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CALCULATION OF THERMODYNAMIC PROPERTIES OF LIQUID AG-AU-SB ALLOYS

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ABSTRACT

The results of calculation of thermodynamic properties of liquid Ag-Au-Sb alloys are presented in this paper. General solution model has been applied in the calculation procedure, based on the starting binary data taken from the COST 531 database. The investigations were done in the sections from each corner with molar ratio of other two components equal to 1:1, 1:3 and 3:1. Thermodynamic quantities were determined at the temperature of 1400K using applied method.

Keywords: thermodynamics, lead-free solders, Ag-Au-Sb system

INTRODUCTION

There are numerous lead-free solder alloys, which are considered nowadays as a possible alternative to conventional Pb-bearing solders [1]. One among different systems, which are the subject of different investigations recently, is the Ag-Au-Sb ternary system. This system could present an important alloy system in the development of substitute solder systems with low freezing points and high strengths, as well as an interesting possibility concerning the high heat loads.

In the Ag-Au-Sb system, three low-order binary subsystems are experimentally well established and thermodynamic evaluation of each system has already been attempted. The most complete reviews of thermodynamic data for constitutive binaries Ag-Au, Ag-Sb and Au-Sb are given in [2], [3] and [4], respectively, and also in the COST531 Database [5].

As a contribution to the more complete knowledge of thermodynamic behavior of this lead-free solder candidate-system, the results of thermodynamic properties calculation for liquid Ag-Au-Sb alloys, using general solution model, are presented in this paper. Such given set of thermodynamic data for liquid Ag-Au-Sb alloys could be useful for further assessment of this system.

THEORETICAL FUNDAMENTALS

The basic equations of general solution model [6,7] are given as follows:

$$\Delta G^E = x_1x_2 (A^o_{12} + A^1_{12} (x_1-x_2) + A^2_{12} (x_1-x_2)^2) + x_2x_3 (A^o_{23} + A^1_{23} (x_2-x_3) + A^2_{23} (x_2-x_3)^2) + x_3x_1 (A^o_{31} + A^1_{31} (x_3-x_1) + A^2_{31} (x_3-x_1)^2) + fx_1x_2x_3 \quad (1)$$

where A^o_{ij}, A^1_{ij}, A^2_{ij} are parameters for binary system "ij" independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta G^E_{ij} = X_iX_j (A^o_{ij} + A^1_{ij} (X_i - X_j) + A^2_{ij} (X_i - X_j)^2 + ... + A^n_{ij} (X_i - X_j)^2) \quad (2)$$

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

$$f = (2\xi_{12} -1)\{A^2_{12} ((2\xi_{12} -1)x_3 + 2(x_1-x_2)) + A^1_{12}\} + (2\xi_{23} -1)\{A^2_{23} ((2\xi_{23} -1)x_1 + 2(x_2-x_3)) + A^1_{23}\} + (2\xi_{31} -1)\{A^2_{31} ((2\xi_{31} -1)x_2 + 2(x_3-x_1)) + A^1_{31}\}, \quad (3)$$

where ξ_{ij} are the similarity coefficients defined by η_i called the deviation sum of squares [6,7]:

$$\xi_{ij}=\eta_i/(\eta_i+\eta_j) \quad (4)$$

where

$$\eta_i = \int_{X_i=0}^{X_i=1} (\Delta G^E_{ij} - \Delta G_{ik})^2 dX_i \quad (5)$$

and

$$X_{i(ij)} = x_i + x_k\xi_{ij} \ . \quad (6)$$

In all given equations, ΔG^E and ΔG^E_{ij} correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system.

RESULTS AND DISCUSSION

The alloys in three sections from the every corner with molar ratio of other two components equal to 1:1, 1:3 and 3:1, and with molar content of main component equal to 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8 and 0.9, were investigated. The investigated system was considered in the order 1-2-3 related to Ag-Au-Sb.

Basic data for the calculation were taken from the COST 531 Database and include characteristic A^k_{ij} (see Eq.2) parameters for liquid phase of each binary system as shown in Table 1.

Table 1. *Starting binary A^k_{ij} parameters for each constitutive binary system*

ΔG^E_{ij}, *kJ/mol*			
System *i-j*	A^o_{ij}	A^1_{ij}	A^2_{ij}
Ag-Au	-16402+1.14T	0	0
Au-Sb	-15437.35-4.63455T	-18854.1+15.64707T	-4271.85
Ag-Sb	-821.8-9.6561T	-19309+4.4239T	-10381.2

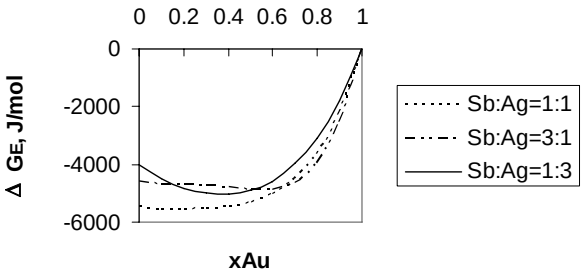
Further, the integral molar Gibbs excess energies for chosen alloys in the Ag-Au-Sb system were calculated using general solution model, given through Eqs. (1-6). Partial thermodynamic quantities were derived using the following equation:

$$G_i^E = \Delta G^E + \left(\frac{\partial \Delta G^E}{\partial X_i} \right) \cdot (1 - X_i), \tag{7}$$

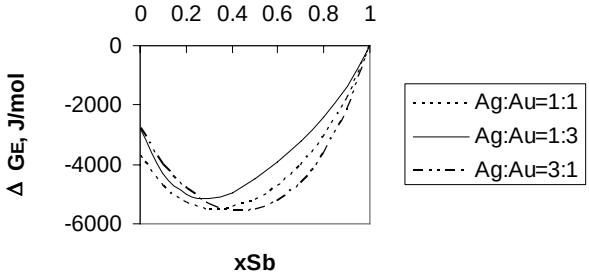
which enabled determination of responding activity coefficients and activities of the *"i"* component. Calculated thermodynamic properties for all investigated alloys at the temperature of 1400K are presented in the form of graphical representations of the dependence of integral molar Gibbs excess energy and activity on composition for different sections in the ternary Ag-Au-Sb, as shown in Fig. 1 and 2, respectively.

Figure 1. *ΔG^E vs. composition for different sections in the Ag-Au-Sb section at 1400K*

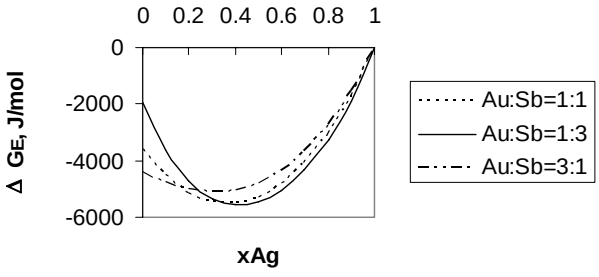
a) *sections from Sb corner*



b) *sections from Au corner*



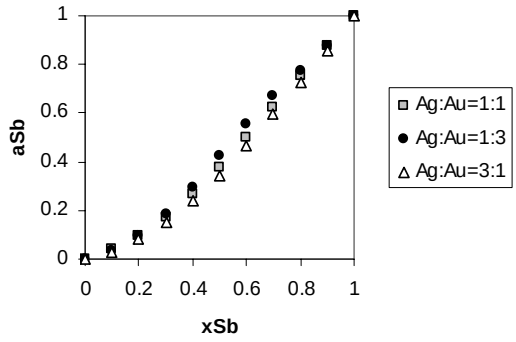
c) *sections from Ag corner*



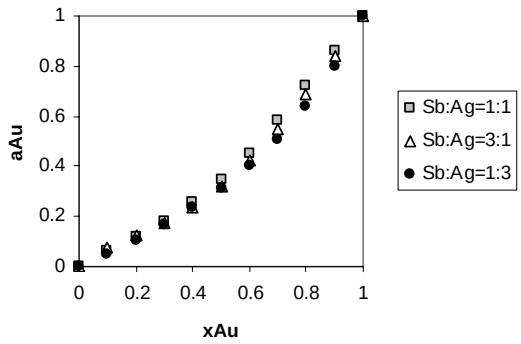
It can be seen that the integral molar excess Gibbs energies in the ternary Ag-Au-Sb system are negative in all investigated sections (Fig.1), with a minimum value of about -6kJ/mol. Activities of all constitutive components in the investigated system show negative deviation from ideal behavior, which indicates to a good mutual miscibility of the present components. Such obtained results may contribute to the thermodynamics of this system, because experimental thermodynamic data are still missing in literature. Also, these results could be used for the further investigations of the Ag-Au-Sb system phase equilibria in order to determine accurate phase diagram of this ternary system.

Figure 2. *Activity vs. composition for different sections in the Ag-Au-Sb section at 1400K*

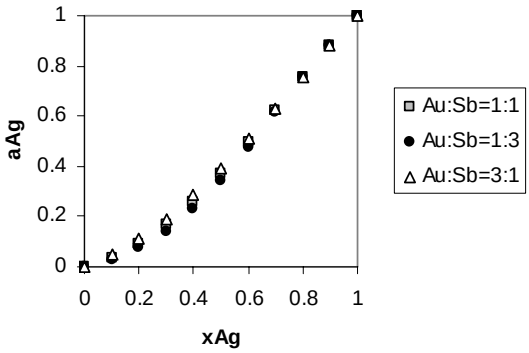
a) *sections from Sb corner*



b) *sections from Au corner*



c) *sections from Ag corner*



CONCLUSIONS

The results of calculation of thermodynamic properties of liquid Ag-Au-Sb alloys are presented in this paper. General solution model has been applied in the investigations done in the sections from each corner with molar ratio of other two components equal to 1:1, 1:3 and 3:1. Thermodynamic quantities were determined at the temperature of 1400K using applied method and may be used for further research of the phase equilibria and thermodynamics of this lead-free solder candidate.

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