Phase stability of Ag–Sn alloy nanoparticles

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ABSTRACT

Nanoparticles often possess phase stabilities that differ from those of bulk materials, as a result of their large surface-to-volume ratio. Park and Lee suggested that the phase diagram of metallic nanoparticles can be calculated using the CALPHAD method through the introduction of the size effect. Based on Park and Lee's model, the thermodynamic parameters for the Ag–Sn nanoparticle system (pure Ag and Sn, the intermetallic compound Ag_3Sn, and liquid and solid solutions (fcc, hcp, and bct)) were optimized as a function of temperature, composition, and the size of the nanoparticle. The phase stability of the Ag_3Sn nanoparticles was affected by the selection of the surface tension value for Ag_3Sn; however, the eutectic temperature and composition are not affected by the phase stability of the Ag_3Sn nanoparticles. When the size of the nanoparticles is decreased, the eutectic temperature decreases, and the eutectic composition approaches the Sn-rich corner. The present results exhibited a reasonable agreement with the reported experimental data.

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1. Introduction

Researchers who seek to design new Pb-free solders are required to simultaneously consider many parameters. The most important factors that are considered when the selecting an alloy are the melting point and reliability. Since the conventional Sn–Pb eutectic alloy exhibits a melting point of 456 K (183 °C), it is reasonable to assume that a new Pb-free solder alloy would possess a melting point close to that of the Sn–Pb eutectic alloy.

Although there are several alloys that possess melting points close to or lower than the Sn–Pb eutectic alloy, many of them cannot be used as solders as a result of their unreliability (poor wetting, broad freezing range, or price, to name a few). For example, Sn–9 wt%Zn alloy exhibits a melting point of 471 K, but the wettability is poor due to the oxidation of Zn [1]. Additionally, this alloy also exhibits poor compatibility with Cu substrates resulting from the formation of an intermetallic compound (Cu_5Zn_8) [2]. Sn–58 wt%Bi alloy has been considered as a potential soldering alloy due to its low melting point (412 K). However, recrystallization of this alloy causes volume expansion which results in deformation at the interface, and thus leads to embrittlement [3]. Sn–6 wt%Bi–6 wt%Zn alloy exhibits a melting point of 441 K, but the Zn and Bi present in this alloy result in poor wettability and a broad freezing range [1]. Sn–20 wt%In–2.8 wt%Ag alloy has a melting point of 451 K and better mechanical property than Sn–3.5 wt%Ag alloy [4]. However, the disadvantage of this alloy is high cost of In. For quaternary or higher multi-component alloy systems, the decrease in

the liquidus temperature is insignificant [1]. Currently, the most popular Pb-free solder alloys are Sn–Ag or Sn–Ag–Cu alloys. The primary drawback of these alloys for soldering purposes is their high melting point (489–498 K).

As an alternative technical approach, several researchers have begun focusing their attention on nanoparticles (NPs), because the melting point of the NPs can be decreased as a result of their high surface-to-volume ratio [5–21]. Pb-free solder NPs have been previously fabricated using the chemical reduction method, the consumable-electrode direct current arc method, the arc discharge method, and the sonochemical reduction method [5–17]. The melting point of solder NPs has decreased significantly: Sn–3.0 wt%Ag–0.5 wt%Cu NPs (5–100 nm) exhibit a melting point of 470–488 K [8–11], Ag–Sn NPs (10–90 nm) exhibit a melting point of 446–501 K [14–17], and Au–(33–84)wt%Sn NPs (2–10 nm) exhibit a melting point of 460–469 K [13]. However, most of the alloy compositions in these studies were selected with respect to bulk Pb-free solder alloys.

Recently, theoretical and experimental studies on the phase stability of NPs have been extensively investigated [8,9,17–25,35,36]. The CALPHAD (Computer Calculation of Phase Diagrams)-type thermodynamic description of alloy NPs is a powerful tool for predicting the phase diagram of NPs equal to or larger than 10 nm in diameter [22], which could save time and lower experimental costs. However, the CALPHAD-type phase diagrams have previously been used to describe fully miscible alloys or simple eutectic alloy systems [23–25,35,36]. For an incongruent melting system containing an intermetallic compound, Sopousek et al. suggested a phase diagram of Sn–Ag alloy, one of the strongest candidates for the Pb-free solder NP system, and a typical incongruent melting

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system. However, in this study, the chemical potential of Ag_3Sn NP was simply assumed as the sum of each fraction of pure Ag and Sn NPs ($\mu_{Ag_3Sn} = 0.75\mu_{Ag} + 0.25\mu_{Sn}$) [17]. Therefore, it is considered that no systematic study has yet been carried out for an incongruent melting system. In this study, calculations for the Sn–Ag NP system have been performed based on the re-optimized thermodynamic variables as a function of temperature, composition, and NP size.

2. Theory

The CALPHAD-type thermodynamic model of an alloy NP system was developed by Park and Lee [24], and was further improved and extended to nanowire and nanofilm systems by Lee and Sim [25]. Herein, the thermodynamic model of a binary NP system is summarized. The present model is a slightly modified version of the original model suggested by Park and Lee [24].

The total Gibbs free energy of an A–B binary system is composed of the bulk and surface Gibbs free energies:

$$G^{Total} = G^{Bulk} + G^{Surface} \tag{1}$$

The Gibbs free energy of bulk alloy is expressed by Eq. (2):

$$G^{Bulk} = X_A G_A^o + X_B G_B^o + RT(X_A \ln X_A + X_B \ln X_B) + G^{Ex,Bulk} \tag{2}$$

where X_A and X_B are the mole fractions of A and B, respectively. G_A^o and G_B^o are the standard Gibbs free energies of A and B, respectively. R is the gas constant, T is the temperature, and $G^{Ex,Bulk}$ is the excess Gibbs free energy, which is typically described by the Redlich–Kister polynomial, expressed by Eq. (3).

$$G^{Ex,Bulk} = X_A X_B \sum L^v (X_B - X_A)^v \quad (v = 0, 1, 2, \ldots) \tag{3}$$

$$L^v = a + bT + cT \ln T + \cdots \tag{4}$$

When the NP is assumed as an isotropic spherical particle, the Gibbs free energy of the surface is expressed by Eq. (5). Here, we assume that the contact angle between the NPs and the substrate is adequately high, and the interface between phases within the NPs is planar:

$$G^{Surface} = \frac{2\sigma V}{r} \tag{5}$$

where V is the molar volume, r is the radius of the NP, and σ is the surface tension.

For a pure element i, the Gibbs free energy of the surface is described by Eq. (6).

$$G_i^{Surface} = \frac{2\sigma_i^o V_i}{r} \tag{6}$$

Although the surface tension of a liquid is identical to the experimental data, that of a solid can be affected by the shape of the NP (resulting anisotropic surface tension of each face), the surface strain, and the uncertainty of the measurements. Therefore, the surface tension of a solid should be expressed with a correction factor c ($\sigma_i^o = c \times \sigma_i$(experiment)), which can be determined by fitting the melting point of pure metallic NPs. A constant value for c is typically sufficient to describe the melting behavior of pure spherical metallic NPs with a radius larger than 5 nm.

Eq. (6) is also valid for stoichiometric intermetallic compounds. If there is no experimental data for the surface tension of an intermetallic compound, it should be estimated indirectly. Iida and Guthrie reported that the surface tension of pure liquid metals at their melting point is proportional to $\Delta H_{LG}/V_i^{2/3}$, where ΔH_{LG} is the enthalpy of evaporation [26]. The correlation between the surface tension of liquid metals and $\Delta H_{LG}/V_i^{2/3}$ at the melting point is given by Eq. (7).

$$\sigma_L \approx 1.8 \times 10^{-9} \frac{\Delta H_{LG}}{V_i^{2/3}} \tag{7}$$

Similarly, we may assume that the surface tension of solid metals at their melting point is proportional to $\Delta H_{SG}/V_i^{2/3}$, where ΔH_{SG} is the enthalpy of sublimation [24]. Fig. 1 displays the relationship between the surface tension of solid metals as a function of $\Delta H_{SG}/V_i^{2/3}$ at their melting points. A similar correlation between the solid metals can be described by Eq. (8).

$$\sigma_s \approx 1.7 \times 10^{-9} \frac{\Delta H_{SG}}{V_i^{2/3}} \tag{8}$$

Most of the surface tension values fit within the predicted values from Eq. (8) within an error of ±20%. The melting point of an intermetallic compound can be computed from the chemical potential equilibrium between the liquid and the intermetallic compound, while the sublimation enthalpy and molar volume at the melting point can be obtained from the literature. Additionally, the surface tension
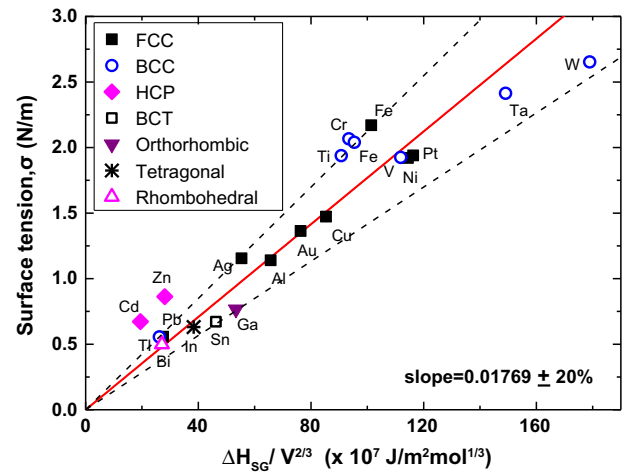

Fig. 1. Relationship between the surface tension and $\Delta H_{SG}/V^{2/3}$ at various melting points.

of the intermetallic compound can be estimated from Eq. (8). If the melting behavior of the NPs composed of the intermetallic compound is measureable, then c can be determined experimentally. However, in many cases, the melting behavior of such NPs is difficult to determine experimentally. In such cases, the correction factor is simply assumed to be unity.

In order to determine the Gibbs free energy of the surface of binary alloy NPs, the molar volume and the surface tension should be separately calculated. The molar volume of the alloy can be regarded as the sum of the contribution of each component, when the excess volume is negligible.

$$V = V_A X_A + V_B X_B \tag{9}$$

The surface tension of the alloy can be evaluated using Butler's equation [27,28]:

$$\sigma = \sigma_A^o + \frac{RT}{A_A} \ln\left(\frac{X_A^{Surface}}{X_A^{Bulk}}\right) + \frac{1}{A_A}\left[G_A^{Ex,Surface}\left(T, X_B^{Surface}\right) - G_A^{Ex,Bulk}\left(T, X_B^{Bulk}\right)\right]$$

$$= \sigma_B^o + \frac{RT}{A_B} \ln\left(\frac{X_B^{Surface}}{X_B^{Bulk}}\right) + \frac{1}{A_B}\left[G_B^{Ex,Surface}\left(T, X_B^{Surface}\right) - G_B^{Ex,Bulk}\left(T, X_B^{Bulk}\right)\right] \tag{10}$$

where the surface tension of a pure element, σ_i^o, is the re-estimated value with the correction factor c ($\sigma_i^o = c\sigma_i$), and the molar surface area of i (for both A and B) is obtained by Eq. (11) when a close-packed surface monolayer is assumed to be present.

$$A_i = 1.091 N_0^{1/3} V_i^{2/3} \tag{11}$$

where N_0 is Avogadro's number. Additionally, the partial excess Gibbs free energies of surface and bulk have a relationship given by Eq. (12) [30].

$$G_i^{Ex,Surface}\left(T, X_B^{Surface}\right) = \beta \times G_i^{Ex,Bulk}\left(T, X_B^{Surface}\right) \tag{12}$$

The physical meaning of β is the ratio of the coordination number between the surface and bulk atoms. Park and Lee showed that the values of β for pure solid and liquid metals are 0.85 and 0.84, respectively [24]. Tanaka et al. argued that the experimentally determined β value includes the effect of surface relaxation, and also assumed that the β value of a mixture is the same as pure elements [27,28]. The calculated surface tension of several binary alloys under these assumptions exhibited reasonable agreements with the experimental values [27–29].

3. Results

The procedure for the optimization of the thermodynamic parameters of the Sn–Ag NP system is summarized below:

(1) Determination of the surface tension of the pure solid phase (Sn and Ag) with the correction factor c.
(2) Determination of the molar volume of the various pure solid phases (Sn(bct), Sn(fcc), Sn(hcp), Ag(fcc), and Ag(hcp)).
(3) Determination of the surface tension of the stoichiometric intermetallic compound (Ag_3Sn).
(4) Determination of the molar volume of the stoichiometric intermetallic compound (Ag_3Sn).