Phase equilibria of the ternary Ag – Cu – In system at 300 ℃

Md. Azizul Haque, and Wojciech Gierlotka

***Abstract*—**The soldering technology is a key-point for electronic industry. Nowadays, only lead-free solders can be used. Among many of them, there is the ternary Ag – Cu – In system. Its isothermal section at 300˚C was determined based on the phase equilibria experiment along with the electron probe microanalysis and the X-ray powder diffraction method. Obtained results revealed significant solubility of a third element in all binary intermetallic compounds. Moreover, the established phase diagram partially confirmed earlier researches.

***Keywords*—**Lead-free solders, phase equilibria, isothermal section, Ag-Cu-In alloys.

I. Introduction

THE soldering technology is a key-point for electronic industry. According to RoHS directive [1], only the lead free solders can be used, what means that a new alloy should replace the traditional Sn37Pb solder. Among many of proposed materials, there is a quaternary Ag – Cu – In – Sn alloy [2]. One of its constituent ternary Ag – Cu – In system was already described in literature [3, 4]; however, the papers show inconsistency. Therefore, the main goal of this work was to check phase equilibria in the ternary Ag – Cu – In system.

II. Literature review

Thermodynamic properties and phase equilibrium data of the constituent binary systems are well known and widely available in literature [5]. The Ag – Cu system is a simple eutectic with 3 phases: liquid, FCC#Ag and FCC#Cu. The binary Ag – In includes: liquid, FCC#Ag and HCP_ζ, Tetragonal(In) and two intermetallic compounds Ag2In and AgIn2. The third binary, Cu – In is quite complicated system that includes: FCC_A1#Cu, Tetragonal_A6(In), BCC_A2, CUIN_δ, CUIN_γ, CUIN_η, CUIN_θ and liquid phases.

The phase equilibria of the Ag – Cu – In system was described by Gebhardt and Dreher [6] by using DTA and metallographic analysis. Later, Woychik and Massalski [3] presented the phase relationships in the ternary Ag-Cu-In system and determined the isothermal section at 506˚C and 676˚C. They [3] showed that the γ phase exists as a continuous solution between Ag – In and Cu – In systems. On the other hand Bahrai et al. [4] determined two isothermal sections at 510˚C and 607˚C as well as 15 isoplethal sections by using X-ray powder diffraction (XRD), electron probe micro analysis (EPMA) and differential scanning calorimetry (DSC) methods. A number of inconsistencies were found between these two papers [3,4]. According to Woychik and Massalski [3] there is a continuity of γ phase from low temperature Ag2In to high temperature CUIN_ γ, while no continuous phase field was reported by Bahrai et al. [3]. Moreover, some ternary equilibria were determined in between different phases in both works[3,4]. The inconsistency between [3] and [4] was a motivation for this work.

III. Experiment

Ternary Ag-Cu-In alloys were prepared from the Ag shot (1-3mm in size and purity of 99.9999 %, AlfaAesar-A Johnson Matthey Company, 30 Bond Street Ward Hill, MA 01835) Cu shot (9mm in size and purity of 99.9999 %, AlfaAesar-A Johnson Matthey Company, 30 Bond Street Ward Hill, MA 01835), and In shot (3-5mm in size and purity of 99%, ALDRICH, Germany). Calculated amounts of pure metals were weighted with METTLER TOLEDO AX204 in order to obtain the samples of 1 g in total mass with high precision. After that, samples were encapsulated in a 8mm ID quartz tube with a 5×10^{-3} Torr vacuum pressure treatment to avoid any contamination by Oxygen or Air. The Sample capsules were placed in the furnace and heated slowly up to 1085°C and kept there for 7 days to ensure that all the elements were molten and the liquid became homogeneously mixed. The molten samples were shaken two times daily for better homogeneity. After being heat treated, the quartz tubes were taken out from the furnace and quenched in the water. The total mass losses of ingot observed during this procedure were less than 0.2% resulting in an accuracy of the nominal compositions within ±0.2 at. %. These quenched samples were used for phase equilibria study.

For the equilibration, the quenched samples were kept in the furnace at 300°C. The annealing time was 3 months that the alloys would take to reach phase equilibrium. After 3 months of reaction time, the samples were removed from the furnace and quenched in water. The equilibrated samples were cut into halves in 1:2 ratios. One part was ground into powders for X-ray diffraction (XRD-6000, Shimadzu LabX) analysis and the other part was mounted by Epo-Fix resin. The mounted samples surfaces were polished by silicon carbide sandpapers

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of different grades and finally polished with 0.3 micrometers alumina (Al2O3) slurry to prepare samples for metallographic examinations. Preliminary microstructures of the phases were examined by the Optical Microscopy (OM-Nikon, Japan) and Backscattered electron image (BEI). Compositional analysis of phases was done using EPMA (JXA–8200M, JEOL) operated at 15 kV.

The detailed information about nominal compositions of the samples and determined phases is given in Table I.

TABLE I
NOMINAL COMPOSITION OF SAMPLES.

Alloy	Nominal Composition			Equilibrium Phases
	Ag (at. %)	Cu(at. %)	In (at. %)	
1	10	80	10	Ag+ $\delta(Cu_7In_3)$ + Cu
2	20	70	10	Ag + $\delta(Cu_7In_3)$ + Cu
3	30	60	10	Ag + $\delta(Cu_7In_3)$ + Cu
4	40	50	10	Ag + $\delta(Cu_7In_3)$ + Cu
5	50	40	10	Ag + Cu
6	60	30	10	Ag+ Cu
7	70	20	10	Ag + Cu
8	80	10	10	Ag
9	10	70	20	Ag + $\delta(Cu_7In_3)$ + Cu
10	20	60	20	Ag+ $\delta(Cu_7In_3)$ + Cu
11	30	50	20	Ag + $\delta(Cu_7In_3)$ + Cu
12	40	40	20	Ag + $\delta(Cu_7In_3)$ + Cu
13	50	30	20	Ag + $\delta(Cu_7In_3)$ + Cu
14	60	20	20	Ag+ $\delta(Cu_7In_3)$
15	70	10	20	Ag+ $\delta(Cu_7In_3)$
16	10	60	30	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
17	20	50	30	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
18	30	40	30	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
19	40	30	30	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
20	50	20	30	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
21	60	10	30	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
22	10	50	40	η + $\gamma(Ag_2In)$ + $Cu_{11}In_9$
23	20	40	40	ζ(HCP) + $Cu_{11}In_9$
24	30	30	40	ζ(HCP) + $Cu_{11}In_9$+L
25	40	20	40	ζ(HCP) + $Cu_{11}In_9$+L
26	50	10	40	ζ(HCP) + $Cu_{11}In_9$+L
27	10	40	50	ζ(HCP) + $Cu_{11}In_9$+L
28	20	30	50	ζ(HCP) + $Cu_{11}In_9$+L
29	30	20	50	ζ(HCP) + $Cu_{11}In_9$+L
30	40	10	50	ζ(HCP) + $Cu_{11}In_9$+L
31	20	49.3	30.7	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
32	30	38.6	31.4	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
33	40	28.3	31.7	$\delta(Cu_7In_3)$ + $\gamma(Ag_2In)$
34	50	17.6	32.4	$\delta(Cu_7In_3)$ + η
35	60	6.7	33.3	$\gamma(Ag_2In)$
36	70	5	25	Ag+ ζ(HCP)
37	60	15	25	Ag+ ζ(HCP)+ $\delta(Cu_7In_3)$

IV. RESULTS AND DISCUSSION

The phase compositions of examined alloys were quantitatively measured by EPMA and results are gathered in Table II.

TABLE II
EPMA ANALYSIS RESULTS.

Alloy	Phase Composition			Equilibrium Phases
	Ag (at %)	Cu (at%)	In (at %)	
1	2.1498	95.5254	2.3248	Cu
	5.1389	66.3435	28.5176	$\delta(Cu_7In_3)$
	48.1415	33.0569	18.8015	Ag
7	5.8236	92.3085	1.8679	Cu
	79.8929	9.5996	10.5075	Ag
9	3.5371	88.9882	7.4747	Cu
	3.7087	68.4002	27.8911	$\delta(Cu_7In_3)$
	31.5086	49.5944	18.897	Ag
10	7.3958	88.9761	3.6281	Cu
	5.5443	66.7072	27.7485	$\delta(Cu_7In_3)$
	71.6476	12.3902	15.9622	Ag
12	12.1492	83.1132	4.7376	Cu
	7.6329	63.4423	28.9249	$\delta(Cu_7In_3)$
	73.7279	9.5815	16.6906	Ag
14	4.0299	65.6315	30.3386	$\delta(Cu_7In_3)$
	80.2127	4.2972	15.4901	Ag
16	6.3128	63.6536	30.0336	$\delta(Cu_7In_3)$
	34.1968	34.6717	31.1316	ζ(HCP)
17	8.6398	60.7849	30.5754	$\delta(Cu_7In_3)$
	53.1892	19.0922	27.7187	ζ(HCP)
18	6.1664	62.8009	31.0327	$\delta(Cu_7In_3)$
	66.3795	6.3444	27.2762	ζ(HCP)
19	2.7041	67.0209	30.275	$\delta(Cu_7In_3)$
	63.4039	6.1665	30.4296	ζ(HCP)
21	4.0328	65.2329	30.7343	$\delta(Cu_7In_3)$
	64.072	5.3614	30.5666	ζ(HCP)
22	60.3587	8.2162	31.4251	$\gamma(Ag_2In)$
	6.3511	51.4088	42.2401	$Cu_{11}In_9$
	5.5955	56.8054	37.5991	η
23	62.6493	2.4222	34.9285	ζ(HCP)
	6.027	51.2486	42.7244	$Cu_{11}In_9$
25	6.2313	50.8376	42.9312	$Cu_{11}In_9$
	63.126	1.6173	35.2566	ζ(HCP)
	0	0	100	L
26	6.106	51.2975	42.5965	$Cu_{11}In_9$
	63.2097	1.7638	35.0265	ζ(HCP)
	0	0	100	L
29	63.174	1.7332	35.0928	ζ(HCP)
	6.0596	50.7766	43.1638	$Cu_{11}In_9$
	10.1625	19.9568	69.8807	L
30	63.289	1.486	35.225	ζ(HCP)
	6.0123	51.9949	41.9928	$Cu_{11}In_9$
	0.0736	0.11	99.8101	L
31	4.4125	64.5	31.0333	δ-(Cu_7In_3)
	52.6904	16.1	31.2075	Ag2In
32	5.4856	62.7	31.7954	δ-(Cu_7In_3)
	52.6055	15.3	32.0736	$\gamma(Ag_2In)$
34	7.58	55.9	36.5112	δ-(Cu_7In_3)
	53.0617	14.9	32.0198	η
35	60.2675	6.9	32.8071	$\gamma(Ag_2In)$
36	74.7799	6.3	18.8563	Ag
	66.3795	6.3	27.2762	ζ(HCP)
37	6.5992	62.3	31.0716	δ-(Cu7In3)
	75.254	6.3	18.363	Ag
	66.5684	6.0	27.3977	ζ(HCP)

The observed phases were also confirmed by XRD examination, which results are listed in Table III..

TABLE III
XRD ANALYSIS RESULTS.

Alloy	No. of Phases	Phases	2Theta	a(Å)	b(Å)	c(Å)
		FCC_A1#Ag	38	4.085		
		FCC_A1#Cu	43.36	3.615		
12	3	$\delta(Cu_7In_3)$	42.22	10.07	9.126	6.724
		$\delta(Cu_7In_3)$	42.38	10.07	9.126	6.724
18	2	$\zeta(Ag_3In)$	39.34	2.97		4.805
		$\zeta(Ag_3In)$	39.34	2.97		4.805
		$Cu_{11}In_9$	41.88	12.81	4.354	7.353
28	3	In	32.94	3.251		4.945
		$\delta(Cu_7In_3)$	34.33	10.07	9.126	6.724
31	2	$\gamma(Ag_2In)$	38.6	2.95		4.80
35	1	$\gamma(Ag_2In)$	38.6	2.95		4.80
		FCC_A1#Ag	44.6	4.085		
		$\delta(Cu_7In_3)$	42.22	10.07	9.126	6.724
37	2	$\zeta(Ag_3In)$	39.90	2.956		4.786

From the EPMA and XRD analysis 8 distinguishable phases were found: FCC#Ag, FCC#Cu, δ(Cu7In3), η, Cu11In9, ζ(Ag3In-HCP), γ(Ag2In) and L(In). All the phases exist in the constituent binary systems. The analysis revealed seven ternary regions: (FCC_A1#Ag + FCC_A1#Cu + δ(Cu7In3), FCC_A1#Ag + δ(Cu7In3) + ζ(Ag3In-HCP), δ(Cu7In3) + ζ(Ag3In-HCP) + γ(Ag2In), γ(Ag2In) + δ(Cu7In3) + η, γ(Ag2In) + Cu11In9) + η , γ(Ag2In) + Cu11In9) + ζ(Ag3In-HCP) and ζ(Ag3In-HCP) + Cu11In9 + L) and fourteen binary ones: FCC_A1#Ag + FCC_A1#Cu, FCC_A1#Ag + δ(Cu7In3), FCC_A1#Cu + δ(Cu7In3), FCC_A1#Ag + ζ(Ag3In-HCP), ζ(Ag3In-HCP) + γ(Ag2In), ζ(Ag3In-HCP) + δ(Cu7In3), γ(Ag2In) + δ(Cu7In3), δ(Cu7In3) + η, η + γ(Ag2In), γ(Ag2In) + Cu11In9, η + Cu11In9, ζ(Ag3In-HCP) + Cu11In9, Cu11In9 + L and ζ(Ag3In-HCP) + L.

The detailed analysis of some samples is shown below. Figure 2 shows the BEI image of Alloy 12 with nominal composition of Ag - 40 at% Cu, -20 at% In, as shown in Table 1. Three different phases were observed in equilibrium. The compositions of dark, gray and bright phases are Ag-90 at %, Cu-3 at % In; Ag-66 at % Cu, -28 at % In; Ag-12 at % Cu-16 at %In, respectively as summarized in Table 2. The dark and bright phases were recognized as FCC_A1 phase region, while gray phase was δ(Cu7In3). This alloy was also selected for XRD analysis to ensure the phases found by the EPMA analysis. Figure 3 shows the diffraction pattern of the examined sample. It can be found that the diffraction results are in good agreement with compositional analysis, what confirmed three phase region: FCC_A1#Ag + FCC_A1#Cu + δ(Cu7In3).

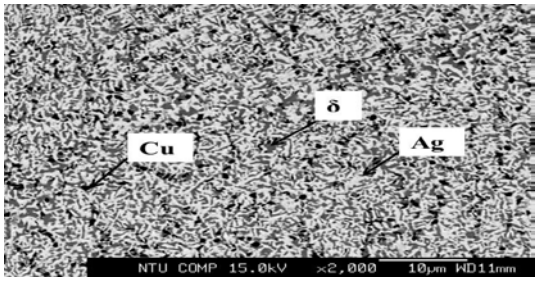

Fig. 1 BEI micrograph of Sample 12.

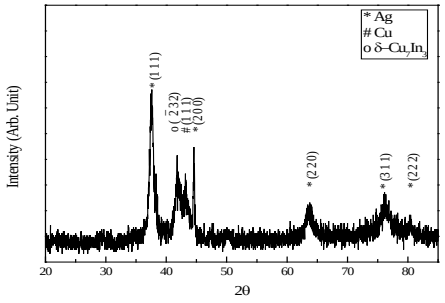

Fig .2 XRD diffraction pattern of Sample 12.

Fig. 3 shows the BEI micrograph of Alloy 19. The nominal composition of this alloy was Ag-30 at % Cu, -30 at % In. In this micrograph one can find larger phase grains than in Alloys 12. From the EPMA analysis, the composition of dark phase was Ag-67 at % Cu,-30 at % In and the bright phase was Ag-6 at % Cu, -31 at % In. According to the binary phase diagram, the dark phase represents ζ(HCP) phase and bright one represents δ(Cu7In3) phase. Other alloys like: 16(Ag-60 at % Cu-30 at % In), 17(Ag-50 at % Cu-30 at % In), 18(Ag-40 at % Cu-30 at % In), 20(Ag-20 at % Cu-30 at % In) and 21(Ag-10 at % Cu-30 at % In) showed exactly the same result.

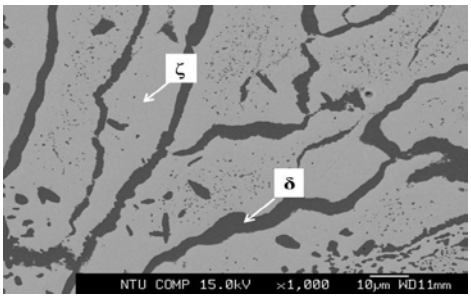

Fig 3. BEI micrograph of Sample 19.

Alloy18 (Ag-40 at % Cu,-30 at % In) was selected from this binary region for XRD analysis to confirm the phases found by EPMA analysis. Result of the X-ray analysis is shown in Figure 4. It can be seen that EPMA and XRD results match each other.

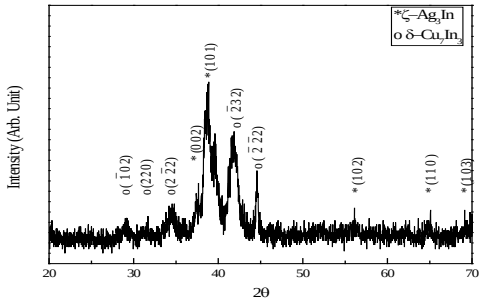

Fig 4. XRD diffraction pattern of Sample 19.

Figure 5 shows the BEI micrograph of alloy 26 (Ag–10 at. % Cu, –40 at.% In). Three different phases were observed by EPMA analysis. The bright phase was indicated as ζ(HCP) phase, blackish gray as Cu11In9 phase and a phase adjacent to the black spot as liquid (In) phase. The individual compositions of these phases are summarized in Table 2. In Fig. 5 can be find big void spaces. Due to the high In concentration the alloy posed high brittleness behavior and the voids were created during polishing procedure. Another four alloys: 24(Ag–30 at. % Cu- 40 at. % In), 25(Ag–20 at. % Cu- 40 at. % In), 27(Ag–40 at. % Cu- 50 at. % In), 28(Ag–30 at. % Cu- 50 at. % In), 29(Ag–20 at. % Cu- 50 at. % In) and 30(Ag–10 at. % Cu- 50 at. % In) revealed the same region and their examination showed the same results.

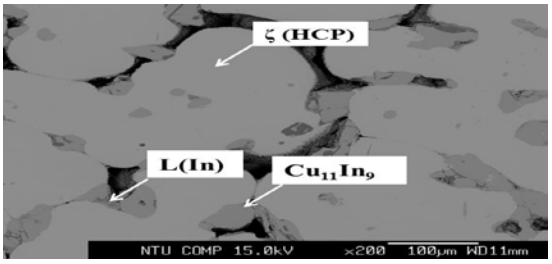

Fig 5. BEI micrograph of Sample 26.

Figure 6 shows the micrograph of alloy 23 of nominal composition: Ag-40 at. % Cu,-40 at. % In. EPMA results revealed ζ (HCP) and Cu11In9 phases. The phases compositions were Ag-2.5 at. % Cu-35 at. % In, and Ag-51 at % Cu, -43 at. % In for ζ (HCP) and Cu11In9 phase, respectively as shown in Table 2. The morphology of the sample shows that ζ(HCP) phase was dispersed in the Cu11In9 phase like floating ice in water.

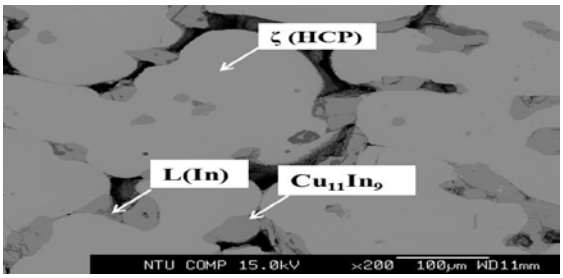

Fig 6. BEI micrograph of Sample 23.

The isothermal section of the ternary Ag-Cu-In system at 300˚C constructed from own experimental results is shown in Figure 7.

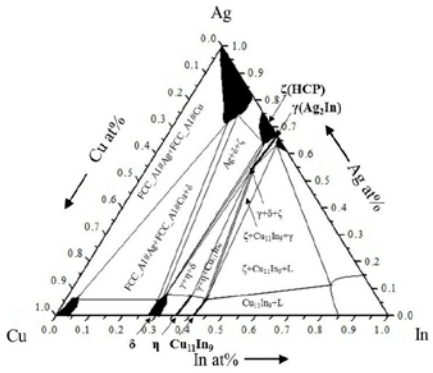

Fig. 7. Isothermal section of the Ag – Cu – In system at 300˚C.

The established phase diagram reveals significant solubility of a third element in all binary intermetallic copounds. The big solubility of Cu in the Ag2In phase at the temperature at which binary Ag2In decomposes suggests that Woychik and Massalski's [3] phase diagram shown proper phase equilibria. Similar, other ternary regions are rather in agreement with Woychik and Massalski [3] than with Baharai et al. [4]. However, taking into account chemical composition analysis, the solubility of Cu in Ag2In phase seems to be smaller than suggested by [3]. It appears that further phase equilibria examination at temperature between 300˚C and 500˚C will be very helpful for full understanding of the relation between Ag2In and gamma-CuIn phases.

V. Conclusions

The isothermal section of the ternary Ag – Cu – In system at 300˚C was proposed based on own experimental results. The chemical compositions of the phases were determined by EPMA measurement. In addition, the phases in equilibrium were confirmed by XRD analysis. The proposed phase diagram includes seven ternary and fourteen binary regions. Moreover, the phase diagram shown in this work partially confirms Woychik and Massalski [3] proposition of phase relationship in the ternary Ag – Cu – In system.

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