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Thermodynamic functions for $U_{0.45}Pu_{0.55}N$

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Abstract

Enthalpy increments of $U_{0.45}Pu_{0.55}N$ were measured in the temperature range of 1025–1775 K by inverse drop calorimetry using a high temperature differential calorimeter. The enthalpy increments were fitted to a polynomial in temperature and the heat capacity, entropy and Gibbs energy functions were computed. The results are presented and discussed in comparison with literature data.

Keywords: Drop calorimetry; Enthalpy increment; Heat capacity; Thermodynamic functions; Uranium–plutonium mixed nitride; Advanced fuel for fast reactors

1. Introduction

Uranium–plutonium mixed nitride (U,Pu)N is a candidate advanced fuel for fast reactors [1]. It has higher thermal conductivity, superior breeding properties due to higher heavy metal density and excellent compatibility with sodium coolant compared to mixed oxide fuel. It is less sensitive to oxidation compared to mixed carbide fuel, and the problems, associated with reprocessing of carbide fuel using the PUREX process are absent with the nitride fuels [2,3]. Yet, in comparison, there is little information on the irradiation behaviour of mixed nitride fuels. We have studied a plutonium-rich mixed nitride, $U_{0.45}Pu_{0.55}N$, that might prove suitable for actinide burning in future fast reactors. Thermodynamic properties of mixed nitride fuels are of importance not only for evaluating the fuel performance under normal and abnormal reactor conditions but also in the fabrication process. In the literature, heat capacity data are available only for the conventional fuel composition, $U_{0.80}Pu_{0.20}N$. The high temperature enthalpy and heat capacity data of $U_{0.80}Pu_{0.20}N$ measured using an Oelson calorimeter in the temperature range 298–1800 K were reported by Alexander et al. [4]. To evaluate the heat capacity of $U_{0.80}Pu_{0.20}N$ in the temperature range 300–3000 K, Kurosaki et al. [5] performed molecular dynamic calculations on UN, PuN and (U,Pu)N. Thermodynamic properties of UN, PuN and $U_{0.80}Pu_{0.20}N$ have been critically assessed by Matsui and Ohse [6] who observed, based on the vapour pressure data, that uranium plutonium mixed nitrides are expected to be ideal solid solutions of UN and PuN. However, the activity coefficients determined by Suzuki et al. [7] have shown that the mixed nitrides become more non-ideal with increasing concentration of PuN. In the present study, the enthalpy increments for $U_{0.45}Pu_{0.55}N$ were measured using a high temperature differential calorimeter. From the measured enthalpy increments, thermodynamic functions such as heat capacity, entropy and Gibbs energy functions were computed. The results are presented and compared with the literature data available for $U_{0.80}Pu_{0.20}N$.

2. Experimental

The $U_{0.45}Pu_{0.55}N$ fuel samples used for the enthalpy increment measurements were prepared, characterized and supplied by the Radiometallurgy Division, BARC, Mumbai [2,3]. The results of chemical characterisation of the $U_{0.45}Pu_{0.55}N$ fuel samples are given in Table 1. Enthalpy increments 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. The equipment is described in more detail elsewhere [8,9]. The calorimeter was calibrated by dropping samples of α-alumina (SRM 720) supplied by NIST, USA. In a typical experiment at a given temperature, five each, of samples and standards, maintained at the ambient temperature were dropped, alternatively, into the calorimeter at the high temperature. The detailed

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Table 1
Specifications of $U_{0.45}Pu_{0.55}N$ fuel pellets

Specification	$U_{0.45}Pu_{0.55}N$
Plutonium (wt.%)	52 ± 1
Plutonium and uranium (wt.%)	≥ 94
Carbon (wt.%)	0.108
Second phase	Nil
Oxygen (wt.%)	0.105
Nitrogen (wt.%)	5.56
Fabrication route	Powder-pellet
Sintered density (%TD)	85 ± 1

experimental procedure adopted has also been described earlier [8].

3. Results and discussion

The error in the enthalpy increments from our measurements had been determined to be 2–4% [8]. The enthalpy increments of $U_{0.45}Pu_{0.55}N$ were measured in the temperature range of 1025–1775 K. They were fitted to a polynomial function 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 heat capacity of the solid solution at 298 K ($C_{p,298} = 48.799\ \mathrm{J\,K^{-1}\,mol^{-1}}$) which was estimated from the assessed values [6] of $C_{p,298}$ for pure UN and PuN by using Neumann–Kopp's molar additivity rule; (iii) $\mathrm{d}C_p/\mathrm{d}T$ at 298 K = 0.095 which was computed by using Neumann–Kopp's rule from the corresponding values for UN and PuN which, in turn, were obtained by fitting literature data for heat capacity of UN and PuN [10,11], respectively. The fit equation obtained for $U_{0.45}Pu_{0.55}N$ is given below:

$$H_T - H_{298}\,(\mathrm{J\,mol^{-1}}) = 45.04835T\,(\mathrm{K}) + 6.28998 \times 10^{-3}T\,(\mathrm{K})^2 + 60.26113 \times 10^{-1}T\,(\mathrm{K})^{-1} - 13,990$$

Table 2
Measured enthalpy increments and fit values of $U_{0.45}Pu_{0.55}N$

T (K)	ΔH_{298}^{T} Measured ($\mathrm{J\,mol^{-1}}$)	ΔH_{298}^{T} Fit	$100 \times ((\Delta H_{298}^{T}$ Fit $- \Delta H_{298}^{T}$ Measured$)/\Delta H_{298}^{T}$ Fit) (%)
1025	38,657	38,793	0.35
1073	41,519	41,588	0.17
1115	43,794	44,058	0.60
1169	46,576	47,267	1.46
1218	49,503	50,210	1.41
1263	52,065	52,939	1.65
1306	54,985	55,571	1.05
1349	57,693	58,226	0.92
1387	59,662	60,592	1.54
1424	62,315	62,913	0.95
1481	65,726	66,522	1.20
1529	69,534	69,594	0.09
1590	73,771	73,538	−0.32
1634	76,547	76,413	−0.18
1681	80,234	79,510	−0.91
1737	84,262	83,237	−1.23
1775	86,861	85,788	−1.25

Table 3
Thermodynamic functions of $U_{0.45}Pu_{0.55}N$ calculated from the measured enthalpy increments

T (K)	$H_T - H_{298}$ ($\mathrm{J\,mol^{-1}}$)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	S_T ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-(G_T - H_{298})/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
298	0	48.799	69.462	69.462
300	90	48.822	69.764	69.463
400	5,035	50.080	83.982	71.393
500	10,106	51.338	95.292	75.079
600	15,303	52.596	104.763	79.258
700	20,626	53.854	112.965	83.500
800	26,074	55.112	120.239	87.646
900	31,648	56.370	126.803	91.638
1000	37,348	57.628	132.807	95.459
1100	44,174	58.886	138.358	99.110
1200	49,125	60.144	143.536	102.598
1300	55,203	61.402	148.400	105.936
1400	61,406	62.660	152.996	109.135
1500	67,735	63.918	157.362	112.206
1600	74,189	65.176	161.528	115.159
1700	80,770	66.434	165.517	118.005
1800	87,476	67.692	169.350	120.752

Table 2 shows the measured enthalpy increment values along with the calculated values from the above fit equation. The equation fits the enthalpy increment data very well. Standard error of the fit is 1.21%. The estimate of the standard deviation for the fit is 740 $\mathrm{J\,mol^{-1}}$. From the above fit equation, heat capacity, entropy and the Gibbs energy functions were computed and are given in Table 3. The S_{298} value needed for the computation of the entropy and the Gibbs energy functions was estimated from the literature data [6] for the S_{298}^{0} values of UN and PuN using the molar additivity rule and adding the ideal mixing entropy.

Fig. 1 shows our measured values of enthalpy increments for $U_{0.45}Pu_{0.55}N$ along with the fit values. Though the results of Suzuki et al. [7] indicate that the solid solutions tend to be more non-ideal with increasing amounts of PuN, the enthalpy increments of the mixed nitride have also been computed by invoking Neumann–Kopp's rule which is based on the assumption that the solid solution is ideal. The present enthalpy increment data for $U_{0.45}Pu_{0.55}N$ are 2–5% lower than the mole average values calculated using the assessed enthalpy data UN and PuN of Matsui and Ohse [6]. As can be seen from the figure, the present data

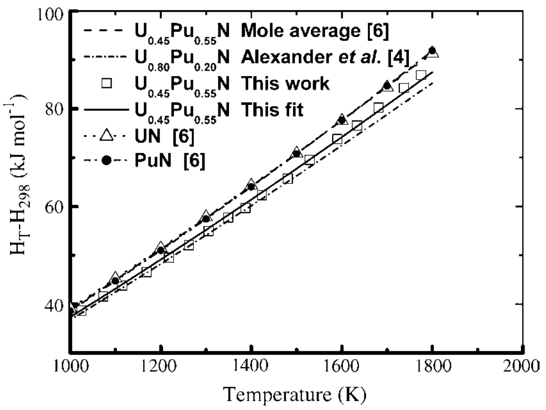

Fig. 1. Enthalpy increments of uranium–plutonium mixed nitride.

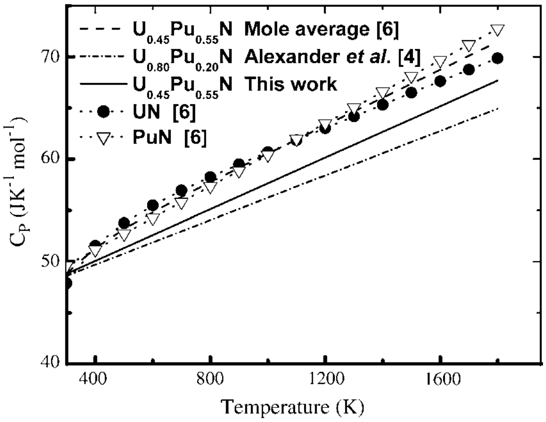

Fig. 2. Heat capacity of uranium–plutonium mixed nitride.

for $U_{0.45}Pu_{0.55}N$ are higher than that of $U_{0.80}Pu_{0.20}N$, reported by Alexander et al. [4], the maximum deviation being 3% at higher temperatures. Fig. 2 shows the present heat capacity data for $U_{0.45}Pu_{0.55}N$ along with the mole average values of the heat capacity computed using those of uranium and plutonium mononitrides given by Matsui and Ohse [6]. The heat capacity data of Alexander et al. [4] for $U_{0.80}Pu_{0.20}N$ are also given in the same figure. As can be seen from Fig. 2, the present data are lower than the mole average values and that the difference between the two sets of data increases with increasing temperature. The maximum deviation is about 6% at temperatures above 1000 K. Similarly, the present data become increasingly higher than those of Alexander et al. [4] for $U_{0.80}Pu_{0.20}N$ with increase in temperature. It must be mentioned here that Matsui and Ohse [6] have also observed that the data of Alexander et al. [4] are much lower than the mole average values. Kurosaki et al. [5] observed that the data of Alexander et al. [4] are in very good agreement with the sum of C_v and C_d obtained by molecular dynamic calculations. As has also been observed by them, the actual heat capacity could be higher because the contributions due to defects, electrons, etc. have not been accounted for.

4. Conclusion

This study presents the first measurements of the enthalpy increments and heat capacity of $U_{0.45}Pu_{0.55}N$.

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