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Interfaces in lead-free solder alloys: Enthalpy of formation of binary Ag–Sn, Cu–Sn and Ni–Sn intermetallic compounds

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Abstract

Standard enthalpies of formation were determined for a number of binary intermetallic compounds in the systems Ag–Sn, Cu–Sn, and Ni–Sn by means of solution calorimetry in liquid Sn in a Calvet-type microcalorimeter. For the pure elements Ag, Cu, and Ni, the limiting partial enthalpies of mixing as well as the enthalpies of solution at infinite dilution in Sn were measured at 773, 873, 973 and 1073 K. The results for the enthalpy of formation for the intermetallic compounds Ag_3Sn, Ag_4Sn, Cu_3Sn, $Cu_{41}Sn_{11}$, Cu_6Sn_5, Ni_3Sn-LT, Ni_3Sn_2-HT, and Ni_3Sn_4 are discussed and compared with the corresponding literature values.

Keywords: Calorimetry; Enthalpy of formation; Lead-free solder alloy; Intermetallic compounds

1. Introduction

Soldering technology is the most important joining technology in the electronics industry [1] and has been used widely for the joining of the modules (first-level package) to printed circuit boards. Soldering technology is now becoming even more important because of the fast-growing usage of the ball-grid array package and flip-chip technology. The Pb–Sn alloys are still the dominating solders in the modern electronics industry. However, because of health and environmental concerns, there are continuous efforts to develop lead-free solders following the RoHS directive of the European Union. This directive requires that all electronic products to be sold in the European Union with some well defined exemptions must not contain Pb after 1 July 2006 [2] and it has an immediate impact on the realization of the movement to Pb-free solders. In the last years several different lead-free solders were developed and established on the market. It quickly turned out that there is no drop-in replacement of Pb–Sn solders. Therefore, a basic understanding of soldering processes is indispensable for a systematic development of new solder materials for different applications.

The fundamental issues that affect the microstructure of solder joints are the metallization scheme, solder chemistry, details of the reflow process, and phase transformations in the solid state under manufacturing and service conditions of a device.

Eutectic and near-eutectic Ag–Cu–Sn alloys are the most prominent candidates as lead-free solders, and Ni is commonly used as diffusion barrier layer material. With the emerging of these Ag–Cu–Sn solders, the Ag–Cu–Sn/Ni contacts play an important role in electronic products. Furthermore, Ni itself is considered as a component of solder alloys. Because solders are low melting temperature alloys, diffusion and interfacial reactions are usually significant at common operating temperatures or even at room temperature. Thus the interfacial reactions between Ni and the solder are becoming more and more important for materials scientists. The fabrication of reliable solder joints in micro-electronic packages depends on the formation of mutual solid solutions and intermetallic compounds (IMCs) between solder and substrate. Particularly the IMCs play an important role in controlling the mechanical and electrical properties of solder joints. In many cases IMCs are quite brittle and their extended formation in solder joints lowers their electric conductivity and reduces their mechanical strength.

The knowledge of the enthalpy of formation of IMCs is essential for the understanding of interfacial reactions, especially for the interpretation and prediction of interfacial diffusion, reaction

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paths and mechanisms. The purpose of this study is to determine the enthalpy of formation of intermetallic compounds formed due to interfacial reaction between Ag–Cu–Sn solders and Ni substrates at low temperatures. As there is no evidence for the formation of ternary IMCs in the quaternary Ag–Cu–Ni–Sn system [3], this study was restricted to the formation enthalpies of binary IMCs stable at low temperatures

Selected literature data for the limiting partial enthalpy of mixing of Ag, Cu or Ni with Sn are collected in Table 1. Likewise, Table 2 contains literature values for the enthalpies of formation of various intermetallic compounds in the three binary systems Ag–Sn, Cu–Sn and Ni–Sn.

2. Experimental procedure

2.1. Sample preparation and analysis

Samples of the intermetallic compounds Ag_3Sn, Ag_4Sn, $Cu_3Sn(\varepsilon)$, $Cu_{41}Sn_{11}(\delta)$, Cu_6Sn_5, Ni_3Sn-LT, Ni_3Sn_2-HT, and Ni_3Sn_4 with the nominal compositions as given in Table 2 were synthesized from high purity materials: Ag shot (99.98%, ÖGUSSA, Vienna, Austria), heated in a carbon crucible at 700 °C for 10 min to remove surface impurities; Cu (99.98% Goodfellow, Cambridge, UK) treated under H_2 flow at 200 °C for 2 h to remove oxide layers. Ni (99.98%) and Sn (99.9985%, both Alfa Johnson Matthey, Karlsruhe, Germany) were used as received and without further treatment.

Weighed amounts of the pure elements were arc melted in an inert argon atmosphere. The reguli were inverted several times and the arc melting process was repeated to ensure complete homogenization of alloys. The alloys were encapsulated in quartz tubes and sealed under vacuum ($\leq$1 Pa), then annealed at appropriate temperatures listed in Table 2. After an annealing time of 21 days, the alloys were removed from the furnace and quenched in cold water.

A Guinier-Huber film camera with Cu $K_{\alpha 1}$ radiation was used in order to analyze the phase composition of the samples. The powdered alloys were fixed on a plastic foil and pure Si (99.9999%) was used as an internal standard. The exposure time was 6 h. Table 2 summarizes information regarding nominal compositions, annealing temperatures and identified phases.

2.2. Calorimetry

The solution calorimetric measurements were carried out in a Calvet-type micro calorimeter (HT1000 Setaram, Lyon, France). Each of the twin cells is surrounded by a thermopile with more than 200 thermocouples. The calorimeter is suitable for temperatures up to 1000 °C and heated by a wire wound resistance furnace. A self-made automatic drop device serves for up to 30 drops, measurement control and data evaluation is performed with the software LabView and HiQ, both supplied by National Instruments. LabView is an instrumentation software based on the graphical programming language G and HIQ is used for evaluation and presentation of numerical data; the syntax is very similar to MATLAB. The whole apparatus was described in details by Flandorfer et al. [18].

Pieces of Sn with a total mass between 4 and 5 g were placed into a BN (Boron nitride) crucible (8 mm in diameter, 68 mm in height) which was put inside the quartz tube that has to be introduced in one of the calorimeter cells. Before starting the experiment, the quartz tube was flushed several times with high purity argon (99.999% with Oxisorb cleaning system). Finally, an argon flow of 30 ml/min was kept constant during measurement. Little pieces (8–15 mg) of pure transition metals or samples were dropped from the automatic drop device at drop temperature (DT ≈ 298 K) into the liquid Sn bath maintained at the measurement temperature (MT = 773, 873, 973, or 1073 K, respectively). At the end of each series of measurements, the calorimeter was calibrated by five additions (approx. 30 mg each) of standard α-Al_2O_3 supplied by NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA).

The drop temperature (DT) and the measurement temperature (MT) for each drop were determined using thermo-resistors and thermocouples. The accuracy is usually better than ±1 °C. Generally, the average values of DT and MT for the different drops in one run were used for the data evaluation. From the scatter of the experimental results it is estimated that the values of $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}$ as well as the final values of the enthalpy of formation should be accurate within ±1 kJ/mol.

3. Results

3.1. Determination of $\Delta_{Sol}\bar{H}$ in liquid tin bath

In the course of the present study, the molar enthalpies of solution of Ag, Cu, and Ni in liquid Sn were determined by successive additions of small pieces of the pure elements to a corresponding bath of pure tin or Sn-alloy (after the first addition). The corresponding results for 773 K are plotted versus the molar fraction of the added transitions metal in Figs. 1–3. In a similar way, enthalpies of solution in liquid Sn were determined for the intermetallic compounds Ag_3Sn, Ag_4Sn, Cu_3Sn, $Cu_{41}Sn_{11}$, Cu_6Sn_5, Ni_3Sn-LT, Ni_3Sn_2-HT and Ni_3Sn_4. As an example, the results for Ag_3Sn, $Cu_{41}Sn_{11}$ and Ni_3Sn_2-HT phases are shown in Figs. 4–6.

The values are the measured heat effects ΔQ of the following reactions:

$$(\mathrm{A})_{\mathrm{DT}} + (\text{Sn or Sn-alloy})_{\mathrm{MT}} \rightarrow (\text{Solution})_{\mathrm{MT}}; \quad \Delta Q/n_{\mathrm{A}} = \Delta_{\mathrm{sol}} H(\mathrm{A}) \tag{1}$$

$$(\mathrm{A}_x\mathrm{B}_y)_{\mathrm{DT}} + (\text{Sn or Sn-alloy})_{\mathrm{MT}} \rightarrow (\text{Solution})_{\mathrm{MT}}; \quad \Delta Q/n_{\mathrm{A}_x\mathrm{B}_y} = \Delta_{\mathrm{sol}} H(\mathrm{A}_x\mathrm{B}_y) \tag{2}$$

$(\mathrm{A})_{\mathrm{DT}}$ refers to the pure elements and $(\mathrm{A}_x\mathrm{B}_y)_{\mathrm{DT}}$ refers to the intermetallic compounds in solid state, both at drop temperature, and n_{A}, $n_{\mathrm{A}_x\mathrm{B}_y}$ refer to their molar amounts.

$(\text{Sn or Sn-alloy})_{\mathrm{MT}}$ refers to the liquid Sn bath at the measurement temperature and ΔQ is the measured heat effect for an individual addition. $\Delta_{\mathrm{Sol}}\bar{H}$ is the total heat effect measured for one mole of the pure elements and intermetallic compounds.

Table 1
Heat of solution at infinite dilution and limiting partial enthalpy of mixing (TM = transition metal)

Phase	T (K)	Present work		Literature
		$\Delta_{\mathrm{sol}}\bar{H}^{\infty}$ (kJ/mol)	$\Delta_{\mathrm{mix}}\bar{H}^{\infty}_{\mathrm{TM}}$ (kJ/mol)	$\Delta_{\mathrm{mix}}\bar{H}^{\infty}_{\mathrm{TM}}$ (kJ/mol)
Ag	773	28.32 ± 0.16	5.73 ± 0.19	4.25 [4]
	873	30.40 ± 0.16	4.48 ± 0.16	4.40 [4]
	973	32.53 ± 0.14	3.79 ± 0.14	4.42 [4]
	1073	35.81 ± 0.13	3.56 ± 0.13	4.34 [4]
Cu	773	24.16 ± 0.57	0.85 ± 0.60	−0.84 [4]
	873	27.39 ± 0.39	1.57 ± 0.18	2.19 [4]
	973	30.74 ± 0.25	2.18 ± 0.09	1.15 [4]
	1073	34.45 ± 0.28	2.85 ± 0.28	1.96 [4]
Ni	773	−29.39 ± 0.31	−58.26 ± 0.89	−53.24 [5]
	873	−22.77 ± 0.32	−53.64 ± 0.43	−52.32 [5]
	973	−16.62 ± 0.18	−52.01 ± 0.18	−50.13 [5]
	1073	−11.56 ± 0.18	−50.13 ± 0.18	−48.96 [5]
$Ag_3Sn(\varepsilon)$	773	30.52 ± 0.35		
$Ag_4Sn(\zeta)$	773	29.75 ± 0.60		
$Cu_3Sn(\varepsilon)$	773	31.45 ± 0.58		
$Cu_{41}Sn_{11}(\delta)$	773	29.05 ± 0.50		
$Cu_6Sn_5(\eta)$	773	28.69 ± 0.70		
Ni_3Sn-LT	773	8.62 ± 0.70		
Ni_3Sn_2-HT	773	26.64 ± 0.80		
Ni_3Sn_4	773	23.49 ± 0.58		

The given errors for $\Delta_{\mathrm{sol}}\bar{H}^{\infty}$ are the standard deviation of the respective linear regression.

Table 2
Comparison of the enthalpy of formation at 298 K with literature data standard states: solid components

Composition (at.%)	Annealing temperature (K)	Phase	Enthalpy of formation (kJ/mol)	
			This work	Literature
$Ag_{0.74}Sn_{0.26}$	613	$Ag_3Sn(\varepsilon)$	−4.2 (±1)	−4.5 (± 0.25), 723 K [6]
$Ag_{0.85}Sn_{0.15}$	913	$Ag_4Sn(\zeta)$	−2.8 (±1)	−2.5 (± 0.25), 723 K [6] −3.6 (±0.10), 723 K [7]
$Cu_{0.80}Sn_{0.20}$	973	$Cu_{41}Sn_{11}(\delta)$	−5.7 (±1)	−5.45 (± 0.2), 723 K [8] −5.46 (± 0.2), 723 K [9]
$Cu_{0.75}Sn_{0.25}$	913	$Cu_3Sn(\varepsilon)$	−8.2 (±1)	−7.81 (±0.2), 723 K [8] −7.53 (±0.2), 723 K [9] −7.82 (±0.2), 298 K [10] −8.36, 723 K [11]
$Cu_{0.55}Sn_{0.45}$	473	$Cu_6Sn_5(\eta)$	−6.1 (±1)	−7.03 (± 0.05), 273 K [12]
$Ni_{0.74}Sn_{0.26}$	1073	Ni_3Sn-LT[a]	−24.9 (±1)	−23 (± 0.28), 293 K [9] −26 (± 0.5), 1060 K [13] −23.4 (± 4), 298 K [14] −19.0 (±2.4), 1332 K [16]
$Ni_{0.58}Sn_{0.42}$	1323	Ni_3Sn_2-HT	−34.6 (±1)	−31 (±0.28), 293 K [9] −32 (± 0.5), 1060 K [13] −31.3 (± 4), 298 K [14] −39 (± 0.2), 1023 K [15] −32.02 (±0.2), 1288 K [16]
$Ni_{0.43}Sn_{0.57}$	873	Ni_3Sn_4	−24.0 (±1)	−25.3 (± 0.5), 1060 K [13] −33.7 (± 0.2), 1023 K [15] −28.52, 298 K [16]; $Ni_{0.44}Sn_{0.56}$[b] −30.30, 298 K [16]; $Ni_{0.47}Sn_{0.53}$[b] −24.9 (±1.0), 846 K [17]

[a] Ni_3Sn-HT cannot be obtained by quenching; see Ref. [20].

[b] Must have been a two-phase sample; see Ref. [20].

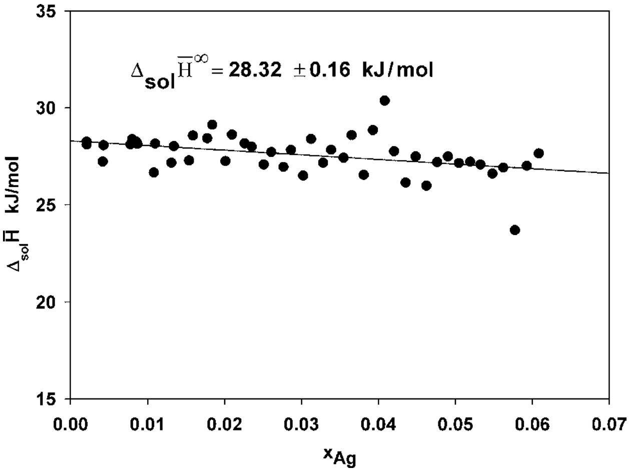

Fig. 1. Molar enthalpies of solution of Ag in a liquid Sn-bath at 773 K. The extrapolated value at infinite dilution ($x_{Ag} = 0$) is given.

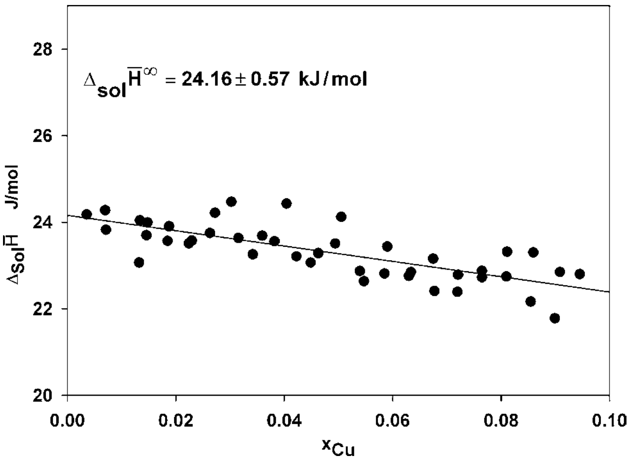

Fig. 2. Molar enthalpies of solution of Cu in a liquid Sn-bath at 773 K. The extrapolated value at infinite dilution ($x_{Cu} = 0$) is given.

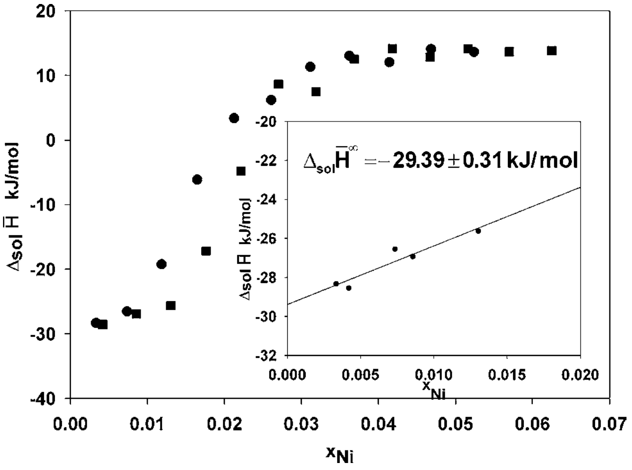

Fig. 3. Molar enthalpies of solution of Ni in a liquid Sn-bath at 773 K. The inset shows the composition range $x_{Ni} \leq 0.02$ where the bath is single phase. The extrapolated value at infinite dilution ($x_{Ni} = 0$) is given.

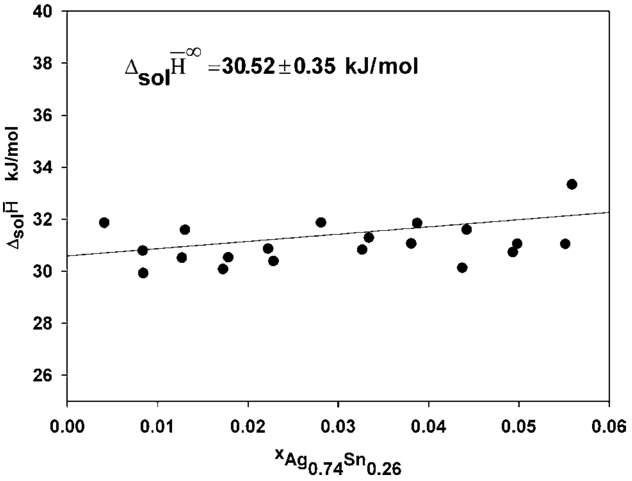

Fig. 4. Molar enthalpies of solution of $Ag_{0.74}Sn_{0.26}$ in a liquid Sn-bath at 773 K. The extrapolated value at infinite dilution ($x_{Comp.} = 0$) is given.

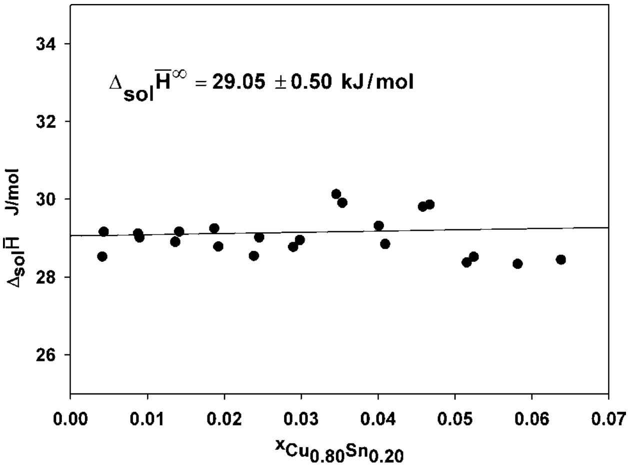

Fig. 5. Molar enthalpies of solution of $Cu_{0.80}Sn_{0.20}$ in a liquid Sn-bath at 773 K. The extrapolated value at infinite dilution ($x_{Comp.} = 0$) is given.

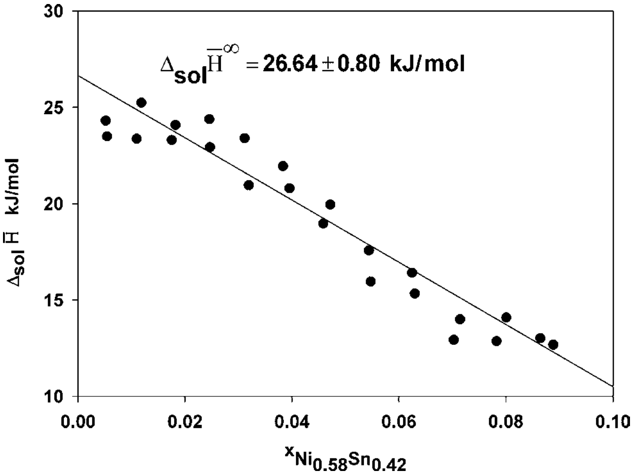

Fig. 6. Molar enthalpies of solution of $Ni_{0.58}Sn_{0.42}$ in a liquid Sn-bath at 773 K. The extrapolated value at infinite dilution ($x_{Comp.} = 0$) is given.

In the composition range investigated, the heat of solution is approximately a linear function of the composition, x_{A} and $x_{\mathrm{A}_x\mathrm{B}_y}$. An exception is the system Ni–Sn, where an intermetallic compound is formed already between 1 and 2 at.% Ni. Fig. 2 shows the heat of solution of Ni in a Sn bath, and it can be seen that the curve shows a kink at about 1.5 at.% Ni, which is caused by the primary crystallization of a solid phase which is most likely Ni_3Sn_4. Due to this reason only few data points are available in a fully liquid state for extrapolation. The $\Delta_{\mathrm{Sol}}\bar{H}$ values were fitted to a polynomial of first order and extrapolated to infinite dilution ($x_{\mathrm{Sn}} = 1$) in order to obtain $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}$. All values of heat of solution at infinite dilution for pure elements and binary IMCs are summarized in Table 1. $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}$ is positive for all elements and compounds except for Ni because of its strongly exothermic enthalpy of mixing with liquid Sn. In addition, the limiting partial enthalpies of mixing of the pure elements in liquid Sn were also determined at 873, 973 and 1073 K. The results are included in Table 1. It can be seen that the values for Ag, Cu and Ni in Sn show a temperature dependency. In the case of Cu and Ni it is a positive temperature dependence and for Ag a negative temperature dependence. This is in disagreement with the findings of Yassin and Castanet [4] who reported a slightly positive temperature dependence of the limiting partial enthalpies of mixing of Ag in Sn based on literature data of various authors. However, the corresponding values show a considerable scatter, and their conclusions of certain temperature dependence are hard to follow.

3.2. *Determination of the enthalpy of formation*

The enthalpies of formation, $\Delta_{\mathrm{f}}H^{298}$, of the considered binary IMCs, were obtained from the difference of the heats of solution at infinite dilution of the pure components and the compounds:

$$\Delta_{\mathrm{f}}H^{298}(\mathrm{A}_x\mathrm{B}_y) = x\Delta_{\mathrm{sol}}\bar{H}^{\infty}(\mathrm{A}) + y\Delta_{\mathrm{sol}}\bar{H}^{\infty}(\mathrm{B}) - \Delta_{\mathrm{sol}}\bar{H}^{\infty}(\mathrm{A}_x\mathrm{B}_y) \qquad (3)$$

- $\Delta_{\mathrm{f}}H^{298}$ is the enthalpy of formation of the intermetallic compound at 298 K referred to the solid components.
- x and y are the mole fractions of the components.
- $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{A})$, $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{B})$, and $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{A_xB_y})$ are the limiting enthalpies of solution of the solid components in liquid Sn. In our case $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{B}) = \Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{Sn})$.

The values $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{A})$ and $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{B})$ consist of the following terms:

- Enthalpy of heating of one mole of the solid component from room temperature (≈298 K) to the temperature of the calorimeter (MT).
- Molar enthalpy of fusion of the component ($\Delta_{\mathrm{fus}}H$).
- Limiting partial enthalpy of mixing $\left(\Delta_{\mathrm{mix}}\bar{H}^{\infty}\right)$ of the component in liquid tin. $\Delta_{\mathrm{mix}}\bar{H}^{\infty}(\mathrm{Sn})$ in Sn is naturally zero, thus $\Delta_{\mathrm{Sol}}\bar{H}^{\infty}(\mathrm{Sn})$ reduces to the first two terms which were calculated from the Dinsdale polynomials [19].

4. Discussion

The enthalpy of formation of a compound can be used as a measure of its stability because the contribution of the entropy of formation is usually small.

Table 2 presents the comparison of the obtained enthalpies of formation of Ag–Sn compounds with literature data. The values of −4.2 kJ/mol for Ag_3Sn and −2.8 kJ/mol for Ag_4Sn are in good agreement with values reported by Kleppa [6]. The value obtained for Ag_4Sn by Laurie et al. [7] is significantly more exothermic.

A comparison of the enthalpies of formation of Cu–Sn compounds is also shown in Table 2. The $\Delta_{\mathrm{f}}H^{298}$ value of $Cu_{41}Sn_{11}$ (−5.7 kJ/mol) is compared to a value obtained by Kleppa [8] and the agreement is very good. Our result for Cu_3Sn (−8.2 kJ/mol) is shown together with the data of Kleppa [8] and three other works [9–11]. In general the agreement is very good. The situation is somewhat different for Cu_6Sn_5 where the only available literature value by Gangulee et al. [12] is slightly more negative than our value of $\Delta_{\mathrm{f}}H^{298} = -6.1$ kJ/mol. However, the deviation is hardly above the error limit.

The formation enthalpies for Ni–Sn intermetallic compounds are again presented in Table 2. The $\Delta_{\mathrm{f}}H^{298}$ value of Ni_3Sn-LT is −24.9 kJ/mol, that of Ni_3Sn_2-HT is −34.6 kJ/mol and that of Ni_3Sn_4 is −24.0 kJ/mol. They are generally in good agreement with previous literature data [9,13–17], except for the data given by Dannoehl and Lukas [15] who obtained much more exothermic values for Ni_3Sn_2-HT and Ni_3Sn_4. Unfortunately there are no standard states given by the authors what makes a comparison difficult. For the latter compound agreement with Torgersen et al. [16] seems to be better but one has to take into account the difference in composition [$Ni_{3.14}Sn_4$ and $Ni_{3.50}Sn_4$ versus $Ni_{3.0}Sn_4$]. According to hitherto published literature and a recent new investigation of the Ni–Sn phase diagram [20] alloys of the given compositions are not single phase but in equilibrium with Ni_3Sn_2-HT. The considerable higher enthalpy of formation of this compound might explain the more exothermic values given in Ref. [16]

In the three binary systems Ag–Sn, Cu–Sn, and Ni–Sn, the most stable intermetallic compounds are Ag_3Sn, Cu_3Sn, and Ni_3Sn_2. From many investigations of the interfacial reactions between Cu–Sn or Ag–Cu–Sn solders and Ni substrate it is well known that $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ intermetallic compounds are primarily formed. Only after long time annealing at temperatures close to the melting of the solder the compounds $(Cu,Ni)_3Sn$ and $(Ni,Cu)_3Sn$ are additionally formed whereas Ni_3Sn_2, the most stable compound, is usually never formed at the respective annealing temperatures. This implies that IMCs formation via interfacial reactions is rather controlled by diffusion kinetics than by the stabilities of the corresponding intermetallic compounds.

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