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Thermodynamic assessments of the Au–Gd and Au–Yb systems

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ABSTRACT

The thermodynamic assessments of the Au–Gd and Au–Yb binary systems have been carried out by the Calculation of Phase Diagram (CALPHAD) method based on the available experimental data. The Gibbs free energies of the solution phases including liquid, fcc, bcc, and hcp were described by the substitutional solution models with the Redlich–Kister equation. All the intermetallic compounds except the βAuYb phase were treated as stoichiometric phases, and the βAuYb phase was modeled using the sublattice model. The thermodynamic parameters of each phase in the Au–Gd and Au–Yb binary systems were obtained, and an agreement between the calculated results and experimental data was obtained in each binary system.

1. Introduction

As convenient electronic packing materials, the Sn–Pb-based solders can cause serious harm to health and environment because of the toxic nature of plumbum. Therefore, the development of Pb-free solders, which should satisfy the criterion regarding plentiful supply, favorable physical and chemical properties and cost benefit, has been considered necessarily [1,2]. As the most promising substitute for leaded solders, Sn–Au eutectic solder has been vastly employed for optoelectronic packages in high-temperature environments with high thermal and electrical conductivities, superior creep resistance and excellent solderability [3,4]. Furthermore, the addition of the appropriate amount of rare earth (RE) elements can refine the microstructure of lead-free solder alloy, which improves the wettability, mechanical property and thermal fatigue behavior of lead-free solder joint significantly [5,6]. As a result, to design the proper alloy compositions, understanding of the phase equilibria of the Sn–Au–RE becomes necessary. In the research program, the thermodynamic database for Au–RE (RE=La, Ce, Pr, Nd, Eu, Gd, Dy, Er, Ho….) will be developed.

Recently, the Au–Gd binary system was thermodynamically optimized in reference [7], where the enthalpies of mixing of liquid phase [8] and activities of components [9] in Au–Gd binary system were not considered. In the present work, the thermodynamic assessments of Au–Gd and Au–Yb systems have been carried out by the Calculation of Phase Diagram (CALPHAD) approach [10], and the thermodynamic database of the Au–RE systems have been developed, which will provide important thermodynamic information for the multi-component Sn–Au–RE alloy systems.

2. Thermodynamic models

2.1. Liquid phases and solid solutions

The Gibbs free energies of the liquid, fcc, bcc, and hcp phases in the Au–RE (RE=Gd and Yb) binary systems are described by the substitutional solution model with using the Redlich–Kister formula [11]. The molar Gibbs free energies of solution phase in the Au–RE systems are expressed as:

$$G_m^{\Phi} = \sum_{i=\mathrm{Au,RE}} {}^{0}G_i^{\Phi} x_i + RT \sum_{i=\mathrm{Au,RE}} x_i \ln x_i + x_{\mathrm{Au}} x_{\mathrm{RE}} \sum_{m=0}^{n} {}^{m}L_{\mathrm{Au,RE}}^{\Phi} (x_{\mathrm{Au}} - x_{\mathrm{RE}}). \tag{1}$$

where ${}^{0}G_i^{\Phi}$ is the Gibbs free energy of pure element i in the respective reference state with the Φ phase, which is taken from the SGTE pure elements database [12], R is the gas constant, T is the temperature, x_i is the molar fraction of component i. ${}^{m}L_{\mathrm{Au,RE}}^{\Phi}$ is the binary interaction parameter and formulated as:

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$${}^{m}L^{\Phi}_{Au,RE} = a_m + b_m T. \quad (2)$$

where the values of a_m and b_m are optimized in the present work.

2.2. Stoichiometric compounds

All the intermetallic compounds except the βAuYb phase in the Au–RE (RE=Gd and Yb) binary systems are treated as stoichiometric phases. The Gibbs free energy per mole of formula unit Au_mRE_n can be expressed, as follows:

$$\Delta^0G_f^{Au_mRE_n} = {}^0G_f^{Au_mRE_n} - m^0G_{Au}^{SER} - n^0G_{RE}^{SER} = a'_m + b'_mT + c'_mT\ln T + d'_mT^2 + e'_mT^3 \quad (3)$$

where the $\Delta^0G_f^{Au_mRE_n}$ indicates the standard Gibbs free energy of formation of the stoichiometric compounds from pure elements. The parameters of a'_m, b'_m, c'_m, d'_m and e'_m are assessed in the present work.

2.3. Intermetallic compound with solubility

The intermetallic compound of the βAuYb phase with certain solubility is modeled by the two-sublattice model $(Au)_{0.5}$:$(Au,Yb)_{0.5}$. The molar Gibbs free energy of the compounds is presented by the following equation:

$$G_m^{\beta AuYb} = y_{Au}^{I}\,{}^0G_{Au:Au}^{\beta AuYb} + y_{Yb}^{I}\,{}^0G_{Au:Yb}^{\beta AuYb} + 0.5RT(y_{Au}^{I}\ln y_{Au}^{I} + y_{Yb}^{I}\ln y_{Yb}^{I}) + 0.5y_{Au}^{I}y_{Yb}^{I}L_{Au:Au,Yb} \quad (4)$$

where y_i^I is the site fraction of element i in the first sublattice. The ${}^0G_{i:j}^{\beta AuYb}$ represents the Gibbs free energies of the βAuYb compound when the first and second sublattices are respectively occupied by elements i and j. $L_{Au:Au,Yb}$ is the interaction energy between Au atoms in the first sublattice when the second sublattice is occupied by Au and Yb, and is expressed as:

$$L^{\varphi}_{Au:Au,Yb} = a'' + b''T + c''\ln T \quad (5)$$

the parameters of a'', b'' and c'' are evaluated in this work.

3. Thermodynamic optimization

The optimization of the thermodynamic parameters was carried out by using PARROT program in the Thermo-Calc software [13], 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 available experimental 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 Au–Gd system

3.1.1. Experimental information

In the Au–Gd system, the terminal solid solubility of Gd in (Au) was experimentally determined to be 0.7 at% Gd by Rider et al. [14], and the intermetallic compounds and the melting point of βAuGd phase was presented by McMasters et al. [15]. Besides these, the crystal structures of the intermetallic compounds (Au_6Gd [15,16], $Au_{51}Gd_{14}$ [15], Au_3Gd [17], Au_2Gd [15,18,19], AuGd (β and α allotropic forms) [15,20,21] and $AuGd_2$ [15]) were obtained. Later, the phase diagram in the Au–Gd system was studied by Saccone et al. [22], who firstly reported the compounds of $Au_{10}Gd_7$ and Au_4Gd_3 phases, and identified four solution phases (liquid, (Au), (αGd), (βGd)) and 9 intermetallic compounds (Au_6Gd, $Au_{51}Gd_{14}$, Au_3Gd, Au_2Gd, $Au_{10}Gd_7$, Au_4Gd_3, βAuGd, αAuGd and $AuGd_2$) with differential thermal analysis (DTA), X-ray diffraction (XRD), optical and scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). Saccone et al. [22] also determined five eutectic reactions (L↔(Au)+Au_6Gd at 11.0 at% Gd and 800 °C, L↔$Au_{51}Gd_{14}$+Au_3Gd at 23.0 at% Gd and 1135 °C, L↔Au_3Gd+Au_2Gd at 29.5 at% Gd and 1110 °C, L↔Au_2Gd+$Au_{10}Gd_7$ at 36.5 at% Gd and 1140 °C, and L↔$AuGd_2$+(αGd) at 79.0 at% Gd and 845 °C), four peritectic reactions (L+$Au_{51}Gd_{14}$↔Au_6Gd at 855 °C, L+Au_4Gd_3↔$Au_{10}Gd_7$ at 1160 °C, L+αAuGd↔Au_4Gd_3 at 1340 °C, and L+αAuGd↔$AuGd_2$ at 935 °C), a polymorphic reaction (βAuGd↔αAuGd at 1475 °C) and a catatectic reaction ((βGd)↔L+(αGd) at 1220 °C).

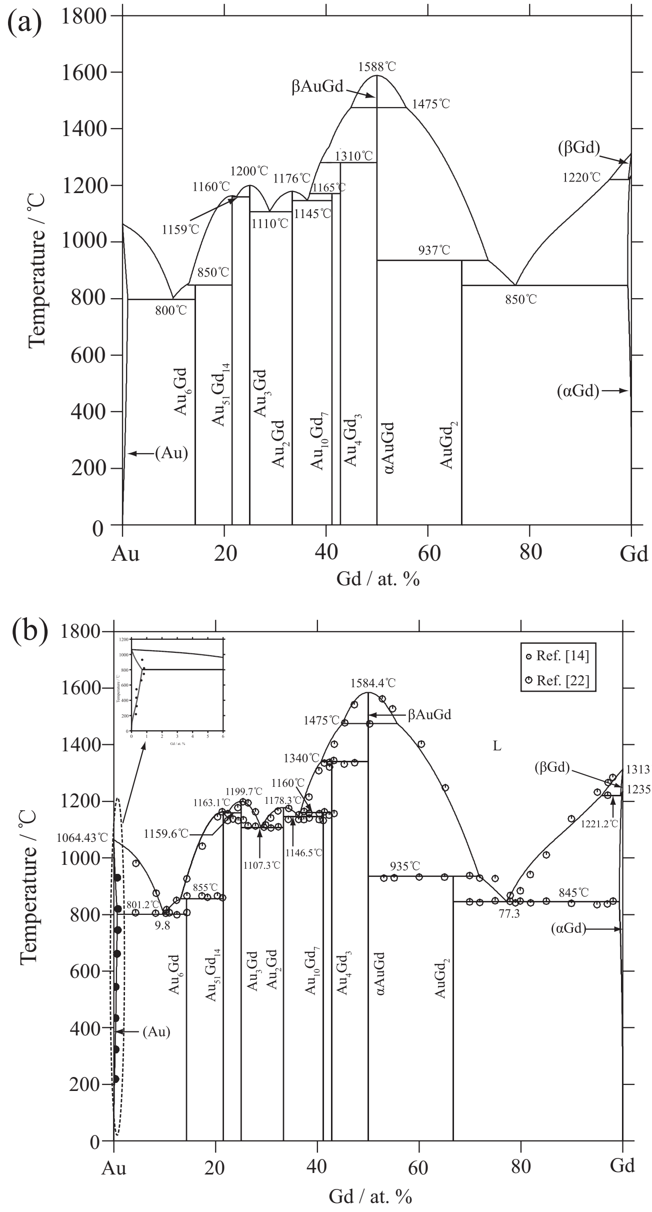

Fig. 1. Calculated phase diagram of the Au–Gd system: (a) from Ref. [7]; (b) in this work compared with the experimental data [14,22].

Additionally, Fitzner and Kleppa [23] experimentally determined the value of standard enthalpies of formation of αAuGd, Au_2Gd and Au_3Gd compounds by using high-temperature direct synthesis calorimety is −82.6 ± 2.7 kJ/mol of atoms, −77.2 ± 2.7 kJ/mol of atoms, −69.9 ± 2.2 kJ/mol of atoms respectively. Later, Ferro et al. [24] reported the value of standard enthalpies of formation of αAuGd phase is −82.0 ± 2.0 kJ/mol of atoms at 27 °C. Witusiewicz and Ivanov [8]