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Thermal analysis of some alloys in the Ag-Cu-Sn ternary system

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The ternary phase transition reactions in the system Ag-Cu-Sn were studied by DTA (Differential Thermal Analysis). The investigated samples were situated along three vertical sections with molar ratios Ag/Cu=1, Ag/Sn=1 and Cu/Sn=1. The liquidus surface and invariant reactions were calculated by the CALPHAD method using thermodynamic parameters included in the COST 531 database. The experimentally determined phase transition temperatures were compared with calculation results and good mutual agreement was noticed.

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Keywords: Ag-Cu-Sn ternary system; Phase diagram; Thermal analysis

1. Introduction

The phase diagram of the Ag-Cu-Sn system is fundamental to the development of technology of lead-free solder alloys. Recent legislations in many countries to eliminate the use of lead containing solder alloys have created renewed interest in this system, especially in the Sn rich region. Apart from this, Ag-Cu-Sn system also forms the basis of several Cu rich dental amalgams.

In this paper, the phase transition temperatures of the Ag-Cu-Sn alloys along three vertical sections were investigated by DTA.

Experimental results were compared with the results of thermodynamic calculation based on the 4.4 SGTE values of Gibbs energies for pure elements **[1]** and thermodynamic data included in the COST 531 thermodynamic database **[2]**.

2. Experimental procedure

The samples were prepared by mixing metals of purity > 99.99% in required proportions and induction-melted in graphite crucibles. Argon gas was purged over the sample crucible to create an inert atmosphere in the heated chamber. The alloys were melted and cooled repeatedly to improve homogeneity. The total mass losses of the prepared ingots were less than 1mass% so the nominal compositions of the alloys were accepted for the further investigation.

The DTA measurements were carried out with the Derivatograph (MOM Budapest) apparatus under following conditions: flowing argon atmosphere, sample masses about 2 g, and alumina as the reference material. A heating rate of 5 ^{o}C /min was employed both for calibration and measurement of the prepared samples.

The temperatures of invariant transitions were taken from the extrapolated onset on heating. The other phase transition temperatures were taken from the peak temperature.

3. Thermodynamic and crystallographic data

Calculation of the Ag-Cu-Sn phase equilibria was done using CALPHAD method **[3-4]**. The thermodynamic data for the Ag-Cu-Sn system, used for the phase diagram calculation in the present work, were taken from an unpublished assessment of Gisby and Dinsdale **[5]** carried out prior the COST 531 Action **[6]** and included in COST 531 Database for Lead Free Solders **[2]**. The assessment was based on calorimetry data of Shen et al. **[7-8]**, studies of the solubility of Cu in Ag-Sn liquids by **[9]** and studies of phase equilibria for various isopleths in the ternary system **[10-15].**

The pure solid elements in their stable form at 298.15 K and under the pressure of 1 bar were chosen as the reference state for the systems (SER). The Version 4.4 of the SGTE Unary Database (Scientific Group Thermodata Europe) of phase stabilities for stable and metastable states of pure elements **[1]** was used.

The phases from constitutive binary subsystems considered for thermodynamic calculation of Ag-Cu-Sn phase diagram with their crystallographic data are listed in Table 1.

Table 1. Phases and crystallographic data [16].

Phase Name in Thermodynamic Database	Common Name	Strukturbericht designation	Pearson Symbol
LIQUID	Liquid		
FCC_A1	(Ag), (Cu)	*A*1	*cF4*
AGSB_ORTHO	ε	*D*0*a*	*oP*8
HCP_A3	ζ	*A*3	*hP*2
DIAMOND_A4	(αSn)	*A*4	*cF*8
BCT_A5	(βSn)	*A*5	*tI*4
BCC_A2	β γ	*A*2 *D*03	*cI*2 *cF*16
CU10SN3	ζ	…	*hP*26
CU41SN11	δ	…	*cF*416
CU3SN	ε	…	*oC*80
CU6SN5_P	η'	…	*mC*44
CUIN_ETA	η	*B*81	*hP*4

Calculated phase diagrams of the constitutive binary systems are shown in Fig. 1.

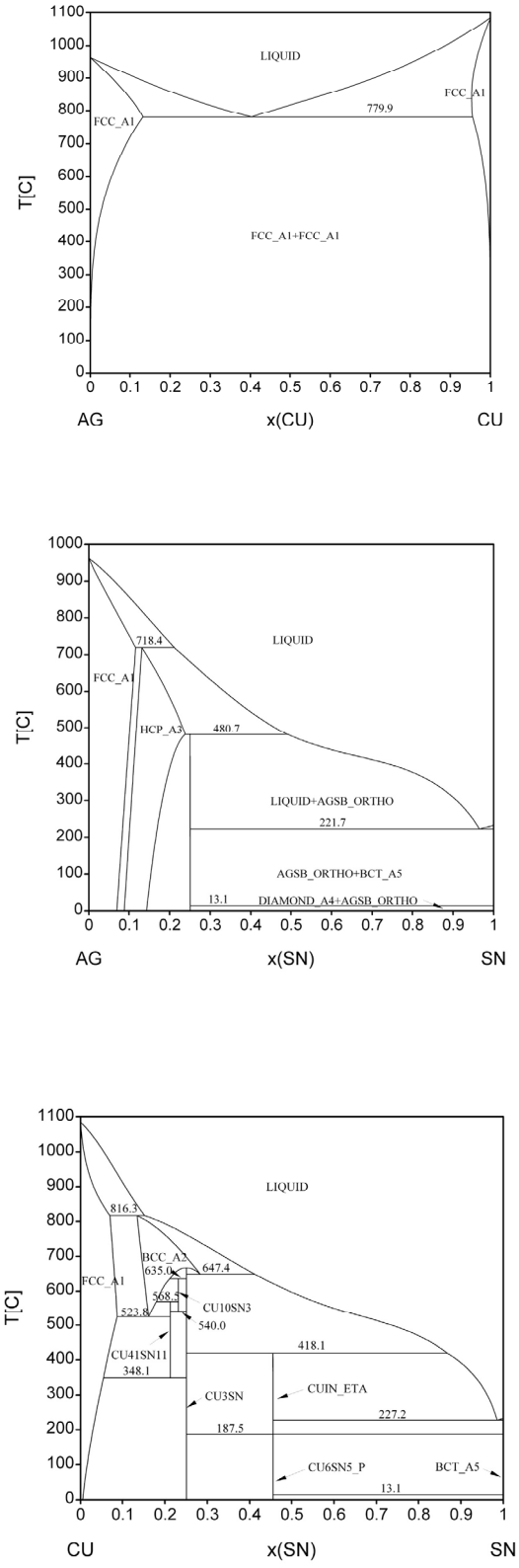

Fig 1. The calculated phase diagrams of the binary boundary systems: a) Ag-Cu system; b) Ag-Sn system; c) Cu-Sn system

The high temperature modification of the Cu_6Sn_5 phase (thermodynamically stable above 187.5 ^oC) in the Cu-Sn binary system was named as CUIN_ETA phase in the thermodynamic database. The reason for the selection of this name is complete solubility of this phase with corresponding phase from the Cu-In binary system, determined during the experimental investigation of ternary Cu-In-Sn system **[16]**. The crystallographic similarity of these two phases from different binary systems required their unique name and thermodynamic model for the accurate calculation of phase equilibria in multicomponent systems. For the same reasons Ag-Sn binary system include phase with the thermodynamic database name AGSB_ORTHO.

4. Results and discussion

Based on thermodynamic parameter values from [2] the liquidus surface of the Ag-Cu-Sn ternary system is calculated and plotted in Fig. 2. Six invariant reactions involving liquid phase and eight primary crystallization regions (Fcc_A1 (Cu based solution), Fcc_A1 (Ag based solution) HCP_A3, AGSB_ORTHO, BCT_A5, CUIN_ETA, CU3SN, BCC_A2) are observed in this ternary system.

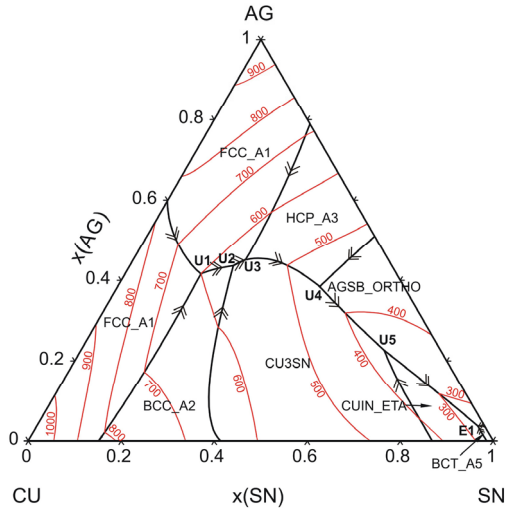

Fig. 2. The calculated liquidus surface of the Ag-Cu-Sn ternary system.

The calculated temperatures of ternary invariant reactions involving liquid phase and the compositions of the corresponding phases are listed in Table 2.

Table 2. Calculated invariant reactions involvig liquid phase in the Ag-Cu-Sn ternary system.

T/ °C Reaction	Type	Phase	Composition	
			xAg	xCu
600.2 LIQUID + FCC_A1 -> BCC_A2 + FCC_A1	U_1	LIQUID	0.415	0.422
		FCC_A1	0.012	0.914
		BCC_A2	0.028	0.821
		FCC_A1	0.896	0.039
560.7 LIQUID + BCC_A2 -> FCC_A1 + CU3SN	U_2	LIQUID	0.436	0.342
		BCC_A2	0.033	0.769
		FCC_A1	0.874	0.022
		CU3SN	0.000	0.750
552.2 LIQUID + FCC_A1 -> CU3SN + HCP_A3	U_3	LIQUID	0.450	0.308
		FCC_A1	0.865	0.019
		CU3SN	0.000	0.750
		HCP_A3	0.857	0.011
441.0 LIQUID + HCP_A3 -> CU3SN + AGSB_ORTHO	U_4	LIQUID	0.383	0.182
		HCP_A3	0.780	0.002
		CU3SN	0.000	0.750
		AGSB_ORTHO	0.750	0.000
349.5 LIQUID + CU3SN -> AGSB_ORTHO + CUIN_ETA	U_5	LIQUID	0.225	0.122
		CU3SN	0.000	0.750
		AGSB_ORTHO	0.750	0.000
		CUIN_ETA	0.000	0.545
217.5 LIQUID -> AGSB_ORTHO + CUIN_ETA + BCT_A5	E1	LIQUID	0.036	0.016
		AGSB_ORTHO	0.750	0.000
		CUIN_ETA	0.000	0.545
		BCT_A5	0.001	0.000

In order to compare experimental results with calculation three vertical sections with the constant molar ratios of Ag/Cu=1, Ag/Sn=1 and Cu/Sn=1, corresponding to the compositions of the prepared samples, are calculated. Phase diagrams with phase transition temperatures from the present DTA measurements are plotted in Fig. 3 (a)–(c). The calculated vertical sections are in good agreement with experimental results.

The curves of thermal analysis were recorded during heating of samples. For the DTA peak related to calculated invariant reaction, the temperature of extrapolated onset was used instead of peak temperature. For all other phase transitions the peak temperature was accepted. For the liquidus temperature, the temperature of the last peak on heating was validated. The overall results of DTA measurements are shown in Table 3.

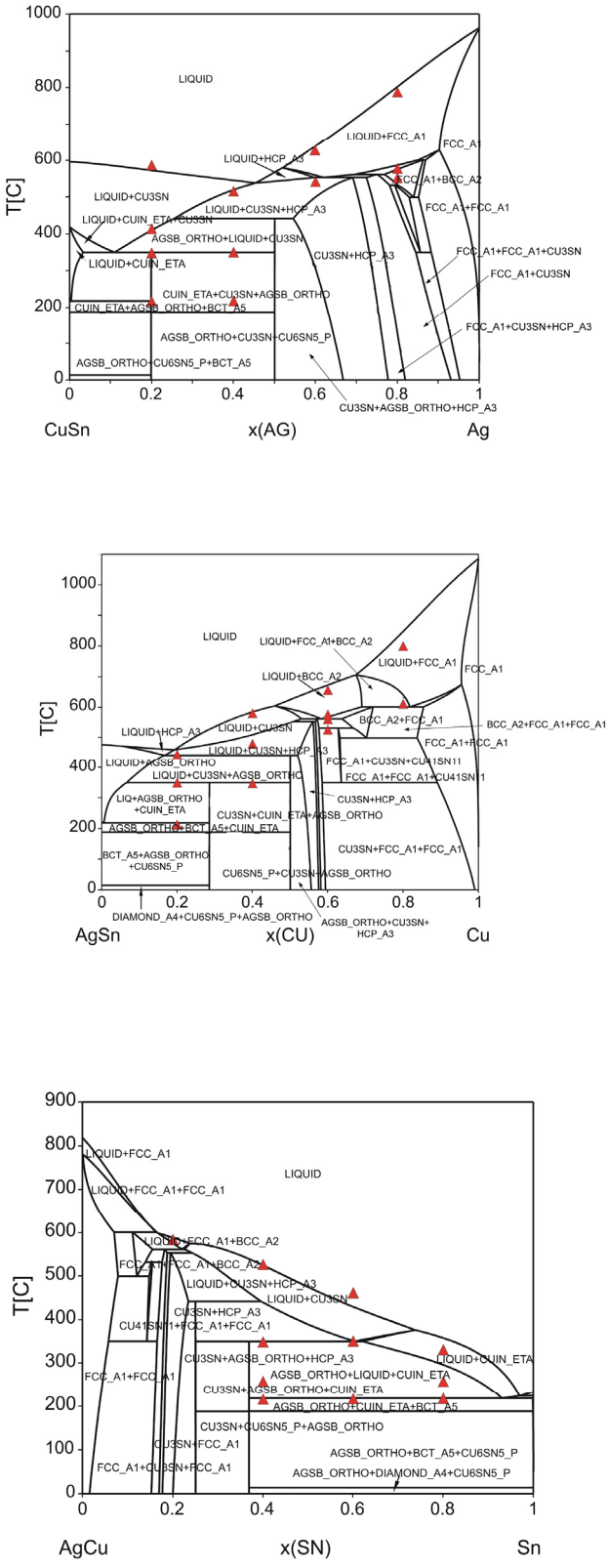

Fig. 3. Calculated vertical sections of the Ag-Cu-Sn ternary system compared with DTA results (triangle) from the present study: a) Cu:Sn=1, b) Ag:Sn=1, c) Ag:Cu=1

Table 3. DTA results for the investigated alloys of the Ag-Cu-Sn ternary system.

Sample composition [at.%]	Phase transition temperature [°C]		
	Invariant reaction	Other transition	Liquidus
$Ag_{20}Cu_{40}Sn_{40}$	217, 348	413	586
$Ag_{40}Cu_{30}Sn_{30}$	218, 350		515
$Ag_{60}Cu_{20}Sn_{20}$		541	625
$Ag_{80}Cu_{10}Sn_{10}$		551, 577	787
$Ag_{40}Cu_{20}Sn_{40}$	214, 349		444
$Ag_{30}Cu_{40}Sn_{30}$	347	479	579
$Ag_{20}Cu_{60}Sn_{20}$		525, 560, 575	655
$Ag_{10}Cu_{80}Sn_{10}$		610	799
$Ag_{40}Cu_{40}Sn_{20}$			583
$Ag_{30}Cu_{30}Sn_{40}$	215, 348	257	526
$Ag_{20}Cu_{20}Sn_{60}$	216	350	461
$Ag_{10}Cu_{10}Sn_{80}$	217	257	330

Fig. 4 shows example of DTA heating curves for some of investigated samples.

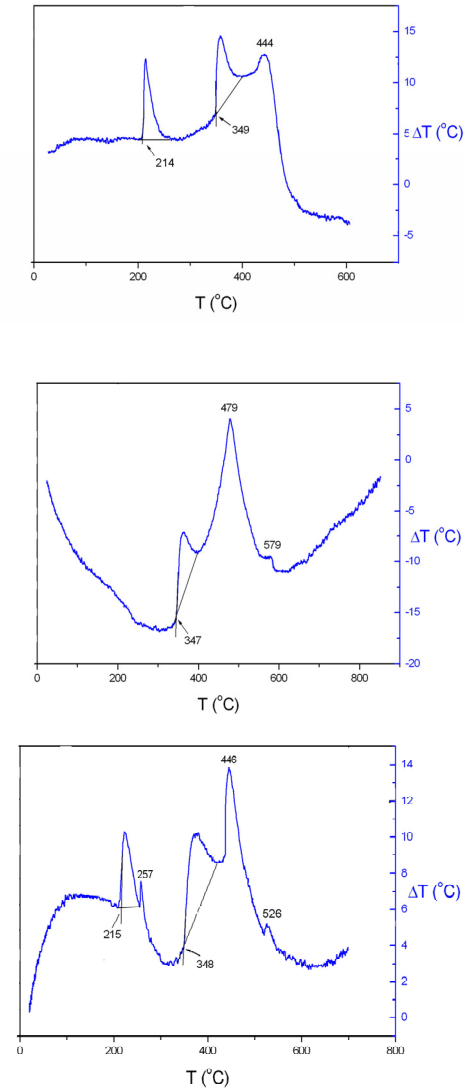

Fig. 4. Example of DTA curve with the determined phase transition temperatures for: a) $Ag_{40}Cu_{20}Sn_{40}$ alloy; b) $Ag_{30}Cu_{40}Sn_{30}$ alloy; c) $Ag_{30}Cu_{30}Sn_{40}$ alloy

Thermal analysis results of investigated samples given in the Table 3 indicate good mutual agreement with the calculated temperatures of two invariant reactions: ternary eutectic reactions at 217.5 °C and quasi-peritectic reaction at 349.5 °C. From Fig. 3 (a)–(c) one can observe that the calculated liquidus surface also show agreement with experimentally measured liquidus temperatures.

5. Conclusion

Thermal behavior of some alloys of the Ag-Cu-Sn ternary systems was investigated using thermal analysis. Twelve samples with the compositions along three vertical sections with Ag/Cu=1, Ag/Sn=1 and Cu/Sn=1 were prepared and measured by DTA. Experimentally determined temperatures of phase transitions were compared with calculated phase diagram of investigated ternary system. The liquidus surface and invariant reactions of the Ag-Cu-Sn ternary system were calculated using optimized thermodynamic parameters included in the COST 531 database. Six invariant reactions in total were calculated: five ternary quasi-peritectic reactions and one ternary eutectic reaction. Our experimental results point to the existence of phase transition reaction at temperature close to 217.5 °C which matched with calculated temperature of ternary eutectic reaction. Also, in majority of investigated samples marked peak with extrapolated onset temperature corresponding to calculated quasi-peritectic reaction at 349.5 °C was identified. For the majority of investigated samples experimentally determined liquidus temperatures are in agreement with calculation.

Acknowledgement

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