

12.4

The Effect of Burnup on the Oxygen Potential of the Fuel.

The burnup of Pu (or U) causes oxygen to be released and the FP's, even though there are 2 of them , cannot combine with all of the oxygen liberated (Hypo--> Hyper)

To find $\overline{\Delta G_{O_2}}$ (function of r) need;

- 1.) decrease of U, Pu and increase in oxygen consuming FP's
 - 2.) Chemical and Physical States of FP's
 - 3.) Redistribution of O₂ and FP's in fuel
 - 4.) Thermochemistry of solid -gas phase
 - 5.) Effectiveness of cladding to remove oxygen and FP's
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12.4.1 Concentration Changes During Burnup Orlander shows

$$N_U = (1 - q)(1 - \beta)(N_U^\circ + N_{Pu}^\circ)$$

$$N_{Pu} = q(1 - \beta)(N_U^\circ + N_{Pu}^\circ)$$

where q = cation fraction of Pu
 β = burnup

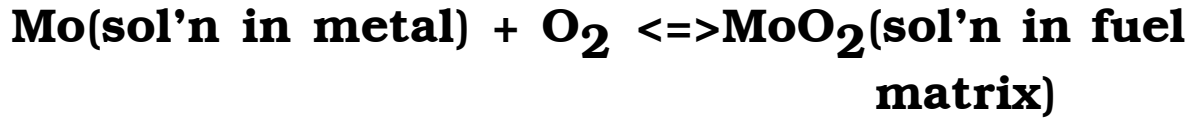
$$q = \frac{q}{1 - \beta} \quad \text{if conversion ratio} = 1.0$$

also,

$$N_i = Y_i \beta (N_U^\circ + N_{Pu}^\circ)$$

12.4.2 Partitioning of Mo

As shown earlier, the free energy of formation of MoO₂ is close to stoichiometric fuel



With ideal solutions, we can replace activities with fractions to give;

$$\Delta G_{\text{Mo}}^{\circ} = RT \ln \Pi_{\text{O}_2} - RT \ln \left(\frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m} \right)$$

Free Energy	$\overline{\Delta G_{\text{O}_2}}$	
of Formation	Oxygen	Fraction of Mo in
MoO₂	Potential	Metal Matrix as MoO₂
	Fuel	

Set up expressions for y_{Mo}^f (12.22) & y_{Mo}^m (12.23)

$$\Delta G_{\text{Mo}}^{\circ} = \overline{\Delta G_{\text{O}_2}} - RT \ln \left\{ \left(\frac{f_{\text{Mo}}}{1 - f_{\text{Mo}}} \right) \left(\frac{Y_{\text{NM}} + (1 - f_{\text{Mo}}) Y_{\text{Mo}}}{\frac{1 - \beta}{\beta} + Y_{\text{Y-Re}} + f_{\text{Mo}} + Y_{\text{ZrNb}} - Y_{\text{BaSr}}} \right) \right\}$$

Unknowns, f_{Mo} = frac of oxidized Mo as MoO₂
 $V_{\text{U}}, V_{\text{Pu}}$ to determine $\overline{\Delta H_{\text{O}_2}}, \overline{\Delta S_{\text{O}_2}} \rightarrow \overline{\Delta G_{\text{O}_2}}$

12.4.3 Oxygen Balance

- Recognize that oxygen can exist in both HM oxides and FP oxides (Zr, Ba, Sr, Y,)

$$N_o^{Ba-Sr} + N_o^f$$

$$3N_{Ba-Sr} (BaZrO_3, SrZrO_3)$$

- Charge balance is maintained by reduction of Pu or oxidation of U

Charge Balance

Hypostoichiometric Fuel Only

($V_U = 4, V_{Pu} < 4$)

$$2N_o^f = 4N_U + V_{Pu}N_{Pu} + 4(N_{Zr-Nb} - N_{Ba-Sr})$$

$$+ 6N_{Ba-Sr} + 3N_{Y-RE} + 4f_{Mo}N_{Mo}$$

Hyperstoichiometric Fuel Only

($V_U > 4, V_{Pu} = 4$)

$$2N_o^f = V_U N_U + 4N_{Pu} + 4(N_{Zr-Nb} - N_{Ba-Sr})$$

$$+ 6N_{Ba-Sr} + 3N_{Y-RE} + 4f_{Mo}N_{Mo}$$

Dividing through by N_U and using burn up def.,

$$2\left(\frac{O}{M}\right) = 4(1 - q)(1 - \beta) + V_{Pu}q(1 - \beta) +$$

$$(2Y_{Ba-Sr} + 4Y_{Zr-Nb} + 3Y_{Y-RE} + 4f_{Mo}Y_{Mo})\beta$$

similar for hyper fuel.

- Use oxygen balance to solve for f_{Mo} and V_U or

V_{Pu}

fraction of Mo oxidized to MoO_2

• Knowing V_U or V_{Pu} , we can solve for $\overline{\Delta G_{O_2}}$
from figures 11.13 and 11.14

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Note figure 12.10 for hypo fuel !

Note difference from figure 11.12
(Mo holds oxygen content down)

$$\beta_{crit} \approx \left(\frac{\left[1 - \left\{ \frac{O}{M} \right\} \left\{ \frac{1}{2} \right\} \right]}{1 - \left[\frac{(2Y_{Ba-Zr} + 4Y_{Zr-Nb} + Y_{Y-Re})}{4} \right]} \right)$$

when

$O/M = 1.99 \quad \beta_{crit} = 1.5\%$

$O/M = 1.97 \quad \beta_{crit} = 4.8\%$

$O/M = 1.95 \quad \beta_{crit} = 6.7\%$

For
 $(U_{0.8}Pu_{0.2})O_{2-x}$

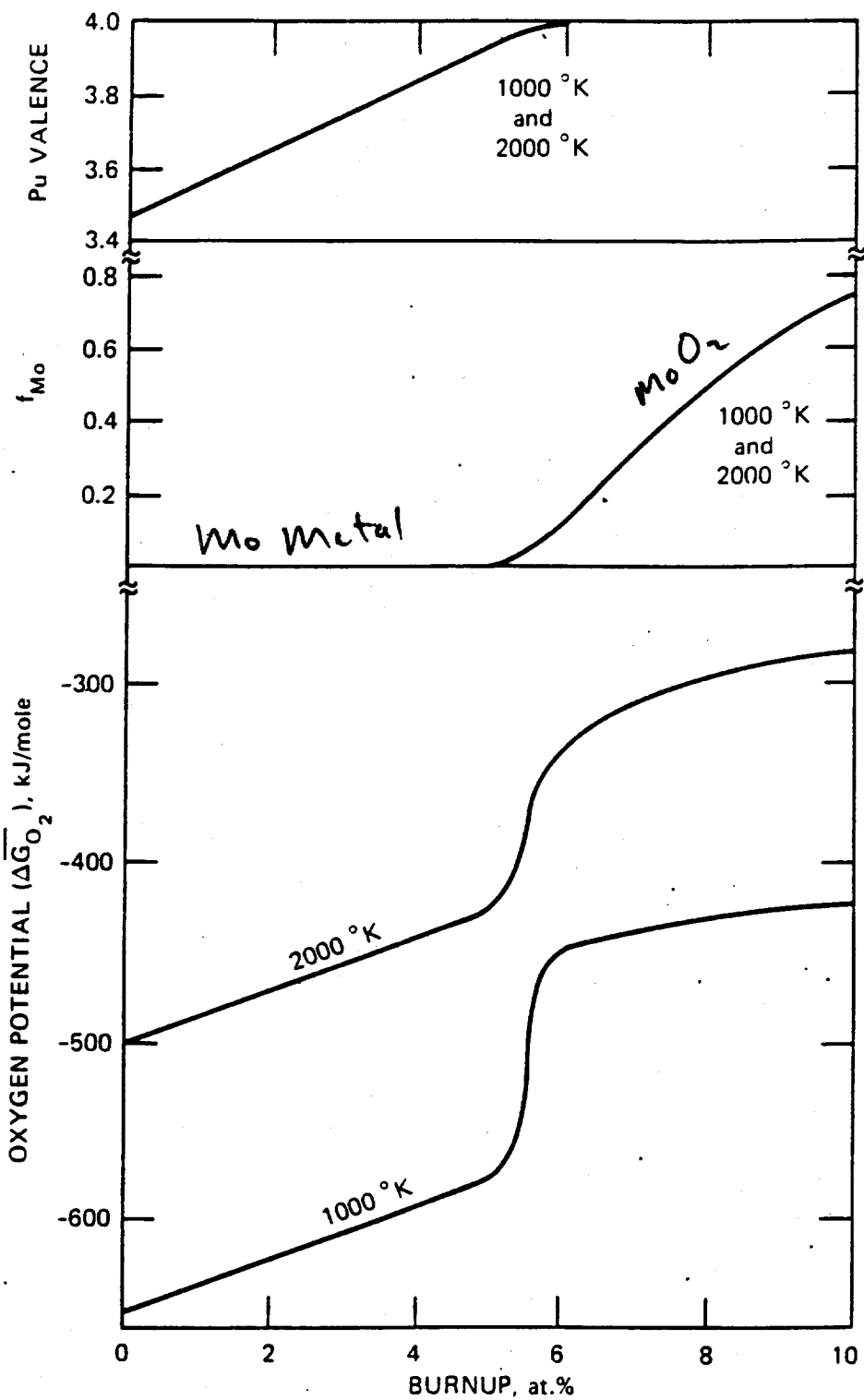


Fig. 12.10 Effect of burnup on the oxygen potential, molybdenum oxidation state, and plutonium valence for fuel of initial composition $(U_{0.85}Pu_{0.15}O_{1.96})$. The effects of oxygen, heavy metal, and fission-product migration and oxygen reaction with the cladding are not considered.

Problem 12.4

After irradiation it was found that where the $T=2000^{\circ}\text{K}$, the Mo was distributed as follows;

- 0.08 mole% MoO_2 in oxide fuel
- 10 at% Mo in metallic inclusions
- 0.01 g of metallic inclusions per gram of irradiated fuel

 a.) Assuming ideal solutions, calculate Π_{O_2}

$$\Delta G_{\text{Mo}}^{\circ} = -574 + 164 \left(\frac{T}{1000} \right) \dots \frac{\text{kJ}}{\text{mole}}$$

for $\text{Mo}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{MoO}_2(\text{s})$

$$K = \exp\left(\frac{-\Delta G_{\text{Mo}}^{\circ}}{RT}\right) = \left(\frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m \sum \Pi_{\text{O}_2}}\right) \text{ (eq. 12.17)}$$

@ 2000 °K,

$$\Delta G_{\text{Mo}}^{\circ} = -574 + 164 \cdot 2 = -246 \text{ kJ/mole}$$

Then oxygen potential is;

$$\Delta G_{\text{O}_2}^{\circ} = RT \ln(\Pi_{\text{O}_2}) = \Delta G_{\text{Mo}}^{\circ} + RT \ln\left(\frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m}\right)$$

$$8.28 \cdot 2 \cdot \ln(0.08/10) = -80 \text{ kJ/mole}$$

$$\Delta G_{\text{O}_2}^{\circ} = -246 - 80 = -326 \text{ kJ/mole}$$

$$\Pi_{\text{O}_2} = \exp\left(\frac{-326}{R \sum 2000}\right) = 2 \times 10^{-9} \text{ atm}$$

b.) Assuming that all the noble metals are in metallic inclusions, calculate the burnup of the fuel. (Assume all At. Wts. of elements in metallic inclusions are 100)

There are 0.01 g of metallic inclusions per g of fuel, or,

$\left(\frac{0.01}{100}\right)$ g atoms of metallic inclusions per
 0.1 cm³ of fuel

However, only 10% (at) of inclusions are of Mo

The Noble Metal (NM) conc. (g atom/cm³ fuel) is

$$N_{NM} = \left(\frac{0.00009}{0.1}\right) = 0.0009 \left(\frac{\text{g - atom.NM}}{\text{cm}^3 \cdot \text{fuel}}\right)$$

=====

$$\begin{aligned} N_U^\circ + N_{Pu}^\circ &= \text{initial heavy metal Conc} \\ &= 10 \frac{\text{g}}{\text{cc}} \sum \frac{1}{270 \frac{\text{g}}{\text{g - atom.HM}}} \end{aligned}$$

$$= 0.037 \text{ g atom HM / cc of fuel}$$

using eq. 12.16

$$\beta = \frac{N_{NM}}{Y_{NM} \sum (N_U^\circ + N_{Pu}^\circ)} = \frac{0.0009}{0.456 \sum 0.037} = 0.053$$

$$\underline{\quad} = 5.3 \%$$

c.) Find the Mo content of the metallic inclusion that should have been found if no Mo had been lost from or gained by the unit volume of fuel under consideration.

From eq. 12.16, total Mo conc. after 5.3% BU ;

$$N_{Mo}^* = (0.206) \sum \beta \sum (N_U^\circ + N_{Pu}^\circ)$$

table 12.1 Part b

$$= 0.0004$$

$$\begin{aligned} (N_{Mo}^{incl})^* &= \text{Mo in metallic inclusions } \left(\frac{\text{g atom}}{\text{cc fuel}} \right) \\ &= 0.001 \left(\frac{\text{g atom incl}}{\text{cc fuel}} \right) \cdot (y_{Mo}^m)^* \end{aligned}$$

assume metallic inclusion are principally NM, use b.)

$$\begin{aligned} (N_{Mo}^f)^* &= \text{Mo in fuel matrix, } \frac{\text{g atom}}{\text{cc fuel}} \\ &= 0.037 \frac{\text{g atom HM}}{\text{cc fuel}} \cdot (y_{Mo}^f)^* \end{aligned}$$

$$N_{Mo}^* = (N_{Mo}^{incl})^* + (N_{Mo}^f)^* = 0.001 (y_{Mo}^m)^* + 0.037 (y_{Mo}^f)^*$$

But the ratio $\frac{(y_{Mo}^f)^*}{(y_{Mo}^m)^*}$ is fixed by ΔG_{O_2} and is the same as the measured value, therefore,

$$(y_{Mo}^f)^* = \frac{0.08}{10} (y_{Mo}^m)^*$$

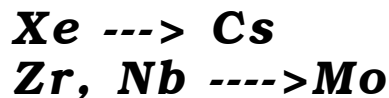
and

$$\begin{aligned} N_{Mo}^* &= (y_{Mo}^m)^* \left[0.001 + \frac{0.037 \Sigma 0.08}{10} \right] \\ &= 0.0013 (y_{Mo}^m)^* \\ (y_{Mo}^m)^* &= \frac{N_{Mo}^*}{0.0013} = \frac{0.0004}{0.0013} \\ &= 0.31 \end{aligned}$$

Metallic inclusions should have contained 31% Mo if none is lost from this spot in the fuel. The fact that only 10 at% of the inclusion was Mo means that $\approx 2/3$ of the Mo produced by fission at the radial location where the measurements were made was removed by some migration process to other radial positions in the fuel pin.

12.5 Fission Product Migration

In addition to vapor transport, solid state diffusion can transport solid fission products around fuel pins. Note that the precursors may be important.



Cesium is classic example which is usually found in colder portions of the fuel

<u>Bad</u>		<u>Good</u>
• Accelerates potential corrosion SS	Cs_2O	• Reduces O_2
• Removes Cs so it can't tie up Iodine	Cs_2MoO_4 Cs_2UO_4	• Oxide less volatile
• Swelling	CsI	• Usually all I is tied up with Cs ($Y_{\text{Cs}} \approx 6Y_{\text{I}}$)

- Figure 12.11, note log scale
- Movement of Mo -Figure 12.1

- Columnar grains concentrate Cs_2MoO_4 at fuel surface

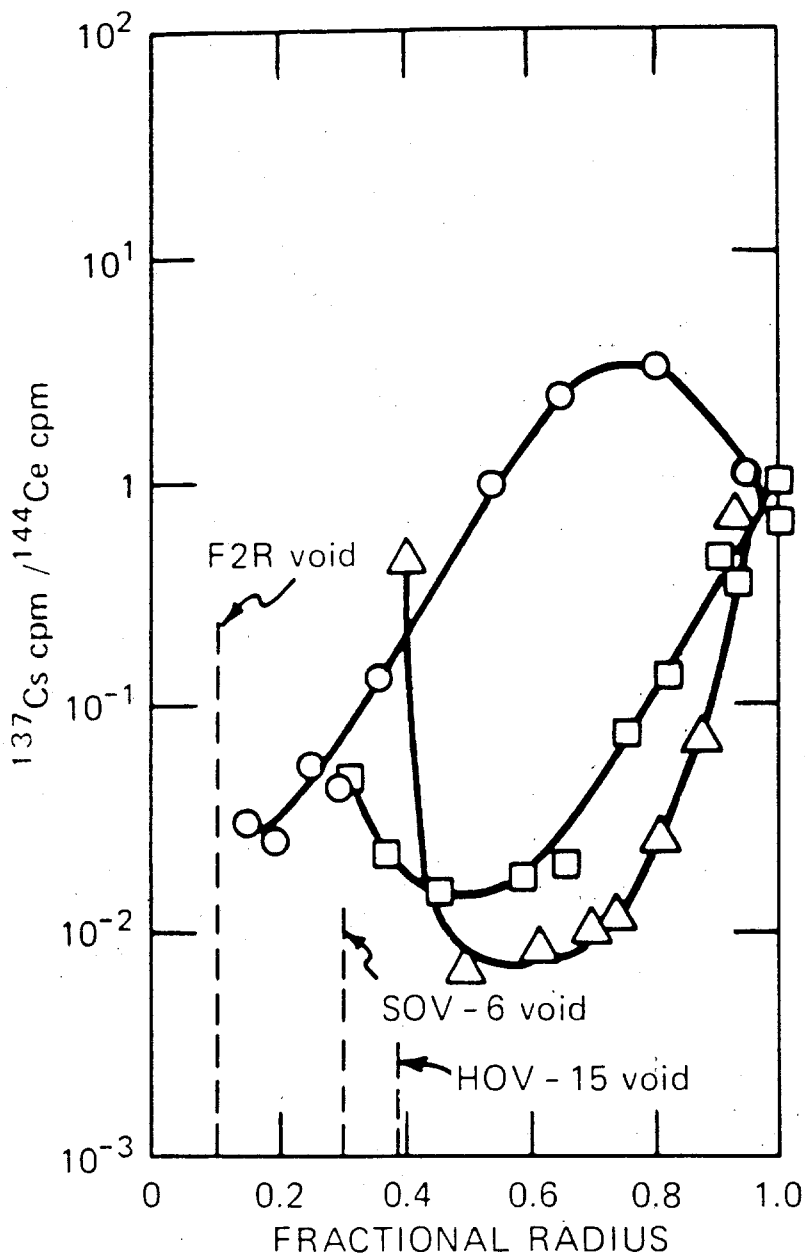


Fig. 12.11 Radial distribution of ^{137}Cs in irradiated mixed-oxide fuel pins. ○, F2R. △, HOV-15. □, SOV-6. (From C. E. Johnson et al., in *Proceedings of the Conference of Fast Reactor Fuel Element Technology*, New Orleans, p. 603, American Nuclear Society, Hinsdale, Ill., 1971.)

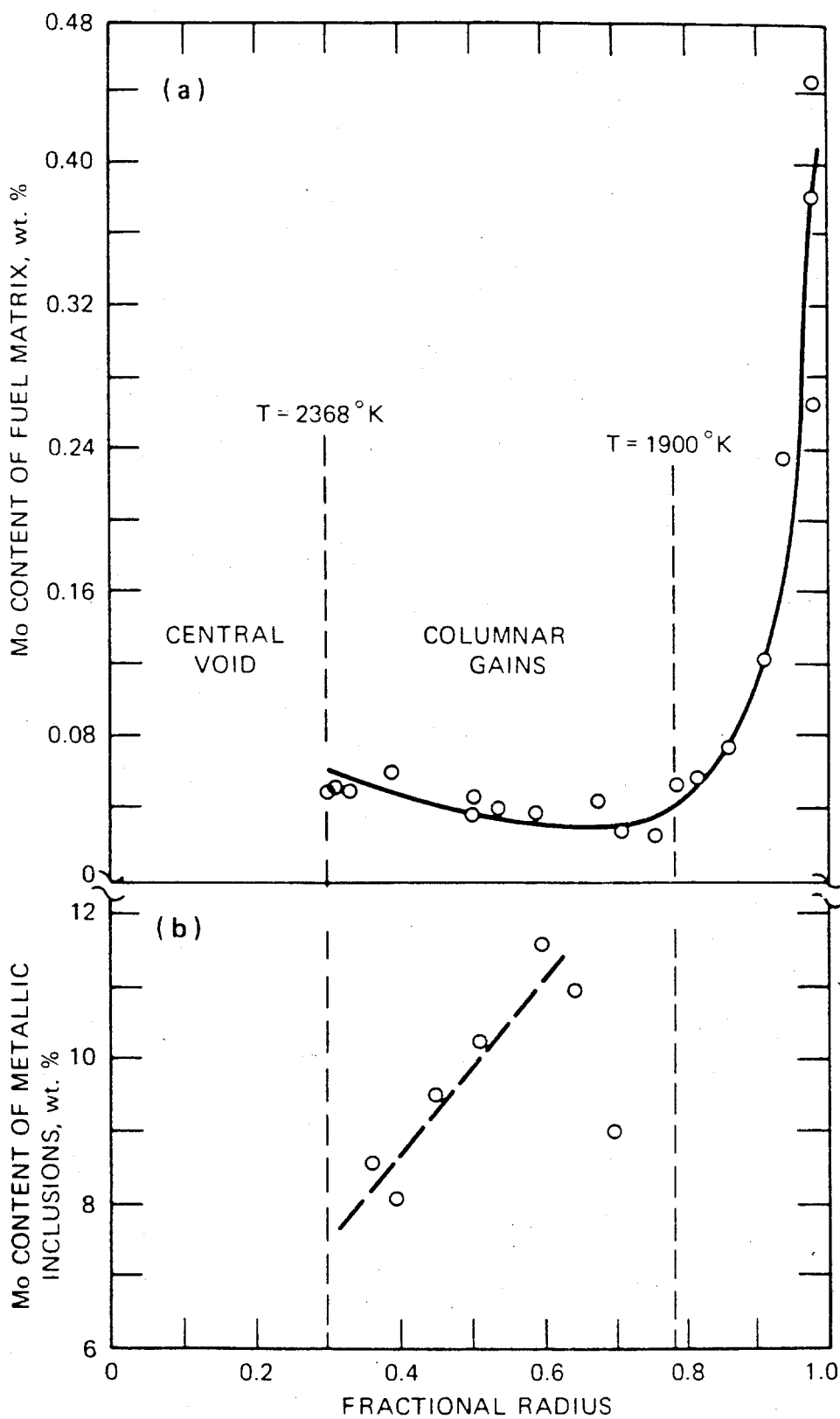


Fig. 12.12 Concentrations of molybdenum in the fuel matrix (a) and in the metallic inclusions (b) of an irradiated mixed-oxide fuel pin. Initial fuel density, 85% of theoretical density; initial oxygen-to-metal ratio, 1.998; burnup, 9.4%; linear power, 425 W/cm. [From I. Johnson et al., *J. Nucl. Mater.*, 48: 21 (1973).]

12.6 Fuel Cladding Interaction

Major problem for high burnup fuels in 316 SS cladding (Not as bad for lower B.U. LWR fuel)

12.6.1

Important thing is to keep Π_{O_2} low to resist oxide formation - Table 12.4

Can do this by keeping fuel hypostoichiometric but that is hard because of vapor transport

Note: If one could keep the O/M ratio at ≈ 1.96 , then the oxygen partial pressure is so low that Cr_2O_3 can't form. This is one reason oxide fuel is fabricated in the hypostoichiometric state.

12.6.2 Observations of Cladding Corrosion by Irradiated Mixed Oxide Fuels

Two types of cladding attack

- a.) Corrosion of inner clad wall
- b.) Transport of clad constituents to fuel

Attack of Cladding

- 1.) Worst "actors"

Cs, Mo, I, Oxygen

- 2.) Depends on T and O_2 potential

Figure 12.16

Note threshold at $\approx 550^\circ C$

Table 12.4 Thermochemical Properties of Fuel and Cladding at 1000° K

Mixed-oxide fuel*		Stainless-steel components†	
Heavy-metal valence	$\overline{\Delta G_{O_2}}$, kJ/mole	Reaction	ΔG° , kJ/mole
4.002	-284	$\frac{4}{3} \text{Cr} + \text{O}_2 = \frac{2}{3} \text{Cr}_2 \text{O}_3$	-573
4.000	-418		
3.98	-561	$2\text{Fe} + \text{O}_2 = 2\text{FeO}$	-393
3.96	-615	$2\text{Ni} + \text{O}_2 = 2\text{NiO}$	-293

*Oxygen potentials taken from Fig. 12.6.

†A typical stainless steel used in fast reactor fuel-element cladding contains 74 wt. % Fe, 18 wt. % Cr, and 8 wt. % Ni. Carbon and boron are minor components.

Mechanism



Low melting point medium to
attack Cr_2O_3

**12.6.3 Transport of Cladding Components to
Fuel---- Read**

12.7 Fuel Swelling Due to Solid Fission Products

$$\left(\frac{\Delta V}{V}\right)_{\text{solid.FP}} = \left(\frac{V - V^\circ}{V^\circ}\right) = \left\{ \sum_{\text{solid.FP}} \left(\frac{Y_i v_i}{v_U} \right) - 1 \right\} \beta$$

Volume of UO_2

Does **not** include gases !!!

Qualifications for Table 12.6

- *It overestimates the DV in hot part and underestimates it in the cold part.*
- *As oxygen potential increases, more MoO_2 forms, increasing DV*

0.15 - 0.45 % per % B.U.

**Table 12.6 Swelling Due to Solid Fission Products
in Pure Uranium Dioxide Fuel***

Fission-product group	Y_i†	v_i/v_U	$Y_i v_i/v_U$
Nb + soluble Zr‡	0.149		
<u>Y + rare earths</u>	<u>0.534</u>		
Total soluble fission products	0.683	1.00	0.683
Mo	0.240		
<u>Ru + Tc + Rh + Pd</u>	<u>0.263</u>		
Total metallic inclusions	0.503	0.36	0.181
Ba + Sr (as zirconates)	0.149	1.74	0.258
Cs + Rb + I + Te	0.238	0.76	0.181
Other fission products	0.027	0.76	0.021
	<u>1.60</u>	Total	1.324

*Solid swelling = $1.324 - 1 = 0.32\%$ per atom percent burnup.

†From Table 12.1.

‡Soluble Zr is the zirconium remaining after fraction in the zirconates in the alkaline earth oxide phase has been removed from the total Zr yield.