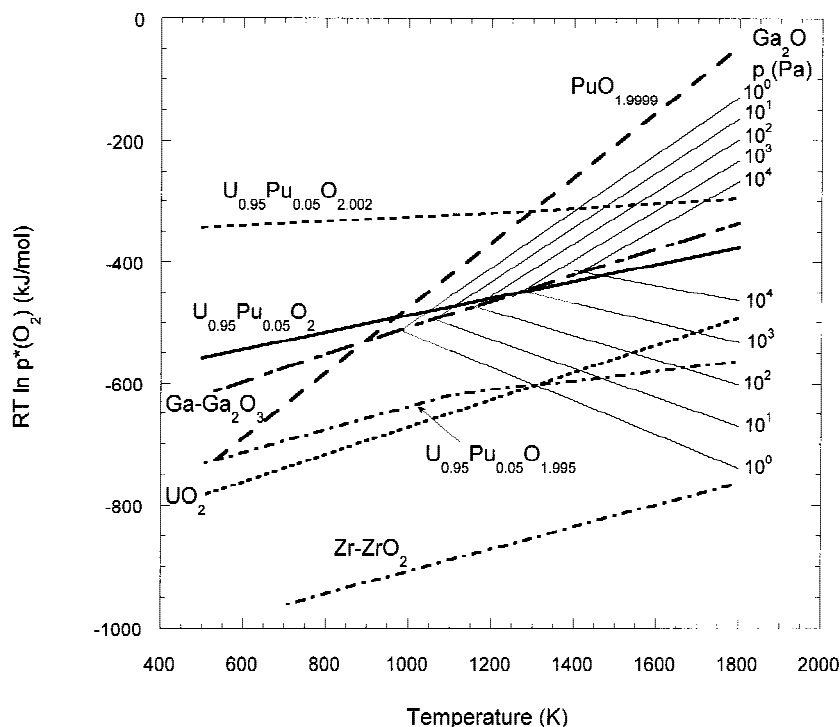


Fig. 1. Plot of temperature versus oxygen potential for the constituents of MOX fuel and gallium. Also included are the isobars for Ga₂O(g) over elemental gallium and Ga₂O₃(s).

oxide phases that bind the released oxygen atoms. Assuming rapid kinetics, the free energy of the reaction necessary to form these oxides governs the priority for the formation of fission-product oxides. The Ellingham diagram of Kleykamp⁶ indicates the oxygen-potential boundaries for the formation of fission-product simple-oxide phases. Using that information, supplemented by the thermochemical data from Barin,³ it is possible to determine the state of the fission products at a specific burn-up.

A set of burn-up calculations for MOX fuel that contained 5 mass% PuO₂ was performed to determine the fuel composition after 52.5 gigawatt-days per tonne (GW·d/t), which is equivalent to ~5% burn-up; the resultant fission-product concentrations are shown in Tables II and III. The first set of fission products is the concentration accumulated in the MOX fuel, which is caused by actinide fissions that occur exclusively in the uranium (i.e., fissioning of uranium and uranium transmuted to the Pu²³⁹ species), and the second set of data represents the concentration in the original PuO₂ aggregate that is generated by fissioning the initial Pu²³⁹ species in the as-fabricated fuel. Approximately 75% of the original Pu²³⁹ species is fissioned, with 1.27 total fissions per initial plutonium atom. The third data set contains the proportional sum of the first two data sets and represents the total fission-product inventory (i.e., the concentration, assuming the fuel is homogeneous), which is applied in the next section.

For the purposes of this assessment, it was assumed that the entire initial concentration of gallium in the original plutonium alloy (1 mass%) was carried over to the fuel. Table II considers fuel that has been prepared such that the gallium is present as

the oxide form, and Table III assumes that the gallium in the fuel is elemental (a slightly lower O/M-ratio fuel). Also given in the tables is the O/M ratio for each of the fission products that form oxides based on the release of oxygen during fissioning and the thermochemistry. If an O/M value is not shown, either the element does not form an oxide or the oxygen potential is insufficient to form the metal oxide. Note that, with the exception of cesium and rubidium (which, if oxidized, are assumed to be present as uranates⁷), all the fission products are assumed to form simple oxides. This assumption is conservative in terms of fission-product interactions, because the formation of any complex oxides will occur at lower oxygen potentials and further stabilize the system. The initial O/M ratio of the fuel is assumed to be 2, although slightly hyperstoichiometric fuel is likely to be fabricated.

The totals of the columns in Tables II and III for oxygen in the fission-product oxides represent the fraction of fission-released oxygen atoms accommodated by fission-product oxides per atom of initial plutonium or actinide atom. These values were determined via comparison with the fraction of oxygen atoms that are released by fission, which is given at the bottom of the columns. Thus, the fission products form oxides, based on their thermochemical affinity for oxidation, until all the fission-released oxygen is consumed. The difference between the released oxygen and the fission-product oxygen was balanced by allowing an appropriate fraction of the metallic fission product, which would oxidize next, to consume the oxygen.

The last two columns in Tables II and III consider the fuel as containing isolated aggregate PuO₂ grains in which all the gal-

Table II. Fission-Product Concentrations Computed for a Burn-up of 52.5 GW·d/t and Their Oxidation State, Assuming Gallium is Present as the Oxide Form in As-Fabricated Fuel

Fission product and MOX	In UO ₂ (atoms/atom of initial U)	In PuO ₂ aggregate (atoms/atom of initial Pu)	Total (atoms/atom of initial actinide)	Fission product O/M ratio in MOX	Oxygen in fission product oxide in homogeneous MOX (atoms/atom of initial actinide)	Fission product O/M ratio in PuO ₂	Oxygen in fission product oxide in PuO ₂ aggregate (atoms/atom of initial Pu)
Se	8.75×10^{-5}	2.55×10^{-3}	2.11×10^{-4}				
Br	3.42×10^{-5}	1.00×10^{-3}	8.27×10^{-5}				
Kr	4.47×10^{-4}	1.13×10^{-2}	9.90×10^{-4}				
Rb	3.73×10^{-4}	9.71×10^{-3}	8.39×10^{-4}	1.00	8.39×10^{-4}	1.00	9.71×10^{-3}
Sr	9.49×10^{-4}	2.30×10^{-2}	2.05×10^{-3}	1.00	2.05×10^{-3}	1.00	2.30×10^{-2}
Y	4.91×10^{-4}	1.16×10^{-2}	1.05×10^{-3}	1.50	1.57×10^{-3}	1.50	1.74×10^{-2}
Zr	4.46×10^{-3}	1.24×10^{-1}	1.04×10^{-2}	2.00	2.08×10^{-2}	2.00	2.48×10^{-1}
Nb	6.56×10^{-5}	7.39×10^{-4}	9.93×10^{-5}	2.00	1.99×10^{-4}	2.00	1.48×10^{-3}
Mo	5.00×10^{-3}	1.58×10^{-1}	1.26×10^{-2}	2.00	2.53×10^{-2}	2.00	3.16×10^{-1}
Tc	1.20×10^{-3}	3.51×10^{-2}	2.90×10^{-3}			2.00	7.01×10^{-2}
Ru	4.67×10^{-3}	1.47×10^{-1}	1.18×10^{-2}			0.72	1.06×10^{-1}
Rh	9.60×10^{-4}	2.68×10^{-2}	2.25×10^{-3}				
Pd	3.11×10^{-3}	1.28×10^{-1}	9.37×10^{-3}				
Ag	2.34×10^{-4}	7.84×10^{-3}	6.14×10^{-4}				
Cd	2.62×10^{-4}	1.36×10^{-2}	9.27×10^{-4}			1.00	1.36×10^{-2}
Sn	1.09×10^{-4}	3.74×10^{-3}	2.90×10^{-4}			2.00	7.48×10^{-3}
Sb	3.13×10^{-5}	9.06×10^{-4}	7.50×10^{-5}			1.50	1.36×10^{-3}
Te	6.51×10^{-4}	2.08×10^{-2}	1.66×10^{-3}			2.00	4.16×10^{-2}
I	3.76×10^{-4}	1.19×10^{-2}	9.54×10^{-4}				
Xe	6.29×10^{-3}	1.94×10^{-1}	1.57×10^{-2}				
Cs	3.66×10^{-3}	1.16×10^{-1}	9.30×10^{-3}	1.00	9.30×10^{-3}	1.00	1.16×10^{-1}
Ba	1.53×10^{-3}	5.15×10^{-2}	4.03×10^{-3}	1.00	4.03×10^{-3}	1.00	5.15×10^{-2}
La	1.28×10^{-3}	3.94×10^{-2}	3.18×10^{-3}	1.50	4.78×10^{-3}	1.50	5.91×10^{-2}
Ce	2.84×10^{-3}	8.29×10^{-2}	6.84×10^{-3}	1.50	1.03×10^{-2}	1.50	1.24×10^{-1}
Pr	1.13×10^{-3}	3.53×10^{-2}	2.84×10^{-3}	1.50	4.26×10^{-3}	1.50	5.29×10^{-2}
Nd	3.57×10^{-3}	1.13×10^{-1}	9.04×10^{-3}	1.50	1.36×10^{-2}	1.50	1.69×10^{-1}
Pm	1.84×10^{-4}	3.26×10^{-3}	3.38×10^{-4}	1.50	5.07×10^{-4}	1.50	4.89×10^{-3}
Sm	8.00×10^{-4}	2.52×10^{-2}	2.02×10^{-3}	1.50	3.03×10^{-3}	1.50	3.78×10^{-2}
Eu	2.10×10^{-4}	7.64×10^{-3}	5.81×10^{-4}	1.50	8.72×10^{-4}	1.50	1.15×10^{-2}
Gd	1.38×10^{-4}	6.65×10^{-3}	4.64×10^{-4}	1.50	6.96×10^{-4}	1.50	9.98×10^{-3}
Tb	4.45×10^{-6}	1.91×10^{-4}	4.23×10^{-6}	1.50	6.34×10^{-6}	1.50	2.87×10^{-4}
Dy		1.06×10^{-4}	5.32×10^{-6}	1.50	7.98×10^{-6}	1.50	1.60×10^{-4}
MOX					5.00×10^{-3}		
Total					1.07×10^{-1}		1.49
Oxygen released					1.07×10^{-1}		1.49

Table III. Fission-Product Concentrations Computed for a Burn-up of 52.5 GW-d/t and Their Oxidation State, Assuming Elemental (Unoxidized) Gallium is Present in As-Fabricated Fuel

Fission product, Ga, and MOX	In UO ₂ (atoms/atom of initial U)	In PuO ₂ aggregate (atoms/atom of initial Pu)	Total (atoms/atom of initial actinide)	Fission product O/M ratio in MOX	Oxygen in fission product oxide in homogeneous MOX (atoms/atom of initial actinide)	Fission product O/M ratio in PuO ₂	Oxygen in fission product oxide in PuO ₂ aggregate (atoms/atom of initial Pu)
Se	8.75×10^{-5}	2.55×10^{-3}	2.11×10^{-4}				
Br	3.42×10^{-5}	1.00×10^{-3}	8.27×10^{-5}				
Kr	4.47×10^{-4}	1.13×10^{-2}	9.90×10^{-4}				
Rb	3.73×10^{-4}	9.71×10^{-3}	8.39×10^{-4}	1.00	8.39×10^{-4}	1.00	9.71×10^{-3}
Sr	9.49×10^{-4}	2.30×10^{-2}	2.05×10^{-3}	1.00	2.05×10^{-3}	1.00	2.30×10^{-2}
Y	4.91×10^{-4}	1.16×10^{-2}	1.05×10^{-3}	1.50	1.57×10^{-3}	1.50	1.74×10^{-2}
Zr	4.46×10^{-3}	0.1237928	1.04×10^{-2}	2.00	2.08×10^{-2}	2.00	2.48×10^{-1}
Nb	6.56×10^{-5}	7.39×10^{-4}	9.93×10^{-5}	2.00	1.99×10^{-4}	2.00	1.48×10^{-3}
Mo	5.00×10^{-3}	1.58×10^{-1}	1.26×10^{-2}	2.00	2.53×10^{-2}	2.00	3.16×10^{-1}
Tc	1.20×10^{-3}	3.51×10^{-2}	2.90×10^{-3}			2.00	7.01×10^{-2}
Ru	4.67×10^{-3}	1.47×10^{-1}	1.18×10^{-2}			0.43	6.33×10^{-2}
Rh	9.60×10^{-4}	2.68×10^{-2}	2.25×10^{-3}				
Pd	3.11×10^{-3}	1.28×10^{-1}	9.37×10^{-3}				
Ag	2.34×10^{-4}	7.84×10^{-3}	6.14×10^{-4}				
Cd	2.62×10^{-4}	1.36×10^{-2}	9.27×10^{-4}			1.00	1.36×10^{-2}
Sn	1.09×10^{-4}	3.74×10^{-3}	2.90×10^{-4}			2.00	7.48×10^{-3}
Sb	3.13×10^{-5}	9.06×10^{-4}	7.50×10^{-5}			1.50	1.36×10^{-3}
Te	6.51×10^{-4}	2.08×10^{-2}	1.66×10^{-3}			2.00	4.16×10^{-2}
I	3.76×10^{-4}	1.19×10^{-2}	9.54×10^{-4}				
Xe	6.29×10^{-3}	1.94×10^{-1}	1.57×10^{-2}				
Cs	3.66×10^{-3}	1.16×10^{-1}	9.30×10^{-3}	1.00	9.30×10^{-3}	1.00	1.16×10^{-1}
Ba	1.53×10^{-3}	5.15×10^{-2}	4.03×10^{-3}	1.00	4.03×10^{-3}	1.00	5.15×10^{-2}
La	1.28×10^{-3}	3.94×10^{-2}	3.18×10^{-3}	1.50	4.78×10^{-3}	1.50	5.91×10^{-2}
Ce	2.84×10^{-3}	8.29×10^{-2}	6.84×10^{-3}	1.50	1.03×10^{-2}	1.50	1.24×10^{-1}
Pr	1.13×10^{-3}	3.53×10^{-2}	2.84×10^{-3}	1.50	4.26×10^{-3}	1.50	5.29×10^{-2}
Nd	3.57×10^{-3}	1.13×10^{-1}	9.04×10^{-3}	1.50	1.36×10^{-2}	1.50	1.69×10^{-1}
Pm	1.84×10^{-4}	3.26×10^{-3}	3.38×10^{-4}	1.50	5.07×10^{-4}	1.50	4.89×10^{-3}
Sm	8.00×10^{-4}	2.52×10^{-2}	2.02×10^{-3}	1.50	3.03×10^{-3}	1.50	3.78×10^{-2}
Eu	2.10×10^{-4}	7.64×10^{-3}	5.81×10^{-4}	1.50	8.72×10^{-4}	1.50	1.15×10^{-2}
Gd	1.38×10^{-4}	6.65×10^{-3}	4.64×10^{-4}	1.50	6.96×10^{-4}	1.50	9.98×10^{-3}
Tb	4.45×10^{-6}	1.91×10^{-4}	4.23×10^{-6}	1.50	6.34×10^{-6}	1.50	2.87×10^{-4}
Dy		1.06×10^{-4}	5.32×10^{-6}	1.50	7.98×10^{-6}	1.50	1.60×10^{-4}
Ga		3.35×10^{-2}	1.68×10^{-3}	1.50	2.51×10^{-3}	1.50	5.03×10^{-2}
MOX					3.00×10^{-3}		
Total					1.08×10^{-1}		1.50
Oxygen released					1.08×10^{-1}		1.50

lium resides, with the fission products bred solely into the PuO₂ aggregate that accommodates the fission-released oxygen atoms. In the case where gallium is present as the oxide form in as-fabricated fuel (Table II), it is expected to remain as the oxide form during burn-up. Several of the metallic fission products will form oxides, either in solution with the fuel or as independent phases, as indicated in Table II.

The oxide phases that will form are considered to be somewhat different from those observed in typical LWR fuel.⁶ LWR fuel will have metallic precipitates that contain molybdenum, technetium, cadmium, tin, antimony, and tellurium; however, under the assumption that the PuO₂ remains as an isolated aggregate in the MOX fuel, these metals are present as oxides. The oxygen balance also indicates that a portion of the ruthenium will exist as an oxide (i.e., its O/M ratios in Tables II and III are a fraction of the value of 2 for RuO₂). The presence of these fission products as oxides instead of metallic precipitates should not have a negative effect on fuel behavior, unless they form precipitates whose volume increase causes mechanical deformation.

Gallium present as the metal (unoxidized) form in unirradiated fuel will oxidize during burn-up to form Ga₂O₃ by using oxygen that is released by the fissioning of the actinide oxides. Thus, the gallium that is present at a level of 1 mass% is also listed in Table III, to allow its inclusion as an oxygen sink. As is apparent in Table III, the presence of elemental gallium at this concentration does not have much effect on the oxidation state of the fission products.

IV. Behavior in Homogeneous MOX Fuel

Next, the MOX fuel is assumed to exist as a true solid solution of 5% PuO₂ in UO₂. The fuel is present as the phase U_{0.95}Pu_{0.05}O_{2±x}.

(I) As-Fabricated Fuel

Besmann and Lindemer⁵ also developed a chemical thermodynamic representation of the fluorite-phase mixed-oxide system that includes U_{0.95}Pu_{0.05}O_{2±x}. The equations that detail the representation are too complex to reproduce here but can be found in the reference. The temperature–oxygen potential relationship for U_{0.95}Pu_{0.05}O_{2±x} can be determined by using these relationships. The expressions for the range of possible nominal production stoichiometries (U_{0.95}Pu_{0.05}O₂, U_{0.95}Pu_{0.05}O_{2.002}, and U_{0.95}Pu_{0.05}O_{1.995}) are plotted in Fig. 1. The discontinuity in the curve for the $\Delta\bar{G}_{O_2}$ value of U_{0.95}Pu_{0.05}O_{1.995} is due to the need to treat the oxygen potential with two different relationships over the temperature range of interest for this composition.⁵ For comparison purposes, the line for stoichiometric UO₂, based on a similar representation by Lindemer and Besmann,⁸ also is shown in Fig. 1.

Figure 1 shows that, at temperatures greater than ~1260 K, the gallium–Ga₂O₃ equilibrium line exists at a more positive oxygen potential than that for U_{0.95}Pu_{0.05}O₂. This observation implies that, if the U_{0.95}Pu_{0.05}O₂ phase fixes the oxygen potential in the fuel, Ga₂O₃ may be reduced to the metal in regions of the fuel at temperatures greater than ~1260 K. If the oxygen potential is fixed by U_{0.95}Pu_{0.05}O_{1.995}, elemental gal-

lium would be the stable phase over the entire temperature range. Finally, the hyperstoichiometric fuel, $U_{0.95}Pu_{0.05}O_{2.002}$, would cause gallium to be present as an oxide.

(2) During Burn-up

The behavior of homogeneous fuel during burn-up is more complex than the case where the PuO_2 is assumed to act as an isolated aggregate. As in typical LWR fuel, during burn-up, the oxygen that is released will increase the oxygen content of the UO_2 - PuO_2 phase, thus increasing its O/M ratio. (PuO_2 , in contrast, cannot have an O/M ratio of >2 , and, therefore, it remains constant at a value of 2.) In addition, the chemical equilibrium state in the fuel also will be affected by the formation of metal fission-product oxides. The global equilibrium composition, which includes the fission products and the MOX, however, is difficult to compute particularly because the oxygen potential representation for the UO_2 - PuO_2 phase is nonlinear and requires the use of iterative solution schemes. Thus, for simplicity, the oxidation states of the fission products have been determined from the Ellingham diagram of Kleykamp,⁶ the assessment of Lindemer *et al.*,⁷ and the O/M ratio of the fuel estimated from the representation of Besmann and Lindemer,⁵ together with the oxygen balance. The UO_2 - PuO_2 initially is assumed to have an O/M ratio of 2.

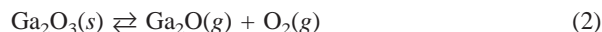
In the case where gallium is present in the unirradiated fuel as the oxide, it is estimated that the O/M ratio of the fuel will increase to ~ 2.005 with the fission-product states, as indicated in Table II. Note that, in the oxygen balance in Tables II and III, the oxidation of the fuel from an O/M ratio of 2 to higher values is included by the MOX entry. The only significant difference from the fission products in typical LWR fuel is the oxidized state of the molybdenum.⁶

Assuming that the gallium in the unirradiated fuel is not oxidized, it becomes a sink for oxygen (Table III). Because of the oxidation of the gallium during burn-up, the O/M ratio of the fuel is estimated to increase only to ~ 2.003 . However, the fission products are considered to exist in the same oxidation state as in the case where gallium is initially oxidized (Table II).

V. Potential for Gallium Vapor Transport

(1) Gallium Vapor Pressure within MOX Fuel

Near the oxygen potentials for MOX fuel, as shown in Fig. 1, the dominant gaseous species will be Ga_2O . The only other gaseous species are elemental gallium and GaO , with only the gallium vapor pressure exceeding that of Ga_2O at oxygen potentials well below those of the gallium- Ga_2O equilibrium. The Ga_2O vapor pressures in the presence of Ga_2O_3 are governed by the reaction



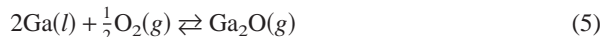
which can be used to compute the species partial pressures. For the sake of simplicity, the free-energy values for the constituents at temperature were computed from the enthalpy of formation (ΔH_f) and entropy (S) at 1000 K (Table I):

$$\Delta G_T = \Delta H_{f,1000K} - T\Delta S_{1000K} \quad (3)$$

where ΔG_T is the change in the Gibbs free energy and ΔS is the change in entropy. This assumption is very accurate if T is within several hundred degrees of the temperature of the enthalpy and entropy values (in this case, 1000 K). Using the thermochemical data of Table I and the above-mentioned equation, the oxygen potential expression for values of the vapor pressure of $Ga_2O(g)$ over $Ga_2O_3(s)$ is given by the equation

$$RT \ln p_{O_2}^* = -970137 + 371.441T - RT \ln p_{Ga_2O} \quad (4)$$

Under lower oxygen potentials where elemental gallium is the stable phase, as opposed to the oxide, the vapor pressure of Ga_2O is determined from the equation



Again, from the data of Table I, the oxygen potential expression can be expressed as

$$RT \ln p_{O_2}^* = -242142 - 84.984T + 2RT \ln p_{Ga_2O} \quad (6)$$

The vapor pressure calculations presume that the condensed gallium species are present as separate phases within the fuel, yet there is no reason why gallium, regardless of its oxidation state, could not be dissolved in the fluorite structure of the fuel. Should that be the case, the equilibrium behavior of the gallium would be modified by its solution in the fuel and governed by its activity in the solution. In the absence of data regarding the activity of gallium in either PuO_2 or UO_2 - PuO_2 , the best assumption is to presume that there are no energetic interactions between the species and that the system acts as an ideal solid solution.⁹ That being the case, the activity of the dissolved gallium species would simply be in direct proportion to its concentration. As a result, the Ga_2O (or any other gallium species) vapor pressure would simply be reduced by a factor equal to the molar concentration of the dissolved gallium species:

$$p_{Ga_2O,(sol)} = [Ga/Ga_2O_3]_{(sol)} p_{Ga_2O} \quad (7)$$

where $[Ga/Ga_2O]$ is the molar concentration of either elemental gallium or Ga_2O_3 in the MOX fuel.

(2) Vapor-Transport Mechanisms

Under constant oxygen potential, or even under the slowly changing oxygen potential of the MOX isocompositional lines (Fig. 1), p_{Ga_2O} will decrease as the temperature decreases, regardless of whether elemental gallium or Ga_2O_3 is present. Thus, a driving mechanism for the vapor transport of Ga_2O from hotter to cooler regions exists, with the potential for condensation of the oxide on the fuel side of the clad or the cooler ends of the fuel rod. Elevated oxygen pressures suppress the Ga_2O vapor pressure over Ga_2O_3 (Fig. 1); thus, significant burn-up could serve to reduce gallium transport. Conversely, increasing oxygen potential increases the Ga_2O vapor pressure over elemental gallium. Deposition of metallic gallium on the clad via such a process is not possible however without another gallium-containing, relatively high-vapor-pressure species with which Ga_2O can form a vapor-transport couple.

VI. Interactions with Zirconium

The zirconium- ZrO_2 equilibrium line, based on the data of Barin,³ is shown in Fig. 1 to allow assessment of the thermochemical behavior of gallium with regard to the cladding. The position of the zirconium/ ZrO_2 boundary at an oxygen potential that is substantially more negative than that of gallium/ Ga_2O_3 indicates that, under equilibrium conditions, zirconium will reduce the Ga_2O_3 phase to gallium metal, thus forming ZrO_2 . This observation implies that Ga_2O_3 that has condensed on, or otherwise transported to, the Zircaloy surface may react such that elemental gallium forms, which allows Zircaloy attack. Given that Zircaloy will have a native ZrO_2 surface film, which may prevent direct contact between Ga_2O_3 and the base metal, the nature and extent of any reaction will be dependent on various transport phenomena, such as diffusion of oxygen or mechanical damage to the film. In addition, there is potential for gallium to dissolve in the ZrO_2 structure.

VII. Conclusion

For the proposed MOX LWR fuel, knowledge of the chemical thermodynamic relationships in the actinide oxide and gallium oxide systems has allowed determination of the state of gallium as a function of temperature and oxygen potential, along with the vapor pressure of the Ga_2O species. The

state of gallium, assuming significant burn-up, also has been considered.

The presumption that the presence of elemental gallium at the Zircaloy surface causes degradation of the clad (although this is yet to be demonstrated) may require that the fuel chemistry be controlled to assure gallium is present in the oxide form. To maintain gallium as an oxide in as-fabricated fuel, the O/M ratio of the fuel should be at least 2. During burn-up, in an isolated PuO_2 aggregate, the fission products molybdenum, technetium, cadmium, tin, antimony, tellurium, and some ruthenium are computed to be present as oxides. This observation is true whether or not the gallium is oxidized in the unirradiated fuel. However, it is in contrast to the situation in typical LWR fuel, where these fission products are present in metallic precipitates.

The results that have been obtained, assuming that the fuel is homogeneous and the gallium is present initially as the oxide, indicate that, of the above-noted metallic fission products, only molybdenum will be oxidized and the O/M ratio of the fuel will increase from an original value of 2 to ~ 2.005 . Thus, with the exception of molybdenum, the fission-product states will be similar to those observed in typical LWR fuel.⁶ The same condition is true even assuming that the 1 mass% of gallium in the weapons plutonium is carried over to the fuel as the metal, although the O/M ratio of the fuel will only increase to ~ 2.003 at the given burn-up. If the formation of complex oxides is included in the analysis, the molybdenum might, at least in part, remain as the metal; thus, the fuel behavior would not differ from that of typical LWR fuel in this respect.

At temperatures that approach 1800 K, the vapor pressure of gaseous Ga_2O will be on the order of 10^4 Pa. In a temperature gradient within the fuel rod, the oxide species may vaporize in significant quantities in the hotter regions and transport to the cooler clad surfaces, where it would condense. If mass transport allows the condensed Ga_2O_3 to be reduced by the zirconium

in the clad, then even the oxide at the clad surface may have detrimental effects. However, Lindemer¹⁰ has persuasively argued that because analogous cesium species are retained within fuel-pellet material and are not transported to the clad, gallium also would not likely migrate to the cladding surface.

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