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CALCULATION OF THERMODYNAMIC PROPERTIES Al-Ga-Sn TERNARY ALLOY USING MUGGIANU AND TOOP MODEL

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Abstract

Since the 1960s, the rapid advancement of information technology (IT) infrastructure has been covered by the innovation of new electronic devices. This progress has not only accelerated industrial growth but also enhanced the quality of human life. Modern electronic devices are highly advanced and contain numerous components. Traditionally, Sn-Pb solder alloys have been the preferred choice due to their many advantages, such as ease of use, low melting point, favorable working conditions, good ductility, and excellent wetting properties on copper and its alloys. However, due to the toxic effects of lead on both health and the environment, limit the use of lead. As a result, the development of lead-free solder alternatives has been a focus for the past thirty years. To investigate new solder materials extensively, it's crucial to understand phase diagrams, phase equilibria, and melting points. Thermodynamic calculations and modeling are key in producing a consistent dataset and predicting thermodynamic properties. Muggianu Model and Model Toop were used to calculate the thermodynamic properties of Al-Ga-Sn liquid alloys. The predicted values were compared with the calculated results of the General Solution Model, and published experimental data confirm that the models are both accurate and practical.

***Keywords**: Muggianu Model, Model Toop, Al-Ga-Sn alloys, thermodynamic properties, activity*

1. INTRODUCTION

For over 60 years, SnPb solder has been widely used in electronic assembly, chosen for its good soldering characteristics, ease of manufacturing, reliability, and low cost [1, 2]. However, health risks of lead, rise concerns about its environmental and human impact. Various regulations have been implemented, regarding the disposal of products containing lead. Mainly, the European Union's Restriction of Hazardous Substances (RoHS) Directive, which is related to Directive 2002/95/EC, does not allow using Sn-Pb solder in consumer electronics within the EU and other countries [3].

Extensive research has been started to find alternatives to lead-free solders [4-6]. Lead-free solders range from binary to ternary systems, mainly based on tin (Sn) with small amounts of other alloying elements such as silver (Ag), copper (Cu), zinc (Zn), indium (In), bismuth (Bi) and others [7]. Commonly studied binary systems include Sn–Ag, Sn–Cu, Sn–Zn, Sn–Bi, and Sn–In, while ternary systems like Sn–Ag–Cu, Sn–Ag–Bi, and Sn–Zn–Bi have also been explored [1, 2, 4, 5, 8-13]. Sn-Ag-Cu (SAC305) solders are widely used in electronic packaging. Their good thermo-mechanical properties and relatively low melting

point make SAC solders a practical substitute for traditional Sn-Pb solders [14]. However, Pb-free solders have limitations; one of them is that they are more expensive due to the presence of silver (Ag) [2, 12, 15]. Producing low-cost alternatives to near-eutectic SAC alloys for lead-free electronics assembly is critical to maintaining the cheap production of electronic devices [16].

One approach is to add aluminum (Al) with tin (Sn) as an additional element while replacing expensive ones like silver (Ag), copper (Cu), bismuth (Bi), and indium (In). M.E. Alam and M. Gupta [17] reported that Sn-Al solder shows high ductility and has a melting point close to lead-free Sn-Cu solder (227°C), with a potential 16% reduction in density. The addition of micro alloying elements like gallium (Ga), nickel (Ni), and zinc (Zn) further improves the performance and reliability of Sn-Al solder [18]. Gallium and its alloys present some advantages for microelectronic interconnections. With its low melting point and non-toxic properties, Ga is a good choice for improving solder performance. This property is partly due to Ga's ability to form stable solid solutions and intermetallic compounds (IMCs) with metals like Cu, Ni, and Al, which have higher melting points. Ga and its alloys can contribute to the miniaturization and flexibility of microelectronic devices [19-21].

To investigate new solder materials, it's important to understand phase diagrams, phase equilibria, and melting points [6, 10, 22-24]. Thermodynamic calculations and modeling are vital in producing a reliable dataset and predicting thermodynamic properties [25-28]. The thermodynamic properties of a ternary system can be calculated using various methods based on the known thermodynamic properties of the binary systems. Besides the General Solution Model (GSM) [29-31], which we used in our previous study [32], is the most popular among existing models, there are also many other models. Therefore, a symmetric Muggianu Model [33] and an asymmetric Model Toop [34] were used to calculate the thermodynamic properties of the Al-Ga-Sn ternary systems. Calculate values were compared with the General Solution Model (GSM) [29-32] and the experimental data from our previous study [32, 35].

2. THEORETICAL BASIS

2.1 Muggianu Model

The Muggianu model [33] was selected from the symmetric models used to predict thermodynamic behavior. Its fundamental equation is as follows:

$$\Delta G^E = \frac{4x_1x_2}{(1+x_1-x_2)(1+x_2-x_1)}\Delta G_{12}^E\left(\frac{1+x_1-x_2}{2};\frac{1+x_2-x_1}{2}\right)+$$
$$+\frac{4x_2x_3}{(1+x_2-x_3)(1+x_3-x_2)}\Delta G_{23}^E\left(\frac{1+x_2-x_3}{2};\frac{1+x_3-x_2}{2}\right)+$$
$$+\frac{4x_3x_1}{(1+x_3-x_1)(1+x_1-x_3)}\Delta G_{31}^E\left(\frac{1+x_3-x_1}{2};\frac{1+x_1-x_3}{2}\right) \quad (1)$$

2.2 Model Toop

The Toop model [34] was selected to predict the thermodynamic properties among the available asymmetric models. The fundamental equation for a ternary system is as follows:

$$\Delta G^E = \frac{x_2}{1-x_1}\Delta G_{12}^E\left(x_1;1-x_1\right)+\frac{x_3}{1-x_1}\Delta G_{13}^E\left(x_1;1-x_1\right)+$$
$$+\left(x_2+x_3\right)\Delta G_{23}^E\left(\frac{x_2}{x_2+x_3};\frac{x_3}{x_2+x_3}\right) \quad (2)$$

where ΔG^E is integral molar excess Gibbs energy for ternary system, and x_i is mole fraction of the component *i*. ΔG_{ij}^E is integral molar excess Gibbs energy for a binary system, and for calculation, we use the followed equation:

$$\Delta G_{ij}^E = x_i x_j\left(A_{ij}^0+A_{ij}^1(x_i-x_j)+A_{ij}^2(x_i+x_j)^2+...+A_{ij}^n(x_i-x_j)^n\right) \quad (3)$$

where A^0_{ij}, A^1_{ij},A^2_{ij} represent Redlich-Kister parameters for binary system "*ij*" which may vary with temperature. x_i and x_j are mole fractions of components "*i*" i "*j*" u "*ij*" binary system.

Partial thermodynamic quantities are calculated according to the equations:

$$G_i^E = G^E+\left(1-x_i\right)\left(\partial G^E/\partial x_i\right)=RT\ln\gamma_i \quad (4)$$

$$a_i = x_i\gamma_i \quad (5)$$

where G_i^E is partial molar excess Gibbs energy, a_i is activity of component *i*, γ_i is activity coefficient of component *i*, *T* is temperature, *R* is gas constant (8.314 $J{\cdot}K^{-1}mol^{-1}$), and G^E is Gibbs energy for the whole system, dependent on composition. Integral molar excess Gibbs energy (ΔG^E) corresponds to the whole system, while partial molar excess Gibbs energy (G_i^E) corresponds to individual components.

3. RESULTS AND DISCUSSION

The thermodynamic properties of the Al-Ga-Sn ternary system were studied across nine sections, from the Al, Ga, and Sn corners, with mole ratios of 1:3, 1:1, and 3:1. The molar content of the third component varied from 0 to 0.9 in the temperature range of 800-1600 K. All thermodynamic properties calculated in this work are related to the liquid phase.

The thermodynamic data for the constituent binary subsystems of Sn-Al [36], Sn-Ga [37], and Al-Ga [38], required for the calculation of thermodynamic properties in the investigated Al-Ga-Sn system, are presented in Table 1.

Table 1. *Redlich–Kister parameters for constitutive binary systems*

System *ij*	L^{o}_{ij} (T)*			L^{1}_{ij} (T)*			L^{2}_{ij} (T)*			Ref
	A	B	C	A	B	C	A	B	C	
Sn-Al	16329.85	-4.98306	/	4111.97	-1.15145		1765.43	-0.5739	/	[36]
Sn-Ga	3369.7	0.03854	/	528.9	-0.1145	/	/	/	/	[37]
Al-Ga	2613.3	-2.94533	/	692.4	-0.09271	/	319.5	/	/	[38]

3.1 Calculation of thermodynamic properties by the Muggianu Model

The thermodynamic properties of the Al-Ga-Sn ternary system were calculated using the Muggianu model, as illustrated in Figures 1 and 2.

For all examined sections, the activities of tin and aluminum exhibit a positive deviation from Raoult's law, with tin showing a more pronounced deviation.

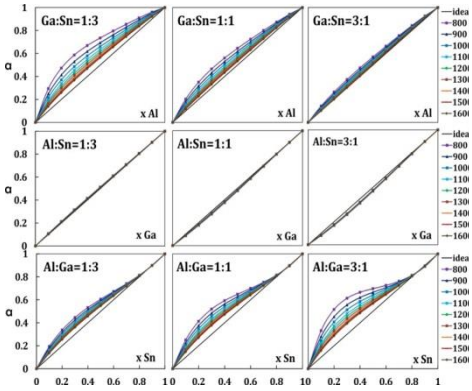

Figure 1. *Activity of Al, Ga and Sn, in the Al-Ga-Sn system according to the Muggianu model*

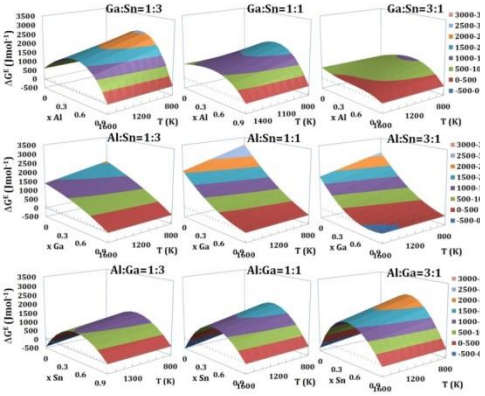

Figure 2. *Integral molar excess Gibbs free energy in the Al-Ga-Sn system, based on the Muggianu model*

For the activities of tin, as the gallium content increases, the deviation from the line of ideal behavior decreases, as well for the activities of aluminum. On the other hand, the activity of gallium aligns closely with the line of ideal behavior. With an increase in aluminum content, the slightly positive deviation in the activity of gallium shifts to a slight negative deviation, but it remains very close to the line of ideal behavior. The values of the integral molar excess Gibbs free energy (Figure 2) range from 0 to 3.5 kJ/mol, with the highest integral molar excess Gibbs free energy observed at the Al-Sn=1:1 ratio.

3.2 Calculation of thermodynamic properties by Model Toop

The thermodynamic properties of the ternary Al-Ga-Sn system were also predicted using model Toop's. The calculated values for tin activity in the temperature range of 800-1600 K (Figure 3) for all examined cross-sections show a positive deviation from Raoult's law. This deviation decreases as the gallium content increases. Similarly, the aluminum activity exhibits a strong positive deviation from Raoult's law, but in this case, the positive deviation increases as the gallium content decreases. The activity of gallium

aligns with the ideal state line, transitioning from nearly ideal behavior to a slight negative deviation as the tin content decreases.

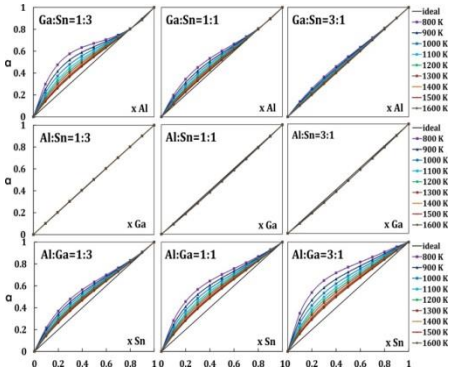

Figure 3. *Activity of Al, Ga and Sn, in the Al-Ga-Sn system according to the model Toop*

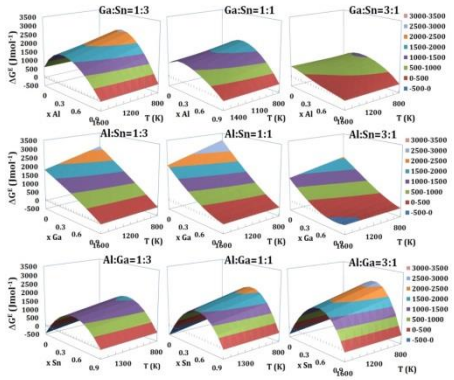

Figure 4. *Integral molar excess Gibbs free energy in the Al-Ga-Sn system based on the model Toop*

The values of the integral molar excess Gibbs energy for the Al-Ga-Sn ternary system within the temperature range of 800-1600 K (Figure 4) span from 0 to 3.5 kJ/mol for all the cross-sections studied. The activity of gallium in the Al-Ga-Sn ternary system at temperatures of 800, 900, and 1000K, as calculated using the Muggianu model [33] and the Toop model [34], was compared with predictions from the GSM model [32] and experimental data obtained via Oelsen calorimetry [35]. The comparison reveals a good correlation, although the experimentally determined gallium activity demonstrates a more pronounced negative deviation at all examined temperatures compared to the predicted values (Figures 5).

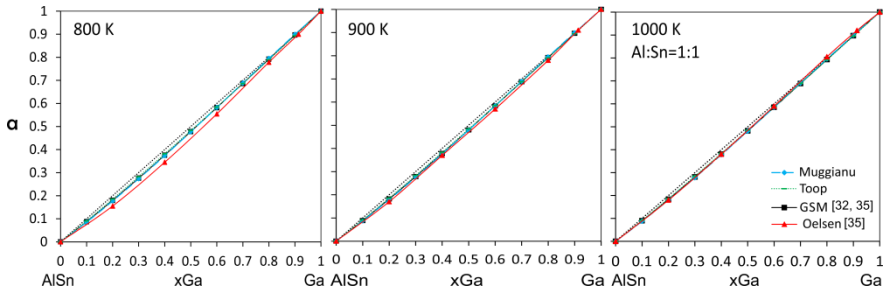

Figure 5. *Activity dependences of gallium in AlSn-Ga section at 800, 900 and 1000 K obtained by the Muggianu, Toop and GSM model [32, 35] and experimentally determined by Oelsen calorimetry [35]*

4. CONCLUSION

The thermodynamic properties of the Al-Ga-Sn system were determined using the Muggianu and Toop models over a temperature range of 800 to 1600 K. This analysis allowed for the calculation of integral molar excess Gibbs energies and activities for all components. The computed integral molar excess Gibbs energies for the examined sections were found to be positive, reaching up to 3.5 kJ/mol. Both aluminum and tin

activities exhibited a positive deviation from Raoult's law across all sections studied. However, for aluminum and tin activities, the deviation decreases for alloys with a high gallium content. Gallium's activity remained close to the ideal behavior line, particularly in alloys with a high gallium concentration. When compared to the predicted results from the General Solution Model and experimental data available in the literature, the accuracy and practicality of the models were confirmed. The thermodynamic data provided for Al-Ga-Sn alloys could be valuable for further phase diagram studies of this system and for completing its thermodynamic description.

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