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EXPERIMENTAL STUDY OF PHASE EQUILIBRIA IN THE SILVER-COPPER-INDIUM ALLOYS

DOŚWIADCZALNE WYZNACZANIE RÓWNOWAG FAZOWYCH W STOPACH SREBRO-MIEDŹ-IND

The brief thermodynamic characteristic of binary subsystems were given, and phase diagrams presented. Then cross-section of ternary system Ag-Cu-In was calculated along the constant Cu/In ratio equal 1, using binary formalism. Considerable discrepancies were observed between calculation results and the known informations about thermodynamic behaviour of the liquid alloys. To explain it, this study was undertaken, employing two experimental techniques: differential thermal analysis, DTA, and differential scanning calorimetry, DSC. Three cross sections were investigated for constant Cu/In ratio equal 3, 1 and 1/3, with silver content varying from 10 at.% to 90 at.%, every 10%. Results are presented in tables and figures, exhibiting two different trends: 1) good agreement of experiment and calculations for higher Ag content (>60%), 2) considerable discrepancies between experiment and calculations for lower silver content, especially for the cross-section Cu/In = 1.

Results of both experimental techniques agree well each other.

Experimental data obtained in this work are to be used for thermodynamic modelling and phase diagram calculations of the system under accord by CALPHAD approach.

Na wstępie przedstawiono wykresy fazowe dwuskładnikowych stopów składowych: Ag-Cu, Ag-In i Cu-In, podając ich krótką charakterystykę termodynamiczną. Następnie obliczono przekrój poprzeczny układu trójskładnikowego Ag-Cu-In wzdłuż linii stałego stosunku zawartości Cu/In, równego 1. Wyniki obliczeń pozostają w znacznej rozbieżności z uzyskanymi już wcześniej informacjami o charakterze termodynamicznym stopów trójskładnikowych. Dla wyjaśnienia tych rozbieżności podjęto niniejsze badania przy zastosowaniu dwóch technik eksperymentu: różnicowej analizy termicznej, DTA, i różnicowej mikrokalorimetrii skaningowej, DSC. Zbadano stopy o składach leżących wzdłuż trzech linii stałej zawartości Cu/In, równej: 3, 1 i 1/3, oraz przy zawartości srebra zmieniającej się od 10% at. do 90% at., co 10%. Wyniki tabeli przedstawiono w tabelach i na wykresach. Uzyskane rezultaty wykazują dwojaką tendencję: 1) dobrą zgodność z wynikami obliczeń dla stopów o wysokiej zawartości srebra (>60%); 2) znaczne rozbieżności z wynikami obliczeń dla stopów o niższej zawartości srebra, największe dla przekroju Cu/In = 1.

Zaobserwowano również dobrą zgodność wyników pochodzących z obydwu zastosowanych metod eksperymentu: DTA i DSC.

Dane eksperymentalne uzyskane w niniejszej pracy będą zastosowane wraz z innymi informacjami do obliczenia diagramu fazowego układu Ag-Cu-In metodą CALPHAD.

1. Introduction

Silver-copper-indium alloys are regarded as one of the possible materials for lead-free solders. Information about its constitution are scarce and contradictory, as stated by Petzow and Effenberg [1]. Thermodynamic properties of the liquid phase has been not known so far. Most recently activities and heats of mixing were determined in the liquid Ag-Cu-In alloys by emf technique and drop calorimetry, respectively by Wierzbicka et. al. [2]. The last information are the good basis to

start thermodynamic modelling of the system of interest, Zabdyr et. al. [3].

2. Binary prediction

Ternary system Ag-Cu-In consists of three binary subsystems: Ag-Cu, Ag-In and Cu-In. Silver-copper is the simple eutectic system with two terminal solid solutions on both sides, as can be seen in Fig. 1 and with moderately positive heat of mixing in the liquid phase, as reported by Hayes et. al. [5].

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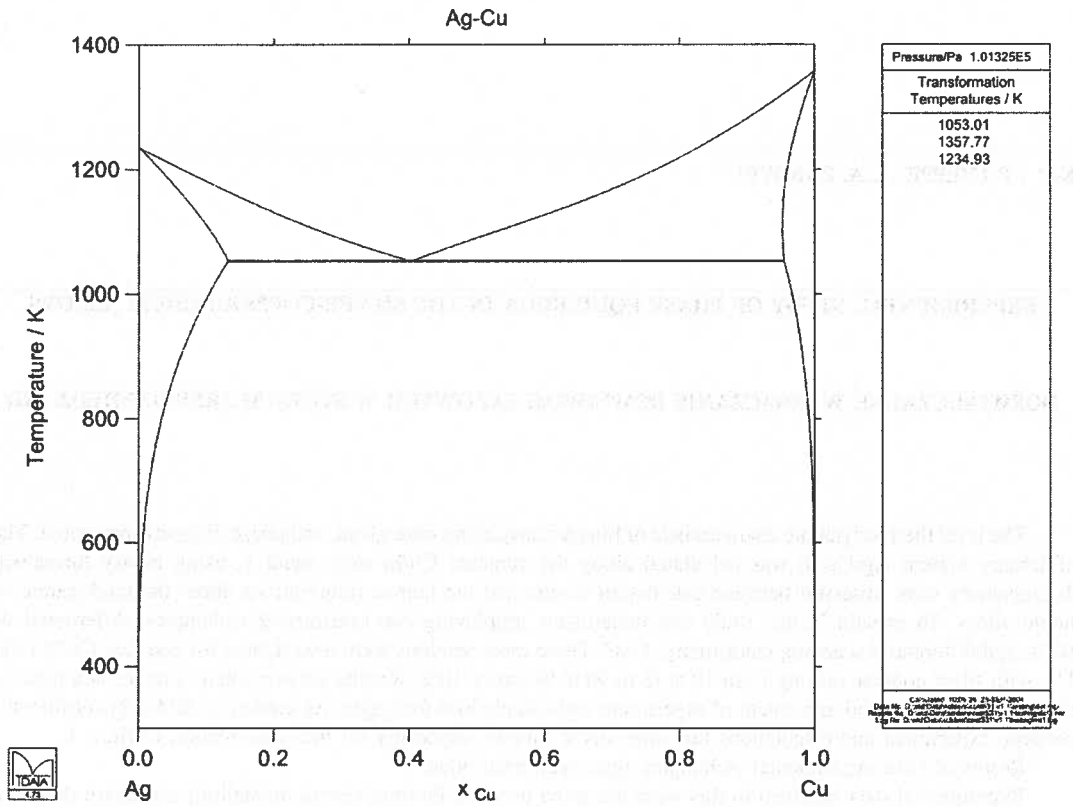


Fig. 1. Ag-Cu phase diagram taken from COST 531 database [4]

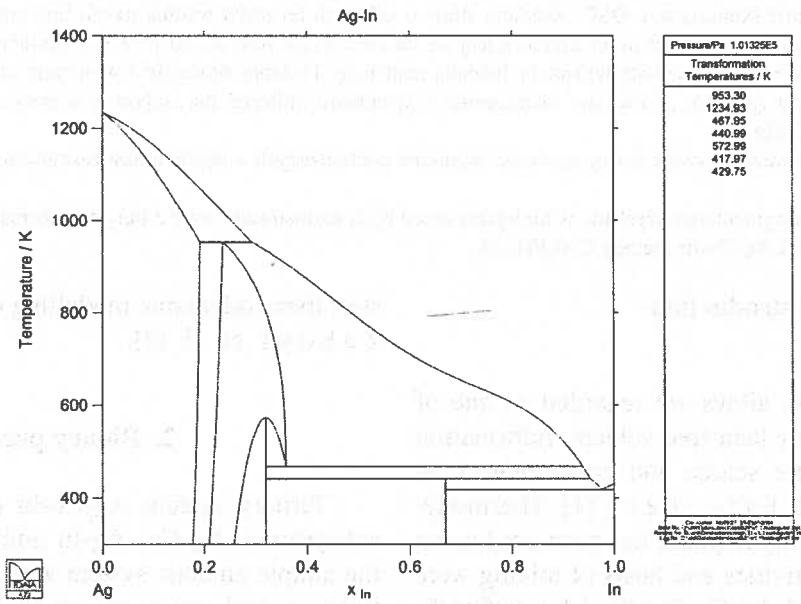


Fig. 2. Ag-In phase diagram [4]

Silver-Indium system is more complicated, with tendency to formation of a couple of intermetallic phases in the solid state, and negative deviation from ideality in the liquid phase.

The Ag-In phase diagram is presented in Fig. 2.

Finally, copper-indium system is similar in its thermodynamic nature to Ag-In, forming a series of intermetallic phases, as seen in Fig. 3.

Combination of those three subsystems should give the predominance of the negative deviation from the ideality in the liquid ternary phase, and the ability for intermediate solid phases formation.

It is usual practice to employ so-called binary formalism to predict thermodynamic properties of ternary system in the case when no information is available about ternary thermodynamics, following the relation below:

$$G_{ABC} = X_A X_B G_{AB} + X_A X_C G_{AC} + X_B X_C G_{BC}, \quad (1)$$

where: X_A , X_B , X_C – molar fractions of component A, B and C, respectively of ternary system ABC; G_{ABC} – predicted thermodynamic property of ternary system ABC; G_{AB} , G_{AC} , G_{BC} – thermodynamic properties of the respective binary subsystems AB, AC and BC.

It should be noted, that this kind of prediction does not take into account *ternary interactions* in the system, and property itself is to the some extent the *average* of binary properties.

In the case of Ag-Cu-In system binary interaction parameters were taken for Ag-Cu, Ag-In and Cu-In system from database [4], and phase diagram calculations were carried out for the cross-section of the system for the Cu:In constant content ratio equal to 1. Resulting isopleth is shown in Fig. 4, below.

The result of calculations is unexpected: huge miscibility gap appears in the central region of the liquid phase, revealing strong positive deviation from ideality. This is in contradiction to our primary prediction on the predominance of negative deviations coming from the thermodynamic nature of both Ag-In and Cu-In binaries. This is also in contradiction to the results of our investigations in ternary system [2]: as well indium activities in ternary liquid display negative deviation from Raoult's rule, as heats of formations are along this cross-section negative. To explain this problem experimental determination of liquidus surface in ternary Ag-Cu-In is needed.

3. Determination of the liquidus surface in ternary Ag-Cu-In system

Experiments were carried out along of three cross-sections of Cu:In constant ratio, equal to: 3, 1 and

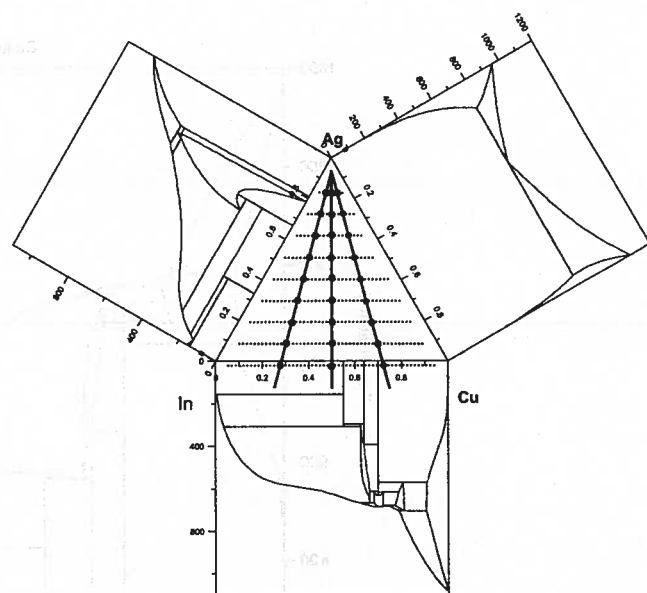


Fig. 5. Ternary sample compositions shown along with the binary subsystem phase diagrams

1/3, and for silver content varying from 10 to 100 at.%, every 10%; scheme of sample compositions along with binary subsystem phase diagrams is shown in Fig. 5.

The differential thermal analysis, DTA, was employed to determine solid-liquid (or liquid-liquid in case of miscibility gap occurrence) equilibria in the system under interest.

3.1. Sample preparation

Pure metals (at least 99.99) were weighted and encapsulated in the quartz ampules under vacuum. The samples were melted in the induction furnace. This method allows to obtain the melting temperature of the alloy in very short time and the most important thing is that samples were mixed during the melting process, what guarantees the homogeneity of the samples in the whole volume. The total mass of the samples was about 2 g.

3.2. Experimental procedure

The heat flux type DSC and the DTA (Du Pont Instruments DSC 910 and DTA1600, respectively) were used in this study to measure liquidus temperatures for Ag-Cu-In alloys in three cross-section of Cu:In constant ratio, equal to: 3, 1 and 1/3 (Fig. 5). The curves were recorded during the heating and cooling process. Both the cooling and heating rate was 10°C/min. The measurements were carried out under argon gas atmosphere to prevent oxidation. Total mass of the samples used were about 15–20 mg for DTA and 40–60 mg for DSC measurements, and small silicon crucibles were applied both in DTA and DSC experiments. When the phase

transformation started, endo- or exothermic heat effect was generated in the curve. The liquidus temperature was determined at the peak temperature of the heat effect on heating and the onset temperature of the effect on cooling, marked as T_{\min} heating and T_{onset} for cooling respectively (Fig. 6).

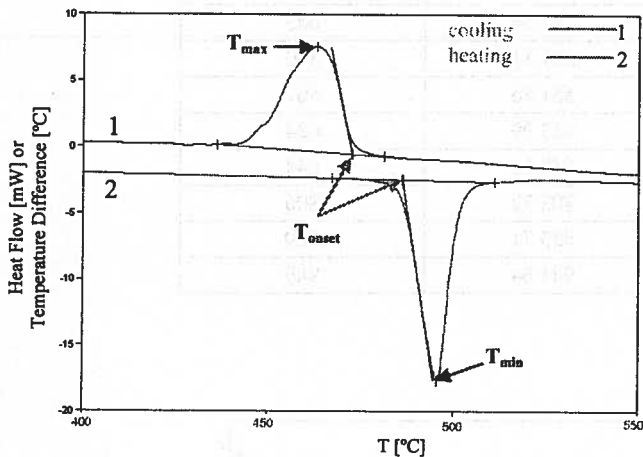


Fig. 6. Determination the characteristic temperatures of the heat effect in heating and cooling curve in DTA and DSC method

The DTA measurements were done for every compositions of the Ag-Cu-In alloys (Fig. 5) but the DSC only for alloys melting below 700°C, the temperature limit of the DSC analyzer.

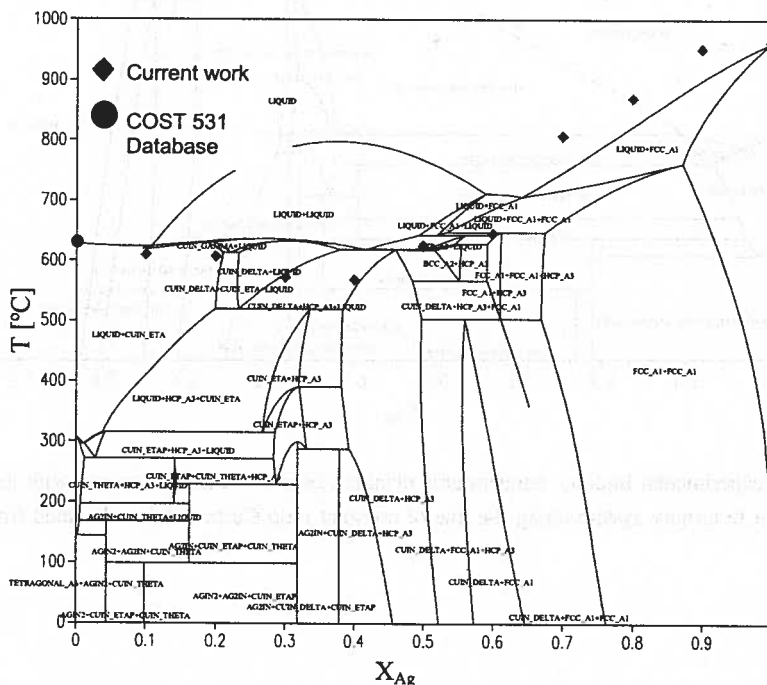


Fig. 7. Comparison of the experimental liquidus temperatures obtained from DTA measurements with the liquidus surface in the cross-section of the Ag-Cu-In ternary system along the line of constant ratio Cu:In = 1, calculated from the binary data only

3.3. Results

Experimental results were compared with the phase boundaries calculated using the binary thermodynamic data base.

As has been shown in figures 7 to 11, comparing measured and modelled liquidus temperatures, experimental temperature values of liquidus T_L for alloys of Ag molar fraction from 0.1 up to 0.6 and $X_{\text{Cu}}:X_{\text{In}} = 1:1$ (Fig. 7, 10), and for 0.1 to 0.5 for $X_{\text{Cu}}:X_{\text{In}} = 1:3$ and 3:1 (Fig. 8, 9, 11), are lower than calculated. The misfit results because ternary interactions were not taken into account. For Ag molar fractions higher than 0.5, T_L values are higher and for proportion of molar fractions $X_{\text{Cu}}:X_{\text{In}} = 1:3$ and 3:1, temperatures fits better to temperatures calculated from the binary system data. This results from the fact, that increasing Ag content in the systems decreases the influence of ternary interactions. In case of $X_{\text{Cu}}:X_{\text{In}} = 1:1$, changes of molar fractions ratio of each alloy component with increasing Ag amount are not significant, thus ternary interaction influence will be high for the whole concentration range.

The consequence of this fact is discrepancy between calculated and experimental liquidus temperature values, occurring for these alloys, for the whole Ag content range. The liquidus lines experimentally determined for three cross-sections have minimum values for the range of 0.3–0.4 Ag molar fraction. The minimum is neither sharp nor deep – is rather flat.

Experimental liquidus temperatures, obtained by DTA method for the $X_{Cu}:X_{In} = 1:1$ cross-section

X_{Ag}	Experimental temperatures			Liquidus temperatures
	heating		cooling	
	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_{min} [°C] ($\pm 2^\circ\text{C}$)	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_L [°C] ($\pm 2^\circ\text{C}$)
0.0				631 [4]
0.1	557.42	607.85	598.37	608
0.2	562.22	605.17	595.34	605
0.3	561.54	570.13	551.11	570
0.4	551.62	566.97	551.86	567
0.5	559.85	623.53	633.99	624
0.6	637.65	643.81	640.16	644
0.7	788.09	806.16	802.72	806
0.8	865.98	868.69	885.71	869
0.9	936.61	949.39	941.64	949

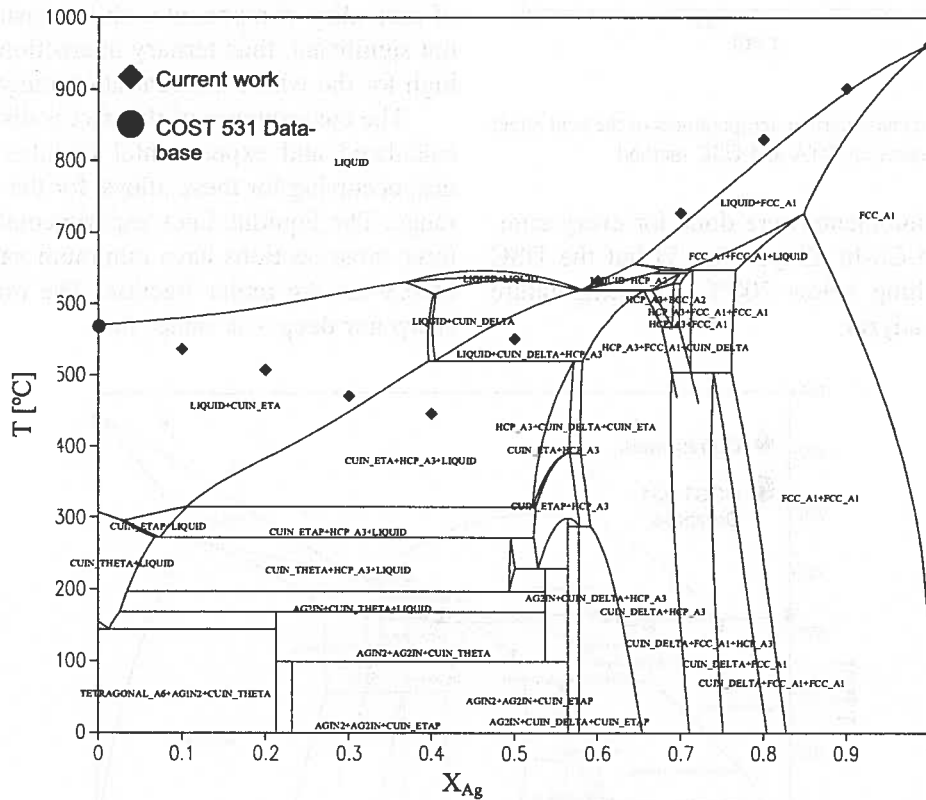


Fig. 8. Comparison of the experimental liquidus temperatures obtained from DTA measurements with the liquidus surface on the cross-section of the Ag-Cu-In ternary system along the line of constant ratio Cu:In = 1:3, calculated from the binary data only

TABLE 3

Experimental liquidus temperatures, obtained by DTA method for the $X_{Cu}:X_{In} = 3:1$ cross-section

X_{Ag}	Experimental temperatures			Liquidus temperatures T_L [°C] ($\pm 2^\circ\text{C}$)
	heating		cooling	
	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_{min} [°C] ($\pm 2^\circ\text{C}$)	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	
0.0				689 [4]
0.1	603.73	653.49	632.40	653
0.2	584.98	612.14	599.66	612
0.3	584.19	593.80	593.41	594
0.4	632.26	653.47	694.55	653
0.5	656.56	695.07	702.39	695
0.6	726.17	753.31	753.54	753
0.7	750.90	805.95	805.42	806
0.8	788.79	850.18	855.27	850
0.9	866.98	905.40	895.71	905

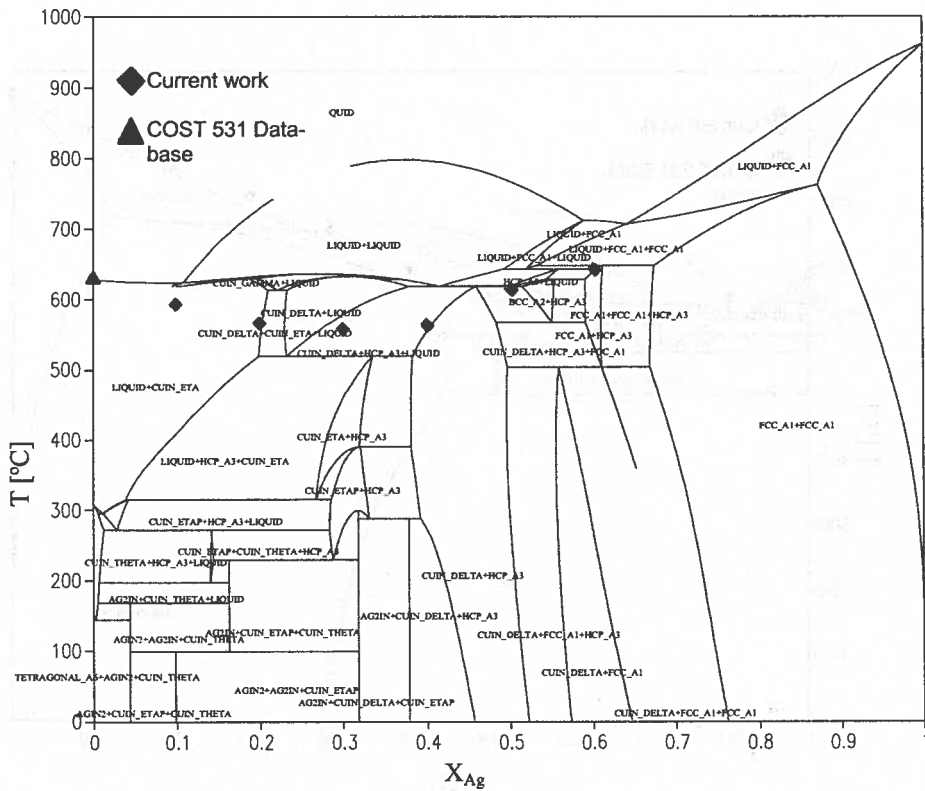


Fig. 10. Comparison of the experimental liquidus temperatures obtained from DSC measurements with the liquidus surface on the cross-section of the Ag-Cu-In ternary system along the line of $Cu:In = 1$ constant ratio, calculated from binary data only

Experimental liquidus temperatures, obtained by DSC method for the $X_{Cu}:X_{In} = 1:1$ cross-section

TABLE 4

X_{Ag}	Experimental temperatures				Liquidus temperatures T_L [°C] ($\pm 2^\circ\text{C}$)
	heating		cooling		
	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_{min} [°C] ($\pm 2^\circ\text{C}$)	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_{min} [°C] ($\pm 2^\circ\text{C}$)	
0.0					631 [4]
0.1	546.72	594.64	583.73	578.01	595
0.2	523.51	566.97	544.87	539.73	567
0.3	516.00	560.59	549.32	543.01	561
0.4	552.74	565.41	547.00	539.19	565
0.5	564.36	615.57	608.27	604.02	616
0.6	637.08	644.29	686.27	681.13	644

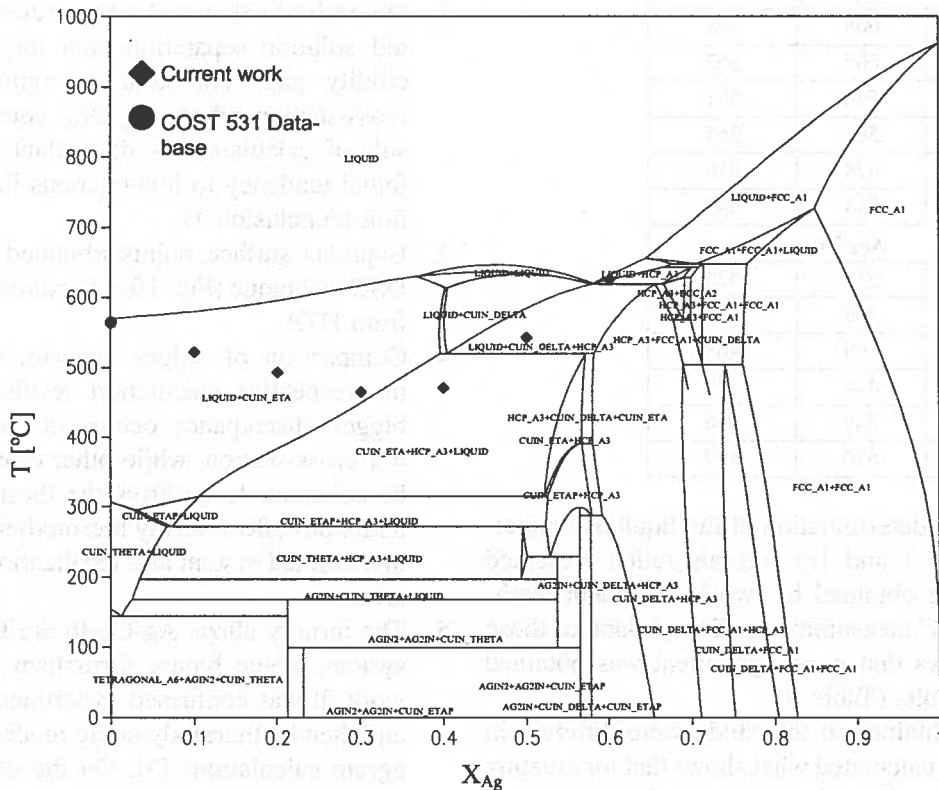


Fig. 11. Comparison of the experimental liquidus temperatures obtained from DSC measurements with the liquidus surface on the cross-section of the Ag-Cu-In ternary system along the $Cu:In = 1:3$ line of constant ratio, calculated from binary data only

Experimental liquidus temperatures, obtained by DSC method for the $X_{Cu}:X_{In} = 1:3$ cross-section

X_{Ag}	Experimental temperatures				Liquidus temperatures T_L [°C] ($\pm 2^\circ\text{C}$)
	heating		cooling		
	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_{min} [°C] ($\pm 2^\circ\text{C}$)	T_{onset} [°C] ($\pm 2^\circ\text{C}$)	T_{min} [°C] ($\pm 2^\circ\text{C}$)	
0.0					567 [4]
0.1	451.56	525.13	517.89	510.77	525
0.2	431.98	496.52	485.26	480.37	497
0.3	444.72	468.10	415.06	446.48	468
0.4	457.85	473.31	453.85	450.17	473
0.5	490.41	546.14	539.25	535.36	546
0.6	602.99	628.54	616.95	614.14	629

TABLE 6
Comparison of the liquidus temperature obtained by DTA
and DSC methods

X_{Ag}	Liquidus temperatures T_L [°C] ($\pm 2^\circ\text{C}$)	
	DTA	DSC
$X_{Cu}:X_{In} = 1:1$		
0.1	608	595
0.2	605	567
0.3	570	561
0.4	567	565
0.5	624	616
0.6	644	644
$X_{Cu}:X_{In} = 1:3$		
0.1	534	525
0.2	505	497
0.3	469	468
0.4	444	473
0.5	549	546
0.6	630	629

The results of determination of the liquidus temperatures for $Cu:In = 1$ and $1:3$ constant ratios presented in this paper were obtained by two independent methods: DTA and DSC measurements. Comparison of those temperatures shows that good agreement was obtained between those results (Table 6).

The results obtained in this study were different in comparison to the calculated what shows that for creating a corrected ternary alloy phase diagram it is necessary to have a good thermodynamic data base for the ternary system. The data for binaries are not sufficient.

4. Conclusions

1. Experimentally determined liquidus surface points were compared to relevant phase boundary lines ob-

tained from calculations (Fig. 7–9). One can see double tendency: conformity of experimental points with calculated line for high Ag content ($X_{Ag} = 0.6 - 0.1$) and for $X_{Ag} = 0$ (liquidus $Cu-In$ calculated from the COST 531 data base) and some misfit between experimental and calculated values for central part of Ag content range.

2. On each of calculated cross-section one can see liquid solution separation area for two phases, miscibility gap. The area is significant for central cross-section where $X_{Cu}:X_{In}$ equals to 1. This result of calculation is discordant to experimentally found tendency to homogenous liquid phase formation (conclusion 1).
3. Liquidus surface points obtained independently by DSC technique (Fig. 10–11) confirm results obtained from DTA.
4. Comparison of values experimentally obtained to the respective calculation results, shows that the biggest discrepancy occurs in the central, $X_{Cu}:X_{In} = 1$ cross-section, while other cross-sections look to be coherent. It confirms the thesis, that ternary interactions affect mostly thermodynamic properties of investigated system and localization of phase boundaries.
5. The ternary alloys $Ag-Cu-In$ are the example of the system, where binary formalism prediction fails to work. It was confirmed experimentally in this work, and then by thermodynamic modelling and phase diagram calculations [3]. On the other hand, there is number of multicomponent alloy systems, where binary formalism works well, giving the reliable approximation of the properties given, and avoiding the long-lasting and costly experimental work. Therefore, there is a good practice to check a binary prediction, before starting any other investigations of thermodynamic properties of multicomponent system.

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