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Partial and integral enthalpies of mixing in the liquid Ag–In–Sn–Zn quaternary alloys

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ABSTRACT

The partial and integral enthalpies of mixing of liquid quaternary Ag–In–Sn–Zn alloys have been measured at 500 °C along seven ternary sections: $In_{0.450}Sn_{0.450}Zn_{0.100}$, $In_{0.375}Sn_{0.375}Zn_{0.250}$, $In_{0.333}Sn_{0.333}Zn_{0.334}$, $In_{0.225}Sn_{0.550}Zn_{0.225}$, $In_{0.100}Sn_{0.800}Zn_{0.100}$, $In_{0.550}Sn_{0.225}Zn_{0.225}$ and $In_{0.800}Sn_{0.100}Zn_{0.100}$. The measurements were carried out using a Calvet-type microcalorimeter and drop calorimetric technique. Additionally, the enthalpies of mixing of the liquid Ag–In–Sn–Zn have been calculated using the traditional Kohler, Muggianu, Toop and Hillert geometric models and compared to the experimental one.

1. Introduction

Lead–tin solders are commonly used in electronic packaging due to their unique combination of electrical, chemical, physical, thermal and mechanical properties. However, lead and lead containing substances are among the top chemicals posing a considerable threat to human life and environment [1]. Over several years, much effort was put into developing alternative lead-free solder alloys. Although it is now widely agreed that there is no drop-in replacement for the standard Sn–Pb solders that have been used worldwide, a range of possible alternatives has been investigated. Because Sn is a common low melting temperature element that forms compounds with many metals of importance in electronic applications, it appears likely that any new alloy will also be Sn-based.

Among many potential candidates, Ag–Sn, Cu–Sn, Zn–Sn, Ag–Cu–Sn . . . , Sn–Zn-based alloys were viewed as very promising candidates [2,3]. In 1994, McCormack and Jin [4,5] reported that the addition of In into the Sn–Zn alloys can positively contribute to the wetting characteristics of the alloys and lower sufficiently their melting temperatures.

The quality and reliability of a solder joint is highly depending on phases and their microstructure formed during solidification. Although interfacial reactions between Sn–In and Sn–Zn binary alloys with those commonly used substrates have been examined, there are no similar studies regarding the interfacial reactions between substrates and In–Sn–Zn alloys.

Among several pure metals with good conductivity, it is found that Ag is a suitable substrate to form only one layer intermetallic compounds (Ag_3Sn) after chemical reactions with most Sn-based solders [6–8]. It is reported that the simple interfacial reaction between Ag and the solders is beneficial to the soldering joint reliability [6–8]. Recently, Chen et al. [9] have examined the interfacial reactions between In–Sn–Zn and Ag at 230 °C.

Therefore, knowledge of Ag–In–Sn–Zn quaternary system is important for the development of solder materials discussed above. Thus, information on thermochemistry and phase relation of these systems forms the base for a systematic alloy design which is desired to avoid complex and time consuming trial and error developing methods. Experimental thermochemical data such as mixing enthalpies are indispensable for the thermodynamic optimization of phase diagrams and the estimation of several physical properties, e.g. surface tension, viscosity and wettability.

Recently, Rechchach et al. [10] have determined the enthalpies of mixing of the liquid In–Sn–Zn ternary alloys at 500 °C over the entire composition range. More recently (2014), Boulouiz and Sabbar [11] have measured and calculated the enthalpies of mixing of Au–In–Sn–Zn quaternary alloys at 500 °C.

To our best knowledge, no data for the enthalpy of mixing of liquid alloys in the Ag–In–Sn–Zn quaternary system are available in the literature.

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In the present work, the partial and the integral enthalpies of mixing of liquid quaternary Ag–In–Sn–Zn alloys were investigated at 500 °C. Additionally, using the traditional geometric models of Kohler [12], Muggianu et al. [13], Toop [14] and Hillert [15], the integral enthalpy of mixing was calculated and compared to the experimental values.

2. Literature survey

In the following, the thermodynamic information (enthalpy of mixing) concerning the limiting binary and ternary alloys have been recalled.

2.1. The binary systems

2.1.1. The In–Sn binary system

Several experimental investigations of the enthalpy of mixing of liquid In–Sn alloys can be found in the literature. They cover the entire composition range and a temperature range from 248 to 900 °C [16–20]. All experimental data show negative values of enthalpy of mixing for the liquid In–Sn alloys. The enthalpy of mixing has been calculated by several authors [21–24]. Good agreement was obtained between calculated and experimental data. Recently, using direct-reaction calorimetry, Rechchach et al. [10] have determined the partial and the integral enthalpies of mixing of the liquid In–Sn alloys at 500 °C and over the entire composition range.

2.1.2. The In–Zn binary system

The enthalpy of mixing in the liquid In–Zn alloys has been measured using calorimetry [25–27] at about 450 °C. The same measurements were investigated by EMF method [28–31] between 427 and 532 °C. All the experimental data show positive values of enthalpy of mixing for the liquid In–Zn alloys. Lee [32], based on the above-mentioned experimental data [25–31], has calculated the enthalpy of mixing of liquid In–Zn alloys. The calculated and experimental results are in good agreement.

2.1.3. The Sn–Zn binary system

Experimental investigations of the enthalpy of mixing of liquid Sn–Zn alloys can be found in the literature [33–39] between 422 and 546 °C. Derived values of enthalpy of mixing were reported using EMF method [40–43]. All experimental data show positive values of enthalpy of mixing for the liquid Sn–Zn alloys. Several assessments of the enthalpy of mixing of liquid Sn–Zn alloys were reported [32,44,45] in comparison with all experimental data [33–43].

2.1.4. The Ag–In binary system

The enthalpies of mixing in the liquid Ag–In alloys have been measured by several authors [16,46–48] between 450 and 1007 °C. The enthalpy of mixing varies with temperature, indicating a change in heat capacity. A thermodynamic assessment of this system was carried out by Korhonen and kivilahti [22] in comparison with some experimental data [16,46,48]. Later, Moser et al. [49] have calculated the enthalpy of mixing in the liquid phase at 727 °C. Fair agreement was obtained between calculated [49] and experimental data [46,48].

2.1.5. The Ag–Sn binary system

Using several techniques (calorimetry, potentiometry, vapour pressure), the enthalpies of mixing of liquid Ag–Sn alloys have been measured by several authors [50–56] from 554 to 1100 °C over a very large composition range. A good agreement was obtained with all experimental data. The mixing enthalpies of molten Ag–Sn alloys have been assessed [57–62]. Recently, Flandorfer et al. [63] have measured the mixing enthalpy of liquid Ag–Sn alloys at 500, 700, 900, 1000, 1100 and 1250 °C.

2.1.6. The Ag–Zn binary system

Direct measurements of the enthalpy of mixing in liquid Ag–Zn alloys are not available in the literature, which is mainly due to the high vapour pressure of zinc. Nevertheless, reliable data about the enthalpy of formation of liquid alloys in this system were obtained indirectly by optimising the other thermodynamic properties available together with the phase equilibria by the CALPHAD technique [64].

2.2. The ternary systems

2.2.1. The In–Sn–Zn ternary system

The enthalpies of mixing of liquid In–Sn–Zn alloys have already been measured by some authors. Fiorani et al. [65] have measured the partial and the integral enthalpies of mixing in the liquid In–Sn–Zn alloys following the three isopletic cuts: $x_{In}/x_{Sn} = 1/1$ at 447 °C, $x_{Sn}/x_{Zn} = 1/1$ at 447 °C and $x_{In}/x_{Zn} = 1/1$ at 483 °C. Later, Anres et al. [66] have investigated by direct reaction calorimetry the enthalpies of mixing in the liquid In–Sn–Zn ternary alloys. Their measurements were explored at 440 and 634 °C following the sections $x_{In}/x_{Sn} = 1/3$, 1/1, 3/1 and $x_{Zn}/x_{In} = 1/3$, 1/1. Cui et al. [67] have calculated the partial mixing enthalpies of In, Sn and Zn at 447, 483 and 447 °C respectively in comparison with the experimental data reported by Fiorani et al. [65]. There is no good agreement between the calculated and experimental data. Xie et al. [68], using CALPHAD technique, have calculated the mixing enthalpies of In–Sn–Zn ternary liquid alloys at 439 °C. The calculated results are in good agreement with the experimental data reported by Anres et al. [66]. Moelans et al. [69], using CALPHAD method, have assessed the mixing enthalpy at 441 and 634 °C for the section $x_{In}/x_{Sn} = 1/3$ in comparison with experimental data reported previously by Anres et al. [66]. Recently, the mixing enthalpy of the liquid In–Sn–Zn alloys has been measured at 500 °C using a drop method calorimetry by Rechchach et al. [10]. The measurements were examined following seven sections: $x_{In}/x_{Sn} = 0.851/0.149$, 0.667/0.333, 0.501/0.499, 0.336/0.664, 0.152/0.848 and $x_{In}/x_{Zn} = 0.702/0.298$, 0.519/0.481.

2.2.2. The Ag–In–Sn ternary system

The enthalpies of mixing of liquid Ag–In–Sn alloys have been measured by calorimetry by Gather et al. [70] following the four isopletic cuts: $x_{In}/x_{Sn} = 1/4$ at 893 °C, $x_{In}/x_{Sn} = 2/3$ at 893 °C, $x_{In}/x_{Sn} = 3/2$ at 980 °C and $x_{In}/x_{Sn} = 4/1$ at 980 °C. Recently, Liu et al. [71] have calculated the enthalpy of mixing in the liquid phase at the same vertical sections investigated by Gather et al. [70]. The results indicate that there is basic agreement between the experimental and calculated results.

2.2.3. The Ag–Sn–Zn ternary system

EMF method was applied by Karlhuber et al. [72] to derive the enthalpy of mixing of this system at 627 °C following the three sections: $x_{Ag}/x_{Sn} = 1/3$, 1/1 and 3/1. Peng et al. [73], using four different models developed by Kohler [12], Toop [13], Mugianu [14] and Hillert [15], have calculated the mixing enthalpy of liquid Ag–Sn–Zn following the same sections investigated by Karlhuber et al. [72]. The calculated values are more negative. Later, Knott et al. [74] have measured the integral enthalpies of mixing in the liquid phase at 700 °C along cross-sections with molar ratios Ag:Sn = 1:3, 1:1, 3:1 and Zn mole fractions from 0 to about 0.4. Very recently, Vassilev et al. [75] have calculated the enthalpy of mixing of the liquid Ag–Sn–Zn alloys at 700 °C with the same molar ratios investigated by Knott et al. [74]. Good agreement between calculated and newer experimental results [74] is obtained.