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Enthalpy of formation of Au–Sn intermetallic phases. Part II

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ABSTRACT

The technique of solution calorimetry with liquid Sn has been used for the determination of enthalpy of formation of intermetallic compounds from the Au–Sn system. The intermetallic phases were prepared and homogenized in a glow-box operated in high purity argon. They were analyzed by an X-ray diffraction method before the calorimetric investigations to confirm their crystallographic structure. The obtained experimental values of enthalpy of formation were -5.8 ± 0.3 and -1.3 ± 0.4 kJ/mole of atoms for ζ′-Au_5Sn, and ζ-Au_5Sn of the composition $Au_{89}Sn_{11}$, respectively. Using the DTA technique the transition temperatures were measured for the following phases: η-$AuSn_4$, ε-$AuSn_2$, δ-AuSn, ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$). It was found that the obtained data in the study agreed very well with the results previously presented in literature, except for the ζ-Au_5Sn ($Au_{89}Sn_{11}$) intermetallic phase, for which a difference of about 50° was observed for the liquidus temperature.

1. Introduction

In spite of a high price the alloys of the Au–Sn system are candidates for new lead-free solders. These alloys have been investigated in COST Action MP0602-HISOLD Advanced Solder Materials for High Temperature Applications. The Institute of Metallurgy and Materials Science Polish Academy of Sciences (IMIM PAS) has performed, in that action, some tasks and one of them concerned the measurement of formation enthalpy of intermetallic Au–Sn compounds. The experimental data of the heat of formation of δ-AuSn, ε-$AuSn_2$ and η-$AuSn_4$ obtained by the tin solution calorimetric method were presented in the first paper [1]. Using the same experimental technique the studies were continued in the present work and the results of calorimetric measurements of ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$) are presented together with the results of differential thermal analysis (DTA) for three intermetallic compounds studied earlier [1] and for two in that work.

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:

$$\Delta_f H = X_{Au}\Delta H^{ef.0}_{Au} + X_{Sn}\Delta H^{ef.0}_{Sn} - \Delta H^{ef.0}_{X_{Au}X_{Sn}} \quad (1)$$

where $\Delta_f H$ – the formation enthalpy of the phase (alloy), X_{Au}, X_{Sn} – concentrations (mole fractions) of the components, $\Delta H^{ef.0}_{Au}$, $\Delta H^{ef.0}_{Sn}$, $\Delta H^{ef.0}_{X_{Au}X_{Sn}}$ – 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 calorimeter used were shown elsewhere [2].

3. Preparation and identification of phases

The intermetallic ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$) phases were prepared in the glove-box operating in high purity argon. Very low concentrations of oxygen and water, lower than 1 ppm, was maintained in the glove-box by a continuous circulation of Ar between the glove-box and the purification system, which consists of reactors filled with the molecular sieve, catalytic copper and titanium sponge. The box worked at 1300 K removing, apart from oxygen, also nitrogen from the Ar. The metals of high purity shown in Table 1 were melted in a graphite crucible at temperature about 50 °C higher than the melting point of the investigated phase. After melting and thorough stirring, the liquid alloy was solidified and the solid alloy was next annealed at various periods of time as shown in Table 2.

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Table 1
Metals used in measurements.

Metal	Purity [wt.%]	
Sn	99.999	Institute of Electronic Materials Technology
Au	99.99	Mennica – Metale Szlachetne S.A.

Table 2
Homogenization conditions of intermetallic phases.

Intermetallic phase	Annealing temperature	Annealing time
ζ′-Au_5Sn	423 K (150 °C)	14 days
ζ-Au_5Sn ($Au_{89}Sn_{11}$)	573 K (300 °C)	1 month

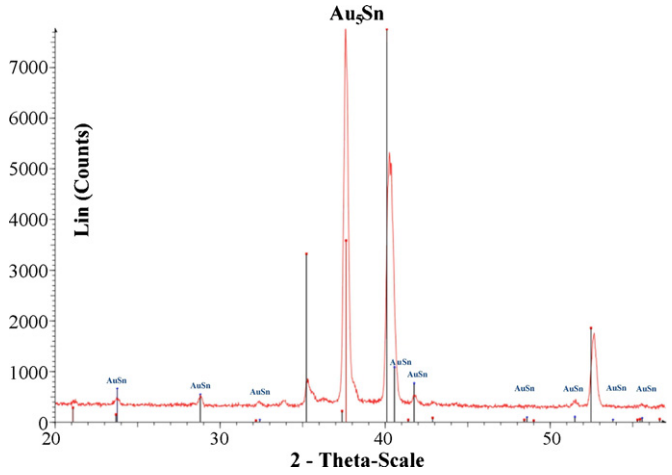

Fig. 1. Diffraction pattern of ζ′-Au_5Sn phase (Au_5Sn = 97.3 wt.%, AuSn = 2.7 wt.%).

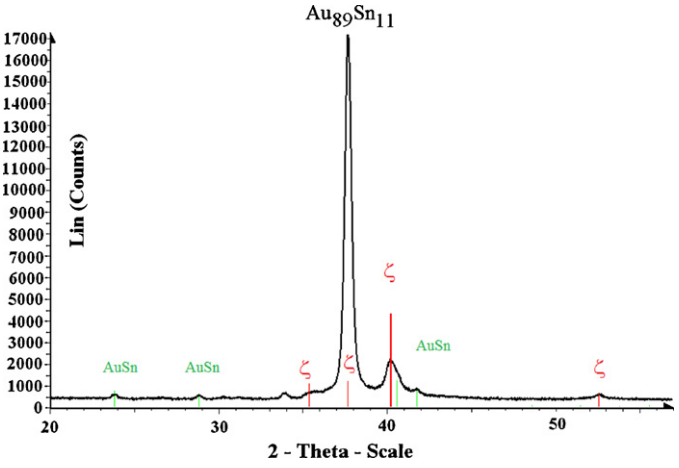

Fig. 2. Diffraction pattern of ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase.

The phases were analyzed by X-ray diffraction after the homogenization. The analysis confirmed the appropriate structure of the investigated intermetallic Au–Sn phases. The X-ray diffraction patterns of ζ′-Au_5Sn, and ζ-Au_5Sn ($Au_{89}Sn_{11}$) are shown in Figs. 1 and 2, in which, a small amount of AuSn phase (2–5 wt.%) was additionally observed in the samples. Therefore, the influence of the AuSn phase on the final result of the enthalpy of formation was taken into account in the calculations.

Since the intensity ration peaks in Figs. 1 and 2 were not as texture in the case of the X-ray pattern for randomized sample (no preferred orientation), the texture analysis was performed. The results of texture measurement for the ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase (Figs. 3 and 4) confirmed the occurrence of the phase discussed. X-

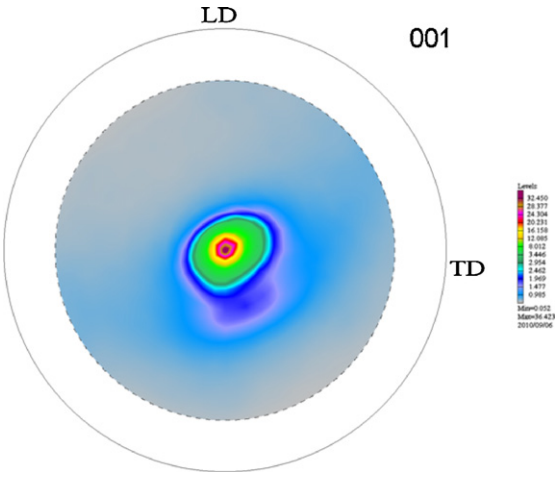

Fig. 3. The texture analysis of ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase. LD, TD denote the longitudinal and transverse directions of sample, respectively.

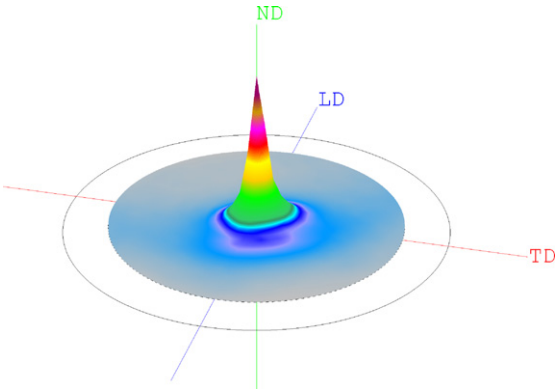

Fig. 4. The texture analysis of ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase. ND – normal direction.

ray diffraction pattern of the ζ-Au_5Sn ($Au_{89}Sn_{11}$) sample given in Fig. 2 shows relatively high intensity of 0 0 2 reflections when compared to its nominal intensity ratio in the crystallographic data base. Registered incomplete back-reflection (0 0 1)-pole figure exhibits a strong preferred crystallographic orientation of the $Au_{89}Sn_{11}$ phase (Figs. 3 and 4). The axial type texture ⟨0 0 1⟩ justifies the abnormal ratio of diffraction intensities observed in the examined sample.

4. Results and discussion

The heat effects obtained from the solution calorimetric method, presented in Tables 3 and 4 were used together with the data of the enthalpy of solution of Au in liquid Sn (at infinite dilution of Au) from an earlier work [1] and with the thermochemical data of metals from the SGTE Substances Database (2001 update: March 1, 2002, Thermo-Calc Software) for the calculation of heat of formation of intermetallic compounds. All obtained values of heat effects and the enthalpy of formation of ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$) are collected in Tables 3 and 4. Since an amount of AuSn phase was recorded in the X-ray analysis the heat effect of the AuSn solution in the Sn bath was taken into account in the calculation of the ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$) enthalpy of formation. The obtained values differed by about −5.8 kJ/mole of atoms, for ζ′-Au_5Sn with the standard deviation 0.3 kJ/mole of atom, and by about −1.3 kJ/mole of atoms, for the ζ-Au_5Sn ($Au_{89}Sn_{11}$) at the standard deviation of 0.4 kJ/mole of atom.

The $\Delta_f H$ values of Au–Sn intermetallic phases available in the literature [3,4,6–10] and these from this work are presented in

Table 3
Heats of formation and heat effects measured for ζ′-Au_5Sn intermetallic phase at 295 K by the solution calorimetry. The bath temperature was 671 ± 2 K.

Phase	Temperature [K]	Measurement no	Heat effect ΔH^{ef} [kJ/mole of atoms]	Enthalpy of formation $\Delta_f H$ [kJ/mole of atoms]
ζ′-Au_5Sn	295	1	−0.8	−6
		2	−0.8	−6.1
		3	−1.5	−5.4
		4	−1	−5.9
		5	−1.4	−5.5
		Average	−1.1	−5.8
		Standard dev.	0.3	0.3

Table 4
Heats of formation and heat effects measured for ζ-Au_5Sn ($Au_{89}Sn_{11}$) intermetallic phase at 300 K by the solution calorimetry. The bath temperature was 672 ± 2 K.

Phase	Temperature [K]	Measurement No	Heat effect ΔH^{ef} [kJ/mole of atoms]	Enthalpy of formation $\Delta_f H$ [kJ/mole of atoms]
ζ-Au_5Sn ($Au_{89}Sn_{11}$)	300	1	−6.9	−1.7
		2	−7.9	−0.7
		3	−7.6	−0.9
		4	−6.8	−1.7
		5	−7.6	−1.0
		6	−7.3	−1.2
		7	−6.8	−1.8
		Average	−7.1	−1.3
		Standard dev.	0.4	0.4

Table 5
Enthalpy of formation of Au–Sn intermetallic phases measured by various authors.

Author	*T* [K]	Phase				
		*δ-AuSn	*ε-$AuSn_2$	*η-$AuSn_4$	ζ′-Au_5Sn	ζ-Au_5Sn ($Au_{89}Sn_{11}$)
This study and *[1]	300	−15.4 ± 0.3	−14.2 ± 0.3	−7.9 ± 0.6	−5.8 ± 0.3	−1.3 ± 0.4
Kleppa [3]	723623515	−14.2	−12.9	−6.8		−1.0 (87 at.%)−1.1 (94 at.%)
Jena et al. [4]	273	−15.1				
	195	−15.0				
	78	−14.9				
	273					−4.24 (84 at.%)
	195					−4.44 (84 at.%)
	78					−3.89 (84 at.%)
	78					−3.16 (86 at.%)
	78					−1.74 (89 at.%)
Misra et al. [6]	273	−15.26 ±0.2	−14.2 ± 0.04	−7.74 ± 0.13		−4.06 ± 0.02 (84.5 at.%)
						−3.5 ± 0.04 (86 at.%)
						−3.32 ± 0.2 (87.5 at.%)
Biltz et al. [7]	363	−17.1	−7.7			

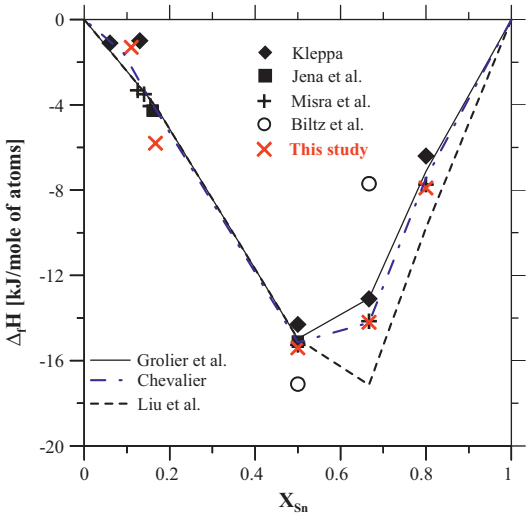

Fig. 5. The formation enthalpy of intermetallic phases from the Au–Sn system.

Table 5 and Fig. 5. A very good agreement for δ-AuSn, ε-$AuSn_2$ and η-$AuSn_4$ intermetallic compounds can be observed. The differences between the data are lower than the estimated experimental errors. It seems that the enthalpies of formation are rather independent of temperature and the slight temperature dependencies found by Jena and Bever [4] for δ-AuSn and ζ-Au_5Sn resulted rather from the measurement error of the heat of solution of gold in the liquid tin which could be noticed when analyzing the data for the example given in [1]. Another factor impacting the low temperature measurements data obtained with the solution calorimetric technique can be the result of the possible phase transition of ζ′-Au_5Sn phase and gold-rich alloys at 268 K (−5 °C) and 206 K (−67 °C) [5].

The results of Misra et al. [6] for the gold-rich alloys are comparable with those of Jena [4] and the results of Biltz et al. [7] for the δ-AuSn compound are about 10% lower and for ε-$AuSn_2$ about 40% higher in comparison with the data of this study, Kleppa [3] and Misra et al. [6].

Such a high difference between the data of Biltz et al. [7] and this study, Kleppa [3] and Misra et al. [6] for ε-$AuSn_2$ can be explained by too short the time and too low the reaction temperature of Sn with Au (363 K (90 °C)) because in such conditions

Table 6
Phase transition temperatures of intermetallic Au–Sn phases IMPs measured with the DTA technique for.

Phase	Liquidus temperature	Melting temperature	Eutectic(oid) temperature	Peritectic(oid) temperature
η-$AuSn_4$	552 K (279 °C)		488 K (215 °C)	525 K (252 °C)
ε-$AuSn_2$	612 K (339 °C)			582 K (309 °C)
δ-AuSn	692 K (419 °C)	692 K (419 °C)		
ζ′-Au_5Sn	970 K (697 °C)		553 K (280 °C)	463 K (190 °C)
ζ-Au_5Sn ($Au_{89}Sn_{11}$)	1173 K (900 °C)			796 K (523 °C)
β-$Au_{10}Sn$				807 K (534 °C)

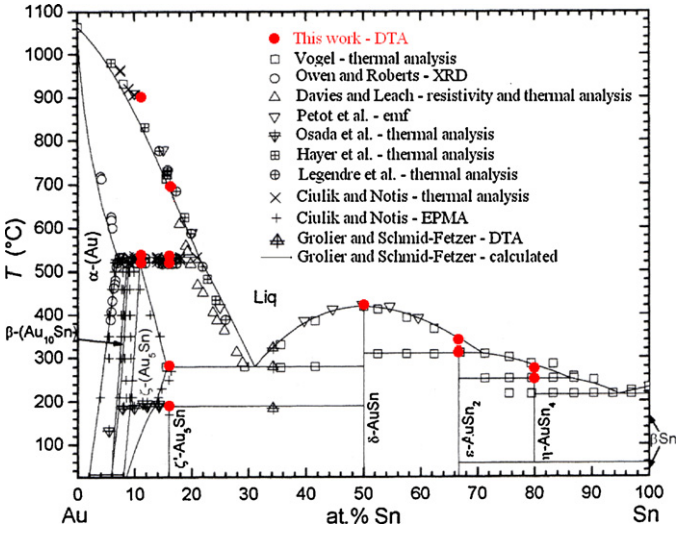

Fig. 6. Results of experimental investigations of the equilibrium temperature phase transitions in the Au–Sn system [11–18] together with the phase equilibria calculated by Grolier and Schmid-Fetzer [9].

the components probably reacted into the ε-$AuSn_2$ compound only partially.

Very close values of the heat of formation for ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase were obtained in the present study and that by Kleppa [3] at 87 at.% and 94 at.% of Au. However, the data of Misra et al. [6] for almost the same composition (87.5 at.%) are by over 2 kJ/mole of atoms lower in comparison with the results of authors of this work and Kleppa's study [3]. In general, it can be said that the experimental values of the heat of formation of the cited authors showed a satisfactory agreement for the most gold-rich phases and for other phases.

Comparing the formation enthalpy of intermetallic phases presented in [1] and those used by Grolier and Schmid-Fetzer [9], Liu et al. [8] and Chevalier [10] for the calculation of the phase diagram one may notice that the values applied by Chevalier [10] are almost identical as those obtained by the solution calorimetric method [1]. The value reported in [8–10] for the ζ′-Au_5Sn ($Au_{89}Sn_{11}$) phase is about 1.5 kJ/mole atoms less exothermic than that presented in this study.

All investigated intermetallic phases in earlier [1] and in this work (η-$AuSn_4$, ε-$AuSn_2$, δ-AuSn, ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$)) were subjected to the DTA studies and the temperatures of phase transitions obtained are shown in Fig. 6 and Table 6.

It was observed that in the case of $Au_{89}Sn_{11}$ phase, the liquidus temperature was about 60 °C higher in comparison with that calculated in [9]. However, as it can be seen from Fig. 6, the DTA results of liquidus and solidus temperature, for the gold-rich alloys, were generally higher by about 10–50 °C than those calculated ones. The analysis of the experimental liquidus data, in the gold-rich region, suggested that the liquidus line should have an evident S-shape in that region. The other DTA results showed good agreement with the calculated and experimental data of phase transition temperatures (read color symbols).

5. Conclusions

Heat effects and enthalpy of formation of ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$) intermetallic phases were measured using the tin solution calorimetric method. The measured value of the enthalpy of formation for the ζ′-Au_5Sn was -5.8 ± 0.3 kJ/mole of atoms, which was about 1.8 kJ/mole of atoms lower in comparison with that earlier measured for $X_{Au} = 0.845$ and about 1.5 kJ/mole lower for $X_{Au} = 0.84$. The formation enthalpy of the ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase, measured in the present study was -1.3 ± 0.4 kJ/mole of atoms, which was almost the same as that of Kleppa and by about 2 kJ/mole of atoms higher than that of Misra with co-workers.

The differential thermal analysis conducted for five intermetallic phases (η-$AuSn_4$, ε-$AuSn_2$, δ-AuSn, ζ′-Au_5Sn and ζ-Au_5Sn ($Au_{89}Sn_{11}$)) showed that the phase transition temperatures measured in that work agreed very well with those measured earlier in other laboratories and calculated except for the ζ-Au_5Sn ($Au_{89}Sn_{11}$) phase, whose measured liquidus temperature was about 60° higher in comparison with that calculated.

Analyzing the data presented in Au–Sn phase diagram, it can be concluded that the correlation between the calculated liquidus and solidus equilibrium lines of the gold-rich alloys are too low and that the recalculation of the Au–Sn system with special consideration paid to that region should be conducted to improve the agreement between the mentioned two sets of data. It seems that the thorough analysis of Chevalier, Grolier and Liu et al. works might give a new set of thermodynamic functions for the calculations of equilibrium lines of the Au–Sn system which would be in good agreement with the experimental data, especially, for Au-rich alloys.

Acknowledgements

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