Thermodynamic modeling of the Ge-Nd binary system

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Abstract

The Ge-Nd has been critically assessed by means of the CALculation of PHAse Diagram (CALPHAD) technique. For the liquid phase, the associate model was used with the constituent species Ge, Nd, Ge\textsubscript{3}Nd\textsubscript{5} and Ge\textsubscript{1.6}Nd in the Ge-Nd system. The terminal solid solution diamond-(Ge), dhcp-(Nd) and bcc\textsubscript{A2}-(Nd) in the Ge-Nd system were described using the substitutional model, in which the excess Gibbs energy was formulated with the Redlich-Kister equation. The compounds with homogeneity ranges, α(Ge\textsubscript{1.6}Nd), β(Ge\textsubscript{1.6}Nd), (GeNd\textsubscript{5}), (GeNd\textsubscript{3}) and (GeNd\textsubscript{5}) were modeled using two sublattices as α(Ge,Nd)\textsubscript{1.6}Nd, β(Ge,Nd)\textsubscript{1.6}Nd, (Ge,Nd)Nd\textsubscript{5}, (Ge,Nd)Nd\textsubscript{3} and (Ge,Nd)Nd\textsubscript{5}, respectively. A self-consistent thermodynamic parameters for each of the Ge-Nd binary systems was obtained. The calculation results agree well with the available experimental data from literatures.

Keywords: Ge-Nd system; Thermodynamic assessment; CALPHAD technique

1. Introduction

Rare earth (RE) alloys are common hydrogen storage materials (Buckley et al., 1995)(Willems and Buschow, 1986)(Notten and Hokkeling, 1991)(Kisiet al., 1992). The previous study (Witham et al., 1997)showed that a small amount of Ni is replaced by Ge in the RE alloys can improve the activation characteristics and the life cycle of the alloy, therefore the element Ge is a potential addition for the RE-based hydrogen storage alloys.

As a continuation of systematic studies, this paper describes thermodynamically the Ge-Nd systems by means of the CALculation of PHAse Diagram (CALPHAD) technique. The thermodynamic parameters involved in the Gibbs energy models of the individual phases are optimized from the experimental thermodynamic properties and phase diagram information.

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2. Experimental information

The phase diagram of the Ge-Nd binary system was firstly constructed by Eremenko et al. (Eremenko et al., 1974). The phase equilibria were investigated using metallography, differential thermal analysis (DTA), dilatometry and X-ray analysis. The alloys were prepared by arc melting in an argon atmosphere using 99.99 at.% pure Ge and 99.34 at.% pure Nd. For the non-stoichiometric compounds, β(Ge1.6Nd) melts congruently at 1760 K with a homogeneity range of 38.4 to 40 at.% Nd, α(Ge1.6Nd) and β(Ge1.6Nd) are the low and the high temperature modifications, respectively, with the transformation temperature 888 K, (GeNd) is crystallized from the melt in the presence of Ge2Nd5 at 1670 K with a homogeneity range of 50 to 51 at.% Nd, (GeNd) is crystallized from the melt in the presence of Ge2Nd5 at 1763 K with a homogeneity range of 56.6 to 57.9 at.% Nd, and Ge3Nd5 melts congruently at 1853 K. Gokhale and Abbaschian (Gokhale and Abbaschian, 1989) summarized the phase diagram based on the experimental results of the phase equilibria reported by Eremenko et al. (Eremenko et al., 1974).

Nikolaenko and Beloborodova (Nikolaenko and Beloborodova, 1978) reported the experimental data of the enthalpies of mixing of liquid and the partial molar enthalpies of Nd and Ge in the liquid phase at 1925 K. By the direct synthesis method, Meschel and Kleppa (Meschel and Kleppa, 1995) measured the enthalpies of formation of Ge3Nd5 and Ge1.6Nd at 298.15 K, and Polotskaya and Buyanov (Polotskaya and Buyanov, 1986) obtained the enthalpies of formation of αGe1.6Nd between 930-1050 K. Based on their e.m.f. experiments, Sidorko and Polotskaya (Sidorko and Polotskaya, 1994) measured the enthalpies of formation of αGe1.6Nd between 760-1050 K. Gordienko et al. (Gordienko et al., 1998) studied the enthalpy of formation of αGe1.6Nd at 298.50 K.

3. Thermodynamic models

3.1. Pure elements

The stable forms of the pure elements, Ge and Nd, at 298.15 K are chosen as the reference states of the system. For the pure element i in its stable or metastable state of the phase φ, the Gibbs energy function is described by an equation of the following form:

\[ G_i^\phi(T) = G_i^{SER}(298.15K) - R T \ln \frac{N_i^\phi}{N_i^{SER}} \]

(1)

where \( G_i^{SER}(298.15K) \) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, diamond for Ge and dhcp for Nd; and a, b, c, ..., h are the coefficients. The Gibbs energy of the element i, in its SER state, is denoted by \( G_{SERi} \) as follows:

\[ G_{SERGe} = G_{Ge}^{diamond}(T) - H_{Ge}^{SER}(298.15K) \]

(2)

\[ G_{SERNd} = G_{Nd}^{dhcp}(T) - H_{Nd}^{SER}(298.15K) \]

(3)

The Gibbs energy functions of pure elements are taken from the SGTE compilation by Dinsdale (Dinsdale, 1991) in the present work.

3.2. Solution phases

In the Ge-Nd system, there are four solution phases, Liquid, diamond-(Ge), dhcp-(Nd) and bcc-(Nd). Diamond-(Ge), dhcp-(Nd) and bcc-(Nd) are described by the substitutional model with Ge and Nd constituting the same lattice. The Gibbs energy function of the substitutional solution phase \( \varphi \) for one mole of atoms is described by the following expression:

\[ G^\phi = x_{Ge} G_{Ge}^\phi + x_{Nd} G_{Nd}^\phi + R T (x_{Ge} \ln x_{Ge} + x_{Nd} \ln x_{Nd}) + G_m^\phi \]

(4)

where \( x_i \) and \( G_i^\phi \) are the mole fraction and the Gibbs energy of the element i (i= Ge and Nd), and R is the gas constant, T the absolute temperature, and \( G_m^\phi \) the excess Gibbs energy expressed by the Redlich-Kister Polynomial:
where $J_{Ge,Nd}$ is the jth interaction parameter between elements Ge and Nd in φ status and takes the form as the following:

$$J_{Ge,Nd} = A_j + B_j T$$

where the constants A and B are to be optimized in the present work.

In the present work, the associate model, which is possible to be integrated in the substitutional model, is chosen for the liquid phase. The constituent species Ge, Nd, Ge3Nd5 and Ge1.6Nd in the Ge-Nd system are considered. The associate species Ge3Nd5 and Ge1.6Nd correspond to the compounds with the highest congruent melting points in the related systems and with the asymmetry liquid phase boundary lines. The excess Gibbs energy expression is as the following:

$$\Delta G_{m}^{E}(T) - H_{m}^{SER}(298.15K) = \sum x_i (\Delta G_{i}^{liq}(T) + RT \ln x_i) + \sum_i \sum_j \sum_k x_j x_k J_{ij,k}^{Liq}$$

where $\Delta G_{i}^{liq}(T)$ (i= Ge, Nd, Ge3Nd5 and Ge1.6Nd) is the molar Gibbs energy of the pure species i in the liquid state, $x_i$ the mole fraction of the species i in the liquid, and $J_{ij,k}^{Liq}$ (i = 0, 1, 2,...; j,k = Ge, Nd, Ge3Nd5 and Ge1.6Nd with j ≠ k ) the ith interaction parameter between the species j and k, which is a function of temperature as in Equ. (6).

### 3.3. Compound solution phases

1. (GeNd)

According to the available experimental information, the intermediate phase (GeNd) is non-stoichiometric compound with the composition range forming the strict stoichiometry 1:1. The two-sublattice model (Ge%, Nd)(Nd) is used for describing this kind of compound solution phases. The Gibbs energy per mole of formula unit is given by the following expression:

$$G_m^{(GeNd)}(T) - H_{m}^{SER}(298.15K) = \sum x_i (\Delta G_{i}^{liq}(T) + RT \ln x_i) + \sum_i \sum_j \sum_k x_j x_k J_{ij,k}^{Liq}$$

where $\Delta G_{i}^{liq}(T)$ and $\Delta G_{i}^{liq}(T)$ represent the Gibbs energies of the hypothetical compounds GeNd and NdNd, respectively. The intermediate phase (GeNd) is the low temperature allotropic compound. The two-sublattice model (Ge%, Nd)(Nd) is used to describe the compound solution phase (GeNd) and (Ge1.6Nd). The Gibbs energy per mole of formula unit $\varphi$ (Ge1.6Nd) and $\beta$ (Ge1.6Nd) is given by the following expression:
\[ G_m^{76\text{Ge}_{1.6}\text{Nd}}(T) - H_{\text{SER}}^{76\text{Ge}_{1.6}\text{Nd}}(298.15\text{K}) = y_{\text{Ge}} y_{\text{Nd}}^* \mathbf{G}_{\text{GeNd}}^{76\text{Ge}_{1.6}\text{Nd}}(T) + y_{\text{Nd}} y_{\text{Nd}}^* \mathbf{G}_{\text{NdNd}}^{76\text{Ge}_{1.6}\text{Nd}}(T) + 1.6RT(y_{\text{Ge}} \ln y_{\text{Ge}}^* + y_{\text{Nd}} \ln y_{\text{Nd}}^*) + E_{\text{m}}^{76\text{Ge}_{1.6}\text{Nd}} \] (10)

\[ E_{\text{m}}^{76\text{Ge}_{1.6}\text{Nd}} = y_{\text{Ge}} y_{\text{Nd}}^* \sum_{i} i^{\text{Ge}_{1.6}\text{Nd}} \left( y_{\text{Ge}} - y_{\text{Nd}}^* \right) \] (11)

where \( \mathbf{G}_{\text{GeNd}}^{76\text{Ge}_{1.6}\text{Nd}}(T) \) and \( \mathbf{G}_{\text{NdNd}}^{76\text{Ge}_{1.6}\text{Nd}}(T) \) represent the Gibbs energies of the hypothetical compounds \( \text{Ge}_{1.6}\text{Nd} \) and \( \text{Nd}_{1.6}\text{Nd} \), respectively. \( L_i^{\text{Ge}_{1.6}\text{Nd}} \) is the \( i \)th interaction parameter between \( \text{Ge} \) and \( \text{Nd} \) in the first sublattice while the second sublattice is occupied only by \( \text{Nd} \).

(3) \( \text{Ge}_{2}\text{Nd}_5 \) and \( \text{Ge}_3\text{Nd}_5 \)

The intermediate phase \( \text{Ge}_{2}\text{Nd}_5 \) is a non-stoichiometric compound with the composition range from 56.6 to 57.9 at.\% \( \text{Nd} \), which is on the \( \text{Nd} \)-rich side of the strict stoichiometry \( \text{Ge}_{4}\text{Nd}_5 = 4:5 \). Similarly, the intermediate phase \( \text{Ge}_3\text{Nd}_5 \) is a non-stoichiometric compound with the composition range from 62.5 to 63.7 at.\% \( \text{Nd} \), which is on the \( \text{Nd} \)-rich side of the strict stoichiometry \( \text{Ge}_{3}\text{Nd}_5 = 3:5 \). The two-sublattice model \( \text{Ge}_{m}\text{Nd}_n \) is used for describing these two compound solid solution phases. The Gibbs energy per mole of formula unit is given by the following expression:

\[ G_m^{\text{Ge}_{m}\text{Nd}_n}(T) - H_{\text{SER}}^{\text{Ge}_{m}\text{Nd}_n}(298.15\text{K}) = y_{\text{Ge}} y_{\text{Nd}}^* \mathbf{G}_{\text{GeNd}}^{\text{Ge}_{m}\text{Nd}_n}(T) + y_{\text{Nd}} y_{\text{Nd}}^* \mathbf{G}_{\text{NdNd}}^{\text{Ge}_{m}\text{Nd}_n}(T) + \mathbf{E}_{\text{m}}^{\text{Ge}_{m}\text{Nd}_n} \] (12)

\[ E_{\text{m}}^{\text{Ge}_{m}\text{Nd}_n} = y_{\text{Ge}} y_{\text{Nd}}^* \sum_{i} i^{\text{Ge}_{m}\text{Nd}_n} \left( y_{\text{Ge}} - y_{\text{Nd}}^* \right) \] (13)

where \( \mathbf{G}_{\text{GeNd}}^{\text{Ge}_{m}\text{Nd}_n}(T) \) and \( \mathbf{G}_{\text{NdNd}}^{\text{Ge}_{m}\text{Nd}_n}(T) \) represent the Gibbs energies of the hypothetical compounds \( \text{Ge}_{m}\text{Nd}_n \) and \( \text{Nd}_m\text{Nd}_n \), respectively. \( L_i^{\text{Ge}_{m}\text{Nd}_n} \) is the \( i \)th interaction parameter between \( \text{Ge} \) and \( \text{Nd} \) in the first sublattice while the second sublattice is occupied only by \( \text{Nd} \).

4. Results and discussion

4.1. Results

The optimized thermodynamic parameters of the Ge-Nd system are given in Table 1. The invariant reactions are calculated and compared with the experimental data, as listed in Table 2.

Table 1  Optimized thermodynamic parameters of the Ge-Nd system

| Phase/ Model | Parameters |
|--------------|------------|
| Liquid       | \( ^0\mathbf{G}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = 3 \times \text{GHSERGE} + 5 \times \text{GHSERND} = 267278 - 50 \times T \) |
| (Ge,Ge\text{Nd1.6Nd,Ge}_{3}\text{Nd5}) | \( ^0\mathbf{G}_{\text{NdNd}}^{\text{Ge}_{1.6}\text{Nd}} = 1.6 \times \text{GHSERGE} + \text{GHSERND} = 196744.8 - 0.05149 \times T \) |
| \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -39426.54 - 23.2 \times T \) | \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -37280 + 26 \times T \) |
| \( ^1\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -321216 + 20.37 \times T \) | \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -44362.266 - 19.0722 \times T \) |
| \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -320996 + 4 \times T \) | \( ^1\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = 42000 \) |
| \( ^2\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -90000 \) | \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -147506.25 \) |
| \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = -361368 + 22.3671 \times T \) | \( ^0\mathbf{F}_{\text{GeNd}}^{\text{Ge}_{1.6}\text{Nd}} = \text{GHSERND} + 10000 \) |

diamond (Ge)
\begin{align*}
(\text{Ge,Nd}) & \quad \theta_{\text{Y}_{\text{Ge,Nd}}} = -144000 \\
\text{dhcp (aNd)} & \quad \theta_{\text{Y}_{\text{Ge}}} = \text{GHSERGE} + 50000 \\
\phi_{\text{Nd}} & \quad \theta_{\text{Y}_{\text{Nd}}} = -273180 + 10 \times T \\
\text{bcc (cNd)} & \quad \theta_{\text{Y}_{\text{Nd}}} = -218776.4 + 18 \times T \\
\phi_{\text{Nd}} & \quad \theta_{\text{Y}_{\text{Nd}}} = 20000 \\
(\alpha\text{Ge,Nd}) & \quad \theta_{\text{Y}_{\text{Ge,Nd}}} = 1.6 \times \text{GHSERGE} + \text{GHSERND} - 205518.89 + 23.0513 \times T \\
(\text{Ge,Nd})_{\beta} & \quad \theta_{\text{Y}_{\text{Ge,Nd}}} = 2.6 \times \text{GHSERND} + 50000 \\
(\beta\text{Ge,Nd}) & \quad \theta_{\text{Y}_{\text{Ge,Nd}}} = 1.6 \times \text{GHSERGE} + \text{GHSERND} - 205470 + 23 \times T \\
(\text{Ge,Nd})_{\text{bcc}} & \quad \theta_{\text{Y}_{\text{Ge,Nd}}} = -237600 + 60 \times T \\
(\gamma\text{Ge,Nd}) & \quad \theta_{\text{Y}_{\text{Nd}}} = -178800 + 45 \times T \\
(\text{GeNd}) & \quad \theta_{\text{Y}_{\text{GeNd}}} = \text{GHSERGE} + \text{GHSERND} - 205540 + 38.8 \times T \\
(\text{GeNd})_{\text{bcc}} & \quad \theta_{\text{Y}_{\text{GeNd}}} = 2 \times \text{GHSERND} + 50000 \\
(\phi\text{Nd}) & \quad \theta_{\text{Y}_{\text{Nd}}} = -140000 \\
(\delta\text{Nd}) & \quad \theta_{\text{Y}_{\text{Nd}}} = -60000 \\
(\text{GeNd})_{\text{Li}} & \quad \theta_{\text{Y}_{\text{GeNd}}} = 4 \times \text{GHSERGE} + 5 \times \text{GHSERND} - 1023900 + 218 \times T \\
(\text{GeNd})_{\text{Ge}} & \quad \theta_{\text{Y}_{\text{GeNd}}} = 9 \times \text{GHSERND} + 200000 \\
(\phi\text{GeNd}) & \quad \theta_{\text{Y}_{\text{Nd}}} = -630000 + 20 \times T \\
(\delta\text{Nd}) & \quad \theta_{\text{Y}_{\text{Nd}}} = -200000 \\
(\text{GeNd})_{\text{Ge}} & \quad \theta_{\text{Y}_{\text{GeNd}}} = 3 \times \text{GHSERGE} + 5 \times \text{GHSERND} - 1095980 + 249 \times T \\
(\text{GeNd})_{\text{Ge}} & \quad \theta_{\text{Y}_{\text{GeNd}}} = 8 \times \text{GHSERND} + 200000 \\
(\delta\text{Nd}) & \quad \theta_{\text{Y}_{\text{Nd}}} = 15000 - 120 \times T
\end{align*}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|}
\hline
Reaction & Compositions ($X_{\text{Nd}}$) & $T$ (K) & Reaction Type & Reference \\
\hline
Liquid$\rightarrow$\beta(Ge$_{1.6}$Nd) & 0.385 & 1760 & Congruent & This work \\
 & 0.385 & 1760 & Congruent & (Eremenko et al., 1974) \\
 & & & & (Gokhale and Abbaschian, 1989) \\
Liquid$\rightarrow$GeNd$_{\delta}$ & 0.625 & 1853 & Congruent & This work \\
 & 0.625 & 1853 & Congruent & (Eremenko et al., 1974) \\
 & & & & (Gokhale and Abbaschian, 1989) \\
(Ge$_{3}$Nd$_{5}$)+Liquid$\rightarrow$(Ge$_{4}$Nd$_{5}$) & 0.625 & 1763 & Peritectic & This work \\
 & 0.523 & 0.571 & & (Eremenko et al., 1974) \\
 & 0.625 & 0.495 & 0.571 & Peritectic & (Gokhale and Abbaschian, 1989) \\
Liquid$\rightarrow$(GeNd$_{\delta}$) & 0.466 & 1670 & Peritectic & This work \\
 & 0.559 & 0.510 & & (Eremenko et al., 1974) \\
 & 0.485 & 0.566 & 0.500 & Peritectic & (Gokhale and Abbaschian, 1989) \\
Liquid$\rightarrow$(GeNd)+\beta(Ge$_{1.6}$Nd) & 0.460 & 1663 & Eutectic & This work \\
 & 0.508 & 0.397 & & (Eremenko et al., 1974) \\
 & 0.480 & 0.500 & 0.400 & Eutectic & (Gokhale and Abbaschian, 1989) \\
(bcc(\beta)Nd)$\rightarrow$dhcp(aNd) & & 1131 & Allotropic transformation & This work \\
 & & 1131 & Allotropic transformation & (Dinsdale, 1991) \\
Liquid$\rightarrow$diamond(\beta)+\beta(Ge$_{1.6}$Nd) & 0.187 & 1083 & Eutectic & This work \\
 & 0.006 & 0.384 & & (Eremenko et al., 1974) \\
 & 0.160 & <0.02 & 0.384 & Eutectic & This work \\
\hline
\end{tabular}
\caption{Invariant reactions in the assessed Ge-Nd phase diagram}
\end{table}
Figure 1 shows the calculated phase diagram of the Ge-Nd binary system with all the critical temperatures labeled. The calculated phase diagram is nearly in accordance with the experimental data reported by Ref. (Eremenko et al., 1974).

Figure 2 is the comparison between the calculated results and the experimental data of the enthalpies of mixing of liquid alloys (at 1925 K and up to 40 at% Nd) (Nikolaenko and Beloborodova, 1978) as well as the literature calculated result (Gokhale and Abbaschian, 1989).

Figure 3 is the comparison between the calculated results and the experimental data of the partial molar enthalpies of Nd and Ge (Nikolaenko and Beloborodova, 1978) in the liquid phase.

Figure 4 is the comparison between the calculated results and the experimental data of the formation enthalpies of the compounds $\alpha$Ge$_{1.6}$Nd, GeNd, Ge$_2$Nd$_5$ and Ge$_3$Nd$_5$ at 298.15 K (Meschel and Kleppa, 1995) (Polotskaya and Buyanov, 1986) (Sidorko and Polotskaya, 1994).

![Fig. 1. The Ge-Nd binary phase diagram. (a) calculated with the present description; (b) compared with the experimental data.](image)
Fig. 2. Calculated enthalpies of formation of liquid phase at 1925 K compared with experimental data and literature calculated result.

Fig. 3. Partial molar enthalpies of Nd and Ge in liquid phase
(a) calculated partial molar enthalpies of Nd compared with experimental data;
(b) calculated partial molar enthalpies of Ge compared with experimental data.
4.2. Discussion

Considering the comparison between the calculated results and the experimental data, the equilibrium phase diagrams and the thermochemical properties of the Ge-Nd system can be reproduced accordingly, except the enthalpies of formation of compounds at room temperature in both of the systems. Since Ge is a high volatile metal and Nd are easily oxidized, experimental errors are likely caused. The battery voltage measurement, the cell reaction irreversibility and the temperature fluctuations in the electromotive force method and the thermal loss, the mess measurement and the temperature variations in the calorimetric method can also lead to a large measurement deviation. Some well-designed investigations are needed to confirm the precise values of the thermochemical properties of the systems.

5. Conclusions

The experimental data of the phase equilibria and the thermodynamic properties in the Ge-Nd system has been critically evaluated. All of the phases of the Ge-Nd system are modeled reasonably, with the associate model for the liquid phase, the substitutional model for diamond-(Ge), dhcp-(Nd) and bcc_A2-(Nd), the two-sublattice model for the non-stoichiometric compounds α(Ge_{1.6}Nd), β(Ge_{1.6}Nd), (GeNd), (Ge_{4}Nd_{5}) and (Ge_{3}Nd_{5}). Based on the experimental measurements from literatures, a set of self-consistent thermodynamic parameters for each of the Ge-Nd binary systems was obtained. The calculation results agree well with the available experimental data.

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