

## STUDY OF THE COPPER – INDIUM – TIN TERNARY SYSTEM BY MEANS OF REACTIVE DIFFUSION

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## STUDIUM TERNÁRNÍHO SYSTÉMU MĚĎ – INDIUM – CÍN POMOCÍ REAKTIVNÍ DIFUZE

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### Abstrakt

Cílem této práce bylo experimentální studium ternárního systému měď – indium – cín za účelem rozšíření údajů publikovaných doposud v odborné literatuře. Experimentální práce byly provedeny na Vysoké škole báňské – Technické univerzitě Ostrava. Byl proveden experimentální výzkum reaktivní difuze vybraných difuzních spojů Cu/Sn, Cu/Sn+In a Cu/In při různém geometrickém uspořádání: rovinné rozpouštění, cylindrické rozpouštění a kapilární zkoušky, při různých teplotách a dobách žhání. Vzorky byly připraveny z kovů o čistotě In – 5N a Sn – 5N a elektrovedné mědi. Tepelné zpracování difuzních dvojic bylo provedeno v laboratorních pecích při teplotních a časových režimech: 400 °C/50 hodin, 600 °C/48 hodin a 600 °C/310 hodin v argonové atmosféře nebo ve vakuu. Vzorky byly po ukončení žhání prudce ochlazeny do vody, případně volně ochlazovány ve vakuové peci. Byly měřeny a studovány následující charakteristiky vzorků: metalografické studium mikrostruktury, celková chemická analýza vzorků (ICP-AES), bodová a liniová chemická mikroanalýza jednotlivých fází v struktuře slitin (WDX, EDX). Pro termodynamické výpočty byl na Masarykově univerzitě v Brně použit program THERMOCALC a termodynamická databáze COST 531. Metodou CALPHAD (Calculation of Phase Diagrams), založenou na výpočtu termodynamických rovnováh, byly vypočteny izotermické řezy v ternárním systému Cu–In–Sn při teplotách 600 a 400 °C. Získané experimentální výsledky měření fázových rovnováh byly porovnány s termodynamickými výpočty. Metoda reaktivní difuze dala reprezentativní výsledky a spolehlivě identifikovala přítomné fáze při současném rozpouštění Cu matrice taveninou pájky Sn, In, resp. In+Sn. Interakce mědi s pájkou byla ovlivněna konvekcí a vysokou difuzivitou v tavenině, což vedlo k vysoké rychlosti pohybu mezifázové hranice solid/likvid.

## Abstract

The aim of the work was an experimental study of the copper – indium – tin ternary system, the purpose of which was to broaden the amount of the data published in the literature. The experimental work was performed at VŠB – Technical University of Ostrava. The experimental research of the reactive diffusion was performed in the selected Cu/Sn, Cu/Sn+In and Cu/In diffusion joints at various geometries of lay-out – plane dissolving, cylindrical dissolving and capillary tests - at different temperatures and time regimes. The samples were prepared from the metals of purities In – 5N, Sn – 5N and high-conductivity copper. The heat treatment of diffusion couples was performed in the laboratory furnaces at the following temperatures and time regimes: 400 °C/50 hours, 600 °C/48 hours and 600 °C/310 hours in the argon atmosphere or in vacuum. Having finished the annealing, the samples were quenched to water or freely cooled in the vacuum furnace. The following characteristics of samples were measured and studied: metallography, total chemical analysis (ICP-AES), spot and line chemical micro-analysis of individual phases in the structure of alloys (EDX, WDX). The program THERMOCALC (Masaryk University in Brno) and thermodynamic database COST 531 was used for thermodynamic calculations. CALPHAD (Calculation of Phase Diagrams) method, based on calculation of thermodynamic equilibria, was used for calculations of isothermal sections in the Cu–In–Sn ternary system at the temperatures of 600 and 400 °C. The obtained experimental results of the measured phase equilibria were compared with the thermodynamic calculations. The method of reactive diffusion provided representative results and identified reliably the present phases at simultaneous dissolving of the Cu matrix by the melt of solders Sn, In, and/or In+Sn. The copper and solder interaction was influenced by convection and high diffusivity in the melt, which resulted in a high speed of movement of the solid/liquid interface boundary.

**Keywords:** Copper–indium–tin ternary system, phase equilibria, reactive diffusion, WDX chemical microanalysis, thermodynamic calculation

## 1. Introduction

Reactive diffusion is the diffusion accompanied by phase changes in materials. It can be observed in cases when the atoms of matrix and diffusant are mutually limitedly miscible or they can form compounds with each other. Solid solutions of basic components A and B form in the diffusion layer and areas of other phases of different widths may be found among them in conformity with the corresponding phase diagram. There is always a concentration jump on the interface boundary if the binary or ternary system does not show a total solubility in the solid state. In this special case the concentration profile shows a continuous concentration course. The result of reactive diffusion is coexistence of several successive layers of solid solutions or chemical compounds (intermetallic phases). The width of the areas, i.e. the thickness of individual phases, will depend on the values of interdiffusion coefficients of elements in each of the present phases.

This phenomenon is often utilized in semiconductor technology, e.g. when creating dielectric layers of oxides or nitrides of silicon, when creating inter-layers of intermetallic compounds and silicides at the reaction of metallic layers with adjacent layers of semiconductors and dielectrics (creation of  $\text{Mo}_3\text{Si}$ ,  $\text{Mo}_5\text{Si}_3$  and  $\text{MoSi}_2$  layers at the diffusion of molybdenum into silicon). Reactive diffusion also occurs at soldering of electronic components on printed circuit cards when reactions between tin and copper proceed and the thin function layer  $\eta(\text{Cu}_{11}\text{Sn}_9)$  creates. Reactive diffusion is also applied when producing function gradient materials, etc.

## 2. Diffusion at the solid and liquid phases contact

At the diffusion in A–B binary system the melt comes into contact with the solid phase and this process happens in case that the two materials A, B have considerably different melting temperatures. The temperature of diffusion heating is selected so that e.g. material A stays in the solid state and material B is molten. In the place of the solid phase/melt contact, the metal A dissolves and diffuses into the melt and this process will last until the melt B is saturated with the diffusant A. It is possible to determine diffusion characteristics of the studied system from the shift of the interface between the solid phase and melt. An equilibrium, time constant concentration of the element A, which can be determined from the phase diagram, sets up on the interface boundary on the side of the melt.

The values of diffusivities in the melt are by three or more orders higher than those in the solid phase. Experimental determination of the values of diffusivity in the melt is quite difficult, especially due to convection, which may totally disturb or homogenize the diffusion concentration profile of the element A in the melt. This was the reason why a number of fundamentally different methods of study of diffusion in melts were developed. Most used are capillary methods, e.g. capillary-reservoir or capillary methods with configurations taken from the study of diffusion in the solid state.

When the metal A dissolves in the melt of metal B, the boundary between the solid phase and melt moves rapidly. In consequence of this interface boundary movement, concentration gradient of metal B on the metal matrix surface rises considerably. It results in essentially faster growth of intermetallic phases in the A–B system, compared with diffusion processes in the solid state, in conformity with the corresponding phase diagram. Phases with decreasing concentration of the element B form and grow in the direction from the surface of the solid/liquid interface inwards the metal A matrix. Thickness of these phases may be influenced:

- 1) by the temperature at reactive diffusion,
- 2) by the time of contact of the metal B melt with the metal A matrix,
- 3) by the thickness of the B melt at the beginning of production.

In dependence on the properties of metals A and B and values of these parameters, the rate of growth of phases under the surface of the metal A matrix at reactive diffusion may be even by an order higher than when utilizing diffusion processes in the solid state. Thicknesses of newly formed layers of individual phases mostly range in orders  $10^{-1}$  to  $10^2$   $\mu\text{m}$ . If convenient combinations of the components A, B, or A, B, C ... are selected, the procedure is highly efficient and applicable not only for binary systems but also for ternary or multi-component systems.

## 3. Binary and ternary phase equilibria in the system Cu–In–Sn

The latest phase diagrams of binary systems copper – tin, copper – indium are published in [1, 2]. These systems are rather complicated, they contain numerous intermetallic phases in the regions of both high and lower temperatures – see Table 1. It is obvious from Table 1 that in both the systems Cu–Sn and Cu–In, phases of similar types form from the structural as well as chemical stoichiometric ratios points of view, e.g. the phase  $\text{Cu}_6\text{Sn}_5$  corresponds to  $\text{Cu}_{11}\text{In}_9$ , the phases  $\beta$ ,  $\delta$  and  $\eta$  occur in both the systems and have the same type of lattice. Köster [3] (see Fig. 4 in [2]) and Liu [4] published the Cu–In–Sn ternary system. A thermodynamic calculation of the system Cu–Sn was also carried out by Shim et al. [5].

Table 1 Areas of the co-existence of individual phases in Cu – Sn and Cu – In binary systems

Cu – Sn system				Cu – In system			
Phase	Co-existence area Sn [at. %]	$T$ [°C]	Chemical formula	Phase	Co-existence area In [at. %]	$T$ [°C]	Chemical formula
(Cu)	max. 9.1	při 520	Cu	(Cu)	max. 10.9	při 574	Cu
$\beta$	13.1-16.5	586-798		$\beta$	18.1-24.5	574-710	
$\gamma$	15-29	520-755		$\gamma$	27.7-31.3	616-684	
$\delta$	20-21	350-590	$\text{Cu}_{41}\text{Sn}_{11}$	$\delta$	29.1-30.6	< 631	$\text{Cu}_7\text{In}_3$
$\zeta$	20.3-22.5	582-640	$\text{Cu}_{10}\text{Sn}_3$				
$\epsilon$	24.5-25.9	< 676	$\text{Cu}_3\text{Sn}$		44	< 307	$\text{Cu}_{11}\text{In}_9$
$\eta$	43.5-44.5	186-415	$\text{Cu}_6\text{Sn}_5$	$\eta'$	43.5-44.5	307-667	
$\eta'$	43.5-44.5	< 189	$\text{Cu}_6\text{Sn}_5$	$\eta$	43.5-44.5	< 389	
(Sn)	100	13-232	$\beta$ Sn	(In)	100	< 156	In

#### 4. Experiment

Our experiments of reactive diffusion of Cu with melts of Sn, In or Sn+In were executed with the following arrangements: cylindrical and plane dissolving, capillary tests.

##### 4.1 Cylindrical arrangement

An orifice  $d = 10$  mm, 18 mm deep, was drilled in the Cu cylinders, diameter 27 mm, and a cylinder of solder, mass 8 g, was thrust into the orifice. The solder chemical compositions were 100 Sn, 75 Sn + 25 In, 50 Sn + 50 In, 25 Sn + 75 In and 100 In (data in at. %). The cylinders were sealed with Cu caps with cylindrical stems, diameter 10 mm. The stem penetrated about 10 mm into the cavity and was situated closely above the inserted solder. The annealing itself took place in a laboratory furnace at the temperature 600 °C, the time was 310 hours. After annealing the specimens were quenched in water.

In specimens with high content of Sn, strong dissolving of Cu in the tin melt was observed, the Cu inner diameter enlarged from initial 10 mm to 13÷15 mm. A cavity with irregular pores of large dimensions created inside the residual Sn region. A narrow region in the shape of annulus coloured yellow – a new phase – created on the Cu/Sn interface. As an example we show the concentration profiles of Cu, In, Sn after reactive diffusion of Cu/75 at. % In + 25 at. % Sn joint.

In specimens with high In content the cylindrical cavity was free of solder which crept up along the Cu stem during annealing and practically “disappeared” from the original region. After annealing the solder was found on the outer surface of the Cu cylinder. Indium reacted with the outer surface of the Cu cylinder and penetrated locally to the depth up to 2 mm. The inner cavity of the Cu cylinders stayed without the diameter change. The cavity inner surface was covered by a thin layer of solder and a new layer of yellow colour, 500÷800  $\mu\text{m}$  wide, formed between the layer and copper.

In further experiment an orifice  $d = 10,5$  mm, 30 mm deep, was drilled in the Cu cylinders, diameter 27 mm. A thread M12x1.5 was made in the upper part of the cylinder. The pin had the same thread on the stem. The reason was to prevent the solder to escape from the cavity. The cylinders filled with the solder were sealed with Cu caps by screwing. Two solders were prepared, 100 at. % Cu and 75 at. % Sn + 25 at. % In. The annealing itself took place in a temperature stabilized laboratory furnace at the temperature 600 °C, the time was 48 hours. After annealing the specimens were quenched in water. As an example, the concentration profile of In and Sn in Cu region and microstructure of the sample Cu/25 at. % In + 75 at. % Sn after annealing 600 °C/48 h is shown on the Fig. 2.

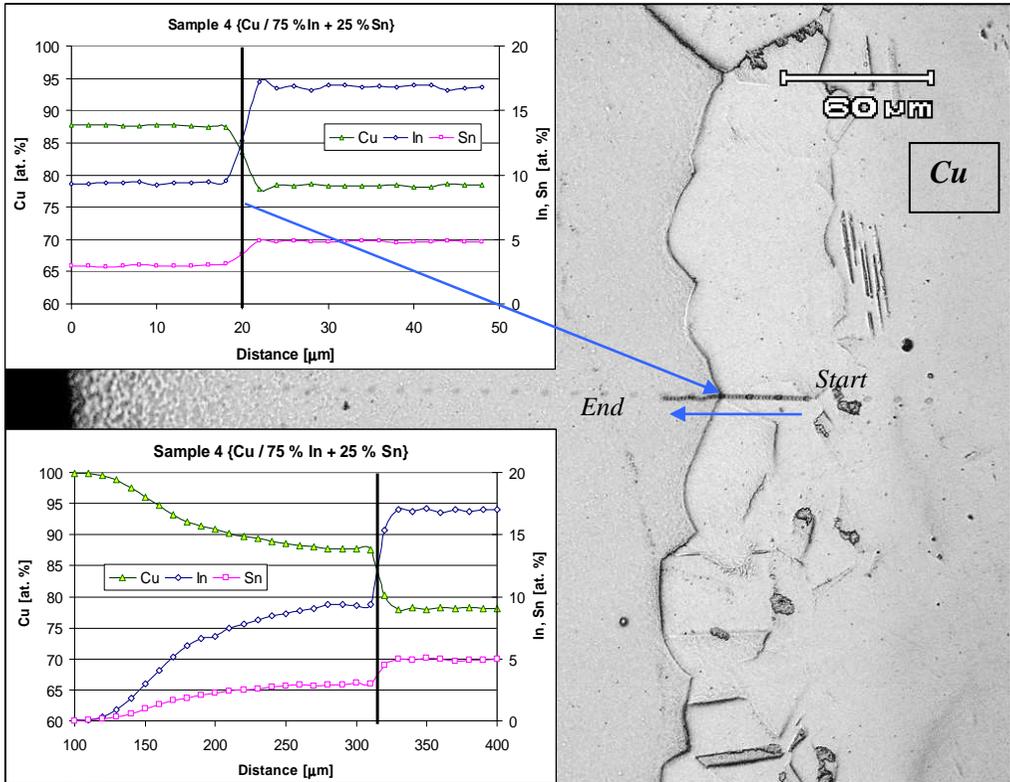


Fig.1 Microstructure and concentration profiles in Cu/75 at. % In + 25 at. % Sn joint (600 °C/310 h) – WDX analysis

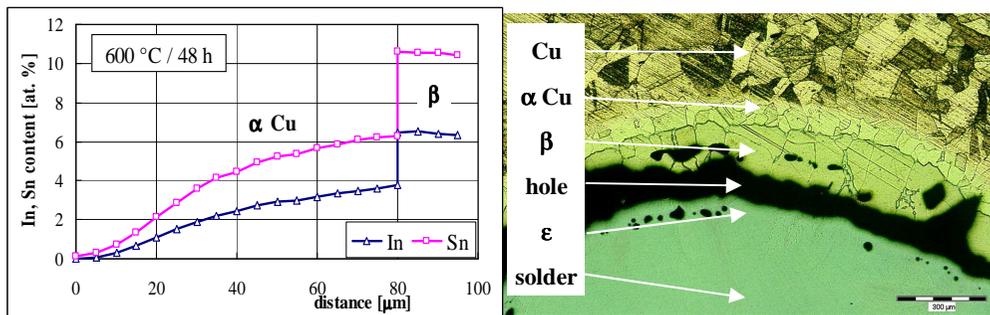


Fig.2 The sample Cu/25 at. % In + 75 at. % Sn – annealing 600 °C / 48 h and quenching, concentration profile of In and Sn in Cu and microstructure of the cross-section

#### 4.2 Plane arrangement

For this purpose, cylinders of pure Cu, outer diameter 40 mm and 25 mm high, were prepared. They were provided with cylindrical orifice inside, the diameter 30 mm, 20 mm deep. Solder 100 % Sn and/or 75 % Sn + 25 % In was placed on the bottom of the cylindrical cavity and covered from above with a Cu cap, diameter 30 mm and height 10 mm, that exactly fitted with the cavity inner diameter (by virtue of perfect solder sealing) and which covered the melt

by dead weight. In addition, a piece of Cu tube was placed on the bottom of the orifice whose task was to limit the melt height. The annealing itself took place at the temperature 400 °C, the time was 50 hours. It was followed by free cooling in the air or quenching in water. Several bubbles appeared in the solidified solder and a local phase  $\eta$  in the shape of small sticks was found in the proximity of Cu. Thin layers of other phases were discovered close to the interface boundary. A contact of the solder and Cu block was preserved. We managed to catch the melt composition at the moment of its final solidification since the eutectic reaction lies in areas between 200 to 240 °C when the melt is gradually deprived of copper. This shows itself by secondary segregation of phases inside the quickly solidifying melt that were identified relatively far from the interface boundary Cu/Sn, and/or Cu/In + Sn.

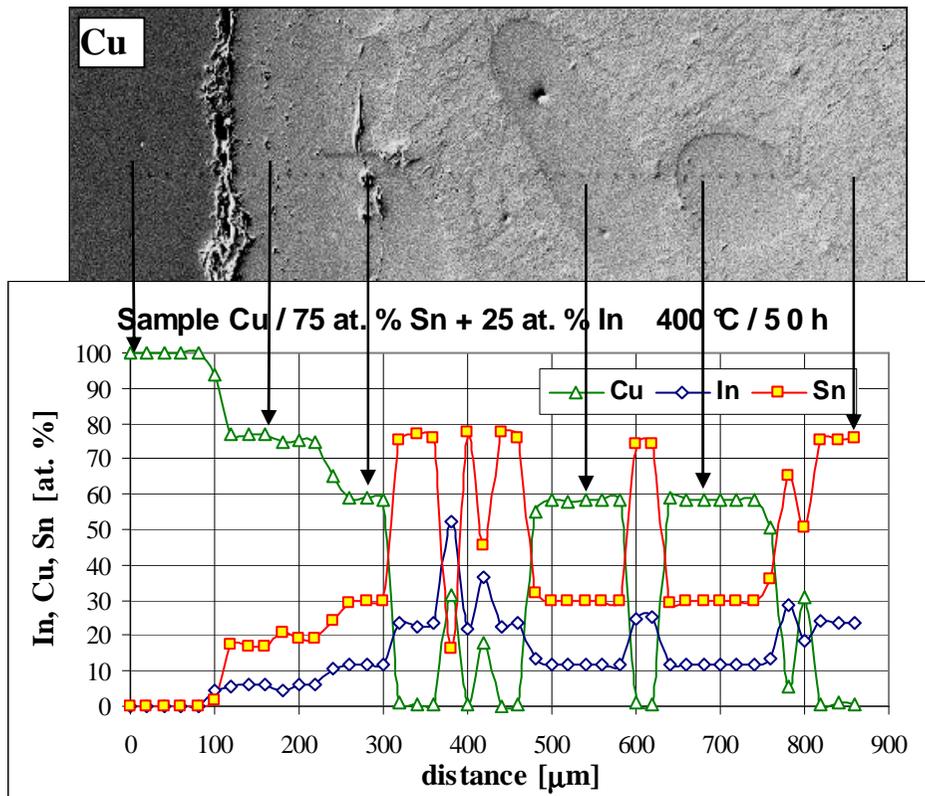


Fig.3 Microstructure (SEI) and concentration profiles (WDX) in Cu/75 at.% Sn + 25 at. % In joint (400 °C/50 h)

Very interesting concentration profiles were measured in sample Cu/75 at.% Sn + 25 at. % In – see Fig. 3. The line analysis in the length 860  $\mu\text{m}$  with the step 20  $\mu\text{m}$  passed through all areas, i.e. from pure copper to the area of solidified melt where it intersected two islets of the phase  $\eta$ . The following phases were gradually identified: Cu (0.1/0.2 = concentration In/Sn in atomic percent), phase  $\zeta$  - width 50  $\mu\text{m}$  (6/17.1), phase  $\varepsilon$  - width 50  $\mu\text{m}$  (5.5/19.7), phase  $\eta$  - width 80  $\mu\text{m}$  (11.7/29.6), solidified melt as the phase  $\gamma$  (Sn,In) width 160  $\mu\text{m}$  (23/76), phase  $\eta$  in the melt - width 120  $\mu\text{m}$  (11.8/29.7), solidified melt as the phase  $\gamma$  (Sn,In) width 40  $\mu\text{m}$  (25/74), another phase  $\eta$  in the melt - width 120  $\mu\text{m}$  (11.8/29.6), solidified melt as the phase  $\gamma$  (Sn,In)

width 40  $\mu\text{m}$  (24/75). The melt crystallized at relatively low temperatures below 200 °C while creating a fine dendritic structure containing the  $\gamma(\text{In},\text{Sn})$  phase the composition of which was practically the same as that of the initial solder. In this solidified melt round islets of the phase  $\eta$  are found, their chemical composition is in exact agreement with the Cu–In–Sn phase diagram according to Köster [3]. The islets were mostly mutually separated or they touched each other. Copper dissolved in the solder up to the distance min. 1 mm from the original interface boundary. Under the conditions of fast cooling, the melt was depleted of copper in conformity with the phase diagram and oversaturated Cu precipitated in the form of the phase  $\eta$ . The character of the precipitated phase  $\eta$  was also influenced by the position of the solder in the orifice of the Cu cylinder, i.e. the influence of convection and diffusion. Therefore the morphology of segregated formations was various, different at the bottom and by the melt surface.

### 4.3 Capillary tests

The aim of these tests was to discover the character of dissolving and influence of convection in the Cu/Sn, In diffusion joint. At the contact of the Cu substrate with the melt of pure Sn or In, and/or with the alloy Sn + In, reactive diffusion between individual components takes place besides preferential dissolving of Cu in the melt of solder and new phases create, mostly in the solid. Convection in the melt, which can influence negatively the character of diffusion processes, plays an important role. That is why the samples were submitted to various temperature and time regimes.

Before the experiment itself, the Cu wire, diameter 2.8 mm and length about 10 mm, with metallographically made up front surface, was placed into the lower part of a quartz capillary, inner diameter 2.8 to 3 mm. The solder samples were prepared in the form of cylinders by sucking the melt into the corresponding capillary so that the contact solder/Cu wire was ensured. Lengths of the solder samples were 2, 4, 6, 8 and 10 mm.

The samples in capillaries were placed into a graphite casing with drilled orifices. The heat treatment was performed in the laboratory furnaces at the temperatures 400 and 600°C and three different times: 24, 48 and 72 hours in the argon protective atmosphere followed by quenching to water or free cooling. However, the furnace was not hermetically leak-proof and there was a great probability of oxidation of samples at high work temperature. Therefore further tests were carried out in the vacuum furnace at the pressure 110 Pa, spontaneously cooled in the furnace in vacuum for about 24 hours. The samples annealed in vacuum presented good metal joints. It is evident that further secondary structural and chemical reactions happened during a relatively slow cooling of samples.

Three types of effects of Sn or In with the Cu wire were discovered by visual observation after mechanical grinding and polishing. Significant dissolving of copper by the solder occurred in all the cases. In the first case the copper dissolving proceeded from the interface Cu/solder inwards Cu gradually top-down, which was observable visually in the form of three regions of different colours. In the second case the solder reacted not only axially, but also radial dissolving of copper from the wire surface towards the centre was observed. In the third case a sharp transition solder/Cu without a visible transitional area was observed while preserving the solder/Cu contact.

The results of the capillary test of a sample after the treatment 600 °C/24 h in vacuum, the Sn height was 4 mm, are presented as an example. Sn penetrated into the Cu region

primarily along the Cu wire surface, so that the reaction of Sn with Cu took place especially in the superficial layer and even in the lower part of wire. The area of pure Cu occupied the wire central part, about 1.5 mm wide and 4 mm long. Such behaviour is atypical and thus difficult to evaluate. From the initial length of the Cu wire the frontal penetration of Sn into Cu was 4 mm deep. Structural characteristics and concentration profiles of both the elements in the area of the Cu/Sn transition, after the given heat treatment regime, are documented in Fig. 4. The sequence of individual identified phases is in conformity with the binary Cu-Sn diagram. An unexpected occurrence of an islet of the phase  $\eta$  is probably connected with crystallization of Sn remainder and its segregation in the structure at low temperatures.

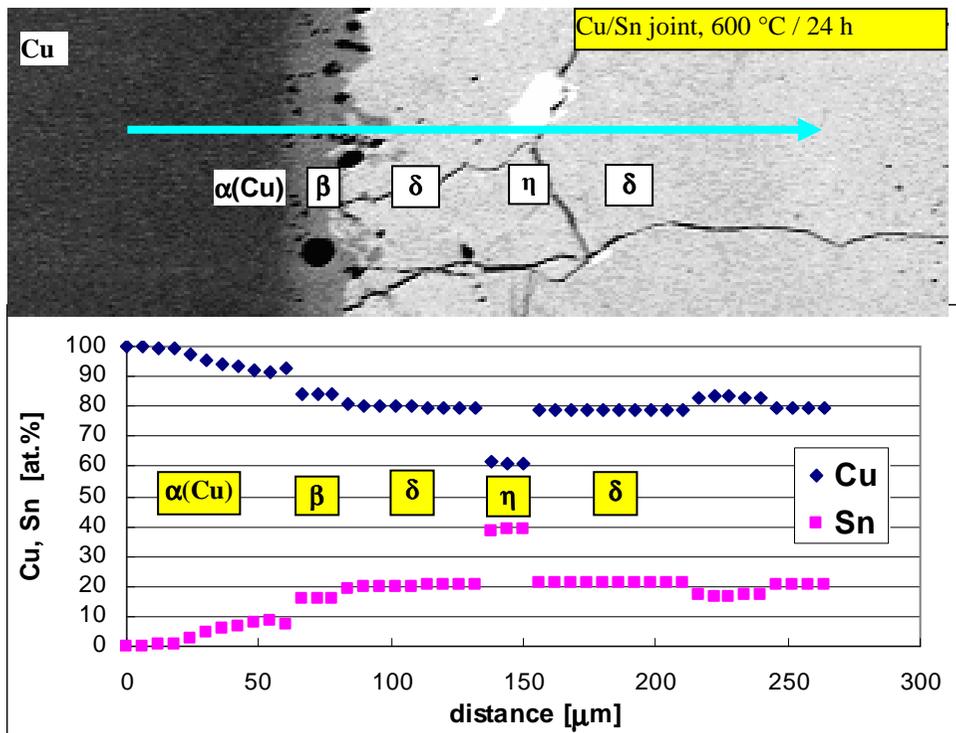


Fig.4 Microstructure (SEI) and concentration profiles (WDX analysis, step 6  $\mu\text{m}$ ) of copper and tin in Cu/Sn joint after annealing (600 °C/24 h) in vacuum furnace (capillary sample)

Concentrations of elements in the given localities determined by WDX method corresponded very well to concentrations of phases according to equilibrium binary diagrams of the systems Cu–Sn, Cu–In, and/or Cu–In–Sn. Dissolving of Cu wire by the melts of Sn, and/or In happened frontally as well as from the wire surface. With growing volume of the melt of Sn and In the region of pure Cu rapidly reduced and it often remained just in the central area of the wire, which was caused by high convection in the melt. In addition, high capillarity, especially of In, but also that of Sn, led to their transport into the lower part of the capillary.

With regard to the discovered structural and phase transformations at the process of cooling of samples (mostly several hours) and promising results when applying vacuum, we propose to perform experiments according to the following procedure: Specimens will be placed

into capillaries made of silica glass and metal in the lower part of semi-sealed capillaries. An appropriate low-melting alloy will be placed above this wire and a contact of both materials will be secured. Then the quartz capillary will be evacuated and the annealing itself will be carried out. The cooling has to be as short as possible, in order of seconds, which is technologically hardly feasible. However, dimensions and volume of specimens will enable to solve this problem by quenching in water or liquid CO<sub>2</sub>. The most suitable method for preserving the melt composition after annealing would be the method of decantation, which is difficult to perform in case of closed ampoule. A certain hope provides the ampoule turning by 180° in the moment of quenching. In this was the remainder of the melt separates from the solid phase and it will be possible to analyse it easily by classic chemical procedures.

### 5. Results of reactive diffusion – summary and recommendations

So far the experiments with Cu dissolving in Sn, In and/or in Sn–In alloys were executed at the temperature 600 °C and times 48 and 310 hours and at the temperature 400 °C and time 48 hours. More experiments were focused on Cu dissolving where the melt was placed in the cylindrical orifice, diameter 1.0 and/or 1.05 cm and it was to present cylindrical dissolving. The other portion of experiments proceeded with cylindrical orifice, diameter 3 cm, and was to model plane dissolving. In further analysis it is necessary to know concentration profile of dissolving Cu in the melt for evaluating the melt homogeneity. It would be convenient to carry out measurements by X-ray micro-analyser with the step 300 ÷ 500 μm and to complete them by analyses of major areas. Only then it will be possible at least to estimate the total amount of dissolved Cu in Sn, the interface boundary shift and size in dependence on the dissolving time and temperature.

The concentration profiles are dependent on the values of diffusion coefficients of individual components. On the phase interface the concentration corresponding to respective isotherm of the phase diagram is established. At the same time, the concentration of Cu dissolving in the melt increases up to the saturation of the melt by Cu. With respect to the large volume of melt, the enrichment of melt by Cu proceeds in the neighbouring region of melt to the substrate only. Dissolving of Cu in the melt is influenced substantially by the temperature and convections. In the case of annealing time long enough, all reactions occurring in the isothermal section should be established. The observed jumps on the concentration profile are important information on a respective existing phase. The region between individual concentration jumps brings information on the domain of existence of a given phase. The role of the three orders higher diffusion coefficient in liquid phase than in solid phase needs to be taken into account.

Utilizing of capillary methods known from the study of diffusion in molten metals and melts enables to reduce or nearly eliminate convection in melts at reactive diffusion if the ceramic capillary diameter is suitably opted. Elimination of convection results in retardation of the solid phase dissolving and, in addition, the values of diffusion coefficients of metals in the solid phase can be determined. For this purpose, it would be convenient to apply so-called method of “long capillary“ situated vertically. A cylinder of Cu, about 1 cm long, would be placed on the bottom of capillary and above it a column of melt (Sn),  $h \approx 5 \div 10$  cm. To eliminate convection, it is suitable to opt the capillary inner diameter about 0.25 cm. Surface diffusion may show itself more markedly at smaller diameters.

In the Table 2, the values of concentrations of individual identified phases obtained by the methods WDX and EDX (line, spot and surface analyses) from concentration profiles are

presented. In most cases the values presented in the table are mean values determined from more measurements, it means that the values are objectively trustworthy. The results presented in Table 2. were confronted with latest binary diagrams Cu–Sn, Cu–In as well as with the ternary diagram Cu–In–Sn according to Köster [3] and Liu [4]. Our experimentally determined concentrations of individual phases were also drawn in the diagram calculated thermodynamically by Vřešťál for the temperatures 873 and 673 K – see Fig. 5 and Fig. 6.

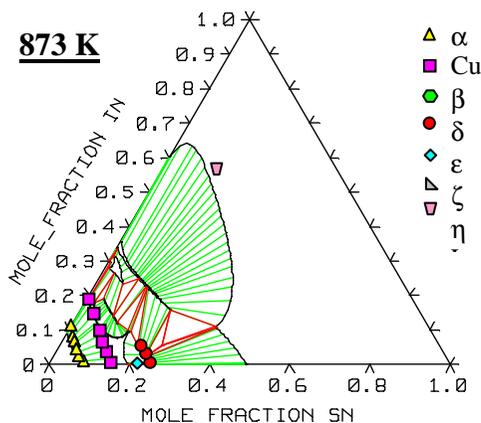


Fig.5 Thermodynamical calculated isothermal section in the Cu – In – Sn ternary system at 873 K

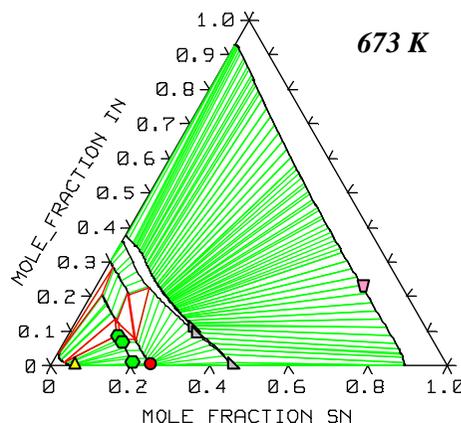


Fig.6 Thermodynamical calculated isothermal section in the Cu – In – Sn ternary system at 673 K

The results shown in the Tab. 2 were reached by chemical line microanalysis (WDX) with proper chosen step. The regions, where the concentration jumps occurred, were analysed in more detail. High-temperature phase  $\gamma$  was detected in no case. The reason can be seen in abruptness of the melt from Cu in this region during the sample quenching from 600 °C into water. In Cu–In and Cu–Sn binary systems the phases detected were in agreement with published data. The region of the melt contained high concentrations of Sn and In, respectively. It was caused by very short time of annealing which was not sufficient for saturation of the melt by Cu. Nevertheless, the phase  $\eta$  was created in the melt in places where the melt was in contact with Cu, sometimes in a large distance from the interface.

Table 2 Experimental results of WDX analysis

Sample	Annealing	Content Sn [at. %]				
		$\alpha$ Cu	$\delta$	$\epsilon$	$\eta$	liquid
Cu - 100 % Sn*	400 °C/50 h	2.9	19.2-21.9	21-24	40-42.5	96-99
Cu - 100 % Sn	400 °C/50 h	6.4	20.4	24.8-25.8	44.5	96-99
Massalski [1]	400 °C	8.1	20.5	24.5-25.1	43.5	84.7

Sample	Annealing	Content Sn [at. %]					
		$\alpha$ Cu	$\beta$	$\gamma$	$\zeta$	$\epsilon$	liquid
Cu - 100 % Sn	600 °C/48 h	9	14.8-15.2	not found	21.7-22.5	24.5-26.2	94-98
Cu - 100 % Sn	600 °C/310 h	9	15				
Massalski [1]	600 °C	9.1	14.9	16.1-20.2	21.7-22.6	24.7-26.1	55

Sample	Annealing	Content In [at. %]			
		$\alpha$ Cu	$\beta$	$\delta$	liquid

Cu - 100 % In	600 °C/310 h	11	19.8			
Massalski [1]	600 °C	10.8	19.5-21.8	29.1-30.9		63

Sample Cu - In/Sn	Annealing	Content In/Sn [at. %]					liquid	η v liq.
		α Cu	ζ or δ?	ε	η			
Cu - 25 / 75	400 °C/50 h	0.1/1	6.3/16.7	5.3/21	12.8/28.4	25/72	12/30	
Cu - 25 / 75	400 °C/50 h	0.2/0.3	10.6-8/13.4-16		11.6/28.7			
Köster [1]	400 °C	1.4/4.1	5.4-5.8/16-17	6-7/18-19	10-11/30-32	23/67		

Sample Cu - In/Sn	Annealing	Content In/Sn [at. %]				liquid
		α Cu	β	γ	ε	
Cu - 25 / 75	600 °C/48 h	3.4/6.3	6.1/10.7	not found	5.4/21.5	
Cu - 25 / 75	600 °C/310 h	1.5/8	2-3/13.5-14.5	not found	3/23	
Köster [1]	600 °C	2.2/7.1	4-4.2/12-12.6	4.4-6/13-17		10.5/30

Sample Cu - In/Sn	Annealing	Content In/Sn [at. %]				liquid
		α Cu	β	γ		
Cu - 50 / 50	600 °C/310 h	5.9/4	9.5-10/7-7.5	11-12/9.5-10		
Köster [1]	600 °C	4.3/4.7	8.7-9.2/8.4-9	10-13/10-13		22.5/22.5

Sample Cu - In/Sn	Annealing	Content In/Sn [at. %]				liquid
		α Cu	β	γ	η	
Cu - 50 / 50	600 °C/310 h	7/3	14.5/5.5-6			
Köster [1]	600 °C	8/2.5	14-15/4.4-4.7	20-22/6.2-7	25-27/8	58/17

\* air cooling

α Cu – fcc solid solution of copper, β – bcc Cu<sub>17</sub>Sn<sub>3</sub> and β – bcc Cu-In, γ – Cu<sub>4</sub>Sn and γ – Cu-In, δ – Cu<sub>41</sub>Sn<sub>11</sub> and δ – Cu<sub>7</sub>In<sub>3</sub>, η – Cu<sub>6</sub>Sn<sub>5</sub>, Cu-In and Cu<sub>17</sub>Sn<sub>3</sub> Cu<sub>0.545</sub>(Cu,In,Sn)<sub>0.122</sub>(InSn)<sub>0.333</sub>, ζ – Cu<sub>10</sub>Sn<sub>3</sub>, ε – Cu<sub>3</sub>Sn [1, 3, 4].

On the base of our analysis (see Tab. 2 and Fig. 5) we found out that the region of ε phase has to extend to the phase diagram more deeply than it is supposed in [3]. Furthermore, we found out that the ζ phase, which exists in binary phase diagram only at temperatures above 582 °C, is supposed in ternary phase diagram [3,4] up to 400 °C. Our experiment does not confirm this assumption and the δ phase is supposed instead.

Phase equilibria determined in this work in ternary system agree well with vertical sections Cu–25In75 Sn and Cu–50In50Sn, published in [3-5]. Composition of phases determined in isothermal sections at 400 °C and 600 °C is also in agreement with calculated phase diagrams (see Fig. 5 and Fig. 6).

The problem of reactive diffusion of metals at dissolving in contact with melt was discussed. In the experimental part, the diffusion in the joints Cu/In-Sn was measured at various temperatures and annealing times. The results of measurement of diffusion in individual regions of solid solutions in the Cu–In–Sn phase diagram agree well with theoretical assumptions and with the results published in literature. The method of diffusion couples is proved to be a reliable method for determination of phase regions in isothermal phase diagrams.

## 6. Conclusion

The problem of reactive diffusion of metals at dissolving in contact with melt was discussed. In the experimental part, the diffusion in the joints Cu/In-Sn was measured at various

temperatures and annealing times. The results of measurement of diffusion in individual regions of solid solutions in the Cu–In–Sn phase diagram agree well with theoretical assumptions and with the results published in literature. The method of diffusion couples is proved to be a reliable method for determination of phase regions in isothermal phase diagrams.

### Acknowledgement

*This work was supported by Ministry of Education, Youth and Sports of the Czech Republic in projects COST OC 531.001, COST OC 531.002, COST OC 531.003 (Project of European Union COST Materials Action 531 „Lead-free Solder Materials“) and MSM 6198910013 „Processes of preparation and properties of highly pure and structural defined materials“. WDX analysis carried out in Vítkovice, Výzkum a vývoj, a.s., is gratefully acknowledged.*

### Literature

- [1] Massalski T.D.: Binary Alloy Phase Diagrams. Second Edition Plus Updates on CD ROM, Ohio, ASM International, Metal Park, 1996.
- [2] Drápala J. , Zlatohlávek P., Smetana B., Vodárek V., Kursá M., Vřešťál J., Kroupa A.: Study of selected alloys on the base of the copper – indium – tin ternary system. Acta Metallurgica Slovaca, 12, 2006, NO. 4, pp. 343-356.
- [3] Köster W., Gödecke T., Heine D.: Der Aufbau des Systems Kupfer-Indium-Zinn im Bereich von 100 bis 50 At.-% Cu. Zeitschrift für Metallkunde, 63, 1972, H. 12, S. 802–807.
- [4] Liu X.J. et al.: Experimental Determination and Thermodynamic Calculation of the Phase Equilibria in the Cu-In-Sn System. Journal of Electronic Materials, vol. 30, 2001, No. 9, pp. 1093-1103.
- [5] Shim J.-H., Oh C.-S., Lee B.-J., Lee D.N.: Zeitschrift für Metallkunde. 87, 1996, pp. 205-212.