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Enthalpy and Gibbs energy of formation of samarium dicarbide

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Abstract

Enthalpy and Gibbs energy of formation of SmC_2 have been determined between 1420 and 1650 K by measuring the CO(g) partial pressure over the invariant $SmC_2(s)$–$SmO_{1.5}(s)$–C(s) three-phase field. The equilibrium CO pressure over the three-phase field was deduced from the effusion pressure by the dynamic effusion MS method. The Gibbs energy of formation of $SmC_2(s)$ in the entire temperature range was deduced from the Gibbs energy of the reaction, $SmO_{1.5}(s) + 3.5\ C(s) = SmC_2(s) + 1.5\ CO(g)$, and by taking the Gibbs energy functions of the other constituents from literature. The recommended Gibbs energy of formation of SmC_2 at 298 K is $-(98 \pm 7)\ kJ\,mol^{-1}$. The enthalpy of formation of $SmC_2(s)$ was derived from the enthalpy of reaction and the enthalpies of formation of $SmO_{1.5}(s)$ and CO(g) taken from literature. The third-law enthalpy of formation of $SmC_2(s)$ at 298 K is $-(85 \pm 8)\ kJ\,mol^{-1}$.

1. Introduction

Samarium is a fission product and also a neutron poison. Samarium forms a brittle dicarbide (SmC_2) which has a metallic gold luster and a calcium carbide crystal structure. In continuation with our earlier programme [1–3] to determine the thermodynamic data of certain solid rare-earth carbides in the temperature range 1200–1700 K, which normally exist in a fuel pin during its irradiation in a nuclear reactor, the results on the SmC_2 system are presented in this paper.

There is no established phase diagram for the Sm–C system. While the structures of the carbides have been adequately studied, the physical and chemical properties are described in very few reports [4–6]. Three binary carbides (viz.) SmC_2, $SmC_{1.5}$ and Sm_3C have been reported so far based on the review of Adachi et al. [4]. As in the case of LaC_2, two types of modifications of SmC_2 exist, the low-temperature tetragonal α-phase and the high-temperature β-phase [4].

A number of workers have studied the thermodynamic properties of samarium dicarbide, mostly by the mass-spectrometric method, but there is considerable scatter in the reported data. Cuthbert et al. [7] have measured the Sm vapour pressure in equilibrium with the dicarbides between 1400 and 2000 K by Knudsen-effusion mass spectrometry. They have indicated that the mono-atomic metal is the only significant vapour species and have reported the enthalpy of formation of $SmC_2(s)$. Avery et al. [8] have measured the Sm vapour pressures over the Sm–C system from 67 to 100 at.% C by the Knudsen-effusion method in a mass spectrometer between 1330 and 2051 K. They have contradicted the conclusions of Cuthbert et al. [7] in reporting the existence of $SmC_2(g)$ along with Sm(g) over the SmC_2–C condensed phase. Faircloth et al. [9] have studied the vapourisation of $SmC_2(s)$ between 1300 and 2400 K and have reported the enthalpy of formation of $SmC_2(s)$ at 298 K assuming the results of Cuthbert et al. [7] that the vapour phase consists of Sm(g) only. The chemical composition, vapour pressure and lattice constants of samarium carbide have been determined by

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Kyshtobaeva et al. [10] using a Langmuir vapourisation technique. Stout et al. [11] determined the vapour pressure of SmC_2 in equilibrium with graphite by the Knudsen-effusion technique, recording the rates of weight loss between 1350 and 2050 K, and have reported the presence of Sm(g) only as the predominant vapour phase. The vapour pressure over the SmC_2–C system was also determined in another study by Seiver and Eick [12]. Haschke and Deline [13] studied the binary and ternary regions of the Sm–O–C system between 1400 and 2200 K and the presence of non-stoichiometric carbides like $SmC_{1.36}$ and $SmC_{1.45}$ was reported. They have also identified a NaCl type oxycarbide with a stoichiometry of $SmO_{0.5}C_{0.4}$ in this system. Based on the ternary phase diagram (Fig. 1) it is obvious that $SmO_{0.5}C_{0.4}$ is in equilibrium with $SmO_{1.5}$(s), $SmC_{1.45}$(s) and Sm(s). There is no conclusive information on the limits of oxygen solubility in SmC_2(s). More recently, Haschke and Deline [14] have studied the vapourisation behaviour and thermodynamic properties of SmC_2 and SmC_y ($1.36 < y < 1.45$) using the target-collection effusion technique between 1548 and 2049 K. The anomalous increase in the equilibrium pressure of samarium in the gaseous phase with temperature and the observed shift of $\Delta_f H^\circ$ (SmC_y) to less negative values with increasing temperature have been attributed to the significant retrograde temperature dependence of the carbon-rich phase boundary of Sm_2C_3. Meschel and Kleppa [15] have calculated the enthalpy of formation of SmC_2(s) at 298 K from the difference in the measured enthalpy of the reaction Sm(s) + 2C(s) = SmC_2(s) at 1273 K and the measured enthalpy increment associated with SmC_2(s) going from 298 to 1273 K. Gschneidner et al. [5,6] provide a theoretical estimate of the Gibbs energy and enthalpy of formation of all the rare-earth carbides. Niessen et al. [16] have estimated the enthalpy of formation of SmC_2 using Miedema's semi-empirical method. A recent compilation of thermodynamic data by Barin [17] contains a listing of enthalpy and Gibbs energy of formation of SmC_2(s) apart from the Gibbs energy and enthalpy functions as a function of temperature.

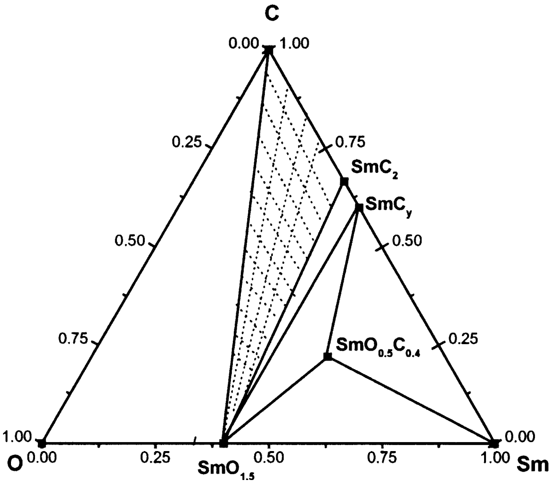

Fig. 1. Ternary phase diagram of the Sm–C–O system [13]. The shaded area is the three-phase field used for the thermodynamic measurements.

As there is considerable discrepancy in the reported thermodynamic data of samarium carbides, this work is aimed at determination of the equilibrium CO(g) pressures over the $SmO_{1.5}$(s)–C(s)–SmC_2(s) (hatched area in Fig. 1) using the dynamic effusion MS method [18] between 1420 and 1650 K, according to the equation:

$$SmO_{1.5}(s) + 3.5C(s) = SmC_2(s) + 1.5CO(g) \qquad (1)$$

and the determination of Gibbs energy and enthalpy of formation of SmC_2(s) by second-law and third-law methods taking appropriate data for $SmO_{1.5}$(s), C(s) and CO(g) from literature [19].

2. Experimental

$SmO_{1.5}$(s) of 99.9% purity procured from M/s. Indian Rare-Earths, India and C(s) with a purity higher than 99.999%, were used for the preparation of the samples. A stoichiometric mixture of $SmO_{1.5}$(s) and C(s), was blended and pelletised at a pressure of 25 MPa to give pellets of 6 mm diameter, 1 mm thickness and weighing about 100 mg. The pellets were heated to the desired temperature and the pressure of CO(g) effusing out of the pellet, p_{eff}, was recorded as a function of time by using a quadrupole mass spectrometer (QMS). An independent high-temperature XRD of the sample between 1373 and 1773 K was done in order to establish the presence of the phases at various temperatures. Details of the experimental procedure employed and the apparatus have been described in our earlier papers [1–3,18].

3. Results and discussion

3.1. Confirmation of the products

The sample was in the expected phase field comprising of SmC_2(s), C(s) and $SmO_{1.5}$(s) as indicated by the XRD results reported in Fig. 2. The lattice parameters of SmC_2(s) were derived from the XRD pattern to be $a = 376$ pm and $c = 634$ pm from the reflections at (1 0 1) and (1 1 0) planes. The lattice parameters for $SmC_{2.0}$ have also been reported by Haschke and Deline [13] [$a = 376.3 \pm 0.1$ pm and $c = 632.1 \pm 0.4$ pm]. The

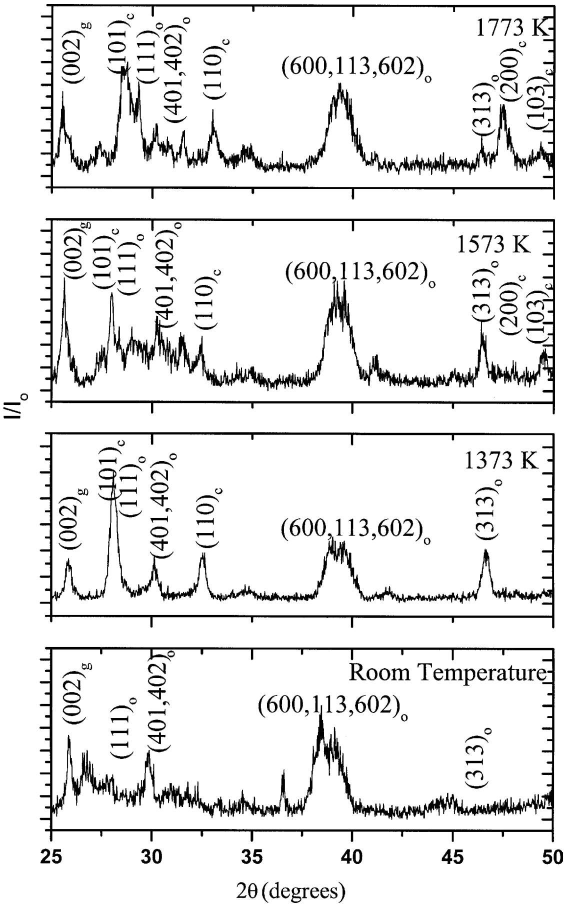

Fig. 2. High-temperature XRD patterns of the Sm–C–O system (subscripts indicate peaks due to various phases: g, graphite; o, $SmO_{1.5}$; and c, SmC_2).

data [$a = 377 \pm 1$ pm and $c = 633 \pm 1$ pm] reported by Spedding et al. [20] have been accepted as reference data by JCPDS. It is obvious that the lattice parameters reported in the present study are in close agreement with both the reports mentioned above. Faircloth et al. [9] have reported a non-stoichiometry in the SmC_2(s) phase and have predicted the limiting composition of the dicarbide to be $SmC_{2.05\pm0.05}$ at 1473–1673 K, which would increase to $SmC_{2.18}$ at about 2573 K. However, the lattice parameters of SmC_2(s) prepared under various conditions in the present study did not show any variation thereby indicating that there is no non-stoichiometry in the SmC_2(s) phase.

The $SmO_{0.5}C_{0.4}$ ($a = 506.6$ pm) phase is one of the oxycarbides reported, and it exhibits a NaCl type symmetry (Fm$\bar{3}$m) [13] while SmC_2(s) has a CaC_2 type tetragonal structure (I4/mmm) below 1443 K. There is no conclusive information on the limits of oxygen solubility in SmC_2(s). The peaks in the XRD pattern show a broad hump around $2\theta = 30°$. This hump may be due to agglomeration of multiple peaks of oxide which occur around this angle.

3.2. Equilibrium CO(g) pressures

The equilibrium CO pressures determined between 1450 and 1650 K for the SmC_2(s)–C(s)–$SmO_{1.5}$(s) three-phase field are given in Table 1. The equilibrium CO(g) pressures were plotted as a function of $1/T$ (Fig. 3) and fitted to a straight line by the least-squares method. The fit equation is

$$\ln p_{CO} = -(52000 \pm 895)/T + (22.6 \pm 0.6) \quad (p_{co} \text{ in bar}). \tag{2}$$

3.3. Gibbs energy of formation of $SmC_2(s)$

The Gibbs energy of reaction (1) at a given temperature was derived from the equilibrium CO(g) pressures at that temperature. The Gibbs energy of formation of SmC_2(s) at various temperatures was derived from the Gibbs energy of reaction (1). The Gibbs energy of formation of SmC_2(s) obtained in the present study is compared with the other literature data in Fig. 4. From the figure it is obvious that there is a scatter in the reported data. The Gibbs energy of formation of SmC_2(s) obtained in the present study agree within the limits of experimental error with the results of Cuthbert et al. [7], Avery et al. [8], Stout et al. [11], Faircloth et al. [9] and that listed in Barin [17]. It must be noted that all of these investigators have worked in the high-carbon region of the Sm–C phase diagram and have used mass-spectrometric techniques for determination of vapour pressures as in the present study. The $\Delta_f G°$ of SmC_2(s) has been derived to be $-(98 \pm 7)$ kJ mol^{-1} and this agrees well with the compiled data (−98.3) listed by Barin [17]. The $\Delta_f S°$ of SmC_2(s) as estimated from the present data is 8 J K^{-1} mol^{-1} in this temperature range.

3.4. Enthalpy of formation of $SmC_2(s)$

The second-law enthalpy of reaction (1) at the mid-temperature of measurement was obtained from the slope of the $\ln p_{CO}$ versus $1/T$ curve. This was converted to the enthalpy at 298 K by taking the enthalpy increments of $SmO_{1.5}$(s), C(s), CO(g) from literature [19]. Thermal functions for SmC_2(s) were estimated using the thermal functions of CaC_2 [9]. The $\Delta_r H°_T$ and $\Delta_r H°_{298}$ were found to be (648 ± 7) and (675 ± 7) kJ mol^{-1}, respectively. It is pointed out that all the researchers have calculated the thermal functions of SmC_2 based on those of CaC_2. The enthalpy of the reaction (1) at 298 K derived based on the thermal functions of $UC_{1.94}$ and $ThC_{1.94}$ was found to be (691 ± 7) and (671 ± 7) kJ mol^{-1}, respectively. The enthalpy of the reaction (1) at 298 K

Table 1
Equilibrium CO(g) pressures over the phase mixture $SmO_{1.5}$(s)–C(s)–SmC_2(s) and the Gibbs energy and enthalpy of reaction as a function of temperature

Runs	Temperature (K)	Equilibrium CO pressure (bar)	$\Delta_rG°$ of reaction (1) (kJ mol^{-1})	$\Delta_rH°_{298}$ of reaction (1)[a] at 298 K (kJ mol^{-1})
Run 1	1443	1.39E−6[b]	242.6	673.3
	1494	5.36E−6	226.1	671.9
	1539	1.50E−5	213.2	672.3
	1578	3.30E−5	203.0	673.6
	1613	5.91E−5	195.8	676.6
Run 2	1443	1.31E−6	243.8	674.5
	1483	3.40E−6	232.9	675.4
	1533	1.04E−5	219.4	676.7
	1573	2.63E−5	206.9	675.9
	1603	4.60E−5	199.7	677.6
Run 3	1443	1.77E−6	238.3	669.0
	1527	1.17E−5	216.4	672.1
	1573	3.71E−5	200.1	669.2
	1623	7.20E−5	193.1	676.9
Run 4	1436	1.39E−6	241.5	670.3
	1519	1.09E−5	216.6	669.9
	1561	2.60E−5	205.6	671.2
	1586	4.18E−5	199.5	672.7
	1612	6.87E−5	192.8	673.6
	1666	2.20E−4	175.0	671.5
Run 5	1428	1.05E−6	245.2	671.6
	1433	1.19E−6	243.8	668.6
	1533	1.58E−5	211.4	670.0
	1643	1.51E−4	180.3	671.5
	1650	1.17E−4	186.3	678.0

[a] Third-law results (based on thermal functions of CaC_2(s)).

[b] Read as 1.39×10^{-6} or 1.39 µbar.

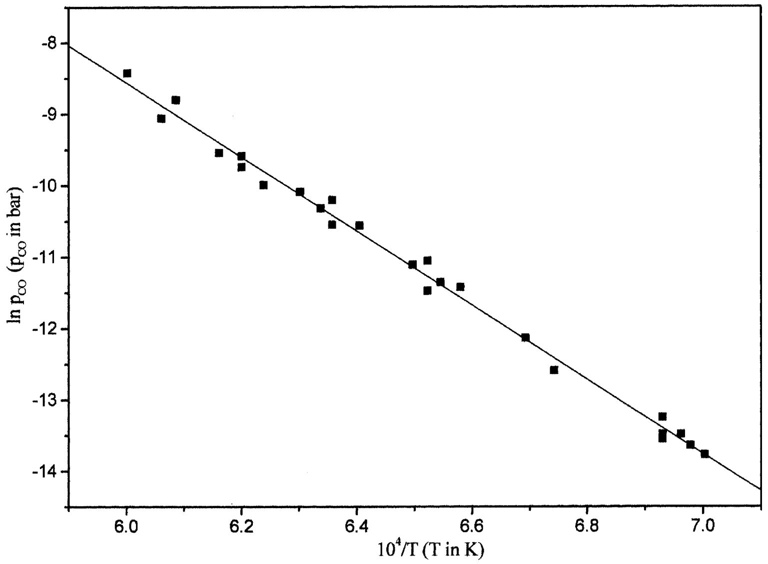

Fig. 3. Plot of equilibrium CO(g) pressure as derived for reaction (1) against reciprocal temperature.

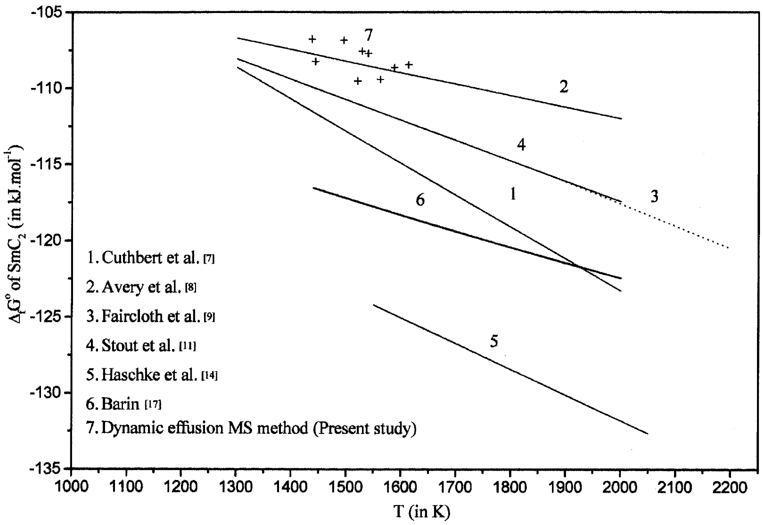

Fig. 4. Gibbs energy of formation of SmC_2(s).

was calculated to be (676 ± 7) kJ mol^{-1} based on the enthalpy increments provided in Barin [17].

The third-law enthalpy of reaction (1) was derived from the p_{CO} value at each temperature and Gibbs energy functions of $SmO_{1.5}$(s), C(s), CO(g) from literature [18] and SmC_2(s) as suggested by Faircloth et al. [9]. The average of the enthalpy of reaction at 298 K calculated using the third-law method was found to be (672 ± 3), (663 ± 3), (662 ± 3) and (668 ± 3) kJ mol^{-1} based on the Gibbs energy functions of SmC_2 estimated from the thermal functions of CaC_2 [19], $UC_{1.94}$ [19], $ThC_{1.94}$ [19] and the listed data in Barin [17], respectively. Data on the enthalpy of formation of SmC_2(s) at 298 K available in the literature are compared with those obtained in the present study (calculated using the thermal functions of SmC_2(s) derived from the thermal functions of CaC_2, $UC_{1.94}$ and $ThC_{1.94}$ and the thermal functions listed in Barin [17]) in Table 2.

The second-law and third-law enthalpies (estimated with the thermal functions of SmC_2 derived from those of CaC_2) of reaction (1) at 298 K obtained from the present study are in agreement with each other, within about 3 kJ mol^{-1}. As it can be seen from Table 1, there is no significant temperature dependent variation of the

Table 2
Enthalpy of formation of SmC_2(s)

Method/technique	$\Delta_f H^\circ_{298}$ (kJ mol^{-1})			Reference
	Second law	Third law	Selected	
Knudsen cell MS	−89.2 ± 8	−63.6 ± 8.4	−63.6 ± 8.4	[7]
Knudsen effusion	−92.9 ± 18	–	−92.9 ± 18	[8]
Knudsen effusion	−82	−65.4 ± 6.7	−65.4 ± 6.7	[9]
Langmuir evaporation	−56.1 ± 2.8	–	−56.1 ± 2.8	[10]
Knudsen cell MS	−97.1 ± 8.4	−99.9 ± 8.4	−97.9 ± 8.4	[11]
Knudsen cell MS	−96.2 ± 7.5	−104.3 ± 3.3	−96.3 ± 7.5	[14]
Synthesis calorimetry	–	–	−77.1 ± 1.1	[15]
Estimation	–	–	−195 ± 30	[16]
Compilation	–	–	−96.2	[17]
				Using thermal functions of
Dynamic effusion MS method (present study)	−71 ± 7	−79 ± 3		Barin [17]
	−72 ± 7	−75 ± 3		CaC_2
	−56 ± 7	−84 ± 3		$UC_{1.94}$
	−76 ± 7	−86 ± 3	−85 ± 8[a]	$ThC_{1.94}$

[a] Recommended value with the overall estimated error in the measurement.

third-law enthalpy of reaction indicating the reliability of the thermodynamic data obtained. The enthalpy of formation as reported in the present study (using the thermal functions derived from CaC_2) is in good agreement with the results of Meschel et al. [15], Cuthbert et al. [7] and Faircloth et al. [9] within the limits of experimental error. The results of Avery et al. [8], Stout et al. [11] and Haschke and Deline [14] are negative in comparison to our results. While the results of Avery et al. [8] and Stout et al. [11] agree with our Gibbs energy of formation of SmC_2(s) data, a significant difference in the enthalpy of formation of SmC_2(s) at 298 K has been attributed to the method of derivation of thermal functions. Haschke and Deline [14] have worked on the metal-rich side of the Sm–C system hence their reported results are not in agreement with our results.

It can be seen that the enthalpy of formation of SmC_2(s) at 298 K by the third-law method using the thermal functions of SmC_2(s) and those of $UC_{1.94}$ and $ThC_{1.94}$ are in good agreement. Hence, the average of these two results, $-(85 \pm 8)$ kJ mol^{-1}, is chosen to be the recommended value for $\Delta_f H^\circ_{298}$ of SmC_2(s).

3.5. Errors in the measurement

The uncertainty in the temperature is ±3 K and the error in the pressure measurements for different samples heated to the same temperature is less than 5%, based on our data. The error in the $\Delta_f G^\circ$ measurements is about 7 kJ mol^{-1}. The enthalpy and Gibbs energy functions of $SmO_{1.5}$(s), C(s) and CO(g) have been taken from a standard data base [19], while the functions of SmC_2(s) are estimated as experimental data are not available. The error in the enthalpy measurements using the second-law treatment is estimated to be about 7 kJ mol^{-1} and by third-law analysis is about 3 kJ mol^{-1}. Considering the error in $\Delta_f G^\circ$, the overall error in the third-law enthalpy is about 8 kJ mol^{-1}.

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