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Review

Thermodynamic reassessment of the Sm–Ni binary system

Z. Rahou*, K. Mahdouk

Laboratory of Thermodynamics and Energetics (L.T.E), Faculty of Sciences, Ibn Zohr University, B.P. 8106, Agadir, Morocco

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ABSTRACT

Based on the available experimental data of phase equilibria and thermodynamic properties from the literature, the Sm–Ni binary system has been thermodynamically assessed using the CALPHAD (CALculation of PHAse Diagrams) method. The solution phases, Liquid, FCC_A1, RHOMB, HCP_A3 and BCC_A2, were modeled as substitutional solution phases, of which the excess Gibbs energies were formulated with Redlich–Kister polynomials. All intermetallic phases Sm_3Ni, Sm_7Ni_3, Sm_3Ni_2, SmNi, $SmNi_2$, $SmNi_3$, Sm_2Ni_7, Sm_5Ni_{19}, $SmNi_5$, and Sm_2Ni_{17} were described as stoichiometric compounds. Subsequently, a set of self-consistent thermodynamic parameters describing various phases in this binary system has been obtained. The calculated results reproduce well the corresponding experimental data.

Contents

1. Introduction

The intermetallic compounds formed by rare earth (RE) elements and transition metals (TM) are of particular interest regarding to their potential usage as high value functional materials, such as permanent magnets [1,2] and hydrogen storage materials (reversible absorption of a large quantity of hydrogen gas at room temperature and nearly at atmospheric pressure) [3,4]. Moreover, many ternary Al–TM–RE systems form amorphous alloys with interesting mechanical properties [5,6] and some rare-earth/transition metal oxides are candidate materials for solid oxide fuel cells [7]. Furthermore, the rare-earth/3d transition metal intermetallic compounds were suggested as being promising candidates for room temperature magnetic refrigeration based on magneto-caloric effect (MCE) [8–10] who has attracted more attention for improved energy efficiency and environmental friendliness compared with traditional compression/expansion gas

* Corresponding author.
E-mail address: rahou.zakarea@gmail.com (Z. Rahou).

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refrigeration [11,12].

On the other hand, the knowledge of thermodynamic data and phase diagrams is essential for developing and checking models of phase transformations, coupling thermodynamics with kinetics [13]. The purpose of the present work is (1) to evaluate recent experimental phase diagram and his relative thermodynamic data and (2) to provide a set of self-consistent parameters for calculation of the phase equilibria and thermodynamic properties in the Sm–Ni binary system using the CALPHAD (CALculation of PHAse Diagram) method [14] and the Thermo-calc software package [15].

2. Thermodynamic models

2.1. Pure elements

The stable forms of the pure elements at 298.15 K and 1 bar were chosen as the reference states of the system. For the thermodynamic functions of the pure elements in their stable and metastable states, the phase stability equations compiled by Dinsdale [16] and adopted by the SGTE (Scientific Group Thermodata Europe) were used in the present work:

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

where H_i^{SER} (298.15 K)is the molar enthalpy of the so-called "Standard Element Reference" (SER), i.e., the enthalpies of the pure elements in their defined reference state at 298.15 K and 1 bar; T is the absolute temperature; $G_i^{\phi}(T)$ is the absolute molar Gibbs energy of the element i (i = Sm and Ni) with structure ϕ in a non magnetic states.

In thermodynamic study, absolute energy is not of importance, so the relative value of Gibbs energy ${}^{0}G_i^{\phi}(T)$ is adopted in CALPHAD approach. The Gibbs energy of the element i (i = Sm or Ni) ${}^{0}G_i^{\phi}(T)$, in its SER state is denoted by $GHSER_i$, i.e.

$$ GHSER_{Sm} = {}^{0}G_{Sm}^{\mathrm{rhomb}}(T) = G_{Sm}^{\mathrm{rhomb}}(T) - H_{Sm}^{SER} \quad (298.15K) \quad (2) $$

$$ GHSER_{Ni} = {}^{0}G_{Ni}^{fcc}(T) = G_{Ni}^{fcc}(T) - H_{Ni}^{SER} \quad (298.15K) \quad (3) $$

2.2. Solution phases

The substitutional solution model was employed to describe the solution phases including Liquid, FCC_A1, RHOMB, BCC_A2 and HCP_A3. The molar Gibbs energy of the solution phase ϕ (ϕ = Liquid, FCC_A1, RHOMB, HCP_A3 and BCC_A2) can be expressed as:

$$ G_m^{\phi} = x_{Ni}{}^{0}G_{Ni}^{\phi} + x_{Sm}{}^{0}G_{Sm}^{\phi} + RT(x_{Ni}\ln x_{Ni} + x_{Sm}\ln x_{Sm}) + {}^{E}G_m^{\phi} + {}^{mg}G_m^{\phi} \quad (4) $$

where G_m^{ϕ} is the molar Gibbs energy of a solution phase ϕ; ${}^{0}G_i^{\phi}$ is the molar Gibbs energy of the element i (i = Sm, Ni) with the structure ϕ in a non-magnetic state; x_i the mole fraction of component i, R gas constant, T temperature; ${}^{E}G_m^{\phi}$ the excess Gibbs energy, and ${}^{mg}G_m^{\phi}$ is the magnetic contribution to the Gibbs energy which will be discussed in section 2.4. The excess Gibbs energy of phase ϕ can be expressed by the Redlich–Kister polynomials [17] as:

$$ {}^{E}G_m^{\phi} = x_{Ni}x_{Sm}\sum_j {}^{j}L_{Ni,Sm}^{\phi}(x_{Ni} - x_{Sm})^j \quad (5) $$

here ${}^{j}L_{Ni,Sm}^{\phi}$(j = 0, 1, 2, …) is the interaction parameter between elements Sm and Ni and is formulated as temperature dependent:

$$ {}^{j}L_{Ni,Sm}^{\phi} = a_j + b_jT + c_jTLnT + d_jT^2 + e_jT^3 + f_jT^{-1} + g_jT^7 + hjT^{-9} \quad (6) $$

Where a_j, b_j, c_j, d_j, e_j, f_j, g_j and h_j are model parameters to be optimized. In most cases, only the two first terms of the above equation are used.

2.3. Intermetallic compounds

All intermetallic compounds, Sm_3Ni, Sm_7Ni_3, Sm_3Ni_2, SmNi, $SmNi_2$, $SmNi_3$, Sm_2Ni_7, Sm_5Ni_{19}, $SmNi_5$, and Sm_2Ni_{17} were treated as stoichiometric phases in the Sm–Ni binary system because no available experimental data are reports homogeneity range for these compounds. The Gibbs energy of a Sm_ANi_B compound is given as:

$$ {}^{0}G_m^{Sm_ANi_B} = \frac{A}{A+B}{}^{0}G_{Sm}^{\mathrm{rhomb}} + \frac{B}{A+B}{}^{0}G_{Ni}^{fcc} + a + bT + {}^{mg}G_m^{Sm_ANi_B} \quad (7) $$

where ${}^{0}G_{Sm}^{\mathrm{rhomb}}$ and ${}^{0}G_{Ni}^{hfcc}$ are the Gibbs energies of the respective pure elements Sm and Ni in the non-magnetic rhomb and fcc structure respectively. The parameters a and b were evaluated in the present work. ${}^{mg}G_m^{Sm_ANi_B}$ is the magnetic contribution to the Gibbs energy discussed in Section 2.4.

2.4. Magnetic contribution to the Gibbs energy

The magnetic contribution to the Gibbs energy ${}^{mg}G_m$ can be described as:

$$ {}^{mg}G_m = RTln(\beta+1)f(\tau) \quad (8) $$

where τ is defined as T/T_c with T_c being the critical temperature for magnetic ordering, i.e. the curie temperature (Tc) for ferromagnetic ordering and the Néel temperature (T_N) for antiferromagnetic ordering; β is a quantity related to the total magnetic entropy and is equal to the Bohr magnetic moment per mole of atoms in most cases; $f(\tau)$ represents the polynomials given by Hillert and Jarl [18] based on the magnetic specific heat of iron, i.e.for $\tau < 1$

$$ f(\tau) = 1 - \frac{79\tau^{-1}/140p + 474/497(1/p - 1)(\tau^3/6 + \tau^9/135 + \tau^{15}/600)}{D} \quad (9) $$