Thermodynamic Re-Assessment of the Ternary System Ni-Sn-Zn using a four-sublattice model and supported by first-principles calculations

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Abstract In this paper CALPHAD (CALculation of PHAse Diagram) method was used for thermodynamic reevaluation of the ternary Ni-Sn-Zn system. The fcc_A1/Ni₃Sn₂-L12 disordered/ordered transition was described using a four-sublattice model. In CALPHAD modeling therefore, the enthalpies of formation of the ternary compounds (τ₁, τ₂, and τ₄) and end-members of the phases at 0 K are essential input thermodynamic parameter in the Ni-Sn-Zn ternary system. Which is computed via first-principles calculations? In the Ni-Sn-Zn ternary system, it was clarified that the ordered Ni-Sn-Zn phase is formed from the liquid phase with the addition of Zn. An optimal set of thermodynamic parameters for the Ni-Sn-Zn system was obtained by taking into consideration of the experimental data from the literature and theoretic values from the present first-principles calculations. Assessments between the calculated and measured phase diagrams signposted, that nearly all the consistent experimental information was agreeably accounted for by the present modeling.

Keyword: Ni-Sn-Zn system, CALPHAD, First-principles calculations

Introduction

Therefore, thermodynamic data for ternary compounds are of the utmost reputation for obtaining consistent thermodynamic accounts of ternary systems. The formation of soldered joint (seam) among the metal to be brazed and the solder heated to a temperature slightly above the solder melting point (Tm) is one of the key stages of the soldering technological process. The formation of intermetallic compounds, solid solutions or eutectics occurs in the seam as a result of the interdiffusion and succeeding crystallization processes. The foremost necessities for soldered joints are their high mechanical strength and satisfactory structural characteristics that afford reliable contact with the surface, corrosion resistance, good thermal and electrical properties as well as the likelihood of heat treatment of elements
encompassing such joints without causing damage to them [1]. To satisfy these necessities it is required to habit solders with definite chemical composition. Powder solders have newly become popular on the world market. Their solicitation provides the reduction of labor intensity in the soldering technological process, accurate material dosing, mechanization and miniaturization of the soldering procedure. Naturally, additional requirements are imposed on the particle size in powder solders.

Moreover, the addition of nickel can lead to the formation of ternary intermetallic compounds and, consequently, it can improve mechanical properties and corrosion resistance of the joint [2]. In this regard, some methods of Zn–Sn–Ni ternary alloy coatings deposition have been developed. These coatings are characterized by higher corrosion resistance, excellent solderability and electrical conductivity in comparison with coatings based on Sn–Zn and Ni–Zn binary alloys [3–4]. As for Zn–Sn–Ni powder alloy, there is no information on its preparation and properties in the literature.

For many investigated ternary compounds, there exist noticeable discrepancies for the measured enthalpies of formation from different sources [6]. Knowledge of phase diagram and thermodynamic properties [5] is of fundamental importance in many applications. High-throughput discovery of new materials strongly depends on the establishment of an accurate thermodynamic database in a multi-component system. Knowledge of thermodynamics is a prerequisite for improving various physical, chemical and mechanical properties of these alloys, and even for exploring new materials [7]. Among the huge number of ternary compounds discovered so far, thermodynamic data are available only for a few percent of the reported compounds [8]. The enthalpy of formation, as the leading term of Gibbs energy, is the predominant quantity among various thermodynamic properties. Thermodynamic descriptions for ternary systems are the nucleus of a multi-component thermodynamic database.

To cure this situation, numerous computational tactics have been developed. The widely used methods to calculate enthalpy of formation include, between others, Miedema model, CALPHAD (CALculation of PHAse Diagram) approach and first-principles calculation. The Miedema model, which was developed by Miedema et al. [9, 10] coalescing thoughts from the thermodynamics of solids with energy band theory in the mid 1970’s, is straightforward. Though, organized deviations from
experimental data are often observed in binary and ternary alloys due to inherent explanations associated with this model [11]. Recently, several modified Miedema models have been proposed in order to obtain more reasonable results [12-14]. CALPHAD method predicts enthalpy of formation for any alloy from the Gibbs energy expressions of individual phases [14]. These expressions are optimized from various experimental phase equilibria and thermodynamic properties. The precision of this process relies on a sound thermodynamic model for each phase, correct experimental information as well as the quality for thermodynamic descriptions of the lower-order systems. Density functional theory (DFT) is the key stream to solve the first-principles equation calculation. DFT became very general in quantum chemistry since 1990s, because of a valuable equilibrium among accuracy and computational cost in the solid state physics. Current calculations show that first-principles method (e.g. density functional theory (DFT)) provides an alternate way to obtain enthalpies of formation. Accurate crystal structure is a prerequisite for obtaining enthalpy of formation by means of first-principles method. For a phase with a few hundred atoms per unit cell, first-principles calculation is, however, extremely time-consuming. Thus, any individual experimental or theoretical method mentioned above cannot give entirely satisfactory results. In the present work, we propose an effective approach to obtain enthalpies of formation for ternary compounds highly efficiently. Such an approach is the integration of Miedema model, CALPHAD approach, first-principles calculations, and high temperature reaction calorimetry (HTRC). To verify this methodology, we focus on the Al-Fe-Si and Al-Mn-Ni ternary systems, which are two important sub-systems of multi-component Al alloys.

In order to fit the first-principles calculated E-V (energy-volume) data points; the four-parameter Birch-Murnaghan equation of state with its linear form [17] is employed. CALPHAD is another theoretical approach to obtain the enthalpy of formation. The essence of this approach is to evaluate the parameters of thermodynamic models for the Gibbs energies of the individual phases via a thermodynamic optimization applied to the measured thermodynamic and phase equilibrium data. With the optimized thermodynamic parameters, any phase equilibria and thermodynamic properties can be
computed. Using the GM model predicted enthalpies of formation as reliable estimates for Gibbs energies of ternary compounds, Du et al. [16] and Liu [21] performed thermodynamic optimizations for the Al–Co–Cr, Al–Co–Ni, Co–Cr–Ni systems, respectively. In this study, my purpose to survey the phase equilibria of the Ni-Sn-Zn system at different temperature range and an attempt compute and validate the previous published data with calphad approaches and results are supported with first principle calculation, Miedema Calculator of the thermodynamic properties of Ni-Sn-Zn system.

2 Appraisal of experimental data in the literature

At the beginning of our investigations only one publication with very little phase diagram information was available Mayer A. et al. [15] for the ternary Ni-Sn-Zn system. On the basis of the experimental data of isothermal sections at 200 °C [16], 500 °C [16, 20], 600 °C [17, 19] 700 °C [16, 18, 24, 27] and 800 °C [16, 18, 24] 900 °C [18] as well as the intermetallic compound and solid solution [12, 21] in the Ni-Sn-Zn system have been reported in the literature. In 1958, Westbrook et al. [33] prepared about 150 ternary alloys and for the first time determined the isothermal section at 1000 °C for the Ni-Sn-Zn system using X-ray diffraction (XRD), metallographic observation, and microhardness measurements. Four ternary compounds (τ₁ to τ₄) were found. The existence of τ₁ to τ₄ was confirmed by subsequent investigations [16-20, 24, 27]. A new two (i.e., τ₁ and τ₂) ternary compound with a composition of Ni₃₆Sn₄₂Zn₂₂ (in at.%). which are derived from α'-Ni₃Sn₂ and β-NiZn, respectively Jian-Lie Liang et al. [20]. while a double layer containing Ni₅Zn₂₁ and Ni₃₅Zn₂₂Sn₄₃ IMCs is formed at temperatures above 325°C is reported by Chiu M Y et al. [21].

Experimental phase equilibria data of the Ni-Sn-Zn system were investigation of more than 60 alloy samples. Two new ternary compounds, designated as τ₂ (Ni₃Sn₄Zn) and τ₃(Ni₃Sn₉Zn₅), were identified at 700, 800 and 900 °C by Schmetterer Clemens et al. [18] and their homogeneity ranges and crystal structures could be described. Whereas τ₃ is only present at 700 °C, the τ₂-phase was found at both 700 and 800 °C. No truly ternary compound could be found in the isothermal section at 900 °C.
Subsequently, the isothermal section, indicate that this phase is a ternary solid solution of Ni₃Sn-HT from constituent binary Ni-Sn. It is stabilized to lower temperatures by additions of Zn, although identified two ternary compounds, i.e. Ni₅ₓSn₄Zn (labelled τ₂) and Ni₅Sn₂Zn (labelled τ₃) at 973 K by Schmetterer et al. [22-23,24 26]. The formation of the ternary intermetallic τ₁ phase (Ni₃ₓSn₄Zn) has been established by Kudaka A.A. et al. [27].

All the binary compounds, excluding Ni₃Sn₄, show a large solubility of the third element reported by Yuan Yuan et al. [19]. The isothermal section at 873 K, including 17 three phase fields, has been determined. The formation of triple intermetallic phases at stated temperature was observed in the study of Sn–Zn–Ni alloys obtained from metallurgical metal powders by K. Ishizuka et al. [25]. And single layer of Ni₅Zn₂, IMC appears at temperatures below 325°C by Chiu M Y et al. [21], while a double layer containing Ni₅Zn₂ and Ni₃5Zn₂2Sn₄3 IMCs is formed at temperatures above 325°C. These new experimental results will provide valuable information to the thermodynamic description of alloy systems relevant for high-temperature lead-free soldering.

3 First-principles calculations for enthalpy of formation

DFT make the scientist can calculate much larger systems than traditional. The Helmholtz energy, F(V,T), of a condensed phase, in terms of the quasiharmonic approach, from first-principles calculations based on DFT is expressed as follows [28-29]: The thermal electronic contribution to the Helmholtz energy is estimated based on the electronic density of states and calculated using Fermi-Dirac statistics for metallic systems [28]. Lattice vibrations are modeled with the Debye-Grüneisen model with the benefit of both accuracy and efficiency; the relevant equations have been described in detail in previous publications [30-31]. In order to predict A2 solution mixing, calculations of the enthalpy of mixing based on special quasirandom structures calculations (SQS) [32]. Radial distribution functions (RDF) of relaxed supercells are compared with the ideal bcc structure after each relaxation step [33]. The Vienna ab-initio Simulation Package (VASP) [34] is used for spin-polarized DFT calculations due to the
ferro- and antiferromagnetic natures of Co and Cr, respectively. Electron-ion interactions are described by the accurate projector augmented-wave (PAW) method [35-36]. The generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE) [37] is used to describe the electron exchange and correlation. Plane-wave cut-off energy of 400 eV is consistently used to ensure enough basis sets are included, as recommended by the VASP manual [38]. Reciprocal k-meshes used for fcc-Al/Co, hcp-Co, bcc-Al/Co/Cr, B2 and σ are 21×21×21, 23×23×12, 17×17×17, 15×15×15, and 6×6×11, respectively. The structures are relaxed by implementing the Methfessel-Paxton method [39] to minimize the forces acting on the atoms. After relaxations, a final calculation using the tetrahedron with Blöchl corrections [40] is applied to ensure an accurate total energy calculation.

The phase relations and thermodynamic properties of the condensed Ni-Mn-In, Al-Co-Cr, Zr-Ni-Sn ternary alloy system using first-principles calculations were investigated by [41, 44, 45], based on density functional theory (DFT). First-principles special quasirandom structures (SQS) calculations predict a large bcc-A2 (disordered)/B2 (ordered) miscibility gap, in agreement with experiments by Xuan L. Liu et al. [44]. A partitioning model is then used for the A2/B2 phase to effectively describe the order-disorder transitions. P. Sauerschnig et al. [45] was considered thermodynamic data in the ternary system only available in the literature for ZrNiSn to observed enthalpy of formation. DFT calculations also provide details on electronic properties and bonding. The phase relations and thermodynamic properties of the Al–Co–Cr, Al–Co–Ni, Co–Cr–Ni ternary alloys using first principles calculations based on DFT (density functional theory). A2/B2 transitions are also shown to agree well with previous experimental findings in the Al–Co–Cr ternary system. To facilitate reading, the symbols used to denote the phases in the Ni-Sn-Zn system are listed in Table 1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Prototype</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>Phase description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ni)</td>
<td>Cu</td>
<td>cF4</td>
<td>Fm3m</td>
<td>SS based on fcc_A1Ni</td>
</tr>
<tr>
<td>(βSn)</td>
<td>αSn</td>
<td>tI4</td>
<td>I4/amd</td>
<td>A5</td>
</tr>
</tbody>
</table>
The first-principles refer to the calculations originating from "first-principles", meaning that the inputs were the atomic coordinates and atomic numbers. The first-principles method computes the interactions between atoms in a periodic supercell. This is determined using quantum mechanical electronic theory that is based on the electronic charge density and does not rely on any empirical data. This section provides a description of the DFT methodology. The Helmholtz energy, $F(V,T)$, of a shortened phase, in terms of the quasiharmonic tactic, from first-principles calculations based on DFT is expressed as follows [32,33]:

$$F(V,T) = E_{0K}(V) + F_{Vib}(V,T) + F_{T-el}(V,T)$$

$F_{Vib}(V,T)$ and $F_{T-el}(V,T)$ symbolize the temperature-dependent vibrational and thermal-electronic contributions in the above expression, respectively. In the present work, the Helmholtz energy is taken approximately as the Gibbs energy due to the negligible ambient pressure used in the modeling. The thermal electronic contribution to the Helmholtz energy is estimated based on the electronic density of states and commutated using Fermi-Dirac statistics for metallic systems [28]. $E_{0K}(V)$ is the static contribution at 0 K without the zero-point vibrational energy.
In order to fit the first-principles calculated E-V (energy-volume) data points, the four-parameter Birch-Murnaghan equation of state with its linear form [49] is employed,

\[ E(V) = A + BV^{-\frac{2}{3}} + CV^{-\frac{4}{3}} + DV^{-2} \]  

(3.1)

where A, B, C and D are fitting parameters. In the present work, the EOS calculations are adopted to get more accurate ground state energy of the corresponding pure elements and compounds than only a single relaxation in the first-principles calculations and 8 data points in the volume range of 0.99-1.15 V₀ are used for the EOS fitting of each structure.

The enthalpy of formation of Niₓ.Snᵧ.Zn_z compound is defined as follows:

\[ \Delta_f E(Ni_xSn_yZn_z) = E(Ni_xSn_yZn_y) - \frac{x}{x+y+z} E(Ni) - \frac{y}{x+y+z} E(Sn) - \frac{z}{x+y+z} E(Zn) \]  

(3.2)

where E (Niₓ.Snᵧ.Zn_z), E (Ni), E (Si), and E (Ti) are equilibrium energies of the compound, Niₓ.Snᵧ.Zn_z, and the pure elements Ni, Sn and Zn in their standard reference structures, respectively, which are acquired by Eq. (3.1). The magnetic contribution from Ni atoms is well-thought-out in the present calculations. Since the calculations are performed at 0 K and 0 Pa, the energy of formation is taken to be the enthalpy of formation.

4. Thermodynamic model

As well as the CALculation of PHAse Diagrams (CALPHAD) method attempted an extrapolation from binary thermodynamic data to obtain Gibbs energy values for ternary liquid alloys [17, 43-49]. Various groups of authors reported partial ternary phase diagrams, especially isothermal sections at different temperatures.

Description of the ternary liquid phase (Gibbs excess energy dependence on the temperature and the composition) was achieved using the available thermodynamic data of the constitutive binary systems (Ni–Zn, Sn–Zn, Sn–Ni). Good agreement of the present assessment with thermodynamically optimized values of the system Sn–Ni–Zn (obtained by the CAL-PHAD approach) was observed by V. Gandova et
al. [43, 45, 48-51]. The calculated isothermal sections at 1000, 1200 and 1350 °C are in good agreement with the experimental data Yang Shu-Yu et al. [45]. The phase equilibria observed experimentally in the isothermal section at 950°C as well as the relevant homogeneity regions of the binary and ternary phases. The invariant three- and four-phase equilibria were involving the liquid show satisfactory agreement between experiment and calculation by P. Sauerschnig et al. [50]. A small number of the reactions show larger differences that will require more parameters for the description of the liquid and solid phase. The Al–Cu–Ni, Cu–Cr–Ni and Cu–Cr–Ag, Al–Co–Mn, Ni–Co–Cr ternary system were validated by comparing various calculations such as invariant reaction equilibria, thermochemical properties, isothermal and isoplethal sections with all available experimental data [53-56]. A vital subsystem of many high entropy alloys (HEAs), which can probably be attributed to the existence of stable ordered and disordered FCC and BCC structures Wei Wanga et al. [53]. The substitutional solution model was used to describe the solution phases. A set of self-consistent thermodynamic parameters of the Cu–Cr–Ni and Cu–Cr–Ag systems was obtained by Chengliang Qiu et al. [54]. Most of the reliable experimental data can be well reproduced by the present thermodynamic modeling. In the modelling, experimental data such as liquidus, solidus, tie lines, and phase boundaries are included. An order–disorder model is used to describe the bcc and B2 phases, showed a good agreement between the present results and experiments Mehdi Noori et al. [55]. In the assessments of the Ni–Co–Cr ternary system and sub-binary systems by the CALPHAD method by Ning Zhao et al. [56], and were well reproduced by the present thermodynamic database. The calculated and experimental diffusion coefficients reach a satisfactory agreement.

The SGTE (Scientific Group Thermodata Europe) database which is compiled by Dinsdale [47], are used the Gibbs energy functions for the elements Ni, Sn and Zn in present modeling. The substitutional solution model is labeled the solution phases, i.e. liquid, fcc_A1 and bcc_A2. The excess Gibbs energy of the solution phases is defined by the Redlich-Kister-Muggianu polynomial [48]. In observation of the experimentally pragmatic negligible homogeneity ranges of the ternary compounds (τ₁
to \( r_3 \) [16, 23], these phases are treated as stoichiometric compounds. For \( Ni_3Sn \) and \( NiZn \) phases, the sublattice models are used,

\[
\Delta G^{ASL}_m (y^{\text{S}}_i) = \sum_{i=Ni}^{3} \sum_{j=Sn}^{2} \sum_{k=Sn}^{Ni} \sum_{l=Sn}^{Ni} \sum_{j=Sn}^{1} \sum_{k=Sn}^{(2)} \sum_{l=Sn}^{(3)} \sum_{j=Sn}^{(4)} \sum_{k=Sn}^{4} \sum_{l=Sn}^{4} \left[ \frac{RT}{4} \sum_{i=Ni}^{Ni} y^{\text{S}}_i \ln(y^{\text{S}}_i) \right] + y^{\text{S}}_N i y^{\text{S}}_S n \left[ \frac{\eta^{(L)}_{Ni,Sn}}{y^{\text{S}}_Ni} + (y^{\text{S}}_Ni - y^{\text{S}}_Sn) \eta^{(L)}_{Ni,Sn} \right] + y^{\text{S}}_N i y^{\text{S}}_Zn \left[ \frac{\eta^{(L)}_{Ni,Zn}}{y^{\text{S}}_Ni} + (y^{\text{S}}_Ni - y^{\text{S}}_Zn) \eta^{(L)}_{Ni,Zn} \right] + y^{\text{S}}_Zn y^{\text{S}}_Sn \left[ \frac{\eta^{(L)}_{Zn,Sn}}{y^{\text{S}}_Zn} + (y^{\text{S}}_Zn - y^{\text{S}}_Sn) \eta^{(L)}_{Zn,Sn} \right] + \sum_{s=1}^{4} \sum_{v=1}^{4} y^{\text{S}}_{Ni} y^{\text{S}}_{Sn} y^{\text{S}}_{Ni} y^{\text{S}}_{Sn} * L_{Ni,Sn} + \sum_{s=1}^{4} \sum_{v=1}^{4} y^{\text{S}}_{Zn} y^{\text{S}}_{Sn} y^{\text{S}}_{Zn} y^{\text{S}}_{Sn} * L_{Zn,Sn} \tag{3.4}
\]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Prototype</th>
<th>Space group</th>
<th>Phase description</th>
<th>Modeling [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ni_3Sn-HT )</td>
<td>BiF3</td>
<td>Fm( \overline{3} )m</td>
<td>( D\overline{0}_3 )</td>
<td>( (Ni,Sn)<em>{0.25(Ni,Sn)</em>{0.25}(Ni)_{0.5}} )</td>
</tr>
<tr>
<td>( Ni_3Sn-LT )</td>
<td>( Ni_3Sn )</td>
<td>P6(/mmc )</td>
<td>( D\overline{0}_1 )</td>
<td>( (Ni,Sn)<em>{0.75(Sn)</em>{0.25}} )</td>
</tr>
<tr>
<td>( Ni_3Sn_2-HT )</td>
<td>( InNi_2 )</td>
<td>P6(/mmc )</td>
<td>( B\overline{8}_2 )</td>
<td>( (Ni)<em>{0.33(Ni,Sn)</em>{0.33(Sn)}_{0.33}} )</td>
</tr>
<tr>
<td>( Ni_3Sn_2-LT )</td>
<td>( Ni_3Sn_2 )</td>
<td>( Pnma )</td>
<td>( Sn)<em>{0.25(Ni,Sn)</em>{0.25}(Ni)_{0.4}} )</td>
<td></td>
</tr>
<tr>
<td>( Ni_3Sn_4 )</td>
<td>C2/m</td>
<td>( C\overline{2}m )</td>
<td></td>
<td>( (Ni,Sn)<em>{0.25(Ni,Sn)</em>{0.25(Sn)_{0.5}}} )</td>
</tr>
<tr>
<td>( NiZn-HT )</td>
<td>( CsCl )</td>
<td>Pm3m</td>
<td>( B2 )</td>
<td>( (Ni,Zn)<em>{1}^{(Va,Zn)</em>{1}} )</td>
</tr>
<tr>
<td>( NiZn-LT )</td>
<td>( AuCu )</td>
<td>P4(/mmm )</td>
<td>( L\overline{1}_0 )</td>
<td>( (Ni,Zn)<em>{1}^{(Va,Zn)</em>{1}} )</td>
</tr>
<tr>
<td>( NiZn_{14} )</td>
<td>( Cu_{3}Zn_{8} )</td>
<td>I( \overline{4} )m</td>
<td>( D\overline{8}_2 )</td>
<td>( (Ni)<em>{1}^{(Zn)</em>{1}} )</td>
</tr>
<tr>
<td>( NiZn_{8} )</td>
<td>( CoZn_{13} )</td>
<td>P6(/mmc )</td>
<td></td>
<td>( (Ni, Va)<em>{1}^{(Ni,Zn)</em>{22(Ni)<em>{4}(Zn)</em>{22}}} )</td>
</tr>
</tbody>
</table>

Table 2 List of the modeling to calculate the Gibbs energies in the phases in the Ni-Sn-Zn system.

In order to represent the Gibbs energies of both ordered \( B_2 \) and disordered \( bcc_A \) phases using a single function, the ternary \( bcc_A \) is described by a model \( (Ni,Sn,Zn,Va)_{1}^{Va}Va_{3} \). In conflicting to the prior modeling work in Table 2 is use in the present work. The ordered \( Ni_3Sn \) phase with \( L1_2 \) structure is designated using a four-sublattice model \( (Ni,Sn,Zn)_{0.25(Ni,Sn,Zn)_{0.25}(Ni,Sn,Zn)_{0.25}(Ni,Sn,Zn)_{0.25}} \). In directive to represent the Gibbs energies of both ordered \( L1_2 \) phase and disordered \( fcc_A \) structure using a single function, \( fcc_A \) is described by a model \( (Ni,Sn,Ti)_{1}^{Va}Va_{1} \). The ordered and disordered states of \( fcc \) phase are usually described using a single formula:

\[
G^{ASL}_m = G^{\text{dis}}_m (x_i) + G^{ASL}_m (y^{\text{S}}_i) - G^{ASL}_m (y^{\text{S}}_i = x_i) \tag{3.5}
\]

Where \( G^{\text{dis}}_m \) represents the Gibbs energy of the disordered fcc phase. \( G^{ASL}_m (y^{\text{S}}_i) - G^{ASL}_m (y^{\text{S}}_i = x_i) \) denotes the Gibbs energy impact from the ordered phase. This differential is identical to zero when the
disordered state is stable. Hence, Eq. (3.5) can represent both the ordered and disordered states of fcc phase.

Trendy interpretation of the crystallographic equivalence of the four sublattices, the thermodynamic properties of every lattice are equal. Further assuming that the interaction parameters within one sublattice are independent to elements in other sublattices, the \( G_m^{SL}(y_i^a) \) in Eq. (3.5) is represented as follows:

\[
\Delta G_{Ni:Ni:Sn:Ni} = \Delta G_{Ni:Sn:Ni:Ni} = \Delta G_{Sn:Ni:Ni:Ni} = \Delta G_{Ni:Sn:Sn:Ni} \quad (3.6)
\]

\[
\]

\[
\]

\[
\Delta G_{Ni:Ni:Zn:Ni} = \Delta G_{Ni:Zn:Ni:Ni} = \Delta G_{Zn:Ni:Ni:Ni} = \Delta G_{Ni:Zn:Ni:Zn} \quad (3.9)
\]

\[
\]

\[
\Delta G_{Zn:Zn:Ni:Ni} = \Delta G_{Zn:Zn:Ni:Zn} = \Delta G_{Zn:Ni:Ni:Zn} = \Delta G_{Ni:Zn:Ni:Zn} = \Delta G_{Ni:Zn:Zn:Zn} = \Delta G_{Ni:Zn:Zn:Zn} \quad (4.1)
\]

\[
\Delta G_{Zn:Zn:Zn:Ni} = \Delta G_{Zn:Zn:Zn:Ni} = \Delta G_{Zn:Zn:Zn:Zn} = \Delta G_{Zn:Zn:Zn:Zn} = \Delta G_{Zn:Zn:Zn:Zn} \quad (4.2)
\]

\[
\Delta G_{Zn:Zn:Sn:Sn} = \Delta G_{Zn:Sn:Zn:Zn} = \Delta G_{Zn:Sn:Zn:Zn} = \Delta G_{Zn:Sn:Zn:Zn} = \Delta G_{Zn:Sn:Zn:Zn} \quad (4.3)
\]

\[
\]

when \( y_i^{(1)} = y_i^{(2)} = y_i^{(3)} \neq y_i^{(4)} \), four sublattice model describe L1_2 structure. When \( y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)} \), it represents the L1_0 structure.

Similarly, the interaction parameters are exposed to the ensuing equations:

\[
^0L_{Ni:Sn:V:V} = ^0L_{V:V:Ni:Sn} = ^0L_{V:V:Ni:Sn} = ^0L_{Ni:Sn} \quad (4.5)
\]

\[
^1L_{Ni:Sn:V:V} = ^1L_{V:V:Ni:Sn} = ^1L_{V:V:Ni:Sn} = ^1L_{Ni:Sn} \quad (4.6)
\]

\[
^0L_{Ni:Zn:V:V} = ^0L_{V:V:Ni:Zn} = ^0L_{V:V:Ni:Zn} = ^0L_{Ni:Zn} \quad (4.7)
\]

\[
^1L_{Ni:Zn:V:V} = ^1L_{V:V:Ni:Zn} = ^1L_{V:V:Ni:Zn} = ^1L_{Ni:Zn} \quad (4.8)
\]

\[
^0L_{Zn:Sn:V:V} = ^0L_{V:V:Zn:Sn} = ^0L_{V:V:Zn:Sn} = ^0L_{Zn:Sn} \quad (4.9)
\]

\[
^1L_{Zn:Sn:V:V} = ^1L_{V:V:Zn:Sn} = ^1L_{V:V:Zn:Sn} = ^1L_{Zn:Sn} \quad (4.10)
\]
The character “V” in a sublattice means that the parameter is independent of the occupation of that sublattice.

5. Results and discussions

All phases occurring in Ni-Sn-Zn hitherto described in literature are summarized in Table 1. Accordingly, the phase relationships of the Ni-Sn-Zn system were deduced for three isothermal sections at 700, 800 and 900 °C; the sections were constructed based on EPMA and XRD results and are shown in Figs. 1-3, respectively. In the diagrams, single-phase regions are shaded and three-phase fields are designated with roman numbers for which the legends can be found in Table 3. Tie lines evaluated by EPMA are indicated by solid lines whereas tie-lines deduced from XRD results only are indicated with dashed lines. DTA measurements served for the rough estimation of liquidus phase boundaries; the respective results are given in Table 4. Six ternary solid solutions were found along with the Ni(Sn, Zn) solid solution. Additionally, two new ternary compounds, designated as τ₂ and τ₃ have been included. In order to construct the full isothermal section at 700 °C, eight three-phase fields could be exactly determined by EPMA and two three-phase fields were estimated from XRD analyses only. The extension of the two-phase field between NiZn-LT and NiZn-HT from Ni-Zn into the ternary system is only estimated from other phase relations such as \([\text{Ni}_3\text{Sn-LT} + \text{Ni}_3\text{Sn}_2\text{-HT} + \text{NiZn-LT}]\) and \([\text{Ni}_3\text{Sn}_2\text{-HT+ τ₂} + \text{NiZn-HT}]\). There is no direct experimental evidence because a sample placed at Ni₅₀Sn₅₀Zn₄₅ did not show two-phases, neither in XRD nor in EPMA. However, NiZn-HT can undergo a martensitic transformation to the LT-modification [14] during quenching and the contrast in an SEM-BSE image is expected to be very low. Also the three-phase field \([\text{Ni}_3\text{Sn}_2\text{-HT} + \text{NiZn-HT} + \text{NiZn-LT}]\) is a rough estimate along with the consideration of other phase relations.
Our most important result, however, is the discovery of two new ternary compounds in the ternary Ni-Sn-Zn system. The first one, designated τ₂, was observed at 700 °C within composition ranges given by Ni₄₄Sn₃₇₋₄₄Zn₉₋₁₄. We decided to designate it shortly as Ni₅Sn₄Zn. There are also structural similarities between the τ₂ phase and the neighboring Ni₃Sn₂-HT solid solution although there is no direct structure/superstructure relation [15]. The second ternary compound found was designated τ₃ or Ni₇Sn₉Zn₅. The homogeneity range at 700 °C can be given as Ni₃₅₋₃₈Sn₃₅₋₄₃Zn₂₃₋₂₇.

Fig. 4.1. Isothermal sections in the Sn-Ni-Zn ternary system (less than 60 at.% Ni) from this study: (a) 800 °C, (b) 500 °C, and (c) 200 °C. [16]

4.2 First-principles results
Stable phase Ni₃Sn, Ni₃Sn₄, Ni₃Sn₂, Ni₄Sn₃, Ni₂Zn₁₁, Ni₁₆Zn₅₃, and Ni-Zn are shown in Fig, which is obtained by using by DFT software package material project.; another phrase such as τ₁ to τ₆ also finds out to set the composition of Ni, Sn, and Zn in DFT calculation, here in Fig red point show the τ₁ (Ni-Sn-Zn).

Fig. 4.2 Use DFT calculations to generate compositional phases, red point τ₃ phase and grand potential phase diagrams

This includes elastic stiffness constants (Cij), volume/atom (V₀), bulk modulus (B₀), and Poisson’s ratio (Voigt–Reuss–Hill effective medium). These results are crucial properties necessary for accurate finite temperature predictions. End-members Ni₃Sn-HT, Ni₃Sn-LT, Ni₃Sn₄, Ni₃Sn, NiZn-HT and NiZn-LT are the only stable end-members results for these are included in Table 2. The stable ternary solid solutions Ni₃Sn-LT, Ni₃Sn₂-HT, Ni₃Sn₄, NiZn-LT, NiZn-HT, Ni₂Zn₁₄ and Ni(Sn, Zn) are in good agreement with the constituent binary systems Ni-Sn [4] and Ni-Zn [2]. The Ni(Sn, Zn) solid solution is much wider along the Ni-Zn side than along Ni-Sn side. Considering the much closer chemical relationship of Ni and Zn compared to Ni and Sn this is not astonishing. All binary phases show a significant ternary solubility. While the monoclinic phase Ni₃Sn₄ dissolves a rather low amount of Zn (1-2 at%), the solubility of Sn in both, NiZn-LT and NiZn-HT, is noticeably high (up to 22 at% Sn). It is noteworthy that NiZn-HT containing dissolved Sn can be stabilized at lower temperatures by quenching. This is not possible with the pure binary phase NiZn-HT as reported by Murakami et al. [14].
Clemens Schmetterer [18] were found along with the solid solution Ni(Sn, Zn) of six ternary solid solutions. Additionally, two new ternary compounds, designated as $\tau_2$ and $\tau_3$ have been included. In order to construct the full isothermal section at 700 °C, eight three-phase fields could be exactly determined by EPMA and two three-phase fields were estimated from XRD analyses only.

**Table 4.2** Calculated DFT elastic stiffness constants and various properties of the end-members of Intermetallic compound.

<table>
<thead>
<tr>
<th>End-member</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$V_0$(Å³/atom)</th>
<th>$B_0$ (GPa)</th>
<th>$G_0$ (GPa)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Sn-HT</td>
<td>233</td>
<td>128</td>
<td>97</td>
<td>103.37</td>
<td>163</td>
<td>72</td>
<td>0.30</td>
</tr>
<tr>
<td>Ni$_3$Sn-LT</td>
<td>261</td>
<td>113</td>
<td>50</td>
<td>51.659</td>
<td>164</td>
<td>66</td>
<td>0.32</td>
</tr>
<tr>
<td>Ni$_3$Sn$_2$-HT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni$_3$Sn$_2$-LT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni$_3$Sn$_4$</td>
<td>150</td>
<td>69</td>
<td>54</td>
<td>127.85</td>
<td>98</td>
<td>47</td>
<td>0.29</td>
</tr>
<tr>
<td>Ni$_3$Sn</td>
<td>149</td>
<td>170</td>
<td>98</td>
<td>51.94</td>
<td>163</td>
<td>11</td>
<td>0.47</td>
</tr>
<tr>
<td>NiZn-HT</td>
<td>222</td>
<td>84</td>
<td>106</td>
<td>24.04</td>
<td>146</td>
<td>63</td>
<td>0.31</td>
</tr>
<tr>
<td>NiZn-LT</td>
<td>51</td>
<td>69</td>
<td>-19</td>
<td>38.2</td>
<td>63</td>
<td>-14</td>
<td>0.62</td>
</tr>
<tr>
<td>Ni$<em>2$Zn$</em>{14}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NiZn$_8$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
It can be seen that in cases the present calculated DFT predicted results coordinate well with experimental results.

4.3 CALPHAD modeling results

Figs. 3 to 6 show the calculated isothermal sections at 800, 700, 500 and 200 °C along with the experimental data [16, 18], respectively. As can be seen from these figures, most of experimental phase diagram data are accounted for by the present modeling.
Fig. 4.3 Calculated Ni-Sn-Zn isothermal sections (solid lines) at 800°C (a), 700°C (b), 500°C (c), and 200°C (d). Experimental phase equilibrium data by Chang J et al. [16]

As seen in Fig. 4.3(a) through (d), the 800, 700, 500 and 200°C isotherms remain nearly identical to experimental work.

Table 4 shows the first-principles calculated the enthalpies of formation for the ternary compounds along with literature data Yu. Plevachuk [24] and the calculated enthalpies of formation of the ones for the end-members of NiSn and NiZn phases, $\tau_1$, $\tau_2$ and $\tau_3$ are present via the first-principles calculations and compared with the CALPHAD approach. Hence, the calculated enthalpy of formation of the present work is considered to be reasonable.

**Table 4.3** Computed enthalpy of formation for the ternary compounds along with literature data [9] and the end-members of the NiSn and NiZn phases in the Ni-Sn-Zn system.

<table>
<thead>
<tr>
<th>Phase/end-member</th>
<th>First-principles calculations, 0 K</th>
<th>CALPHAD, 298.15 K</th>
<th>MIEDEMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (Ni-Sn-Zn)</td>
<td>-19.65</td>
<td>-20.63</td>
<td>-18.14</td>
</tr>
<tr>
<td>$\tau_2$ (Ni$_3$Sn$_2$Zn)</td>
<td>-22.87</td>
<td>-23.87</td>
<td>-21.62</td>
</tr>
<tr>
<td>$\tau_3$ (Ni$_7$Sn$_9$Zn$_5$)</td>
<td>-18.90</td>
<td>-20.09</td>
<td>-17.38</td>
</tr>
</tbody>
</table>
The first principles computed enthalpies of formation for the four end-members, in which NiZn$_8$ and Ni$_3$Sn$_2$ show minimum (-6.25 kJ/mol-atoms) and maximum (23.19 kJ/mol-atoms) energies, respectively. However, the end-member of Ni$_3$Sn$_2$-HT, which is supposed to possess the largest enthalpy of formation since all the sites are occupied by anti-atoms, shows an unexpected intermediate value (-23.19 kJ/mol-atoms). Therefore, the hypothesis that the enthalpy of formation of the end-member is the largest if all its sites are occupied by anti-atoms may not be true according the present first-principles calculations. Again, these results demonstrate that first-principles calculation is an effective and powerful technique to provide necessary thermodynamic information for valid CALPHAD assessment, especially when the experimental data are unavailable. As a consequence, with the help of first-principles calculations, the obtained thermodynamic parameters in the present work are more physically meaningful.

**Conclusion**

All the phase diagram and thermodynamic data available in the literature over the last century for the Ni-Sn-Zn system are critically evaluated. Ten ternary compounds are stable in this ternary system. The stability and melting behavior of the Ni$_3$Sn$_2$-HT ordered phase are clarified. The enthalpies of formation for the ternary compounds ($\tau_1$, $\tau_2$ and $\tau_3$) and end-members of Ni$_3$Sn$_4$ and Ni$_3$Zn$_{14}$ at 0 K in the Ni-Sn-Zn ternary system are computed via first-principles calculations to provide necessary thermodynamic data for the present modeling in order to improve the physical meaning of the optimized parameters.
A thermodynamic modeling of the Ni-Sn-Zn system over the entire arrangement and temperature ranges is approved out based on the experimental data from the literature and the present first-principles calculations. An optimal set of thermodynamic parameters for the Ni-Sn-Zn system is obtained. Obvious enhancements have been ended, in comparison with the previous modeling.

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