Journal of Alloys and Compounds 491 (2010) 173–177

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Enthalpy of formation of intermetallic phases from the Au–Sn system

A. Dębski*, W. Gąsior, Z. Moser, R. Major

Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25, Reymonta Street, 30-059 Kraków, Poland

ARTICLE INFO

Article history:
Received 7 October 2009
Received in revised form 29 October 2009
Accepted 2 November 2009
Available online 5 November 2009

Keywords:
Gold–tin system
Au–Sn
intermetallics
Heat of formation
Solution calorimetry
Thermodynamic properties

ABSTRACT

Solution calorimetry with liquid Sn has been used for the determination of enthalpy of solution of Au and enthalpy of formation of intermetallic compounds from the Au–Sn system. Enthalpy of solution of liquid Au in liquid Sn was measured at 667 K to be -34.3 ± 0.5 kJ/g-atom and it was almost the same as cited in many earlier references. Based on the literature and this study data parabolic equations of temperature dependence of enthalpy of gold solution in liquid tin were worked out for three groups of data. Intermetallic phases were prepared and homogenized in the glow-box operated in high purity argon. They were analyzed by X-ray diffraction method before the calorimetric investigations to confirm their crystallographic structure. The obtained experimental values of enthalpy of formation were -15.3 ± 0.3, -14.2 ± 0.3 and -7.9 ± 0.6 kJ/mol of atoms for AuSn, $AuSn_2$ and $AuSn_4$, respectively. It was found that the obtained data in the study agreed very well with the results previously presented in literature. The observed differences were not higher than 0.5 kJ/mol of atoms.

1. Introduction

The investigations of high temperature lead-free solder materials for the microelectronics, automobile, space and biomedical industry have been the fundamental task of the COST MPO602 action. The low temperature lead-free solders were the subject of interest for the COST 531 Project, in which the Institute Metallurgy and Materials Science, Krakow, Poland has also participated. The lead-free solders, based on alloys from the Au–Sn system, modified by third additions, belong to the solders which could be used in electronic devices of highest reliability designed for special applications. It is also possible that the solders could be applied in future in the microelectronics based on new semiconductors working at elevated temperatures unlike these commonly used now.

The phase diagram of Au–Sn system, presented in 1990 by Okamoto and Massalski [1] was not completely investigated (Fig. 1) at high concentrations of Au and some equilibrium lines were simply only predicted. Recently, Okamoto [2] has worked out the Au–Sn system based on new experimental data shown in Fig. 2. Meanwhile, in the frame of the COST ACTION 531, the thermodynamic parameters of all phases have been established and the equilibria in Au–Sn system calculated [3] (Fig. 3). However, there is still lack of the agreement between authors [2] and [3] on the peritectoidal transformation at 300 K (27 °C). The Au–Sn phase diagram [1–3] show the presence of six intermetallic compounds in the solid state, $Au_{10}Sn(\beta)$, $Au_5Sn(\zeta)$, AuSn(δ), $AuSn_2(\varepsilon)$, $AuSn_4(\eta)$ and ζ' phase solid solution of known structures.

Two earlier versions of Au–Sn system with two eutectic temperatures 488–490 K (215–217 °C) and 552 ± 1 K (279 °C) and compositions ranging from 4.6 to 6.3 and 71 at.% Au, respectively [1,2] are presented in Figs. 1 and 2. The modification of these eutectics by the additions the Cu or Ag or another metal can, on one hand, diminish the costs of the solder production and on the other hand improve mechanical properties and the wettability parameters.

The heats of solution of Au in liquid Sn were examined at different temperatures in various studies [4–14] and except for the Kleppa's data [5], which are about 1 kJ/mol less exothermic than theirs, the results of other authors [4,6–14] are very consistent with each other. The heat of formation of AuSn, $AuSn_2$ and $AuSn_4$ were measured at 623 K, 515 K and 515 K by Kleppa [15], respectively using solution calorimetry and by Jane and Bever [16], for AuSn phase at 273 K, 195 K and 78 K with the same technique. The obtained results for AuSn phase of both authors are almost the same and the observed differences are comparable with the experimental error, indicating that the heat of formation of AuSn is independent of temperature.

The preparation, identification by X-ray analysis and the measurements of the enthalpy of solution of Au in liquid Sn and enthalpy of formation of AuSn, $AuSn_2$ and $AuSn_4$ intermetallic phases using the solution calorimetric technique was the main aim of this work. It is simultaneously the first stage of investigations of the enthalpy of formation of all existing phases in the Au–Sn system, which, finally, will be used for the recalculation of the Au–Sn phase diagram.

* Corresponding author.
E-mail address: nmdebski@imim-pan.krakow.pl (A. Dębski).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.11.003

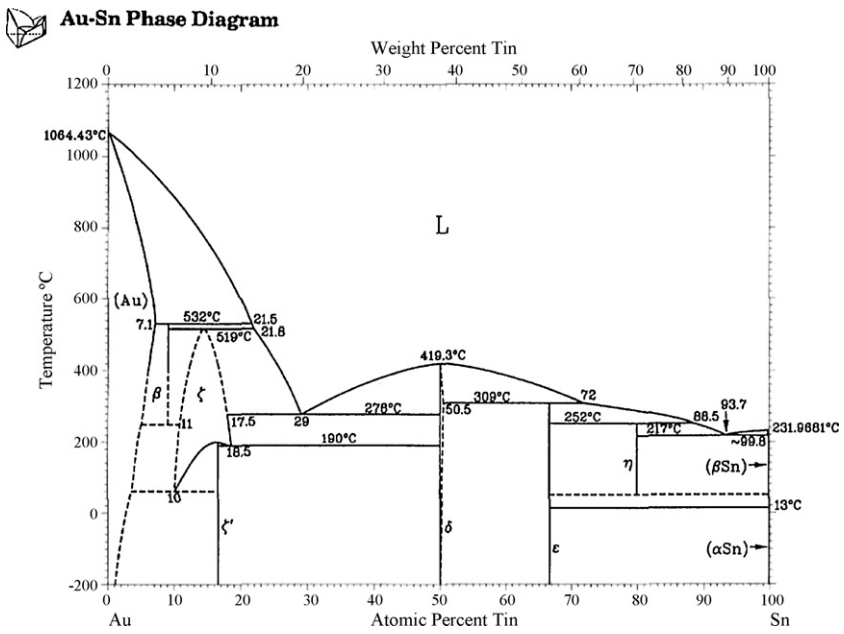

Fig. 1. Phase diagram of the Au–Sn system worked out by Okamoto and Massalski [1].

2. Determination of the enthalpy of formation of intermetallic phases based on solution calorimetric technique

The enthalpy of formation, $\Delta_f H$ of the considered phase, determined with this method, is obtained from the difference of heat effects accompanying the dissolution of the studied phase and its components in the tin bath. In the case of two-component phase the following equation is applied:

$$\Delta_f H = X_{Au}\Delta H_{Au}\text{ef}\circ + X_{Sn}\Delta H_{Sn}\text{ef}\circ - \Delta H_{X_{Au}X_{Sn}}\text{ef}\circ \quad (1)$$

where $\Delta_f H$ is the formation enthalpy of the phase (alloy), X_{Au}, X_{Sn} are concentrations (mole fractions) of the components, $\Delta H_{Au}\text{ef}\circ$, $\Delta H_{Sn}\text{ef}\circ$, $\Delta H_{X_{Au}X_{Sn}}\text{ef}\circ$ are heat effects accompanying the dissolution of the components and the phase (alloy) in the bath.

The solid state of Au and Sn was chosen as the reference state. The construction details of the used calorimeter were shown elsewhere [17]. Before each experimental run, the calorimeter was evacuated with a diffusion pump and flushed with high purity argon many times either at room or at elevated temperature. At the beginning of each run, the calibration was conducted by dissolving several Sn samples in tin bath at a fixed temperature. During calorimetric measurements the Sn bath was continuously stirred. The voltage signal from the thermopile situated directly on the crucible with the Sn-bath was registered in a digital form by computer and the heat effects and the enthalpies of formation were calculated using special software.

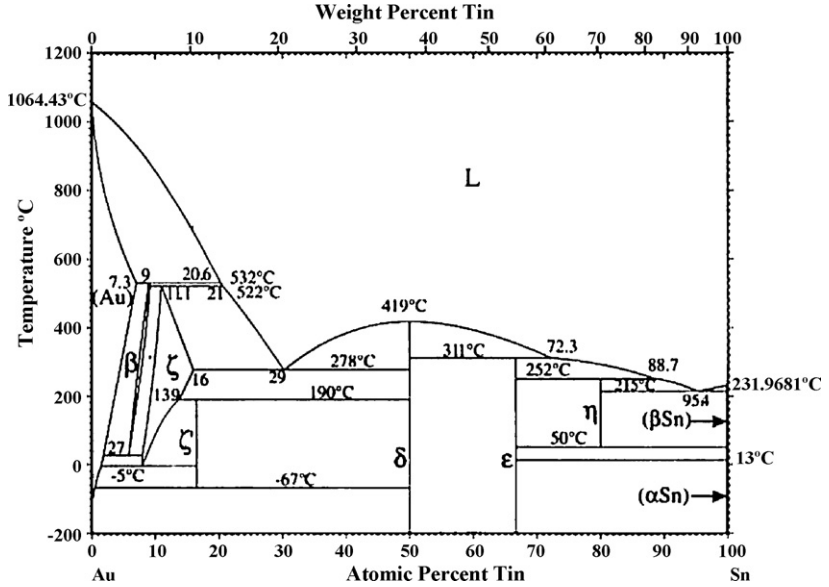

Fig. 2. The Au–Sn phase diagram proposed by Okamoto [2].