Enthalpies of Formation of (Cu,Ni)$_3$Sn, (Cu,Ni)$_6$Sn$_5$-HT and (Ni,Cu)$_3$Sn$_2$-HT

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Standard enthalpies of formation of ternary phases in the Cu-Ni-Sn system were determined along sections at 25, 41 and 45.5 at.% Sn applying tin solution drop calorimetry. Generally, the interaction of Ni with Sn is much stronger than that of Cu with Sn. Along all sections the enthalpy of formation changes almost linearly with the mutual substitution of Cu and Ni within the respective homogeneity ranges. Thus no additional ternary interaction promoting the formation of further Cu-Ni-Sn phases can be assumed. The results are discussed and compared with literature values relevant to this system.

Keywords
- enthalpy of formation, experimental thermodynamics,
- intermetallics, metallic alloys, thermodynamic properties

1. Introduction

Within the efforts of the electronics industry to develop a more environmentally friendly and less toxic technology, e.g. the switch to lead-free solders, the ternary Cu-Ni-Sn system assumed a key role, due to the focus on mostly Cu and Sn-bearing solders and Ni as a surface coating on the metallization. In recent years a number of investigations were carried out to determine the phase equilibria in this system that are the basis for targeted material design, especially for more sophisticated solder related technologies like transient liquid phase bonding. However, the elements involved are characterized by quite different melting temperatures and reliable experimental phase diagram investigations are hampered by uncertainties concerning the establishment of equilibrium at temperatures relevant for soldering in the high melting parts.

By combining experiments at higher temperatures with thermodynamic modelling of the phase equilibria (CALPHAD method) these difficulties can be overcome. This is a semi-empirical method and thus relies on available thermodynamic data. The phases usually formed in solder joints are Cu$_6$Sn$_5$, Ni$_3$Sn$_2$ and after long term annealing Cu$_3$Sn. The enthalpies of formation of these phases (as well as a number of others) were determined by Flandorfer et al.[1] using drop-solution calorimetry and discussed together with other results from literature. Their work was limited to the binary compounds, but it is known from phase diagram studies that the high temperature (HT) phases of Cu$_3$Sn and Ni$_3$Sn (both DO$_3$, BiF$_3$ structure type) form a temperature dependent mutual solid solution in the ternary Cu-Ni-Sn system.[2] Such a complete mutual solution was not found for the Cu$_5$Sn$_3$ and Ni$_5$Sn$_3$ HT phases (both partially filled InNi$_2$ type structures), but both of them dissolve considerable amounts of the respective third element.

In contrast to the binary compounds,[1] the enthalpies of formation of their ternary solid solutions have so far not been determined experimentally. First principles studies on Cu$_5$Sn$_3$ and Cu$_6$$_3$Ni$_3$Sn$_5$ were conducted by Ghosh and Asta[3] and Yu et al.,[4] respectively. In the latter work four different substitutions of Cu by Ni in the Cu$_6$Sn$_5$-low temperature crystal structure were investigated. In all cases the enthalpy of formation values indicated a stabilization of the compound by the admixture of Ni. Cu$_5$Ni$_2$Sn$_5$ was found to be the most stable one among these.

It was therefore considered of interest to provide experimental enthalpies of formation for several compositions within the homogeneity ranges of the various phases in the ternary Cu-Ni-Sn system using drop solution calorimetry.

2. Materials and Methods

Ternary samples were prepared along three sections at 25 at.% Sn from Ni$_3$Sn to Cu$_3$Sn, at 41 at.% Sn starting from Ni$_5$Sn$_2$ and at 45.5 at.% Sn starting from Cu$_6$Sn$_5$. Their compositions can be found in Table 1. The continuous solid solution between Ni$_3$Sn HT and Cu$_3$Sn HT is strongly temperature dependent and does not appear as such at a single temperature (in isothermal sections of the phase diagram) due to the different thermal stability ranges of the binary phases. Therefore, at 973 K the phases Ni$_3$Sn LT, t$_1$ or Cu$_3$Sn HT were found in samples P2-P8, as shown in Table 1 (see also Ref 2). Ni$_5$Sn$_2$ HT and Cu$_6$Sn$_5$ HT even at
Table 1 Sample composition, measurement details and enthalpy of formation results

| Sample Number | Cu, at.% | Ni, at.% | Sn, at.% | Phase present after annealing | Space group | Structure type | Lattice constants pm | Annealing temperature, K | Drop T, K | Measurement T, K | ΔfH^298, kJ/mol atom | Value, kJ/mol atom | Error ±, kJ/mol atom |
|---------------|---------|----------|----------|-----------------------------|-------------|----------------|---------------------|--------------------------|-----------|----------------|---------------------|-------------------|---------------------|
| P2            | 60      | 15       | 25       | Cu₃Sn HT (Cu) traces         | Fm-3 m      | BiF₃           | 598.658(6)         | 973                      | 304       | 873           | 30.6                | 11.7              | 1                   |
| P3            | 50      | 25       | 25       | Cu₃Sn HT                    | Fm-3 m      | BiF₃           | 596.752(5)         | 973                      | 310       | 873           | 27.9                | 14.1              | 1                   |
| P4            | 40      | 35       | 25       | Cu₃Sn HT                    | Fm-3 m      | BiF₃           | 595.194(8)         | 973                      | 312       | 873           | 25                  | 16.2              | 1                   |
| P5            | 30      | 45       | 25       | Cu₃Sn HT                    | Fm-3 m      | BiF₃           | 593.575(9)         | 973                      | 304       | 873           | 22.1                | 18.3              | 1                   |
| P7            | 12      | 63       | 25       | t1                          | Cmcm        | β-Cu₃Ti        | 537.6/429.6/451.0  | 973                      | 307       | 873           | 16.4                | 21.6              | 1                   |
| P8            | 5       | 70       | 25       | Ni₁Sn LT                    | P6̅/3mmc     | Mg2Cd          | 529.98/426.092     | 973                      | 308       | 873           | 14.6                | 23.3              | 1                   |
| P9            | 30      | 29       | 41       | Ni₁Sn₂ HT                   | P6̅/3mmc     | InNi₂          | 415.628/515.366    | 973                      | 307       | 873           | 33.2                | 22.1              | 1                   |
| P10           | 20      | 39       | 41       | Ni₁Sn₂ HT                   | P6̅/3mmc     | InNi₂          | 413.455/518.125    | 973                      | 304       | 873           | 32.3                | 26.1              | 1                   |
| P11           | 10      | 49       | 41       | Ni₁Sn₂ HT                   | P6̅/3mmc     | InNi₂          | 411.799/518.894    | 973                      | 304       | 873           | 30.1                | 28.9              | 1                   |
| P12           | 27.5    | 27       | 45.5     | Cu₃Sn₅ HT (Sn traces)       | I4/amd      | β-Sn           | 402.604(3)/510.604(5) | 673                      | 304       | 873           | 30.2                | 18.2              | 2                   |
| P13           | 37.5    | 17       | 45.5     | Cu₃Sn₅ HT (Sn traces)       | I4/amd      | β-Sn           | 583.222(9)/318.188(7) | 673                      | 304       | 873           | 33.3                | 16.2              | 2                   |
varying temperature do not form a continuous solid solution. Furthermore, they differ in their Ni:Sn and Cu:Sn ratios according to the binary phase diagrams which resulted in the chosen placement of the samples.

The samples were prepared from Cu (99.98%, Goodfellow, Cambridge, UK), Ni (99.98%) and Sn (99.9985%, both Alfa Johnson Matthey, Karlsruhe, Germany). Before use, Cu was treated under H₂ flow at 473 K in order to remove oxide layers, while the other metals were used as received.

The weighed pure metals were fused together in an arc furnace in Ar atmosphere. The sample pellets were remelted three to four times and turned upside down in order to ensure homogeneity. After alloying, the samples were sealed in evacuated quartz glass tubes and annealed at 973 and 673 K, respectively—see Table 1. The samples were then quenched in cold water.

Prior to the calorimetric measurements, the samples were characterised by means of x-ray diffraction (XRD) which was carried out on a Bruker D8 diffractometer in Bragg-Brentano geometry (Bruker AXS, Karlsruhe, Germany) using Cu Kα₁ radiation and an exposure time of two hours. The obtained diffractograms were analyzed using the Topas 3 software (Bruker AXS, Karlsruhe, Germany) in order to check that the desired phase had formed and to determine possible traces of impurity phases.

Drop solution calorimetry used to determine the enthalpies of formation was done on a Calvet-type micro calorimeter (HT1000 Setaram, Caluire, France). This calorimeter consists of a twin cell for sample and reference. Each cell is surrounded by a thermopile of more than 200 thermocouples. It is heated by a wire wound resistance furnace suitable for operating temperatures up to 1273 K. A self-made drop device was used for dropping up to 30 sample pieces during each experiment, while measurement control and data recording were done using the software LabView and HiQ (both National Instruments). A more detailed description of the setup was given by Flandorfer et al.[5]

The experimental setup consisted of a quartz glass tube inserted into the measurement cell, which housed a BN (boronitride) crucible containing the Sn-bath (4-12 g). Before each measurement, the whole apparatus was flushed several times with high purity Ar (99.999% with Oxisorb cleaning system) and a constant Ar flow of 30 mL/min was established during the measurement. Small pieces (10-40 mg) of the pure transition metals or the alloys were dropped from the automatic drop device at the drop temperature (DT; see Table 1) into the Sn-bath kept at the measurement temperature (MT = 873 K). Calibration was done at the end of each measurement by dropping pieces of α-Al₂O₃ standard (~30 mg each) supplied by National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Temperature measurement was done using thermocouples and thermo-resistors with accuracy higher than ±1 K. For the evaluation the average values of DT and MT of each drop in an experiment were taken.

The quantity measured in the experiments is the enthalpy of solution, ΔsolH(A), where A represents either a pure metal or a compound. This was obtained by successive additions of the respective material to the bath of pure Sn or Sn-alloy (after the first drop). Recalculation of the measured heat effects to a basis of one mole of dropped substance yielded the approximate partial heat of solution ΔsolH(A) for dropping a sample piece from DT to the tin bath at MT. This is valid only if the masses of dropped substance are very small compared to the mass of material in the crucible.

In order to derive the enthalpy of formation of a compound, ΔfH°, the limiting partial enthalpies of solution at infinite dilution ΔsolH°(A) need to be known. They are obtained by extrapolating the values of ΔsolH(A) of each drop made during an experiment to a mole fraction of zero. In the composition range very close to pure tin ΔsolH(A) can be treated as a linear function of composition. If this condition is not fulfilled over the entire composition range, only the linear part can be used or another function needs to be used for extrapolation. Examples for both cases are shown in Fig. 1 and 2 for samples P10 and P12, respectively.

The enthalpy of formation was then derived as the difference between the limiting enthalpies of solution at infinite dilution of the pure elements and the respective alloy in liquid Sn as expressed by Eq 1:

\[ \Delta_{f}H° = 32.3 \text{kJ/mol atom} \]

\[ \Delta_{f}H° = 30.2 \text{kJ/mol atom} \]
\[ \Delta_t H^{298} = x \cdot \Delta_{\text{sol}} H^\infty (\text{Cu}) + y \cdot \Delta_{\text{sol}} H^\infty (\text{Ni}) + z \cdot \Delta_{\text{sol}} H^\infty (\text{Sn}) - \Delta_{\text{sol}} H^\infty (\text{Cu}_x \text{Ni}_y \text{Sn}_z), \quad (\text{Eq } 1) \]

- \( \Delta_t H^{298} \) is the enthalpy of formation of the intermetallic compound at 298 K with the pure solid metals being the reference state.
- \( x, y \) and \( z \) are the mole fractions of \( \text{Cu}, \text{Ni} \) and \( \text{Sn} \).
- \( \Delta_{\text{sol}} H^\infty (A) \) are the limiting enthalpies of solution at infinite dilution of the pure elements or the compound in liquid \( \text{Sn} \).

The \( \Delta_{\text{sol}} H^\infty \) values contain the following contributions:

\[
\Delta_{\text{sol}} H^\infty (A) = \int_{\text{Tm}(A)}^{\text{MT}} \text{Cp}(A, s) \, dT + \int_{\text{Tm}(A)}^{\text{MT}} \text{Cp}(A, l) \, dT + \Delta_{\text{fus}} H(A, \text{Tm}) + \Delta_{\text{mix}} H^\infty (A) \quad \text{for } MT > \text{Tm}
\]

\[
\Delta_{\text{sol}} H^\infty (A) = \int_{\text{DT}} \text{Cp}(A, s) \, dT + \Delta_{\text{fus}} H(A, \text{MT}) + \Delta_{\text{mix}} H^\infty (A) \quad \text{for } MT < \text{Tm}
\]

\( (\text{Eq } 2) \)

- Integral over \( \text{Cp} \)—relative enthalpies of heating of solid and liquid component over the respective temperature ranges
- Enthalpy of fusion—\( \Delta_{\text{fus}} H \)
- Limiting partial enthalpy of mixing of the component or alloy with liquid \( \text{Sn}—\Delta_{\text{mix}} H^\infty \).

The terms in Eq 2 can either be taken from available literature or need to be determined in the course of the experiments. \( \Delta_{\text{mix}} H^\infty \) is zero for dropping \( \text{Sn} \) into a \( \text{Sn} \)-bath so that \( \Delta_{\text{sol}} H^\infty (\text{Sn}) \) can simply be calculated from available SGTE data \(^6\) and does not need to be determined experimentally. Equation 1 is valid only under the assumption that the limiting enthalpies of mechanical mixtures of \( \text{Cu} \) and \( \text{Ni} \) in liquid \( \text{Sn} \) are a linear combination of the limiting enthalpies of the pure compounds. The error of the measured \( \Delta_{\text{sol}} H^\infty \) and of the calculated final \( \Delta H \) was determined from the experimental scatter and is smaller than \( \pm 1 \) kJ/mol unless otherwise stated.

### 3. Results and Discussion

Values of \( \Delta_{\text{sol}} H^\infty \) and \( \Delta_t H^{298} \) for the investigated alloys are presented in Table 1. A graphical representation of the \( \Delta_t H^{298} \) values is given in Fig. 3 (25 at.% Sn section) and Fig. 4 (41 and 45.5 at.% Sn sections). The values for the limiting binary compounds were taken from Flandorfer et al.\(^1\) Within limits of error in all sections, a linear dependency between the enthalphy of formation and the change in composition (change in the \( \text{Cu}/\text{Ni} \) ratio) is observed. Interestingly, at 25 at.% \( \text{Sn} \), this linear trend is unaffected by the presence of different phases: \( \text{Cu}_3\text{Sn} \) HT phase, \( \text{Ni}_3\text{Sn} \) LT phase, squares the \( \tau_1 \) ternary compound and triangles the \( \text{Ni}_3\text{Sn} \) LT phase.

![Fig. 3](image329x585.png) Enthalpies of formation of alloys at a constant \( \text{Sn} \)-content of 25 at.% (samples P2-P8). Circles represent the \( \text{Cu}_3\text{Sn} \) HT phase, squares the \( \tau_1 \) ternary compound and triangles the \( \text{Ni}_3\text{Sn} \) LT phase.

![Fig. 4](image329x507.png) Enthalpies of formation of alloys at a constant \( \text{Sn} \)-content of 41 at.% (squares: \( \text{Ni}_3\text{Sn}_2 \) HT, samples P9-P11) and 45.5 at.% (circles: \( \text{Cu}_6\text{Sn}_5 \) HT, samples P12-P13).

et al.\(^1\) It has to be noted that sample P2, \( \text{Cu}_{60}\text{Ni}_{15}\text{Sn}_{25} \), contained trace amounts of (\( \text{Cu} \)), which can be considered negligible (only 2% according to XRD), while sample P7, \( \text{Cu}_{12}\text{Ni}_{63}\text{Sn}_{25} \), contains the stable and metastable variants of \( \tau_1 \) and \( \tau_1' \) in equal amounts. Both phases crystallize in the \( \beta \)-\( \text{Cu}_3\text{Ti} \) type structure and only differ in the free parameters of the atom positions and variations of the lattice parameters.\(^2\) Any influence on the enthalphy of formation should therefore be negligible.
The enthalpy of formation can be regarded as a measure for the stability of a compound, since the entropy of formation is usually very small and influences the stability only at very HT.[1] According to the present results, the addition of Ni enhances the stability of the Cu-Sn compounds whereas the addition of Cu to Ni-Sn systems has the reverse effect. A stronger electronic interaction of Ni with Sn due to the even number of valence electrons of both elements is assumed to be responsible for this behaviour. A similar effect can also be observed in the enthalpies of mixing of liquid state in the systems Cu-Sn and Ni-Sn, where Flandorfer et al.[6] reported minima of $-3.6$ kJ/mol at $x_{Cu} = 0.73$ and $-20.6$ kJ/mol at $x_{Ni} = 0.60$, respectively at 1373 K. This assumption is supported by the occurrence of short range order in the liquid state.

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**Table 2** Enthalpy of formation values of (Cu,Ni)$_6$Sn$_5$ LT as reported in Ref 4

| Composition  | Cu, at.% | Ni, at.% | Sn, at.% | $\Delta H$ at 0 K, kJ/mol atom | Cu atom site substituted by Ni as in Ref 4 |
|--------------|----------|----------|----------|-------------------------------|-----------------------------------------|
| Cu$_6$Sn$_5$ | 54.55    | 0.00     | 45.45    | $-26.32$                      | 8f (Cu1)                                |
| Cu$_5$NiSn$_5$ | 36.36    | 18.18    | 45.45    | $-53.73$                      | 8f (Cu2)                                |
| Cu$_5$NiSn$_5$ | 36.36    | 18.18    | 45.45    | $-59.12$                      | 4a (Cu3)                                |
| Cu$_5$NiSn$_5$ | 45.45    | 9.09     | 45.45    | $-50.03$                      | 4e (Cu4)                                |

Another sample, Cu$_{68}$Ni$_7$Sn$_{25}$, had initially been prepared, but in none of the preparation runs the Cu$_3$Sn HT phase could be fully retained. Instead, this sample partially decomposed into Cu$_{41}$Sn$_{11}$ (40%) and (Cu) (20%); its values are therefore not given in Table 1. However, the enthalpy of formation of this sample was determined to be $-9.8$ kJ/mol atom, which corresponds to the observed linear trend.

From these observations, it can be concluded that the enthalpy of formation of Cu-Ni-Sn phases at 25 at.% Sn predominantly depends on the replacement of Cu by Ni rather than on the actual type of phase present in the sample. Indeed, the crystal structures of the phases found along this section show some clear relationships. The most obvious relation can be found between the cubic DO$_3$ type (Cu,Ni)$_3$Sn HT phase and the orthorhombic t1 phase which are both composed of (Cu,Ni)- and Sn-chains. While the arrangements of these two kinds of chains is regular in the Cu$_6$Sn$_5$ HT phase according to the cubic symmetry, an offset between the chains along the c-axis can be noticed in the t1 phase which breaks the cubic symmetry and necessitates the orthorhombic setting. Nevertheless, the coordination of the individual atoms remains similar in the two phases which indicates similar (Cu,Ni)-Sn bonds. As the local environment of the atoms appears to be similar in all phases, the exchange of Cu and Ni has the main influence on the enthalpy of formation rather than the actual phase formed.

An equally linear trend was found for the Ni$_3$Sn$_2$ HT and Cu$_6$Sn$_5$ HT phases (samples P9-P11, and P12, P13), respectively. As Ni$_3$Sn$_2$ HT is a congruently melting compound, single phase samples could easily be prepared. On the contrary, despite having the same crystal structure, Cu$_5$Sn$_5$ HT is formed in a peritectic reaction in the binary Cu-Sn system. In the ternary system, too, it was therefore not possible to obtain single phase samples despite prolonged annealing. Samples P12 and P13 contain trace amounts of (Sn) according to XRD which are considered longed annealing. Samples P12 and P13 contain trace amounts of (Sn) according to XRD which are considered longed annealing. Samples P12 and P13 contain trace amounts of (Sn) according to XRD which are considered longed annealing. Samples P12 and P13 contain trace amounts of (Sn) according to XRD which are considered longed annealing. Samples P12 and P13 contain trace amounts of (Sn) according to XRD which are considered longed annealing. Samples P12 and P13 contain trace amounts of (Sn) according to XRD which are considered longed annealing.

Yu et al.[4] calculated enthalpy of formation values for the admixture of Ni to the Cu$_6$Sn$_5$ LT phase (see Table 2) using first principles calculations. Their values are in general lower than those reported in the present study and well established values in the literature,[1] but are valid for 0 K and the low temperature phase. However, they show the same trend as the data in the present work valid at 298 K for the HT phase, i.e. increasing exothermic enthalpy of formation by the admixture of Ni to Cu$_6$Sn$_5$ HT.

The enthalpy of formation can be regarded as a measure for the stability of a compound, since the entropy of formation is usually very small and influences the stability only at very HT.[1] According to the present results, the addition of Ni enhances the stability of the Cu-Sn compounds whereas the addition of Cu to Ni-Sn systems has the reverse effect. A stronger electronic interaction of Ni with Sn due to the even number of valence electrons of both elements is assumed to be responsible for this behaviour. A similar effect can also be observed in the enthalpies of mixing of liquid state in the systems Cu-Sn and Ni-Sn, where Flandorfer et al.[6] reported minima of $-3.6$ kJ/mol at $x_{Cu} = 0.73$ and $-20.6$ kJ/mol at $x_{Ni} = 0.60$, respectively at 1373 K. This assumption is supported by the occurrence of short range order in the liquid state.