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Thermodynamic assessment of the Ag–Au–Bi system

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Abstract

The Ag–Au–Bi system has been thermodynamically assessed through the Calphad approach by combining recently derived experimental data, in particular the phase diagram equilibria and the integral enthalpies of mixing of its liquid phase. A good agreement is obtained between the calculation and the experimental data. The resulting assessment will be incorporated into the thermodynamic description of the quaternary Ag–Au–Bi–Sb system, which is of interest in the lead-free soldering process for electronic materials.

Keywords: Ag–Au–Bi ternary phase diagram; Thermodynamic assessment; CALPHAD method

1. Introduction

For the development of new lead-free soldering and brazing materials because of the prohibition of lead in electronic materials, Zoro et al. [1–3] studied two ternary systems Ag–Au–Bi and Ag–Au–Sb.

For the Ag–Au–Bi system, no experimental data were available in the literature up to the recent determinations made by this author [1–3], except an attempt made by [4], but not published and only presented at the XIVth JEEP in Marseille in 1988.

First of all, we have revised the three binary systems Ag–Au, Ag–Bi, and Au–Bi. The thermodynamic parameters for the Ag–Au and Ag–Bi systems were taken from Cost 531 (COopération Scientifique et Technique) [5]. As for the Au–Bi system, we reoptimized it [6], using the recent experimental data on the phase equilibria and integral enthalpies of mixing of the liquid phase for different compositions and temperatures published by Zoro et al. [2].

In the ternary Ag–Au–Bi system, no ternary compound was found.

2. Experimental information

2.1. Phase diagram data

We used the experimental data on phase diagrams determined by Zoro et al. [3] on four isopleth sections: 20 at.% Ag, 50 at.% Bi, 85 at.% Bi, and the section with ratio Ag:Au = 1:4, that is:

- the liquidus temperature and
- the invariant phase equilibria which are gathered in Table 1.

An isothermal section at 503K studied by electron probe micro analysis (EPMA) gave the extension of the Au_2Bi compound in the ternary system and its two and three-phase domains.

2.2. Thermodynamic data

The thermodynamic properties used were the measurements of the integral enthalpies of mixing of the Ag–Au–Bi liquid phase from the direct reaction calorimetry determined on five sections: Ag–$Au_{0.10}Bi_{0.90}$ at 673 K, Ag–$Au_{0.11}Bi_{0.89}$ at 773 K, with x(Ag) increasing from 0 to 0.4, Ag–$Au_{0.27}Bi_{0.73}$ at 773 K, Au–$Ag_{0.11}Bi_{0.89}$ at 773 K and Au–$Ag_{0.24}Bi_{0.76}$ at 773 K, with x(Au) increasing from 0 to 0.25.

The experimental methodology was indicated in Zoro et al. [2]. The integral enthalpy of formation of the liquid Ag–Au–Bi

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Table 1
Calculated temperature compared with the experimentally obtained one for the invariant transitory peritectic reaction U for the Ag–Au–Bi ternary system

Invariant reaction		Calculated T (K)	Reference	Experimental T (K)	Reference
U	Fcc + $L \leftrightarrow Au_2Bi$ + (Bi)	525.4	*This work*	516.0 ± 0.5	[3]
e_1	$L \leftrightarrow$ Fcc_A1 + (Bi)	535.7	*This work*	535.4	[1]
e_2	$L \leftrightarrow Au_2Bi$ + (Bi)	514.0	[6]	515.1 ± 0.1	[3]

The experimental and calculated temperatures of the eutectic reactions of the binary systems Ag–Bi and Au–Bi are also given.

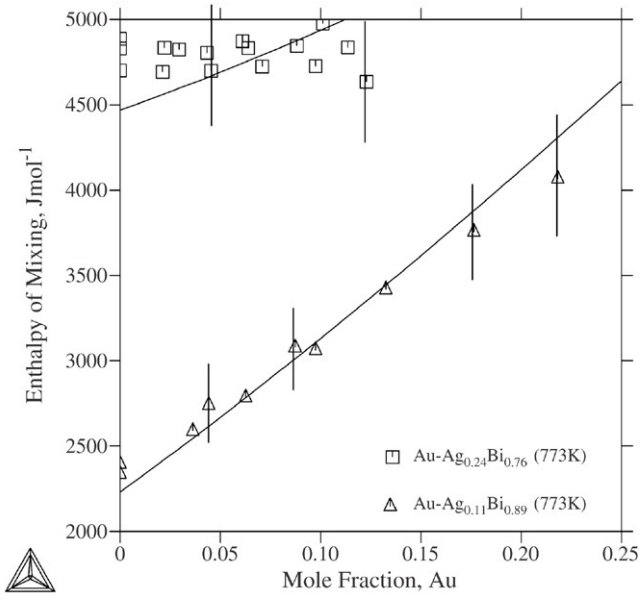

Fig. 1. Comparison of the calculated and experimental integral enthalpies of mixing of the liquid alloys $Ag–Au_x - Bi_{1-x}$. The reference states were Ag, Au solid fcc, and Bi liquid at T (773 K) and 1 bar. The reproducibility of the heat effect was better than ±8% [3].

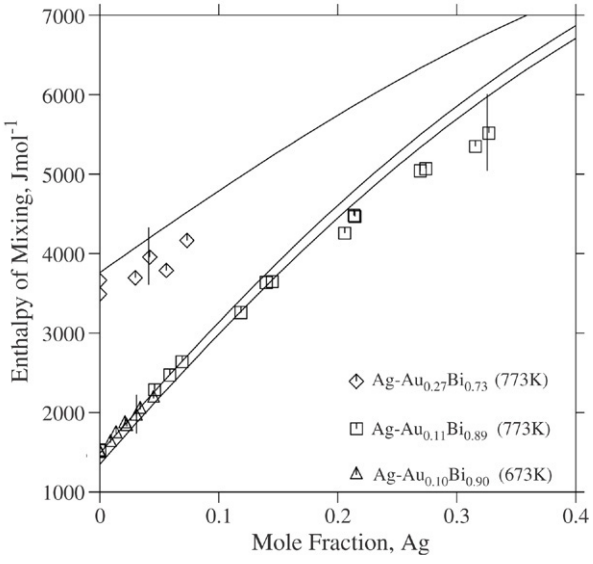

Fig. 2. Comparison of the calculated and experimental integral enthalpies of mixing of the liquid alloys $Au–Ag_x - Bi_{1-x}$. The reference states were Ag, Au solid fcc, and Bi liquid at T (673 and 773 K) and 1 bar. The reproducibility of the heat effect was better than ±8% [3].

alloys were measured using the high temperature calorimeter SETARAM HT1000.

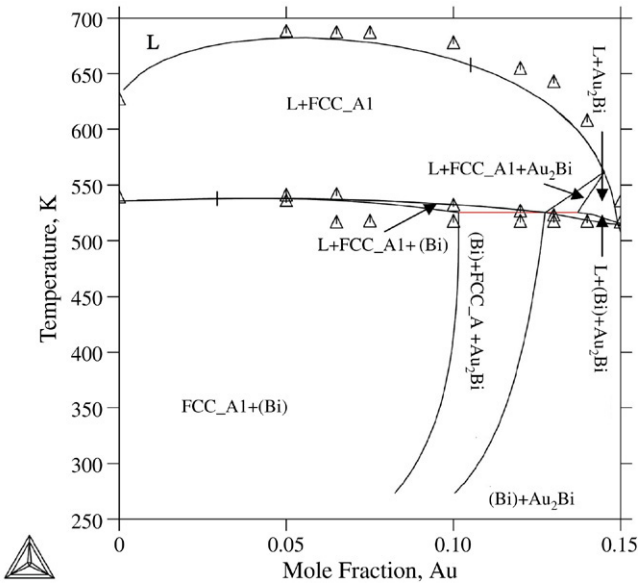

Fig. 3. Calculated and experimental isopleth sections at 85 at.% Bi for the Ag–Au–Bi system. The experimental data obtained by Zoro et al. [2] are included. The error bar on T is ±5 K.

The reference states were the corresponding solid pure elements for the dropped metals (Ag then Au, or Au then Ag) and liquid pure element for the bath (Bi) in the calorimeter cell at experimental temperature.

The alloy samples were prepared from Ag (5 N), Au (4 N) and Bi (5 N). The temperature was measured by thermocouples made of Pt/Pt—10 wt%Rh.

The heat effects were measured by the successive dropping of a series of solid samples (pure elements) at room temperature through a charging stainless steel tube into a silica crucible containing liquid bismuth first (for the determination of the enthalpy of formation of the binary liquid alloys), and then in a second stage, the liquid Ag_xBi_{1-x} or Au_xBi_{1-x} alloys formed at the end of the first stage, for the determination of the enthalpies of formation of the ternary liquid alloys.

Each series was performed at least twice. The gained signals were recorded and automatically integrated. At the end of each series, the calorimeter was calibrated by four drops of NIST Standard Al_2O_3 [7]. The reproducibility of the heat effects was better than ±8%. The thermal effect, ΔQ, due to the dissolution of a metal dropped into the calorimetric bath, was calculated from the "heat flow Φ versus time" pattern by integration ($\Delta Q = \int_{t_1}^{t_2} \Phi \, dt$) between t_1 and t_2 (time of the beginning and end of reaction) using the SETARAM software. The area S of the pattern is proportional to the exchanged heat $\Delta Q = KS$, where K is the calibration constant. We briefly recall that the