ELSEVIER

Journal of Alloys and Compounds 217 (1995) 235–239

Journal of
ALLOYS
AND COMPOUNDS

Standard enthalpies of formation of some neodymium and gadolinium carbides, silicides and germanides by high-temperature direct-synthesis calorimetry

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Received 1 July 1994

Abstract

The standard enthalpies of formation of some congruent-melting compounds in the binary systems Nd + X and Gd + X (where X = C, Si, Ge) have been determined by direct-synthesis calorimetry at 1473 ± 2 K. The following values of ΔH_0^f (kJ/g.atom) are reported: NdC_2, −29.2 ± 1.4; $NdSi_2$, −62.0 ± 1.9; NdSi, −78.7 ± 2.5; Nd_5Ge_3, −72.1 ± 1.6; $NdGe_{1.6}$, −80.2 ± 1.9; GdC_2, −24.8 ± 1.6; Gd_5Si_3, −68.0 ± 2.3; $GdSi_2$, −59.0 ± 2.1; Gd_5Ge_3, −82.0 ± 2.6. The results are compared with some earlier experimental data (all derived from e.m.f. or vapor pressure measurements), with predicted values from Miedema's semi-empirical model, and with earlier calorimetric data for NdX_3 and GdX_3 (where X = Sn, Pb).

Keywords: Enthalpies of formation; Neodymium; Gadolinium; High temperature direct synthesis calorimetry

1. Introduction

During very recent years we have pursued systematic studies of the enthalpies of formation of rare-earth carbides, silicides and germanides based on high-temperature direct-synthesis calorimetry. These investigations started with the work of Topor and Kleppa [1,2] on some characteristic silicides of the Group III metals, and of Jung and Kleppa [3] on the corresponding germanides. In the past year our study has been extended by the present authors to the enthalpies of formation of the Group III carbides [4], and most recently to the carbides, silicides and germanides of the lanthanide metals cerium and praseodymium [5]. In the present investigation we are extending our work to the carbides, silicides and germanides of neodymium and gadolinium.

The information in the literature regarding the phases considered is less extensive than for the corresponding La, Ce and Pr compounds. For example, there are no established phase diagrams for the Nd + C and the Gd + C systems [6]. However, the structural properties are quite adequately covered [7–12]. The published literature offers some enthalpy of formation values for the carbides, and also for some of the silicides, but very little for the germanides [13–18]. All the earlier data were obtained by e.m.f. and mass spectrometric methods; we found no calorimetric values for the compounds which we studied.

We will compare our results with the published e.m.f. and vapor pressure values in the literature and with predictions based on Miedema's semi-empirical model [19]. We shall also compare our results for the carbides with our new data for the silicides and germanides and with calorimetric data for compounds of Nd and Gd with Sn and Pb reported by Palenzona [20], by Palenzona and Cirafici [21] and by Bacha et al. [22].

Our new data allow us to make a quantitative comparison of the enthalpies of formation for carbides, silicides and germanides for five lanthanide elements from La to Gd. The data also enable us to further test the systematic correlation of the heats of formation of the lanthanide elements considered with the five elements in the IVb column of the periodic table (5).

2. Experimental details and materials

The experiments were carried out at 1473 ± 2 K in a single-unit differential microcalorimeter which has been described in an earlier communication from this laboratory [23]. All the experiments were performed under a protective atmosphere of argon gas, purified

SSDI 0925-8388(94)01342-X

by passing it over titanium chips at about 900 °C. A boron nitride crucible was used to contain the samples.

All the materials were purchased from Johnson Matthey/Aesar, Ward Hill, MA; Nd and Gd were in ingot form. The purities of the samples ranged from 99.0% for carbon to 99.999% for germanium. The particle sizes of the powders used were about −80 mesh for the Nd and Gd metals, −150 mesh for Ge, −300 mesh for C and −325 mesh for Si. The Nd and Gd samples were hand-filed from the ingots immediately prior to the preparation of the sample pellets, to avoid as much as possible oxidation by air. The carbon was in the crystalline graphite modification. As purchased, the Ge had an average particle size of −10 mesh. We ground this sample in an agate mortar and sifted it through a 150-mesh sieve to obtain a suitable particle size for the calorimetric experiments.

The two components were carefully mixed in the appropriate molar ratio, pressed into 4-mm pellets, and dropped into the calorimeter from room temperature. In a subsequent set of experiments the reaction products were also dropped into the calorimeter from room temperature in order to measure their heat contents. Between the two sets of experiments the samples were kept in a vacuum dessicator to prevent reaction with oxygen or moisture.

Calibration of the calorimeter was achieved by dropping weighed segments of 2-mm high-purity copper wire from room temperature into the calorimeter at 1473±2 K. The enthalpy of pure copper at this temperature, 46 465 J/g.atom, was obtained from Hultgren et. al. [24]. The calibrations were reproducible to within ±1.2%.

The reacted samples were examined by X-ray diffraction to assess their structures and to ascertain the absence of unreacted metals. When possible, the samples were also subjected to scanning electron microscopy (SEM) and X-ray microprobe analyses. As we noted in our earlier communication [4], the rare-earth carbides cannot be tested by this method, since they decompose on mounting.

There is no published phase diagram for the Nd+C system; however, some structural data are reported [6]. The melting point of NdC_2 is estimated to be 2260 °C [13]. This compound undergoes a structural transformation from tetragonal to cubic at a temperature of about 1150±20 °C. Only the structure of the low-temperature modification is known. We prepared NdC_2 according to the procedure which we described in detail for other rare-earth carbides in our earlier communication [4]. The X-ray diffraction pattern of this phase agreed well with that of the tetragonal modification in the ASTM Powder Diffraction File. There was no evidence for the presence of unreacted metal or other carbide phases. However, we observed a small amount of Nd_2O_3, approximately 1%.

The phase diagram of the Nd+Si system shows two congruently melting phases: $NdSi_2$, which melts at 1757 °C, and NdSi, melting at 1677 °C [6]. We prepared both compounds in the calorimeter. The X-ray diffraction pattern of $NdSi_2$ showed good agreement with the pattern of the orthorhombic, low-temperature modification of this stoichiometry. Since the ASTM Powder Diffraction File listed only the pattern of the high-temperature, tetragonal modification, we generated the pattern for the low-temperature modification from the unit-cell parameters for $NdSi_2$ and the atomic coordinates for $GdSi_2$. These coordinates are not available for $NdSi_2$ [25]. There was no evidence for the presence of unreacted metal or any other phase in the reaction product. Even Nd_2O_3 was not detected within our limits. SEM and X-ray microprobe analyses confirmed that $NdSi_2$ was single-phase. The X-ray diffraction pattern of NdSi indicated the presence of about 5% $NdSi_2$.

The phase diagram of the Nd+Ge system shows two congruently melting phases: Nd_5Ge_3, melting at 1580 °C, and $NdGe_{2-x}$, melting at 1487 °C [6]. Massalski et al. report that the latter compound exists as a single phase at $X_{Ge}=0.60$–0.616, corresponding to a ratio $X_{Ge}/X_{Nd}=1.6$ [6]. The X-ray diffraction patterns of both phases showed that there were no unreacted metals and that only the dominant phases were present. These patterns agreed well with the patterns in the ASTM Powder Diffraction File. $NdGe_{1.6}$ undergoes a transformation from an orthorhombic to a tetragonal structure at 615–680 °C [6]. We observed only the tetragonal modification. SEM and X-ray microprobe analyses confirmed that both Nd_5Ge_3 and $NdGe_{1.6}$ were single-phase structures.

There is no published phase diagram for the Gd+C system [6]. However, some structural data are reported [10]. For GdC_2, only the structure of the room-temperature, tetragonal modification is known. Our X-ray diffraction pattern showed good agreement with this pattern in the ASTM Powder Diffraction File. However, we observed a small amount of a second phase, about 5% or less of Gd_2C_3.

The published phase diagram for the Gd+Si system is a composite of several studies [6]. Four congruently melting phases are reported; however, the melting points are given only for two of these. We selected Gd_5Si_3 and $GdSi_2$, which melt congruently at 1650 °C and 2100 °C, respectively, for study [6]. The X-ray diffraction patterns of both compounds showed excellent agreement with the patterns in the ASTM Powder Diffraction File. There was no evidence for the presence of unreacted metal, or of other phases, and we did not find Gd_2O_3.

The phase diagram for the Gd+Ge system shows only one congruently melting phase, Gd_5Ge_3, which melts at 1790 °C [6]. Our X-ray diffraction pattern of this compound showed excellent agreement with the pattern in the ASTM Powder Diffraction File. There was no evidence for the presence of unreacted metal or of other phases.

3. Results and discussion

The standard enthalpies of formation of the rare-earth carbides, silicides and germanides determined in this study were obtained as the difference between the results of two sets of measurements. In the first set the following reaction took place in the calorimeter:

$$\text{RE(s,298 K)} + m\text{X(s,298 K)} = \text{REX}_m(s\text{,1473 K}) \qquad (1)$$

Here m represents the molar ratio X/RE, RE is the considered rare earth metal, X represents C, Si or Ge and s denotes solid. The reaction pellets were reused in a subsequent set of measurements to determine their heat contents:

$$\text{REX}_m(s\text{,298 K}) = \text{REX}_m\text{(s,1473 K)} \qquad (2)$$

The standard enthalpy of formation is given by:

$$\Delta H_f^0 = \Delta H(1) - \Delta H(2) \qquad (3)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes per gram atom associated with reactions (1) and (2).

The experimental results are summarized in Table 1. The heat effects associated with reactions (1) and (2) are given in kJ/g.atom as the averages of 5–7 consecutive measurements with the appropriate standard deviations. The last column shows the standard enthalpies of formation of the phases considered. The standard deviations in this column also reflect a contribution from the uncertainties in the calibrations.

Even though the melting point of Nd_5Ge_3 was listed as 1580 °C, we found that the sample melted in the crucible and could not be removed. In order to measure the heat content we prepared Nd_5Ge_3 by arc-melting on a water-cooled copper hearth. This sample was tested by X-ray diffraction and SEM as mentioned previously.

Table 2 compares the standard enthalpies of formation reported in the present work with experimental values from the published literature and with predicted values from Miedema's semi-empirical model [19]. It should be noted that all the earlier experimental data were derived from e.m.f. or vapor pressure measurements. We found no calorimetric data in the literature.

Our value for the heat of formation of NdC_2 agrees very well with the value of Anderson and Bagshaw based on e.m.f. measurements [26], but differs considerably from the vapor pressure value of Faircloth et al. [27]. No detailed comparison can be made for $NdSi_2$, $NdGe_{1.6}$ and $GdSi_2$, since the reported enthalpy values are not referred to room temperature [16–18]. We found no enthalpies of formation for NdSi, Nd_5Ge_3, Gd_5Si_3 and Gd_5Ge_3. However, our value for Gd_5Ge_3 is quite comparable with the value for $GdGe_{1.63}$ determined by the e.m.f. method [17] (−80.2 kJ/g.atom). Our enthalpy of formation for GdC_2 is less exothermic than the values based on e.m.f. and on mass spectrometry [26,28].

Table 2 shows that Miedema's predicted values are in reasonable agreement with our measurements for $NdSi_2$, NdSi, Nd_5Ge_3, $NdGe_{1.6}$ and Gd_5Si_3. However, for $GdSi_2$ the predicted value is more exothermic, while for Gd_5Ge_3 it is less exothermic than the experimental values. As we noted already in our earlier work, the predicted values for the carbides are very different from our experimental values [4,5].

In Fig. 1 we present a systematic graph which shows the standard enthalpies of formation of carbides, silicides and germanides for the five lanthanide metals studied in this laboratory. The value for La_5Ge_3 was reported by Jung and Kleppa [3], the other values by the present authors [4,5]. In this figure we give only the enthalpies of formation for the dominant structures in the considered binary systems: REC_2 for the carbides, $RESi_2$ for the silicides and RE_5Ge_3 for the germanides. Heats of formation for other phases in these systems are included in Tables 1 and 2 and in Refs. [3,5].

Table 1
Standard enthalpies of formation for some Nd and Gd carbides, silicides and germanides. Data in kJ/g.atom

Compound	m.p. (°C)	$\Delta H(1)$	$\Delta H(2)$	ΔH_f^0
NdC_2	2260 [a]	+4.7±0.7(6)	33.9±1.2(6)	−29.2±1.4
$NdSi_2$	1757	−27.6±1.0(6)	34.4±1.6(6)	−62.0±1.9
NdSi	1677	−43.5±1.7(5)	35.2±1.9(5)	−78.7±2.5
Nd_5Ge_3	1580	−36.3±1.0(6)	35.8±1.3(6)	−72.1±1.6
$NdGe_{1.6}$	1487	−44.3±0.7(5)	35.9±1.8(6)	−80.2±1.9
GdC_2		+1.5±0.7(5)	26.3±1.4(6)	−24.8±1.6
Gd_5Si_3	1650	−35.1±1.8(5)	32.9±1.4(7)	−68.0±2.3
$GdSi_2$	2100	−25.7±1.5(5)	33.3±1.5(6)	−59.0±2.1
Gd_5Ge_3	1790	−51.8±1.9(5)	30.2±1.8(8)	−82.0±2.6

[a] Estimated value.

Table 2
Comparison of the ΔH_f^0 data for some Nd and Gd carbides, silicides and germanides with literature values and with predictions from Miedema's semi-empirical model. Data in kJ/g.atom

Compound	ΔH_f^0(expt.), this work	ΔH_f^0(expt.), literature	Method	ΔH_f^0(pred.) Ref. [19]
NdC_2	-29.2 ± 1.4	-29.6 ± 3.5 -17.4	E.m.f. (26) vapor pressure (27)	-63
$NdSi_2$	-62.0 ± 1.9	-89 ± 3.4	E.m.f. (16) 930–1020 K	-69
NdSi	-78.7 ± 2.5	–		-77
Nd_5Ge_3	-72.1 ± 1.6	–		-74
$NdGe_{1.6}$	-80.2 ± 1.9	-103.6 ± 4.9	E.m.f. (16) 930–1050 K	-86
GdC_2	-24.8 ± 1.6	-33.8 ± 3.5 -41.8 ± 12.6	E.m.f. (26) mass. spec. (28)	-65
Gd_5Si_3	-68.0 ± 2.3	–		-64
$GdSi_2$	-59.0 ± 2.1	-79.3 ± 3.3	E.m.f. (18) 885 K	-68
Gd_5Ge_3	-82.0 ± 2.6	–		-74

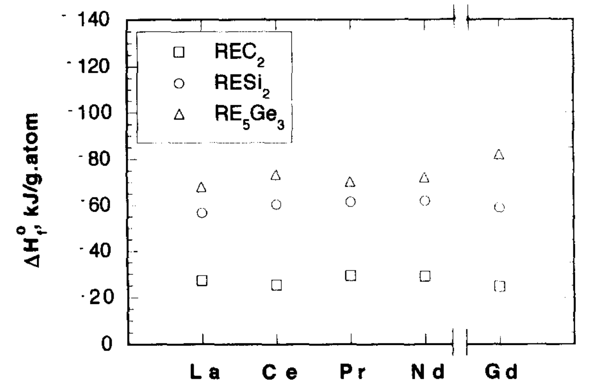

Fig. 1. Standard enthalpies of formation of characteristic carbides, silicides and germanides for La, Ce, Pr, Nd and Gd. The broken axes indicate that there are three missing elements (Pm, Sm, Eu) between Nd and Gd for which we do not report data.

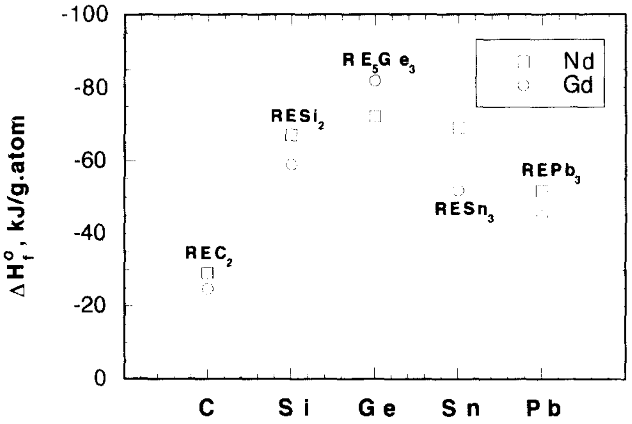

Fig. 2. Standard enthalpies of formation for characteristic compounds of Nd and Gd with Group IVb elements C, Si, Ge, Sn and Pb.

Fig. 1 shows that the values in each set of compounds are quite comparable for La,Ce,Pr,Nd and Gd. However, the negative value for Gd_5Ge_3 is slightly larger than for the other germanides; this may reflect the fact that its melting point is more than 200 °C higher than for the other four germanides. The magnitude of the enthalpy of formation increases from carbide to silicide to germanide, as one would expect from the position of C, Si and Ge in the periodic table. In Fig. 2 we compare our results for the Nd and Gd carbides, silicides and germanides with calorimetric data for their compounds with Sn and Pb. The enthalpy of formation for $NdSn_3$ was measured by Palenzona [20], and that for $GdSn_3$ by Bacha et al. [22]. The values for $NdPb_3$ and $GdPb_3$ were reported by Palenzona and Cirafici [21]. As we noted in our earlier communication [5], for the corresponding La, Ce and Pr systems, the change from C through Si, Ge and Sn to Pb is roughly parabolic. We see an increase in $-\Delta H_f^0$ from carbide to germanide, a noticeable peak at Ge, and a subsequent decrease from Ge to Sn to Pb. It is interesting to note that, for all compounds but the germanides, the Nd alloy has the more exothermic heat of formation than the Gd alloy. It is also worth noting that the enthalpies of formation for the Sn and Pb compounds differ considerably more in the Nd and Gd alloys than in the previously studied La, Ce and Pr alloys [5].

Acknowledgements

This investigation has been supported by the Department of Energy and has also benefited from the MRL facilities at the University of Chicago. We are indebted to Dr. Joseph Pluth who generated the X-ray diffraction pattern for the low-temperature modification of $NdSi_2$ from its unit-cell parameters, and the atomic coordinates for $GdSi_2$.

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