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Thermodynamic assessment of the Nd–Zn system

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Abstract

The Nd–Zn binary system has been optimized by CALPHAD method, using the available experimental thermodynamic and phase diagram information. The system contains eight intermetallic compounds: NdZn, $NdZn_2$, $NdZn_3$, Nd_3Zn_{11}, $Nd_{13}Zn_{58}$, Nd_3Zn_{22}, Nd_2Zn_{17} and $NdZn_{11}$. They were treated as stoichiometric compounds. The standard enthalpies of formation of these compounds were calculated in this work. Good agreement was obtained between the calculation and experimental results. A set of self-consistent thermodynamic model parameters was derived.

Keywords: Rare earth; Zinc; Phase diagrams; Thermodynamic properties

1. Introduction

During the last few decades the investigation of intermetallic compounds between rare earth and transition metals has received additional impetus [1]. The research of special hot dip galvanizing alloys of low cost and high capability is the object of many scientific researchers. The minim addition of rare earth metals into hot dip galvanizing alloys can decrease the thickness of the zinc alloyed coatings, advance the corrosion resistance, and improve the performance of the coatings [2]. The investigation of the galvanization of silicon-containing steels indicates that the addition of RE in zinc liquid affects jointly the prevention of the abnormal growth of the ζ phase when zinc reacts with iron [3]. Therefore, the phase diagrams and thermodynamic properties of the RE–Zn system have very important economical and social benefits for the development of hot dip galvanizing technique. Nevertheless, thermodynamic studies and experimental data of these systems are lacking. Furthermore, there is no effective check for the consistency between the reported phase diagram and the thermodynamic data. For this, the CALPHAD technique [4] provides an available method. By modeling the Nd–Zn alloy, a self-consistent description of the phase relations and thermodynamic data was obtained in present work.

2. Thermodynamic models

2.1. Pure elements

The Gibbs energy of the pure element i, referred to the enthalpy of its stable state at 298.15 K, is described as a function of temperature by

$$ {}^{0}G_i - {}^{0}H_i^{\mathrm{SER}}(298.15K) = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (1) $$

where a through h are coefficients taken from the work of Dinsdale [5].

2.2. Solution phases

The liquid and body-centered cubic (bcc) phases are treated with the substitutional solution model for which the Gibbs energy expression is described as

$$ G_{\mathrm{m}}^{\phi} = X_{\mathrm{Nd}}^{0}G_{\mathrm{Nd}}^{\phi} + X_{\mathrm{Zn}}^{0}G_{\mathrm{Zn}}^{\phi} + RT(X_{\mathrm{Nd}}\ln X_{\mathrm{Nd}} + X_{\mathrm{Zn}}\ln X_{\mathrm{Zn}}) + {}^{\mathrm{E}}G_{\mathrm{m}}^{\phi} \quad (2) $$

where ${}^{0}G_{\mathrm{Nd}}^{\phi}$ and ${}^{0}G_{\mathrm{Zn}}^{\phi}$ are, respectively, the molar Gibbs energies of pure neodymium and zinc with structure ϕ in the non-magnetic state [5]. X_{Nd} and X_{Zn} are the mole fractions of Nd and Zn. ${}^{\mathrm{E}}G_{\mathrm{m}}^{\phi}$ is the excess Gibbs energy, expressed as a

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Redlich–Kister polynomial [6]:

$$^{E}G_{m}^{\phi} = X_{Nd}X_{Zn}\sum_{i} {}^{i}L_{Nd,Zn}^{\phi}(X_{Nd} - X_{Zn})^{i} \quad (3)$$

where $^{i}L_{Nd,Zn}^{\phi}$ called the binary interaction parameter represents the interaction energy between the two elements. $^{i}L_{Nd,Zn}^{\phi}$ can be temperature dependent and two coefficients are usually sufficient, given by

$$^{i}L_{Nd,Zn}^{\phi} = a_i + b_i T \quad (4)$$

where a_i and b_i are the parameters evaluated in this work.

2.3. Stoichiometric intermetallic compounds

The intermetallic phases NdZn, $NdZn_2$, $NdZn_3$, Nd_3Zn_{11}, $Nd_{13}Zn_{58}$, Nd_3Zn_{22}, Nd_2Zn_{17} and $NdZn_{11}$ in the Nd–Zn system are treated as strict stoichiometric compounds. The Gibbs energies per mole of formula unit Nd_AZn_B can be expressed as

$$G_{Nd:Zn}^{Nd_AZn_B} = A\,{}^{0}G_{Nd}^{dhcp} + B\,{}^{0}G_{Zn}^{hcp} + A_0 + B_0T \quad (5)$$

where $^{0}G_{Nd}^{dhcp}$ and $^{0}G_{Zn}^{hcp}$ are the Gibbs energies of the respective pure elements in the dhcp and hcp phase structures. The coefficients A_0 and B_0 are the lattice stability parameters to be evaluated in the present work.

3. Experimental information

The Nd–Zn system has been investigated by many researchers [7–15]. Kuz'ma et al. [7,8] confirmed the existence of $NdZn_{11}$ and Nd_2Zn_{17}. Iandelli and Palenzona [9,10] investigated compounds NdZn, Nd_2Zn_{17} and $NdZn_{11}$. Fornasini and Merlo [11] researched $NdZn_2$ in detail. In a later study, Veleckis et al. [12] reported the compounds $NdZn_2$, $NdZn_3$, Nd_3Zn_{11}, $NdZn_{4.3}$, $NdZn_{6.5}$, Nd_2Zn_{17} and $NdZn_{11}$. Bruzzone et al. [13] investigated some structural characteristics of the compounds $NdZn_2$, $NdZn_{4.46}$ and Nd_3Zn_{22}. Chiotti and Mason [14] determined the phase relationship of Nd–Zn system by means of metallurgy, thermodynamics and X-ray diffraction analyses. They confirmed the existence of eight intermetallic compounds, namely NdZn, $NdZn_2$, $NdZn_3$, Nd_3Zn_{11}, $Nd_{13}Zn_{58}$, Nd_3Zn_{22}, Nd_2Zn_{17} and $NdZn_{11}$. They also reported the existence of $NdZn_{12}$ with the same structure of $SmZn_{12}$ and concluded the existence of inter-transformation between $NdZn_{11}$ and $NdZn_{12}$, but did not indicate the inter-transformation temperature. Veleckis et al. [12] reported the inexistence of $NdZn_{11}$ above 1173 K. In the present optimization, the data from Chiotti and Mason [14] are used.

In the diagram of Chiotti and Mason [14], NdZn, $NdZn_2$ and Nd_2Zn_{17} melt congruently, respectively, at the temperature 1196, 1198 and 1254 K. $NdZn_3$ is a peritectoid compound; Nd_3Zn_{11}, $Nd_{13}Zn_{58}$ and Nd_3Zn_{22} are peritectic compounds. The eutectic reaction, Liq. → β-Nd(bcc) + NdZn, occurs at 903 K, 23.1 at.% Zn. The eutectic reaction, Liq. → NdZn + $NdZn_2$, occurs at 1141 K, 57.5 at.% Zn. The eutectic reaction, Liq. → $NdZn_2$ + Nd_3Zn_{11}, occurs at 1127 K, 73.7 at.% Zn. The eutectoid reaction, β-Nd(bcc) → α-Nd(dhcp) + NdZn, occurs at 895 K, 8.4 at.% Zn.

All the invariant reactions are listed in Table 1.

Borzone et al. [16] measured the enthalpies of formation of compounds of Nd–Zn system using direct calorimetry and acid solution calorimetry. Chiotti and Mason [17] measured the zinc vapor pressure data using the dewpoint method and developed the appropriate thermodynamic relations for the phases present in Nd–Zn system.

Table 1
Invariant reactions in the Nd–Zn system

Reaction	T (K) ($X_{Zn}^{Liq.}$)	
	Present work	Ref. [14]
β-Nd(bcc) → α-Nd(dhcp) + NdZn	895.5 (0.086[a])	895 (0.084[a])
Liq. → β-Nd(bcc) + NdZn	901.5 (0.235)	903 (0.231)
Liq. → NdZn	1195	1196
Liq. → NdZn + $NdZn_2$	1143 (0.588)	1141 (0.575)
Liq. → $NdZn_2$	1194	1198
Liq. → $NdZn_2$ + Nd_3Zn_{11}	1134 (0.746)	1127 (0.737)
$NdZn_2$ + Nd_3Zn_{11} → $NdZn_3$	1122	1122
Liq. + $Nd_{13}Zn_{58}$ → Nd_3Zn_{11}	1142 (0.759)	1143 (0.759)
Liq. + Nd_3Zn_{22} → $Nd_{13}Zn_{58}$	1174 (0.802)	1175 (0.802)
Liq. + Nd_2Zn_{17} → Nd_3Zn_{22}	1127 (0.851)	1223 (0.867)
Liq. → Nd_2Zn_{17}	1250	1254
Liq. + Nd_2Zn_{17} → $NdZn_{11}$	1055 (0.990)	Above 1003

[a] *Note*: The composition of Zn in β-Nd (at.%).

4. Assessment procedure

Most of the experiment information mentioned above was available during the evaluation of the thermodynamic parameters. Due to the lack of experimental and thermodynamic data, $NdZn_{11}$ and $NdZn_{12}$ were treated as only one compound. All the compounds were strictly treated as stoichiometric compounds.

The optimization was carried out by using a software package THERMO-CALC [18]. The experimental phase diagram data and thermodynamic information of compounds were used as input to the program. All the solution phases and stoichiometric compounds were described by available thermodynamic models. All the data used were critically reviewed and selected before input. Each piece of selected information was given a certain weight by personal judgment, and changed by trial and error during the assessment, until most of calculated results were reappeared within the expected uncertainty limits.

The optimization was carried out step by step. The parameters for the liquid phase were first optimized by the experimental data of liquidus line. Then the congruent intermetallic compounds were investigated. The parameters for the intermetallic compounds were consequently optimized using the phase diagram data and the enthalpies of formation of compounds.

Finally, all the parameters were evaluated together to give the best representing of the Nd–Zn system. All evaluated parameters are listed in Table 2.

5. Results and discussions

Fig. 1 shows the calculated phase diagram with experimental values used in the optimization. Table 2 gives the optimized parameters of the Nd–Zn system. The calculated phase diagram is in well agreement with that reported by Chiotti and Mason [14]. All the assessed and experimental invariant equilibriums in the Nd–Zn system are listed in Table 1. An agreement within 7 °C between the temperatures of calculated and experimentally

Table 2
The optimized parameters describing the thermodynamic properties of the Nd–Zn system

Liquid	${}^0L^{\text{Liq.}}_{\text{Nd,Zn}} = -102649.0 + 27.1096T$
	${}^1L^{\text{Liq.}}_{\text{Nd,Zn}} = 70636.9 - 41.0381T$
bcc	${}^0L^{\text{bcc}}_{\text{Nd,Zn}} = -66703.1$
	${}^1L^{\text{bcc}}_{\text{Nd,Zn}} = 28406.5$
NdZn	${}^0G^{\text{NdZn}}_{\text{Nd:Zn}} - {}^0G^{\text{dhcp}}_{\text{Nd}} - {}^0G^{\text{hcp}}_{\text{Zn}} = -69149.4 + 12.7061T$
$NdZn_2$	${}^0G^{\text{NdZn}_2}_{\text{Nd:Zn}} - {}^0G^{\text{dhcp}}_{\text{Nd}} - 2{}^0G^{\text{hcp}}_{\text{Zn}} = -107196.3 + 21.9361T$
$NdZn_3$	${}^0G^{\text{NdZn}_3}_{\text{Nd:Zn}} - {}^0G^{\text{dhcp}}_{\text{Nd}} - 3{}^0G^{\text{hcp}}_{\text{Zn}} = -133825.7 + 32.0133T$
Nd_3Zn_{11}	${}^0G^{\text{Nd}_3\text{Zn}_{11}}_{\text{Nd:Zn}} - 3{}^0G^{\text{dhcp}}_{\text{Nd}} - 11{}^0G^{\text{hcp}}_{\text{Zn}} = -444171.0 + 106.7787T$
$Nd_{13}Zn_{58}$	${}^0G^{\text{Nd}_{13}\text{Zn}_{58}}_{\text{Nd:Zn}} - 13{}^0G^{\text{dhcp}}_{\text{Nd}} - 58{}^0G^{\text{hcp}}_{\text{Zn}} = -2143820.7 + 524.1522T$
Nd_3Zn_{22}	${}^0G^{\text{Nd}_3\text{Zn}_{22}}_{\text{Nd:Zn}} - 3{}^0G^{\text{dhcp}}_{\text{Nd}} - 22{}^0G^{\text{hcp}}_{\text{Zn}} = -669762.2 + 181.8252T$
Nd_2Zn_{17}	${}^0G^{\text{Nd}_2\text{Zn}_{17}}_{\text{Nd:Zn}} - 2{}^0G^{\text{dhcp}}_{\text{Nd}} - 17{}^0G^{\text{hcp}}_{\text{Zn}} = -465559.7 + 117.7031T$
$NdZn_{11}$	${}^0G^{\text{NdZn}_{11}}_{\text{Nd:Zn}} - {}^0G^{\text{dhcp}}_{\text{Nd}} - 11{}^0G^{\text{hcp}}_{\text{Zn}} = -253011.8 + 68.5991T$

The values are given in SI units per mole of formula units.

determined invariant reactions has been obtained. The calculated temperature of invariant reaction, Liq. + Nd_2Zn_{17} → $NdZn_{11}$, is 1055 K. This agrees with the experimental data reported by Chiotti and Mason [14] and Veleckis et al. [12]. Fig. 2 shows the enlarged part of calculated liquidus line between $NdZn_3$ and Nd_2Zn_{17}.

Fig. 3 shows the assessed enthalpies of formation at 298 K in comparison with experimental data [16,17]. The experimental standard enthalpies of formation for Nd–Zn system are plotted in the figure, too. The calculated standard enthalpies of formation of NdZn, $NdZn_2$, $NdZn_3$, Nd_3Zn_{11}, $Nd_{13}Zn_{58}$, Nd_3Zn_{22} and Nd_2Zn_{17} are −34.58, −35.73, −33.46, −31.73, −30.22, −26.78 and −24.50 kJ/mol, respectively.

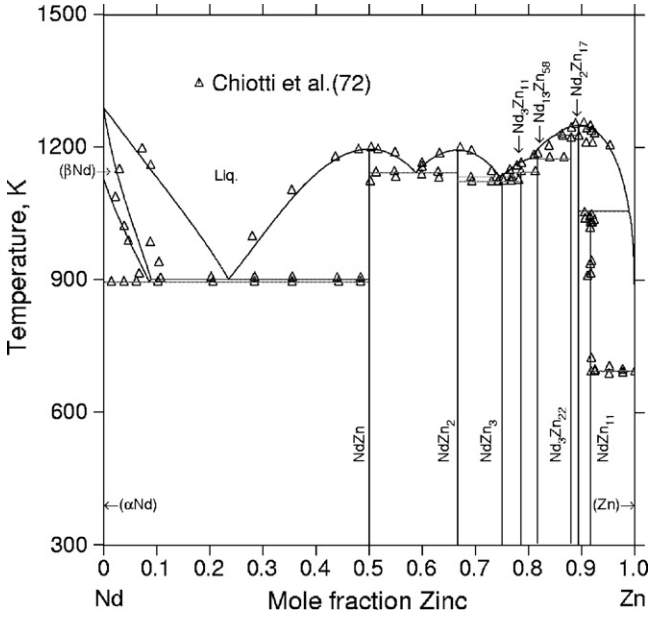

Fig. 1. The Nd–Zn phase diagram calculated from the present thermodynamic description compared with experimental measurements [14].

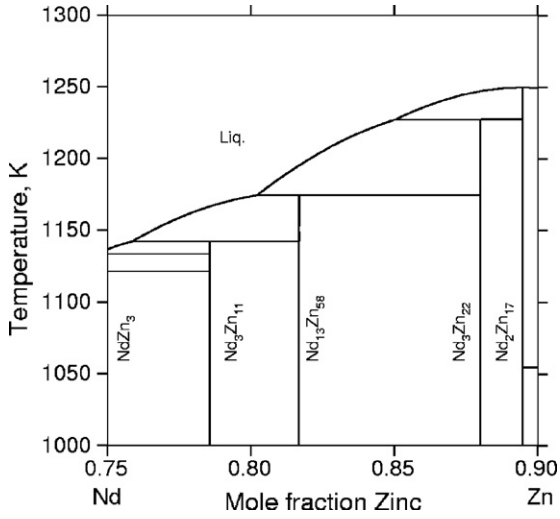

Fig. 2. The enlarged part of calculated liquidus line between $NdZn_3$ and Nd_2Zn_{17}.

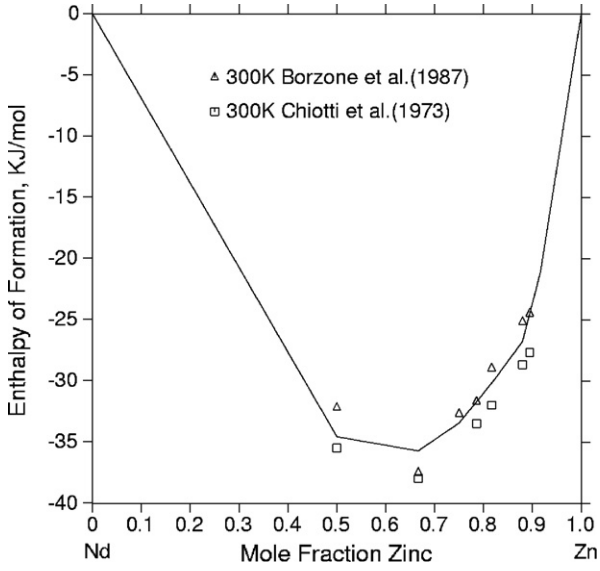

Fig. 3. The calculated standard enthalpies of formation of Nd–Zn intermediate phases compared with experimental measurements [16,17].

6. Conclusions

The phase relations and thermodynamic properties of the Nd–Zn system were evaluated from experimental information available in the literature. A consistent set of thermodynamic parameters was derived. The calculated phase equilibria agree well with most of the data reported in literatures. More experiment work on this system especially for the Zinc-rich corner may be necessary to improve the description.

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