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A theoretical investigation of integral mixing enthalpies in the ternary Ag–In–Zn alloys

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Abstract
The results of the calculation of integral enthalpies of mixing in liquid state for ternary Ag-In-Zn alloys using the general solution model of Chou are presented in this paper. Five selected sections with x_{In}/x_{Zn} = 1/1, 1/2, 2/1, 1/3 and 3/1 were investigated at 773K. The other traditional geometric models such as Kohler, Muggianu, Toop and Hillert are also included in calculations for comparison and discussion.

Keywords: Pb-free solders; Integral enthalpy of mixing; Geometric models; Ag-In-Zn ternary system.

1. Introduction
In accordance with the Directives of the European Parliament and of the Council on "waste electrical and electronic equipment" and on "restriction of use of certain hazardous substances", lead is banned from production of new electrical and electronic devices from 1 July 2006 [1]. The traditional lead-tin solders have to be replaced with new solders, free of lead .Other alloys with a melting temperature close to the commonly used Sn-Pb eutectic (183 °C) and having appropriate properties should be found. For industrial usage of a new soldering material, the physical properties (electrical, chemical, thermal, mechanical…) in the solid as well as in the liquid state should be well known.
Among many potential candidates, Ag–Sn, Cu–Sn, Zn–Sn, Ag–Cu–Sn, Ag-In-Sn, In-Sn-Zn, Ag-In-Sn-Zn…alloys were viewed as very promising candidates [2-4]. The enthalpy of mixing of the quaternary Ag-In-Sn-Zn system has already been studied by our research group at 500 °C [5]. The Ag-In-Zn is one of the four sub-ternaries, the study of this system at the same temperature seems to be important in order to have more information about the interaction between the four metals.
Gold and silver-based alloys are known for good mechanical and thermal properties as well as corrosion consistency and can be considered as potential candidates. In, and Zn are being solder alloy components and Au or Ag as a possible substrate element.
It is well known that for industrial applications, it is necessary to have access to reliable thermochemical properties (enthalpy of mixing, free enthalpy of mixing …) of various kinds of solution, especially for multicomponent systems. In our previous work [6], the integral enthalpies of mixing of the ternary Au-In-Zn system were calculated by using Chou, Kohler and Toop models.
In this work, the calculation of the integral enthalpies of mixing of liquid phase in the Ag-In-Zn alloys at 773K using different geometric models such as Kohler [7], Muggianu [8], Toop [9] and Hillert [10] models. In addition, a general solution model of Chou [11] has been introduced in the calculations for comparison and discussion. Five cross sections have been studied in order to explore a large domain of alloys, and to have significant information about the influence of silver.

2. Literature survey

2.1. Binary Ag-In

From the literature, considerable amounts of data are available on the enthalpy of mixing of liquid Ag-In alloys. Kleppa [12] and Castanet *et al*. [13] used direct-reaction calorimetry to measure the liquid enthalpies of mixing at different temperatures. The results suggest that the enthalpy of mixing is slightly temperature dependent, especially for higher in concentrations and temperatures close to the liquidus line. Moser *et al*.,[14] and Sabbar *et al*.[15] assessed the experimental data and presented an optimized version of the thermodynamic parameters; however, they did not take into account the temperature dependence of the enthalpy of mixing.

2.2. Binary Ag-Zn

Direct measurements of the enthalpy of mixing in liquid Ag–Zn alloys are not available in the literature, which is mainly due to the high vapour pressure of zinc. Nevertheless, reliable data about the enthalpy of formation of liquid alloys in this system were obtained indirectly by optimizing the other thermodynamic properties available together with the phase equilibira by the CALPHAD technique [16].

2.3. Binary In-Zn

The enthalpy of mixing for liquid In-Zn alloys was determined calorimetrically [17-19]. Emf methods were applied to derive the corresponding values [20-22]. All experimental data show positive values for the enthalpy of mixing. Lee [23] presented a thermodynamic assessment based on the above-mentioned experimental data [20-22]. The calculated and experimental results were in good agreement.

2.4. Ternary Ag-In-Zn system

To the best knowledge of the authors, there is no data for the enthalpy of mixing of liquid Ag-In-Zn available in literature.

3. Theoretical fundamentals

3.1. A general solution model of Chou [11]

There are several methods for calculating thermodynamic properties based on binary information [7-10]. The method provided recently by Chou [11] has been proved to be the most reasonable one in all aspects among current geometrical models. This model can not only generalize various kinds of situations, break down the boundary between symmetrical and asymmetrical systems, but can also thoroughly rule out any human interference in the calculation process. The correctness of this model has already been proved theoretically and the accuracy of calculation has also been shown in some practical examples [24, 25]. Therefore, this model is applied for calculating the thermodynamic properties of the Ag-In-Zn ternary system.

When the Chou's model is applied to the Ag-In-Zn ternary system, first of all, it is necessary to calculate the similarity coefficients ξ_{ij} for three binaries which are defined by η_i called the deviation sum of squares:

$$\xi_{12} = \frac{\eta_{\mathrm{I}}}{\eta_{\mathrm{I}}+\eta_{\mathrm{II}}} \qquad \xi_{23} = \frac{\eta_{\mathrm{II}}}{\eta_{\mathrm{II}}+\eta_{\mathrm{III}}} \qquad \xi_{31} = \frac{\eta_{\mathrm{III}}}{\eta_{\mathrm{III}}+\eta_{\mathrm{I}}}$$

Where

$$\eta_{\mathrm{I}} = \int_0^1 (\Delta_{mix} H_{12} - \Delta_{mix} H_{13})^2 \mathrm{d}X_1 \qquad \eta_{\mathrm{II}} = \int_0^1 (\Delta_{mix} H_{21} - \Delta_{mix} H_{23})^2 \mathrm{d}X_2$$

$$\eta_{\mathrm{III}} = \int_0^1 (\Delta_{mix} H_{31} - \Delta_{mix} H_{32})^2 \mathrm{d}X_3$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12} \qquad X_{2(23)} = x_2 + x_1\xi_{23} \qquad X_{3(31)} = x_3 + x_2\xi_{31}$$

The basic equation of the general solution model, derived by Chou, is given as follows:

$$\Delta_{mix} H_{123} = x_1 x_2 \sum_{\nu} L_{12}^{\nu} (x_1 - x_2)^{\nu} + x_2 x_3 \sum_{\nu} L_{23}^{\nu} (x_2 - x_3)^{\nu} + x_3 x_1 \sum_{\nu} L_{31}^{\nu} (x_3 - x_1)^{\nu} + x_1 x_2 x_3 f$$

$\Delta_{mix} H_{123}$ is an integral enthalpy of mixing for a ternary 1-2-3 system, x_1, x_2, x_3 are the mole fractions of a ternary alloy, L_{ij}^{ν} are parameters for binary "ij" independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta_{mix} H_{ij} = X_i X_j \sum_{\nu} L_{ij}^{\nu} \left(X_i - X_j\right)^{\nu}$$

Where X_i and X_j indicate the mole fraction of component "i" and "j" in "ij" binary system. The function *f* is the ternary interaction coefficient expressed by:

$$f = (2\xi_{12} - 1)\left[L_{12}^{2}\left((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)\right) + L_{12}^{1}\right] + (2\xi_{23} - 1)\left[L_{23}^{2}\left((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)\right) + L_{23}^{1}\right] + (2\xi_{31} - 1)\left[L_{31}^{2}\left((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)\right) + L_{31}^{1}\right]$$

3.2. A traditional Kohler [7], Muggianu [8], Toop[9], and Hillert [10] models

There are several traditional models used to extrapolate the ternary thermodynamic properties based on the three constitutive binary systems, which are classified, into two categories: symmetrical [7, 8] and asymmetrical [9, 10]. The use of a symmetrical model when an asymmetrical model is more appropriate can often give rise to errors.

The four different extrapolation models [7-10] were used to calculate the enthalpy of mixing in the ternary Ag-In-Zn system. A ternary system contains three binary systems, and the information of all these binary systems should be known before using the models.

The various predictive extensions from the binary to ternary systems are shown below.

Kohler model [7]:

$$\Delta_{\text{mix}} H_{123} = (x_{1+}\, x_2)^2 \Delta_{\text{mix}} H_{12}\left(\frac{x_1}{x_1 + x_2}; \frac{x_2}{x_1 + x_2}\right) + (x_{1+}\, x_3)^2 \Delta_{\text{mix}} H_{13}\left(\frac{x_1}{x_1 + x_3}; \frac{x_3}{x_1 + x_3}\right) + (x_{2+}\, x_3)^2 \Delta_{\text{mix}} H_{23}\left(\frac{x_2}{x_2 + x_3}; \frac{x_3}{x_2 + x_3}\right)$$

Muggianu model [8]:

$$\Delta_{\text{mix}} H_{123} = \frac{4x_1 x_2}{(1 + x_{1-}\, x_2)(1 + x_{2-} x_1)} \Delta_{mix}\ H_{12}\left(\frac{1 + x_1 - x_2}{2}; \frac{1 + x_2 - x_1}{2}\right) + \frac{4x_1 x_3}{(1 + x_{1-}\, x_3)(1 + x_{3-} x_1)} \Delta_{mix}\ H_{13}\left(\frac{1 + x_1 - x_3}{2}; \frac{1 + x_3 - x_1}{2}\right) + \frac{4x_2 x_3}{(1 + x_{2-}\, x_3)(1 + x_{3-} x_2)} \Delta_{mix}\ H_{23}\left(\frac{1 + x_2 - x_3}{2}; \frac{1 + x_3 - x_2}{2}\right)$$

Toop model [9]:

$$\Delta_{\text{mix}} H_{123} = (x_{2+}\, x_3)^2 \Delta_{\text{mix}} H_{23}\left(\frac{x_2}{x_2 + x_3}; \frac{x_3}{x_2 + x_3}\right) + \frac{x_2}{(1 - x_1)} \Delta_{\text{mix}} H_{12}(x_1 ; 1 - x_1) + \frac{x_3}{(1 - x_1)} \Delta_{\text{mix}} H_{13}(x_1 ; 1 - x_1)$$

Hillert model [10]:

$$\Delta_{mix} H_{123} = \frac{x_2 x_3}{v_{23} v_{32}} \Delta_{mix} H_{23}(v_{23}; v_{32}) + \frac{x_2}{(1 - x_1)} \Delta_{mix} H_{12}(x_1 ; 1 - x_1) + \frac{x_3}{(1 - x_1)} \Delta_{mix} H_{13}(x_1 ; 1 - x_1)$$

Where $\boldsymbol{v_{23}} = \frac{\mathbf{1}+x_2-x_3}{\mathbf{2}}$; $v_{32} = \frac{\mathbf{1}+x_3-x_2}{\mathbf{2}}$

4. Results and discussion

The calculations in the investigated ternary system Ag-In-Zn were carried out along the lines of a constant x_{In}/x_{Zn}. The five selected cross sections are given in Table 1.

Table 1: The five investigated sections

Section	A	B	C	D	E
x_{In}/x_{Zn}	3/1	2/1	1/1	1/2	1/3

For our calculation we used the data of Hultgreen et al. [26] for the three sub-binary Ag–In, In-Zn and Ag–Zn systems (Table 2).

Table 2: Binary interaction parameters of Ag-In, In-Zn and Zn-Ag sub-binary systems at 773 K.

Binary system	$L^{(0)}$	$L^{(1)}$	$L^{(2)}$
Ag-In	-17452	-13714	-6800
In-Zn	13095	-2682	0
Zn-Ag	-27678	6526	1791

Using the Equations developed by Chou, the deviation sum of squares and the similarity coefficients for the three binaries Ag-In, Ag-Zn and In-Zn are listed in Table 3.

Table 3: Deviation sum squares and similarity coefficients for Chou's model [11] applied on Ag-In-Zn.

Deviation sum of squares (J^2/mol^2)	η_I=3012207,16		η_{II}=34435789,6		η_{III}=379309161	
Interaction of	Ag-In	Ag-Zn	In-Ag	In-Zn	Zn-Ag	Zn-In
Similarity coefficients	ξ_{Ag-In}=0,08043707		ξ_{In-Zn}=0,38592011		ξ_{Zn-Ag}=0,9478918	

From the values of similarity coefficients (Table 3), one can conclude that the integral enthalpies of mixing of Ag-In and Ag-Zn are more similar to each other than to In-Zn, respectively. These ξ values indicate also that this system could be an asymmetrical system. The calculated results for the five models in all the ternary investigated sections (A-E) are summarized in Table 4 and illustrated in Figure 2.

Table 4: Integral enthalpies of mixing of Ag-In-Zn system at 773 K predicted by different models

x_{Ag}	Kohler [7]	Muggianu [8]	Toop [9]	Hillert [10]	Chou [11]
Section A: x_{In}/x_{Zn}=3/1					
0	2707	2707	2707	2707	2707
0,1	476	421	241	510	490
0,2	-1572	-1842	-1972	-1509	-1541
0,3	-3344	-3862	-3836	-3262	-3299
0,4	-4748	-5442	-5262	-4659	-4695
0,5	-5690	-6439	-6164	-5604	-5635
0,6	-6072	-6748	-6457	-5999	-6023
0,7	-5795	-6298	-6062	-5743	-5759
0,8	-4759	-5042	-4902	-4731	-4739
0,9	-2862	-2949	-2904	-2854	-2856
Section B: x_{In}/x_{Zn}=2/1					
0	2711	2711	2711	2711	2711
0,1	907	810	686	907	923
0,2	-752	-1036	-1146	-743	-717
0,3	-2256	-2735	-2759	-2234	-2205
0,4	-3558	-4189	-4101	-3525	-3496
0,5	-4576	-5274	-5090	-4537	-4513
0,6	-5191	-5852	-5618	-5154	-5135
0,7	-5249	-5769	-5551	-5220	-5207
0,8	-4560	-4870	-4724	-4543	-4536,
0,9	-2898	-2998	-2947	-2892	-2890
Section C: x_{In}/x_{Zn}=1/1					
0	3274	3274	3274	3274	3274
0,1	1109	912	1205	1205	1187
0,2	-1020	-1207	-688	-688	-728
0,3	-2974	-3030	-2369	-2369	-2428
0,4	-4596	-4485	-3775	-3775	-3846
0,5	-5736	-5494	-4823	-4823	-4895
0,6	-6257	-5960	-5402	-5402	-5466
0,7	-6039	-5772	-5378	-5378	-5426
0,8	-4981	-4809	-4595	-4595	-4622
0,9	-2994	-2935	-2871	-2871	-2879
Section D: x_{In}/x_{Zn}=1/2					
0	3109	3109	3109	3109	3109
0,1	898	823	615	914	882
0,2	-1124	-1441	-1619	-1098	-1161
0,3	-2889	-3490	-3509	-2860	-2942
0,4	-4316	-5132	-4975	-4288	-4380
0,5	-5315	-6209	-5932	-5290	-5380
0,6	-5785	-6605	-6293	-5766	-5842
0,7	-5615	-6235	-5971	-5602	-5657
0,8	-4683	-5037	-4876	-4677	-4708
0,9	-2859	-2969	-2916	-2857	-2867
Section E: (x_{In}/x_{Zn}=1/3)					
0	2204	2204	2204	2204	2204
0,1	582	481	404	574	595
0,2	-912	-1172	-1231	-915	-883
0,3	-2284	-2696	-2695	-2277	-2240
0,4	-3497	-4023	-3943	-3481	-3445
0,5	-4473	-5049	-4898	-4451	-4420
0,6	-5090	-5633	-5445	-5066	-5042
0,7	-5181	-5610	-5433	-5161	-5145
0,8	-4537	-4796	-4675	-4525	-4517
0,9	-2909	-2994	-2950	-2905	-2903

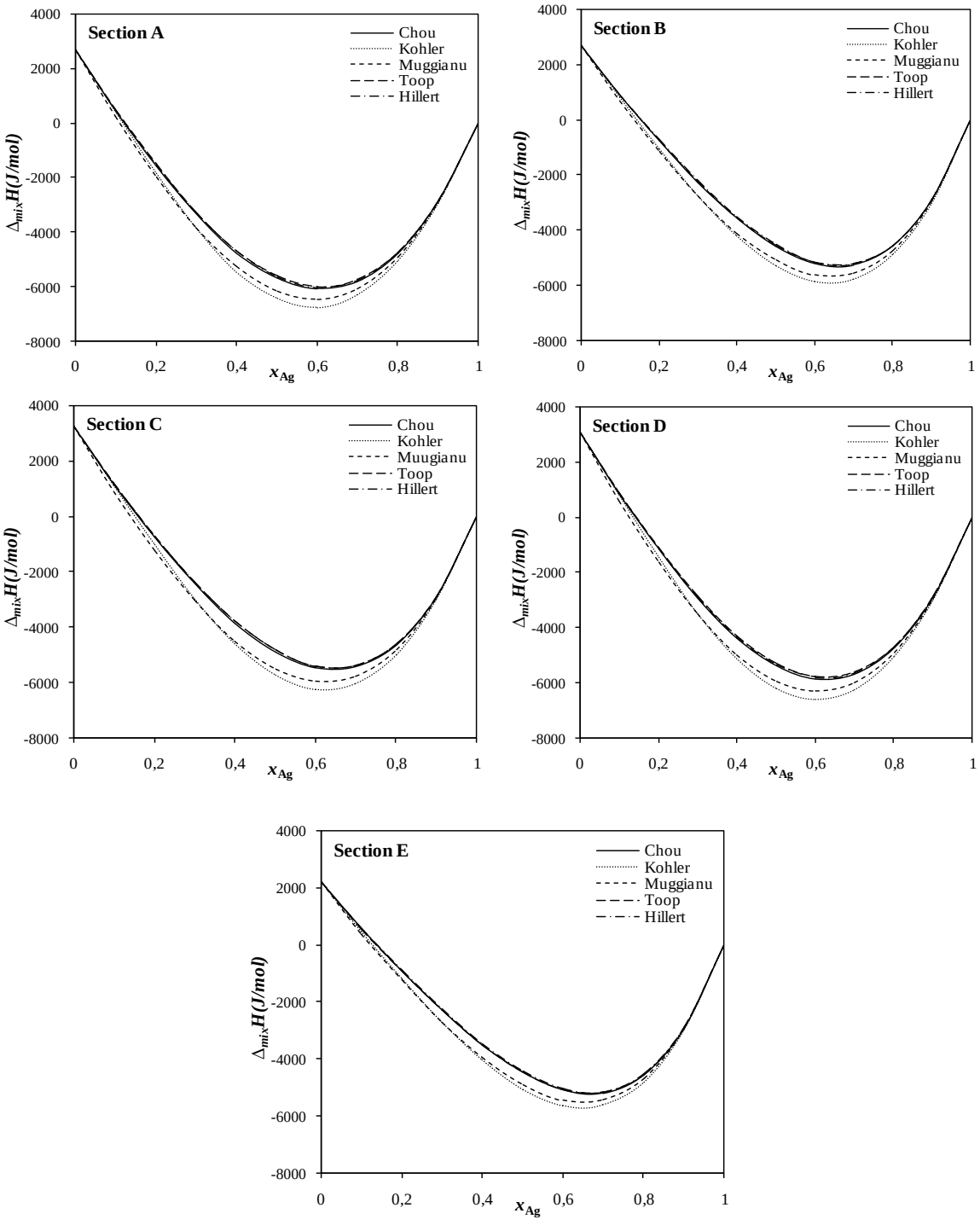

Figure 2: Integral enthalpies of mixing in the liquid Ag-In -Zn alloys at 773 K using the different studied models.

The predicted results $\Delta_{mix}H$ = f (x_{Ag}) at 773 K show that the curves for the five selected sections have a narrow endothermic range ($0 \leq x_{Ag} \leq 0{,}15$) and a large exothermic range. The coordinate of the minima is $\Delta_{mix}\boldsymbol{H}_{min} \simeq$ -6kJ/mol and $\boldsymbol{x}_{Ag} \simeq 0{,}6$. The enthalpy values obtained by symmetric models are more exothermic than those obtained by the asymmetric ones. Indeed, it could be concluded that predicted values of integral enthalpies of

mixing for the five selected sections obtained by Chou's model are in better agreement with the results obtained by the Toop and Hillert asymmetrical models.

Conclusion

The integral enthalpies of mixing of the ternary Ag-In-Zn system were calculated using Chou, Kohler, Muggianu, Toop and Hillert models. The values obtained by Kohler and Muggianu are more exothermic than those obtained by Toop and Hillert models. The predicted enthalpy values of Chou's model's are in good agreement with those of Toop and Hillert models.

In order to verify our predicted results and to determinate the symmetry or asymmetry of the Ag-In-Zn system, some experimental studies are necessary.

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