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Enthalpy and Gibbs energy of formation of dysprosium dicarbide

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Abstract

The equilibrium CO(g) pressures have been determined over the univariant three-phase field $DyO_{1.5}$(s)–C(s)–DyC_2(s) by means of the dynamic effusion MS method, in the temperature range 1360–1590 K. The carbide phase was generated in situ by the carbothermic reduction of the oxide using a quadrupole mass spectrometer, the effusion pressure of carbon monoxide was monitored. The enthalpy of the carbothermic reduction reaction was calculated by second- and third-law methods. By combining the appropriate thermal functions and enthalpies of other constituents from standard thermodynamic tables, the enthalpy of formation of the dicarbide at 298 K has been calculated. The Gibbs energy of formation of the dicarbide in this temperature range has also been calculated. The recommended values of enthalpy and Gibbs energy of formation of DyC_2(s) at 298 K are $-(131 \pm 19)$ kJ mol^{-1} and $-(165 \pm 6)$ kJ mol^{-1}, respectively.

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1. Introduction

Dysprosium is a fission product representative of the heavy lanthanide group elements. High thermal neutron absorption cross-section, insignificant swelling and high melting points of its compounds make them suitable candidates for nuclear control rod materials. In continuation with our earlier programme [1–4] to generate thermodynamic data of solid rare-earth carbides in the temperature range 1200–1700 K, we present the results of dysprosium carbide in this paper.

The heavy lanthanide carbon systems starting from samarium to lutetium do not have a complete phase diagram, barring some information about the formation and the crystal structure of the carbides. The yttrium–carbon phase diagram is regarded as the best prototype for compounds of the heavy lanthanide elements with carbon [5]. The element dysprosium forms a number of binary carbides such as Dy_2C, $Dy_{15}C_{13}$, Dy_2C_3 and DyC_2. The DyC_2(s) is the carbide in equilibrium with free graphite. The phase transformation temperature of DyC_2(s) from α (CaC_2-type tetragonal form) to β (KCN-type cubic form) phase occurs at around 1573 K.

A few investigators have tried to study the thermodynamic properties of dysprosium dicarbide. Balducci et al. [6] determined the enthalpy of formation of DyC_2(s) by studying the vaporization of

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$DyC_2(s)$ by the Knudsen effusion mass spectrometric technique in the temperature range 2083–2500 K. The ion intensity of Dy^+ was measured from which the other thermodynamic data were derived. Anderson et al. [7] used a solid state calcium fluoride galvanic cell to determine the thermodynamic data of a number of rare earth carbides including $DyC_2(s)$ in the temperature range 1033–1263 K. Meschel and Kleppa [8] have determined the enthalpy of formation of $DyC_2(s)$ using a high-temperature direct synthesis calorimetric technique recently. A compilation of the thermodynamic data of all the rare earth carbides is available in the review article of Gschneidner and Calderwood [9]. Miedema et al. [10] have predicted the enthalpy of formation of $DyC_2(s)$ using a semi-empirical model.

As there is considerable discrepancy in the available thermodynamic data of dysprosium carbides, the thermodynamic data of the dicarbide, $DyC_2(s)$, was derived in the temperature range 1360–1590 K by the dynamic effusion MS method [11]. The dicarbide was generated in situ in a high-vacuum chamber (ultimate pressure 10^{-9} bar) from a mixture of $DyO_{1.5}$ and graphite as per the following reaction:

$$DyO_{1.5}(s) + 3.5C(s) = DyC_2(s) + 1.5CO(g). \qquad (1)$$

The equilibrium carbon monoxide pressure of the resulting phase field $DyO_{1.5}(s)$–$C(s)$–$DyC_2(s)$ was derived from the effusion pressure of CO(g) of the sintered pellet as determined by means of a quadrupole mass spectrometer(QMS). From the temperature dependence of the equilibrium carbon monoxide pressures, the Gibbs energy of formation of $DyC_2(s)$ and the enthalpy of formation of $DyC_2(s)$ at 298 K by second- and third-law treatments were derived, after taking appropriate data for $DyO_{1.5}(s)$, C(s) and CO(g) from the literature [12]. The derived data were then compared with the earlier reports in literature.

2. Experimental

$DyO_{1.5}(s)$ of 99.9% purity procured from M/s. Indian Rare-Earths, India and C(s) with a purity greater than 99.999%, were used for the preparation of the samples.

A stoichiometric mixture of $DyO_{1.5}(s)$ 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 using the quadrupole mass spectrometer (QMS). Details of the experimental procedure employed and the apparatus have been described in our earlier papers [1–4,11]. The procedure was repeated for four different runs. High-temperature XRD patterns of the initial oxide–graphite mixture were also recorded in the temperature range 1373–1773 K using a Phillips XPERT diffractometer.

3. Results and discussion

3.1. Confirmation of the phases

The high-temperature XRD patterns of the sample mixture are depicted in Fig. 1. These patterns indicate the presence of the $DyC_2(s)$ phase along with the oxide and graphite phase from 1373 K onwards up to 1773 K. The lattice constants of the tetragonal $DyC_2(s)$ at 298 K have been derived to

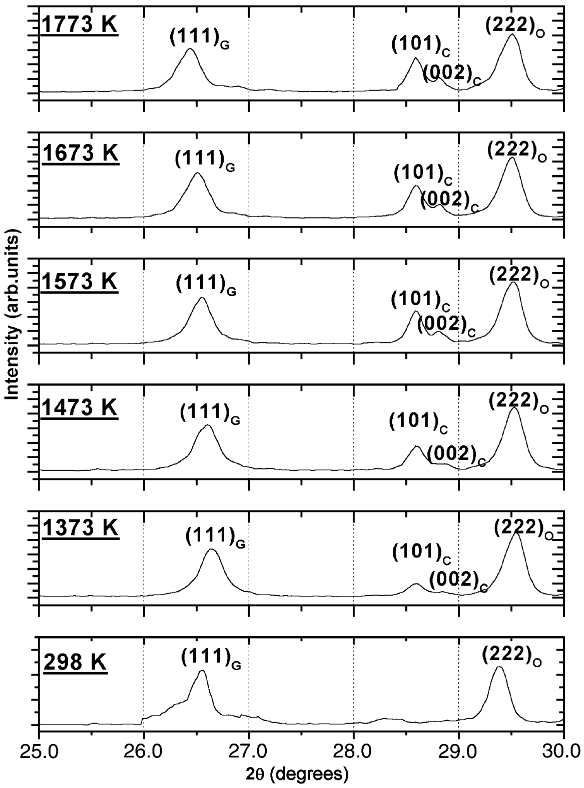

Fig. 1. High-temperature XRD patterns of the $DyO_{1.5}(s)$–$C(s)$–$DyC_2(s)$ three-phase field in the Dy–C–O system (subscripts indicate peaks due to various phases: G, graphite; O, $DyO_{1.5}$ and C, DyC_2).

be $a = 361$ pm and $c = 618$ pm. This result indicates the presence of the expected three-phase field $DyO_{1.5}$(s)–C(s)–DyC_2(s) in the entire temperature range of measurement, which is a requirement for making meaningful equilibrium CO(g) pressure determinations.

In the reaction of carbon with dysprosium oxide compounds such as $Dy_{15}C_{19}$(s) and Dy_2OC(s) are expected to be formed according to the studies of Hajek et al. [13]. The formation of these two compounds was prevented by taking a stoichiometric excess of graphite in the starting mixture, as the phase diagram as reported by Brozek et al. [14] indicates that $DyO_{1.5}$(s), C(s) and the DyC_2(s) cannot co-exist with $Dy_{15}C_{19}$(s) or the oxicarbide phase. Further, the XRD patterns also indicate the presence of the oxide, graphite and DyC_2(s) phases only in the entire experimental temperature range. This result proves the presence of only the expected phases at the time of measurement of equilibrium CO pressures.

3.2. Equilibrium CO pressure measurements

The equilibrium CO pressures recorded in the temperature range 1360–1590 K for this system are given in Table 1. The carbon monoxide pressures were plotted as a function of $1/T$ (Fig. 2) and were fitted to a straight line by the method of least squares. The fit equation was found to be

$$\ln p_{CO} = -(51\,282 \pm 1449)/T + (23.8 \pm 0.9) \times (p_{CO} \text{ in bar}). \tag{2}$$

The Gibbs energies of reaction (1) at different temperatures were then derived from the corresponding equilibrium constants. The Gibbs energies of formation of DyC_2(s) is calculated according to the following equation:

Table 1
Equilibrium CO(g) pressures over the three-phase field $DyO_{1.5}$(s)–C(s)–DyC_2(s) and the Gibbs energy of the reaction (1) at various temperatures and enthalpy of reaction at 298 K

Runs	Temperature (K)	Equilibrium CO pressure (bar)	$\Delta_r G^0$ of reaction 1 (kJ mol^{-1})	$\Delta_r H^0_{298}$ of reaction 1[a] at 298 K (kJ mol^{-1})		
				Based on CaC_2	Based on $UC_{1.94}$	Based on $ThC_{1.94}$
Run 1	1358	2.04E-07[b]	192.1	633.5	653.4	629.3
	1396	3.48E-07	185.5	626.0	646.8	622.4
	1434	9.17E-07	173.4	623.0	644.7	620.1
	1473	3.21E-06	157.8	634.9	657.5	632.7
	1511	5.42E-06	151.2	631.2	654.8	629.7
	1549	2.01E-05	134.9	624.5	649.1	623.9
Run 2	1358	1.87E-07	193.2	634.4	654.3	630.2
	1396	3.52E-07	185.3	626.5	647.3	623.0
	1434	8.97E-07	173.7	637.9	659.6	635.0
	1473	3.93E-06	155.2	634.3	656.9	632.1
	1549	2.04E-05	134.7	621.9	646.5	621.3
	1587	5.21E-05	123.0	624.3	649.8	624.5
Run 3	1358	1.66E-07	194.7	634.2	654.1	630.1
	1396	3.70E-07	184.7	626.2	647.0	622.7
	1434	7.72E-07	175.5	638.3	660.0	635.4
	1473	5.56E-06	150.9	633.9	656.6	631.8
	1511	2.05E-05	134.6	632.1	655.7	630.6
Run 4	1358	1.93E-07	134.4	624.0	648.6	623.4
	1396	8.55E-07	192.8	633.5	653.4	629.3
	1587	5.27E-05	174.2	625.6	646.4	622.1
	1434	3.11E-06	122.9	620.2	645.8	620.4
	1473	3.27E-06	158.1	626.6	648.3	623.8
	1511	5.60E-06	157.5	634.3	656.9	632.1
	1549	5.35E-05	150.8	631.3	654.9	629.8
	1587	5.68E-05	122.7	620.3	644.9	619.7

[a] Third-law results (the Gibbs energy functions of DyC_2(s) in each case have been derived from the corresponding functions of the carbide indicated).

[b] Read as 2.04×10^{-7}.

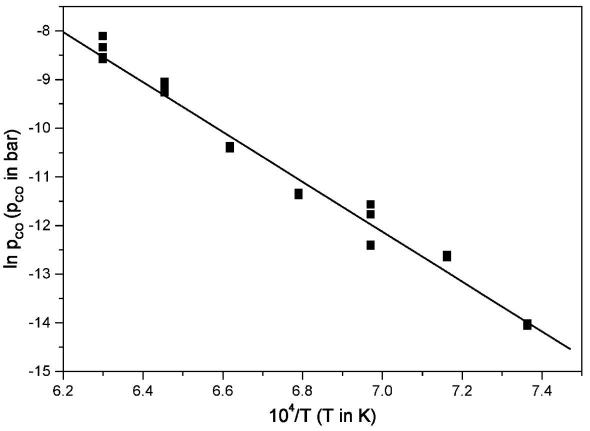

Fig. 2. Plot of ln p_{CO} of the $DyO_{1.5}$(s)–C(s)–DyC_2(s) phase field against reciprocal temperature.

$$2/3DyO_{1.5}(s) + 7/3C(s) = 2/3DyC_2(s) + CO(g) \quad \Delta_rG^0, \qquad (3)$$

$$2/3Dy(l) + 1/2O_2(g) = 2/3DyO_{1.5}(s), \quad \Delta_fG^0, \qquad (4)$$

$$2/3Dy(l) + 1/2O_2(g) + 7/3C(s) = 2/3DyC_2(s) + CO(g) \quad \Delta_rG^{0'}. \qquad (5)$$

The Gibbs energies of formation of DyC_2(s) at various temperatures were derived from the Gibbs energies of reaction (1) (listed in Table 1) using appropriate Gibbs energy of formation data of $DyO_{1.5}$(s) from the literature [12]. The Gibbs energy of formation of DyC_2(s) conforms to the equation:

$$\Delta_fG^0 DyC_2(s) = -110.3 - 0.027 * T, \ \text{kJ mol}^{-1}, \qquad (6)$$

in the temperature range 1360–1590 K.

3.3. Enthalpy of formation of $DyC_2(s)$

3.3.1. Second-law method

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. The enthalpy of the reaction was converted to the enthalpy of reaction at 298 K by including the enthalpy increments of $DyO_{1.5}$(s), C(s), CO(g) from the literature [12]. Thermal functions for DyC_2(s) were estimated by using the thermal functions of iso-structural CaC_2 [12], in order to compare the results in the present study with other literature reports wherein similar methodology has been used. The $\Delta_rH^0_T$ (T = 1473 K) and $\Delta_rH^0_{298}$ were found to be (640 ± 18) kJ mol^{-1} and (659 ± 18) kJ mol^{-1} respectively, for the reaction (1). The enthalpy increments of DyC_2(s) were also calculated using the corresponding thermal functions of $UC_{1.94}$ [12] and $ThC_{1.94}$ [12] and were used for deriving the enthalpy of reaction (1). The enthalpy of the reaction (1) at 298 K derived on the basis of the thermal functions of $UC_{1.94}$ and $ThC_{1.94}$ was found to be (676 ± 18) kJ mol^{-1} and (654 ± 18) kJ mol^{-1}, respectively.

3.3.2. Third-law method

The third-law enthalpy of reaction (1) was derived from the p_{CO} at each temperature and Gibbs energy functions of $DyO_{1.5}$(s), C(s), CO(g) from the literature [12] and DyC_2(s). The enthalpy of the reaction calculated by the third-law method for each equilibrium CO(g) pressure by deriving the Gibbs energy functions of DyC_2(s) from those of CaC_2 [12], $UC_{1.94}$ [12] and $ThC_{1.94}$ [12] have been listed in Table 1. From the table it is obvious that there is no significant temperature dependent variation of the third-law enthalpy of reaction indicating the reliability of the thermodynamic data obtained. The average of the enthalpy of the reaction at 298 K calculated by using the third-law method was found to be (651 ± 5) kJ mol^{-1}, (629 ± 5) kJ mol^{-1}, and (627 ± 5) kJ mol^{-1} based on the Gibbs energy functions of DyC_2(s) estimated from those of CaC_2 [12], $UC_{1.94}$ [12] and $ThC_{1.94}$ [12] respectively.

The enthalpy of formation of DyC_2(s) at 298 K was then derived from the enthalpy of reaction at 298 K, as determined in the present study and the enthalpy of formation of $DyO_{1.5}$(s), C(s) and CO(g) taken from the literature [12]. The enthalpy of formation of DyC_2(s) at 298 K as calculated using the thermal functions of DyC_2(s) derived from those of $UC_{1.94}$ is −(83 ± 18) kJ mol^{-1} (second-law) and −(130 ± 5) kJ mol^{-1} (third-law). The enthalpy of formation of DyC_2(s) at 298 K as calculated based on thermal functions of DyC_2(s) derived from those of $ThC_{1.94}$ is −(105 ± 18) kJ mol^{-1} (second-law) and −(132 ± 5) kJ mol^{-1} (third-law). Data on the enthalpy of formation of DyC_2(s) at 298 K available in the literature are compared with those obtained in the present study in Table 2.

Enthalpy of formation of DyC_2(s) at 298 K reported in the present study (derived from the thermal functions of DyC_2(s) and generated from the corresponding functions of CaC_2(s)) are agreeable within the limits of uncertainty with the results obtained by Anderson and Bagshaw [7]. The results of the present study are on the higher side in comparison to the reports of Meschel and Kleppa [8] Due to the variation in the thermal functions of $UC_{1.94}$(s) and $ThC_{1.94}$(s), a difference in the second

Table 2
Comparison of the enthalpies of formation of DyC_2(s) with the data available in the literature

Method/technique	$\Delta_f H^0_{298}$ (kJ mol^{-1})			References
	Second law	Third law	Selected	
Knudsen effusion MS	-46 ± 4	–	-46 ± 4	Balducci et al. [6]
EMF	–	-94.2 ± 10	-94.2 ± 10	Anderson et al. [7]
Calorimetry	–	–	-85.8 ± 6	Meschel et al. [8]
Calculation	–	–	-198	Niessen et al. [10]
CO pressure (dynamic effusion MS method)	-100 ± 18	-107 ± 5		Present study (from CaC_2)[a]
	-83 ± 18	-130 ± 5		(from $UC_{1.94}$)[a]
	-105 ± 18	-132 ± 5	-131 ± 19[b]	(from $ThC_{1.94}$)[a]

[a] The thermal functions of DyC_2(s) for calculation in the present study were derived from the corresponding thermal functions as mentioned. The thermal functions used for calculation by other workers are based on thermal functions CaC_2(s).

[b] Overall error in measurement.

Table 3
Comparison of the enthalpies of formation of various rare earth dicarbides derived using the dynamic effusion MS method

Dicarbide	$\Delta_f H^0_{298}$ (kJ mol^{-1}) based on the thermal functions of the dicarbide derived from the corresponding functions of						
	CaC_2(s)		$UC_{1.94}$(s)		$ThC_{1.94}$(s)		Selected value[b]
	Second law	Third law	Second law	Third law	Second law	Third law	
LaC_2 (s)[1]	-90.6 ± 8.4	-80.1 ± 3.6	-75.4 ± 8.4	-57.8 ± 3.6	-95.4 ± 8.4	-59.5 ± 3.6	-58.6 ± 10.1
CeC_2 (s)[3]	-95.5 ± 9.0	-96.8 ± 1.4	-80.1 ± 9.0	-118.8 ± 1.4	-100.1 ± 9.0	-121.4 ± 1.4	-120.1 ± 11.0
NdC_2 (s)[2]	-70.1 ± 8.6	-67.3 ± 1.0	-51.5 ± 8.6	-90.1 ± 1.0	-74.7 ± 8.6	-91.6 ± 1.0	-90.8 ± 6.0
SmC_2 (s)[4]	-72.0 ± 7.0	-75.0 ± 3.0	-56.0 ± 7.0	-84.0 ± 3.0	-76.0 ± 7.0	-86.0 ± 3.0	-85.0 ± 8.0
DyC_2 (s)[a]	-100 ± 18	-107 ± 5	-83 ± 18	-130 ± 5	-105 ± 18	-132 ± 5	-131 ± 19

[a] Present study.

[b] Overall error in the measurement.

and third-law enthalpy has been observed, as in previous reports [1–4]. Since there is a good agreement between the enthalpy of formation obtained in the present study by the second and third-law methods (derived from CaC_2), the differences arising in the case of $UC_{1.94}$(s) and $ThC_{1.94}$(s) may be attributed to the errors in the thermal functions in each case.

The third-law treatment is more widely acclaimed as it is evaluated for each and every experimental data point. It can be seen that the enthalpy of formation of DyC_2(s) at 298 K obtained by the third-law method using the thermal functions of DyC_2(s) and those of $UC_{1.94}$ and $ThC_{1.94}$ are in good agreement. Hence, the average of these two results, $-(131 \pm 19)$ kJ mol^{-1}, is chosen to be the recommended value for $\Delta_f H^0_{298}$ of DyC_2(s). The entropy of formation of DyC_2(s) at 298 K was found to be 106 J K^{-1} mol^{-1} (using the entropy increment of DyC_2(s) derived from those of CaC_2(s), which is close to the compiled data 103.77 J K^{-1} mol^{-1}) of Gschneidner et al. [9].

The enthalpy of formation of DyC_2(s) obtained in this study is compared with the corresponding values of other rare earth dicarbides, determined during our earlier course of experiments, as depicted in Table 3 [1–4]. The trend in the variation of the enthalpy of formation of the dicarbides is similar to the trend observed for the enthalpy of formation of the rare earth oxides, as can be seen from Fig. 3.

3.4. 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 $\Delta_f G^0$ measurements is about 6 kJ mol^{-1}. The enthalpy and Gibbs energy functions of $DyO_{1.5}$(s), C(s) and CO(g) have been taken from well established data bases, while the functions of DyC_2(s) are estimated as experimental data are not available. The error in the enthalpy measurements by using second-law

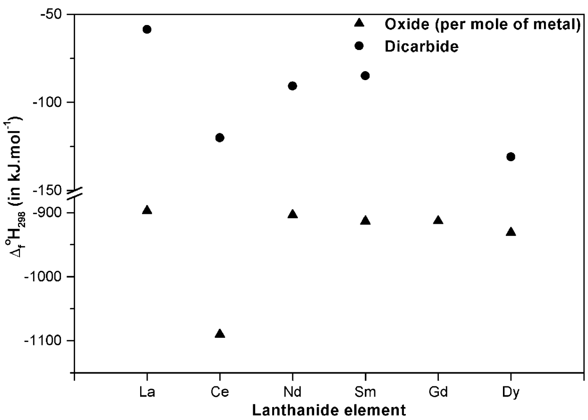

Fig. 3. Comparison of $\Delta_fH^0_{298}$ of some oxides and dicarbides of lanthanide elements.

treatment is about 18 kJ mol^{-1} and by third-law analysis is about 5 kJ mol^{-1}. Considering the error in Δ_fG^0, the overall error in the reported enthalpy of formation is about 19 kJ mol^{-1}.

4. Summary

The equilibrium carbon monoxide pressures over the three-phase mixture of $DyO_{1.5}$(s), C(s) and DyC_2(s) were measured in order to arrive at the thermodynamic data on DyC_2(s). The recommended value of enthalpy of formation and Gibbs energy of formation of DyC_2(s) at 298 K are $-(131 \pm 19)$ kJ mol^{-1} and $-(165 \pm 6)$ kJ mol^{-1} respectively.

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