Thermochemical Aspects of High Plutonia (44%Pu) MOX Fuel

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Abstract

Use of high plutonia MOX as fuel is contemplated from the point of view of rapid disposition of plutonium and from economic power generation. As part of the fuel development programme, high plutonia MOX (44%) is undergoing test irradiation at FBTR, Kalpakkam. Several thermophysical and thermochemical properties need to be evaluated for this composition. This includes phase stability, melting temperature, vapour chemistry, oxygen potential, component redistribution under steep thermal gradient and compatibility studies between fuel-clad and fuel-coolant. Some of the thermochemical aspects are summarized in this paper.

Keywords: Mixed Oxide fuel; 44% plutonia; thermophysical; thermochemical properties

1. Introduction

Uranium-plutonium mixed oxide fuel undergoes structural and chemical changes during burnup in the reactor. The observations during Post Irradiation Examination (PIE) are the cumulative manifestation of several phenomena. To understand the fuel behavior, a comprehensive modeling approach, encompassing several fields of research is essential.

Thermochemical modeling is resorted to explain some of the chemistry aspects of fuel behaviour. Presence of plutonium in MOX, as oxide solid solution, substantially affects the thermochemistry of the fuel. Much literature information is available for 25%Pu-MOX fuel as this was the reference composition. Only limited information is available for higher compositions. Currently there is an emphasis on the use of high plutonia MOX towards rapid disposition of plutonium as well as to enhance the power economy. As part of the fuel development programme in India, studies on high plutonium MOX was initiated. Irradiation of a test pin with 44%Pu-MOX in FBTR, Kalpakkam is in progress.
Essential concerns in using the high plutonia MOX as fuel are its phase segregation; higher oxygen potentials enhancing the fuel-clad chemical interaction and the issue of chemical compatibility between MOX fuel and liquid sodium coolant in the event of clad breach.

In this work, phase stability of MOX fuel, melting temperatures, oxygen potential, vapour pressures, oxygen redistribution and compatibility studies between fuel-clad and fuel-coolant (sodium) are summarized for 44%Pu-MOX fuel.

2. Phase stability

Literature information [1,2] indicate that mixed oxide with O/M=1.985 or 2.00 would exhibit a single phase down to room temperature. However, hypo-stoichiometric MOX fuel with high Pu would undergo phase segregation leading to formation of two phase mixture at low temperatures. For below ~45%Pu, the fuel segregates into two fcc phases with differing (O/M) and Pu fraction. One of the fcc phases is having (O/M)=1.985 and the other fcc phase exhibits a tendency to lower the valency of Pu to (III) resulting in a (O/M) value corresponding to the lower limit of (O/M) for a given Pu fraction in MOX. For above 50%Pu fraction in MOX, fcc+bcc phases segregate at low temperatures, below ~723 K. The bcc phase is also a solid solution of uranium and plutonium oxides with an approximate composition of MnO3 and lattice parameter slightly higher than that of the fcc phase [2].

The transition temperature can be a function of Pu content and (O/M) value. The transition temperature for 42%Pu-MOX with (O/M) = 1.97 is ~723 K [1]. As the two phases are themselves MOX solid solutions of differing compositions it is believed that thermal cycling across the transition temperature may not develop much dimensional strain.

Dilatometric measurements on 44%Pu-MOX with an (O/M)= 1.98±0.02 from ambient temperature to 1473 K do not indicate dimensional variation due to phase segregation [3]. However, the slight change in the sample size observed after the cycle was attributed to the thermal lag between thermal cycles [3]. Data on the extent of segregation of Pu is not available. Recently, the phase segregation in MOX was modeled using thermochemical methods [4].

3. Solidus and liquids temperatures for MOX

The melting temperatures of UO2 was assessed as 3128±13 K [5] and that of PuO2 as 2701±35 K[6]. UO2 melts at a higher temperature, by above 425 K, than PuO2 and MOX fuel melts at temperatures (solidus) which lie between that of pure PuO2 and UO2. Both burnup and deviation from stoichiometry lowers the melting temperature.

The solidus and liquidus temperatures can be estimated using thermochemical principles. Usage of ideal solution formalism for UO2-PuO2 was suggested by Epstein [7]. The data used in the present estimation are:

<table>
<thead>
<tr>
<th>oxide</th>
<th>(T_m) (K)</th>
<th>(\Delta H_m) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO2</td>
<td>3128±13</td>
<td>70±4</td>
</tr>
<tr>
<td>PuO2</td>
<td>2701±35</td>
<td>67±3</td>
</tr>
</tbody>
</table>

The estimated solidus and liquidus temperatures for the UO2-PuO2 pseudo-binary system is shown in Fig.1. The present estimate falls between the estimates of Adamson et al. [6] and Konno et al. [8]. Recent measurements by Kato et al. [9] give higher values for both solidus and liquidus. The solidus data of Kato et al. lie beyond the liquidus data prevailing in the literature. This is attributed to the usage of higher melting temperature for PuO2, 2843 K [9].
The composition dependence of the solidus and liquidus temperature are given by,

\[ T_s(p) = 3128 - 599p + 227p^2 - 55p^3 \]
\[ T_l(p) = 3128 - 390p - 22p^2 - 15p^3 \]

The uncertainty varies from 15 to 32 K for the solidus from p=0.02 to p=0.98 and is ±28 K at p=0.45. Similarly the uncertainty varies from 14 to 51 K for liquidus from p=0.02 to p=0.98 and is ±26 at p=0.45. The solidus temperature for p=0.44 is found as 2904±28 K.

4. Thermophysical properties

Thermal conductivity data reported earlier for 21%, 28% and 40% Pu-MOX indicate that thermal conductivity is a sensitive function of plutonia content [10]. Specific heat measurements on 21%, 28%, 40%, 45%, 55% and 65% Pu-MOX indicate that MOX solid solution obeys Neumann-Kopp’s additive rule [11].

5. Oxygen potential

Oxygen potential controls the chemical state of fission products, interaction of fission products with the fuel and redistribution of fuel and fission product constituents; it also influences fuel-clad chemical interaction and fuel-coolant chemical interaction in the event of clad failure.

The experimental data for oxygen potential are generally reported for discrete fuel compositions at various temperatures [10]. However, theoretical models are needed to provide correlations between discrete experimental data.

5.1. MOX model

In this work, MOX fuel, \((U_{1-p}Pu_pO_{2+z})\) is treated as a pseudo-quaternary solid solution of \(UO_2-U_{1-p}Pu_{p}O_{2+z}\), where \(a, b, c\) and \(d\) are stoichiometric coefficients. The plutonium oxide \(Pu_{p}O_{b}\) is typically a \(Pu_{p}O_{1.5}\)-type phase \((b = 1.5a)\) predominant in the description of hypo-stoichiometry fuel and \(U_{1-p}O_{d}\) is \(UO_{2.25}\)-type oxide \((d = 2.25c)\) predominant in the description of hyper-stoichiometric fuel. For these oxides, the coefficient \(a\) can assume values 1, \((4/3)\) [12], 2 [13] or higher and the coefficient \(c\) can assume values 1, 2, 4 or higher. All the solid solutions were assumed ideal with a provision to incorporate regular solution behaviour, for any further extension of the model.

In the schema shown in Fig.2, the factor \(s\) gives the fraction of plutonium present in the form of \((1/a)Pu_{p}O_{b}\) and the factor \(h\) gives the fraction of uranium present in the form of \((1/c)U_{1-p}O_{d}\). The mass balance expressions for U-O and Pu-O subsystems can be derived using stoichiometric correlations [14].

Fig.2. Schematic representation of mixed oxide fuel solid solution and its components.

5.2. Diamond Plot

In a simple representation, the hypo-stoichiometric fuel can be viewed as \(UO_2-PuO_2-(1/a)Pu_{p}O_{b}\) pseudo-ternary system, ignoring \(U_{1-p}O_{d}\) as it becomes significant only at higher oxygen potentials. Similarly, the hyper-stoichiometric fuel can be viewed as \(UO_2-(1/c)U_{1-p}O_{d}-PuO_2\) pseudo-ternary system. The ‘Diamond plot’ is a graphical representation in which the pseudo-ternaries are adjoined at \(UO_2-PuO_2\) binary, shown in Fig.3.
5.3. Equilibrium

At equilibrium the oxygen potential can be calculated using PuO$_2$-Pu$_4$O$_9$ or UO$_2$-U$_4$O$_9$ equilibrium. For the PuO$_2$-Pu$_4$O$_9$ equilibrium: Pu$_4$O$_9$ + (a/4) O$_2$ = a PuO$_2$. For the UO$_2$-U$_4$O$_9$ equilibrium: c UO$_2$ + (c/8) O$_2$ = c U$_4$O$_9$. The oxygen potential is estimated by invoking the constraint that at equilibrium the oxygen potentials of Pu-O system and U-O system are equal. Initial compositions were obtained from the expressions pertaining to Diamond plot.

Iterative procedure refines the compositions towards equilibrium values subject to the equilibrium constraint. However, it was found that the initial composition obtained from the Diamond plot was indeed the equilibrium composition for most cases. The iterations were effective only for fuel compositions very close to exact stoichiometry, $z > 0.005$.

5.4. Configurational entropy

The oxygen potential has both thermal contributions and configurational contributions. The thermal contributions are independent of the values of the stoichiometric coefficients $a$ and $c$. Using the Gibbs energy data, the thermal term can be identified. The configurational term for Pu-O and U-O subsystems are given by:

$$
\Delta S_{\text{Pu-O}}^{\text{conf}} = \left( \frac{4}{a} \right) RT \ln \left( \frac{N_{\text{PuO}_2}}{N_{\text{Pu}_4\text{O}_9}} \right)
$$

$$
\Delta S_{\text{U-O}}^{\text{conf}} = \left( \frac{8}{c} \right) RT \ln \left( \frac{N_{\text{U}_4\text{O}_9}}{N_{\text{UO}_2}} \right)
$$

Fig.3. The ‘Diamond plot’

Fig.4(a) Oxygen potential as a function of (O/M). Value at exact stoichiometry is marked.

Fig.4(b) Oxygen potential as a function of temperature. Dashed lines indicate threshold for fuel coolant interaction.
The choice of stoichiometric parameters $a$ and $c$ affects the relative contribution of the configurational entropy to the oxygen potential. These parameters affect the slopes near exact stoichiometry in the ‘S’-type curves. It is seen that $a=2$ or 4 and $c=8$ provides a closer representation of experimental data [15]. Using the stoichiometric parameters $a$ and $c$ as 2 and 8, the model is explored for various possibilities.

5.5. Estimations for 44%Pu-MOX

The model is applied for MOX fuel with 44% plutonium and the results of oxygen potential variation with respect to (O/M) at several temperatures are shown in Fig.4(a)-4(d). As expected, the oxygen potential exhibits a typical ‘S’-type curve which shifts towards higher oxygen potential as temperature increases. As plutonium fraction is increased the curves shift towards higher oxygen potential values.

6. Fuel-clad & fuel-sodium chemical interaction

The oxygen potential for the reaction of sodium with oxide fuel $(U_{0.7}Pu_{0.3})O_{2-x}$ and $(U_{0.3}Pu_{0.7})O_{2-x}$ is given by Mignanelli and Potter [16].

\[
\Delta G_{eq}^{O_2} = -920.355 + 0.2301 T \text{ kJ/mol } O_2 \quad \text{and} \quad \Delta G_{eq}^{O_2} = -908.514 + 0.2046 T \text{ kJ/mol } O_2
\]

respectively. The threshold oxygen potentials for oxide fuel with 30% and 70% PuO$_2$ are shown in Fig.4b. For oxide fuel with 44% PuO$_2$, the threshold (O/M) for fuel coolant chemical interaction is well below 1.9 as shown in Fig.4b. Fuel-clad chemical interaction, FCCI, occurs at oxygen potentials higher than -585 kJ/mol at 1000 K [17]. In this context, (O/M)=1.97 was advocated for 44% Pu-MOX[18].

7. (O/M) redistribution

The oxygen in the fuel lattice undergoes redistribution under the steep thermal gradient prevailing across the fuel radius. Synergetic vapour and solid state transport mechanism are suggested [19,20]. Accordingly the redistribution can be estimated using,

\[
\ln \left( \frac{z_2}{z_1} \right) = \frac{Q^*}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

where $z_2$ and $z_1$ represent the deviation from stoichiometry at temperatures $T_2$ and $T_1$ corresponding to different fuel radii, R is universal gas constant and $Q^*$ is transport enthalpy given below with $V_{Pu}$ as the valency of plutonium in MOX fuel.

\[Q^* = (-3960+2370 V_{Pu} - 356 V^2_{Pu}) 1000\]
Using the above correlation, the (O/M) redistribution for (U_{0.56}Pu_{0.44})O_{2-z} was estimated for various nominal (O/M), Fig.5. Parabolic temperature distribution was assumed across the fuel radius with fuel central line temperature as 2600 K and fuel surface temperature as 1250 K.

Fig.5. (O/M) redistribution for (U_{0.56}Pu_{0.44})O_{2-z}.

8. Vapour pressures over MOX

The fuel pellets are subjected to a steep temperature gradient, \( \sim 1700 \) K drop across a radius of 2.5 mm. The vapour pressures of various species depend on the local temperature; vapour pressure is high at the fuel pellet center and relatively low at the pellet surface. The difference in pressure can cause evaporation-condensation of such species.

Several experimental and modeling works were reported in the literature. Recently, the vapour pressure was estimated by Viswanathan and Krishnaiah [21] for MOX and Maeda et al. [22] for the oxide fuels at 2000 K containing minor actinides.

8.1. Estimation of vapour pressure

In the present work, vapour pressures for 44\%Pu-MOX were estimated using thermochemical methods. The MOX model shown in Fig.2 was used. The thermochemical data needed for the calculations were resourced from Cordfunke and Könings [23]. The computations were carried out using the code EQUIt# developed during this work. The code is based on free energy minimization technique. The condensed phase consisted the pseudo-quaternary solid solution with ideal behaviour. The vapour phase consisted of nine species; O, O_2, Pu, PuO, PuO_2, U, UO, UO_2 and UO_3. Oxygen forms integral part of the vapour phase along with other species and oxygen potential was not estimated independently. The vapour pressures were estimated at 2000 K as a function of (O/M) for each plutonium composition.

Results for 44\%Pu-MOX fuel is presented in Fig.6(a)-6(d). A few general observations on the vapourisation of uranium plutonium mixed oxide can be made. The estimated pressures of various species depend on temperature, plutonium fraction and (O/M) of the condensed phase. MOX vapourisation is incongruent: the net vapour phase composition is not equal to that of the solid phase. The vapour pressures of individual species show a drastic change across exact stoichiometry, (O/M)=2.000, except for UO_2 and PuO_2 vapours. Close to exact stoichiometry, the dominant vapour species for uranium is uranium trioxide (UO_3) and for plutonium is plutonium dioxide (PuO_2).

The total pressure of all species exhibits a minimum with respect to (O/M) in the hypo-stoichiometry range. The net (O/M) ratio in the vapour phase is lower than that of the condensed phase up to certain (O/M) of the condensed phase, it become equal and shows a marked increase for higher (O/M) values. There exists a pseudo-congruent composition in the condensed phase at which (O/M) ratio in the vapour phase is equal to that of condensed phase.

Similarly, there exists another pseudo-congruent composition in the condensed phase at which (Pu/M) fraction in the vapour phase is equal to that of condensed phase. The net pressure of all the uranium bearing species is higher than that of the plutonium bearing species. Close to exact stoichiometry (>1.99), the vapour phase is richer in uranium and oxygen compared to condensed phase. This might lead to some amount of hypo-stoichiometry in the condensed phase.

As reported in literature, the uranium bearing species are abundant in the vapour phase compared to that of plutonium. This is one of the mechanisms attributed for the radial distribution of plutonium under the steep temperature gradient. Vapour pressure of atomic oxygen is higher than that for the molecular oxygen. UO_2 is the dominant species of all uranium bearing vapours in the hypo-stoichiometric range. Pressure of UO_2 remains almost invariant with respect to (O/M). Close to exact
stoichiometry, (O/M)>1.99, the pressure of UO₃ becomes dominant. PuO₂ is the dominant species of all plutonium bearing vapours. Pressure of PuO₂ shows a very little increase across the exact stoichiometry.

The total vapour pressure of all the species over MOX fuel exhibits a minimum with respect to (O/M). It was shown that MOX fuel undergoes incongruent vaporization [21,24]. For a given plutonium fraction in MOX, there exists two pseudo-congruent compositions; (i) with respect to (O/M) ratio and (ii) with respect to plutonium fraction. The (O/M) ratio corresponding to the total pressure minima almost coincides with that of pseudo-congruency with respect to (O/M).

9. Fuel-coolant chemical interaction

The capability to continue the operation of commercial LMFBRs to a scheduled refueling can be limited by fuel pin failures. Average fuel pin failures between 1 to 2 per reactor operating year is reported [25].

Following the breach in the cladding, sodium comes into contact with the fuel. The mixed oxide fuel, 20%PuO₂ having O/M ratio greater than ~1.96, is incompatible with coolant and reacts to give sodium urano-plutonate Na₃MO₄ (M=U₁₋ₓPuₓ) as the product. Na₃MO₄, due to its lower density than the fuel, increases the stress level of the cladding: this can further increase the size of the initial leak or cause a secondary crack. Eventually, fissile material fragments can be released into the coolant stream. In addition, potential cooling disturbances are also envisaged.

9.1. Kinetic experiments

From capsule equilibration of fuel/surrogate with sodium, followed by high sensitivity X-radiography, a series of images was recorded at different time intervals. The dimensional changes were measured for UO₂+sodium, 28%CeO₂-(U, Ce)O₂+Sodium [26]. From the results of (U, Ce)O₂ at 513 K the trends were found to be similar to that of 30%Pu-MOX [27]. Such studies indicate that the reaction is not instantaneous; it takes several hours for the completion of the reaction.

9.2. UO₂ – sodium reaction

Two annular UO₂ pellets were capsule equilibrated at 1073 K for 100 h and the radiographic results did not indicate any reaction. This is in confirmation with results of Mignanelli and Potter [28]. Stoichiometric UO₂ reacts with sodium only if oxygen level above a threshold is present in sodium. Alternatively, hyper-stoichiometric UO₂+x reacts with clean sodium. In either approach, the product is Na₃UO₄ which is isomorphous with sodium urano-plutonate, Na₃(U,Pu)O₄. The reaction product Na₃UO₄ was prepared in a separate experiment and the XRD pattern of the resultant powder confirms the formation.
9.3. MOX – sodium reaction

Two annular 44%Pu-MOX pellets were capsule equilibrated with sodium at 1073 K for 140 h inside an active glove box. At the end of equilibration, the sample was subjected to X-radiography, shown in Fig.7. It may be noticed from the images that the MOX fuel did not crumble or change its shape after the reaction. However, overall swelling was observed. Since the product formation on the fuel surface is not expected to be uniform, the dimensions were measured at several cross sections of the pellets and the average pellet volume was arrived at. The relative volume change was compared with the empirical correlations of Housseau et al. [29] and it was found that all the observations are above the predicted line. This is attributed to asymmetric growth of the product on fuel surface.

![Fig. 6(c) (O/M)$_{\text{vap}}$/[O/M]$_{\text{MOX}}$ ratio vs [O/M]$_{\text{MOX}}$](image)

![Fig. 6(d) (Pu/M)$_{\text{vap}}$/[Pu/M]$_{\text{solid}}$ ratio vs [O/M]$_{\text{MOX}}$](image)

Fig. 6(c) (O/M)$_{\text{vap}}$/[O/M]$_{\text{MOX}}$ ratio vs [O/M]$_{\text{MOX}}$.

Fig. 6(d) (Pu/M)$_{\text{vap}}$/[Pu/M]$_{\text{solid}}$ ratio vs [O/M]$_{\text{MOX}}$.

Fig.7 X-radiographic image of 44%Pu-MOX in liquid sodium, after equilibration at 1073 K for 140 h.

10. Conclusion

A summary on phase stability on fcc solid solution segregation, an assessment on melting temperatures, estimate of oxygen potential and vapour pressure data for 44%Pu-MOX is presented. The segregation of solid solution, if any, does not lead to dimensional variation of the fuel pellet. The melting point for 44%Pu-MOX is 2904±28 K. The oxygen potential for 44%Pu-MOX is higher than that for 21 and 28%. For example, oxygen potential for (O/M) =2.000 at 1200K is -361, -351 & -332 kJ/mol. for 21, 28 and 44%Pu-MOX respectively.

The vapour pressure for 44%Pu-MOX are higher than that for 21% and 28%Pu-MOX. The pseudo congruency (O/M) coincides with total pressure minima.

Experimental results on fuel-coolant chemical interaction confirms the formation of the product and pellet swelling due to reaction. The pellet retained its integrity at the end of the experiment. The kinetic experiments indicate that that the reaction is not instantaneous, may take several hours depending on the availability of oxygen, pellet temperature etc.
References