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TIN ACTIVITY DETERMINATION IN THE Ag-Cu-In-Sn SYSTEM

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ABSTRACT
In this paper the results of thermodynamic prediction of Ag-Cu-In-Sn system by geometric sollution model are presented. Tin activity was determined for all investigated sections with constant molar ratio In:Ag:Cu=8:1:1; 6:2:2; 4:3:3; 2:4:4 at temperature 873 up to 1673K
.**Keywords:** Ag-Cu-In-Sn, thermodynamic prediction

1. INTRODUCTION
According to WEEE [1], lead, as a highly toxic metal, has been removed from different materials, especially electronic, although it was widely used in industry, particularly microelectronics, before. Therefore, lead-based solders are under way to be replaced by lead-free alloys, so significant work has been done and is still going on to find a substitute for common Pb-Sn solder alloy.
Due to the specific properties of Pb-Sn solder alloys, the candidates for their replacement are usually tin-based multicomponent alloys, since the investigated binary systems do not satisfy some features (temperature, for example). The question on melting temperature is one of the most difficult problems in the lead-free soldering transition.
Different characteristics of lead-free solder alloys - melting temperature, wettability, reliability, etc., have been studied a lot and widely discussed [2-7]. Phase equilibria for the system Sn-In-X (X=Ag, Bi, Zn, Sb) was investigated by I. Ohnuma, Y. Cui, J. Liu, et al. [3]. Using Thermo Calc software, the appropriate thermodynamic database was formed, and based on that, invariant reactions of the system, as well as isotermal sections at 373 and 473 K, were given in the paper. Also, the phase equilibria for the Sn-Ag-In system was obtained from experimental values (DSC and optical microscopy) and optimised binary data, by X. J. Liu, Y. Inohana, et al. from Japan, and Z. Moser, W. Gasior i J. Pstrus [4,5], from Poland.
Based on large experimental work (optical microscopy, DSC, XRD, SEM, microhardness), Ag-In-Sn alloys were investigated by G.P. Vassilev et al. [6], and the isotermal section at 553 K was obtained.
Phase equilibria for the system Cu-In-Sn was investigated by X.J.Liu, H.S.Liu, I.Ohnuma, et al. [7], based on experimental results (DSC and optical microscopy) and optimized values for binary systems. Also, in that paper the liquidus projection for the Cu-In-Sn system and 8 isotermal sections at 110-900°C, were given.

Considering these facts, Ag-In-Sn-Cu alloys might be potentional candidates for replacement of standard lead solder alloys, so the results of thermodynamic prediction are presented in this paper.

2. THEORETICAL FUNDAMENTALS

Calculation of thermodynamic properties in five investigated sections with molar ratio In:Cu:Ag=8:1:1; 6:2:2; 4:3:3 2:4:4; and 7:2:1, have been done using different predicting methods – Toop [8], Muggianu [9] and Kohler [10], at different temperatures in range 873÷1673K.
The basic equations of these predicting models are given as follows:

Toop model [8]:

$$\Delta G_{1234}^{xs} = \frac{X_2}{1-X_1}\Delta G_{12}^{xs}\left(X_1;1-X_1\right) + \frac{X_3}{1-X_1}\Delta G_{13}^{xs}\left(X_1;1-X_1\right) + \frac{X_4}{1-X_1}\Delta G_{14}^{xs}\left(X_1;1-X_1\right) + \left(1-X_1\right)^2 \Delta G_{234}^{xs}\left(\frac{X_2}{1-X_1};\frac{X_3}{1-X_1};\frac{X_4}{1-X_1}\right) \quad (1)$$

Muggianu model [9]:

$$\Delta G_{1234}^{xs} = \frac{4X_1X_2}{(1+X_1-X_2)(1+X_2-X_1)}\Delta G_{12}^{xs}\left(\frac{1+X_1-X_2}{2};\frac{1+X_2-X_1}{2}\right) + \frac{4X_1X_3}{(1+X_1-X_3)(1+X_3-X_1)}\Delta G_{13}^{xs}\left(\frac{1+X_1-X_3}{2};\frac{1+X_3-X_1}{2}\right) + \frac{4X_1X_4}{(1+X_1-X_4)(1+X_4-X_1)}\Delta G_{14}^{xs}\left(\frac{1+X_1-X_4}{2};\frac{1+X_4-X_1}{2}\right) + \left(1-X_1\right)^2 \Delta G_{234}^{xs}\left(\frac{X_2}{1-X_1};\frac{X_3}{1-X_1};\frac{X_4}{1-X_1}\right) \quad (2)$$

Kohler model [10]:

$$\Delta G_{1234}^{xs} = \left(X_1+X_2\right)^2 \Delta G_{12}^{xs}\left(\frac{X_1}{X_1+X_2};\frac{X_2}{X_1+X_2}\right) + \left(X_1+X_3\right)^2 \Delta G_{13}^{xs}\left(\frac{X_1}{X_1+X_3};\frac{X_3}{X_1+X_3}\right) + \left(X_1+X_4\right)^2 \Delta G_{14}^{xs}\left(\frac{X_1}{X_1+X_4};\frac{X_4}{X_1+X_4}\right) + \left(1-X_1\right)^2 \Delta G_{234}^{xs}\left(\frac{X_2}{1-X_1};\frac{X_3}{1-X_1};\frac{X_4}{1-X_1}\right) \quad (3)$$

In all equations ΔG_{234}^{XS} and ΔG_{1234}^{XS} correspond to the integral molar excess Gibbs energy for ternary and quaternary system, while X_1, X_2, X_3, X_4 correspond to the mole fraction of components in investigated system. Integral molar excess Gibbs energies for constitutive binary systems, ΔG_{ij}^{XS} (i,j=1,…,4) are obtained using Redlich-Kister parameters from COST531 Database [1].

3. RESULTS AND DISCUSSION

Basic data for the thermodynamic calculation were the values of integral molar excess Gibbs energies for constitutive binary systems, ΔG_{ij}^{XS}, which are calculated using Redlich-Kister parameters from COST531 Database [1].
The values of integral molar excess Gibbs energies for the alloys in Ag-In-Sn-Cu investigated sections were calculated using Toop, Kohler and Muggianu models. The comparative graphical presentation for In:Ag:Cu=7:2:1 section at 1673K is shown in Fig.1. As can be seen in Fig.1, there is no essential difference between ΔG_{ij}^{XS} trends for Toop, Kohler and Muggianu models. So, both - symetric and asymmetric models are appropriate to this system.
The ΔG_{ij}^{XS} values for different sections as well as activity values at 873K, are shown in Figures 2 and 3. From figure 2 it can be seen that sections with higher indium fraction (8:1:1; 6:2:2; 7:2:1) have the same ΔG_{ij}^{XS} trend, and the other ones (4:3:3; 2:4:4), different.

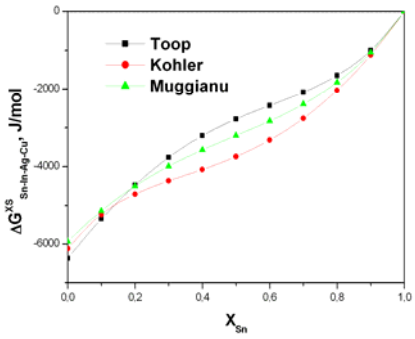


Figure 1. Integral molar excess Gibbs energies for section In:Ag:Cu=7:2:1 at 1673K

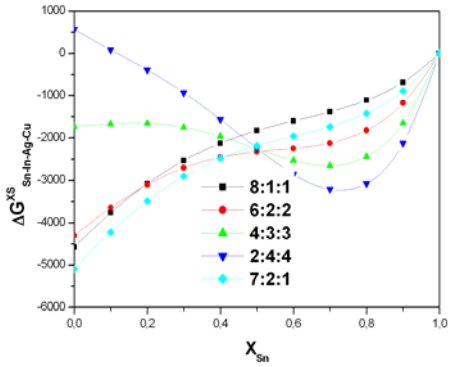


Figure 2. Integral molar excess Gibbs energies for Ag-Cu-In-Sn system at 873K (Toop method)

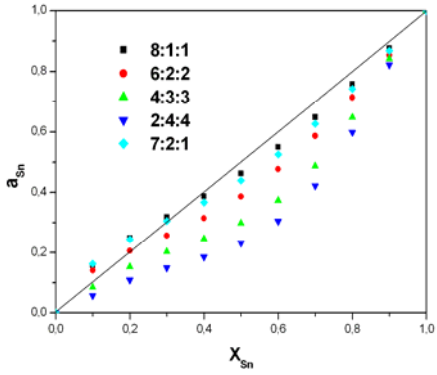
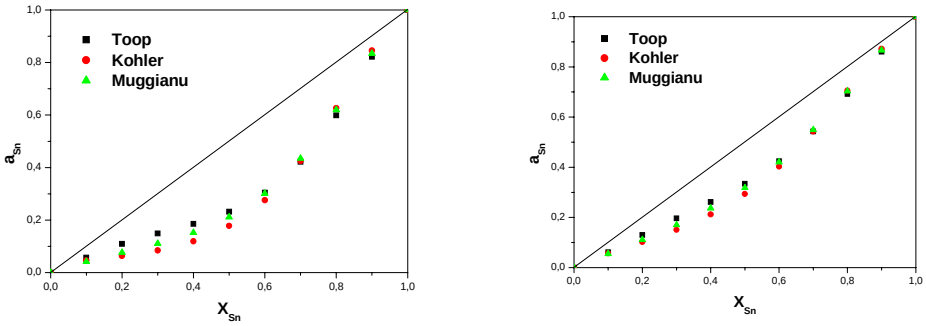


Figure 3. Activity values for Sn-In-Ag-Cu system at 873K (Toop method)

The activity values for all investigated sections have negative deviation from Raoults line for alloys with X_{Sn}>0,4. Further, sections In:Ag:Cu=2:4:4 and 4:3:3 have negative deviation in whole concentration range. Comparison between models is presented at Fig.4 for In:Ag:Cu=2:4:4 section, at 873 and 1673K.



a)873K b)1673K

Figure 4. Tin activity comparison for In:Ag:Cu=2:4:4 section

Negative deviation in whole concentration range pointed out to intermetallic compounds creation, especially for In:Ag:Cu=2:4:4 section.

4. CONCLUSION

The results of thermodynamic prediction of chosen alloys from the Ag-In-Sn-Cu system were presented in this paper, enabling better understanding of these type of potential lead-free solder alloys based on tin.

5. ACKNOWLEDGEMENT

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