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Effect of indium on the microstructure of the interface between Sn3.13Ag0.74CuIn solder and Cu substrate

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ABSTRACT

Influence of indium in Sn3.13Ag0.74Cu solder containing 4, 15, 30, 50 and 75 at.% In on the microstructure at the solder/Cu interface after wetting at 523 K for 1800 s was studied. The scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX), standard and spatially resolved X-ray diffraction (XRD) techniques were used to determine the phases present at the solder/Cu interface. It was found that for In concentration up to 30 at.% the interface is formed by Cu_6Sn_5 phase. For higher In content (50 and 75 at.% In) interface consists of copper rich $Cu_{41}Sn_{11}$ phase.

1. Introduction

The paper [1] of most of the authors of the present manuscript was dedicated to the measurements of density and surface tension of the Sn3.13Ag0.74Cu + In liquid alloys at In concentration 2–75 at.%. For the same alloys wetting conditions of copper substrate were studied in the temperature interval 523–593 K up to 1800 s. Sessile drop method of contact angle measurement was used. Wetting angle decreases from ~37° to ~22° with temperature of wetting and also with increasing indium concentration in solder. Similar results were obtained studying the wetting of copper substrate by copper-free (Sn3.5AgIn) solder [2], the angles ranging, however, from ~60° to ~35° for 0 to 9% In.

This contribution is a continuation of Part I [1] and it is directed to the use of the same alloys (solders) to study the interfacial phenomena between the copper substrate and relevant solder after wetting the copper at 523 K and 1800 s.

In the past several years a number of studies have been published on various aspects of the reactions between Sn–Ag, Sn–Cu and Sn–Ag–Cu alloys and various substrates, eg. Ref. [3]. Reaction between Sn in these molten solders and Cu substrate at the Cu/solder interface results in the formation of η (Cu_6Sn_5) layer. For longer solder time between η and Cu substrate a thin layer of ε (Cu_3Sn) is observed to form. Thickness of both layers and grain size of scalloped η phase increased with increasing solder time for all three solders [4], but the fastest growth was for the SnAgCu solder and the lowest one for the SnAg.

The present paper shows the influence of indium (4–75 at.%) addition to the Sn–3.13Ag–0.74Cu (in at.%) solder on the microstructure of the interface between the solder and copper substrate after reaction the substrate at 523 K and 1800 s. The aim of this contribution is to find the relation between the wettability increase observed in Ref. [1] and In content as well as the microstructure at the solder/Cu interface.

2. Experimental

Lead-free solder alloys based on close to eutectic Sn–3.13Ag–0.74Cu (in at.%) alloys containing 2, 3, 4, 15, 30, 50 and 75 at.% indium were prepared in the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences. They were used for study of wetting conditions (sessile drop method) of copper substrate [1] as well as for study of interaction product(s) originated during wetting process (in this paper). Copper substrate was square form with edge length of 25 mm and thickness of 1.5 mm. Prior the experiment substrates were mechanically polished and cleaned in alcohol followed by etching in 10% sulphuric acid in metanol. Specimens of solder were of cube form with edge length of ~4 mm. Prior to experiment they were grinded and cleaned in alcohol. Before placing the assembled specimen into the furnace (cold zone) both parts (substrate and solder) were daubed by rosin moderately activated flux and the furnace was heated up. After reaching the required temperature speci-

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men was placed into the thermally stabilized furnace zone (air atmosphere). Photos of drops were taken with digital camera up to 1800 s after melting (reached after ~30 s) at given temperatures (523, 553 and 593 K) and contact angles were measured by computer. The wetting angles decreased with temperatures and increasing indium concentrations in the solders from ~37° for the solder without indium at 523 K down to ~22° for the solder with 75 at.% indium at 593 K [1].

Specimens after wetting the copper by solders containing indium in the interval 4–75 at.% at 523 K and 1800 s were used for study of interaction phenomena at the boundary between copper plates and solder.

These specimens with solidified drop were cut perpendicularly to the substrate plane. Cross-sections of the specimen were metallographically prepared by grinding, polished by 1 μm diamond paste and etched in solution of picric and hydrochloric acids in alcohol.

Microstructure of the interface between the solder and copper substrate as well as microstructure of the solder itself were studied by scanning electron microscopy (SEM) JEOL JSM 53-10. An energy-dispersive X-ray spectrometer (EDX) KEVEX DELTA 4 was used to measure the chemical composition of the interface between the solder and substrate as well as bulk solder. After SEM investigation most of the copper substrate was cut away to increase relatively the volume of solder and the interface between the substrate and the solder. After such modification the specimens were exposed to X-ray diffraction.

Two X-ray diffraction methods were used. The first one was standard X-ray diffraction—provided phase analysis from the specimen. The overall microstructure and phase composition of the solder–substrate interface were analyzed in a classical manner by X-ray diffraction (XRD) using conventional HZG-4 diffractometer with Cu-Kα radiation in Bragg–Brentano configuration with graphite monochromator in the diffracted beam (Fig. 6a–e).

The other method, X-ray diffraction (X-scan) was employed to obtain diffraction profile from the phase(s) situated at the interface between the solder and substrate to determine small amount of phase(s) adjacent to the substrate. Two modifications of this method were used. First modification is based on setting the diffraction conditions (θ–2θ) to the strongest X-ray line of given or assumed phase. This is accomplished by scanning across the interface between substrate and solder by moving the specimen. Settings (θ–2θ) are repeated for the strongest line of other phases. X-ray diffraction intensity of the relevant line and position of this maximum gives us the location of the phase in regard to the boundary. This spatially resolved phase analysis in the direction perpendicular to the Cu–solder interface was performed using horizontal X-ray diffractometer equipped with an 18 kW Cu rotating anode. The horizontal beam size was restricted by a primary divergence slit, yielding a beam width of 0.05 mm; vertical size of the beam was limited to 6 mm. The X-scans were performed typically in the range of ±3 mm from the position of the interface with step size of 0.05 mm. Curves in Figs. 7, 8 and 11 are constructed from many points (each 0.05 mm is one value of intensity) and only some points are drawn.

The other modification is based on the measurements of complete 2θ diffraction patterns from e.g. 30° to 90° starting with the position of primary X-ray beam with narrow slits (0.1 mm × 6 mm) partially also on copper substrate and taking several X-ray diffraction patterns, moving the specimen 0.1 mm step by step up to 1 mm length from the origin after each scan. An X-ray mapping in the direction perpendicular to the plane of the Cu–solder interface obtained in this manner allowed to verify the observations from both SEM and classical X-ray scan on the phases existence (Figs. 9 and 10).

3. Results

3.1. Morphology and chemistry of the solder/copper interface by SEM and EDX

Figs. 1–5 show the microstructure of the interface between the SnAgCuIn solder and copper substrate and microstructure of the solders after wetting at 523 K for 1800 s with the content of indium 4,15, 30, 50 and 75%, respectively, obtained by SEM. Reaction layers in all specimens except for specimen with 75 at.% indium have scalloped interface with the solder while the interfaces with copper are relatively flat. The thickness of these layers was calculated from the measured surfaces (by PC Sigma Scan Pro 5) and the length of the layers. The thicknesses of the interface layers (which were identified by X-ray diffraction) are given in Table 1.

The microstructure of the drop after 1800 s wetting of the solder containing 4% In at 523 K (Fig. 1) consists of phases (based on EDX results) Sn, and Cu_6Sn_5 and Cu from the substrate. The results of EDX measurements of the composition in points shown in Fig. 1 are listed in Table 2.

For solder containing 15% In (Fig. 2) the phase with composition corresponding to Ag_3In was detected. The second phase present was Cu_6Sn_5 and Sn (Table 3).

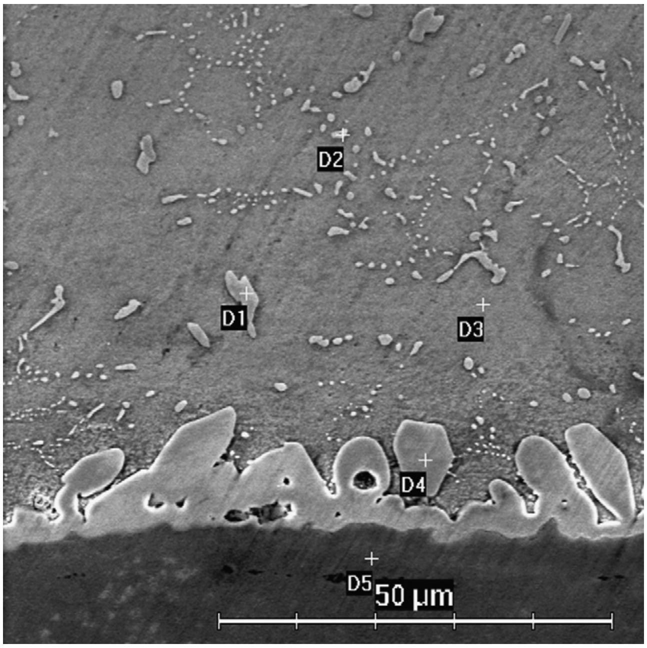

Fig. 1. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–4In after wetting at 523 K, 1800 s.

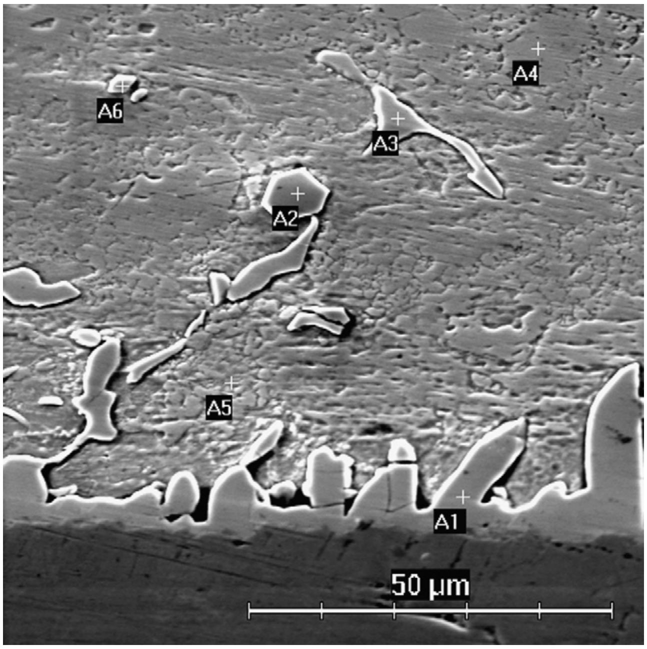

Fig. 2. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–15In after wetting at 523 K, 1800 s.

Table 1
Average thicknesses of interface layers between the solder and substrate after wetting the substrate at the temperature 523 K and 1800 s.

Amount of In in solder (at.%)	Average thickness (μm)	Interface layer(s)
4	8.2	Cu_6Sn_5
15	9.7	Cu_6Sn_5
30	8.5	$Cu_{41}Sn_{11}$; Cu_6Sn_5
50	7.7	$InSn_4$; $Cu_{41}Sn_{11}$
75	5.5 (2.8)	$Cu_{41}Sn_{11}$; Cu_6Sn_5 (discontinuous)

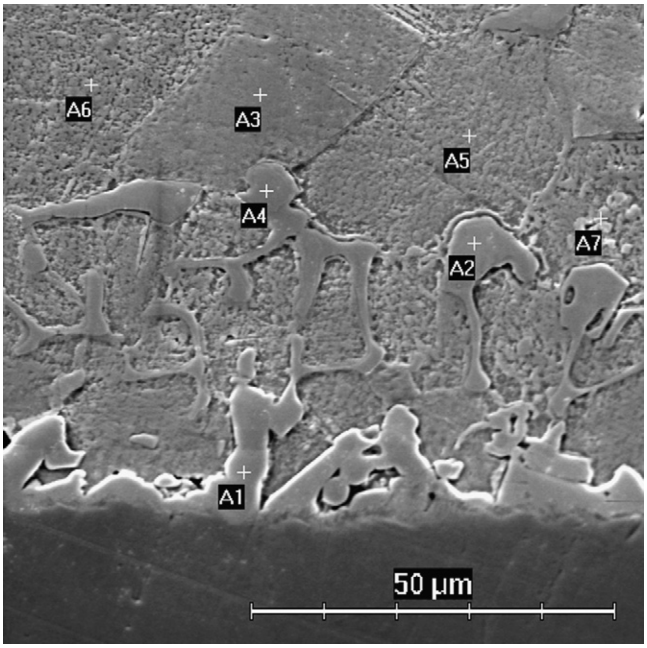

Fig. 3. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–30In after wetting at 523 K, 1800 s.

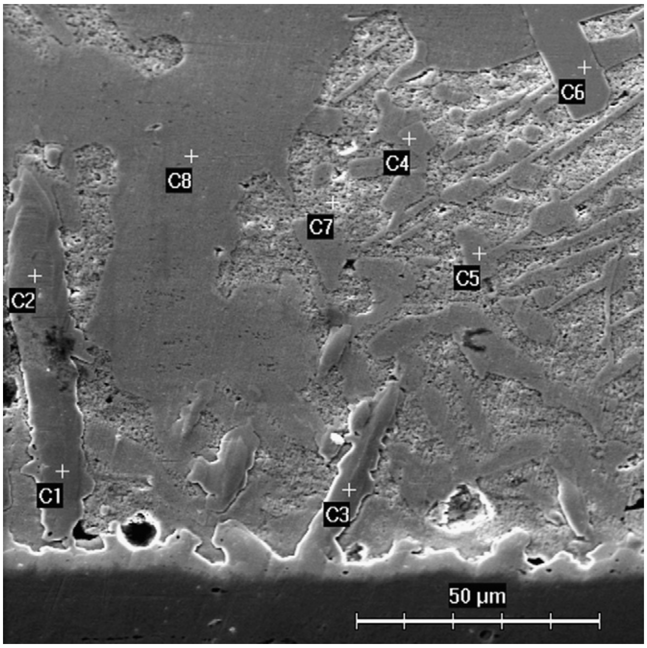

Fig. 4. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–50In after wetting at 523 K, 1800 s.

Table 2
The results of EDX analysis performed at the positions indicated in Fig. 1.

At.% In	Point	Cu	Ag	In	Sn	Possible phases
4	D1	51.3	0.2	0.0	48.5	Cu_6Sn_5
	D2	0.0	41.0	0.0	59.0	Ag_3In
	D3	0.0	0.4	0.0	99.6	Sn
	D4	54.4	0.0	0.0	45.6	Cu_6Sn_5
	D5	100.0	0.0	0.0	0.0	Cu

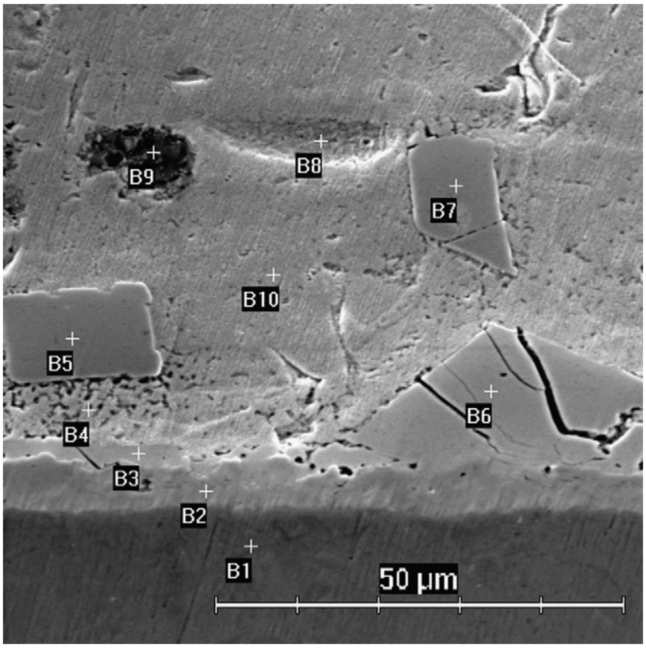

Fig. 5. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–75In after wetting at 523 K, 1800 s.

Table 3
The results of EDX analysis performed at the positions indicated in Fig. 2.

At.% In	Point	Cu	Ag	In	Sn	Possible phases
15	A1	60.6	0.7	0.7	38.0	Cu_6Sn_5
	A2	56.3	0.5	0.5	42.7	Cu_6Sn_5
	A3	2.5	70.8	24.0	2.7	Ag_3In
	A4	0.7	1.0	0.0	98.3	Sn
	A5	1.4	0.6	0.1	97.9	Sn
	A6	54.7	0.7	3.6	41.0	Cu_6Sn_5

Fig. 3 shows the microstructure of the solder containing 30 at.% In on the Cu substrate. Results of EDX measurements are shown in Table 4. Except the phase at the interface (point A1 in Fig. 3) which may correspond to Cu_6Sn_5 also Ag_3In and $InSn_4$ phases together with Sn are present. Measurement of the concentration across the interface showed presence of two phases, one with high copper content (∼66 at.% Cu) which may correspond to Cu_3Sn with high amount of tin (∼34 at.%) or to $Cu_{41}Sn_{11}$ which is adjacent to copper substrate and a relatively thick layer of Cu_6Sn_5 phase.

In the solder with 50 at.% In (Fig. 4) EDX measurements (Table 5) show Sn-rich phases (C4, C5, C8) and Cu-rich phases (C1, C2, C3) which may correspond to $InSn_4$ and $Cu_3(Sn,In)$ or $Cu_{41}Sn_{11}$, respectively.

Fig. 5 shows the microstructure of the specimen with 75 at.% In near the copper/solder interface. The EDX microanalysis showed the appearence of $Cu_{41}Sn_{11}$ phase at B2 point and the presence of In rich phases with composition close to In_3Sn (Table 6).

Table 4
The results of EDX analysis performed at the positions indicated in Fig. 3.

At.% In	Point	Cu	Ag	In	Sn	Possible phases
30	A1	63.6	1.2	3.4	31.8	Cu_6Sn_5
	A2	0.9	70.5	25.5	3.1	Ag_3In
	A3	2.4	0.1	6.5	90.9	Sn
	A4	0.8	70.0	26.7	2.5	Ag_3In
	A5	2.1	0.8	9.0	88.1	$InSn_4$
	A6	1.4	0.8	0.4	97.4	Sn
	A7	2.6	1.5	6.9	89.0	$InSn_4$

Table 5
The results of EDX analysis performed at the positions indicated in Fig. 4.

At.% In	Point	Cu	Ag	In	Sn	Possible phases
50	C1	67.2	0.1	10.5	22.2	$Cu_{41}(Sn,In)_{11}$
	C2	72.4	0.3	8.1	19.2	$Cu_{41}(Sn,In)_{11}$
	C3	65.0	0.6	11.5	22.9	$Cu_{41}(Sn,In)_{11}$
	C4	2.4	3.1	21.1	73.4	$InSn_4$
	C5	1.9	0.4	10.3	87.4	$InSn_4$
	C6	13.9	20.5	49.1	16.6	
	C7	1.1	0.6	66.2	32.1	In_2Sn
	C8	1.1	0.2	9.9	88.8	$InSn_4$

Table 6
The results of EDX analysis performed at the positions indicated in Fig. 5.

At.% In	Point	Cu	Ag	In	Sn	Possible phases
75	B1	99.7	0.0	0.2	0.1	Cu
	B2	74.5	0.3	17.7	7.5	$Cu_{41}(Sn,In)_{11}$
	B3	58.7	0.9	27.9	12.5	$Cu_6(Sn,In)_5$
	B4	0.9	0.5	72.2	26.4	In_3Sn
	B5	30.7	4.2	50.4	14.7	
	B6	28.1	3.7	50.8	17.4	
	B7	16.4	1.4	62.2	20.0	$In_2(In,Sn)$
	B8	0.5	0.6	72.7	26.2	In_3Sn
	B9	1.0	0.9	73.2	24.9	In_3Sn
	B10	1.6	0.8	73.3	24.3	In_3Sn

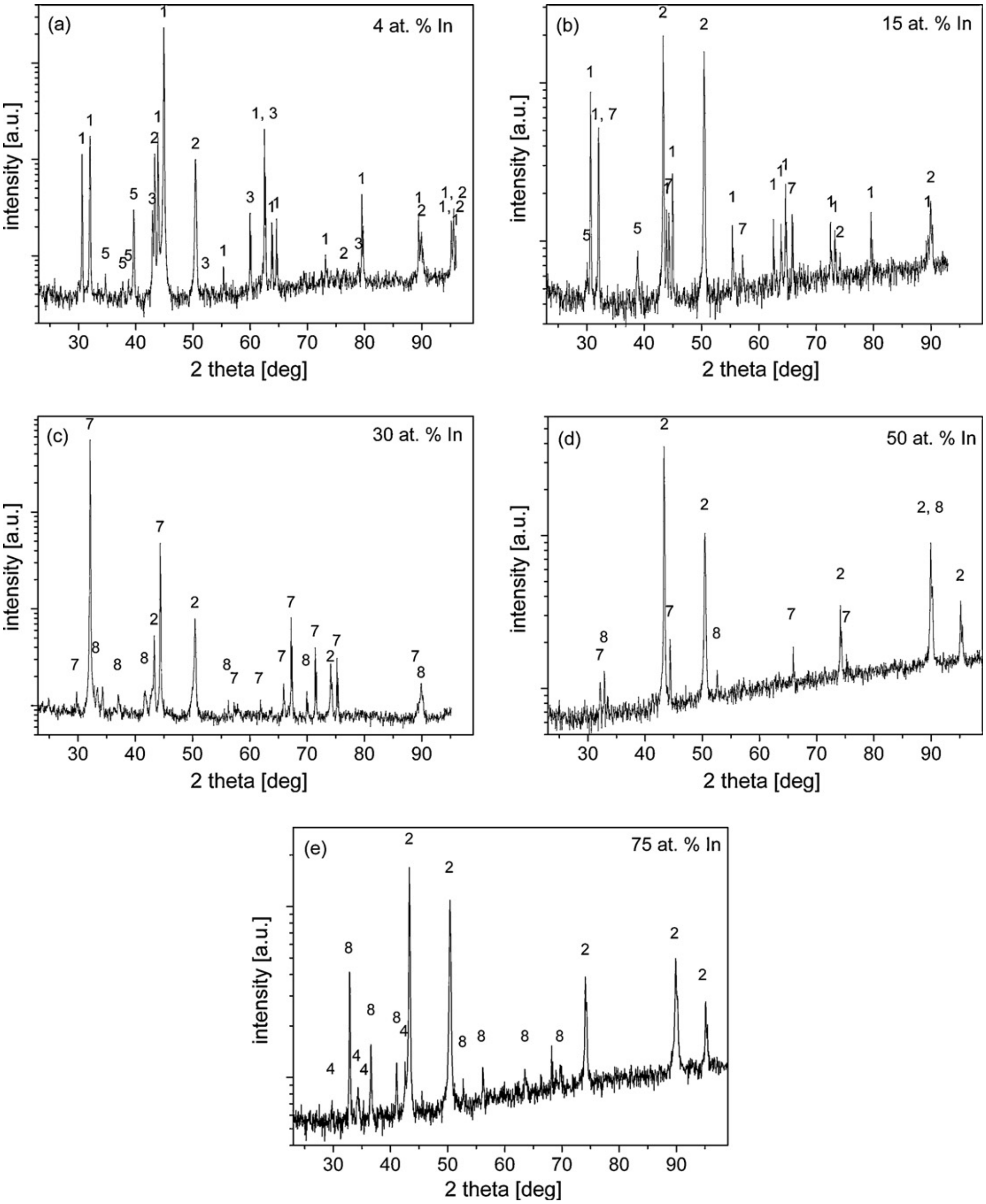

Fig. 6. X-ray diffraction profiles from the cross-sections of SnAgCuIn/Cu couple for numbers at different In content; (a) 4 at.%, (b) 15 at.%, (c) 30 at.%, (d) 50 at.% and (e) 75 at.%. The diffraction maxima refer to appropriate phases: (1) Sn, (2) Cu, (3) Cu_6Sn_5, (4) $Cu_{41}Sn_{11}$, (5) Ag_3In, (7) $InSn_4$ and (8) In_3Sn.

Table 7
The results of X-ray phase analysis of the SnAgCu solder containing various amount of indium after 30 min wetting on copper substrate at 250 °C.

At.% In in solder	Fig. No.	Phase identified
4	6a	Sn, Cu_6Sn_5, Ag_3In,
15	6b	Sn, Ag_3In, $InSn_4$
30	6c	In_3Sn, $InSn_4$
50	6d	In_3Sn, $InSn_4$
75	6e	In_3Sn, $Cu_{41}Sn_{11}$

The phases indicated in the last column of Tables 2–6 are possible phases deduced from the measurement of concentrations at particular points. The situation where it is not possible to assign a specific phase (C6 in Table 5 and B5, B6 in Table 6) means that the measured chemical composition does not correspond clearly to any phase present in the relevant phase diagram.

3.2. *Phase identification by classical X-ray diffraction*

Measurements of concentration by EDX spectroscopy gave us the values at individual points. Additional information about the phase identification in the solder one can obtain by X-ray diffraction from the surface of the specimen.

Standard X-ray diffraction profiles from the particular specimens with different content of indium in the solder are in Fig. 6a–e. The phases identified based on the obtained diffraction patterns are collected in Table 6. It is to be noted that the phases Ag_3In and Ag_3Sn give similar reflections and it is difficult to distinguish between them from the obtained X-ray diffraction patterns.

Copper reflections are almost in all X-ray profiles as they are from the Cu substrate which was not fully eliminated from the specimen.

3.3. *Phase identification and location by X-scan*

X-ray diffraction from the copper substrate and relevant solder does not indicate the reflections from the Cu_6Sn_5 phase probably because of relatively low amount of interface phase comparing with the rest of solder except for the interface with the solder containing 4% of indium. Evaluation of X-ray diffraction profile from the solder containing 4% In is in Fig. 6a. Results are summarized in Table 7.

Similar structure is observed also in the case of the solder containing 15% indium. Morphology of the interface layer (Fig. 2) is similar to the solder containing 4% indium. X-ray diffraction profile does not show the presence of Cu_6Sn_5 phase in the solder (Fig. 6b) even though EDX measurement shows composition in points A1 and A2 (Table 3) close to the composition of Cu_6Sn_5 phase.

To analyze the phases at the interface (because of small volume of phases) X-scan method [5] was used for the specimens containing 30, 50 and 75% of indium. In the case of solder with 30 at.% indium the morphology of the interface layer is also similar to that of the solder with 4% indium. EDX measurement shows in A1 point, which is close to the Cu substrate, higher amount of copper (63.6 at.%) (Table 4). Standard X-ray diffraction profile (Fig. 6c) does not show the presence of Cu_6Sn_5 phase.

Its presence, however, was observed with the help of X-scans. X-ray diffraction conditions were set to two copper lines (1 1 1) and (2 0 0) to determine the position of the interface, two lines (0 0 0 1) and (0 1 0 1) of $InSn_4$ phase and two lines (1 0 1) and (2 0 2) of Cu_6Sn_5 phase (Fig. 7). This figure shows the presence of Cu_6Sn_5 phase, which is adjacent to the substrate together with $InSn_4$ phase. In the bulk of solder besides $InSn_4$ also In_3Sn phase is present (Fig. 6c).

Composition of interface layer in the case of solder with 50 at.% In may correspond to $Cu_{41}(Sn,In)_{11}$ phase (Table 5). Standard X-ray diffraction profile (Fig. 6d) shows the presence of $InSn_4$ and In_3Sn phases.

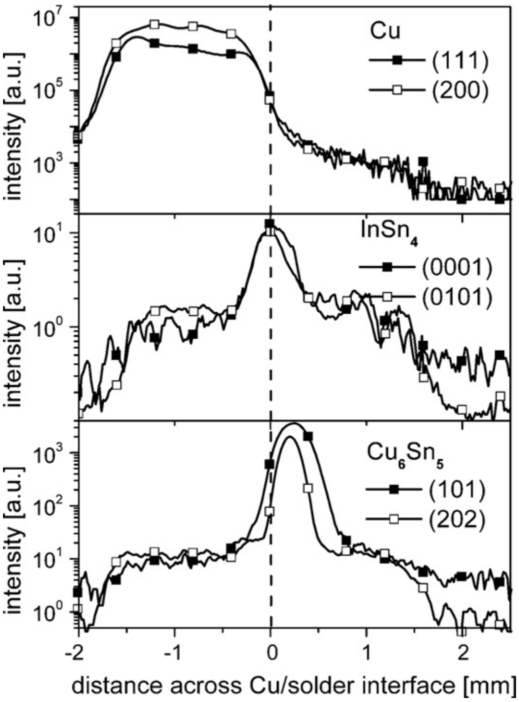

Fig. 7. X-ray diffraction profile (X-scan) of the interface between Cu substrate and solder containing 30 at.% indium.

Fig. 8 shows X-ray diffraction profile (X-scan) around the interface between Cu substrate and solder containing 50% indium with the maximum of (1 1 1) and (2 0 0) lines of copper (boundary-line) and several lines of $InSn_4$ phase; two of them, namely (0 0 0 1) and (0 0 0 2) are shown in the graph.

Neither standard X-ray diffraction (Fig. 6d) nor X-ray diffraction profile (X-scan, Fig. 8) show existence of copper rich phase at the interface observed by SEM and EDX (see high Cu content in point C3, Table 5). For this reason we measured complete 2θ diffraction patterns from 30° to 90° starting with the position of primary X-ray beam with narrow slits (as mentioned above) partially also on copper substrate and taking 10 X-ray diffraction patterns, moving the specimen from the origin into the solder 0.1 mm step by step up to 1 mm length after each scan.

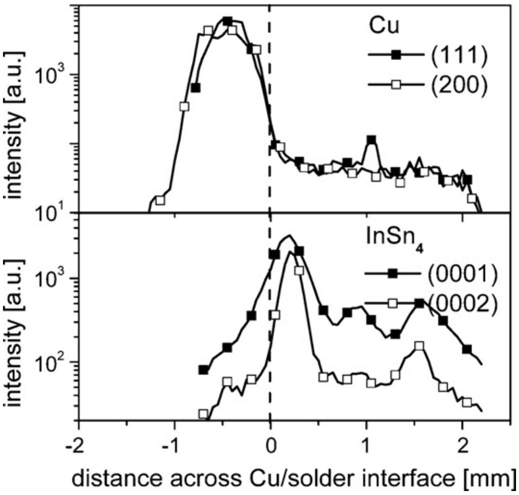

Fig. 8. X-ray diffraction profile (X-scan) of the interface between Cu substrate and solder containing 50 at.% indium.

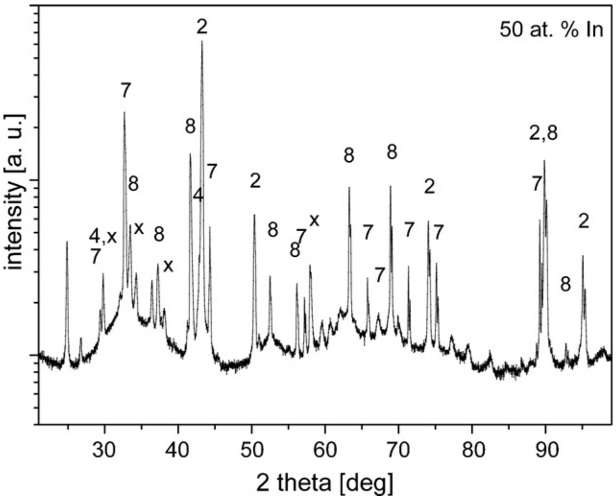

Fig. 9. X-ray diffraction profile (average intensities from 10 measurements) at the interface between Cu substrate and solder containing 50 at.% In. (2) Cu, (4) $Cu_{41}Sn_{11}$, (7) $InSn_4$, (8) In_3Sn and (×) corresponding to Sn oxides.

An X-ray mapping in the direction perpendicular to the plane of the Cu–solder interface obtained in this manner allowed to verify the observations from both SEM and classical X-ray diffraction about the phases present. Fig. 9 represents the average intensity of each line from all 10 measurements of X-ray diffraction spectrum. Fig. 10 shows individual X-ray diffraction patterns at the origin (at the position on the boundary of substrate–solder) (lower curve of Fig. 10) and after moving the specimen by 1 mm from this place into the solder (upper curve of Fig. 10). Besides the phases $InSn_4$ and In_3Sn marked in Fig. 9 there is visible also the presence of $Cu_{41}Sn_{11}$ phase. Fig. 10 shows the vanishing of copper lines and the presence of $Cu_{41}Sn_{11}$ phase. Lines marked by "×" do not change the intensity over the entire range of displacement; their position is very close to those corresponding to Sn oxides.

EDX measurements of the concentration in the solder with 75 at.% In show the composition close to Cu_3Sn phase (point B2, Fig. 5, Table 6). Standard X-ray diffraction profile (Fig. 6e) shows $Cu_{41}Sn_{11}$ and In_3Sn phases.

Fig. 11 shows X-ray diffraction profile (X-scan) around the interface between copper substrate and solder containing 75% indium. Maximum corresponds to (2 2 0) and (2 2 2) copper lines, indicating the position of copper substrate, (5 5 1) line of $Cu_{41}Sn_{11}$ phase, which is adjacent to the copper substrate and (4 2 1) line of In_3Sn phase. $Cu_{41}Sn_{11}$ layer at the interface is relatively smooth on both boundaries, with Cu substrate as well as with Cu_6Sn_5 layer (point B3 in Fig. 5). This layer is discontinuous and its thickness is about 3 μm. It was not detected by X-ray diffraction. Solder contains relatively big particles (points B5, B6 and B7) concentration of which corresponds to $Cu(In,Sn)_2$.

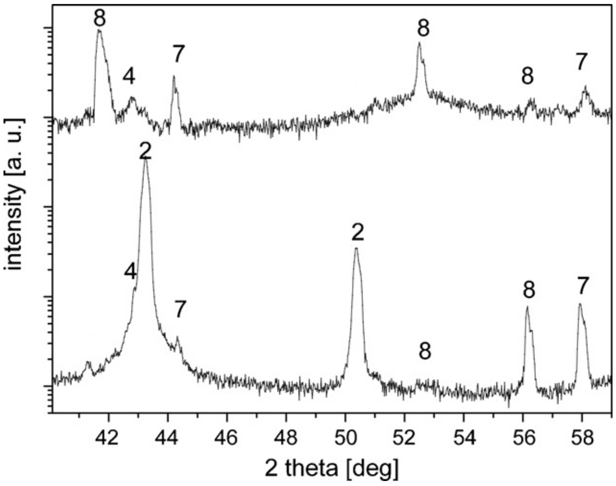

Fig. 10. X-ray diffraction profile of the interface between Cu substrate and solder containing 50 at.% In from the origin of the interface (lower curve) and after moving the specimen for 1 mm from this point into the solder (upper curve). (2) Cu, (4) $Cu_{41}Sn_{11}$, (7) $InSn_4$ and (8) In_3Sn.

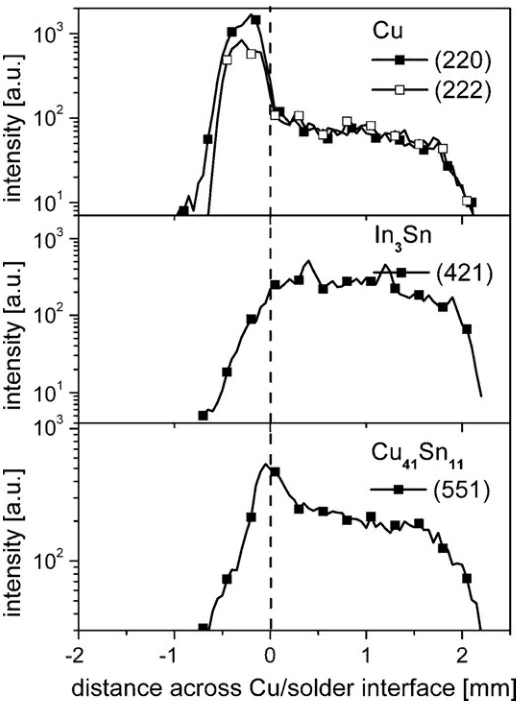

Fig. 11. X-ray diffraction profile (X-scan) of the interface between Cu substrate and solder containing 75 at.% indium.

4. Discussion

It is generally known that product of interaction of copper with molten tin based solder in the temperature range of interest (below ~573 K) results in the formation of Cu_3Sn and Cu_6Sn_5 layers [3], where Cu_6Sn_5 is the first phase to form at the liquid/Cu interface. Cu starts to dissolve rapidly to liquid solder, until the solder becomes supersaturated with Cu more or less uniformly. This dissolution is a non-equilibrium process and locally very high concentration of Cu can be realized in the very vicinity of the Cu/liquid interface (e.g. points A1, A2 in Table 2 or point A1 in Table 4).

Wojewoda et al. [6] studied the formation of intermetallic phases and their growth kinetics in joining process Cu–Cu with the eutectic alloy In–48 at.% Sn. It was revealed that η [$Cu_6(Sn,In)_5$] phase appeared as the first one in the solid–liquid reaction between the Cu and In–Sn liquid and possessed dual morphology of fine and coarse grains. The second intermetallic phase δ [$Cu_{41}(Sn,In)_{11}$] was formed in the solid–solid reaction between the copper and η phase. It was observed either at lower temperatures after longer annealing time (tens of hours) or after short time (minutes) at 573 K and higher temperatures.

More authors studied the interfacial reactions of the Sn–50 wt.% In/Cu couples at low temperatures. Romig et al. [7] found $Cu_2(Sn,In)$ and Cu_2In_3Sn at the temperatures at 343 and 363 K. Chuang et al. [8] studied the Sn–51 wt.% In/Cu couple at 423–673 K, and they found ε-$Cu_3(In,Sn)$ and η-$Cu_6(In,Sn)_5$. Sommadossi et al. [9] studied the interfacial reactions of the Sn–52 wt.%In/Cu couples. They also found the formation of η-Cu_6Sn_5 at 453 K and ε-Cu_3Sn and η-

Cu_6Sn_5 at 563 K. Vianco et al. [10] examined the Sn–50 wt.% In/Cu couples at temperatures varied from 328 to 373 K, and they found the formation $Cu_{26}Sn_{13}In_8$ and $Cu_{17}Sn_9In_{24}$. It is presumed these two phases are Cu_6Sn_5 with high In solubility, and $CuIn_2$ with high Sn solubility. Composition in points B5, B6 and B7 in Table 6 is very similar to the composition $CuIn_2$ with decreasing Cu concentration taking into account the distance of the particle from the Cu substrate (concentration of Cu decreases with the length from the substrate). As mentioned by Laurila et al. [3] the formation of Cu_3Sn is to be expected thermodynamically (and has been observed), however, for times longer than the times used in our experiment. No indication of the presence of Cu_3Sn has been observed in our experiments even for the longest wetting times (1800 s), which is by 50% shorter than the times used in Ref. [3].

EDX measurements concentration, generally, might not suffice to definite result to identify the phase. Because of that diffraction methods were used. Except the standard X-ray diffraction method to be able to identify the phase and/or phases being present in the specimen in small volume, X-ray diffraction scanning was used. Using all these methods, phases present in the solders differ from each other by the content of indium were identified. As can be seen from Table 1 indium influences the growth of copper based phases as well as creation of phases containing indium. For the solder with 4 at.% of indium the interface is formed by Cu_6Sn_5 phase. This is confirmed by both EDX as well as X-ray diffraction methods. For the given treatment (523 K, 1800 s) there is no other phase at the interface. For the solder with higher indium concentration (15 at.%) the thickness of interface phase (again only Cu_6Sn_5 phase) is mildly higher. One can suppose that indium supports the diffusion of copper into the solder. For the solder with 30 at.% of indium there rise two phases at the interface (Cu_6Sn_5 and $InSn_4$). Their thickness is lower than for the solder with 15 at.% of indium because part of the indium is consumed to form $InSn_4$ phase.

The measurement of the composition across the interface for sample with 30 at.% In (Fig. 3) by EDX showed besides the Cu_6Sn_5 phase also the existence of another layer with increased amount of copper which is adjacent to copper substrate. Because we did not obtain X-scan diffraction profile from this layer it is very hard to give a more detailed characterization. Because for solders with higher indium concentration the phase observed at the interface is $Cu_{41}Sn_{11}$, one can suppose that this phase starts to originate already for solder with 30% indium.

EDX results from the wetting the copper substrate by solder with 50 at.% indium show the presence of copper rich phase ($Cu_{41}Sn_{11}$) close to the interface (points C1–C3 in Table 4). Neither standard X-ray diffraction nor X-ray diffraction profile (X-scan) show the presence of this phase. Fig. 9 shows the result from the measurements of this specimen moving it from the origin (copper boundary) to the solder up to 1 mm length by 0.1 mm step. Fig. 9 shows the presence of $Cu_{41}Sn_{11}$ phase (lines with No. 4). Another phase occurred at the interface is $InSn_4$ phase. Interface between copper substrate and solder containing 75 at.% indium consists of $Cu_{41}Sn_{11}$ and In_3Sn phases. Cu_6Sn_5 phase, even though it is shown in Table 5 (point B3), was not found by diffraction methods because of its low thickness.

Wetting angle of Cu substrate by the solder Sn3.13Ag0.74CuIn (at 523 K and 1800 s) [1] decreases with the increase of indium in the solder. Surface tension σ_{LV} of the solder does not practically change with the increase of indium, because surface tensions of both metals are close to each other (surface tension of Sn3.13Ag0.74Cu solder without indium at 523 K is 539.1 mN/m, surface tension of this solder containing 75% indium at 523 K is 543.9 mN/m) [1]. Neither does interfacial tension σ_{SV} change with the amount of indium. Therefore, it can be assumed that the observed decrease of wetting angle is a result of the increase of the interfacial tension σ_{SL} due to increased indium content (S, L, V are for solid, liquid and vapor, respectively).

5. Conclusions

Influence of indium in lead-free solder Sn3.13Ag0.74CuIn in the amount of 4–75 at.% on the interaction products with copper substrate after wetting of copper by the solder at 523 K and 1800 s is presented. Methods of scanning electron microscopy, standard X-ray diffraction and X-ray scan were used. Phase analysis of the bulk solder obtained by X-ray diffraction is given. The phase at the interface between the solder and substrate is changing with increasing content of indium. For all indium concentration (4–75 at.%) in Sn3.13Ag0.74CuIn solder, the phase at the interface between the copper substrate and the solder is copper rich phase. Indium enhances the diffusion of Cu into solder and at the same time creates conditions for formation of In-based phases. Thus an interplay of these two effects leads to increase of the interface layer thickness for lower In content while higher In content leads to the formation of In-based phases which in turn hinder the diffusion of Cu and lead to a decrease of the thickness of the interfacial copper-rich layer. For In concentrations (4, 15 and 30 at.%) Cu_6Sn_5 phase is adjacent to copper substrate. For higher In concentration (50 and 75 at.%) copper rich phase $Cu_{41}Sn_{11}$ is adjacent to the substrate. Increase of indium in the solder is assumed to result in the increase of the interfacial tension between solid substrate and liquid solder. Increase of this tension results in decrease of wetting angle.

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