

Enthalpy of mixing of liquid Ag–Bi–Cu alloys at 1073 K

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ARTICLE INFO

Article history:

Received 26 September 2013

Received in revised form

19 November 2013

Accepted 19 November 2013

Available online 27 November 2013

Keywords:

Ag–Bi–Cu

Drop solution calorimetry

Enthalpy of mixing

Liquid alloys

ABSTRACT

The Ag–Bi–Cu system is among those ternary systems which have not been fully studied yet, in particular the thermodynamic description of the liquid phase is missing. Partial and integral enthalpies of mixing of liquid ternary Ag–Bi–Cu alloys were determined over a broad composition range along six sections: $x(\text{Ag})/x(\text{Bi}) = 0.25, 1, 4$; $x(\text{Ag})/x(\text{Cu}) = 1.5$; $x(\text{Bi})/x(\text{Cu}) = 1.86, 4$. Measurements were carried out at 1073 K using two Calvet type microcalorimeters and drop calorimetric technique. It was found that integral enthalpies of mixing are small and endothermic, similarly to limiting binary alloys. The ternary data were fitted on the basis of an extended Redlich–Kister–Muggianu model for substitutional solutions. There are no significant additional ternary interactions.

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1. Introduction

Worldwide legislation restricted the use of lead in electronic products. This concerns also the use of high-lead containing Pb–Sn solders for high-temperature soldering applications. Research projects were initiated with the aim to design and characterize alternative solder systems [1,2]. Phase diagrams provide basic information which is crucial to the design of Pb-free solders. Phase diagrams can be easily calculated using commercial software based on the CALPHAD method and suitable databases of thermodynamic properties of different binary and ternary alloys in the parametric form. However, to construct a parametric set of data of each system, all available experimental data need to be collected and critically assessed [3]. These data include topological data from DTA/DSC measurements of phase transitions occurring with temperature, and the phase equilibrium information from annealed alloys, as well as thermodynamic data such as activities of components or heats of formation of phases and heats of mixing in liquid phase. Drop solution calorimetry [4] is a useful and direct tool for the determination of the enthalpy of mixing, as the heat effects associated with dissolution of one component in liquid alloy can be measured directly.

The Ag–Bi–Cu system is interesting because of the Ag–Bi subsystem which is still considered as one of the prospective high temperature solders [5,6] for joining on Cu-based substrates.

Ag–Bi–Cu is a subsystem of quaternary Ag–Bi–Cu–Sn, which is also a promising solder material [7]. Therefore, knowledge of phase equilibria in the Ag–Bi–Cu system would help for better understanding of the interactions between the solder and joint parts. So far no experimental thermodynamic data on Ag–Bi–Cu system were reported. Therefore, the purpose of this work is to experimentally determine the enthalpy of mixing in liquid Ag–Bi–Cu alloys.

2. Literature survey

To the best of our knowledge there are no reports on the measurements of enthalpy of mixing of liquid Ag–Bi–Cu alloys. Limiting binaries of the Ag–Bi–Cu system are well studied on the other hand.

The enthalpy of mixing of liquid Ag–Bi alloys was studied by a number of researchers. Hassam et al. [8] critically reviewed preceding literature including the data calculated from electrochemical studies of activity in this system. Two conclusions they have drawn: enthalpy of mixing does not show dependence on temperature, the literature data are significantly scattered. Based on reviewed literature they decided to reinvestigate this system with high temperature solution calorimetry and found their results in agreement with the data calculated from one set of emf measurements [9]. Recently, Gasior et al. [10] reinvestigated the liquid Ag–Bi with emf technique within a reassessment of thermodynamic properties. Based on this they calculated mixing enthalpy and found their results in very good agreement with calorimetric data [8]. For this reason these data [8] are adopted for limiting Ag–Bi binary in the present work.

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Table 1
Binary and ternary interaction parameters relevant to present investigations.

System	Parameter	Reference
Ag–Bi	${}^0L = 6967$	[8]
	${}^1L = -6580$	
	${}^2L = -1942$	
Ag–Cu	${}^0L = 14,463$	[11]
	${}^1L = -934$	
Bi–Cu	${}^0L = 17,810$	[12]
	${}^1L = 3331$	
Ag–Bi–Cu	${}^0M = -2447$	Present study
	${}^1M = 967$	
	${}^2M = -32,654$	

In the case of Ag–Cu system, enthalpy of mixing of liquid alloys was studied by Fitzner et al. [11] with the so called ‘in situ mixing’ technique at 1375 K. They found their results in very good agreement with preceding literature [12]. Recent thermodynamic assessment of the Ag–Cu phase diagram takes these results into account [13]. According to Witusiewicz et al. [13] most of the experimental mixing enthalpy data are consistent and temperature independent. The enthalpy of mixing calculated from Calphad-derived thermodynamic data [13] is in a very good agreement with the data of Fitzner. For this reason data of Witusiewicz are adopted for the Ag–Cu binary system.

Recently, Flandorfer et al. [14] restudied the enthalpy of mixing of liquid Bi–Cu at 1073 K and 1273 K and found that it is weakly dependent on temperature. They found the maximum enthalpy at 50 at.% Bi and 5000 J/mol (1273 K), which is close to the maxima earlier reported: 6100 J/mol at 50 at.% Cu (1416 K) [15], 5600 J/mol at 59 at.% Cu (1614 K) [16]. Since there is no subsequent thermodynamic assessment, and the data of Flandorfer [14] were obtained in the same laboratory as the present work, these data are adopted for Bi–Cu binary system.

For each of the binary systems the mixing enthalpy data could be fitted based on the Redlich–Kister polynomial [17] (Eq. (1)).

$$\Delta_{\text{mix}}H = \sum_i \sum_{j>i} \left[x_i x_j \sum_{\nu} {}^{\nu}L_{ij}(x_i - x_j)^{\nu} \right] \quad (1)$$

In Eq. (1) i and j are equal to elements 1 and 2 in alphabetical order, respectively. ${}^{\nu}L_{ij}(\nu = 0, 1, 2, \dots)$ are the binary interaction parameters, which are collected in Table 1 for the limiting binary systems according to [10,13,14].

3. Experimental

Measurements were performed at 1073 K along six cross-sections of constant ratios: $x(\text{Ag})/x(\text{Bi}) = 0.25, 1, 4$; $x(\text{Ag})/x(\text{Cu}) = 1.5$; $x(\text{Bi})/x(\text{Cu}) = 1.86, 4$, as illustrated in Fig. 1. Calorimetric measurements of four cross-sections were performed in a Calvet-type microcalorimeter MHTC (Setaram, Lyon, France) with thermopile of 20 thermocouples, graphite resistance type furnace, with manual drop device for up to 23 drops. For the two remaining cross sections, namely $x(\text{Ag})/x(\text{Bi}) = 4$ and $x(\text{Bi})/x(\text{Cu}) = 1.86$, another Calvet-type calorimeter HT 1000 (Setaram, Lyon, France) with two thermopiles consisting of more than 200 thermocouples each, a wire wound resistance furnace and an automatic drop device for up to 30 drops was used [19]. To avoid oxidation, measurements were performed under high purity Ar (99.9999%) flow (approximately 20–30 ml/min). Metals of high purity (mass%) Bi 99.999, Ag 99.99, Cu 99.99 were used for measurements. Prior measurements copper was isothermally heated for 5 h at 573 K under hydrogen flow to remove oxides from the surface, while bismuth was cleaned by filtering the liquid metal through glass wool under high purity Ar. Silver was used without special preparation. As a starting

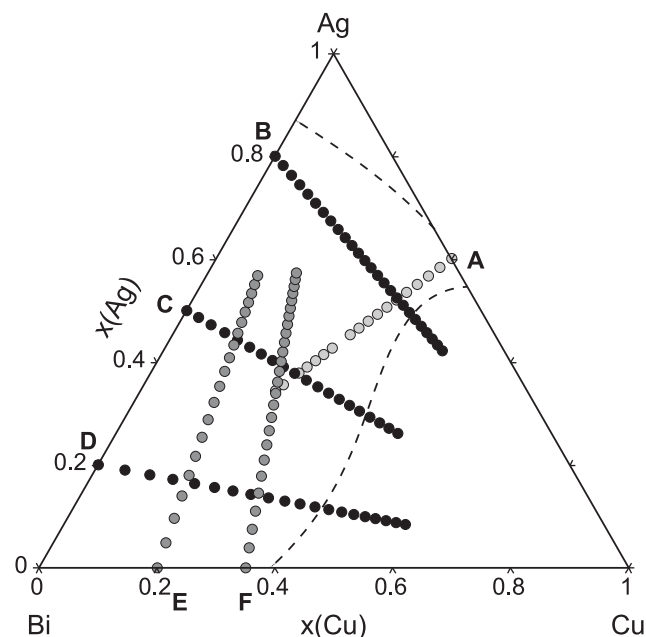


Fig. 1. Measured sections in the ternary Ag–Bi–Cu system at 1073 K. Dashed lines denote the estimated liquidus limit [18].

point of each cross-section, Ag–Bi and Bi–Cu binaries were prepared by melting weight amounts of the respective elements at 1073 K for 20 h in evacuated quartz capsules and later quenching in water. Ag–Cu alloy was prepared under electric arc furnace. The mass loss of such prepared ingots was below 0.5%. Approximately 1000–2000 mg of a binary alloy was placed in a graphite crucible inside the calorimeter, which after evacuation and flushing with Ar was heated up to 1073 K. After stabilizing the temperature for 12 h, 19 drops of respective third component followed by 4 pieces of sapphire were dropped into the bath in 40 min interval with the MHTC instrument, and 25 drops followed by 5 pieces of sapphire in 40 min interval with the HT1000 instrument. Sapphire was used for calorimeter calibration. The obtained signals were recorded and integrated using the evaluation software purchased with the calorimeter. The measured enthalpy (integrated heat flow at constant pressure) is:

$$\Delta H_{\text{signal}} = n_i [H_{i(l),\text{TE}} - H_{i(s),\text{DT}}] + \Delta H_{\text{reaction}} \quad (2)$$

where n_i is the number of moles of the added sample, H_i denotes molar enthalpies, TD is the drop temperature, and TE is the calorimeter temperature of the respective measurement in Kelvin. The molar enthalpy difference ($H_{i(l),\text{TE}} - H_{i(s),\text{DT}}$) was calculated using the so-called Dinsdale polynomials [20]. Because of the rather small additions compared to the total sample amount, the partial enthalpies can be directly given as:

$$\Delta_{\text{mix}}\bar{H}_i = \frac{\Delta H_{\text{reaction}}}{n_i} \quad (3)$$

The integral enthalpy of mixing was calculated by summarizing the respective reaction enthalpies and division by the total molar amount of substance:

$$\Delta_{\text{mix}}H = \frac{\sum_i \Delta H_{\text{reaction},i}}{n_{\text{binary}} + \sum_i n_i} \quad (4)$$

Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal integration and ‘chemical errors’, e.g. incomplete reaction or impurities [14]. Considering many calibration measurements done by dropping NIST standard sapphire, the standard

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