

Chemical states of fission products in irradiated $(U_{0.3}Pu_{0.7})C_{1+x}$ fuel at high burn-ups

Renu Agarwal *, V. Venugopal

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Received 19 April 2005; accepted 1 August 2006

Abstract

The chemical states of fission products have been theoretically determined for the irradiated carbide fuel of Fast Breeder Test Reactor (FBTR) at Kalpakkam, India, at different burn-ups. The SOLGASMIX-PV computer code was used to determine the equilibrium chemical composition of the fuel. The system was assumed to be composed of a gaseous phase at one atmosphere pressure, and various solid phases. The distribution of elements in these phases and their chemical states at different temperatures were calculated as a function of burn-up. The FBTR fuel, $(U_{0.3}Pu_{0.7})C_{1+x}$, was loaded with C/M values in the range, 1.03–1.06. The present calculations indicated that even for the lowest starting C/M of 1.03 in the FBTR fuel, the liquid metal phase of (U, Pu), should not appear at a burn-up as high as 150 GWd/t.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

The MARK I fuel of FBTR (Fast Breeder Test Reactor) of Kalpakkam in India, is a mixed carbide fuel with $Pu/(U + Pu) = 0.7$. It is a biphasic fuel containing a monocarbide phase, $(U, Pu)C$, in equilibrium with 3–6 mol% sesquicarbide phase, $(U, Pu)_2C_3$. The fuel has already exceeded a burn-up of 100 GWd/t. In case of hyper-stoichiometric mixed-carbide fuel, the C/M ratio of the fuel decreases with burn-up [1]. A look at the ternary phase diagram of the U–Pu–C system [1–3], shows that the monocarbides of uranium and plutonium have very narrow non-stoichiometry. Therefore,

the hyper-stoichiometric carbide should consist of $(U, Pu)C + (U, Pu)_2C_3$ phases and the hypo-stoichiometric carbide should consist of $(U, Pu)C + (U, Pu)$ phases. Hence, at high burn-ups when the C/M decreases to less than one, the sesquicarbide phase will disappear and due to the narrow non-stoichiometry of the monocarbide phase [1,2], a low melting (U, Pu), metallic phase will appear. This can result in the appearance of liquid phase in the fuel and the amount of liquid phase will continue to increase with burn-up. Due to difference in the Gibbs energy values of PuC and UC, the metallic phase in equilibrium with the monocarbide phase will be highly rich in plutonium [3–5]. The appearance of the metallic phase will result in a sudden increase in the partial pressure of plutonium and uranium in the fuel. These elements will diffuse from the high temperature center to the low temperature

* Corresponding author.

E-mail address: arenu@barc.gov.in (R. Agarwal).

fuel surface. On the surface they may form low melting eutectics with the components of stainless-steel clad, resulting in clad breaching, which can be detrimental to the fuel element. To be able to predict the burn-up at which metallic phase may appear in the carbide fuel, it is important to know the change in C/M with burn-up. The C/M of the fuel is related to the chemical states of all the fission products. The equilibrium state of the fission products is a result of many competing chemical reactions. The system with the minimum Gibbs energy is the stable system. In actual reactor scenario, under temperature gradient, the equilibria at micro-system level can be used for comparing the partial pressures and chemical potentials of the components. This data combined with transport coefficients can be used for studying the migration behaviour of different species in the dynamic system. However, the scope of the present work is limited to the equilibrium thermodynamic calculations at different temperatures and burn-ups.

2. Input data

To determine the chemical states of various fission product elements, modeling calculations were carried out using a computer program, SOLGASMIX PV [6]. The fission product yields of various isotopes for FBTR fuel were obtained from Pandikumar [7], calculated using ORIGEN (Oak Ridge Isotope Generation and Depletion) computer code [8].

Similar calculations to determine the chemical state of the burnt fuel at different burn-ups, using SOLGASMIX PV, were carried out previously by Imoto [9] for UO₂ fuel and Arai et al. [10] for UC fuel. Matzke [11] has given an estimated change in C/M at 10 at.% burn-up for (U,Pu)C fuel by a simplistic approach of accounting for the carbon attached to various fission products. However, this approach cannot compare the competing chemical reactions with very small Gibbs energy differences where the fission elements can coexist as two or more different compounds. Moreover, these estimations cannot account for the effect of solubility on the stabilizations or destabilization of a compound in a solution phase (see Tables 1 and 2).

To understand the method used in the present calculations, it is important to briefly explain the functioning of the computer program, SOLGASMIX PV. The program needs an input file containing the overall composition of each element in the

system and Gibbs energies of formation of all the compounds that may be formed from these elements in a given system. In case of solution phases, the program assumes ideal solution behaviour for every component unless the activity coefficient of the component is defined by the user. One can select the temperature and pressure of the system. The present calculations were carried out under isothermal and isobaric conditions. The limit of the program is that it can take maximum twelve elements at a time. The program then calculates the stable chemical states of each element based on the principle that the system will try to achieve the lowest Gibbs energy state while maintaining the mass-balance.

Before starting the calculations it was important to understand the constitution of the irradiated carbide fuel and the various phases present in it. Some simulation studies and post-irradiation investigations reported in the literature were used to obtain this information [12–18]. According to these studies, the principal condensed phases appearing in the irradiated mixed carbide fuel can be classified as follows:

1. (U,Pu)C and (U,Pu)₂C₃ type solid solution.
2. UMoC₂ and U₂RuC₂ type ternary compounds.
3. Intermetallic compounds.
4. Carbides of the fission products.
5. A gas phase containing He, Kr, Xe, CsI, Te, I, I₂, CO etc.

During fission of the fuel about 50 fission product elements are formed. But all these elements do not play an important role in the chemistry of the fuel. Some of these elements were excluded from the present calculations on the basis of their negligible fission yields. The remaining 26 elements were grouped together based on the similarity of their chemical behaviour, e.g., Ba and Sr, Cs and Rb, I and Br, Se and Te, and lanthanides. The noble gases like Xe and Kr were taken together as a part of the cover gas required for maintaining the pressure over the system.

During the grouping of the elements, the Gibbs energies of formation of their compounds were also taken into account. Some elements form similar compounds but due to large differences in their Gibbs energies of formation, these elements needed to be treated separately because they form different compounds in the present multi-component fuel system. This was observed in the case of noble metal alloys. Among the noble metals, Mo, Pd and Ru are

Table 1
The Gibbs energies of formation of the compounds used in the present calculations

	ΔG (J/mol) = A + BT		References
	A	B	
$U(s) + 3Pd(s) \rightarrow UPd_3(s)$	-524000	10.00	[39]
$2U(s) + 3C \rightarrow U_2C_3(s)$	-196271.4	-13.70	[40,41,5]
$Cs(s) + 0.5I_2(g) \rightarrow CsI(g)$	-157000	-132.0	[32]
$2Cs(s) + I_2(g) \rightarrow Cs_2I_2(g)$	-461000	143.0	[41]
$Ce(s) + 2Ru(s) \rightarrow CeRu_2(s)$	-216000	0.00	[10]
$2Ce(s) + 3C(s) \rightarrow Ce_2C_3(s)$	-190000	-14.00	[20]
$Zr(s) + C(s) \rightarrow ZrC(s)$	-225099.2	33.10	[42]
$U + Mo + 2C \rightarrow UMoC_2$	-194000	-2.90	[43]
$U(s) + 3Ru(s) \rightarrow URu_3$	-225000	35.00	[30]
$U + Mo + 1.7C \rightarrow UMoC_{1.7}$	-169000	-2.90	[43]
$2Pu(s) + 3C(s) \rightarrow Pu_2C_3(s)$	-164314	-5.52	[40,41,5]
$Pr(l) + 2C(s) \rightarrow PrC_2(s)$	-162757.6	25.90	[44]
$Ce(l) + 2C(s) \rightarrow CeC_2(s)$	-151460.8	18.40	[44]
$Y(s) + 2C(s) \rightarrow YC_2(s)$	-99997.6	-25.50	[44]
$2Y(s) + 3C(s) \rightarrow Y_2C_3(s)$	-125436.3	0.00	[44]
$U(s) + C \rightarrow UC(s)$	-110085.2	1.17	[40,41,5]
$Sm(l) + 2C(s) \rightarrow SmC_2(s)$	-87864	-14.60	[44]
$Nd(l) + 2C(s) \rightarrow NdC_2(s)$	-76985.6	-23.80	[44]
$La(l) + 2C \rightarrow LaC_2(s)$	-84935.2	-11.70	[11]
$Ce(s) + C(s) \rightarrow CeC(s)$	-116733.6	34.30	[44]
$Pr(s) + C(s) \rightarrow PrC(s)$	-127193.6	45.20	[44]
$Y(s) + C(s) \rightarrow YC(s)$	-64266.2	0.00	[44]
$Pu(s) + C(s) \rightarrow PuC(s)$	-57990.2	-0.75	[40,41,5]
$2Mo(s) + C(s) \rightarrow Mo_2C(s)$	-50208	-5.86	[20]
$Mo(s) + (1 - x)C \rightarrow MoC_{1-x}(s)$	-9204.8	-10.90	[44]
$Cs(s) \rightarrow Cs(l)$	2090	-6.94	[32]
$2U(s) + (Rh,Ru) + 2C \rightarrow U_2(Rh,Ru)C_2$	-335000	32.90	[3,28]
$Sr(s) + 2C(s) \rightarrow SrC_2(s)$	-81600	-16.10	[45,52]
$Ba(s) + 2C \rightarrow BaC_2(s)$	-90300	2.60	[45,52]
$Ba(s) + Te \rightarrow BaTe(s)$	-269400	12.30	[46]
$Pd(s) + Te(s) \rightarrow PdTe(s)$	-37650	-2.26	[46]
$0.5 I_2(g) \rightarrow I(g)$	106780	-122.6	[46,51]
$Te(s) \rightarrow Te(g)$	211700	-132.89	[46]
$2Te(s) \rightarrow Te_2(g)$	160400	-159.48	[46]
$Cs(s) \rightarrow Cs(g)$	76650	-90.46	[47]
$2Cs(s) \rightarrow Cs_2(g)$	10600	-113.6	[47]
$Cs(s) + 0.5I_2(s) \rightarrow CsI(l)$	-321700	-7.50	[32]
$Cs(s) + I_2 \rightarrow CsI(l)$	-321700	-7.5	[48,51]
$2Cs(s) + Te(s) \rightarrow Cs_2Te(s)$	-284500	45.77	[49]
$Zr(s) + 2I_2(s) \rightarrow ZrI_4(g)$	-537000	120.00	[50,51]

the elements with reasonably high fission yields. They show different chemistry in carbide fuels, therefore, they were considered separately. The remaining noble metals, Nb, Rh and Tc were grouped together and the symbol used for this group in present document is, Nm. The highly negative Gibbs energy of formation of UPd_3 compared to all other possible compounds of uranium or palladium meant that all the palladium should be stable as UPd_3 ($T_m \sim 1900$ K). With this assumption, palladium was excluded from further Gibbs energy minimization calculations. In the compound UPd_3 ,

U:Pd is in the ratio of 1:3. The exclusion of palladium as UPd_3 had to be in conjunction with a reduction of corresponding amount of uranium from the total uranium content used for further calculations. Hence, one third of the moles of palladium were subtracted from the total number of moles of uranium used for the SOLGASMIX calculations. Similarly, another noble metal element, ruthenium forms a very stable compound, $CeRu_2$ ($T_m = 1840$ K). The fission yield of cerium is a little more than half that of ruthenium, therefore, by assuming that all the ruthenium is present as $CeRu_2$,

Table 2
The elemental fission yield of the FBTR fuel for given burn-ups [7]

Fission product	Fission yield (moles/t) for given burn-up			
	50 (GWd/t)	100 (GWd/t)	120 (GWd/t)	150 (GWd/t)
Ba	14.5942	29.17414	34.86104	44.05326
Br	0.404954	0.800805	0.946628	1.176663
Ce	29.58392	55.03241	63.17888	77.73323
Cs	46.87533	93.66311	111.038	138.7141
Eu	1.163637	2.277148	2.684177	3.333508
I	4.273562	8.267337	9.742201	12.06232
Kr	3.705877	7.396482	8.77845	10.98616
La	12.70183	25.30641	30.033	37.58012
Mo	41.37423	86.22415	103.2143	129.8606
Nb	1.331528	1.371596	1.270495	1.362167
Nd	28.70782	61.16221	73.9731	94.2323
Pd	29.11654	62.47927	76.07077	97.64481
Pm	3.635291	6.136613	6.693452	7.600284
Pr	10.80019	22.43246	26.78664	33.66763
Rb	3.276878	6.561824	7.797392	9.770638
Rh	13.23444	28.09899	33.4972	41.93449
Ru	45.25557	85.05605	99.23619	122.4089
Se	0.841394	1.680638	1.995235	2.49671
Sm	6.912048	15.14972	18.67126	24.22321
Sr	8.427251	16.01896	18.80136	23.30247
Tb	0.045576	0.089098	0.104909	0.12951
Tc	13.62852	27.0227	31.95212	39.67966
Te	5.362565	10.53742	12.4897	15.60794
Xe	52.61012	105.2795	125.0486	156.6343
Y	4.388084	8.296885	9.732138	12.08909
Zr	35.03565	68.9142	81.59452	102.0288

we could exclude Ru from the further calculations and the cerium content used for the calculations was adjusted accordingly.

Finally the elements used for the present Gibbs energy minimization calculations using SOLGAS-MIX PV were, C, Pu, U, I, Te, Sr, Mo, Cs, Zr, lanthanides (Ln) and noble-metals (Nm). In addition to these elements, a few moles of noble gases were taken for the cover gas to maintain a constant pressure of a unit atmosphere. As discussed above, Ru and Pd were excluded from the SOLGAS-MIX program calculations by assuming them to be stable as CeRu_2 and UPd_3 , respectively. These elements, Ru and Pd, were not included in the group of metals covered by Nm. The existence of barium and strontium monocarbides could not be established, as the thermodynamic or XRD and thermodynamic data of these compounds was not available in the literature, therefore, dicarbides of these elements were assumed to be the only stable carbides.

The FBTR design is such that the fuel surface temperature is ~ 1000 K and centerline temperature is ~ 1500 K. Therefore, the present calculations were

carried out at these temperatures and an intermediate temperature, 1200 K.

3. Results and discussion

By comparing the Gibbs energies of formation of various carbides for one mole of carbon (same carbon activity) at 1500 K, the stability of carbides can be written in the following order, $\text{ZrC} > \text{U}_2(\text{Rh}, \text{Ru})\text{C}_2 > \text{UC} > \text{UMoC}_{1.7} > \text{UMoC}_2 > \text{CeC} > \text{U}_2\text{C}_3 > \text{Ce}_2\text{C}_3 > \text{CeC}_2 > \text{PuC} > \text{Mo}_2\text{C} > \text{Pu}_2\text{C}_3 > \text{SrC}_2$. The Gibbs energy of formation of ZrC is the lowest among the carbides that can be formed in this fuel system but Gibbs energy of formation of ZrI_4 is lower than that of ZrC . Hence, among the zirconium compounds, ZrI_4 is more stable than zirconium carbide. As the fission yield of iodine is less than 15 at.% of that of zirconium, zirconium should form ZrI_4 as well as carbide. But the present calculations showed that all the zirconium got stabilized as ZrC and iodine reacted preferably with another fission product, cesium, to form CsI . This was due to many competing reactions in this multi-component system, where,

SOLGASMIX PV tried to find out the set of products that minimized the total Gibbs energy of the whole system.

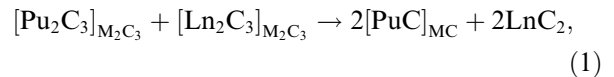
The sesquicarbides of uranium and plutonium and monocarbide of uranium are more stable than the dicarbides of barium and strontium. But barium and strontium dicarbides are more stable than plutonium monocarbide therefore, these alkaline earth elements formed dicarbides. On the other hand tellurides of alkaline-earths are more stable than their carbides. Due to lower fission yield of tellurium, only part of the alkaline-earth elements got converted into tellurides and the rest of the alkaline-earths formed dicarbides. These calculations showed the co-existence of alkaline-earth elements as tellurides and dicarbides. The studies carried out by Peatfield et al. [19] also showed that in U–Sr–C and U–Ba–C systems, U_2C_3 phase can coexist only with SrC_2/BaC_2 and not with Sr/Ba metal. This also indicates that the non-metallic fission products like tellurium and iodine cannot be ignored, as some of the metallic elements make more stable compounds with them compared to carbon. This results in less binding of carbon by the fission products.

In the beginning of these calculations, it was assumed that the noble metals, Ru and Pd were stable as $CeRu_2$ and UPd_3 . These assumptions were supported by various experimental results published in the literature. The results of optical and electron microscopic analysis of $(U_{0.85}Pu_{0.15})C$ fuel irradiated to a burn-up of 4.5 at.% are reported by Bramann et al. [20]. They found that most of the palladium was present in the fuel as intermetallic compounds and ruthenium formed $CeRu_2$. According to the present calculations, the remaining noble metals should be present in the burnt fuel as $UMoC_2$, U_2NmC_2 . Kleykamp [21] and Dienst et al. [22] have also indicated that the noble metal elements (Nm) always coexist as lanthanides-noble metal intermetallic compounds of the type $CeRu_2$ and a dicarbide phase of the type $(U,Pu)_2NmC_2$, regardless of the C/U, at all burn-ups. According to them, with increase in burn-up, the amount of $CeRu_2$ phase increases. Ohmichi et al. [16] and Dienst et al. [22] have also reported the presence of the phases like $(U,Pu)MoC_2$, $(U,Pu)_2RuC_2$ in carbide fuels, based on their studies of simulated fuel with burn-up up to 10 at.% and post-irradiation studies with burn-up up to 7 at.%.

The change in chemical composition of the fuel as a function of burn-up at 1000 K, for starting

C/M = 1.03 are shown in Fig. 1. According to the present calculations, the general trend of change in amounts of different solid phases with burn-up remained similar for different C/M or temperatures. As can be seen from the figure, the amount of M_2C_3 phase increases with burn-up because more and more lanthanides get stabilized as Ln_2C_3 and dissolve in this phase. The increase in various carbon-bonding species with burn-up is accompanied by a decrease in the amount of MC phase.

Lanthanides make stable sesquicarbides and dicarbides. The carbon potential of Pu_2C_3/PuC equilibrium is higher than that of LnC_2/Ln_2C_3 . Assuming that all the compounds are pure solids, one would expect that as long as Pu_2C_3 phase is present in the fuel, all the lanthanides should be present as LnC_2 . In the present system, Pu_2C_3 , Ln_2C_3 and PuC were assumed to be present in solution phases. Though, LnC_2 is also known to dissolve completely in an isomorphous actinide dicarbide phase but the present fuel system did not have a $(U,Pu)C_2$ phase. Therefore, LnC_2 was assumed to be present as a pure compound. The high dilution of Ln_2C_3 in sesquicarbide lattice stabilized this compound compared to LnC_2 , as can be understood from the following relations:



$$\Delta_r G = (2\Delta_f G_{PuC}^0 + 2\Delta_f G_{LnC_2}^0 - \Delta_f G_{Pu_2C_3}^0 - \Delta_f G_{Ln_2C_3}^0) + RT \ln \left(\frac{x_{PuC}^2}{x_{Pu_2C_3} x_{Ln_2C_3}} \right). \quad (2)$$

where, $\Delta_f G_{PuC}^0$, $\Delta_f G_{LnC_2}^0$, $\Delta_f G_{Pu_2C_3}^0$ and $\Delta_f G_{Ln_2C_3}^0$ are the standard Gibbs energies of formation of, PuC , LnC_2 , Pu_2C_3 and Ln_2C_3 , respectively, at temperature T and $\Delta_r G$ is the change in Gibbs energy of the reaction (1). The symbols, x_{PuC} , $x_{Pu_2C_3}$ and $x_{Ln_2C_3}$ are the mole fractions of PuC , Pu_2C_3 and Ln_2C_3 , respectively, in the lattices marked as subscript outside the square brackets given in the reaction Eq. (1). The first part of the Eq. (2), is negative for all the lanthanides. But for most of the lanthanides, a very low value of $x_{Ln_2C_3}$ in the second part of the equation made it positive enough to offset the first part of the Eq. (2). Thus the overall value for $\Delta_r G$ was positive, therefore, favouring the stabilization of Ln_2C_3 instead of LnC_2 . Among the lanthanide carbides, we found that even after stabilization of Ce_2C_3 by dissolution in M_2C_3 phase, some CeC_2 was stable at low temperatures. Therefore, according to the present calculations, at high

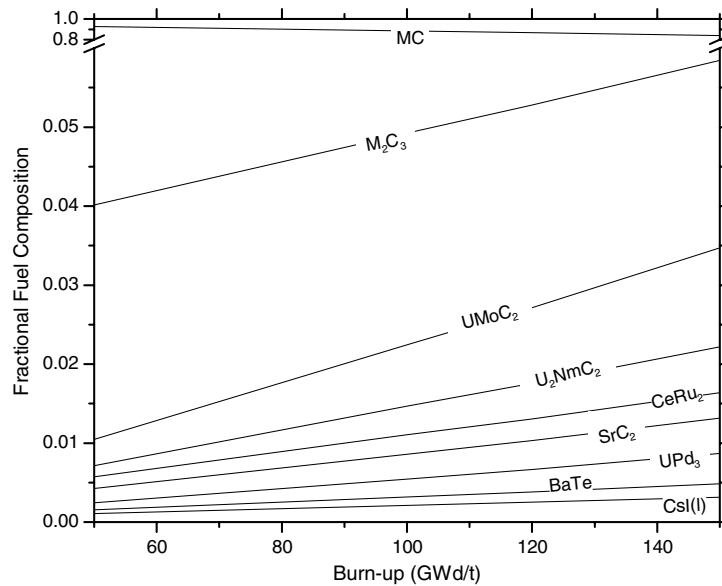


Fig. 1. Change in the fractional amounts of condensed phases with burn-up for the fuel with starting C/M = 1.03 at 1000 K.

burn-up, along with Ce_2C_3 and CeC dissolved in M_2C_3 and MC lattices, some CeC_2 was also formed as a separate phase. However, the presence of CeC_2 did not have much effect on the carbon potential of the system due to buffering effect of Ce_2C_3/CeC dissolved in respective fuel lattices.

Other relevant carbides of lanthanides are their monocarbides. However, only the lanthanides with small atomic radii, e.g., Sc, Y, Sm, Lu, form stable monocarbides or subcarbides. The important fission product lanthanides, in decreasing order of their fission yields are Ce, Nd, La, Pr and Sm. Therefore, most of the lanthanides relevant for the present calculations do not form stable monocarbides, but they get stabilized by dissolution in UC or PuC lattice. The solubility of LnC is very limited in UC and PuC [23]. Even the sesquicarbides of most of these lanthanides show limited solubility in isostructural uranium sesquicarbide. However, most of the relevant Ln_2C_3 dissolve in Pu_2C_3 to form solid-solution over the whole composition range. Haines and Potter [23] and Holleck [2] have presented detailed studies on the phase diagrams of ternary systems, U–Ln–C and Pu–Ln–C. Many researchers [14,23–29] have indicated low solubility of higher carbides of lanthanides in respective uranium carbides but high solubility in respective plutonium carbides. Haines and Potter [23] have given phase diagrams of U–Ln–C and Pu–Ln–C (Ln = La, Ce, Pr, Nd) in the temperature range, 1073–1273 K. Their results

are in good agreement with other reported results [26,27]. According to them, the monocarbides, with more than 6 mol.% lanthanides coexist either with higher carbides and/or lanthanide metals, depending on the C/M of the system. It was observed that in high burn-up, irradiated and simulated carbide fuels, the solubility of lanthanides in carbide fuel is much lower than the sum total of solubilities of the individual lanthanide carbide [29–31]. As the sesquicarbide phase of the plutonium rich carbide fuel of FBTR is almost Pu_2C_3 , all the Ln_2C_3 was assumed to be dissolved in M_2C_3 phase. The calculations were carried out with an assumption of ideal solution of Ln_2C_3 in M_2C_3 matrix. However, the same was not valid for the solution of lanthanide monocarbides in MC matrix as LnC shows limited solubility in MC matrix. Initially the calculations were carried out by making a simple assumption of ideal solution for both (U,Pu,Ln,Zr)C and (U,Pu,Ln) $_2C_3$. But the calculated carbon activity of the fuel increased with increase in burn-up. This was in contradiction to the observation made on burnt carbide fuel. Therefore, the calculations were repeated with the assumption of non-ideal solution behaviour for (U,Pu,Ln,Zr)C. Using 6 mol.% solubility limit of LnC in (U,Pu)C and with the assumption of Raoultian behaviour for the solvent, i.e., (U,Pu,Zr)C and applying Henry's law on the solute, i.e., LnC, an activity coefficient of 24.5 was calculated for LnC in (U,Pu,Ln,Zr)C solution.

The calculations were repeated using this value for non-ideal solution behaviour of monocarbide solution phase but ideal solution behaviour for sesquicarbide solution phase. The carbon activity of the fuel, calculated using these assumptions, decreases with burn-up. The amount of M_2C_3 phase increases and amount of MC phase decreases with burn-up, the carbon activity of the fuel decreases with burn-up. The compositions and not the amounts of these phases determine the carbon activity of the fuel. In Fig. 2, the calculated fractional compositions of MC and M_2C_3 solution phases are shown as a function of burn-up. As can be seen from this figure, the fraction of Ln_2C_3 dissolved in M_2C_3 phase increases sharply with burn-up, whereas, amount of Pu_2C_3 decreases. The fraction of U_2C_3 in M_2C_3 phase is negligible, therefore, it is not seen in the figure.

In Fig. 3, the carbon activity of the fuel calculated for different starting C/M values are compared at different temperatures. The carbon activity calculated for the fuel with starting C/M = 1.03 and assuming ideal solution behaviour for MC and M_2C_3 phases is also given in the figure. The carbon activity of the fuel was calculated from the equilibrium fractions of plutonium in MC and M_2C_3 matrices using the following relation:

$$a_C = \frac{x_{Pu_2C_3}}{x_{PuC}^2} \times \exp \left[\frac{\Delta G_{Pu_2C_3}^0 - 2\Delta G_{PuC}^0}{RT} \right], \quad (3)$$

where, $x_{Pu_2C_3}$ is the mole fraction of Pu_2C_3 in M_2C_3 matrix and x_{PuC} is the mole fraction of PuC in MC matrix. In case of plutonium rich carbide fuel, limited solubility of lanthanides in plutonium-rich monocarbide phase results in decrease in carbon potential of the fuel with burn-up. The carbon potential of $(U_{0.3}Pu_{0.7})C_{1+x}$ with 3 mol% M_2C_3 at 1000 K, before burn-up was calculated to be -45.95 kJ/mol. After 100 GWd/t burn-up, the carbon potential of the fuel decreased to, -46.6 kJ/mol. As can be seen from Fig. 3, the effect of burn-up on the carbon potential of the fuel is more pronounced at high temperatures. With increase in burn-up, the difference in carbon activity of the center and the surface decreases, which should result in reduced mass transfer of carbon from the center to the surface. Therefore, most of the clad carburization should take place in the beginning of the burn-up and should decrease with increase in burn-up. The effect of temperature on the carbon activity is more prominent than the effect of C/M.

In the absence of any other data, the estimated Gibbs energy of formation equation for CeC, given by Besmann and Lindemer [32], was used for all the lanthanide carbides. In the present calculations, the Gibbs energies of formation of Ce_2C_3 and CeC were used for all the lanthanide carbides. However, the actual difference in the values of other lanthanide carbides will impact the distribution of lanthanides

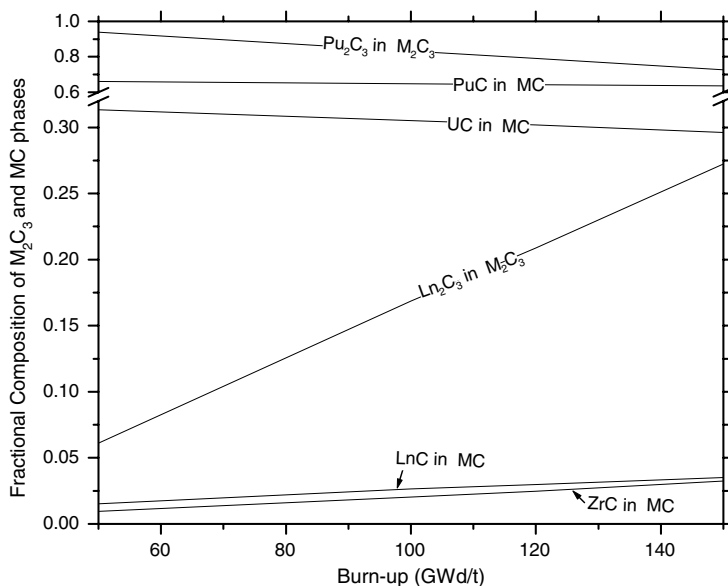


Fig. 2. Change in the fractional compositions of MC and M_2C_3 solution phases of $(U_{0.3}Pu_{0.7})MC_{1.03}$ starting fuel with burn-up, at 1000 K.

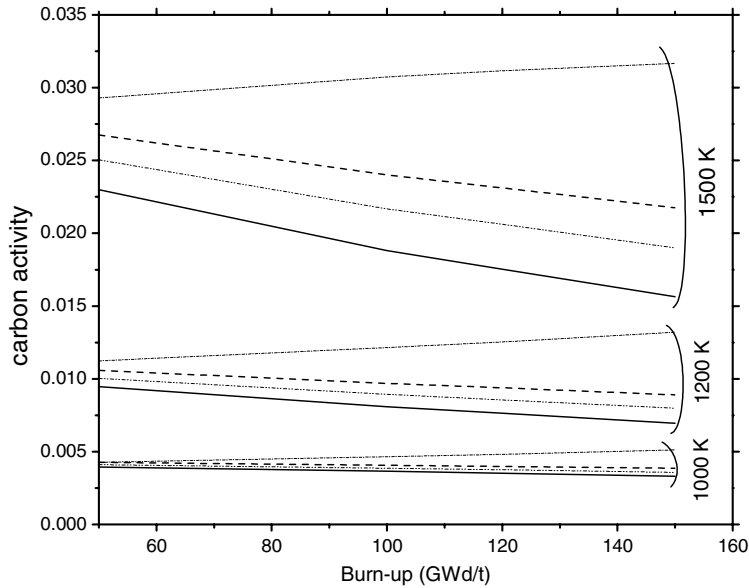


Fig. 3. Effect of burn up on the carbon activity of the fuel at different temperatures and starting C/M values. (— $MC_{1.03}$, ---- $MC_{1.045}$, $MC_{1.06}$ for non-ideal MC-solution and — $MC_{1.03}$ for ideal MC-solution)

in the two matrices, thus affecting the carbon activity of the fuel. It was observed that with the exception of lanthanide carbides, the differences between the Gibbs energies of formation of the compounds are large enough to accommodate the discrepancies in their values without affecting the results of the present calculations.

In the present calculations, the presence of oxygen and nitrogen impurities in the fuel was ignored. However, the starting FBTR fuel contained ~5000–6000 ppm oxygen and ~1000 ppm nitrogen. The presence of these impurities increases the carbon potential of the fuel [4]. According to a computer program described elsewhere [4], for the ($U_{0.3}$ - $Pu_{0.7}$)CNO fuel, containing 1000 ppm nitrogen and 5700 ppm oxygen and 3 mol.% M_2C_3 , the carbon potential of the starting fuel is -43.3 kJ/mol at 1000 K. According to the present calculations, the carbon activity of this fuel after a burn-up of 100 GWd/t should be -44.5 kJ/mol. Whereas, the carbon activity calculated for the fuel with the same sesquicarbide content but without oxygen and nitrogen impurities was, -46.6 kJ/mol, at the same temperature and burn-up. This increase in the carbon activity of the fuel in the presence of oxygen and nitrogen is due to formation of Ln_2O_3 compounds. The sesqui-oxides of lanthanides are more stable than the oxides of uranium or plutonium. In fact both lanthanides and alkaline earths act as oxygen

getters in the carbide fuels. Thus with increase in burn-up the oxygen dissolved in MC phase reduces [33]. Post irradiation examinations of carbide fuel reported in literature have also confirmed the presence of oxides of lanthanides and alkaline earths [18,34,35]. As discussed earlier, formation of the stable sesquicarbide of lanthanides decreases the carbon potential of the carbide fuel with burn-up, but oxygen in the fuel binds some of the lanthanides thus diluting this effect on carbon potential.

The change in plutonium chemical potential with burn-up, shown in Fig. 4, was calculated using the following relation:

$$RT \ln p_{Pu} = (3\Delta G_{PuC}^0 - \Delta G_{Pu_2C_3}^0) + RT \ln \left[\frac{x_{PuC}^3}{x_{Pu_2C_3}} \right], \quad (4)$$

where, x_{PuC} and $x_{Pu_2C_3}$ are the mole fractions of PuC and Pu_2C_3 in the MC and M_2C_3 matrices, respectively. As expected the chemical potential of plutonium increased with increase in burn-up for the assumption of non-ideal behaviour of LnC in MC. The calculations carried out with the assumption of ideal solution behaviour of LnC in MC showed decrease in the plutonium chemical potential with increase in burn-up. The value of chemical potential, even at 150 GWd/t, is so low that it cannot have any detrimental effect on the clad.

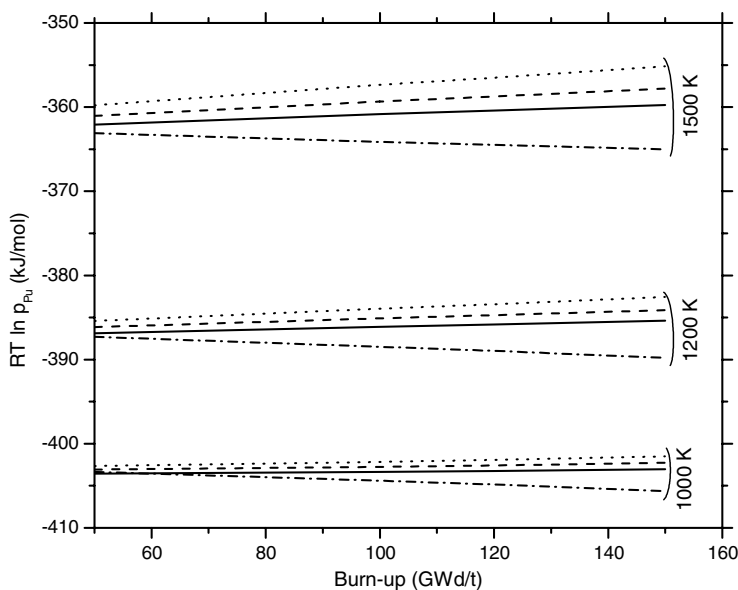


Fig. 4. The effect of burn-up, temperature and starting C/M on plutonium chemical potential. (----MC_{1.03},MC_{1.04}, - - -MC_{1.06} for non-ideal MC-solution and ———MC_{1.03} for ideal MC-solution.)

4. Conclusion

The present calculations did not indicate the formation of (U, Pu) metallic phase even at burn-ups as high as 150 GWd/t. According to the present calculations, cesium and tellurium partial pressures were high compared to other species and their partial pressures increased with burn-up. Therefore, they can affect the fuel-clad compatibility. In most of the fast breeder reactors, containing oxide fuel, the cesium attack on stainless-steel cladding is one of the most detrimental factors due to formation of the stable cesium–chromium oxides [36]. Whereas, the absence of any stable cesium–chromium carbide in carbide fuels prevents corrosive affect of cesium on the cladding material. Tellurium attack on cladding is also greatly reduced in carbide fuels, as tellurium is bound by the cesium or alkaline earth metals. Free iodine is considered to be the main fission product that reacts with the cladding of carbide fuels [36]. The present calculations showed that most of the iodine available in the irradiated fuel should be present as cesium compounds, Cs₂I₂ and CsI. Due to the formation of these compounds, the corrosive effects of iodine will reduce drastically because gaseous cesium iodide molecules are very stable thermodynamically. However, Cubicciotti and Davies [37] have postulated that in the γ -radiation field of the reactor, cesium iodide molecules dissociate followed by ionization. Konashi

et al. [38] have calculated an increase in iodine pressure by a factor of $\sim 10^7$ in presence of radiation field of a fast breeder reactor, compared to no radiation field. Gotzmann and Hofmann [36] carried out some compatibility experiments of steel with simulated hyper-stoichiometric uranium carbide fuel with fission products, Cs, Te, I, Se, corresponding to a burn-up of 10 at.%. They observed that microhardness of the cladding material was increased when it was kept in contact with virgin UC_{1+x} fuel. Whereas, in the presence of Cs, Te, I and Se, carburization of the cladding was reduced, therefore, the microhardness of the cladding remained unchanged. This shows that most of the carburization of the clad takes place in the beginning of the fuel irradiation. This observation is in complete agreement with the present results. Based on the present calculations we can conclude that in case of mixed carbide fuels, iodine is the main fission product that can cause some problem but the important limiting factor in the fuel performance will be the mechanical interaction of the fuel with the clad due to swelling of the fuel [22].

References

- [1] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.
- [2] H. Holleck Thermodynamics of Nuclear Materials 1974, Vol. II, IAEA, Vienna, 1975, p. 213.
- [3] E. Smailos, GfK Rep. KFK 1953 and EUR FNR-1179, 1974.

- [4] Renu agarwal, V. Venugopal, D.D. Sood, 'Thermodynamic analysis of U–Pu–C–N–O system', BARC/1992/E/002, 1992.
- [5] P.E. Potter, K.E. Spear, *Thermodynamics of Nuclear Materials*, Vol. 2, 1979, IAEA-SM-236/40, IAEA, Vienna, 1980, p. 195.
- [6] T.M. Besmann, SOLASMIX-PV, A computer program to calculate equilibrium relationships in complex chemical systems, ORNL/TM-5775, Oak Ridge National Laboratory, Oak Ridge, TN, April, 1977.
- [7] G. Pandikumar, Reactor Physics Division, IGCAR, India (Private Communication).
- [8] M.J. Bell, ORIGEN-2 Code, Oak Ridge National Laboratories, Report ORNL-TM4397, 1973.
- [9] Imoto, *J. Nucl. Mater.* 140 (1986) 19.
- [10] Y. Arai, T. Iwai, T. Ohmichi, *J. Nucl. Mater.* 151 (1987) 63.
- [11] Hj. Matzke, *Sc. Advanced LMFBR Fuels*, North Holland Physics Publishing, 1986.
- [12] M. Coquerelle, Proceedings of Technical Committee meeting, October 1997, IAEA-TECDOC-970, p. 93.
- [13] T. Iwai, Y. Arai, K. Nakajima, Y. Kimura, T. Sukegawa, Y. Suzuki, Japan Atomic Energy Research Institute, Tokyo, Japan, JEARI-Research-96-065, December 1996, 53 p.
- [14] Y. Suzuki, A. Maeda, T. Awai, H. Kanazawa, H. Mimura, Y. Arai, Japan Atomic Energy Research Institute, Tokyo, Japan, JEARI-M-91-192, November 1991, 30 p.
- [15] U. Benedict, in: Proceedings of the International Symposium on 'Thermodynamics of Nuclear Materials', Juelich, Germany, F.R. 29 January–2 Feb, 1979, Vienna, IAEA, 1980, vol. 1, 5860., p. 453.
- [16] T. Ohmichi, Y. Suzuki, A. Maeda, K. Shiozawa, M. Handa, Japan Atomic Energy Research Institute, Tokyo, Japan, JEARI-M-84-161, September 1984, 35 p.
- [17] Y. Suzuki, Y. Arai, T. Iwai, K. Nakajima, International conference on 'Future nuclear systems, Challenge towards second nuclear era with advanced fuel cycles', Yokohama, Japan, 1997, vol. 1588, p. 522.
- [18] H. Kleykamp, 'Advanced LMFBR Fuels', eds. J.J. Leary and H. Kittle, US Report ERDA-4455, 1977, p. 166.
- [19] M. Peatfield, N.H. Brett, P.E. Potter, *J. Nucl. Mater.* 89 (1) (1980) 35.
- [20] J.I. Bramann, R.M. Sharoe, R. Dixson, *J. Nucl. Mater.* 38 (1971) 226.
- [21] H. Kleykamp, *J. Nucl. Mater.* 47 (1973) 271.
- [22] W. Dienst, H. Kleykamp, G. Muhling, H. Reiser, H. Steiner, F. thusmmler, H. Wedemeyer, P. Weimar, in: Proc.: Nuclear Power and its Fuel Cycle, Vol. 3, IAEA, Vienna, 1977, IAEA-CN-36/108, 493.
- [23] H.R. Haines and P.E. Potter, *Thermodynamics of Nuclear Materials*, Vol II. in: Proceedings of a symposium, Vienna, 21–25 October 1974, IAEA, Vienna, 1975, p. 145.
- [24] P. Stecher, A. Neckel, F. Benesovsky, H. Nowotny, *Planseeber, Pulvermet* 12 (1964) 181.
- [25] H. Holleck and W. Wagner, KFK 643 (1967), *Thermodynamics of Nuclear Materials*, in: Proc. Symposy. (Vienna, 1967) p. 667.
- [26] N. Lorenzelli, J.P. Marcon, *J. Less Common Met.* 26 (1972) 71.
- [27] N. Lorenzelli, CEA Report R-4465, 1973.
- [28] H. Holleck, H. Kleykamp, *J. Nucl. Mater.* 32 (1969) 1.
- [29] E. Smailos, KFK-1953 (1974).
- [30] U. Benedict, EUR 5766e (1977).
- [31] U. Bendict, G. Giacchetti, Hj. Matzke, K. Richter, C. Sari, H.E. Schmidt, *Nucl. Technol.* 35 (1977) 154.
- [32] T.M. Besmann, T.B. Lindemer, *Nucl. Technol.* 40 (1978) 297.
- [33] H. Kleykamp, *J. Nucl. Mater.* 300 (2002) 273.
- [34] G. Giacchetti, C. Sari, C.T. walker, TU Progress Report TUSR 18 (1974).
- [35] F.T. Ewart, B.M. Sharpe, R.G. Taylor, UK Report AERE-R 7962 (1975).
- [36] O. Gotzmann, P. Hofmann, in: Proc. IAEA Symp. On Fuel and Fuel Elements for fast Reactors, Brussels, July 2–6, 1973, Vol. 1 (1974) 233.
- [37] D. Cubicciotti, J.H. Davies, *Nucl. Sci. Eng.* 60 (1974) 314.
- [38] K. Konashi, T. Yato, H. Kaneko, *J. Nucl. Mater.* 114 (1983) 86.
- [39] M.S. Chandrasekhariah, *J. Nucl. Mater.* 130 (1985) 366.
- [40] E.K. Storms, R.J. Ackermann and M.H. Rand, IAEA Panel on the Thermodynamics Properties of the U–C, Pu–C and (U,Pu)C- Systems, Grenoble (1974).
- [41] P.E. Potter, *J. Nucl. Mater.* 42 (1972) 1.
- [42] H. Holleck, H. Kleykamp, *J. Nucl. Mater.* 45 (1972/73) 47.
- [43] J.W. Harrison, L.M. Davies, *J. Nucl. Mater.* 27 (1968) 239.
- [44] D.C. Fee and C.E. Johnson, US Report ANL-AFP-10 (1975).
- [45] R.H. Flowers, E.C. Rauh, *J. Inorg. Nucl. Chem.* 28 (1966) 1355.
- [46] O. Kubaschewski, C.B. Alcock, *Metallurgical Thermochemistry*, 5th ed., Pergamon, New York, 1979.
- [47] D.R. Stull and H. Prophet, Project Directors, JANAF Thermodynamical Table, 2nd ed., NSRDS-NBS37 (National Bureau of Standards, 1971).
- [48] M.G. Adamson, E.A. Aitken, T.B. Lindemer, *J. Nucl. Mater.* 130 (1985) 375.
- [49] T.B. Lindemer, T.M. Besmann, C.E. Johnson, *J. Nucl. Mater.* 100 (1981) 178.
- [50] C.E. Holley Jr., M.H. Rand, E.K. Storms, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 6, in: F.L. Oetting (Ed.), *The Actinide Carbides*, IAEA, Vienna, 1984.
- [51] P. Hofmann, J. Spino, *J. Nucl. Mater.* 127 (1985) 205.
- [52] D.R. Stull and G.C. Sinke, *Thermodynamic Properties of the Elements*, Adv. in Chem, 1956.