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Thermodynamic properties of liquid Au–Cu–Sn alloys determined from electromotive force measurements

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ABSTRACT

The thermodynamic properties of the ternary Au–Cu–Sn system were determined with the electromotive force (EMF) method using a liquid electrolyte. Three different cross-sections with constant Au:Cu ratios of 3:1, 1:1, and 1:3 were applied to measure the thermodynamic properties of the ternary system in the temperature range between the liquidus temperature of the alloys and 1023 K. The partial free energies of Sn in liquid Au–Cu–Sn alloys were obtained from EMF data. The integral Gibbs free energy and the integral enthalpy at 900 K were calculated by Gibbs–Duhem integration. The ternary interaction parameters were evaluated using the Redlich–Kister–Muggianu polynomial.

1. Introduction

Development of the new lead-free solders has been a global trend due to environmental and health concerns for Pb toxicity. Au–Sn based alloys have been considered as a potential material to replace the Pb-containing solders especially for the high-temperature applications [1–3]. Currently eutectic 80Au–20Sn (wt.%) solders are already used as high-temperature solders in optoelectronics industry [4]. But the main disadvantage of this kind of solders is the high price, so another component should be added to reduce the cost. Metallic copper behaves chemically like Au and copper alloys have excellent electrical properties, so Au–Cu–Sn alloys have been proposed as promising lead-free solders.

Thermodynamic properties are of great use for the development of a lead-free solder database, for design of new lead-free solders, and for the prediction of various alloy properties like the wetting behavior, the surface tension and the viscosity [5]. So far, two investigations of the thermodynamic properties on Au–Cu–Sn system have been reported. Knott et al. [6] used calorimetric measurements to determine the integral enthalpy of mixing of Au–Cu–Sn system. However, measurements were performed at constant 1273 K and the Gibbs energies cannot be obtained, so it is necessary to employ other experimental methods, such as vapour pressure measurements or electromotive force (EMF) measurements, for the determination of a complete thermodynamic description [7,8]. Recently, an EMF method with solid electrolyte was carried out by Wierzbicka-Miernik et al. [9] in the temperature range from 900 to 1360 K, to study the thermodynamic data of this system. The activities of tin in Au-Cu-Sn system are calculated from Ref. [9] and plotted in Fig. 1. It can be seen that the results at 1273 K show good consistency, but the fluctuations of the values at 900 K are too large at all three cross-sections. It is obvious that the results given by Ref. [9] are not reliable for the lower temperature range. Furthermore, although the enthalpy values of nine alloys were given in Ref. [9], the procedure of calculation could not be found in the paper, so the thermodynamic data of the entire ternary system is still not available for us.

In order to build a complete and accurate thermodynamic description of the ternary Au–Cu–Sn system, an EMF method with liquid electrolyte was carried out at the lower temperature range from the liquidus temperature of the alloys to 1023 K. Two types of electrolyte: liquid and solid, each with characteristic advantages and disadvantages, were described in detail by Ipser et al. [10]. The partial thermodynamic properties were calculated from the EMF data. The Gibbs–Duhem integration was used to determine the integral thermodynamic properties of the entire ternary system. Results from the earlier studies [6,9] were compared and discussed in this work.

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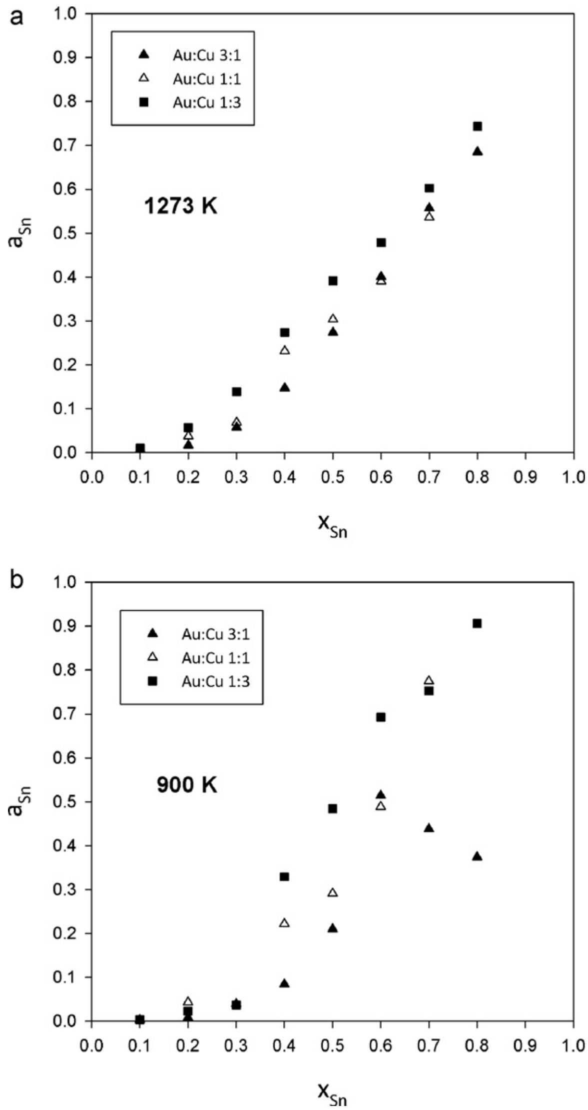

Fig. 1. Activities of tin in ternary Au–Cu–Sn system calculated from Ref. [9] (a) at 1273 K; (b) at 900 K.

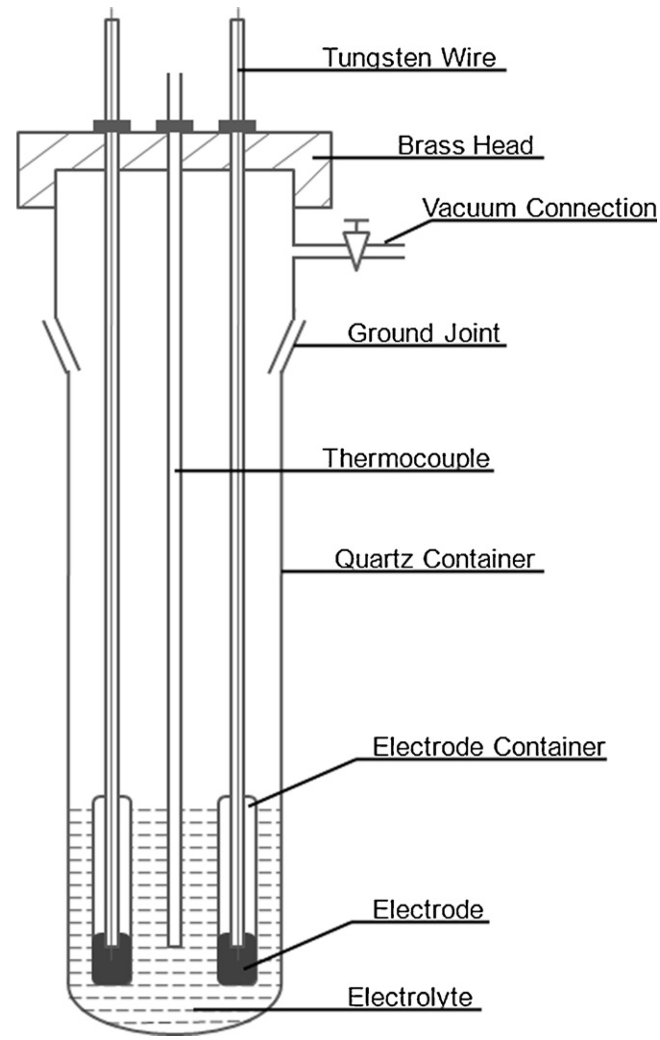

Fig. 2. Galvanic cell assembly.

2. Experimental procedures

2.1. Materials

The ternary alloys were prepared from high purity metals (gold sheet, purity 99.95%; copper wire, purity 99.9%; tin ingots, purity 99.999%). Gold was a product of Ögussa, Austria, whereas copper and tin were products of Johnson Matthey GmbH, Germany. In order to remove the oxide layer from the surface, copper wire was heated for 3 h at 573 K under hydrogen flow and tin ingots were polished with a fine sand paper. Gold was used without further purification. The metals were prepared with the target compositions (three different cross-sections with constant Au:Cu ratios of 3:1, 1:1, and 1:3), sealed in quartz tube under vacuum and melted at 1173 K for one week. Afterwards the samples were quenched in ice water. Approximately 2 g of each alloy was used for the measurements. The eutectic mixture KCl (Merck, Germany, mass fraction purity >0.995) and LiCl (Merck, Germany, mass fraction purity >0.99) with addition of about 0.5 at.% $SnCl_2$ (Johnson Matthey GmbH, Germany, mass fraction purity >0.99) was used as the liquid electrolyte. The cleaning of the electrolyte was described by Mikula [11].

2.2. EMF technique

The schematic cell arrangement is shown in Fig. 2. Four electrodes were used for each measurement. One is the reference electrode which should be the most electropositive pure metal in the system (pure tin was used in this work), and the other three are alloys with different compositions which were measured. A vertical furnace was used to heat the whole cell and the four electrodes were inserted into the liquid electrolyte after it melted. A Ni/NiCr thermocouple was put into the central quartz tube to measure the temperature simultaneously during the measurement. Measurements were carried out on heating and cooling with a rate of 10 K/h. The EMF values were continuously measured by a voltmeter with an impedence larger than 10^{10} Ohm. The temperature and EMF values were automatically recorded every 5 min. During the experiment, the measurement was kept at the high and low temperature limits for a longer period of time (about 6 h) to check the stability of the EMF values. In this work, the cooling curve was taken to evaluate the thermodynamic properties of this system.

2.3. Differential thermal analysis

Before the EMF measurement the liquidus of the alloys were determined by differential thermal analysis so that the temperature range for the EMF measurement could be determined. Thermal analysis was performed on a 404S DTA-instrument (Net-