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The equilibrium phase diagram of the copper–indium system: a new investigation

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Abstract

The entire phase diagram of the Cu–In system was investigated using differential scanning calorimetry (DSC), powder X-ray diffraction (XRD), metallography and electron probe microanalysis (EPMA) studies. The results indicate the existence of a solubility region of In in Cu with the limit of the solid solution at 5.20 at.% In at 400 °C and of six intermediate phases, the three low-temperature phases δ, η and $Cu_{11}In_9$, and the three high-temperature phases γ, η′ and β. The boundaries of each phase were defined with respect to temperature and composition.

Keywords: Phase diagram; Binary system; Copper–indium alloys; Liquid–solid equilibria; Solid–solid equilibria

1. Introduction

In the preparation of an experimental investigation of the ternary alloy Ag–Cu–In we examined earlier studies of the three binary systems Ag–Cu, Ag–In and Cu–In given in the literature. The system Cu–In is complicated and the literature data are conflicting. Therefore, we devoted a study to this system which is a part of a large work devoted to the lead and cadmium free solder materials.

The Cu–In phase diagram was entirely studied by Weibke et al. [1]. These authors showed the existence of a solubility region of In in Cu and of seven intermediate phases, the three low-temperature phases δ-Cu_7In_3, η-Cu_2In and φ (at 42 at.% In) and the four high-temperature phases γ-Cu_7In_3, η′-Cu_2In, β-Cu_4In and ε (at 31.3 at.% In). Several sets of authors have later devoted studies to this binary system. However they limited their studies to only one of the phases earlier described by Weibke and Eggers.

Subramanian and Laughlin [2] presented a compilation and an assessment of different works [1,3–6] on the Cu–In binary phase diagram. However, data in the range of 32–100 at.% In were given by low precision (Fig. 1a). Later, Bolcavage et al. [7] studied the Cu–In phase diagram in the range of 33–60 at.% In. They found only two η/η′-phases and, for higher In content, the stable $Cu_{11}In_9$ compound at room temperature (Fig. 1b). This disagrees with Subramanian and Laughlin who showed a series of five phases h, A, A′, B and C (Fig. 1a) and the stable $Cu_{11}In_9$ compound above 157 °C.

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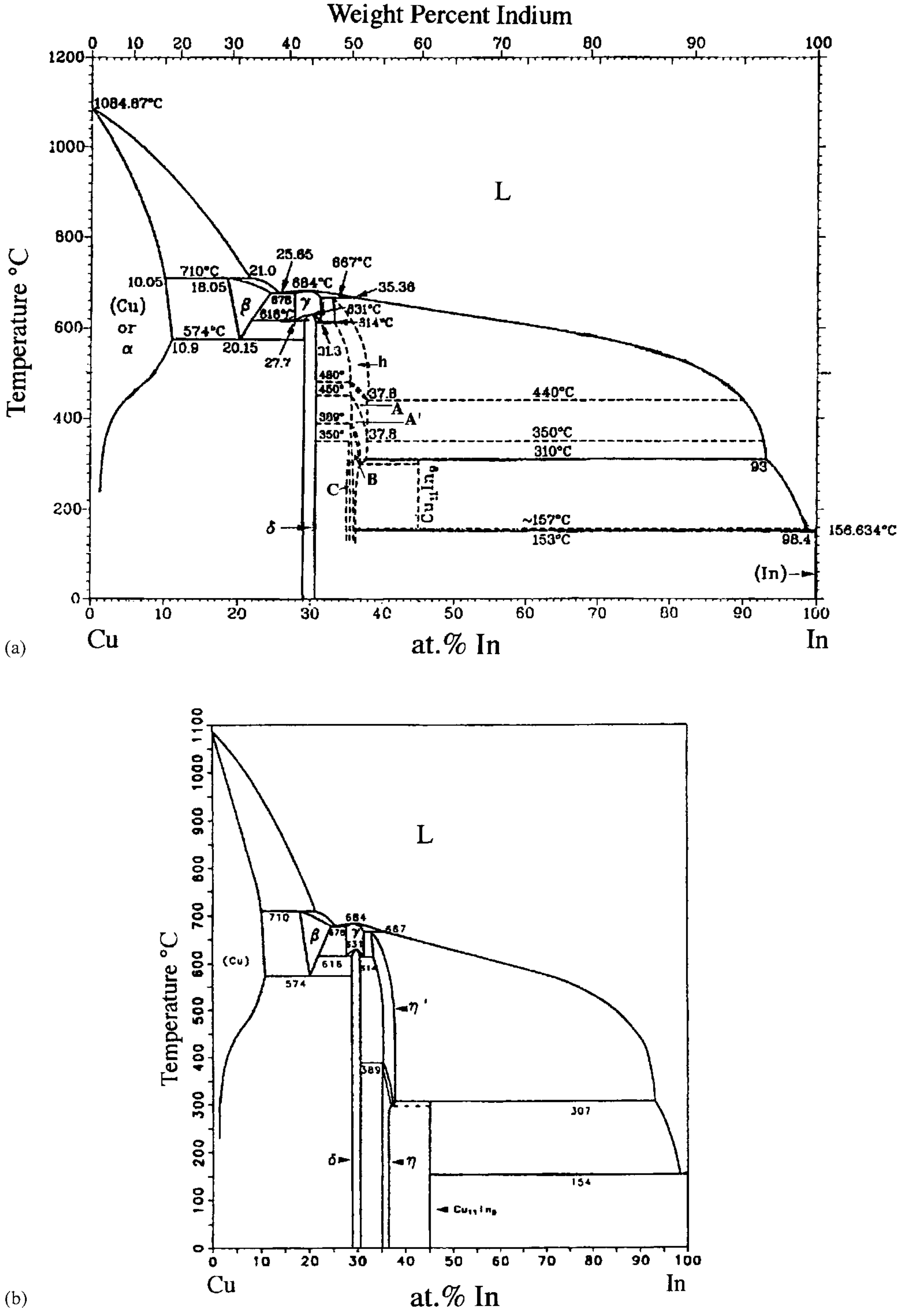

Fig. 1. (a) Phase diagram of the Cu–In binary system according to Subramanian and Laughlin [2]; (b) phase diagram of the Cu–In binary system according to Bolcavage et al. [7].

2. Experimental procedure

The Cu–In phase system was studied by differential scanning calorimetry (DSC), powder X-ray diffraction (XRD), metallography and electron probe microanalysis (EPMA) studies.

The samples were prepared from Cu shavings (99.999% pure, Hoboken, Belgium) and In lumps (99.999% pure, Aldrich, France). Blending of known amounts of elements were introduced into evacuated (10^{-2} Pa) silica ampoules. After melting at 1100 °C, the samples were slowly cooled and annealed at 150 °C for 1 month or longer.

The DSC measurements were carried out with a DSC121 and a multi-HTC (both Setaram, France). The DSC121 was standardized using the melting temperatures of the elements (minimum purity grade of 99.99%) In, Sn, Pb, Zn and Sb [8], and the multi-HTC using the melting temperatures of Ag, Au and Cu [8]. The weights of the samples varied from 200 to 300 mg, and the heating rate was 1, 0.5 or 0.02 °C min^{-1}. The temperature values of the liquidus were obtained from peak temperatures and all the other temperature values were obtained from the onset temperatures.

The phase compositions of the samples were studied by XRD measurements using a Philips 1729 diffractometer (equipped with a goniometer driven by a software developed by Fraisse [9]) using the Cu Kα radiation. The calibration has been checked with pure Si.

The EPMA measurements were carried out with a Camebax SX 50 (Cameca, France) using wavelength dispersive spectroscopy (WDS) to analyze separated phases. Cu and In were used as standard materials. Before the EPMA analysis the surfaces of the polished specimens were examined by a metallographic microscope, Reichert type M.F.2 (Reichert, Austria).

The density measurements were carried out by pycnometry with dibutyl phthalate ($C_{16}H_{22}O_4$; $d = 1.04$ at 25 °C).

3. Results and discussion

3.1. Liquidus

Weibke et al. [1] determined the liquidus curve of Cu–In alloys in the entire composition and Reynolds et al. [4] confirmed this plotting in the range of 26.3–34.8 at.% In. Our results agree very well with the results given by these authors. All our temperature values differ from those reported in these earlier studies by less than 3 °C at each composition given (Table 1, Fig. 6).

3.2. α-phase boundary

3.2.1. The α-phase boundary above 715 °C

Studies of the α-phase boundary above 715 °C have earlier been performed by Muschik and Hehenkamp [10] below 9.45 at.% In using a differential analysis technique and in an earlier study by Weibke et al. [1] using thermal analysis.

Fig. 2 shows that our solidus curve corresponds well with the one given by Muschik and Hehenkamp [10]. On the other hand, these two solidus curves deviate appreciably from the solidus given by Weibke et al. [1].

3.3. The α-phase boundary below 715 °C

Below 715 °C, Weibke et al. [1] used an XRD method to determine the α-phase boundary. They

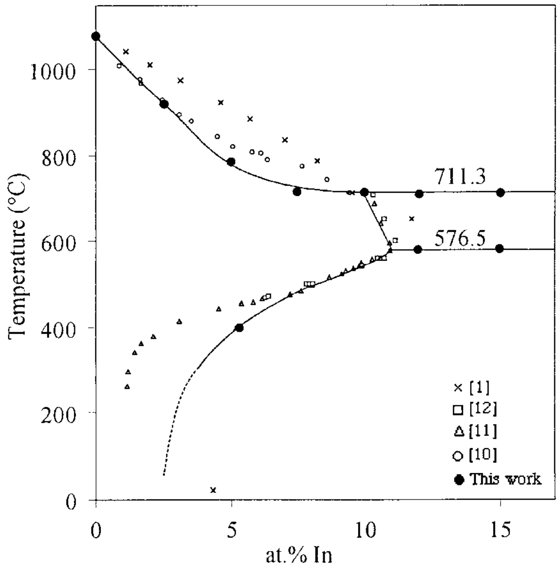

Fig. 2. α-Phase boundary of the Cu–In binary system (the point at 400 °C is identically coincident with the corresponding point of Weibke and Eggers).

Table 1
Experimental DSC data obtained in this work

X(In) (at.%)	T (liquidus, °C)	T (solidus, °C)	T (solvus, °C)	T (invariants, °C)		
2.5	1055.9	923.7				
5.0	1022.4	782.2				
7.5	983.0	713.2				
10.0	950.0			711.1		
12.0	919.3			711.1		
15.0	876.0			711.0		576.3
17.0	806.1			711.3		577.0
19.0	756.0		708.0	711.5		576.0
20.0			701.9	711.3		576.8
21.0			697.3	711.6		576.5
				711.3 (2)[a]		
21.0			597.0			
22.0	705.8		689.9		618.0	576.1
23.0	698.4		683.5		620.8	576.5
24.0	690.5			678.5	619.5	576.4
25.0	684.6			678.8	620.0	576.5
26.0	681.6			678.8	619.3	576.1
27.0				679.8	620.4	576.7
				679.0 (6)[a]		
28.0	682.0		638.0		620.0	577.0
28.5	683.7		626,4		620.2	576.4
29.0	683.9		631.4		620.3	576.9
					620.1 (5)[a]	576.5 (3)[a]
29.4	684.1		631.5			
29.4			630.1			
29.8	683.3	681.1	632.2			
30.0	683.3	679.9	631.8			
30.3	683.0	678.7	630.2			
30.6	682.9	676.7	630.1		618.7	
32.0	682.4			670.5	617.5	386.4
33.3	680.7			669.8	617.3	388.0
					617.8 (7)[a]	
34.5	673.0			670.6		389.0
35.0	673.0		630.0	670.5		390.0
35.6	672.3			669.8		
				670.2 (4)[a]		388.3 (1.5)[a]
36.4	669.0			306.5		
36.5	668.0			305.6		
37.0	667.1			305.5		
37.5	665.0			305.7		
38.0	664.0			305.3	276.9	
39.0	662.9			305.1	277.0	
40.0	659.6			305.3	276.0	
					276.6 (6)[a]	
42.0	652.4			305.9		
42.5	650.8			306.0		
43.3	647.7			305.8		
45.0	643.0			305.3		
50.0	630.3			305.1		155.1
60.0	605.2			306.0		155.6
67.0	583.3			306.3		155.5
70.0	576.8			305.6		155.7
80.0	546.6			305.1		155.6
90.0	482.6			306.8		155.6
95.0	393.0			306.8		155.6
96.0	370.3			306.6		155.6
97.0	346.4			306.6		155.6
				305.8 (6)[a]		155.5 (2)[a]

[a] Mean value with standard deviation in parentheses.

annealed their samples at 650 and 400 °C and the solubilities were found to be 11.7 and 5.18 at.% In, respectively. At 20 °C the solubility was 4.3 at.% In.

Jones and Owen [11] studied the same system using an XRD method. They completed an earlier work presented by Owen and O'Donnell Roberts [12]. They gave the maximum solubility of 10.85 at.%. In at 575 °C. In the range of 710–470 °C their values agree very well with the results of Owen and O'Donnell Roberts. Further, the boundary curve between 250 and 470 °C given by Jones and Owen shows a point of inflection at 470 °C at much lower indium content than the boundary curve proposed by Weibke et al. [1].

Based on XRD measurements the studies of Chatterjee and Gupta [13] gave the relations between lattice parameters and three compositions of copper-rich samples (4, 7 and 10 at.% In) at different quenching temperatures of 200, 400, 550 and 650 °C. These results indicate the existence of an α-phase in this range. Fig. 2 shows the discrepancies between the authors.

We prepared alloys containing 2, 2.5, 3.5, 5, 6, 7.5, 10 and 15 at.% In by melting in evacuated silica ampoules. The samples were annealed at 600 °C for 21 days to ensure the formation of a homogenous α-phase. They were then quenched in cold water, and heated again at 400 °C where they were annealed for another 21 days and subsequently quenched in cold water before analysis. This choice of temperature was done bearing in mind the point of inflection at 470 °C given by Jones and Owen [11].

Fig. 3 shows the parameter value as a function of indium content obtained from our XRD data and gives the limiting solubility of indium in copper equal to 5.20 at.% In. This value, which is in excellent agreement with the value 5.18 at.% In given by Weibke et al. [1], was incorporated into the phase diagram (Fig. 2). This result lends support to the conclusion that there should not be the inflection point at 470 °C on the α-phase boundary that was proposed in earlier study [11]. Consequently, we observe a larger solubility region of copper at low temperatures compared with phase diagrams earlier published.

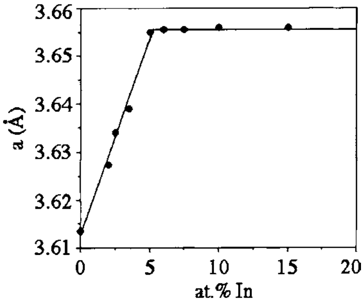

Fig. 3. Variation of lattice parameter of (Cu) with In content at 400 °C.

3.4. *β-phase*

The β-phase boundary has earlier been determined by Weibke et al. [1] in the range of 18.22–23.74 at.% In using thermal analysis between 574 and 715 °C.

By the use of metallographic examination Hume-Rothery et al. [3] determined the limiting composition of β between 18.05 at.% In, at the peritectic temperature of 710 °C (our work: 711.3 °C), and 24.5 at.% In, at the eutectic temperature of 676 °C (our work: 679 °C). The same authors also reported data concerning the α + β/β and α/α + β phase boundaries.

The β-phase structure was determined as a bcc structure β-brass type for 20.66 at.% In with the lattice parameter of 3.008 Å for the alloys quenched from 650 °C [1] and with the lattice parameter of 3.04 Å for the alloys quenched from 672 °C [14].

The boundaries of the β-phase given by Weibke et al. [1] were confirmed by our DSC data. An XRD spectrum of the alloy 20 at.% In, annealed at 620 °C for 1 month and quenched in ice water, was indexed as crystallized in the cubic system with a lattice parameter of 3.027 Å (Table 2).

3.5. *δ/γ-phases*

The previous studies concerning the δ/γ-phases have earlier been reviewed by Bahari et al. [15].

Table 2
XRD pattern of the 20 at.% In alloy, annealed at 620 °C for 1 month

θ (°)	d (Å)	I/I_M (%)	hkl
14.81	3.0133	6.58	1 0 0
21.19	2.1309	100.00	1 1 0
24.61	1.8496	7.61	1 1 1
30.74	1.5069	11.63	2 0 0
36.19	1.3045	9.26	2 1 0
38.90	1.2266	17.80	2 1 1

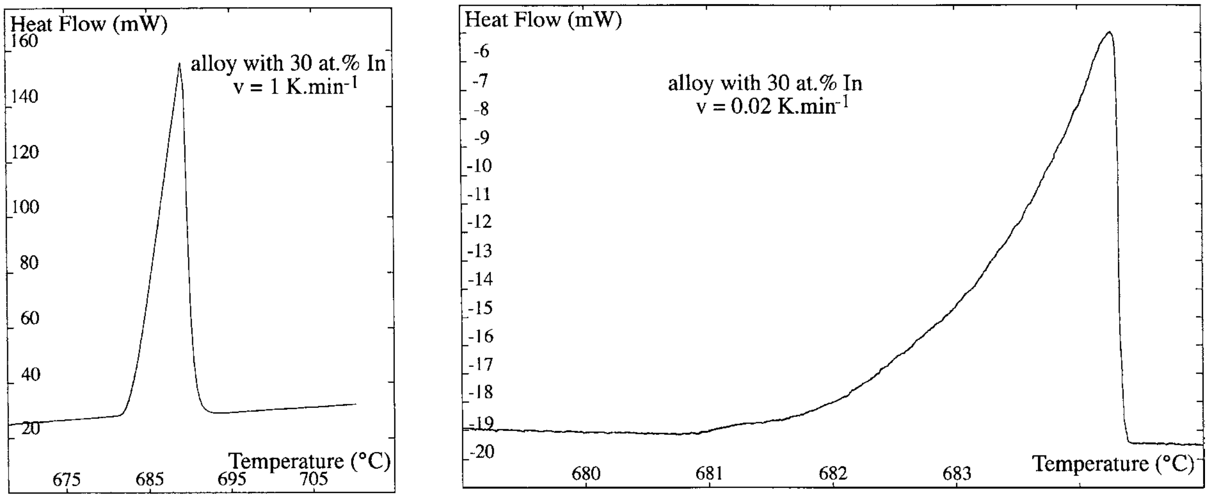

Fig. 4. DSC heating curves at 30 at.% In alloy (the recorded temperature values T_{rec} gave the experimental temperature values T_{exp} using the following calibration equation: $T_{\mathrm{exp}} = 0.995,\ T_{\mathrm{rec}} + 2.430$).

Our results give a δ/γ maximum transformation at 632.2 °C for 29.75 at.% In instead of the value 630 °C for 30.15 at.% In given by Reynolds et al. [4]. Also, our results show a γ maximum temperature at 684.1 °C for 29.35 at.% In instead of the value 682.3 °C for 29.6 at.% In given by Reynolds et al. [4]. In this region, no separation into different domains (δ/δ + γ, δ + γ/γ and γ/γ + Liq) could be found using the heating rate of 1 K min^{-1} as only one thermal effect was observed. However, at a heating rate of 0.02 K min^{-1} small thermal effects preceded the thermal effect obtained at a heating rate of 1 K min^{-1}. Fig. 4 shows the DSC curves at 30 at.% In using the heating rates of 1 and 0.02 K min^{-1}.

We determined the density of four samples (29.4, 29.7, 30 and 30.3 at.% In) in the miscibility range of the δ-phase. This gives rise to Fig. 5 that shows a positive linear variation of density as a function of the composition. This linear variation indicates a substitutional solid solution. The single point ($\delta = 8.92$ at 30.0 at.% In) given by Lidin et al. [16] in this interval agrees very well with our data.

3.6. *η/η′-phases*

Five h, A, A′, B and C phases were given between 31 and 45 at.% In by Jain et al. [5]. Bolcavage et al. [7] could find only two η/η′-phases in this region.

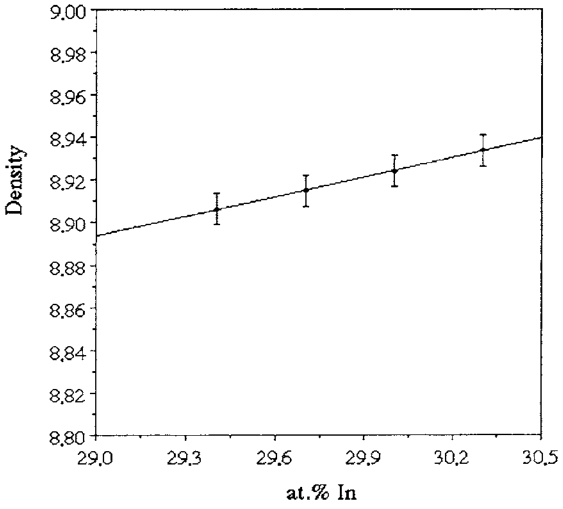

Fig. 5. Variation of δ-phase density with composition at 298 K.

Recently, Elding-Pontén et al. [17] studied the η-phase by electron diffraction. They confirmed the B and C phases cited by Jain et al. [5] and merged the three high-temperature phases (h, A, A′) into only one phase (A).

By the use of DSC measurements we were not able to find more than two phases. This confirms the value of the transition temperature for Cu-rich alloys which corresponds to the $\eta' + \delta \rightleftarrows \eta$ reaction at 388.3 °C,

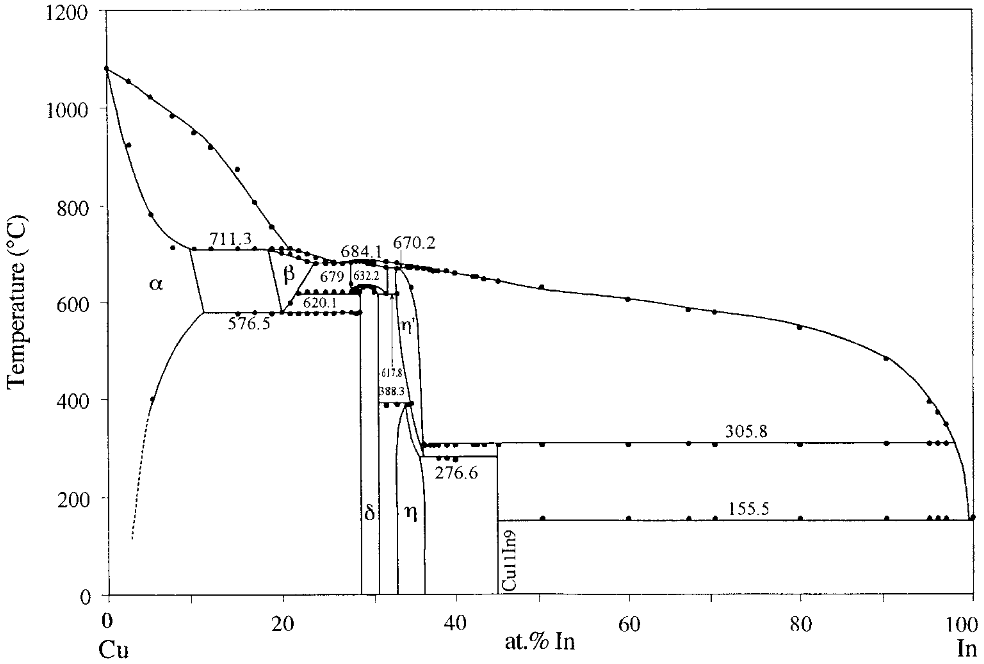

Fig. 6. Phase diagram of the Cu–In system in this work.

given by Bolcavage et al. [7] at 389 °C. A transition corresponding to the $\delta + B \rightleftarrows C$ reaction has been given by Jain et al. [5] and Elding-Pontén et al [17]. Our results, Fig. 6, do not lend support to this finding as we were not able to observe any other endothermic peak in this region with the exception of the peak at 388.3 °C. For the In-rich alloys, besides the endothermic peak at 307 °C related to the peritectic reaction $\eta' + L \rightleftarrows Cu_{11}In_9$, we could find an endothermic peak at 276.6 °C which corresponds to the $\eta' \rightleftarrows \eta + Cu_{11}In_9$ reaction given by Bolcavage et al. [7] as a dotted line.

3.7. $Cu_{11}In_9$ phase

We analyzed samples slowly cooled front the melt, with composition on both sides of $Cu_{11}In_9$ phase. The result showed the peak at 155.5 °C corresponding to the eutectic temperature $L \rightleftarrows In + Cu_{11}In_9$. If the $Cu_{11}In_9$ phase exists at room temperature, this peak was not supposed to appear in the region between the η-phase and $Cu_{11}In_9$. Therefore, we examined alloys annealed at 150 °C for 2 months. We observed that the peak does not completely disappear but decreased in intensity for an alloy with 43.3 at.% In after annealing, whereas for an alloy with 50 at.% In, the intensity of the peak was the same before and after annealing.

Our conclusion is that the $Cu_{11}In_9$ phase exists at room temperature and the peak observed between η-phase and $Cu_{11}In_9$ should disappear completely for samples annealed for more than 2 months. Thus, on the contrary to Subramanian and Laughlin [2], we were able to confirm the existence of the $Cu_{11}In_9$ phase at room temperature. Our results are further in accordance with the result given by Bolcavage et al. [7]. We could not observed two endothermic peaks, one

Table 3
Experimental data points from EPMA measurements

Nominal sample composition		Measured composition of the phases		Phase field
at.% Cu	at.% In	at.% Cu	at.% In	
60	40	62.32	37.68	η
		55.33	44.67	$Cu_{11}In_9$
50	50	54.12	45.83	$Cu_{11}In_9$
33	67	54.18	45.72	$Cu_{11}In_9$
		0.16	99.75	In

related to the formation of $Cu_{11}In_9$ phase and the second related to the eutectic reaction.

Table 3 shows the experimental data front EPMA measurements which confirms the existence of the $Cu_{11}In_9$ phase at room temperature.

4. Conclusion

The binary Cu–In system was studied in all composition using DSC and XRD, and our results agree on the whole very well with the diagram given by Bolcavage et al. [7]. The major disagreement encountered is essentially due to the α-phase boundary below 715 °C with the limit of the solid solution at 5.20 at.% In instead of 3.0 at.% In. We are also able to give the temperature of the transition η/η′ (388.3/276.6 °C). Some minor differences were discovered in the temperature of the eutectic and peritectic binary reactions.

Six stable intermediate phases exist in the Cu–In system: β-Cu_4In, δ-Cu_7In_3, γ-Cu_7In_3, η-Cu_2In, η′-Cu_2In and $Cu_{11}In_9$. The three phases β, η′ and $Cu_{11}In_9$ decompose in peritectic reactions. Only the γ-phase shows a congruent melting point. Our results cannot lend support to the existence of a binary phase between $Cu_{11}In_9$ and pure In mentioned by Bolcavage et al. [7].

The next step of the study of this binary system will be the optimization of the thermodynamic data in view to calculate the phase diagram and include these results in a database devoted to solders.

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