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Journal of Nuclear Materials 295 (2001) 228–232

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Enthalpy and Gibbs energy of formation of neodymium dicarbide

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Received 11 September 2000; accepted 3 March 2001

Abstract

CO partial pressures over the univariant three-phase region containing $NdO_{1.5}(s)$, C(s) and $NdC_2(s)$ were measured by using a quadrupole mass spectrometer (QMS) between 1403 and 1588 K. The $NdC_2(s)$ phase was generated in situ starting from a mixture of $NdO_{1.5}(s)$ and C(s). The second-law and third-law enthalpies of the reaction $NdO_{1.5}(s) + 3.5\ C(s) = NdC_2(s) + 1.5\ CO(g)$ at 298 K were calculated. The enthalpy of formation of $NdC_2(s)$ was derived from the enthalpy of reaction and the enthalpies of formation of $NdO_{1.5}(s)$ and CO(g) taken from the literature. The Gibbs energy of formation of $NdC_2(s)$ was derived from the Gibbs energy of formation of $NdO_{1.5}(s)$ and CO(g) from the literature. The third-law enthalpy of the reaction is (648.1 ± 1.0) and (647.6 ± 1.0) kJ mol^{-1} based on thermal functions of $NdC_2(s)$ derived from those of $UC_{1.94}$ and $ThC_{1.94}$, respectively. The recommended enthalpy and Gibbs energy of formation of $NdC_2(s)$ at 298 K are $-(90.8 \pm 6.0)$ and $-(122.2 \pm 6.0)$ kJ mol^{-1}, respectively.

1. Introduction

Neodymium is an important fission product owing to its high fast fission yield of about 15% [1]. Although a complete phase diagram is not available for the Nd–C binary system, its features are generally similar to that of La–C [2]. Typical of a light lanthanide–carbon system, the existence of a dicarbide (NdC_2) and a sesquicarbide (Nd_2C_3) is observed in the Nd–C system. There are also reports of a high-temperature $NdC_4(g)$ phase [3]. Like the lanthanum dicarbide, the neodymium dicarbide is also expected to exist in two types of modification, the high-temperature β-$NdC_2(s)$ having a cubic CaF_2-type structure with the space group $Fm\bar{3}m$, and the room temperature α-$NdC_2(s)$ having a tetragonal structure of the CeC_2-type with the space group I4/mmm. The transformation temperature of $NdC_2(s)$ from α to β phase is reported to be about 1423 K [2]. Precise information on the solubility of oxygen in $NdC_2(s)$ is not available, though oxycarbides are reported to exist. A detailed XRD pattern of cubic β-$NdC_2(s)$ is not available in the literature.

The vaporisation behaviour and the composition of the vapour in rare-earth metal–carbon systems have been studied extensively. Gschneidner et al. [4] have compiled the thermodynamic data of all the rare-earth carbides, nitrides and sulphides in the year 1971, based on the available data till then. Adachi et al. [5] have reviewed the available information up to 1991 on thermodynamic and other physical properties of rare-earth carbides. Chupka et al. [6] pointed out the pseudo-oxygen character of the C_2^{2-} radical, and showed the similarity between the bonding enthalpies of R–O and R–C_2. De Maria et al. [7] have investigated the gas phase in thermodynamic equilibrium with the condensed neodymium–carbon systems by means of a combined Knudsen-cell mass-spectrometric technique in the temperature range 1950–2160 K. They have apportioned the apparent vapour pressures to the partial pressures of Nd(g) and $NdC_2(g)$ from the ratio of Nd(g)/$NdC_2(g)$ reported De Maria et al. [7]. The vaporisation pattern of

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0022-3115/01/$ - see front matter
PII: S0022-3115(01)00537-2

the $NdC_4(g)$ molecule was studied by using a Knudsen-cell mass spectrometric technique in the temperature range 2210–2350 K by Balducci et al. [3].

There are only two reports available on the thermodynamic data of $NdC_2(s)$. Faircloth et al. [8] have obtained the apparent vapour pressure data in the temperature range 1670–2330 K by employing the Knudsen effusion target collection method and using neodymium dicarbide as the starting sample. Anderson et al. [9] have obtained the thermodynamic data for neodymium dicarbide from a study of the two-phase dicarbide/carbon region employing a solid state galvanic cell with calcium fluoride solid electrolyte in the temperature range 900–1300 K. There is a discrepancy of about 35 kJ mol^{-1} in the reported enthalpy of formation data of $NdC_2(s)$ at 298 K. The Gibbs energy variation with temperature reported by the two workers are in opposite directions. The aim of this work is to determine the enthalpy and Gibbs energy of formation data of $NdC_2(s)$ by a relatively simple method in the temperature range 1403–1588 K, where no other experimental data are available.

The rare-earth dicarbides are usually prepared by arc-melting the metal powder with graphite, or by reduction of the fluorides with barium in carbon crucibles. These methods are expensive and time consuming. Carbothermic reduction of the oxide is by far the well established method for synthesising a carbide which is simple as well as cost effective [10]. A well defined phase diagram for the Nd–C–O system is not available in the literature. Nevertheless, a phase diagram similar to the one proposed for Sm–C–O system can be assumed in this case also [11]. The phase diagram indicates the presence of oxycarbide phases like $NdO_{0.5}C_{0.4}(s)$ and $Nd_2O_2C_2(s)$ and $Nd_4O_3C(s)$. Though there is no report either on the formation or properties of $NdO_{0.5}C_{0.4}(s)$, there is a report on the preparation and some properties of $Nd_2O_2C_2(s)$ by Butherus et al. [12]. They have measured the CO(g) partial pressures over the three-phase field $NdO_{1.5}(s)$–$Nd_2O_2C_2(s)$–C(s) in the temperature range 1700–2200 K. Butherus et al. [13] have also studied the formation of $NdO_{0.5}C_{0.4}(s)$, and have reported an fcc structure with $a = 514.07$ pm for the compound. No other systematic study on vapour pressure measurements have been reported.

In continuation of our studies to generate thermodynamic data on rare-earth carbide systems [14,15], the enthalpy and Gibbs energy of formation of neodymium dicarbide were determined employing a new method [16]. In the present study, the dicarbide was generated in situ in a high-vacuum chamber (ultimate pressure 10^{-9} bar) from a mixture of $NdO_{1.5}$ and graphite according to Eq. (1):

$$NdO_{1.5}(s) + 3.5C(s) = NdC_2(s) + 1.5CO(g) \quad (1)$$

The equilibrium carbon monoxide pressure of the resulting phase field $NdO_{1.5}(s)$–C(s)–$NdC_2(s)$ was determined by measuring the effusion pressure of carbon monoxide from the sintered pellet by means of a quadrupole mass spectrometer (QMS). From the temperature dependence of the equilibrium carbon monoxide pressures, the enthalpy and the Gibbs energy of formation of $NdC_2(s)$ were derived by taking the corresponding data of $NdO_{1.5}(s)$, C(s) and CO(g) from the literature [17]. The derived thermodynamic data are also compared with those available in the literature.

2. Experimental

$NdO_{1.5}(s)$ of 99.99% purity procured from M/s. Koch Light Laboratories, UK, and C(s) with a purity greater than 99.999%, were used for the preparation of the samples.

A stoichiometric mixture of $NdO_{1.5}(s)$ 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 the QMS. Details of the experimental procedure employed and the apparatus have been described in our earlier papers [14,16].

3. Results

3.1. Errors in measurement

The uncertainty in the experimental values of the Gibbs energy and enthalpy of formation of the carbides as presented in this paper are the standard deviations in the least-squares regression analysis. Uncertainties in the measurement of the pressure and temperature are the main sources of random errors. The Gibbs energy of formation is derived from the expression

$$\Delta_f G^\circ = 1.5RT \ln p_{\mathrm{CO}}, \quad (2)$$

where $p_{\mathrm{CO}} = p_O Tk^{-1}\mathrm{C}$. Taking differentials,

$$\mathrm{d}(\Delta_f G^\circ) = (\delta \Delta_f G^\circ/\delta T)\,\mathrm{d}T + (\delta \Delta_f G^\circ/\delta \ln p)\,\mathrm{d}\ln p.$$

Both the terms constitute the random errors in the measurement. The enthalpy of formation of $NdC_2(s)$ is derived from $\Delta_f G^\circ$ by second-law and third-law methods. The error in enthalpy measurements is due to the error in $\Delta_f G^\circ$, the error in the enthalpy functions (in the case of second-law analysis) and the error in Gibbs energy functions (in the case of third-law analysis).

The uncertainty in the temperature is (±3 K), and the error in the pressure measurements for different samples

Table 1
Equilibrium CO(g) pressures over the phase mixture $NdO_{1.5}(s)$–C(s)–$NdC_2(s)$ and the Gibbs energy and enthalpy of reaction as a function of temperature

Temp. (K)	Equilibrium CO pressure (bar)	$\Delta_r G^\circ$ of reaction 1 (kJ mol^{-1})	$\Delta_r H^\circ_{298}$ of reaction[a] at 298 K (kJ mol^{-1})
1403	6.09E-7[b]	250.3	670.3
1453	2.35E-6	234.8	670.1
1503	6.67E-6	223.3	670.7
1503	8.59E-6	218.6	670.8
1508	8.36E-6	219.8	671.5
1513	1.08E-5	215.7	670.4
1553	2.99E-5	201.7	671.4
1583	4.19E-5	199.0	672.9
1588	4.67E-5	197.4	669.2
Average $\Delta_r H^\circ_{298}$ of reaction 1 = (670.8 ± 1.0) kJ mol^{-1}			

[a] Third-law results (based on thermal functions of $CaC_2(s)$).
[b] Read as 6.09×10^{-7}.

heated to the same temperature is less than 5%, based on our data. The error in the $\Delta_f G^\circ$ measurements assuming all these factors is about 5 kJ mol^{-1}. The enthalpy and Gibbs energy functions of $NdO_{1.5}(s)$, C(s) and CO(g) have been taken from the well established data base, while the functions of $NdC_2(s)$ are estimated as experimental data are not available. The error in the enthalpy measurements by using second-law treatment is about 9 kJ mol^{-1} and by third-law analysis is about 1 kJ mol^{-1}. Considering the error in $\Delta_f G^\circ$, the overall error in the third-law enthalpy is about 6 kJ mol^{-1}.

3.2. Gibbs energy of formation of $NdC_2(s)$

The effusion pressures of carbon monoxide recorded in the temperature range 1403–1588 K are given in Table 1. The carbon monoxide pressure was plotted as a function of $1/T$ (Fig. 1) and fitted to a straight line by the method of least-squares. The fitted equation was found to be (p_{CO} in bar)

$$\ln p_{CO} = -(53013 \pm 698)/T + (23.5 \pm 0.5). \quad (3)$$

The Gibbs energy of reaction (1) at different temperatures was then derived from the respective equilibrium constants. The Gibbs energy of formation of $NdC_2(s)$ at various temperatures was derived from the Gibbs energy of reaction (1) by using appropriate Gibbs energy of formation data of $NdO_{1.5}(s)$ and CO(g) from the literature [17]. A comparison of Gibbs energies of formation of $NdC_2(s)$ with the data available in the literature is indicated in Fig 2.

3.3. Enthalpy of formation of $NdC_2(s)$

The second-law enthalpy of reaction (1) at the mid temperature of measurement was obtained from the slope of the $\ln p_{CO}$ vs $1/T$ curve. This was converted to the enthalpy at 298 K by taking the enthalpy increments of $NdO_{1.5}(s)$, C(s), CO(g) from the literature [16]. Thermal functions for $NdC_2(s)$ were estimated as sug-

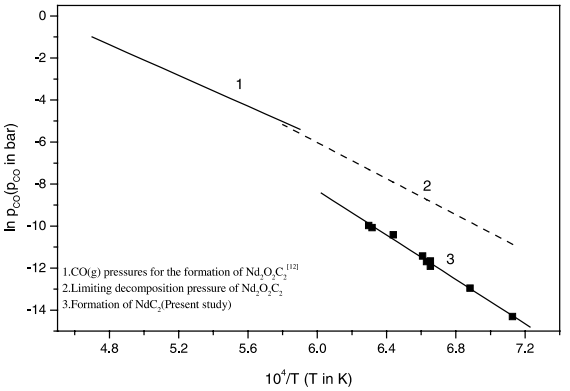

Fig. 1. A plot of equilibrium CO(g) pressure as derived for reaction (1) against reciprocal temperature.

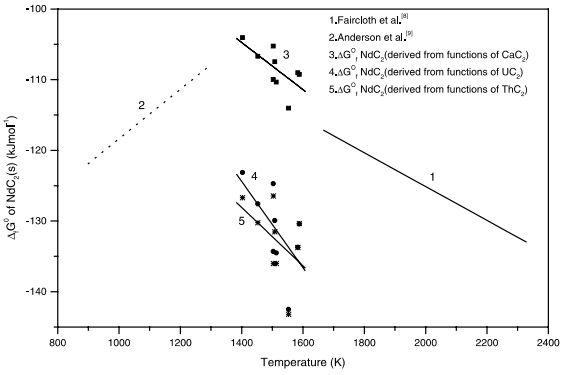

Fig. 2. A comparison of the Gibbs energy of formation of $NdC_2(s)$ obtained from the present study (calculated from thermal functions of CaC_2) with literature reports.

Table 2
Comparison of the enthalpy of formation of $NdC_2(s)$ with the literature data

Method/technique	$\Delta_f H^\circ$ at 298 K (kJ mol^{-1})			Reference
	Second law	Third law	Selected	
Knudsen effusion	−52.3±10	-58.6 ± 1.6	-52.3 ± 10	Faircloth et al. [8]
EMF	−153.4	−88.1	−88.1	Anderson et al. [9]
CO pressure				Present study
	−70.1±8.7	-67.3 ± 1.0		(from CaC_2)[a]
	−51.5±8.7	-90.1 ± 1.0		(from $UC_{1.94}$)[a]
	−74.7±8.7	-91.6 ± 1.0	-90.8 ± 6.0[b]	(from $ThC_{1.94}$)[a]

[a] The thermal functions of $NdC_2(s)$ used for calculation in the present study were derived from the corresponding thermal functions as mentioned, while the other experimentators have derived them based on the thermal functions of NdC_2 as deduced from those of $CaC_2(s)$.
[b] Recommended value with the overall estimated error in the measurement.

gested by Faircloth et al. [8]. The $\Delta_r H^\circ_T$ and $\Delta_r H^\circ_{298}$ were found to be (661.1 ± 8.7) and (668.0 ± 8.7) kJ mol^{-1}, respectively. Similarly, the third-law enthalpy of reaction (1) was derived from p_{CO} at each temperature and the Gibbs energy functions of $NdO_{1.5}(s)$, C(s), CO(g) from the literature [17] and $NdC_2(s)$ as suggested by Faircloth et al. [8]. The enthalpy data calculated using the third-law method at each temperature of measurement are listed in Table 1. The average of the enthalpy of the reaction was found to be (670.8± 1.0) kJ mol^{-1}.

The enthalpy increments and Gibbs energy functions of $NdC_2(s)$ were also calculated by using the corresponding thermal functions of $UC_{1.94}$ [17] and $ThC_{1.94}$ [17] and were used for deriving the enthalpy of reaction (1) using the second-law and third-law methods, respectively. The enthalpy of the reaction derived using the second-law method was found to be (686.6 ± 8.7) and (663.4 ± 8.7) kJ mol^{-1}, respectively. The average enthalpy of reaction using the third-law method was determined to be (648.1 ± 1.0) and (647.6 ± 1.0) kJ mol^{-1}, respectively.

The enthalpy of formation at 298 K for $NdC_2(s)$ was then derived from the enthalpy of reaction (1), as determined in the present study and the enthalpy of formation of $NdO_{1.5}(s)$, C(s) and CO(g) have been taken from the literature [17]. Data on the enthalpy of formation of $NdC_2(s)$ at 298 K available in the literature are compared with those obtained in the present study (calculated using the thermal functions of $NdC_2(s)$ derived from the thermal functions of CaC_2, $UC_{1.94}$ and $ThC_{1.94}$) in Table 2.

4. Discussion

The XRD pattern of the sample indicated the presence of the three-phase mixture $NdO_{1.5}(s)$, $NdC_2(s)$ and C(s). The lattice parameters of $NdC_2(s)$ were deduced to be $a = 382$ pm and $c = 640$ pm. The $Nd_2O_2C_2(s)$ phase is one of the oxycarbides known, and it exhibits a monoclinic symmetry [12] while $NdC_2(s)$ has a tetragonal structure below 1423 K. The absence of $Nd_2O_2C_2(s)$ peaks in the XRD pattern of the present study indicated that the measurements were carried out in the $NdO_{1.5}(s)$–$NdC_2(s)$–C(s) phase field and not in the $NdO_{1.5}(s)$–$Nd_2O_2C_2(s)$–C(s) phase field. The p_{CO} values as a function of temperature, reported by Butherus et al. [12], for the phase field $NdO_{1.5}(s)$–$Nd_2O_2C_2(s)$–C(s), are indicated in Fig 1 along with the data obtained in the present study. It can be seen from the plot that the p_{CO} values obtained in the present study are lower in the entire temperature range of measurement. For example at 1600 K, p_{CO} over the three-phase field $NdO_{1.5}(s)$–$Nd_2O_2C_2(s)$–C(s) is 1.3×10^{-3} bar ($\ln p_{CO} = -6.672$) as compared to 6.48×10^{-5} bar ($\ln p_{CO} = -9.643$) over the phase field $NdO_{1.5}(s)$–$NdC_2(s)$–C(s). The limiting pressures for the decomposition of $Nd_2O_2C_2(s)$ to $NdC_2(s)$ have been calculated based on the results from the present study and those of Butherus et al. [12] and have been plotted in Fig 1. The lower p_{CO} pressures obtained in the present study are taken as a confirmation of absence of the oxycarbide phase. Though another oxycarbide phase like $NdO_{0.5}C_{0.4}(s)$ is expected based on the studies of Haschke et al. [11], no systematic study on the crystal data or vaporisation studies of this compound are available for comparison with our results.

A comparison of the Gibbs energy of formation of $NdC_2(s)$ obtained in the present study (calculated using the thermal functions of NdC_2 derived from those of CaC_2) with the literature reports is given in Fig 2 From the figure it is obvious that there is a lot of scatter in the reported data. The results of Anderson et al. [9] show a very steep temperature variation of the Gibbs energy of formation. The slope has an opposite sign. When extrapolated to higher temperatures, it can be seen that the Gibbs energy of formation of $NdC_2(s)$ obtained in the present study is within the error limits of the results of Faircloth et al. [8]

The calculated second-law and third-law enthalpies (based on the thermal functions of NdC_2 derived from those of CaC_2) of reaction (1) obtained from the present study are in good agreement with each other. As it can be seen from Table 1, there is no significant temperature dependent variation of the third-law enthalpy of reaction indicating the reliability of the thermodynamic data obtained.

Faircloth et al. [8] apportioned the total pressure, measured over $NdC_2(s)$, between p_{Nd} and p_{NdC_2} by taking the ratio of Nd/NdC_2 as reported by De Maria et al. [5] The second-law and third-law enthalpies of the reaction

$$NdC_2(s) = Nd(g) + C(s) \quad (4)$$

derived by Faircloth et al. [8] differed by about 6 kJ mol^{-1}, which is reflected in the enthalpy of formation reported by them (see Table 2). They have chosen the enthalpy of formation obtained by the second-law method as the recommended value. Faircloth et al. [8] have obtained the $NdC_2(s)$–C(s) phases by heating the mixture of neodymium and graphite in a Knudsen-cell above 2000 K. At such temperatures, the possibility of the formation of non-stoichiometric $NdC_2(s)$, cannot be completely ruled out. The thermodynamic data derived by Faircloth et al. [8] are from total pressure measurements, and the partial pressure data are assumed to be sensitive to the Nd/NdC_2 ratio.

Anderson et al. [9] have measured the thermodynamic data by using an EMF technique. There is a large disagreement between second-law (-153.4 kJ mol^{-1}) and third-law (-88.1 kJ mol^{-1}) results of their study (see Table 2). Anderson et al. [9] analysed their data in detail to explain this difference and recommended their third-law value. As discussed earlier, the entropy of formation has an opposite sign. As indicated by the authors, caution should be exercised in using galvanic cells to determine reliable thermochemical information on refractory materials. Unless the cells are operating under conditions of complete inner equilibrium, which usually implies a fairly high temperature, Anderson et al. [9] suggest the practice of other techniques like vaporisation and gas buffer equilibration.

As described in the earlier paper [16], it is necessary to calculate the enthalpy of formation of NdC_2, based on the thermal functions of NdC_2 derived from those of $UC_{1.94}$ and $ThC_{1.94}$, by using second-law and third-law methods. The enthalpy of formation of NdC_2 at 298 K as calculated using the thermal functions of NdC_2 derived from those of $UC_{1.94}$ is $-(51.5 \pm 8.7)$ (second law) and $-(90.1 \pm 1.0)$ kJ mol^{-1} (third law). The enthalpy of formation of NdC_2 at 298 K as calculated based on thermal functions of NdC_2 derived from those of $ThC_{1.94}$ is $-(74.7 \pm 8.7)$ (second law) and $-(91.6 \pm 1.0)$ kJ mol^{-1} (third law). It can be seen that the enthalpy of formation of NdC_2 at 298 K by the third-law method using the thermal functions of NdC_2 and those of $UC_{1.94}$ and $ThC_{1.94}$ are in good agreement. Hence, the average of these two results, $-(90.8 \pm 6.0)$ kJ mol^{-1}, is chosen to be the recommended value for $\Delta_f H^\circ_{298}$ of $NdC_2(s)$.

5. Summary

The equilibrium carbon monoxide pressures over the three-phase mixture of $NdO_{1.5}(s)$, C(s) and $NdC_2(s)$ were measured in order to arrive at the thermodynamic data on $NdC_2(s)$. The enthalpy of formation and the Gibbs energy of formation of $NdC_2(s)$ at 298 K recommended in the present study are $-(90.8 \pm 6.0)$ and $-(122.2 \pm 6.0)$ kJ mol^{-1}, respectively.

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