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Thermodynamic optimizations of the Nd-Sn and Sn-Tb systems

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ABSTRACT

The thermodynamic optimizations of the Nd-Sn and Sn-Tb binary systems were carried out by means of the Calculation of Phase Diagram (CALPHAD) method on the basis of the available experimental data including the thermodynamic properties and phase equilibria. The Gibbs free energies of the liquid, bcc, bct, dhcp and hcp phases were described by the substitutional solution model with the Redlich-Kister equation, while all of the intermetallic compounds (Nd_5Sn_3, Nd_5Sn_4, $Nd_{11}Sn_{10}$, NdSn, Nd_3Sn_5, $NdSn_2$, Nd_3Sn_7, Nd_2Sn_5, $NdSn_3$, Sn_3Tb, βSn_7Tb_3, αSn_7Tb_3, Sn_2Tb, Sn_5Tb_4, $SnTb_4$, $Sn_{10}Tb_{11}$, Sn_4Tb_5 and Sn_3Tb_5) were described by the sublattice model. A set of self-consistent thermodynamic parameters of each phase in the Nd-Sn and Sn-Tb binary systems has been obtained, and the calculated results are in good agreement with the available experimental data.

1. Introduction

In the traditional electronic industry, Pb-Sn solder is widely used in manufacturing and assembly of electronic products owing to its unique combination of material properties and excellent wettability on the Cu substrate. However, the Pb is considered harmful to the human health and environment [1–4]. Therefore, it is important to develop the lead-free solder, which should have the same microstructure stability and mechanical properties as eutectic Pb-Sn solder. So far, a number of investigations have been focused on the lead-free solder alloys such as Sn-Bi, Sn-Ag, Sn-Cu, Sn-In, and Sn-Zn systems [1,5]. Among all these alloys, Sn-Zn system draws much attention because of its excellent properties. For instance, the eutectic temperature (199 °C) of the Sn-Zn alloy is very close to that of eutectic Sn-Pb (183 °C). In addition, the Sn-Zn alloy is less expensive and the mechanical properties such as tensile strength and creep resistance are better than those of the Sn-Pb alloy [6]. Unfortunately, due to the presence of the active zinc, the Sn-Zn based lead-free solders is easily to be oxidized in air, which will result in poor wetting ability [7]. With the addition of the rare earth (RE) elements, the properties such as microstructure, mechanical and wettability of Sn-Zn system were all improved [8,9]. Thus RE elements can be used as additive elements in Sn-Zn-based solders. Therefore, to design the appropriate solder compositions in the Sn-Zn-RE systems effectively, it is important to have a fundamental knowledge about the Sn-RE systems, such as information about the phase equilibria and the related thermodynamic data.

Recently, the Nd-Sn and Sn-Tb binary systems were thermodynamically optimized by Kim et al. [10,11] with using the Modified Quasichemical Model for liquid phase. However, with the CALPHAD approach [12], the Gibbs free energies of solution phases are described by the substitutional solution model and those of intermetallic compounds are modeled by the sublattice model, which make the thermodynamic parameters like the Gibbs energy of mixing of solution and the Gibbs energy of formation of the compounds are different from the work of Kim et al. [10,11]. Considering the compatibility of the thermodynamic parameters, the thermodynamic optimizations of the Nd-Sn and Sn-Tb binary systems have been carried out by using the CALPHAD method, which was adopted in the process of the development of the lead-free thermodynamic database in our group. The thermodynamic optimizations of the Nd-Sn and Sn-Tb binary systems will provide important thermodynamic information for the multicomponent Sn-Zn-RE alloy systems, and the present study is part of the thermodynamic database development of the lead-free solder alloys.

2. Thermodynamic

2.1. Solution phases

In the Sn-RE (RE = Nd, Tb) binary systems, the Gibbs free energies of the liquid, bcc, bct, dhcp, and hcp phases are described by the

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substitutional solution model, as follows:

$$G_m^{\Phi} = \sum_{i=Sn,RE} {}^0G_i^{\Phi} x_i + RT \sum_{i=Sn,RE} x_i ln x_i + \Delta^E G_m^{\Phi} \quad (1)$$

where ${}^0G_i^{\Phi}$ is the Gibbs free energy of the pure component i in the respective reference state with Φ phase, which is taken from the SGTE pure element database [13]; RE means the element Nd or Tb; X_i denotes the mole fraction of the component i; R is the gas constant; T is the absolute temperature; and the term $\Delta^E G_m^{\Phi}$ presents the excess Gibbs free energy, which is expressed by a Redlich-Kister polynomial [14] as:

$$\Delta^E G_m^{\Phi} = x_{Sn} x_{RE} \sum_{m=0}^{n} {}^mL\Phi_{Sn,RE}(x_{Sn} - x_{RE})^m \quad (2)$$

$${}^mL_{Sn,RE}^{\Phi} = a + bT \quad (3)$$

where ${}^mL_{Sn,RE}^{\Phi}$ is the binary interaction parameter, and the coefficients of *a and b* are constants to be evaluated on the basis of available experimental data.

2.2. Stoichiometric intermetallic compounds

The intermetallic compounds of the Nd_5Sn_3, Nd_5Sn_4, $Nd_{11}Sn_{10}$, NdSn, Nd_3Sn_5, $NdSn_2$, Nd_3Sn_7, Nd_2Sn_5, and $NdSn_3$ phases in the Nd-Sn binary system and the Sn_3Tb, βSn_7Tb_3, αSn_7Tb_3, Sn_2Tb, Sn_5Tb_4, $SnTb_4$, $Sn_{10}Tb_{11}$, Sn_4Tb_5, and Sn_3Tb_5 phases in the Sn-Tb system are all treated as stoichiometric phases and described by the sublattice model [15]. The Gibbs energy per mole of formula unit Sn_pRE_q can be expressed, as follows:

$${}^0G_{Sn:RE}^{Sn_pRE_q} = p\,{}^0G_{Sn}^{SER} + q\,{}^0G_{RE}^{SER} + \Delta^0 G_f^{Sn_pRE_q} \quad (4)$$

where the $\Delta^0 G_f^{Sn_pRE_q}$ indicates the standard Gibbs free energy of formation of the stoichiometric compound from pure elements, which is described as:

$$\Delta^0 G_f^{Sn_pRE_q} = a' + b'T \quad (5)$$

where the parameters of a' and b' are evaluated in the present work.

3. Thermodynamic optimizations

The optimization of the thermodynamic parameters was carried out by using the PARROT program in the Thermo-Calc software [16], which can handle various kinds of experimental data. The experimental data of the phase diagram and thermodynamic properties were used as input to the program. Each piece of selected information was given a certain weight based on the importance of data, and changed by trial and error during the assessment, until most of the selected experimental information was reproduced within the expected uncertainty limits.

3.1. The Nd-Sn system

3.1.1. Literature information

The Nd-Sn system consists of four solid solution phases (bcc (βNd), bct (αSn), dhcp (αNd) and hcp (βSn) phases) and nine intermetallic compounds (Nd_5Sn_3, Nd_5Sn_4, $Nd_{11}Sn_{10}$, NdSn, Nd_3Sn_5, $NdSn_2$, Nd_3Sn_7, Nd_2Sn_5 and $NdSn_3$ phases).

Firstly, the melting temperature of $NdSn_3$ was determined to be 1138 °C by Palenzona [17] using dynamic differential calorimetry. Later, with the thermal analysis and microscopic examination, Kulagina et al. [18] studied the Sn-rich region of the phase diagram 75–100 at% Sn) and found the melting temperature of $NdSn_3$ compound phase to be 1137 ± 4 °C, which agreed with the Ref. [17]. Based on the DTA, XRD and metallographic analysis, Eremenko et al. [19] investigated the Nd-Sn system in the composition range of 0–50 at% Sn, where there are two intermetallic compounds: Nd_5Sn_3 (m.p. 1640 ± 10 °C) and Nd_5Sn_4 (m.p. 1500 °C), an eutectic reaction: L (12.0 at% Sn) ↔ Nd_5Sn_3 + βNd at 870 ± 10 °C and an eutectoid reaction: βNd (6 at% Sn) ↔ αNd + Nd_5Sn_3 at 820 °C. With the same method, Eremenko et al. [20] investigated the Nd-Sn system in the composition range of 45–100 at% Sn, and confirmed the melting temperature of Nd_5Sn_3 and Nd_5Sn_4 to be 1660 °C and 1558 ± 11 °C respectively. Four intermediate phases were additionally found: $Nd_{11}Sn_{10}$ (1396 ± 15 °C), NdSn (1257 ± 4 °C), Nd_3Sn_5 (1130 ± 2 °C) and $NdSn_3$ (1170 °C) [20]. However, the investigation was not adequate. The phases of $NdSn_2$, Nd_3Sn_7 and Nd_2Sn_5 were found in the later studies, the eutectoid temperature of Nd_3Sn_5 (1130 ± 2 °C) and the congruent temperature of $NdSn_3$ (1170 °C) were refined to be 1140 °C and 1150 °C respectively.

According to the reported experimental data obtained by Eremenko et al. [19,20], Massalski [21] established the complete Nd-Sn phase diagram, where there are six intermetallic compounds: Nd_5Sn_3 (m.p. 1660 °C), Nd_5Sn_4, $Nd_{11}Sn_{10}$, NdSn, Nd_3Sn_5 and $NdSn_3$ (m.p. 1170 °C), two eutectic reactions: L ↔ NdSn + $NdSn_3$ at 1159 °C and L ↔ βNd + Nd_5Sn_3, and an eutectoidal transformation is also reported: βNd ↔ αNd + Nd_5Sn_3 at 820 °C. Weitzer et al. [22] discovered three additional compounds: $NdSn_2$, Nd_3Sn_7, and Nd_2Sn_5, and clarified the phase relationship between them. Thus, the eutectic reaction between $NdSn_3$ and NdSn reported by Eremenko et al. [20] was unfeasible. Saccone et al. [23] studied the Nd-Sn phase diagram in the 55–80 at% Sn range by differential thermal analysis, X-ray powder diffraction, optical and scanning electron microscopy and electron probe microanalysis. The sample alloys were prepared in an induction furnace and fused in tantalum crucibles with the starting materials, 99.9% Nd and 99.999% Sn. In this range, five intermediate phases were identified: $NdSn_3$ (m.p. 1150 °C), Nd_2Sn_5, Nd_3Sn_7, $NdSn_2$ (m.p. 1180 °C) and Nd_3Sn_5, where the melting temperature of $NdSn_3$ was altered to be 1150 °C from 1170 °C determined by Eremenko et al. [20]. Two eutectic equilibria were found at 1130 °C and 60.5 at% Sn and 1130 °C and 73 at% Sn. On the basis of the reported experimental data [19–22], Saccone et al. [23] modified the Nd-Sn phase diagram, where there are four eutectic reactions: L (73.0 at% Sn) ↔ Nd_2Sn_5 + $NdSn_3$ at 1130 °C, L (60.5 at% Sn) ↔ NdSn + Nd_3Sn_5 at 1130 °C, L (12.0 at% Sn) ↔ Nd_5Sn_3 + (βNd) at 870 °C, L ↔ $NdSn_3$ + (βSn) at 230 °C, six peritectic reactions: L + Nd_5Sn_3 ↔ Nd_5Sn_4 at 1558 °C, L + Nd_5Sn_4 ↔ $Nd_{11}Sn_{10}$ at 1396 °C, L + $Nd_{11}Sn_{10}$ ↔ NdSn at 1257 °C, L + $NdSn_2$ ↔ Nd_3Sn_7 at 1145 °C, L + $NdSn_2$ ↔ Nd_3Sn_5 at 1140 °C, L + Nd_3Sn_7 ↔ Nd_2Sn_5 at 1135 °C and an eutectoid reaction: βNd ↔ αNd + Nd_5Sn_3.

In addition, the enthalpy of formation of the compound $NdSn_3$ phase was carried out by Palenzona [17] using dynamic differential calorimetry with a conventional DTA apparatus. And by means of the direct synthesis calorimetric, Meschel and Kleppa [24] measured the enthalpy of formation of the Nd_5Sn_3 compound. With the Miedema model, Takeuchi and Inoue [25] summarized that the value of the enthalpy of mixing of liquid phase with the reference states of pure liquid metals at 50 at% Sn in the Nd-Sn system is −53 kJ/mol. However, no temperature dependence was given in the work of Ref. [25]. By using liquid-metal solution calorimeter, Peluso and Pool [26] and Lundin and Pool [27] measured the heats of solution of solid (dhcp) Nd in liquid Sn at 750 K in the Nd-dilute composition range. The partial enthalpy of mixing of Nd at infinite dilution at 750 K was calculated to be −251 kJ/mol [26] and −294 kJ/mol [27], respectively. With emf measurements, Kulagina and Bayanov [28] determined the activities of Nd in liquid solution at 773 K, 873 K and 973 K. Later, Matigorova and Bayanov [29] reported the activity values for the same temperature. Based on the reported partial Gibbs energy of Nd, Kober et al. [30] determined the activity of Nd in the two phases (L + $NdSn_3$) at 1000 K.

3.1.2. Thermodynamic optimizations

The optimized phase diagram of 55–80 at% Sn region was constructed based on the work of Saccone et al. [23], and the other composition range based on the experimental data of Eremenko et al. [17–20]. The calculated Nd-Sn phase diagram compared with the experimental data [17–20,23] is shown in Figs. 1, and 2 presents the