ELSEVIER Journal of Nuclear Materials 270 (1999) 301–308

journal of nuclear materials

Calculation of thermodynamic parameters of U–Pu–N system with carbon and oxygen impurities

R. Agarwal, V. Venugopal *, D.D. Sood

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

Received 17 August 1998; accepted 8 December 1998

Abstract

Mixed nitride fuels are being considered for advanced FBR, but very little is known about the thermodynamic properties of these fuels. For an overall composition of the nitride fuel with small amounts of oxygen and carbon impurities, thermodynamic properties, e.g. carbon activity and partial pressures of nitrogen, carbon-monoxide, plutonium and uranium, were calculated in present work. These calculations were based on standard Gibbs free energies of the binary compounds, present in this multi-component system (U,Pu)–C–N–O. For an over all composition of the fuel, stable phase-field was determined by minimization of the Gibbs free energy of the system. The fabrication experiences of various workers, reported in literature, have shown that depending on the impurity content, nitride fuel can exist in two phase fields, mono-nitride phase in equilibrium with sesquinitride phase or mono-nitride phase in equilibrium with dioxide phase. Therefore, in present calculations special attention was given to the thermodynamic behavior of these two phase-fields. A comparison of calculated thermodynamic properties indicated that nitride fuel with dioxide as second phase will be superior to the one with sesquinitride. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Mixed uranium–plutonium nitride fuels are being considered for advanced fast breeder reactors due to their high breeding ratio and good thermal conductivity [1–4]. However, limited thermodynamic data of this fuel is available in literature. Therefore, present calculations were carried out to find out important thermodynamic properties of the mixed nitride in the composition range of relevance to the nuclear fuel. Phase diagram calculations of this fuel are reported previously by Sood et al. [5]. The thermodynamic properties calculated and discussed in present work are: carbon activity and partial pressures of nitrogen, carbon-monoxide, plutonium and uranium.

2. Calculations

The method of calculation is discussed in details in a previous publication by Sood et al. [5]. For the sake of clarity a short description will be presented here. These calculations were focused near the mononitride composition range of the system (U,Pu)–C–N–O with limited carbon and oxygen impurity ($O + C \leqslant 5000$ wt ppm). As a first step, various relevant phase fields of U–Pu–C–N–O system were defined. These phase fields were: (U,Pu)CNO + C; (U,Pu)CNO + (U,Pu); (U,Pu)CNO + $(U,Pu)O_2$; (U,Pu)CNO + $UN_{1.5}$; and (U,Pu)CNO + $UN_{1.5}$ + C. In all these phase fields multi-component mononitride phase (U,Pu)CNO was in equilibrium with a small amount of a second phase. The composition of the total fuel was presented as $(U_{(1-p)}Pu_p)N_n(C_c,O_\phi)$. The mononitride phase (U,Pu)CNO can be expressed in full as $(U_{(1-x)}Pu_x)N_zO_yC_{(1-y-z)}$. A typical phase diagram of (U,Pu)–C–N is given in Fig. 1.

As discussed by Sood et al. [5], these calculations were based on standard molar Gibbs energies of

---

* Corresponding author. Fax: +91-22 556 0750.

PII: S0022-3115(99)00012-4

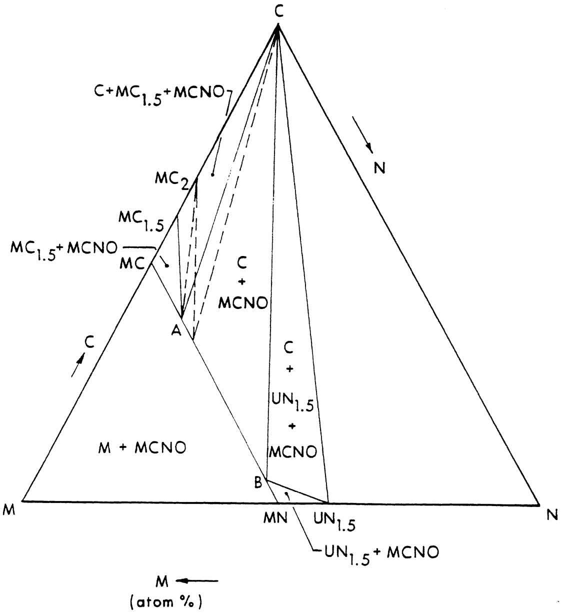

Fig. 1. Schematic phase diagram of the M–C–N system containing oxygen impurity, where, M represents (U,Pu) [5,20].

formation of the binary compounds, given in Table 1. Following assumptions were made during these calculations: (1) solid solutions behave ideally [6–8]; (2) binary components of one phase do not dissolve in another equilibrium phase [9,10]; (3) all the binary compounds, UN, UC, UO, UO_2, $UN_{1.5}$, PuN, PuC, PuO, PuO_2, have been assumed to be stoichiometric [7,11]; (4) $UN_{1.5}$ is the only stable sesquinitride compound [12,13]; (5) the system does not have any ternary compounds.

For a given total composition of the fuel, distribution of various binary compounds in a phase field was calculated using mass balance equations and chemical equilibria. Then the total Gibbs energy of the phase field was calculated using the standard molar Gibbs energies of formation of binary compounds. The calculated Gibbs energies of all the above mentioned relevant phase fields were compared. The phase field with minimum Gibbs energy was considered to be the stable phase field. Thermodynamic parameters of the stable phase field were calculated. A FORTRAN program was written to carry out these calculation.

Table 1
The Gibbs free energies of formation of the binary compounds used for the calculations as a function of temperature $4\Delta G_f^0 = A + BT + CT\ln(T)$ (J mol^{-1})

Compound	A	B	C	Ref.
PuN	−302 825	97.28	0.0	[20]
UN	−297 357	86.19	0.0	[20]
PuC	−57 990	−0.75	0.0	[7]
UC	−110 085	1.17	0.0	[21]
UO	−505 758	94.18	0.0	[7]
PuO	−557 250	92.34	0.0	[7]
$UN_{1.5}$	−367 326	133.05	0.0	[20]
PuO_2	−1 060 560	219.58	−14.43	[22]
UO_2	−1 082 225	170.92	0.0	[22]
(Pu)	331 498	−91.71	0.0	[23]
(U)	488 273	−110.88	0.0	[23]
(CO)	−111 713	−87.70	0.0	[24]

For each relevant phase field a set of equilibrium equations were written to calculate various thermodynamic parameters. A typical example of nitrogen pressure calculation for different phase fields is presented here.

For the phase fields (U,Pu)CNO + $UN_{1.5}$ and (U,Pu)CNO + $UN_{1.5}$ + C the chemical equilibrium used was

$$4UN_{1.5} = 4[[UN]_{PuN}]_{UCO} + (N_2), \tag{1}$$

$$p_{N_2} = \frac{\exp((4\Delta G_f^0(UN_{1.5}) - 4\Delta G_f^0(UN))/RT)}{x_{UN}^4}, \tag{2}$$

where, x_{UN} is the mole fraction of UN present in mononitride phase, $(U_{(1-x)}Pu_x)N_zO_yC_{(1-y-z)}$ and $\Delta G_f^0(UN_{1.5})$ and $\Delta G_f^0(UN)$ are Gibbs free energies of formation of the compounds $UN_{1.5}$ and UN, respectively. The square brackets in $[[UN]_{PuN}]_{UCO}$ represent solid solution of UN in PuN, and the mixed mononitride is in solution with monocarbides and monoxides.

Similarly for the phase field (U,Pu)CNO + C, following equilibrium was used:

$$2[[UN]_{PuN}]_{UCO} + 2C = 2[[UC]_{PuC}]_{UNO} + (N_2), \tag{3}$$

$$p_{N_2} = \frac{\exp((2\Delta G_f^0(UN) - 2\Delta G_f^0(UC))/RT)}{x_{UC}^2/x_{UN}^2}, \tag{4}$$

where x_{UN} and x_{UC} are the mole fractions of UN and UC in mononitride solid solution.

For the phase field (U,Pu)CNO + $(U,Pu)O_2$:

$$2[[UN]_{PuN}]_{UCO} + 2[UO_2]_{PuO_2} = 4[[UO]_{PuO}]_{UCN} + (N_2), \tag{5}$$

$$p_{N_2} = \frac{\exp((2\Delta G_f^0(UN) + 2\Delta G_f^0(UO_2)) - 4\Delta G_f^0(UO))/RT)}{x_{UO}^4/x_{UO_2}^2 x_{UN}^2}, \tag{6}$$

where, x_{UN} and x_{UO} are mole fractions of UN and UO in mononitride solid solution and x_{UO_2} is mole fraction of UO_2 in $(U,Pu)O_2$ solid solution.

For the phase field (U,Pu)CNO+(U,Pu):

$$2[[UN]_{PuN}]_{UCO} = 2[U]_{Pu} + (N_2), \tag{7}$$

$$p_{N_2} = \frac{\exp(2\Delta G_f^0(\mathrm{UN})/RT)}{x_U^2/x_{UN}^2}, \tag{8}$$

where, x_U is mole fraction of uranium in metal phase and x_{UN} of UN in mononitride solid solution.

Similar equilibrium equations were used for the calculation of carbon activity and partial pressures of carbon-monoxide, uranium and plutonium, over the relevant phase fields.

3. Results and discussion

3.1. Nitrogen partial pressures

The calculated nitrogen pressure of nitride fuel consisting of (U,Pu)O_2 and (U,Pu)CNO phases is lower than that of $UN_{1.5}$ and (U,Pu)CNO for an equivalent percent of the second phase. The effect of composition and temperature on the thermodynamic properties of the fuel in phase field (U,Pu)O_2 + (U,Pu)CNO and $UN_{1.5}$ + (U,Pu)CNO are given in Tables 2 and 3 respectively. In (U,Pu)O_2 + (U,Pu)CNO phase field, nitrogen pressures are very low even at temperatures much above the fuel surface temperature (1200 K) as shown in Table 2. Experimentally it has been observed that nitride fuel in the phase field (U,Pu)O_2 + (U,Pu)CNO does not react with cladding material even at high temperatures [14]. These calculations show that partial pressure of nitrogen is influenced more by the change in the carbon impurity of the fuel than of nitrogen or oxygen. For the $UN_{1.5}$ + (U,Pu)CNO phase field the pressure of nitrogen which is controlled by $UN_{1.5}$ phase does not change much with change in non-metal content. In (U,Pu)O_2 + (U,Pu)CNO and $UN_{1.5}$ + (U,Pu)CNO phase fields, partial pressure of nitrogen increases with increase in temperature.

3.2. Carbon activity and carbon-monoxide partial pressure of the fuel

The carbon activity of the fuel with (U,Pu)O_2 and (U,Pu)CNO phases is lower than that of the fuel with $UN_{1.5}$ and (U,Pu)CNO phases for the same mole percent of the second phase as shown in Tables 2 and 3. In (U,Pu)O_2 + (U,Pu)CNO phase field, the carbon activity is quite low at and below 1200 K, therefore, carburization of the clad by direct chemical interaction is not expected. This is in agreement with the experimental observation of Bauer [14]. These calculations also indicate that carbon activity and partial pressure of carbon-monoxide are influenced more by the change in carbon

Table 2
The effect of composition and temperature variation on the thermodynamic parameters of the fuel in phase field (U,Pu)CNO + (U,Pu)O_2 (where the numbers in brackets $(-x) = 10^{-x}$ and $x_{(U,Pu)O_2}$ is mole-fraction of (U,Pu)O_2 phase in the fuel)

Pu/(U + Pu)	N/(U + Pu)	[O] wt ppm	[C] wt ppm	$x_{(U,Pu)O_2}$	P_{pu} (kPa)	P_U (kPa)	P_{CO} (kPa)	P_{N_2} (kPa)	a_C
1000 K									
0.2	0.96	3000	100	0.009	9.8(−14)	1.6(−20)	6.5(−18)	8.7(−17)	5.4(−7)
					2.1(−13) [a]	3.4(−20) [a]	1.9(−18) [a]	1.8(−17) [a]	2.4(−7) [a]
0.8	0.96	3000	100	0.009	9.1(−14)	7.8(−22)	1.3(−16)	2.1(−15)	1.0(−5)
					3.5(−08) [a]	2.9(−16) [a]	5.8(−25) [a]	1.4(−27) [a]	2.9(−11) [a]
0.2	0.97	3000	100	0.019	8.7(−15)	1.3(−21)	2.6(−16)	1.2(−14)	6.4(−6)
					1.9(−14) [a]	2.9(−21) [a]	8.1(−17) [a]	2.6(−15) [a]	3.0(−6) [a]
0.2	0.96	3000	600	0.020	6.7(−15)	1.0(−21)	2.3(−15)	2.1(−14)	5.1(−5)
					1.4(−14) [a]	2.1(−21) [a]	7.5(−16) [a]	4.7(−15) [a]	2.4(−5) [a]
0.2	0.96	3500	100	0.017	5.1(−14)	8.3(−21)	1.7(−17)	3.1(−16)	1.0(−6)
					1.1(−13) [a]	1.8(−20) [a]	5.4(−18) [a]	6.8(−17) [a]	4.8(−7) [a]
2000 K									
0.2	0.96	3000	100	0.009	3.1(−3)	4.6(−6)	5.2(−7)	1.1(−4)	7.7(−6)
					4.6(−3) [a]	6.6(−6) [a]	3.0(−7) [a]	5.5(−5) [a]	5.3(−6) [a]
0.8	0.96	3000	100	0.009	3.5(−3)	2.7(−7)	5.6(−6)	2.0(−3)	8.4(−5)
					2.1 [a]	1.6(−4) [a]	3.7(−10) [a]	5.5(−9) [a]	1.4(−7) [a]
0.2	0.97	3000	100	0.019	2.8(−4)	3.9(−7)	2.0(−5)	1.6(−2)	9.0(−5)
					4.1(−4) [a]	5.7(−7) [a]	1.2(−5) [a]	7.6(−3) [a]	6.3(−5) [a]
0.2	0.96	3000	600	0.020	2.1(−4)	2.9(−7)	1.8(−4)	2.6(−2)	7.1(−4)
					3.1(−4) [a]	4.2(−7) [a]	1.1(−4) [a]	5.0(−2) [a]	1.3(−4) [a]
0.2	0.96	3500	100	0.017	1.7(−3)	2.4(−6)	1.4(−6)	4.1(−4)	1.5(−5)
					2.4(−3) [a]	3.4(−6) [a]	8.1(−7) [a]	2.0(−4) [a]	1.0(−5) [a]

[a] calculations with interaction parameter.

Table 3
The variation of thermodynamic parameters of (U,Pu)CNO + $UN_{1.5}$ fuel with change in temperature and composition (where numbers in brackets $(-x) = 10^{-x}$) and $x_{(U,Pu)N_{1.5}}$ is fraction of $(U,Pu)N_{1.5}$ phase in the fuel)

Pu/(U + Pu)	N/(U + Pu)	[O] wt ppm	[C] wt ppm	$x_{(U,Pu)N_{1.5}}$	P_{pu} (kPa)	P_U (kPa)	P_{CO} (kPa)	P_{N_2} (kPa)	a_C
$T = 1000$ K									
0.2	0.998	500	50	0.014	5.6(−20)	7.5(−27)	3.3(−6)	3.7(−4)	0.568
					5.6(−20) [a]	7.5(−27) [a]	5.2(−6) [a]	3.7(−4) [a]	0.568 [a]
0.2	0.995	500	50	0.008	5.6(−20)	7.5(−27)	3.3(−6)	3.7(−4)	0.56
					5.8(−20) [b]	7.8(−27) [b]	8.5(−9) [b]	3.5(−4) [b]	0.54 [b]
0.2	0.995	550	50	0.009	5.5(−20)	7.5(−27)	3.6(−6)	3.7(−4)	0.56
					5.6(−20) [a]	7.5(−27) [a]	5.7(−6) [a]	3.7(−4) [a]	0.56 [a]
0.2	0.998	500	10	0.012	5.6(−20)	7.5(−27)	6.7(−7)	3.7(−4)	0.113
					5.6(−20) [a]	7.5(−27) [a]	1.0(−6) [a]	3.7(−4) [a]	0.113 [a]
$T = 1200$ K									
0.2	0.998	500	50	0.014	9.2(−16)	2.5(−21)	5.5(−4)	0.152	0.266
					9.2(−16) [a]	2.6(−21) [a]	7.8(−4) [a]	0.152 [a]	0.266 [a]
0.2	0.995	500	50	0.007	9.2(−16)	2.6(−21)	5.3(−4)	0.152	0.263
					9.2(−16) [a]	2.6(−21) [a]	9.2(−4) [a]	0.152 [a]	0.263 [a]
0.2	0.995	550	50	0.009	9.2(−16)	2.6(−21)	6.0(−4)	0.152	0.26
					9.2(−16) [a]	2.6(−21) [a]	8.6(−4) [a]	0.152 [a]	0.26 [a]
0.2	0.998	500	10	0.012	9.2(−16)	2.6(−21)	1.1(−4)	0.152	5.3(−2)
					9.2(−16) [a]	2.4(−21) [a]	1.5(−4) [a]	0.152 [a]	5.3(−2) [a]
$T = 1400$ K									
0.2	0.998	500	50	0.013	9.6(−13)	2.3(−17)	2.0(−2)	10.91	0.15
					9.6(−13) [a]	2.3(−17) [a]	2.8(−2) [a]	10.91 [a]	0.15 [a]

[a] calculations with the interaction parameters.

[b] calculation with the interaction parameters, the stable phase field is $(U,Pu)O_2$+(U,Pu)CNO.

impurity content of the fuel than that of nitrogen or oxygen. The increase in temperature increases carbon-monoxide pressures and carbon activity in $(U,Pu)O_2$ + (U,Pu)CNO, whereas in $UN_{1.5}$ + (U,Pu)CNO phase field the calculated carbon activity decrease with the increase in temperature.

3.3. Plutonium and uranium partial pressures

The $(U,Pu)O_2$ phase in equilibrium with (U,Pu)CNO is highly plutonium rich and plutonium partial pressure over the fuel is controlled by oxides of plutonium according to the following equilibrium:

$$2[[\mathrm{PuO}]_{\mathrm{UO}}]_{\mathrm{PuCN}} = [\mathrm{PuO_2}]_{\mathrm{UO_2}} + (\mathrm{Pu}).$$

Hence oxygen impurity of the nitride fuel will affect plutonium partial pressure. An increase in temperature results in increased plutonium partial pressures over $(U,Pu)O_2$ + (U,Pu)CNO and $UN_{1.5}$ + (U,Pu)CNO phase fields.

Calculations indicate lower uranium partial pressure than plutonium partial pressure over the nitride fuel which is in agreement with the experimental results by Suzuki et al. [15]. Therefore, preferential plutonium transfer by diffusion may take place under temperature gradient [16]. A comparison of data in Tables 2 and 3 shows that uranium and plutonium partial pressures are higher over $(U,Pu)O_2$ +(U,Pu)CNO phase field than $UN_{1.5}$ + (U,Pu)CNO phase field. But even for $(U,Pu)O_2$ + (U,Pu)CNO phase field the partial pressures of uranium or plutonium are less than 10^{-3} kPa at temperatures up to 2000 K. This rules out any significant redistribution of the metal by vapour phase at temperatures lower than 2000 K. But at higher temperatures there can be considerable redistribution of the actinides in the $(U,Pu)O_2$ + (U,Pu)CNO phase field as experimentally observed by Richter and Sari [17].

3.4. Effect of interaction parameters on thermodynamic properties of the fuel

As discussed in Section 2, these calculations are based on ideal solution behavior. However, the computer program written for present calculations can also use interaction parameters of the compounds, if available, to consider non-ideal solution behavior of the system. Potter and Spear [7] have suggested an interaction parameter ($\chi_{\mathrm{PuN-PuO}}$) of 33.5–46.0 kJ/mol for PuO–

PuN system. Therefore, calculations were repeated with an interaction parameter of 46.0 kJ/mol for PuO–PuN. The activities of the compounds PuO and PuN in the mono-nitride solution were calculated as follows:

$$\chi_{\mathrm{PuN\text{-}PuO}} = \mathrm{RT}\ \ln(\gamma_{\mathrm{PuO}})/(x_{\mathrm{PuN}})^2, \qquad (9)$$

$$\chi_{\mathrm{PuN\text{-}PuO}} = \mathrm{RT}\ \ln(\gamma_{\mathrm{PuN}})/(x_{\mathrm{PuO}})^2, \qquad (10)$$

$$a_{\mathrm{PuO}} = x_{\mathrm{PuO}}\gamma_{\mathrm{PuO}}, \qquad (11)$$

$$a_{\mathrm{PuN}} = x_{\mathrm{PuN}}\gamma_{\mathrm{PuN}}. \qquad (12)$$

Consideration of PuO–PuN interaction parameter shows a slight increase in plutonium and uranium partial pressures and decrease in carbon-monoxide and nitrogen partial pressures for uranium rich fuel (U/(U,Pu) = 0.8) consisting of (U,Pu)O_2 + (U,Pu)CNO phases. For plutonium rich nitrides (Pu/(U,Pu) = 0.8), the effect is significant as shown in Table 2.

For $UN_{1.5}$ + (U,Pu)CNO phase field, the effect of PuO–PuN interaction parameter was small, though noticeable difference in carbon-monoxide partial pressure was observed, as seen in Table 3. More experimental data is required to define the interaction parameter for these compounds as a function of composition and temperature.

3.5. Effect of plutonium concentration

With increase in plutonium concentration of the nitride fuel, the phase field $UN_{1.5}$ + (U,Pu)CNO becomes more unstable. In the phase field (U,Pu)O_2 + (U,Pu)CNO, plutonium enrichment results in enhanced carbon activity and partial pressures of nitrogen and carbon-monoxide as can be seen from Table 2. This trend of the nitride fuels is different from that of carbide fuels where the plutonium enrichment reduces carbon activity and carbon-monoxide partial pressure because plutonium sesquicarbide is more stable than uranium sesquicarbide. In nitride fuels, introduction of interaction parameter for PuN–PuO results in reduction of carbon activity. The partial pressures of carbon-monoxide and nitrogen decrease, whereas those of uranium and plutonium increase. A knowledge of the exact value of interaction parameters may be detrimental for the fuel. It will also help us to decide whether plutonium enrichment will be advantageous or not.

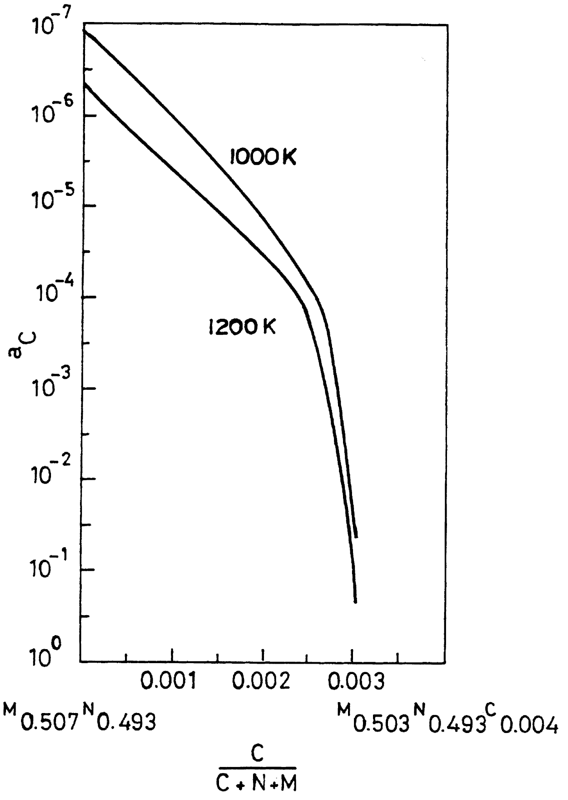

Fig. 2. Effect of carbon on the carbon activity in (U,Pu)CNO + (U,Pu)O_2 phase-field, where, Pu/(U + Pu) = 0.2 and [O] = 2000 wt ppm.

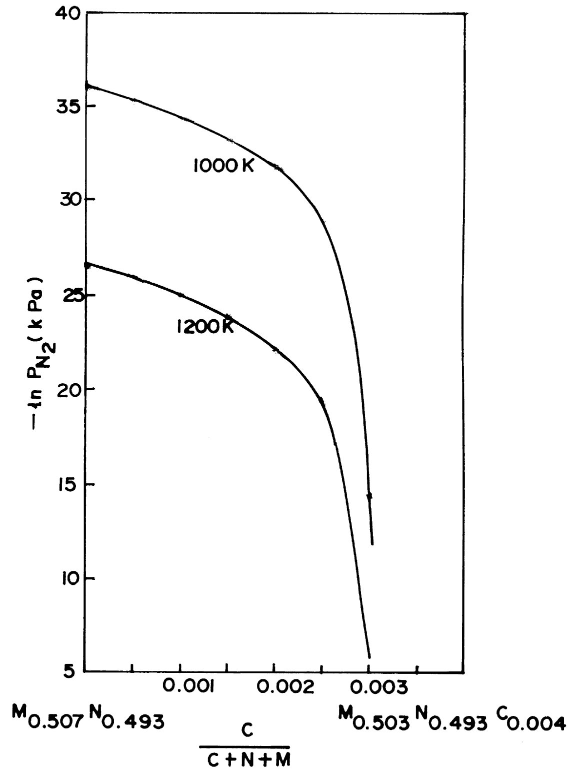

Fig. 3. Effect of carbon on the nitrogen partial pressure in (U,Pu)CNO + (U,Pu)O_2 phase-field, where, Pu/(U + Pu) = 0.2 and [O] = 2000 wt ppm.

3.6. Effect of carbon impurity on (U,Pu)O2+(U,Pu)C-NO phase field

Effect of carbon impurities on carbon activity and partial pressures of carbon-monoxide, nitrogen and plutonium over $(U,Pu)O_2$ + (U,Pu)CNO phase field are shown in Figs. 2–5. These pseudo binary plots were drawn for the fuel composition varying from $(U,Pu)_{0.507}N_{0.493}$ to $(U,Pu)_{0.503}N_{0.493}C_{0.004}$ with high oxygen impurity (2000 wt ppm) and Pu/(Pu + U) = 0.2, at 1000 K and 1200 K. For reference please see partial phase diagram of M–C–N given in Fig. 3, by Sood et al. [5], where M = (U,Pu). In this phase diagram, $M_{0.507}N_{0.493}$–$M_{0.503}N_{0.493}C_{0.004}$ is the axis starting at composition $M_{0.507}N_{0.493}$ and running parallel to the main axis $M_{0.51}N_{0.49}$–$M_{0.49}N_{0.49}C_{0.02}$. In these plots nitrogen and oxygen contents of the fuel are constant. As can be seen from these plots, carbon activity and partial pressures of carbon-monoxide, plutonium and nitrogen are very low for reasonable amount of carbon impurity. As seen in these figures, the thermodynamic parameters, except plutonium partial pressure, show a steep increase near the composition $(U,Pu)_{0.504}N_{0.4935}C_{0.0025}$. Free carbon precipitation starts when carbon impurity level exceeds the composition $(U,Pu)_{0.504}N_{0.493}C_{0.003}$ (~300 wt ppm carbon).

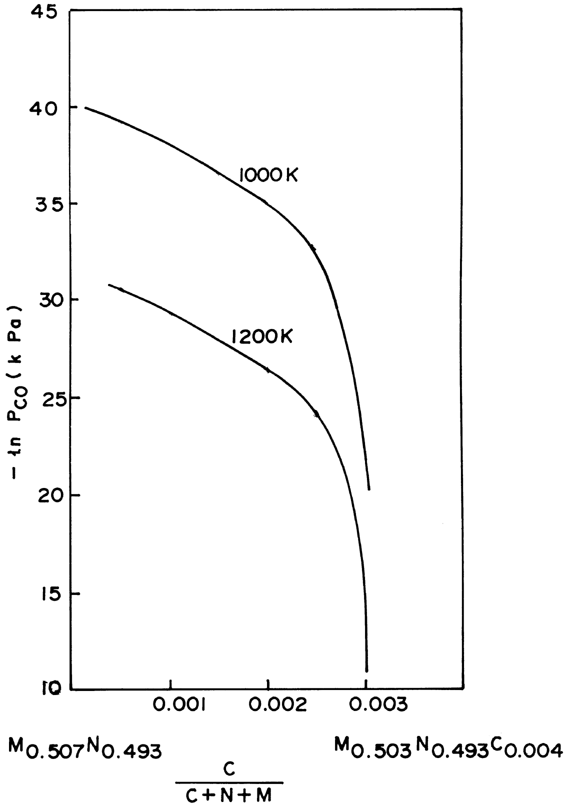

Fig. 4. Effect of carbon on the carbon-monoxide partial pressure in (U,Pu)CNO + $(U,Pu)O_2$ phase-field, where, Pu/(U + Pu) = 0.2 and [O] = 2000 wt ppm.

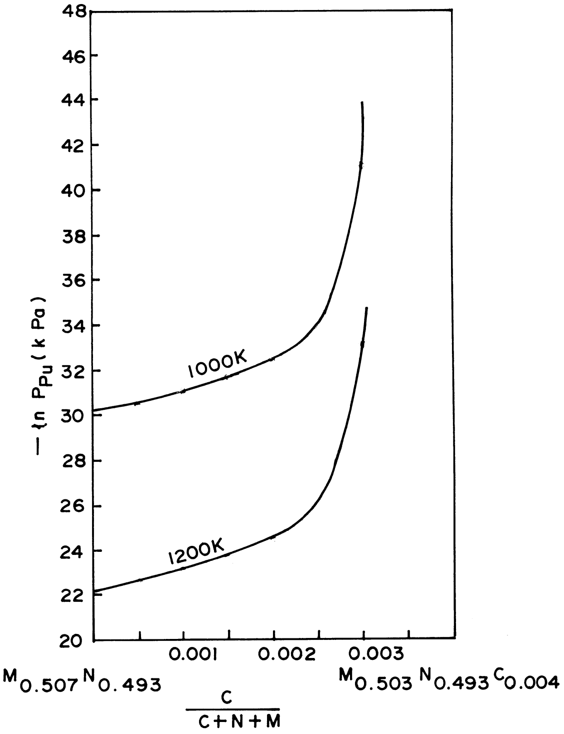

Fig. 5. Effect of carbon on the plutonium partial pressure in (U,Pu)CNO + $(U,Pu)O_2$ phase-field, where, Pu/(U + Pu) = 0.2 and [O] = 2000 wt ppm.

4. Discussion

A comparison of experimentally determined nitrogen partial pressures of carbonitride and nitride fuels with the present calculations is shown in Table 4. A good agreement of the results indicates the reliability of these calculations and validity of the assumptions made during these calculations.

Keller [18] reported partial pressures of nitrogen, uranium and plutonium over the mixed nitride fuel without mentioning the non-metallic composition and phase analysis. The data is given in Table 5. A comparison of the experimental data with calculated results indicated that the fuel composition used for the measurements was probably $(Pu_{0.2}U_{0.8})N_{0.955}$ with 500 wt ppm of carbon and 3000 wt ppm of oxygen having $(U,Pu)O_2$ and (U,Pu)CNO phases.

Nitride fuel has to be biphasic as non-stoichiometry of the mononitride is negligible [19]. Therefore, it is important to decide what second phase should coexist with mononitride phase. Nitride fuels are prepared by

Table 4
A comparison of the experimental and calculated partial pressures of nitrogen over the carbonitride and nitride fuels

Composition	Temperature (K)	Experimental $-\log(P_{N_2}/\text{kPa})$	Calculated $-\log(P_{N_2}/\text{kPa})$	Ref.
U–UN	1500	9.5	9.7	[25]
	1750	6.4	6.7	[25]
	1750	6.0	6.7	[26]
	2000	2.9	4.5	[26]
U–$UC_{0.7}N_{0.3}$	1750	7.3	7.8	[26]
	2000	5.3	5.6	[26]
U–$UC_{0.52}N_{0.48}$	1750	6.7	7.4	[26]
	2000	4.7	5.2	[26]
U–$UC_{0.31}N_{0.69}$	1750	6.2	7.1	[26]
	2000	4.2	4.8	[26]

Table 5
Comparison of the experimental and calculated nitrogen and plutonium partial pressures at different temperatures over the nitride fuel with Pu/(U,Pu) = 0.2 (where, 'exp.' is experimental data [18] and 'calc.' is calculated for (U,Pu)CNO + $(U,Pu)O_2$ phase field with [O] = 3000 wt ppm, [C] = 500 wt ppm)

Temp. (K)	exp. P_{pu} (kPa)	exp. P_U (kPa)	exp. P_{N_2} (kPa)	calc. P_{pu} (kPa)	calc. P_U (kPa)	calc. P_{N_2} (kPa)
1400	2.0×10^{-8}	1.0×10^{-12}	3.0×10^{-9}	5.9×10^{-8}	1.6×10^{-12}	2.3×10^{-9}
1600	1.5×10^{-6}	3.0×10^{-10}	2.5×10^{-7}	4.4×10^{-6}	6.5×10^{-10}	3.0×10^{-7}
1800	5.1×10^{-5}	6.4×10^{-8}	8.9×10^{-6}	1.3×10^{-4}	6.9×10^{-8}	1.4×10^{-5}
2000	6.8×10^{-4}	4.0×10^{-6}	1.1×10^{-4}	2.0×10^{-3}	2.8×10^{-6}	2.8×10^{-4}
2200	5.9×10^{-3}	7.1×10^{-5}	2.0×10^{-3}	1.9×10^{-3}	7.1×10^{-5}	3.4×10^{-3}
2400	3.1×10^{-2}	8.2×10^{-4}	5.5×10^{-3}	1.3×10^{-2}	8.1×10^{-4}	2.6×10^{-2}

carbothermic reduction of mixed oxides in presence of nitrogen atmosphere. Heat treatment to obtain pure products will lead in heavy loss of plutonium metal. Therefore, it is preferred to have some unreacted oxide left in the end product instead of unreacted carbon. Present calculations also indicate clearly that the thermodynamic behavior of the fuel containing mixed dioxide phase along with mononitride phase will be superior to any other phase field. Other candidate phase field for nitride fuel is $UN_{1.5}$ + (U,Pu)CNO. However, not only the thermodynamic properties of the phase field $(U,Pu)O_2$ + (U,Pu)CNO is superior to that of $UN_{1.5}$ + (U,Pu)CNO but it is also stable over a wider composition range [5].

References

[1] H. Blank, K. Richter, M. Conquerelle, Hj. Matzke, M. Kampana, C. Sari, I.L.F. Ray, J. Nucl. Mater. 166 (1989) 95.

[2] C. Prunier, P. Bardelee, J.P. Pages, K. Richter, R.W. Stratton, G. Legergerber, Proceedings of the International Conference On Fast Reactor and Related Fuel Cycles, vol II, Session 15, Paper 9, Kyoto, Japan, 1991.

[3] Y. Arai, S. Fukushima, K. Shiozawa, M. Handa, J. Nucl. Mater. 168 (1989) 280.

[4] Hj. Matzke, Science of Advanced LMFBR Fuels, Elsevier, Amsterdam, 1986, p. 532.

[5] D.D. Sood, R. Agarwal, V. Venugopal, J. Nucl. Mater. 247 (1997) 293.

[6] T. Matsui, R.W. Ohse, High Temp. High Press. 19 (1987) 1.

[7] P.E. Potter, K.E. Spear, Thermodynamics of Nuclear Materials, vol. II, Proc. Symp. Julich, 1979, IAEA, Vienna, 1980, p.195.

[8] J.M. Leitnaker, Thermodynamics of Nuclear Materials, Proc. Symp. Vienna, 1967, IAEA, 1968, p. 317.

[9] H. Holleck, T. Ishii, Thermal Analysis, Proceedings of the third International Conference Davos, vol. 2, Birkhauser, Basel, 1971, p. 137.

[10] A.G. Ermolaev, A.M. Lebedev, V.F. Petrunin, B. Khalikov, Neorg. Mater. 29 (1993) 230.

[11] M.H. Rand, R.J. Ackermann, F. Gronvold, F.L. Oetting, A. Pattoret, Paper presented at the CNRS-IUPAAV Conference on Refractory Oxides for High Temperature Power Sources, Odeillo, France, 1977, Rev. Int. Hautes Temp. Refract. 15 (1978) 355.

[12] R. Lorenzelli, Contribution a L'Etude du Systeme (U, Pu)C,N, CEA Report R-3536, 1968.

[13] A.A. Bauer, Reactor Technol. 15 (2) (1972) 87.

[14] P.E. Potter, J. Nucl. Mater. 47 (1973) 7.

[15] Y. Suzuki, A. Maeda, Y. Arai, T. Ohmichi, J. Nucl. Mater. 188 (1992) 239.
[16] M.H. Bradbury, Hj. Matzke, J. Nucl. Mater. 75 (1978) 68.
[17] K. Richter, C. Sari, J. Nucl. Mater. 184 (1991) 167.
[18] D.L. Keller, Annual Report, Progress on Development of Mateiral and Technology for Advanced Reactors During July 1968–June 1969, Battelle Memorial Institute, USAEC Report BMI-1868, pp. A15–A19.
[19] C.L. Hoening, J. Am. Ceram. Soc. 54 (1971) 391.
[20] P.E. Potter, Plutonium 1975 and other Actinides, Proceedings of the fifth International Conference Baden-Baden, September 10–13, 1975, Elsevier, New York and North-Holland, Amsterdam, 1976, p. 211.
[21] E.K. Storms in: R.J. Ackermann, F.L. Oetting, P.E. Potter, M.H. Rand, E.K. Storms (Eds.), The Uranium–Carbon, Plutonium–Carbon and Uranium–Plutonium–Carbon Systems, Report based on a Consultants' Meeting, Grenoble, 1974, AERE, Harwell.
[22] M.H. Rand, R.J. Ackermann, F. Gronvold, F.L. Oetting, A. Pattoret, paper presentated at CNRS-IUPAAC Conference on Refractory Oxides for High Temperature Power Sources, Odeillo, France, 1977, rev. Int. Hautes Temp. Refract. 15 (1978) 355.
[23] P.E. Potter, J. Nucl. Mat. 34 (1970) 193.
[24] R.J. Ackermann, M.S. Chandrashekhariah, Thermodynamics of Nuclear Materials 1974, vol II, IAEA-SM-190/44, IAEA, Vienna, 1975, p. 3.
[25] H. Tagawa, J. Nucl. Mater. 51 (1974) 78.
[26] Y. Ikeda, M. Tamaki, G. Matsumoto, J. Nucl. Mater. 59 (1976) 103.