



## Thermodynamic studies of uranium–gadolinium–carbon system through the carbothermic reduction of the oxides

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### Abstract

The formation of solid solutions of  $(U_{1-y}Gd_y)_C_2$  (where  $0.2 \leq y \leq 0.8$ ) in the high carbon region, has been studied in the temperature range 1063–1673 K. The solid solutions were prepared by blending the stoichiometric amounts of oxides with graphite and heating the mixture in the form of a pellet to the reaction temperature in a high vacuum chamber. The effusion of CO from the pellet was monitored by means of a quadrupole mass spectrometer. The effusion pressures of CO in the vacuum chamber were correlated to the equilibrium pressure of the system, according to a new method developed in our laboratory [R. Vidhya, M.P. Antony, C.K. Mathews, *J. Phys. Chem.* 99 (1995) 16468]. The reported solubility [T.C. Wallace, N.H. Krikorian, P.L. Stone, *J. Electrochem. Soc.* 111(12) (1964) 1404] of ‘GdC<sub>2</sub>’ in ‘UC<sub>2</sub>’ was verified by XRD. The Gibbs energies of formation of the different solid solutions have been calculated. © 1997 Elsevier Science B.V.

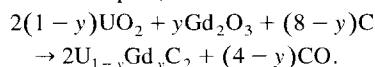
### 1. Introduction

The mixed carbide of uranium and plutonium is the fuel for the fast breeder test reactor (FBTR) situated at Kalpakkam. In order to understand the problems relating to burn-up behavior or compatibility of the burnt fuel with the cladding materials, the knowledge of the phase relationships of the individual fission product elements with fuel materials such as uranium, plutonium and carbon is required. As a first step to have an idea of the chemical constitution of irradiated fuel, a number of systems, with one component in addition to the U and C in uranium carbide, have been analyzed by many workers [1–4]. Holleck and Kleykamp [1] have studied the isothermal and concentration phase diagrams of ternary and quaternary UC systems. Fee and Johnson [2] have described in detail the fission product–uranium–carbon systems in detail in their report. The effect of fission products on the constitution of U–Pu–C has been studied by Haines and Potter [3]. The solubility of fission products in the carbides and nitrides of U and Pu has been discussed by Benedict [4], based on lattice parameter differences. Rare earth fission products constitute roughly one-third of the total fission

products generated in the irradiated fuel. Hence, a study of the rare earth metal–uranium–carbon system can be important in deciding about the carbon potential and other thermodynamic parameters of the irradiated fuel. It can be seen from the literature that there is not enough data on the thermodynamic properties of the uranium–rare earth metal–carbon systems at temperatures below 1700 K.

The rare earth–carbon systems are characterized by two compounds, the sesquicarbide and the dicarbide. The rare-earth sesquicarbides and dicarbides are isomorphous with the corresponding uranium compounds [3]. However, they are only partially soluble in the corresponding uranium compounds [4]. The U–Gd–C system is interesting because it has been reported [5] to form a continuous series of solid solutions above 2063 K, owing to the similarity in the structure. GdC<sub>2</sub> and UC<sub>2</sub> both exist in a tetragonal structure below 1573 K and in a cubic structure above this temperature. According to the authors the UC<sub>2</sub>–GdC<sub>2</sub> solid solution is not stable below 1900 K.

In the present investigation, the formation of solid solutions of  $(U_{1-y}Gd_y)_C_2$  (where  $0.2 \leq y \leq 0.8$ ) from uranium oxide and gadolinium oxide by the carbothermic reduction of the stoichiometric mixtures of the oxides has been attempted, since this method is simple [6]:



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The reported solubility [5] of tetragonal  $\text{GdC}_2$  in tetragonal  $\text{UC}_2$  has been verified in the temperature range 1063–1673 K. The formation of the solid solution was analyzed in this temperature range. Apart from this, the present study involves the measurement of equilibrium pressures of CO, during the progress of the reaction, for each composition, by a new method developed in our laboratory [7]. This method involves the observation of the generation of the solid solution phase in situ and monitoring the rate of effusion of CO from the sintered pellet, as measured by a quadrupole mass spectrometer. The Gibbs energies of formation of the different solid solutions have been calculated in the temperature range 1458–1673 K.

## 2. Experimental

Reactor grade  $\text{UO}_2$  (NFC, India), pure  $\text{Gd}_2\text{O}_3$  (BDH, England) and ultra high purity graphite (purity greater than 99.999%) were used in sample preparation. The oxides were blended with graphite slightly in excess of the stoichiometric amount in an agate mortar for about 45 min. The samples were then pelletized at 4 t, by using a hydraulic press, to give pellets of 6 mm diameter, 1 mm thickness and weighing about 100–110 mg. The pellets were degassed at around 473 K for 12 h before the actual experiment.

The samples were then loaded into a degassed tantalum crucible which was then heated by means of an induction generator in a vacuum chamber. The details of the set up have been reported [7].

The pellets were heated rapidly at a rate of 100 K/min to the reduction temperatures and maintained there for short time periods. The evolution of CO was monitored as a function of time by means of a quadrupole mass spectrometer. The CO pressure increases to a maximum value initially and then decreases exponentially. Pressure measurements were repeated at least thrice at every experimental temperature for accuracy.

On completion of the reaction, the pellet was transferred to a leak-tight container. The samples were weighed and were crushed into powder. The powder obtained was analyzed for the phases present by X-ray diffraction employing  $\text{Cu K}_\alpha$  radiation.

## 3. Results and discussion

### 3.1. Vapor pressure measurements

The pressures of CO in the chamber effused out from the sample at a given temperature were plotted against the reaction time. The decay portion of the curve was fitted to an exponential function of the form

$$P_{\text{eff}} = P_0 * \exp(-k * t),$$

Table 1  
Temperature dependence of Gibbs energies of formation of different compounds

Compound	Gibbs energy of formation (kJ/mol)	Temperature range (K)
$\text{UC}_2$ [9]	$-83.1 + 0.016T$	1500–1800
$\text{U}_{0.8}\text{Gd}_{0.2}\text{C}_2$	$-223.5 + 0.024T$	1498–1603
$\text{U}_{0.6}\text{Gd}_{0.4}\text{C}_2$	$-312.8 + 0.070T$	1458–1653
$\text{U}_{0.5}\text{Gd}_{0.5}\text{C}_2$	$-372.7 + 0.078T$	1562–1658
$\text{U}_{0.4}\text{Gd}_{0.6}\text{C}_2$	$-399.4 + 0.116T$	1573–1668
$\text{U}_{0.2}\text{Gd}_{0.8}\text{C}_2$	$-410.5 + 0.219T$	1533–1673
$\text{GdC}_2$	$-461.8 + 0.291T$	1208–1443

where  $P_{\text{eff}}$  is the effusion pressure of CO from the pellet as measured by means of the quadrupole mass spectrometer,  $P_0$  is the maximum CO pressure in the chamber,  $k$  is a constant for a sample at that temperature and  $t$  is the time of the reaction. From the values of  $P_0$  and  $k$  for a particular temperature, the equilibrium CO pressure for that temperature was calculated according to the equation [7]

$$P_{\text{eq}} = P_0 * T/k,$$

where  $T$  is the reaction temperature.

### 3.2. Formation of the solid solutions

The reduction of the  $\text{UO}_2$ – $\text{Gd}_2\text{O}_3$  mixture to the corresponding solid solution of the carbide (according to the stoichiometry) was studied from 1063 K onwards. The different solid solutions that were synthesized are  $\text{U}_{1-y}\text{Gd}_y\text{C}_2$  ( $y = 0.2, 0.4, 0.5, 0.6$  and  $0.8$ ). It was observed that the reaction proceeded at a measurable rate

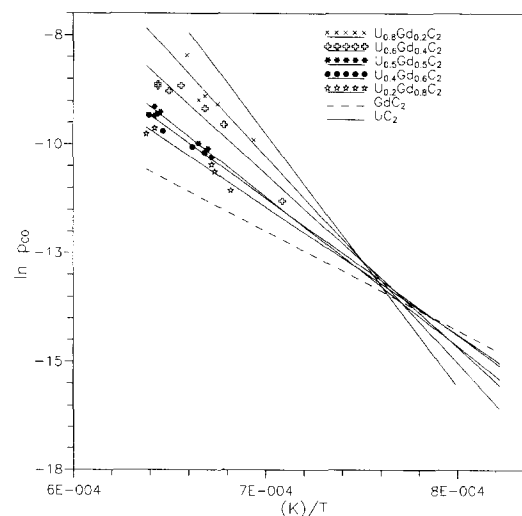


Fig. 1. Plot of  $\ln P_{\text{CO}}$  against reciprocal temperature for the formation of different solid solutions of  $(\text{U}, \text{Gd})\text{C}_2$ .

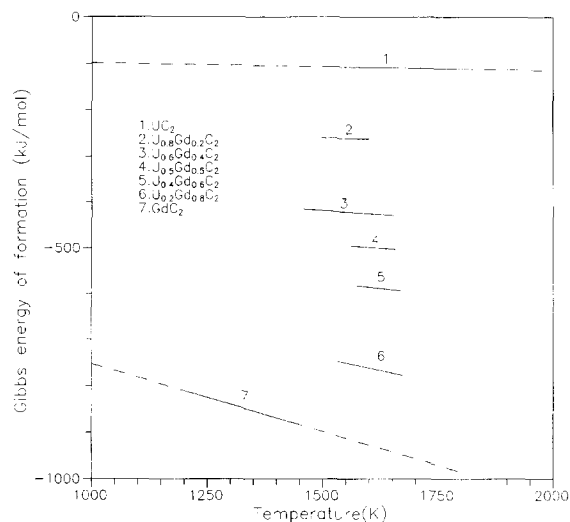


Fig. 2. Plot of Gibbs energies of formation of different solid solutions plotted along with the values for pure phase compounds.

only beyond 1458 K. Below this temperature the measured equilibrium pressures were the same for all compositions of the solid solutions. This indicated that the solid solutions were not formed at the temperature. This observation is in concurrence with that reported by Wallace et al. [5]. Apart from this, the formation of  $\text{GdC}_2$  from  $\text{Gd}_2\text{O}_3$  and graphite was studied.

### 3.3. Confirmation of the solid solution phases

The XRD pattern revealed that all the solid solution phases are of the tetragonal structures. The reflection of (1, 1, 0) and (0, 0, 2) of the solid solution peaks were recorded. These peaks were registered with a constant shift in angle (to the higher angle) depending on the increasing mole fraction of  $\text{GdC}_2$  in the solid solution. A rough estimate of the lattice parameter could be calculated from the two peaks mentioned above. It was observed that the lattice parameters ( $a$ ,  $c$ ) increased with the increasing mole fraction of  $\text{GdC}_2$  in the solid solution.

### 3.4. Thermodynamic properties of the carbide solid solutions

A least square fit of the logarithm of the equilibrium CO pressures against reciprocal temperature for the different solid solutions is given in Fig. 1 (the plots have been extrapolated beyond the temperature range studied for comparison in different phases).

From the equilibrium CO pressures calculated, the Gibbs energies of formation of the different solid solutions

were determined, by taking the appropriate free energy data of the oxides, graphite and the CO phases from standard thermodynamic tables [8]. The temperature dependencies of the Gibbs energies of formation are given in Table 1, along with the temperature range in which these expressions are valid. The data for  $\text{UC}_2$  have been taken from the calculated results of Anthonysamy et al. [9].

A plot of the free energies of formation of the solid solutions along with that for pure phases of  $\text{GdC}_2$  and  $\text{UC}_2$  [9] are included for comparison in Fig. 2. It can be seen that the Gibbs energies of formation show a clear trend corresponding to the different amounts of solubility of ' $\text{GdC}_2$ ' in ' $\text{UC}_2$ '.

## 4. Conclusion

The solid solutions of  $\text{U}_{1-y}\text{Gd}_y\text{C}_2$  ( $y = 0.2$  to  $0.8$ ) have been successfully prepared by heating a mixture of the stoichiometric amounts of the oxides and graphite, in a high vacuum system. The formation of the phases has been confirmed by XRD. The equilibrium CO pressures formed were determined by a new method developed in our laboratory. The Gibbs energies of formation of the carbide solid solution have been calculated. The results indicate that the fission product Gd can exist in the fuel as a solid solution in the  $\text{UC}_2$  phase.

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