

STUDY OF GROWTH KINETICS OF INTERMETALLIC PHASES IN Cu-Sn SOLDER JOINTS UNDER THE CONDITIONS OF REACTIVE DIFFUSION

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Abstract

The content of the paper is a brief description of the basic characteristics of the reactive diffusion in the dissolution of solid copper in the melt of tin solder. Furthermore, it deals with the theory of growth kinetics of intermetallic phases during heat treatment, and a description of lead-free solders and related problems during soldering. Experimental part contains layout and design of experiments suitable for the study of reactive diffusion, metallographic study and x-ray EDX microanalysis of samples, the calculations of diffusion flows and determination of the rate constants of dissolution.

Keywords: Reactive diffusion, dissolving, lead-free solders, tin-copper system, intermetallic phase

1. INTRODUCTION

The reactive diffusion occurs at connecting two solid phases of different chemical compositions as well as at the contact of the solid phase A with the melt B [1-10]. The solid phase metal A dissolves in metal B and atoms of metal A diffuse into the melt B, usually at the presence of natural convections. Atoms B from the melt diffuse into metal A, which dissolves simultaneously and a number of intermetallic phases A_mB_n may form at the metal A surface. These phases grow in metal A with the growing dissolving time. At experiments the temperature T is opted so that it is higher than the melting temperature of metal B and lower than the melting temperature of metal A. The rate of dissolving and the growth of phases depend significantly on the temperature and time. At higher temperatures these processes are very fast compared with the processes in the solid phase. The melt B is gradually enriched with the dissolving metal A until saturation is achieved and the process of dissolving terminates stops. Concentrations corresponding to the relevant phase diagram – i.e. equilibrium concentrations, stabilize on interface boundaries in the solid phase.

Analogical behavior and formation of new phases can also be expected in more complicated binary or ternary systems, in which more intermetallic compounds exist (**Figure 1**). The reactive diffusion will result in co-existence of several consecutive phases of solid solutions. A characteristic feature of multiphase diffusion is a gradual course of the curve demonstrating the dependence of the concentration $c(x,t)$ on the coordinate x . This gradual character of the curve is caused by the fact that primary solid solutions and intermetallic phases create at the reaction between two mutually diffusing substances (components). Two-phase areas separating solid solutions and intermetallic phases in equilibrium diagrams do not create. This shows discordance between the course of diffusion and the equilibrium diagram. The height of individual grades is given by width of two-phase areas in the equilibrium diagram. The width of the creating phase depends on the concentration curve of each phase and its rate of growth [11]. Some our results at the study of the reactive diffusion were published in the journal Defect and Diffusion Forum [12-14].

Unlike the diffusion in single-phase systems, reactions taking place on the interface between individual phases assert at diffusion in multiphase systems. It is important whether these reactions are efficiently fast and do not

retard the course of diffusion. At the beginning of the diffusion process, when the concentration differences are significant, this retardation has to be taken into account. As soon as layers of individual intermetallic phases (even if very thin) create, the retardation effect of reaction rates on the phase interface generally disappears.

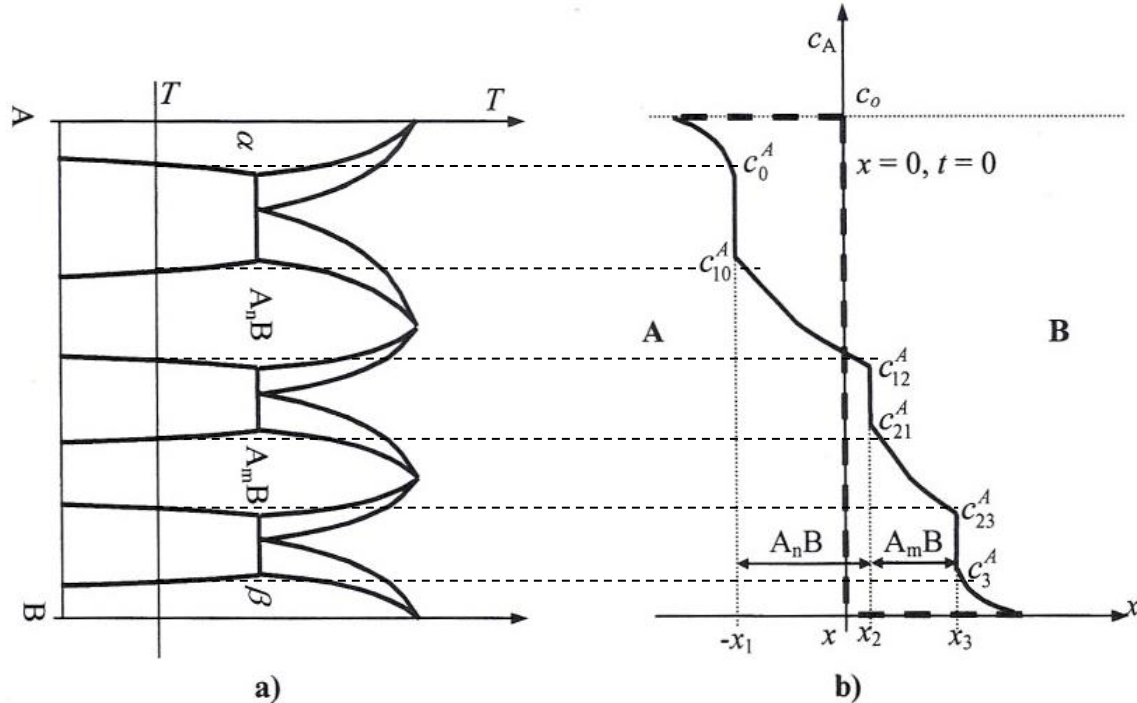


Figure 1 Multiphase diffusion in the A-B binary system a) hypothetic binary system, b) gradual course of concentration

A growth of phases in metal A after long-term heating and detecting the thickness of layers in the diffusion couples metal A – melt B in systems copper – lead free solder will be presented in this paper.

2. THEORY OF THE PLANAR DISSOLUTION

For the planar interface boundary when the interface shift during the dissolution is perpendicular to the interface, the relation is obtained [12-17]

$$\chi(t) = \frac{\rho_2}{\rho_1} \frac{1 - e^{-K_0 t}}{\frac{1 - c_0}{c_0} + e^{-K_0 t}} l_0, \tag{1}$$

where: l_0 is the width of the melt column at time $t = 0$, ρ_2, ρ_1 are densities of the solid and liquid phases, $\chi(t)$ is the shift of the interface boundary during dissolution and c_0 is the saturated concentration of the metal A in the melt B at the temperature T . The following holds for the time dependence $c(t)$ of the metal A in the melt B

$$c(t) = \frac{\chi(t)}{a + \chi(t)}, \quad a = \frac{\rho_2 l_0}{\rho_1}. \tag{2}$$

Relation (1) describes the time dependence of planar dissolution. K_0 is the rate constant of dissolution. Neither the diffusion of atoms B from the melt into solid phase A nor the volume changes during dissolution were taken into account in the model. Convection in the melt will influence the rate of dissolution and therefore the exact value K_0 will partly depend on the geometry, in which the planar dissolution takes place. The relation (1) may be used for an approximate evaluation of the rate constant of dissolving K_0 under precisely defined experimental conditions. **Figure 2** illustrates the calculated dependences $\chi(t)$ for Cu – Sn system. The values

of density ratios $\rho_2 / \rho_1 \approx 0.766$ for $T = 400$ °C, $c_o = 0.115$ (from the phase diagram Cu – Sn), $l_o = 1$ cm at $K_o = (0.3 \div 1.2) \cdot 10^{-5} \text{ s}^{-1}$ were used in the calculations. Time dependences of the component A concentration in the melt, assuming perfect melt homogenisation, are obtained from relations (1) and (2)

$$c_A(t) = c_o (1 - e^{-K_o t}) \quad (3)$$

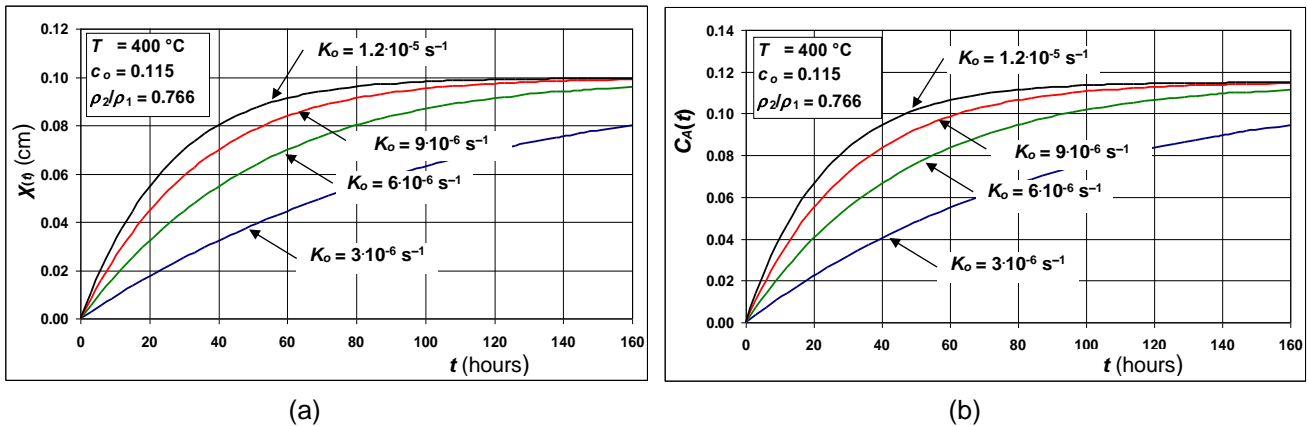


Figure 2 Graphs of functions (a) $\chi(t)$ – eq. (1) and (b) $c_A(t)$ – eq. (3) for the liquid temperature 400 °C in Cu – Sn system and various values of $K_o = (0.3 \div 1.2) \cdot 10^{-5} \text{ s}^{-1}$ for planar dissolution

3. EXPERIMENT

3.1. Experimental study of growth of phases and reactive diffusion on planar specimens

The uni-directional experiment was realized using the “sandwich” specimens. A layer of a tin-based solder was inserted between two Cu plates. Three compositions of lead-free solder alloys were used: pure Sn, Sn97Cu3, Sn95.5Ag3.8Cu0.7 (in wt%). Two plates of high-purity copper were 0.5 mm thick, the other dimensions were 20 x 10 mm. The Sn-based solders inserted between the two Cu plates were rolled down to the thickness 0.6 mm. Copper plates were covered by a layer of suitable flux. The soldered joint was created using a heating element. The sandwiches were held at the temperature $255 \div 285$ °C (above liquid) for 40 - 120 seconds. Prepared specimens were subsequently annealed at $T = 300$ °C for 18, 24, 48 and 92 h.

The η -Cu₆Sn₅ grows into during annealing at the temperature $T = 300$ °C on the interface with the Cu. Copper dissolves in liquid Sn-based solder up to the saturation concentration about 4 at.% (2.2 wt.%) Cu. As a consequence of Sn diffusion into solid Cu, phase η grows with time and subsequently phase ϵ (Cu₃Sn, 75 at.% Cu and 25 at.% Sn) appears close to the pure Cu. The specimens were cooled on the air after annealing and the temperature decreased relatively quickly below the eutectic temperature 227 °C. The joint Cu/Sn95.5Ag3.8Cu0.7 is shown in **Figure 3** after 24 hours of annealing as an example.

At X-ray microanalyses we only obtain this value on the straight line, which should be perpendicular to the interface boundary. X-ray microanalysis of concentration profiles for Cu/Sn joint is in **Figure 4**.

The growth of phase ϵ should proceed with time according to parabolic law $\chi_\epsilon(t) = \alpha \sqrt{t}$ where $\chi_\epsilon(t)$ is the thickness of ϵ and α phases, it is the constant which characterizes the rate of phase growth. The values $\chi_\epsilon(t)$ can be obtained experimentally using the metallographic pictures from relatively large areas. The evaluated values α from the metallography and X-ray EDX microanalysis are presented in **Table 1**. The calculated values α for Cu/Sn, Cu/Sn97Cu3 and Cu/SnAg3.8Cu0.7 joints from EDX measurements were in very good agreement. They were determined for $t = 18$ to 92 hours.

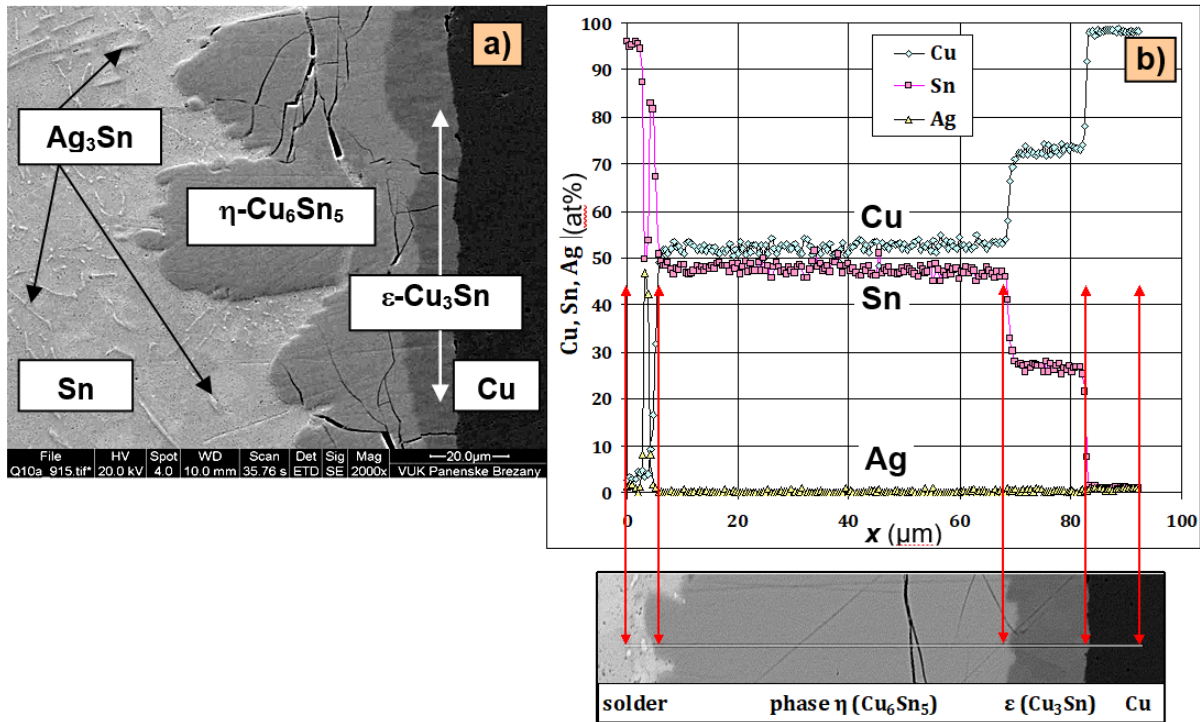
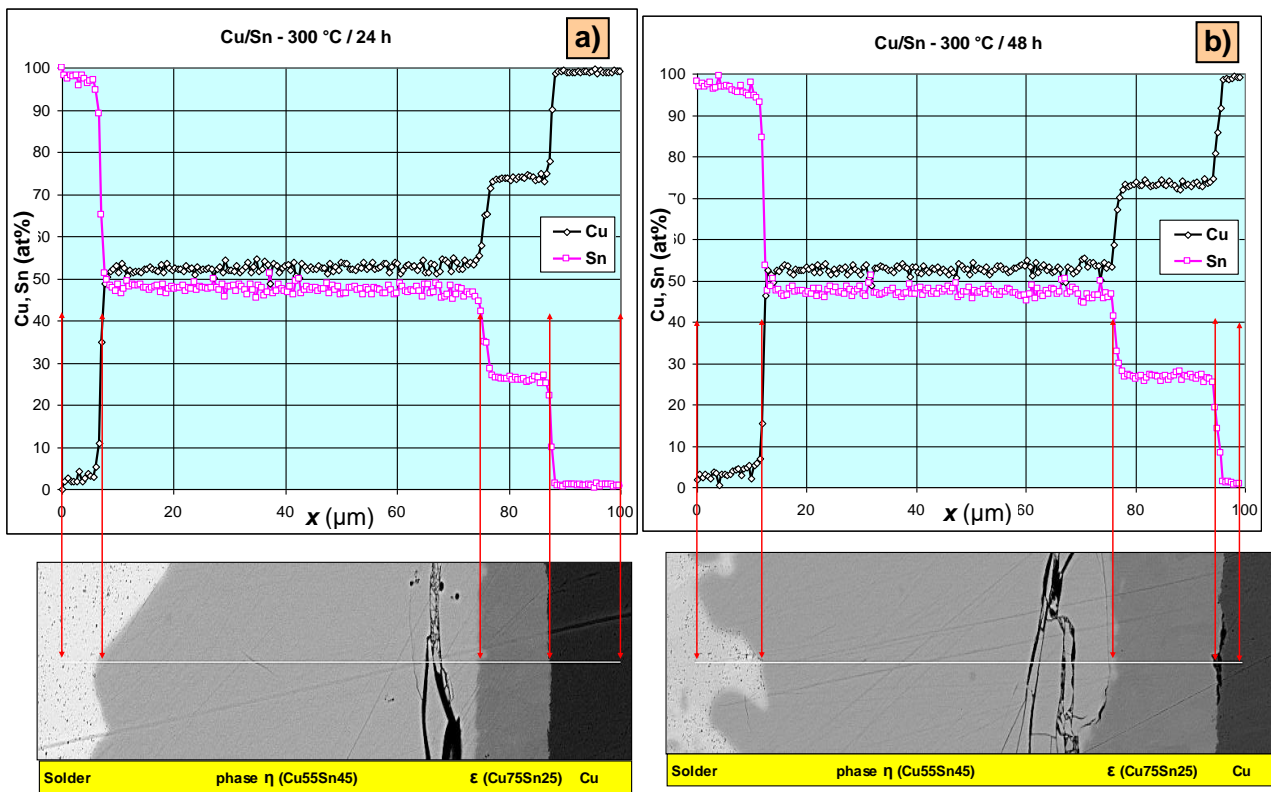


Figure 3 Microstructure a) and concentration profiles b) in the joint Cu/SnAg3.8Cu0.7 annealed at 300 °C for 24 hours



a) $T = 300\text{ }^{\circ}\text{C}$, $t = 24\text{ h}$

b) $T = 300\text{ }^{\circ}\text{C}$, $t = 48\text{ h}$

Figure 4 Microstructure and concentration profiles in the Cu/Sn joint

Table 1 Evaluation of the rate of growth of phase ε in „sandwich“ specimens at temperature $T = 300\text{ }^{\circ}\text{C}$

EDX analysis	T (h)	$\alpha \cdot 10^6$ (cm/s ^{1/2})	mean $\alpha \cdot 10^6$ (cm/s ^{1/2})	Metallography	T (h)	$\alpha \cdot 10^6$ (cm/s ^{1/2})	mean $\alpha \cdot 10^6$ (cm/s ^{1/2})
Cu/Sn			3.33	Cu/Sn	18	5.84	5.57
	24	3.23			24	5.10	
	48	3.43			48	4.38	
					92	6.95	
Cu/Sn97Cu3			3.25	Cu/Sn97Cu3	18	6.50	5.41
	24	3.16			24	6.23	
	48	3.34			48	4.0	
					92	4.92	
Cu/Sn95.5 Ag3.8Cu0.7	18	6.12	4.76	Cu/Sn95.5 Ag3.8Cu0.7	18	6.6	4.27
	24	3.42			24	3.63	
	48	4.30			48	2.40	
	92	5.21			92	4.46	

3.2. Calculation of Sn diffusivities at $T = 300\text{ }^{\circ}\text{C}$ based on the growth of the phase ε into Cu

This tentative calculation was performed using Wagner relation [15-17]. Based on the X-ray analysis of concentration curves we searched for the size of interval Δx , where the Sn concentration in Cu decreased nearly to zero. We can estimate the diffusivity D from the value Δx and the known time of annealing t using the equation:

$$\frac{\Delta x}{2\sqrt{Dt}} \approx 1.5; \quad \operatorname{erfc}(1.5) = 0.034. \quad (4)$$

Diffusion joint: Cu/Sn, $t = 48\text{ h}$, $T = 300\text{ }^{\circ}\text{C}$, $\Delta x = 2\text{ }\mu\text{m}$, $D \approx 2.6 \times 10^{-14}\text{ cm}^2/\text{s}$.

Diffusion joint: Cu/Sn97Cu3, $t = 24\text{ h}$, $T = 300\text{ }^{\circ}\text{C}$, $\Delta x \approx 2\text{ }\mu\text{m}$, $D \approx 5.1 \times 10^{-14}\text{ cm}^2/\text{s}$.

4. DISCUSSION

Binary system A–B, when element A is in the solid phase, was opted as a model example. During the dissolution of the melt B is being saturated with metal A, the melt viscosity may change and then natural convection in the melt decelerates with time. This also partly decelerates the rate of dissolution. We have to realize that the values of rate constant of dissolution K_0 determined experimentally only correspond exactly to a particular geometry and conditions of experiment considering the character of convections in the melt corresponding to particular experimental arrangement.

At dissolution an increased concentration of substance A in melt B is near the interface boundary and at the experiments in question the melt homogenization proceeds due to natural convection in the melt, e.g. even due to small temperature gradient, different densities in the solid phase and melt, vibrations and shakes, etc. With extending the time of dissolution during experiments, the rate of convection decreases due to increasing the substance A concentration in the melt, because the viscosity of melt usually increases. When the saturated concentration in the melt is achieved, dissolution is terminated, equilibrium is set and the interface boundary movement may only proceed in consequence of diffusion in the solid phase. However, this process is mostly by several orders slower than the interface boundary movement at the metal dissolution in the melt and that is why it was neglected in deriving of the interface boundary movement at dissolution. It has to be marked that the values of the rate constant of dissolution K_0 determined experimentally only correspond to a particular

geometry and conditions of experiment due to the character of the convection in the melt pertaining to a particular experimental arrangement.

When observing the growth of phases in system Cu–Sn on planar specimens at the temperature $T = 300\text{ }^{\circ}\text{C}$ a very irregular growth of phase η , especially into the melt, was discovered and estimates of the rate of growth of phase ε into Cu according to the parabolic law were performed as well for the other lead-free solders.

A fast growth of phases in metal A after long-term heating and detecting the thickness of layers with these phases, i.e. $\chi_{\varepsilon}(t)$, $\chi_{\eta}(t)$ etc. pose considerable time demands on structural and chemical microanalyses of specimens.

5. CONCLUSION

In this paper the problems of reactive diffusion at the contact of solid phase with solder melt were outlined briefly. Examples of particular experimental arrangements were presented. The main intention was to calculate time courses of the solid phase dissolution for the cases of planar geometry. The calculations were started from the equation (1) describing the kinetics of dissolution. As an example we presented concentration profiles in the joints Cu/SnAg_{3.8}Cu_{0.7} annealed at 300 °C for 24 hours and Cu/Sn at 300 °C for 24 and 48 hours.

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