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Journal of Nuclear Materials 360 (2007) 99–103

journal of nuclear materials

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Enthalpy measurements of $La_2Te_3O_9$ and $La_2Te_4O_{11}$

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Received 12 June 2006; accepted 13 September 2006

Abstract

Enthalpy increment measurements on $La_2Te_3O_9$(s) and $La_2Te_4O_{11}$(s) were carried out using a Calvet micro-calorimeter. The enthalpy values were analyzed using the non-linear curve fitting method. The dependence of enthalpy increments with temperature was given as: $H^\circ(T) - H^\circ(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = 360.70T + 0.00409T^2 + 133.568 \times 10^5/T - 149923$ ($373 \leqslant T\ (\mathrm{K}) \leqslant 936$) for $La_2Te_3O_9$ and $H^\circ(T) - H^\circ(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = 331.927T + 0.0549T^2 + 29.3623 \times 10^5/T - 114587$ ($373 \leqslant T\ (\mathrm{K}) \leqslant 936$) for $La_2Te_4O_{11}$.

1. Introduction

The stoichiometry of the $(U,Th)O_2$ fuels does not change much during burnup, which is similar to the situation encountered in LWR UO_2 and $(U,Pu)O_2$ fuels, where the O/M shift is negligible during the burnup since oxygen transport across the fuel is very fast and the excess oxygen is gettered by the Zircaloy. In $(U,Th)O_2$ fuel, however, the oxygen diffusion through the fuel is orders of magnitude less and so oxygen transport through the fuel is very slow. This results in a sharp built-up of the oxygen potential within the fuel without any appreciable change in the stoichiometry.

Most of the fission products precipitate as multi-component oxide phases and multi-component metallic phases [1]. Rare earths (RE) and tellurium are among the fission products formed with burnup of the fuel. Usually the oxygen potential inside the oxide fuel does not go beyond the value of Mo/MoO_2 buffer system and Te remains alloyed with the metallic fission products and the RE elements remain dissolved in the fluorite lattice of the fuel matrix and are components of the ceramic precipitates. The fission-generated oxygen is taken up by reactive fission products (RE, Y, Sr, Ba, Zr and Mo), ternary compounds of Cs/Rb, and the fuel itself. In thoria rich fuels, the oxygen uptake by the fuel is low. The concentration of the left-over oxygen is governed by its diffusion outwards to the Zircaloy clad [2]. In thoria rich fuels, oxygen diffusion takes place predominantly by self-diffusion, so the transport rate is orders of magnitude slower than in urania rich fuel. Under such circumstances Mo oxidation might not be as fast as oxygen accumulation inside the fuel leading to interaction of Te with RE oxide components in the presence of oxygen forming ternary compounds. The formation would depend on the oxygen potential and also on the tellurites stabilities. In the context of using thoria rich fuel,

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doi:10.1016/j.jnucmat.2006.09.006

information regarding the thermodynamic stability of rare earth tellurites has relevance. Consequently, the standard molar enthalpies of formation of $La_2Te_3O_9$ and $La_2Te_4O_{11}$ at 298.15 K were determined in our laboratory using isoperibol solution calorimetry [3]. Some DSC studies on the determination of the standard enthalpy of formation of yttrium, lanthanum and praseodymium tellurites have been reported by other investigators [4]. To evaluate the feasibility of formation of the tellurites in the fuel at normal as well as accidental condition the stability values are required as a function of temperature covering the operating range of the fuel. Thus in additions to the measured data of standard molar enthalpies of formation, the temperature dependent heat capacities of the tellurites are required in the evaluation. As heat capacity values are not reported, we undertook the measurements of enthalpy increments of $La_2Te_3O_9$ and $La_2Te_4O_{11}$ using high-temperature Calvet calorimeter in the temperature range of 298–900 K. The heat capacity values were derived from the measured thermal functions.

2. Experimental

2.1. Preparation

The metal tellurites were prepared from high-purity La_2O_3 (99.99%) and TeO_2 (Aldrich, purity 99.99%). For preparation of $La_2Te_3O_9$, a mixture of La_2O_3 and TeO_2 were taken in molar proportions of 1:3 and ground. The ground mixture was taken in a sealed quartz ampoule and heated at 1173 K for three days. $La_2Te_4O_{11}$ was prepared by heating a mixture of La_2O_3 and TeO_2 in 1:4 molar proportions in a sealed quartz ampoule at 923 K for two days with one intermittent grinding.

2.2. Characterization

The compounds formed were characterized by the XRD technique using the Debye–Scherrer method in a Philips X-ray generator PW-1729 with wide-angle goniometer PW-1820 using Ni filtered CuKα radiation. Thermogravimetric runs for the compounds and DTA runs for the compounds as well as pure TeO_2 were taken in a commercial TG-DTA apparatus (Setaram, 92-16.18) in pure argon atmosphere at a heating rate of $10\ K\ min^{-1}$ up to 1173 K. The purity of the compounds formed (single phase) was established from the chemical analysis using the ICP–AES technique.

2.3. Calorimetric measurements

Dry samples of $La_2Te_3O_9$ and $La_2Te_4O_{11}$ were made into pellets of 4 mm diameter and 1 mm thickness under a pressure of 80 MPa. These pellets were annealed in air at 800 K overnight and stored in a desiccator for $H°(T) - H°(298.15\ K)$ measurements. A Calvet calorimeter, model SETARAM HT-1000, was used for enthalpy increment measurements of $La_2Te_3O_9$ and $La_2Te_4O_{11}$ by the 'drop calorimetry' technique. The sample in the form of a pellet, maintained at 298.15 K in the holder, was dropped into the sample cell which consisted of a quartz tube inserted inside the usual alumina holder maintained at the experimental temperature, T. The temperature of the isothermal block was measured using a platinum–platinum + 10% rhodium thermocouple. The heat flow between the isothermal block and either of the cells was recorded in the form of millivolt signals. The details followed in the calorimetric measurements have been described elsewhere [5]. The heat calibration was carried out using a synthetic sapphire [NIST SRM 720].

3. Results and discussion

The XRD patterns of the compounds $La_2Te_3O_9$ and $La_2Te_4O_{11}$ matched well with that reported in JCPDS file No. 22-0376 and 22-0646, respectively. No lines due to the starting components La_2O_3 and TeO_2 were found.

Thermal analysis of pure TeO_2 gave a sharp melting peak at 733 °C [6], which corresponds to its reported melting point. For both the compounds no DTA peak was observed up to 900 °C. This proves the absence of TeO_2 as pure phase in the compounds. They also showed no weight loss up to 900 °C indicating their stability within the temperature range of measurement.

The results of the chemical analysis of the tellurites show that the mass percentage of La and Te are 34.7 and 47.6 against the respective calculated values of 34.53 and 47.57 for $La_2Te_3O_9$. For $La_2Te_4O_{11}$ the analyzed mass percentages for La and Te are 29.0 and 52.5, respectively, against the respective calculated values of 28.81 and 52.93.

The $H°(T) - H°(298.15\ K)$ values for $La_2Te_3O_9$ and $La_2Te_4O_{11}$ obtained at different temperatures are given in Tables 1 and 2, respectively. These values when fitted to suitable polynomials showing their proper temperature dependence can be represented by the following equations:

$$H^\circ(T) - H^\circ(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = 360.70T\ (\mathrm{K}) + 0.00409T^2 + 133.568 \times 10^5/T - 149\,923 (373 \leqslant T\ (\mathrm{K}) \leqslant 936) \quad \text{for } \mathrm{La_2Te_3O_9}, \tag{1}$$

$$H^\circ(T) - H^\circ(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = 331.927T\ (\mathrm{K}) + 0.0549T^2 + 29.3623 \times 10^5/T - 114\,587 (373 \leqslant T\ (\mathrm{K}) \leqslant 936) \quad \text{for } \mathrm{La_2Te_4O_{11}}. \tag{2}$$

Table 1
Experimental enthalpy increment values of $La_2Te_3O_9(s)$

Mass of sample taken (g)	T (K)	$H°(T) - H°(298.15\ K)$ (J mol^{-1})		
		Experimental	Values from the fitted functions	% Error[a] (relative)
0.05295	374.7	21 218 ± 1210	21 456	−1.11
0.08310	425.9	35 698 ± 2300	35 803	0.29
0.09025	476.6	51 406 ± 820	50 948	−0.90
0.13630	502.1	58 820 ± 760	58 810	−0.02
0.05235	527.6	67 228 ± 1560	66 832	−0.59
0.05475	553.4	75 433 ± 1763	75 069	−0.48
0.11800	578.7	83 584 ± 1855	83 263	−0.39
0.14000	681.3	113 601 ± 531	117 310	3.16
0.09520	706.5	127 824 ± 1757	125 877	−1.55
0.17870	731.9	134 807 ± 2112	134 515	−0.22
0.17690	783.3	149 753 ± 4210	152 166	1.59
0.16445	808.9	159 760 ± 3521	161 020	0.78
0.16525	834.6	172 596 ± 2086	169 972	−1.54
0.13840	860.1	182 271 ± 987	178 868	−1.90
0.11090	936.2	203 543 ± 591	205 632	1.02

[a] % Error = (Fit. value − measured value)100/Fit. value.

Table 2
Experimental enthalpy increment values of $La_2Te_4O_{11}(s)$

Mass of sample taken (g)	T (K)	$H°(T) - H°(298.15\ K)$ (J mol^{-1})		
		Experimental	Values from the fitted functions	% Error[a] (relative)
0.13395	374.4	24 508 ± 309	24 571	0.26
0.10135	425.6	44 116 ± 739	43 775	−0.78
0.07620	450.9	53 473 ± 1231	53 180	−0.55
0.19630	476.5	63 005 ± 365	62 675	−0.53
0.18890	502.0	72 648 ± 1194	72 155	−0.68
0.11405	527.5	79 577 ± 4191	81 665	2.56
0.12845	553.1	91 819 ± 1021	91 515	−0.33
0.15465	578.7	99 573 ± 2269	100 892	1.31
0.09655	604.2	108 625 ± 1548	110 642	1.82
0.13330	655.3	131 866 ± 2690	130 083	0.39
0.12560	681.2	142 348 ± 921	140 184	−1.54
0.15080	706.4	153 216 ± 685	150 052	−2.11
0.29240	731.7	157 480 ± 3012	160 018	1.59
0.18540	757.2	174 068 ± 3560	170 172	−2.29
0.20355	783.3	178 822 ± 1899	180 687	1.03
0.20370	808.3	188 308 ± 1776	190 841	1.33
0.14585	834.2	204 083 ± 2078	201 486	−1.29
0.14630	859.9	211 776 ± 3975	212 144	0.17
0.12890	885.4	216 348 ± 5551	222 789	2.89
0.11800	936.3	248 535 ± 4532	244 467	−1.66

[a] % Error = (Fit. value − measured value)100/Fit. value.

The first differential of Eqs. (1) and (2) gives the molar heat capacity for $La_2Te_3O_9$(s) and $La_2Te_4O_{11}$(s), respectively. The resulting equations are

$$C^{\circ}_{p}\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 360.70 + 0.00818T - 133.568 \times 10^{5}/T^{2} \quad (373 \leqslant T\ (\mathrm{K}) \leqslant 936) \text{ for } La_2Te_3O_9, \tag{3}$$

$$C^{\circ}_{p}\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 331.927 + 0.1098T - 29.3623 \times 10^{5}/T \quad (373 \leqslant T\ (\mathrm{K}) \leqslant 936) \text{ for } La_2Te_4O_{11}. \tag{4}$$

Plots of the variation of C_p with temperature from present study as well as using the additivity rule (Neumann–Kopp rule) for $La_2Te_3O_9$(s) and $La_2Te_4O_{11}$(s) are shown in Figs. 1 and 2, respectively. It is observed that for both the compounds the additivity data are significantly higher than the data obtained in the present study but when an enthalpy change is calculated using these two C_p data in a typical temperature interval of 298–900 K, for example, the difference is about 10–15 kJ/mol.

The heat capacity data expressed in Eqs. (3) and (4) were used to evaluate the standard molar enthalpies of formation of $La_2Te_3O_9$ and $La_2Te_4O_{11}$ at 298.15 K from the reported results of high-temperature DSC studies of the compounds measured by Gospodinov et al. [4]. The evaluated values of the two $\Delta_f H^0_{298.15}$ as −2748.16 kJ mol^{-1} and −3098.62 kJ mol^{-1} for $La_2Te_3O_9$ and $La_2Te_4O_{11}$, respectively, were compared with our reported data of −2814.6 kJ mol^{-1} and −3116.5 kJ mol^{-1}, respectively, based on room temperature solution calorimetry of the two compounds [3]. In our earlier work [3] the estimated heat capacities (using Neumann–Kopp rule) for $La_2Te_3O_9$(s) and $La_2Te_4O_{11}$(s) were used to translate the reported high-temperature data of the enthalpy of formation [4] to the standard values at 298.15 K as −2790.6 kJ mol^{-1} and −3113.2 kJ mol^{-1} respectively. Although there appears to be no improvement by using our heat capacity data it might be due to the errors involved in the measurement of the heat of reaction of these two compounds at high temperature using the DSC method [4].

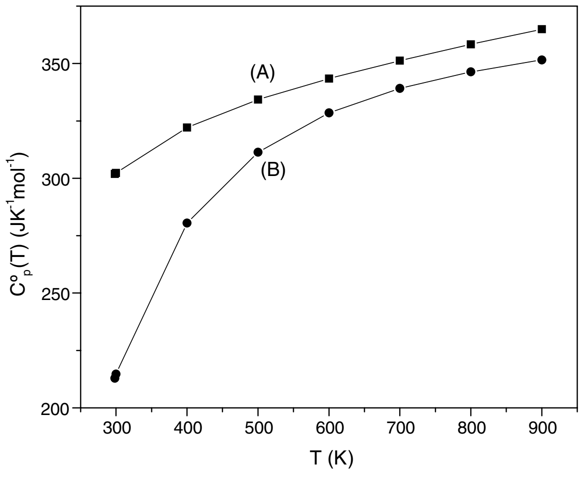

Fig. 1. Change in heat capacity values with temperature for $La_2Te_3O_9$(s). A, using additivity rule; B, present data.

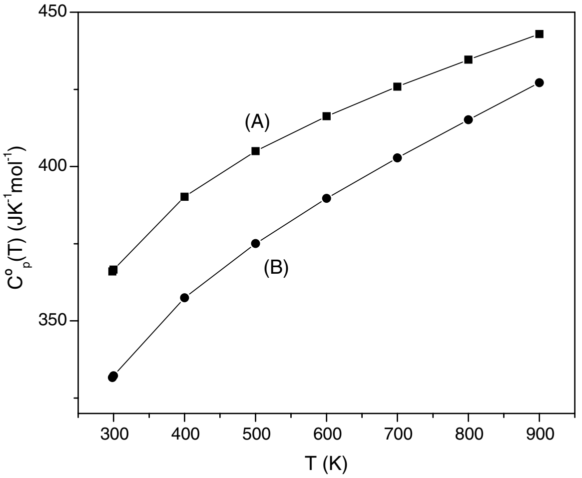

Fig. 2. Change in heat capacity values with temperature for $La_2Te_4O_{11}$(s). A, using additivity rule; B, present data.

4. Conclusion

Enthalpy increment measurements were done for $La_2Te_3O_9$ and $La_2Te_4O_{11}$ using high-temperature Calvet calorimeter. From these measurements the heat capacity–temperature relationship of these two compounds were obtained in the temperature range of 298–948 K as

$$C^{\circ}_{p,m}\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 360.70 + 0.00818T - 133.568 \times 10^{5}/T^{2} \quad (La_2Te_3O_9(s),\ 373 \leqslant T\ (\mathrm{K}) \leqslant 936), \tag{5}$$

$$C^{\circ}_{p,m}\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 331.927\ (\mathrm{K}) + 0.1098T - 29.3623 \times 10^{5}/T \quad (La_2Te_4O_{11}(s),\ 373 \leqslant T\ (\mathrm{K}) \leqslant 936). \tag{6}$$

This is the first report on the heat capacity measurements of these two compounds. An estimation regarding the probability of formation of these compounds in the nuclear fuel comprising of approximately 3 mol% UO_2 and 97 mol% ThO_2 is done at a typical temperature of 1000 K. Using our data for the compounds and taking Te to be in the dissolved state in the metallic precipitates and La_2O_3 in the ThO_2 matrix, the equilibrium oxygen partial pressures over the pure phase of these compounds ($La_2Te_3O_9$ and $La_2Te_4O_{11}$) come out to be in the order of 10^{-5} bar which is much higher than the Mo/MoO_2 oxygen partial pressure at 1000 K. So under normal reactor conditions these compounds do not have any chance of getting formed inside the fuel pin. However, under the situation where Mo fails to buffer the oxygen pressure because of kinetic reasons, these oxygen rich phases can precipitate. Some estimates are also done to judge the competitive dissolution behavior of Te in the fuels and in the separate precipitates like lanthanum tellurites. It is found that the equilibrium oxygen partial pressure over Te dissolved as TeO_2 in the fuel would be of the order of 10^{-20} bar. This indicates that Te would be preferentially remain in the dissolved condition in the fuel than form ternary phases like $La_2Te_3O_9$ and $La_2Te_4O_{11}$.

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