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Thermodynamic description of the Ag–Bi–Sb system

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ABSTRACT

The thermodynamic optimization of the Ag–Bi–Sb system was critically carried out by means of the CALPHAD (CALculation of PHAse Diagram) technique. The solution phases, liquid, fcc, rhomb and hcp_A3(ζ) were described by the substitutional solution model. The compound $\varepsilon(Ag_3Sb)$ was treated as the formula $(Ag, Sb)_{3/4}(Ag, Sb)_{1/4}$ using two sublattice model in the Ag–Bi–Sb ternary system, which is directly from the Ag–Sb binary system. A self-consistent thermodynamic description of the Ag–Bi–Sb system was developed. The vertical sections at 10 at.% Bi, 10 at.% Ag and 70 at.% Ag, the isothermal section at 300 K, the projection of the liquidus surfaces, and the complete reaction scheme for the Ag–Bi–Sb system in the literature were reproduced in the present work.

1. Introduction

In view of environmental and health concerns [1], many investigations have been made in research and development of lead-free substitute solders as replacement of the most commonly used Pb–Sn solder [2,3]. Knowledge about phase diagram and thermodynamic properties of the studied alloys is required to predict the thermal behavior, the microstructure evolution of the solder itself and the possible interfacial reactions between solder and substrate. The Ag–Bi–Sb ternary system is one of the important lead-free systems. Thermodynamic modelling of phase equilibria in perspecive systems represents first necessary step for development of new lead-free soldering materials. For this purpose, the Ag–Bi–Sb system is firstly optimized in this work.

This work deals with a thermodynamic assessment of the Ag–Bi–Sb system by means of the CALPHAD (CALculation of PHAse Diagram) technique. In this method, the thermodynamic properties of the alloy systems are studied using thermodynamic models for the Gibbs energy of the individual phases. The thermodynamic parameters involved in the models are optimized using the experimental thermodynamic and phase diagram information.

2. Binary systems

To obtain a thermodynamic description of a ternary system, the thermodynamic description of each involved binary system is necessary.

2.1. Ag–Bi system

The available experimental information regarding the Ag–Bi system was determined and compiled by several authors [4–11]. The reviewed phase diagram for the Ag–Bi system is based on the work made by Kleppa [4], Nathans [5], Predel [7] and Zimmermann [10]. The maximum solubility of Bi in fcc(Ag) is 2.615 at.% at 723 K. The solid solubility of Ag in rhomb(Bi) is negligibly small. Fig. 1 presents the calculated phase diagram of Ag–Bi system using the thermodynamic description of Zoro et al. [12,13]. The thermodynamic parameters obtained by Zoro et al. [12,13] are adopted in the present work.

2.2. Ag–Sb system

The boundaries of the range of existence of the phase $\varepsilon(Ag_3Sb)$ were measured by Feschotte et al. [14] using X-ray powder diffraction. The Ag–Sb system had been assessed by Lee et al. [15]. However, their thermodynamic parameters could not well reproduce the determined phase diagram in the temperature range below 500 K, and the calculated heats of formation of the solid phases showed large discrepancies from the experimental ones. Later, the available experimental information regarding the Ag–Sb system was compiled by Oh et al. [16], who preformed the thermodynamic re-assessment in 1996. The thermodynamic parameters obtained by Oh et al. [16] are adopted in the present work. Fig. 2 presents the calculated phase diagram of Ag–Sb system using the thermodynamic description of Oh et al. [16].

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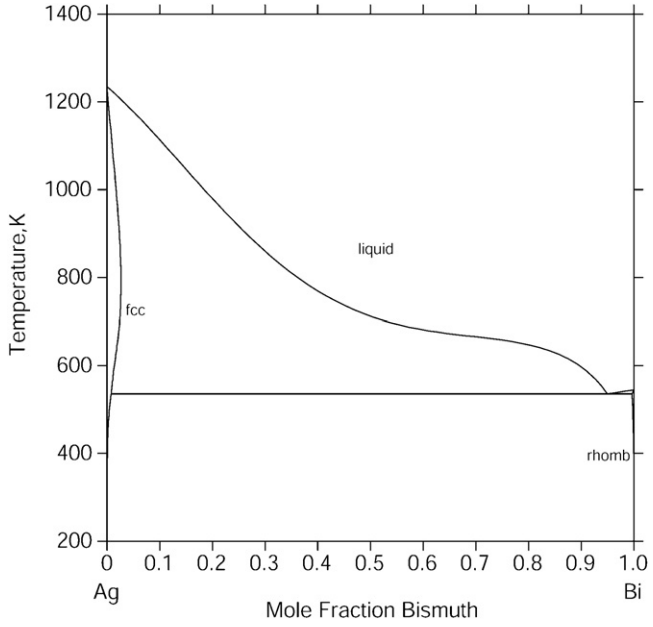

Fig. 1. Calculated Ag–Bi phase diagram by Zoro et al. [12,13].

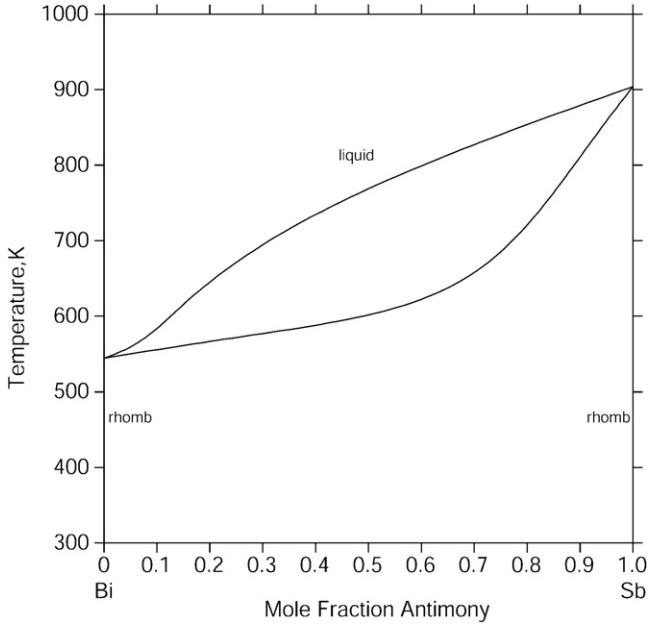

Fig. 3. Calculated Bi–Sb phase diagram by Dinsdale et al. [17].

2.3. Bi–Sb system

There are two equilibrium phases, liquid and rhomb (Bi, Sb) solid solution, in the Bi–Sb system. The Bi–Sb system is very simple and assessed by Dinsdale et al. [17]. The calculated results using the thermodynamic parameters [17] were in good agreement with the experimental data, which was accepted in the assessment of the Bi–Sb–Sn system [18]. The thermodynamic parameters obtained by Dinsdale et al. [17] are adopted in the present work. Fig. 3 presents the calculated phase diagram of Bi–Sb system using the thermodynamic description of Dinsdale et al. [17].

3. Experimental information on the Ag–Bi–Sb system

The information about the Ag–Bi–Sb system is very scarce. Recently, the phase diagram of the Ag–Bi–Sb ternary system has been determined using X-ray powder diffraction analysis and differential scanning calorimetry by Hassam et al. [19]. Hassam et al. [19] investigated the vertical sections at 10 at.% Bi, 10 at.% Ag and 70 at.% Ag, presented the isothermal section at solid equilibria, the projection of liquidus surfaces and the complete reaction scheme of the Ag–Bi–Sb system. However, the vertical section at 10 at.% Ag was not given in the paper [19].

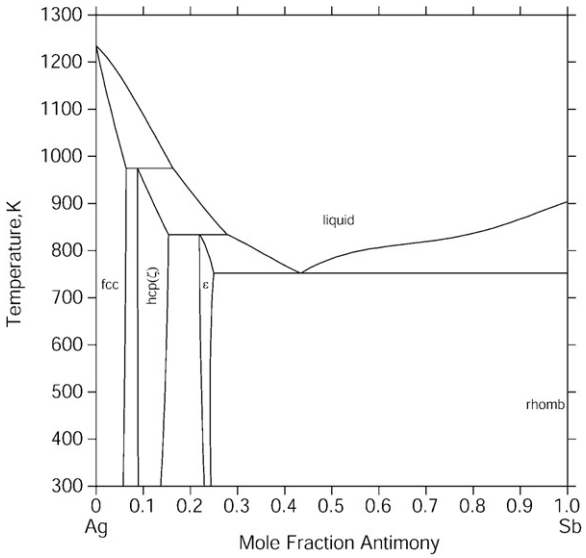

Fig. 2. Calculated Ag–Sb phase diagram by Oh et al. [16].

4. Thermodynamic models

4.1. Unary phases

The Gibbs energy function for the element i (i = Ag, Bi, Sb) in the phase ϕ (ϕ = liquid, fcc, rhomb) is described as follows,

$$G_i^{\phi}(T) = {}^{0}G_i^{\phi}(T) - H_i^{\mathrm{SER}}(298.15\,\mathrm{K})$$

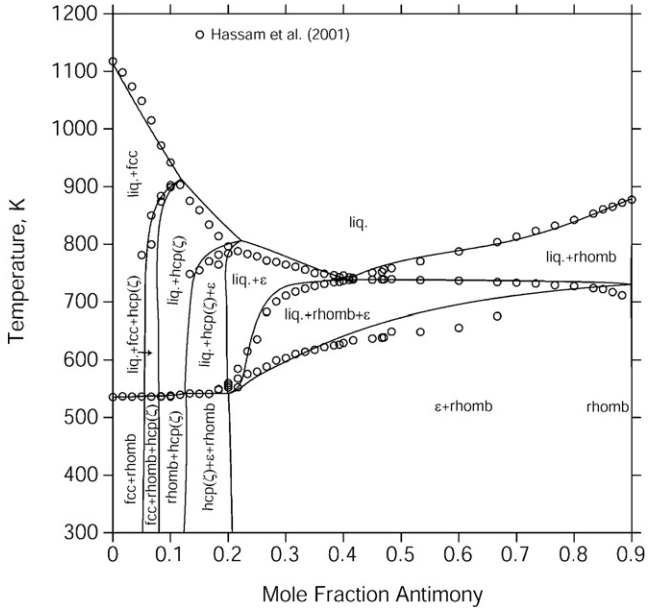

Fig. 4. Calculated vertical section of the Ag–Bi–Sb system at 10 at.% Bi by the present description and comparison with the experimental data [19].