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Thermodynamic properties of uranium plutonium mixed carbides

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Abstract High plutonium containing hyperstoichiometric mixed carbide fuels are used as driver fuel in the Fast Breeder Test Reactor at Kalpakkam, India. The enthalpy increment of the mixed carbide fuels were measured in the temperature range 1000–1800 K using a high temperature drop calorimeter. The results are presented and compared with the data available in the literature.

Keywords Calorimetry · Heat capacity · Actinides · Carbide fuels · Fast breeder test reactor

Introduction

Uranium–plutonium mixed carbides have been successfully irradiated up to a burn-up of 159 GWd/t in the Fast Breeder Test Reactor (FBTR) in Kalpakkam for the first time in the world. FBTR uses a high plutonium containing hyperstoichiometric mixed carbides namely, $(U_{0.3}Pu_{0.7})C$ (Mark-I) and $(U_{0.45}Pu_{0.55})C$ (Mark-II) as driver fuels. Thermodynamic properties of Mark-I and Mark-II fuels are of importance for understanding and predicting the fuel behaviour during irradiation. Besides enabling extrapolation of measured thermodynamic data to other temperature ranges, heat capacity data of the Mark-I and Mark-II fuels are also required to derive the thermal conductivity from the measured thermal diffusivity data. In the literature, thermodynamic data are available only for the conventional $(U_{0.8}Pu_{0.2})C$ fuel. Tetenbaum et al. [1] calculated the thermodynamic properties for $(U_{0.8}Pu_{0.2})C$ by assuming it to be an ideal solution of UC and $PuC_{0.88}$. Fisher and Leibowitz [2] reported measurement of the enthalpy increments of $(U_{0.8}Pu_{0.2})C$ from 1039 to 2421 K with an induction heated drop calorimeter. Preusser [3] has given an empirical equation for the heat capacity of $(U_{0.8}Pu_{0.2})C$, based on the hypothetical overpower excursion model data of Nickerson and Kastenberg [4], Gebhardt et al. [5] and Hoffmann [6]. As no thermodynamic data are available for the Mark-I and Mark-II fuel compositions of FBTR, high temperature drop calorimetric measurements were carried out to determine the enthalpy increments, in the temperature ranges 1018-1765 K. Thermodynamic functions such as heat capacity, entropy and Gibbs energy functions were computed from the measured enthalpy increments.

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Experimental

The mixed carbide samples of Mark-I and Mark-II fuels used for the enthalpy increment measurements were prepared, characterized [7, 8] and supplied by the Radiometallurgy Division, BARC, Mumbai. The important specifications of Mark-I and Mark-II fuels for FBTR are given in Table 1. The enthalpy increments of Mark-I and Mark-II fuels were determined by using a high temperature differential calorimeter (Model HT 1500 of M/s. SETARAM, France) which has been enclosed in an argon atmosphere active glove box system. Besides being radiotoxic the mixed carbide fuel pellets are prone to oxidation and hydrolysis in the presence of oxygen and moisture as well as highly pyrophoric. Hence for carrying out the calorimetric measurements on these radioactive samples, the calorimeter has been attached to a leak tight glove box with a high purity argon atmosphere. The glove

Table 1 Specifications of uranium-plutonium mixed carbide (Mark-I and Mark-II) fuel

Specification	Mark-I	Mark-II
Chemical		
Plutonium (wt%)	66 ± 1	51.9 ± 1
Plutonium and uranium (wt%)	≥94	≥94
Carbon (wt%)	≤5.05	≤5.05
Americium (wt%)	Not specified	0.3 maximum
Oxygen (ppm)	≤6000	≤5000
Oxygen + Nitrogen (ppm)	≤7500	≤6000
M_2C_3 (wt%)	5–20	5–15
Tungsten (ppm)	≤200	≤200
Total impurities (ppm) (excluding oxygen, nitrogen and americium)	≤3000	≤3000
Physical		
Diameter (mm)	4.18 ± 0.04	4.18 ± 0.05
Height (mm) (nominal)	7.00 ± 0.04	7.00 ± 0.04
Density (%TD)	90 ± 1	86 ± 2
Linear Mass (g/cm)	1.67 ± 0.04	1.60 ± 0.04

box pressure was maintained at a negative pressure of 25 mm WG (Water Gauge) with respect to the ambient and the moisture and oxygen impurity levels were maintained,<10 vpm (volume parts per million) each. The high temperature drop calorimeter and the argon atmosphere active glove box system to which the calorimeter is attached have been described elsewhere [9, 10]. In a typical experiment at a given temperature, samples and standards, five each, maintained at the ambient temperature was dropped, alternatively, into the calorimeter at the high temperature. α-alumina (SRM 720) supplied by NIST, USA, was used as the standard. Heat flow was recorded as a function of time and the peak area associated with each drop corresponds to the respective enthalpy increment. Enthalpy increment of sample was obtained from the measured heat flows for the sample, α-alumina (SRM 720) and the critically accessed enthalpy increment values [11] of α-alumina. The detailed experimental procedure adopted has also been described earlier [9].

Results and discussion

The accuracy of the enthalpy increments from our measurements had been determined to be 2–4% [9]. Enthalpy increments of Mark-I and Mark-II fuels were measured in the temperature ranges of 1021–1759 K and 1018–1765 K, respectively. They were fitted to polynomial functions in temperature by the least squares method using the following three constraints: (i) $H_T - H_{298} = 0$ at 298 K; (ii) the derivative of the function at 298 K is equal to the value of heat capacity at 298 K ($C_{p,298}$) for the Mark-I and Mark-II fuels (50.87 and 51.26 JK^{-1} mol^{-1}, respectively) which were estimated from the assessed values [12] of $C^0_{p,298}$ for uranium carbide and plutonium carbide proportional to the weight fraction present in Mark-I and Mark-II fuels of FBTR. (iii) dC_P/dT at 298 K = 0.044 and 0.047, respectively, for Mark-I and Mark-II fuels. For the estimation of S_{298} values, needed for computing entropy and Gibbs energy functions, the contribution of ideal entropy of mixing, besides the molar additivity of S^0_{298} values for uranium carbide and plutonium carbide proportional to the weight fraction present in the fuel were taken from the literature [13, 14]. The fit equations thus obtained for Mark-I and Mark-II fuels are given below:

Mark-I Fuel

$$H_T - H_{298}/\mathrm{Jmol}^{-1} = 44.542(T/K) + 10.609 \times 10^{-3}(T/K)^2 + 31.477 \times 10^{-1}(K/T) - 14223 \quad (1)$$

Mark-II Fuel

$$H_T - H_{298}/\mathrm{Jmol}^{-1} = 45.662(T/K) + 9.387 \times 10^{-3}(T/K)^2 + 35.087 \times 10^{-1}(K/T) - 14449 \quad (2)$$

The standard errors of the fit are 2.2% and 2.3% and the estimate of the standard deviations for the fit are 1527 and 1572 J mol^{-1} for Mark-I and Mark-II fuels, respectively. The measured enthalpy increments of Mark-I and Mark-II fuels are given in Tables 2 and 3 along with their fit values. From the above fit equations, heat capacity, entropy and Gibbs energy function have been computed which are also given in the Tables 2 and 3.

Figure 1 shows the present measured values of enthalpy increments along with the data from the fit for Mark-I and Mark-II fuels as well as those computed using Neumann–

Table 2 Thermodynamic functions of Mark-I mixed carbide fuel

T (K)	$H_T - H_{298}$ (kJ mol^{-1})		T (K)	$H_T - H_{298}$ (kJ mol^{-1})	C_P	S_T	$-(G_T - H_{298})/T$
	Measured	From fit			(J K^{-1} mol^{-1})		
1021	41.284	42.313	298	0	50.87	78.84	78.84
1073	44.829	45.785	300	0.094	50.91	79.15	78.84
1115	47.588	48.630	400	5.291	53.03	94.09	80.86
1169	51.491	52.344	500	10.700	55.15	106.15	84.75
1219	54.951	55.838	600	16.321	57.27	116.39	89.19
1306	60.718	62.043	700	22.154	59.39	125.38	93.73
1345	63.411	64.877	800	28.200	61.52	133.45	98.20
1382	66.221	67.596	900	34.458	63.64	140.82	102.53
1423	69.243	70.642	1000	40.928	65.76	147.63	106.71
1481	73.988	75.012	1100	47.610	67.88	154.00	110.72
1525	77.152	78.375	1200	54.504	70.00	160.00	114.58
1585	83.045	83.027	1300	61.610	72.13	165.68	118.29
1633	87.746	86.804	1400	68.929	74.25	171.11	121.87
1669	91.732	89.669	1500	76.460	76.37	176.30	125.33
1726	95.587	94.261	1600	84.202	78.49	181.30	128.67
1759	99.073	96.951	1700	92.158	80.61	186.12	131.91
			1800	100.325	82.73	190.79	135.05

Table 3 Thermodynamic functions of Mark-II mixed carbide fuel

T (K)	$H_T - H_{298}$ (kJ mol^{-1})		T (K)	$H_T - H_{298}$ (kJ mol^{-1})	C_P	S_T	$-(G_T - H_{298})/T$
	Measured	From fit			(J K^{-1} mol^{-1})		
1018	40.046	41.764	298	0	51.26	77.20	77.20
1063	43.085	44.698	300	0.095	51.30	77.52	77.20
1113	46.726	48.002	400	5.318	53.17	92.53	79.23
1163	49.868	51.354	500	10.729	55.05	104.60	83.14
1199	52.494	53.796	600	16.328	56.98	114.80	87.59
1238	55.448	56.469	700	22.115	58.81	123.72	92.12
1279	57.693	59.310	800	28.089	60.68	131.69	96.58
1321	60.233	62.253	900	34.251	62.56	138.95	100.89
1363	63.711	65.229	1000	40.601	64.44	145.63	105.03
1403	67.216	68.094	1100	47.139	66.32	151.86	109.01
1435	69.476	70.408	1200	53.864	68.19	157.71	112.83
1493	73.721	74.650	1300	60.777	70.07	163.25	116.50
1529	77.388	77.315	1400	67.878	71.95	168.51	120.02
1575	82.056	80.756	1500	75.167	73.83	173.54	123.43
1607	85.370	83.173	1600	82.643	75.70	178.36	126.71
1633	87.211	85.151	1700	90.307	77.58	183.01	129.88
1671	89.486	88.065	1800	98.159	79.46	187.49	132.96
1713	91.861	91.317					
1765	96.000	95.389					

Kopp's rule from the enthalpy data of uranium and plutonium carbides recommended by IAEA [12]. The values from the fit are within ±3% of the measured values. Present enthalpy increment data are in agreement within 5% with the values calculated using Neumann-Kopp's rule for Mark-I and Mark-II fuel compositions. In Fig. 2, the present enthalpy increment data for Mark-I and Mark-II fuels are compared with the literature data [1–3] for $(U_{0.8}Pu_{0.2})C$. It shows, as expected, that the present data are much higher than the values for $(U_{0.8}Pu_{0.2})C$. However,

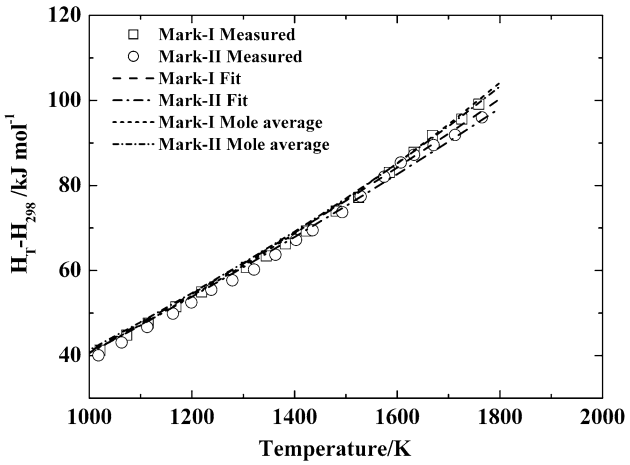

Fig. 1 Enthalpy increments of Mark-I and Mark-II fuels of FBTR

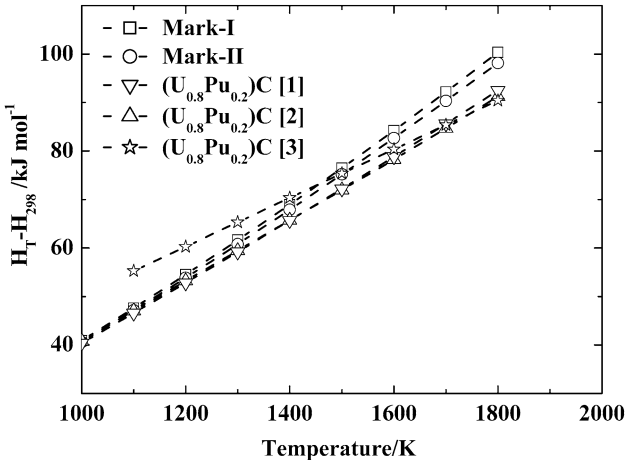

Fig. 2 Comparison of the enthalpy increment data for Mark-I and Mark-II fuels of FBTR with $(U_{0.8}Pu_{0.2})C$

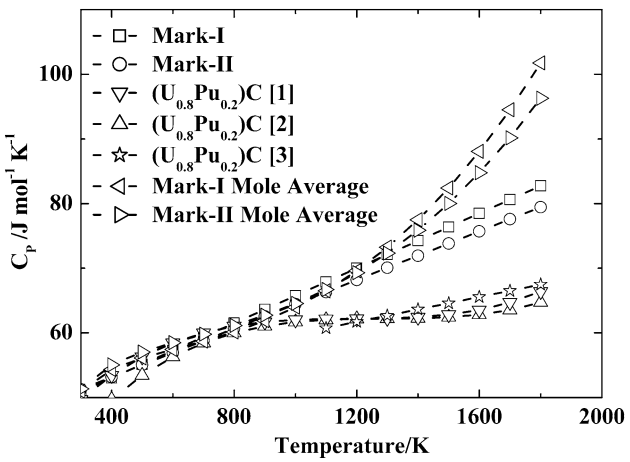

Fig. 3 Comparison of the heat capacity data of Mark-I and Mark-II fuels of FBTR with $(U_{0.8}Pu_{0.2})C$ fuel

at lower temperatures, the enthalpy data of Preusser [3] are much higher than those of Fischer and Leibowitz [2] as well as Tetenbaum et al. [1]. Figure 3 shows the present heat capacity data for Mark-I and Mark-II fuels along with the heat capacity data computed from the literature data for the carbides of uranium and plutonium by using the Neumann-Kopp's rule for Mark-I and Mark-II fuel compositions as well as the heat capacity data from literature [1–3] for conventional $(U_{0.8}Pu_{0.2})C$ fuel. As can be seen from the Fig. 3, the present heat capacity data are lower than the values computed using Neumann–Kopp's rule. The deviations are about 5% at 1500 K and are increasing with increase in temperature.

Summary

The present study provides the first experimental enthalpy increment data for high plutonium content hyperstoichiometric mixed carbide fuels using a high temperature drop calorimeter.

References

1. Tetenbaum M, Sheth A, Olson M. A review of the thermodynamics of the U-C, Pu-C and U-Pu-C systems, Argonne National Laboratory, Report ANL-AFP-8; June 1975.
2. Fisher DF, Leibowitz L. Enthalpy of uranium-plutonium carbide from 298 K to the melting point. J Nucl Mater. 1977;67:244–8.
3. Preusser T. Modeling of carbide fuel rods. Nucl Technol. 1982; 57:343–71.
4. Nickerson GM, Kastenberg WE. Preliminary assessments of carbide fuel pins during mild overpower transients in LMFBRs. Nucl Eng Des. 1976;36:209–33.
5. Gebhardt E, Thummler F, Seghezzi HD. Werstoffe Reaktor. Teil 2: Keramische und pulvermetallurgische Werkstoff. Stuttgart: B.G. Teubner-Verlag; 1969.
6. Hoffmann H. Thermische Ausdehnung, Spezifische Warme, Zustandsgleichung, Karbidische Kernbrennstoffe fur Schnelle, Brutreaktoren, Kernforschungszentrum, Bericht 1111, KfK Karlsruhe; 1969.
7. Sengupta AK, Banerjee J, Jarvis T, Kutty TRG, Ravi K, Majumdar S. Out-of-pile properties of hyperstoichiometric $(U_{0.45}Pu_{0.55})$ fuel for the Fast Breeder Test Reactor. Nucl Technol. 2003;142:260–8.
8. Majumdar M, Sengupta AK, Kamath HS. Fabrication, characterization and property evaluation of mixed carbide fuels for a test Fast Breeder Reactor. J Nucl Mater. 2006;352:165–75.
9. Nagarajan K, Saha R, Babu R, Mathews CK. Thermodynamic functions of Barium and Strontium Zirconates from calorimetric measurements. Thermochim Acta. 1985;90:297–304.
10. Babu R, Kandan R, Ganapathy M, Ravisankar G, Nagarajan K, Vasudeva Rao PR. Incorporation of a high temperature differential calorimeter in an argon atmosphere glove box system. Report IGC-240; 2002.
11. Synthetic Sapphire Al_2O_3, Certificate of Standard Reference Materials 720, 1982. National Bureau of Standards, U.S. Department of Commerce, Washington, DC, 20234, USA; 1982.

12. Holley Jr CE, Rand MH, Storms EK. The chemical thermodynamics of actinide elements and compounds, Part 6. In: Oetting FL, editor. The actinide carbides, IAEA, Vienna; 1984.
13. The uranium-carbon and plutonium-carbon systems, A thermochemical assessment, Technical Reports, Series No. 14, IAEA Vienna, Vienna; 1963.
14. Haines HR, Hall ROA, Lee JA, Mortimer MJ. The low temperature specific heats of three plutonium carbides. J Nucl Mater. 1980;88:261–4.