A NEW THERMODYNAMIC DESCRIPTION OF THE BINARY Sb – Zn SYSTEM

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Abstract

The Sb – Zn alloys are important from technological point of view. Antimony – zinc alloys are not only part of lead-free solders but also thermoelectric materials. A good thermodynamic description of this system is essential for further investigations of multi-components materials that include Sb and Zn. A new assessment was proposed in this work based on recently published experimental reports. Good agreement between calculations and experiments was found. Moreover, two models were used for describing the liquid phase: substitutional solution and associated solution.

Keywords: CALPHAD; lead-free solder; thermoelectric materials;

1. Introduction

The Sb – Zn alloys are in a big interest of material science community. Antimony and zinc are components very often used in lead-free soldering technology and the ternary Sb – Sn – Zn system was proposed as a lead-free solder material [1]. Moreover, the intermetallic compounds (IMCs) that can be found in the binary antimony – zinc system show thermoelectric properties. It is worth to mention, that Sb – Zn alloys were reported in the original Seebeck’s work on thermoelectricity [2]. Furthermore, in 1997 Caillat et al. [3] reported very high figure of merit for the Sb,Zn₄. It is obvious, that the knowledge of phase relationship as well as thermodynamic description will play a key-role in the future works on Me – Sb – Zn thermoelectric materials. Available descriptions of the Sb – Zn system show some conflicts about temperatures and kinds of phase transformations.

2. Literature review


The liquidus line of the binary Sb – Zn system was described by Monkmeyer [25], Zemczuzny [26], Curry [27], Gosselin [28] and Heycock and Neville [29] who used differential thermal analysis (DTA) technique. Liu et al. [30] reported a part of liquidus line determined by DSC measurement. Izard et al.
[31] described liquidus line and temperatures of phase transformations. They also discussed stability of intermediate phases with the aid of XRD experiment. Adjadj et al. [5] used the DSC technique for liquidus and phase transformation temperatures investigation. Takei [32] used resistometric as well as DTA measurement techniques to describe a liquidus line. The intermediate cooling, towards 633 K in agreement with reaction 3 order-disorder transformation of Sb3Zn4 was omitted. Besides that, in Zabdyr [36] work the strange shape of mixing enthalpy at low (843 K) temperature. The first description reproduced liquid phase: substitutional solution and associated liquid. The thermodynamic functions are taken from SGTE Unary (Pure elements) TDB v5.0 [39]. The Gibbs energies of pure elements with respect to temperature $G_{i}^{0}(T)=G_{i}^{0}(298.15\text{ K})+H_{i}^{0}(T)-T \Delta_{f}^{0}H_{i}(T)$ are represented by Equation 1:

$$G_{i}^{0}(T)=a+bT+cT \ln(T)+dT^{2}+eT^{3}+fT^{4}+iT^{5}+jT^{6}+kT^{7}+lT^{8}$$

The $G_{i}^{0}(T)$ data are referred to the constant enthalpy value of the standard element reference $H_{i}^{0}(298.15\text{ K})$ at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [39]. The reference states are Rhombohedral_A7 (Sb) and HCP_ZN (Zn). The $G_{i}^{0}(T)$ expression is given for several temperature ranges, where the coefficients a, b, c, d, e, f, i, j, k have different values. The $G_{i}^{0}(T)$ functions are taken from SGTE Unary (Pure elements) TDB v5.0 [39].

The solid Sb and Zn were treated as pure components because neither there is information about solubility of Sb in solid zinc nor about solubility of Zn in solid antimony. In this case, the Gibbs energies of Sb and Zn were directly taken from the SGTE Unary database [39].

3. Thermodynamic models

This modeling of the binary Sb-Zn system includes 8 phases: Rhombohedral_A7 (Sb), HCP_ZN (Zn), Sb,Zn,(β), Sb,Zn,(γ), Sb,Zn,(γ'), Sb,Zn,(ζ), Sb,Zn,(η) and liquid. The description of the crystal structures is given in Table 1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>Strukturbericht designation</th>
<th>Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>hP2</td>
<td>P6 3/mmc</td>
<td>A3</td>
<td>Mg</td>
</tr>
<tr>
<td>Sb,Zn,(β)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb,Zn,(γ)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb,Zn,(γ')</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb,Zn,(ζ)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb,Zn,(η)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb2Zn3(η)</td>
<td>oP32</td>
<td>Pmmm</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb2Zn3(ζ)</td>
<td>oI</td>
<td>Pmmm</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb2Zn3(η)</td>
<td>oP16</td>
<td>Pbc</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Sb2Zn3(β)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

The Gibbs energies of pure elements with respect to temperature $G_{i}^{0}(T)=G_{i}^{0}(298.15\text{ K})+H_{i}^{0}(T)$ are represented by Equation 1:

$$G_{i}^{0}(T)=a+bT+cT \ln(T)+dT^{2}+eT^{3}+fT^{4}+iT^{5}+jT^{6}+kT^{7}+lT^{8}$$

where

$$G_{Sb,\text{Zn}}^{0}=a+bT+i \cdot \text{GHSERSB}+j \cdot \text{GHSERZN}$$

Liquid phase was described by the substitional
solution model [40]:

\[ G_a(T) = \sum_i x_i G_i(T) + RT \sum_i x_i \ln(x_i) + + \sum_{i<j} x_i x_j \left( \sum_i L_i (x_i - x_i^a) \right) \]  

(3)

where the \( \sum_{i<j} x_i x_j \left( \sum_i L_i (x_i - x_i^a) \right) \) part is the Redlich-Kister polynomial for excess Gibbs free energy.

### 3.2 Associated solution

The liquid phase was also described by associated solution model [41]. The liquid associate was supposed to be \( \text{Sb}_3\text{Zn}_4 \). The Gibbs energy of one mole liquid is given by equation (4):

\[ G_a(T) = \sum_i y_i G_i(T) + RT \sum_i y_i \ln(y_i) + \sum_{i<j} y_i y_j L_{ij}(y_i - y_j) \]

where \( y_i \) denotes a site fraction, \( i, j \) denote constituents of the liquid phase: Sb, Zn and liquid associate \( \text{Sb}_3\text{Zn}_4 \).

### 3.3 Optimization procedure

The thermodynamic parameters for all phases in the system were optimized using ThermoCalc software [42]. For this optimization, thermodynamic data for the liquid phase, invariant reactions and phase equilibrium data were used. To each piece of the selected information was given a certain weight based on experiment accuracy. The optimization was carried out step by step in agreement with Schmid-Fetzer’s et al. [43] guideline. First, the optimization of the liquid phase was performed, and then the solid phases were assessed. All parameters were finally evaluated together to provide the best description of the system. The calculated interaction parameters are shown in Table 2. For checking the results of optimization, the system was also calculated using Pandat [44] software. The last step of modeling was to change a description of the liquid model. During this step description of solid phases was kept unchanged. After optimization the results were checked again in Pandat [44] software.

### 4. Results and discussion

Figure 1 shows calculated phase diagram of the binary Sb – Zn system superimposed with experimental data given by Adjadj et al. [5], Liu et al. [31] and Takei [33]. The calculated liquidus line agrees well with experimental data.

It can be seen, that data given by Liu et al. [31] and Takei [33] shows discrepancy at the composition range 0.6 – 0.8 mole fraction of Zinc; however, the calculated line is located between these 2 datasets. Zoomed part of the phase diagram for composition range from 0.45 to 0.65 mole fraction of zinc is shown in Figure 2 together with DSC data obtained by Adjadj et al. [5]. One can see, that all the phase transformation temperatures agree well with Adjadj et al. [5] data. Calculated order-disorder transformation occurs 2 degree lower than it was revealed by experiment.

### Table 2. Calculated interaction parameters.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SbZn} )</td>
<td>( ^G G = -21827.976 + 7.9927 \times \text{GHSERSB} + \text{GHSERZN} )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\beta) )</td>
<td>( ^G G = -81723.458 + 32.2801 \times \text{GHSERSB} + 4 \times \text{GHSERZN} )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\gamma) )</td>
<td>( ^G G = -361793.319 - 236.8462 \times \text{GHSERSB} + 39 \times \text{GHSERZN} )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\gamma') )</td>
<td>( ^G G = -397804.613 - 1.1087 \times \text{GHSERSB} + 31 \times \text{GHSERZN} )</td>
</tr>
<tr>
<td>( \text{Sb}_2\text{Zn}_3(\zeta) )</td>
<td>( ^G G = -37109.540 - 3.6646 \times \text{GHSERSB} + 3 \times \text{GHSERZN} )</td>
</tr>
<tr>
<td>( \text{Sb}_2\text{Zn}_3(\eta) )</td>
<td>( ^G G = -361793.319 - 236.8462 \times \text{GHSERSB} + 39 \times \text{GHSERZN} )</td>
</tr>
<tr>
<td>( \text{Liquid substitional} )</td>
<td>( ^L L = -47736.194 + 32.5303 \times \text{T} + 42.2936 \times \text{TnT} )</td>
</tr>
<tr>
<td>( \text{SbZn} )</td>
<td>( ^L L = -37454.769 + 32.5303 \times \text{T} - 42.2936 \times \text{TnT} )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\beta) )</td>
<td>( ^L L = -393.624 )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\gamma) )</td>
<td>( ^L L = -6050.661 )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\gamma') )</td>
<td>( ^L L = -393.624 )</td>
</tr>
<tr>
<td>( \text{Sb}_2\text{Zn}_3(\zeta) )</td>
<td>( ^L L = -208903.328 + 2503.5852 \times \text{T} + 441.8588 \times \text{TnT} )</td>
</tr>
<tr>
<td>( \text{Sb}_2\text{Zn}_3(\eta) )</td>
<td>( ^L L = 216478.405 - 1917.5183 \times \text{T} - 289.6028 \times \text{TnT} )</td>
</tr>
<tr>
<td>( \text{Liquid associated} )</td>
<td>( ^L L = -46464.4274 - 114.7774 \times \text{T} )</td>
</tr>
<tr>
<td>( \text{SbZn} )</td>
<td>( ^L L = 192.800.132 + 166.0501 \times \text{T} - 85.5694 \times \text{TnT} )</td>
</tr>
<tr>
<td>( \text{Sb}_3\text{Zn}_4(\beta) )</td>
<td>( ^L L = -293498.096 + 3.3584 \times \text{T} + 36.0324 \times \text{TnT} )</td>
</tr>
</tbody>
</table>
Table 3 shows detailed comparison of calculated invariant reactions with experimental data. The Gibbs energies of formation of IMCs obtained from EMF experiment were taken into account for this optimization. Generally speaking, calculated Gibbs energies of formation show quite good agreement with experimental data, except results for Sb\_3Zn\_4(β) phase.

The comparison between calculated energies of formation and literature data is given in Table 4. Figure 3 shows calculated mixing enthalpy of liquid phase at 843 K and 913 K superimposed with data given by Scheil and Lukas [7] and Witting and Gehring [8]. The calculated functions reproduce experimental information well; only two points reported by Scheil and Lukas [7] exhibit significant deviation from calculation. In the same picture it is shown enthalpy of mixing calculated from previous optimization given by Li et al. [38]. It can be easily found out, that previously proposed description produces extra maximum of the function near composition 0.1 mole fraction of Zn.

The experimental information does not suggest this shape of a function and the additional extreme seems to be an artifact connected with proposed description. The same additional maximum on mixing enthalpy of liquid can be found in Liu’s et al. [31] proposition. Figure 4 shows calculated activity of Sb and Zn at 823 K superimposed with experimental data reported by Rubin and Komarek [6] and Hultgren [10]. The calculation shows very good agreement with experimental data.

The literature reveals, that atoms in the liquid phase tend to have short-range ordering (SRO) and
The existence of the associate was confirmed by Asanovich et al. [45] who used resistivity measurement, Sinha and Miller [46] by viscosity measurement and Matuyama [47] who determined density of a liquid phase. Considering presence of the SRO in a liquid phase, the associate solution model [40] was also applied for an assessment of the liquid phase in this work. During optimization of the liquid, Gibbs energies of solid phases were taken from the previous step (optimization with substitional solution model for liquid phase) and kept unchanged. As it can be seen from Table 2, number of parameters is the same as in the case of substitional solution. The results of calculation are shown in Figures 5 – 7. Figure 5 shows calculated Sb – Zn phase diagram superimposed with experimental data. The liquidus line is reproduced well. Also temperatures of phase transformation agree with experimental data given by Adjadj et al. [5]. Figure 6 shows calculated mixing enthalpy of liquid phase at 843 K and 913 K superimposed with data given by Scheil and Lukas [7] and Witting and Gehring [8]. It can be seen, that calculated function agree with experimental data well; however, for the Zn-rich compositions, the calculation exhibits slightly less exothermic values than experimental points at temperature 843K. Comparing calculated enthalpy of mixing to Zabdyr’s [37] result it can be seen that in [37] calculated enthalpy of mixing at 843K poses an additional extreme for compositions close to pure antimony. This artifact is identical with artifacts obtained by Liu et al. [31] and Li et al. [38] for substitional solution model. Calculated activity of antimony and zinc at 823 K together with experimental data is shown in Figure 7. The

Table 4. Gibbs energies of intermetallic compounds in the binary Sb – Zn system.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Gibbs energy T[K]</th>
<th>Reference state</th>
<th>Reference state</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbZn</td>
<td>-9236 420</td>
<td>Rhombohedral</td>
<td>HCP_ZN</td>
<td>This work</td>
</tr>
<tr>
<td>SbZn</td>
<td>-9700 420</td>
<td>Rhombohedral</td>
<td>HCP_ZN</td>
<td>[20]</td>
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<tr>
<td>SbZn</td>
<td>-8204 804</td>
<td>Liquid</td>
<td>Liquid</td>
<td>This work</td>
</tr>
<tr>
<td>SbZn</td>
<td>-8115 804</td>
<td>Liquid</td>
<td>Liquid</td>
<td>[12]</td>
</tr>
<tr>
<td>SbZn(γ)</td>
<td>-8018 826</td>
<td>Liquid</td>
<td>Liquid</td>
<td>This work</td>
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<tr>
<td>SbZn(γ)</td>
<td>-8032 826</td>
<td>Liquid</td>
<td>Liquid</td>
<td>[12]</td>
</tr>
<tr>
<td>SbZn(γ)</td>
<td>-8189 806</td>
<td>Liquid</td>
<td>Liquid</td>
<td>This work</td>
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<tr>
<td>SbZn(γ)</td>
<td>-7903 806</td>
<td>Liquid</td>
<td>Liquid</td>
<td>[12]</td>
</tr>
<tr>
<td>SbZn(γ)</td>
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<td>Rhombohedral</td>
<td>Liquid</td>
<td>This work</td>
</tr>
<tr>
<td>SbZn(γ)</td>
<td>-7126 800</td>
<td>Rhombohedral</td>
<td>Liquid</td>
<td>[19]</td>
</tr>
<tr>
<td>Sb,Zn(β)</td>
<td>-9767 420</td>
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<td>HCP_ZN</td>
<td>This work</td>
</tr>
<tr>
<td>Sb,Zn(β)</td>
<td>-8800 420</td>
<td>Rhombohedral</td>
<td>HCP_ZN</td>
<td>[20]</td>
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<tr>
<td>Sb,Zn(β)</td>
<td>-8922 600</td>
<td>Rhombohedral</td>
<td>HCP_ZN</td>
<td>This work</td>
</tr>
<tr>
<td>Sb,Zn(β)</td>
<td>-6990 600</td>
<td>Rhombohedral</td>
<td>HCP_ZN</td>
<td>[19]</td>
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<td>Sb,Zn(ζ)</td>
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<td>Rhombohedral</td>
<td>Liquid</td>
<td>This work</td>
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<tr>
<td>Sb,Zn(ζ)</td>
<td>-6916 800</td>
<td>Rhombohedral</td>
<td>Liquid</td>
<td>[19]</td>
</tr>
</tbody>
</table>
calculated function shows good agreement with experimental data. From the results discussed above one can see that both models (substitutional solution and associated solution) described liquid phase well. It can be also found out that even the associated solution model is more suitable from physical point of view, the number of parameters is not smaller than in a case of substitutional solution model application. The asymmetrical “S” shapes of liquid mixing enthalpy and activity functions need quite complicated mathematical description for fitting all the data. The associate solution model did not make description easier, what is in agreement with previous comparison of application both models done by Zabdyr [37]. Both models reproduced thermodynamic properties and liquidus line well; however, the associated solution model could be preferred as more realistic than substitutional solution.

5. Summary

The binary Sb – Zn system was remodeled according to recent phase equilibria data given by Adjadj et al. [5]. Substitutional and associated solution models were used for description of the liquid phase. Both of them reproduce experimental data well; however, the associated solution model could be preferred as more realistic. Modeled liquidus and solidus lines as well as solid phases equilibrium are in good agreement with experimental data.

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References
