структуры и скорости распространения ламелярного структуры в период роста. Сравнение с экспериментом представляется вполне удовлетворительным.

O.Yu. Liashenko

PECULIARITIES OF THE NUCLEATION AND GROWTH OF THE INTERMETALLIC PHASES AT SOLDERING: AMBIGUOUS EXPERIMENTAL RESULTS AND RECENT DEVELOPMENTS IN MODELLING

The interactions between tin or tin-based alloys (in the solid or liquid state) with a copper substrate are reviewed. The majority of studies show that the η-Cu₆Sn₅ phase is a first to grow rapidly during reflow. The nucleation sequence of the intermetallics and their growth kinetics depend on the supersaturation of copper in the liquid tin droplet and on the rate of the removal of this supersaturation in the solder ball. The η phase grows by the well-known law of growth with time exponent 1/3 (interface controlled regime) or law of growth with time exponent 1/2 (volume diffusion control) but also obeys to other laws of the growth kinetics during reflow. The successful models that describe the suppression and growth of the intermetallics are reviewed. During solid-state ageing, the experimental results show that the intermetallic growth kinetics, their competition as well as voiding at the interfaces depend on the kind of the Cu substrate, namely its structure.

Keywords: soldering, nucleation, growth, phase competition, reliability.

Introduction

Soldering is the key technological way to join the separate metallic parts with use of the filler metallic alloy or pure metal in the medium. Known for thousands of years the technique is still in the great interest being the one mostly used in microelectronic industry to join the under-bump metallization layers (UBM), namely the Cu thin films on the printed boards, Cu wires, etc. The Cu-Sn system is the most in demand system in the soldering technology and the Sn-based solder are used in all the packaging techniques. The solders are basically the pure tin or tin-based eutectic alloys in the form of the ball. The permanent trend of miniaturization produces the new challenges. The most crucial are the reliability issues. The

significant decrease of the solder size obeys the following tendency [1]: 1) the modern flip-chip technology operates with solder balls with diameter of 100 μm; 2) the transition to 3D-integrated circuits lowers the size to 20 μm; 3) the forecast is that the solder joint diameter could be reduced to 1 μm.

The conventional solder reaction that develops during so-called reflow process incorporates reactive wetting of the copper substrate with instantaneous growth of common intermetallic compounds (IMC) at the solid substrate/liquid solder interface [2]. Reflow operation is the heating cycle, during which the temperature exceeds the melting eutectic temperature of solder by two-three tens of degrees and the allotted time of reaction is fixed to be couple of minutes (typically 2-3 minutes).

As it was mentioned above, the copper is commonly used as the UBM and interacts with tin. Usually the soldering reactions proceed at the temperatures below 350^0C. As can be seen from the phase diagram, the reaction on the Cu/Sn interface leads to formation of ε-Cu_3Sn and η-Cu_6Sn_5 compounds [3] at such temperature (see Figure 1). There are two allotropic forms of the Cu_6Sn: η´ with monoclinic structure, which is stable for the temperatures less than 187,5 ^{0}C and η with hexagonal structure, which is stable for the temperatures above 187,5 ^{0}C.
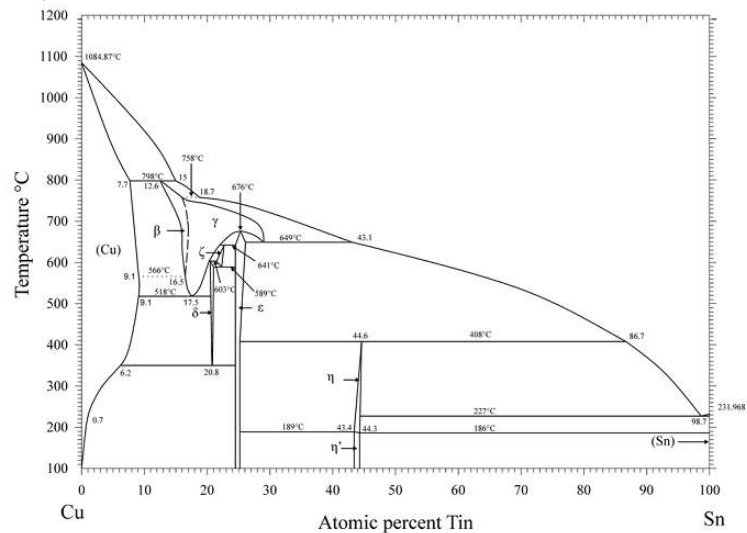

Figure 1. The Cu-Sn phase diagram [3].

No matter of the size of the solder joint, the prolonged heating of the joint during operation of the device results in the solid-state aging of the joint with slow but constant growth of the IMC layers. The reliability issues connected with voiding and subsequent mechanical weakening of the solder joint due to the thickening of the IMC's are emerging during long-term solid-state annealing [2, 4].

The aim of this review is to demonstrate the recent developments and ambiguous results of the study of growth kinetics of the IMC phases during solid-state aging of solder joints and during reflow.

Reflow of the solder joint
General issues
The interaction between solid copper and liquid tin or tin-based solder starts with rapid dissolution of copper till the metastable solubility of tin by copper is reached [5]. The metastable solubility is always higher than the stable one, so even during reaction of copper with pre-saturated tin-based solder the dissolution should happen. The copper diffusion in liquid tin is a very rapid process, as it is well known that the magnitude of the diffusion coefficient in liquids can be as high as 10^{-9} m^2/s. As a result, the copper concentration profile

of the "diffusion profile" type emerges rapidly in the liquid tin or tin-based solder. The conventional solder balls of size of 100 μm can be saturated in Cu at time less than 10 s [6].

As it was emphasized before, the formation of the reaction layers proceeds in the metastable state. It is generally accepted that the growth of the η-Cu_6Sn_5 crystallites is dominant for the initial stages of the reaction [5, 7-8]. As it will be shown below the growth the thickness of η-Cu_6Sn_5 layer exceeds drastically the thickness of the ε-Cu_3Sn phase at any moment of the reaction between liquid tin and solid copper.

Experimental studies of the reflow process and reaction between solid copper and liquid tin

R.A. Gagliano et al. [5] have dipped the Cu foils in the tin bath (heated up in the range of temperatures of 240-300^{0}C) for the very short time of 1s. The foils were quenched subsequently in the cold water. It was shown that the copper substrate is completely covered by η-Cu_6Sn_5 crystallites even after such short time of reaction whatever the temperature of the tin bath (see Figure 2).

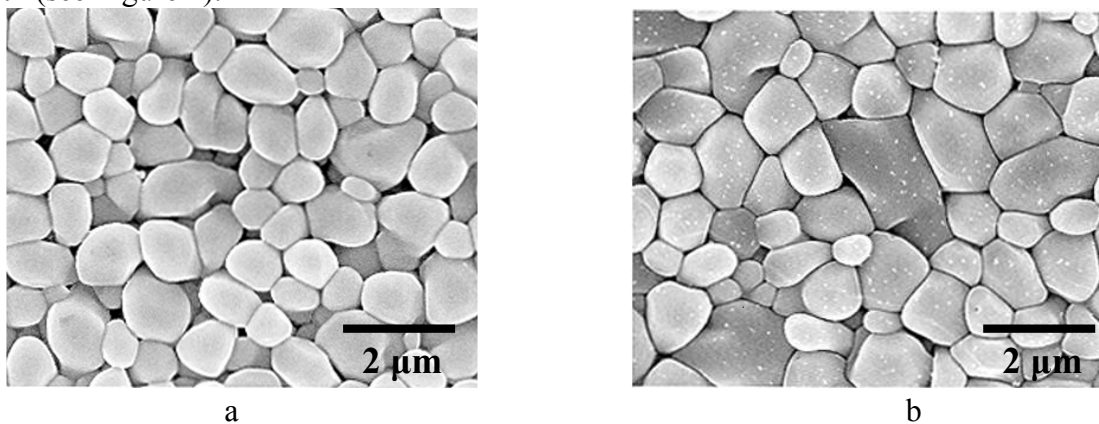a   b

Figure 2. The top-view SEM images showing the microstructure of the Cu_6Sn_5 after dipping in the molten tin for 1s at a – 240^{0}C and b – 300^{0}C [7].

The morphology of the η grains can be very different, depending on the temperature [9], Cu or Ni UBM crystallographic orientation [10-13], solder composition [14]. The variety of the η grains growing during reaction between Cu and liquid tin includes: scallop-like [9], faceted [14] or longitudinal [15].

One example of the morphology evolution can be given on the basis of the work of R.A. Gagliano et al. [15]. The study of the reaction layers of the Sn/Cu couple revealed the formation of the longitudinal η phase grains (see Figure 3 and Figure 4). It was found that the aspect ratio (namely ratio between grain height and width) is growing with annealing time (Figure 3) and with annealing temperature (Figure 4).
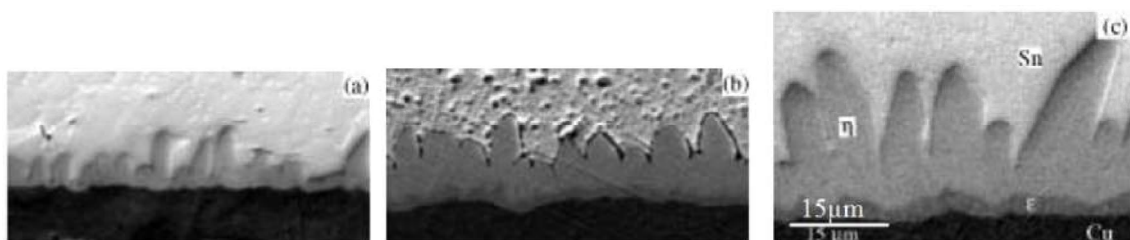

Figure 3. Morphology evolution of the η-phase grains during solid Cu/liquid tin reaction at 275^{0}C for a –3 min, b – 45 min and c – 180 min
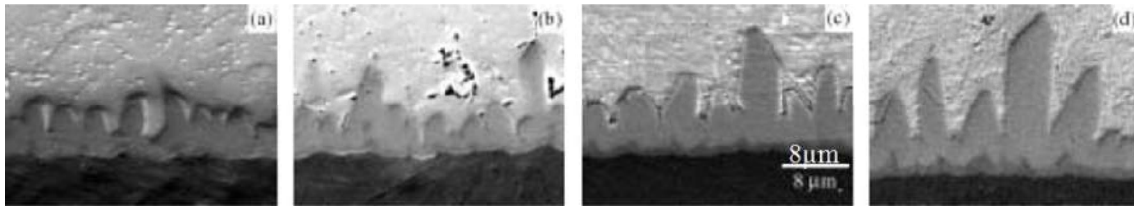(the same magnification is given for three images) [15].

Figure 4. Morphology evolution of the η-phase grains during solid Cu/liquid tin reaction at different temperature. for a – 3 min, b – 45 min and c – 180 min
(the same magnification is given for three images) [15].

In their work J.O. Suh et al. [14] have shown that faceted dendrites of the η-phase are formed at the interface between Cu and pure Sn (see Figure 5a) at 250^0C after 2 min reaction. The clearly different morphology, namely round scallop-like η-phase scallops, was observed by M. Yang et al. [9] after reaction at almost identical temperature of 240^0C after 2 min reaction (see Figure 5b). In both studies it was found that the mean size of dendrites grows with time and temperature following the Ostwald ripening mechanism.
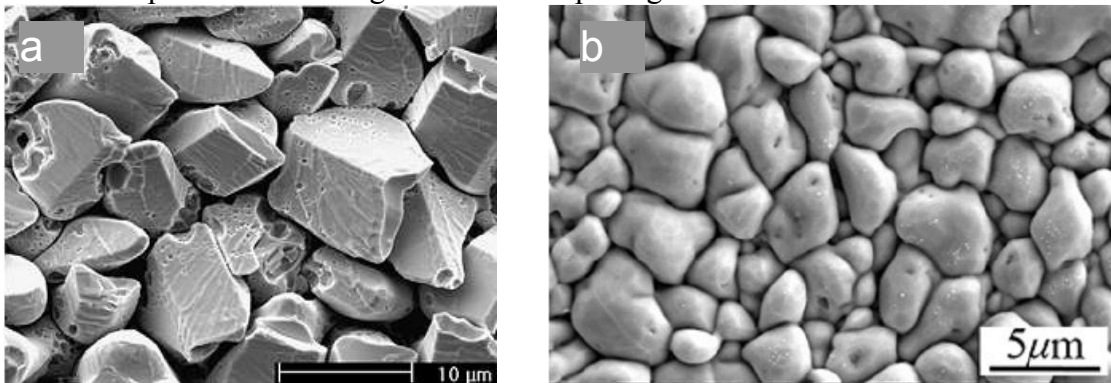

Figure 5. Top view SEM image on the η-phase after 2 min reaction between solid Cu and pure liquid Sn: formation of the faceted dendrites at 250^0C [14] (a) and formation of round the scallop-like dendrites at 240^0C [9] (b).

Recently, a couple of studies implemented synchrotron radiation to track the different stages of the η-phase growth *in situ* [16-17]. M.L. Huang et al. [16] implemented synchrotron radiation *in situ* observation technique for pre-annealed Cu/pure Sn couple at 260^0C for 2h. The heating cycle during observation was as following: start from the room temperature → heating up to 280^0C with a heating rate 15^0C/min → dwelling for 226s at 280^0C → cooling down with a cooling rate 10^0C/min. Authors succeed to detect the decrease of the single grain aspect ratio (see Figure 6a) as well as average IMC thickness (see Figure 6b) during heating stage. The change in aspect ratio values indicates the transition from the longitudinal to the scallop-like shape during the heating stage. During dwelling stage both aspect ratio and average thickness stayed almost constant. During cooling stage the Cu_6Sn_5 compound re-precipitated on the existing Cu_6Sn_5 grains resulting in the significant increase of the aspect ration of individual scallops as well as the average thickness of the IMC. The proposed model fitted well the experimental data on the basis of the suggested parameters (see Figure 6b).

The initial stage of the soldering reaction was studied by M.A.A. Mohd Salleh et al. [17]. The growth of the IMC was tracked from the very beginning of the reaction between Cu and Sn-0.7wt%Cu solder at the melting temperature of the solder (~227^0C) and subsequent cooling. Authors detected the formation of the planar (within resolution of the imaging) layer of the IMC. The IMC layer develops to the scallop-like morphology subsequently. The voids were also detected in the vicinity of the IMC. The reaction kinetics was also studied at higher temperature of 244^0C after placing the liquid droplet of solder on the substrate at this

temperature. Authors measure the IMC thickness versus time (see Figure 7a) as well as logarithmic dependence of the layer thickness with time (see Figure 7b) in order to identify the growth constants. The planar IMC layer precipitates at the very beginning (~ 1s) of the wetting reaction. As can be seen, the growth of the IMC is not monotonic, three different regimes were distinguished: 1) the initial slow growth with time exponent 0,07 within first 10 s of reaction at 244^0C; 2) the rapid growth with time exponent 0,31 at 10-50 s of reaction time; 3) slow growth during cooling to 213^0C (unfortunately, the cooling rate is not specified) the growth exponent decreased significantly to 0,03. Cooling stage took approximately 110 s.
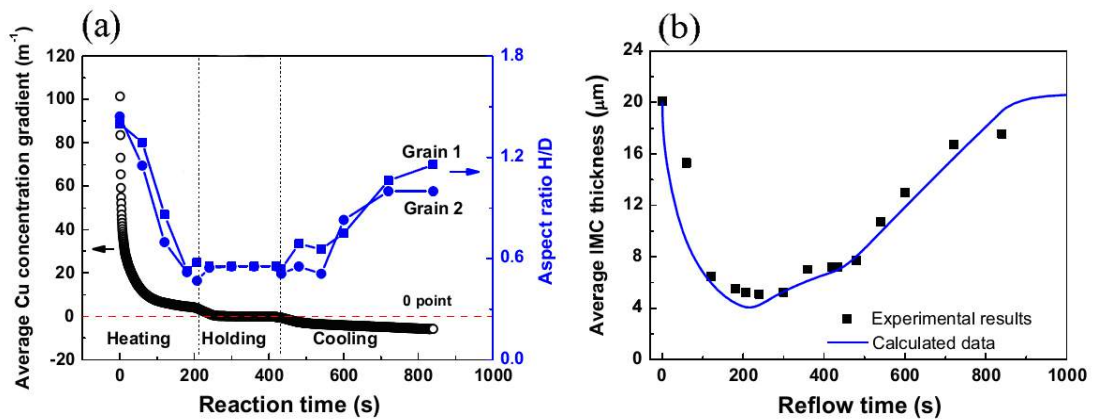

Figure 6. The aspect ratio of two individual grains and the average Cu concentration gradient – a and the average IMC thickness – b as a function of a reaction (reflow) time [16].
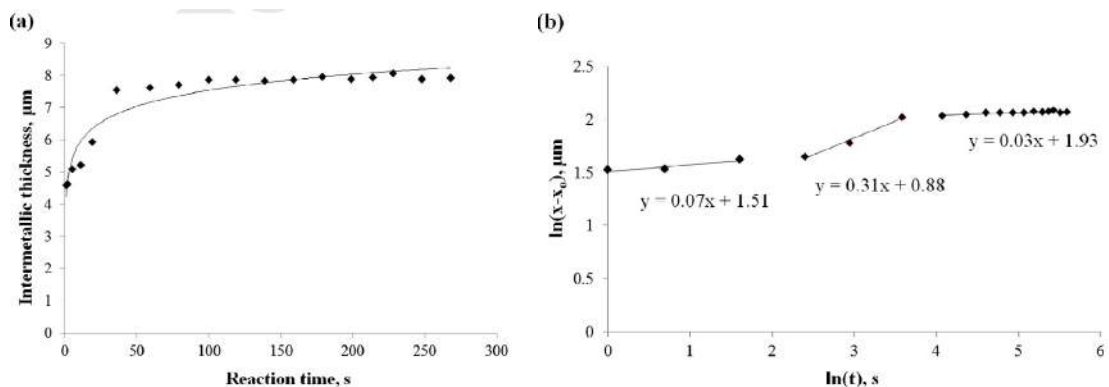

Figure 7. a – the mean IMC thickness versus time; b – ln-ln dependence between IMC thickness and time indicating three stages of the IMC growth during reflow process (temperature range 213-244^{0}C) [17].

It is believed in majority of studies that the formation of the ε-phase is suppressed initially for some period time ranging from 8-10 s [8, 18-19] to 80 s [15]. Normally, after reflow process that lasts few minutes the ε-phase is formed in the form of the continuous and relatively uniform layer. Therefore, during reaction between solid copper and liquid tin the interfacial system consists of two intermetallic layers η-Cu_6Sn_5 and ε-Cu_3Sn organized in the following way: Cu/ε/η/Sn. The interfacial layers formed after prolonged reaction of copper with liquid tin are shown on the Figure 8. Normally, during soldering reaction, when the peak temperature exceeds the melting temperature of the solder by some tens of degrees the ε-phase is much thinner than η-phase.
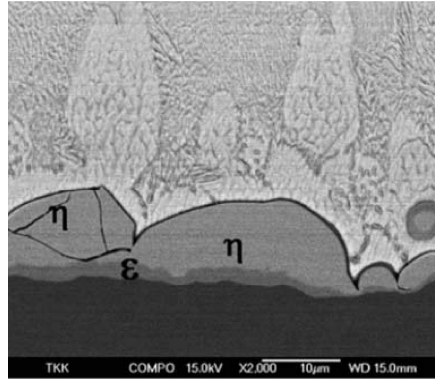
Figure 8. SEM micrographs showing the interfacial zone after Cu-Sn reaction
for 64 minutes at 250^0C [5].

The average thickness of the η-Cu_6Sn_5 phase above which ε-Cu_3Sn phase starts to grow as a continuous layer at Cu/Cu_6Sn_5 interface during liquid Sn/solid Cu interaction has been evaluated from thermodynamic and kinetic considerations [20]. The model predicts that ε-Cu_3Sn phase layer can overcome suppression by η-Cu_6Sn_5 phase after mean size of scallops exceeds about 1 micron.

The growth kinetics of the IMC layer has been studied extensively up to the day (see for example [9, 15, 18, 21]). The systematic study of the reaction between solid Cu and liquid Sn is presented by S. Bader et al [18]. The authors have studied the reaction at the initial stage starting from 5 s to 2.5 minutes. Such duration of reaction is corresponding to the reaction time during conventional soldering procedure. In their study [18] authors studied the reaction between micrometric layers of copper and tin deposited by physical vapor deposition (or PVD). The reaction temperature was 240^0C and 330^0C and whatever the temperature the authors found the linear variation of the thickness of both IMC phases: ($l_\eta < 3$ μm) and ε ($l_\varepsilon < 1$ μm).

R.A. Gagliano and M.E. Fine [15] studied extensively the reaction between Cu and liquid Sn in the range of temperatures from 250^0C to 325^0C (Figure 9). It was found that the η phase growth is governed by cubic power law of time, whereas the evolution of the ε phase is diffusion controlled following the parabolic growth regime. The layer thickness l_i (i = η or ε) could be described by the following relations:

$$l_i = k_i t^n \text{ and } k_i = k_i^0 \exp\left(\frac{-Q_i}{RT}\right),$$
(1)

where $k_\varepsilon^0 = 0{,}026$μm·$s^{1/2}$; $k_\eta^0 = 0{,}103$μm·$s^{1/2}$ and $Q_\varepsilon = 53{,}1$kJ·$mole^{-1}$; $Q_\eta = 13{,}4$kJ·$mole^{-1}$.
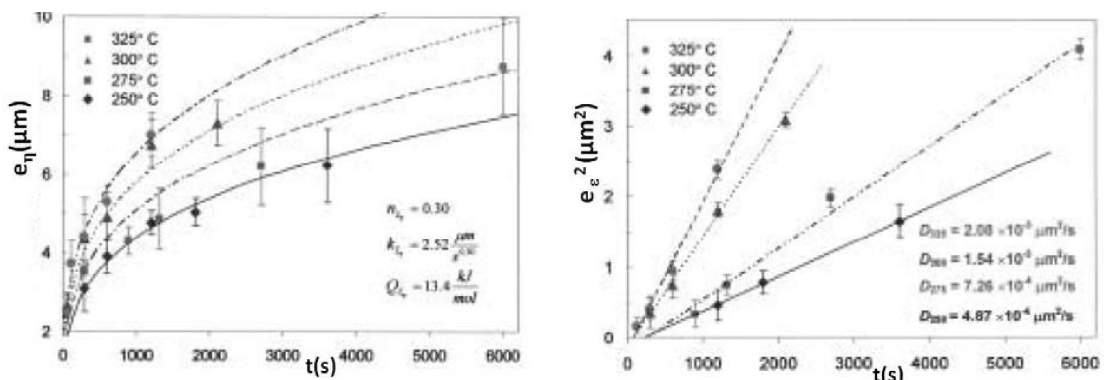
Figure 9. The growth kinetic of the a – η-Cu_6Sn_5 phase and b – ε-Cu_3Sn phase in the temperature range 250-325 ^{0}C [15].

The parabolic growth of the ε-Cu_3Sn phase and cubic law of growth of the η-Cu_6Sn_5 phase were also detected by M. Yang [9] at $T = 240^0C$ and $T = 280^0C$. Nevertheless, the transition from cubic with n ≈ 1/3 to parabolic regime n ≈ 1/2 of growth was detected for η-Cu_6Sn_5 phase at later stages of reaction, namely after reaching 30 min of reaction at both experimental temperatures. The ε-Cu_3Sn phase was growing following the parabolic regime with n ≈ 1/2 whatever the time and temperature. The growth constants of the η-Cu_6Sn_5 phase at the initial stages of reaction ($t < 30$ min) could be determined as $k_\eta = 0{,}139 \mu m \cdot s^{1/2}$ and $k_\eta = 0{,}179 \ \mu m \cdot s^{1/2}$ for $T = 240^0C$ and and $T = 280^0C$ respectively. The growth constants of the η-Cu_6Sn_5 phase at the initial stages of reaction ($t < 30$ min) were determined to be $k_\varepsilon = 0{,}021 \mu m \cdot s^{1/2}$ and $k_\varepsilon = 0{,}032 \ \mu m \cdot s^{1/2}$ for $T = 240^0C$ and and $T = 280^0C$ respectively. These values were calculated on the basis of the growth exponents measured by authors.
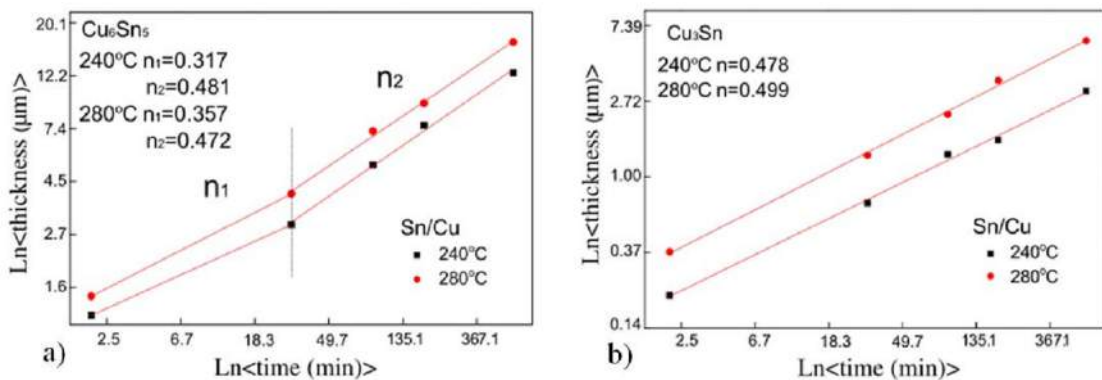

Figure 10. The growth kinetic of the a – η-Cu_6Sn_5 phase and b – ε-Cu_3Sn phase at $T = 240$ and $T = 280 \ ^0C$ [9].

M.L. Huang and F. Yang [22] have conducted the experiments with Sn-xAg-yCu solder balls of different size varying from 200 to 500 µm and demonstrated that the growth kinetics depends on the size of the solder balls. The Figure 11 gives the variation of the IMC layer thickness with time during reaction between Cu and Sn-3.0Ag-0.5Cu solder alloy (Figure 11a) and Cu and Sn-3.5Ag solder (Figure 11b). Authors have also proposed the model of growth called the concentration gradient controlled (CGC) model but as can be seen from Figure 11in some cases it overestimates or underestimates the IMC growth rates in comparison with experimentally measured values.
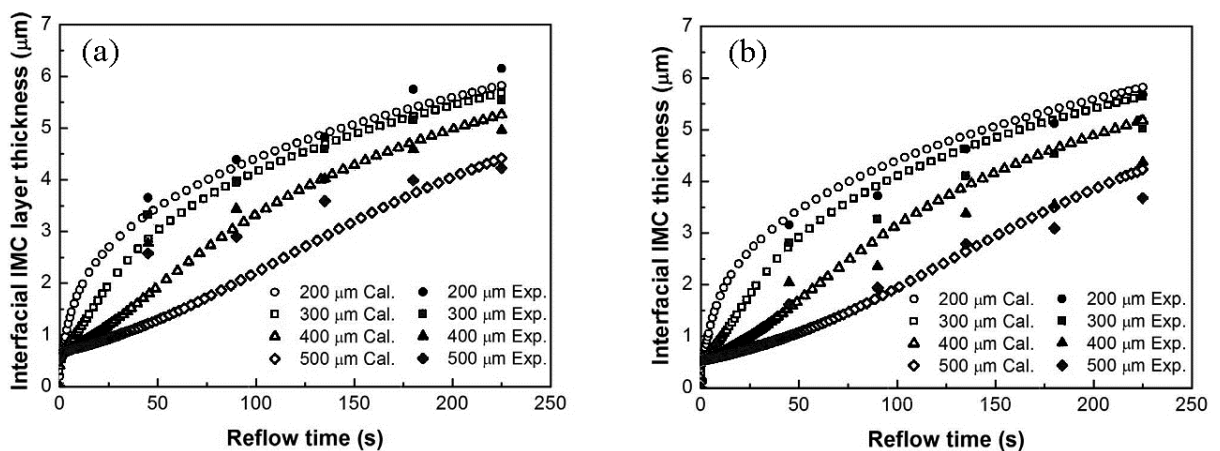

Figure 11. Variation of the IMC thickness with time during a – Cu/Sn-3.0Ag-0.5Cu reaction, b – Cu/Sn-3.5Ag reaction at $T = 250^0C$ [22].

Modeling of the phase growth and competition during reflow

In their work A.M. Gusak and K.N.Tu [23] established a theory called Flux-Driven Ripening (FDR) theory that was called to model the growth of the IMC layer during the soldering reaction. Two important constraints were used in modeling the system:

1)   The *geometrical* constraint is that the interface of the reaction stays constant. By assuming that the scallops have hemispherical shape (Figure 12a), it means that the total surface of the growing scallops is equal to the double surface between scallops and copper substrate (in their model [23] neglected the formation of the ε-Cu₃Sn phase). In fact, authors were considering the ripening process at which the growth of one scallop is happening at expense of other. As can be seen from Figure 12a the existence of the nanometric liquid channels between scallops was suggested, but the fracture of the channels total cross-section was considered to be negligible, so the total interface are between scallops and melt can be expressed as:

$$S^{\text{scallops/melt}} = \sum_{i=1}^{N} 2\pi R_i^2 = 2 \times \sum \pi R_i^2 = 2S^{\text{total}} = \text{const}. \qquad (2)$$

2)   The second constraint is the *conservation of mass* which determines that all the in-flux of Cu atoms is used for the scallop construction. In algebraic representation it means that:

$$n_i C_i \frac{dV_i}{dt} = J^{\text{in}} S^{\text{free}}, \qquad (3)$$

where n_i and C_i are atomic density and mole fraction of copper in the intermetallic respectively. The in-flux is found by applying Fick's law and knowing the average gradient equal to the ratio between equilibrium supersaturation $\Delta C = C^b - C^e$ and mean size of the scallops

$$J^{\text{in}} \cong -nD \frac{C^e - C^b}{\langle R \rangle}, \qquad (4)$$

where $\langle R \rangle$ is the average size of a grain, D is the diffusion coefficient of Cu in the melt and the supersaturation corresponds to the difference between equilibrium concentration of Cu in the liquid alloy near the substrate C^b and equilibrium concentration of Cu in the liquid alloy near the top of the IMC C^e. Both equilibrium concentrations can be found by constructing the common tangents if the thermodynamic assessment of the system is known (see Figure 12b).
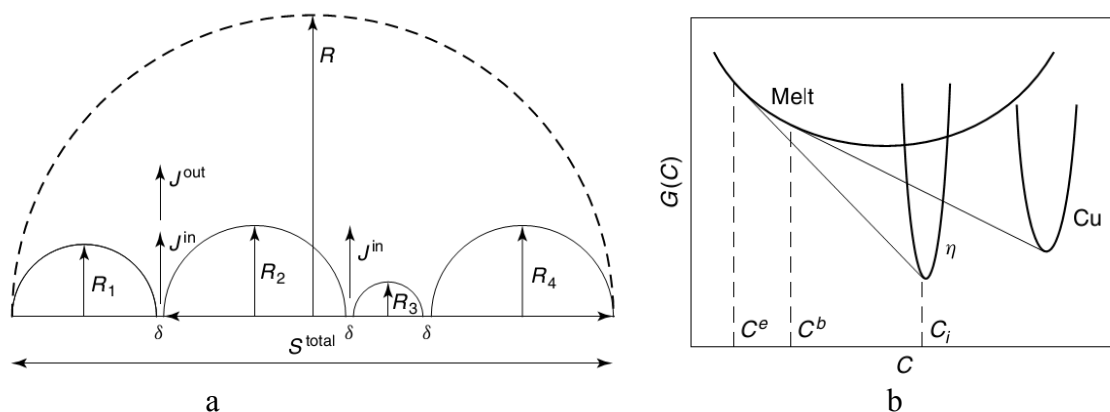

Figure 12. a – Schematic diagram of the cross section of an array of scallops on Cu [23]. There J_{in} is an input flux of copper from substrate, which is supplied by liquid channels of width δ, J_{out} is a flux of "unused" Cu atoms which haven't been incorporated in building IMC phase; b – Schematic dependence of Gibbs free energy on composition.

The final result of the model is derivation of the well-known interface controlled regime of the growth with power 1/3 dependence:

$$\langle R^3 \rangle = kt \,, \tag{5}$$

where the growth rate k is determined as:

$$k = \frac{9}{2} \frac{n}{n_i} \frac{D \left(C^b - C^e \right) \delta}{C_i} \,. \tag{6}$$

The FDR theory was tested in various studies and proved its efficiency. For example, J.O. Suh et al. [14] compared the experimentally measured distributions of scallop sizes obtained by reaction of Cu with 55Sn45Pb solder with theoretical curves from the FDR theory and obtained nice correspondence for reaction times varying from 30s to 8 min (see Figure 13). After fixing $D \approx 10^{-5}$ cm^{2}s^{-1} and $C^b - C^e \approx 0.001$ the width of the liquid channels was determined to be $\delta = 2.54$ nm.
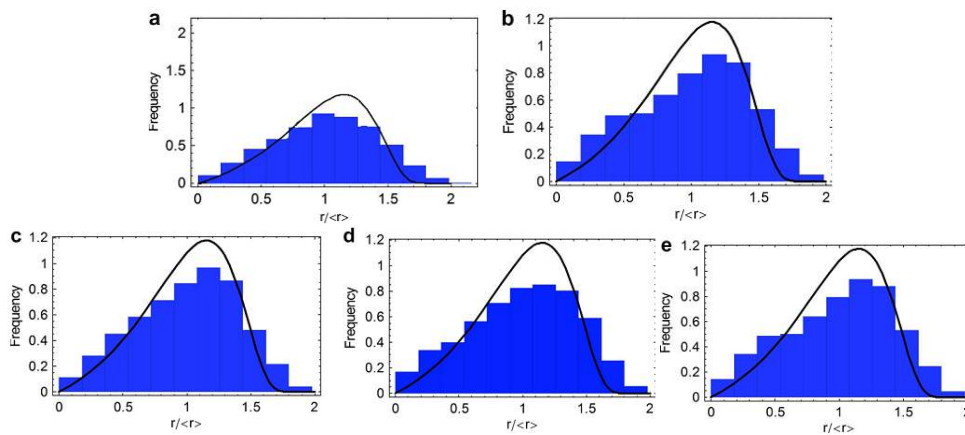
Figure 13. Size distribution of Cu$_6$Sn$_5$ scallops after a – 30s, b – 1 min, c – 2 min, d – 4 min and e – 8 min reflow at $T = 200^0$C. The solid curve corresponds to theoretical calculations from FDR theory [14].

The nature of the path of the fast transport of Cu to the IMC surface is still under discussion. The alternative opinion is that there are no liquid channels between Cu$_6$Sn$_5$ scallops but instead there are grooves [19]. In the vicinity of the substrate the existence of the prewetted grain boundaries (with permittivity of Cu comparable to the high one in the liquid solder) is suggested. Alternative idea [14] is that there agglomerates of the preferentially oriented Cu$_6$Sn$_5$ scallops staying on the separate Cu grains of the substrate. The idea is that the quantity of the liquid channels can be related not to the amount of the scallops itself but the amount of the agglomerates.

Reactions during solid state
General issues
The interfacial reactions between copper and solid tin were studied extensively for the moment but stay in the area of the great interest for industry and researchers. Nevertheless, some results of research are not always similar, describing principally different morphology evolution or giving different theoretical explanation of the growth rate limiting processes. The data on the growth kinetics of phases and their competition is ambiguous: there is no clear answer on the question, what phase grows faster within the temperature range 125-220^{0}C. It still under discussion, what is the most mobile specie during reaction: Cu or Sn.

Experimental studies of the reaction between solid copper and solid tin

The early stages of solid-state reaction Cu and Sn were extensively studied in the works K.N. Tu [24-25], K. N. Tu and R. D. Thompson [26], R. Chopra et al. [27]. The formation of the IMC starts even during deposition of the basic materials. The η-Cu_6Sn_5 phase is first to be formed, whereas ε-Cu_6Sn_5 phase appears after certain incubation time or increase of the temperature of reaction. As an example, during reaction in thin film (deposited by e-gun under vacuum) the Cu_6Sn_5 phase forms even after annealing at -2^0C during the period of one year. It was checked by the transmission electron microscopy (TEM) that Cu_3Sn phase starts accompanying the growth of Cu_6Sn_5 only after temperature reaches 60^0C [24-26]. Modern soldering technology incorporates electroplating as effective and cheap method of the material deposition. In the works of W.M. Tang [28] et al. it was shown that Cu_6Sn_5 phase is formed at the Cu/Sn interface even during deposition. Besides, the electronic microscope analysis with energy-dispersive x-ray spectroscopy (EDX) of the specimen aged for 76 days at ambient temperature (Figure 14) revealed very clearly the Cu_6Sn_5 layer with thickness less than 1μm.
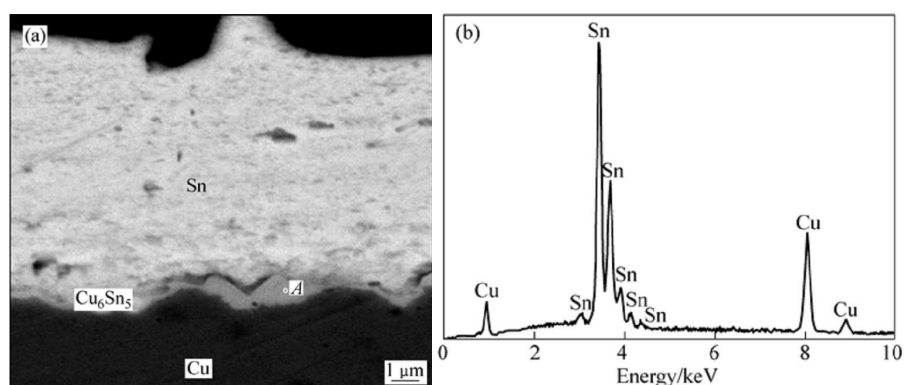

Figure 14. a – SEM image and b – EDX spectrum taken from point A of Cu/Sn couple after solid state aging at room temperature for 76 days [28].

The reactions at the Cu/Sn interfaces in the solid state at the range of temperatures 70-220^0C were studied in literature in details. Two types of experiments could be distinguished: the one based on the diffusion couple Cu/Sn or Cu/Sn-based alloys. Such kind of experiments need: 1) to incorporate accurate metallographic preparation of the surface of two solids; 2) to be performed either under secondary vacuum, either under the air but with use of the acidic flux to exclude the oxidation of the surfaces. The initial contact can be also realized by fast dipping of a copper into the flux and then into the bath with melted tin and subsequent cooling to room temperature. After the couple Cu/Sn-based alloy is isothermally aged for the certain time (up to 170 days [5]). The main number of the studies reports the presence of two phases, namely Cu_6Sn_5 and Cu_3Sn at the interface.
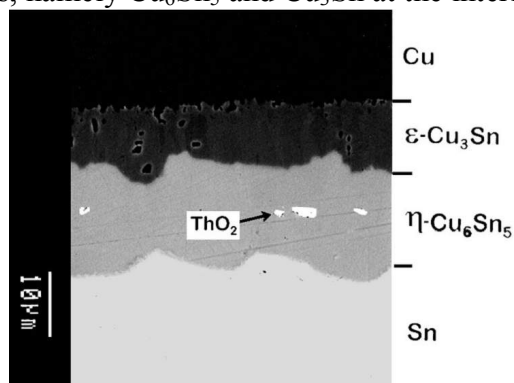

Figure 15. SEM image of the Cu/Sn interfacial zone developed after reaction at 215^0C in vacuum for 225 hours [29].

The Figure 15 shows the scanning electron microscopy (SEM) image of the interfacial zone of the Cu/Sn diffusion couple after aging at 215^0C for 225h under the vacuum [29]. The micrometric inert ThO_2 particles were placed as markers at the initial interface. Two phases Cu_6Sn_5 and Cu_3Sn with the thickness 10-15µm and 7-10µm respectively are seen. As can be seen, the Cu/ε interface is relatively plane in comparison with irregular ε/η and η/Sn interfaces. The marker ThO_2 particles moved in the middle of the Cu_6Sn_5 layer.

In their study M. Onishi et al [30] measured the average thickness of each phases (ε and η) as a function of reaction time up to 900h in the range of temperatures between 190^0C and 220^0C. The growth kinetics of both phases obeys parabolic, what means that the growth of reaction layers is limited by diffusion. Authors report that the growth rate of the η phase was higher than the one of the ε phase whatever the annealing time in the range of temperatures between 190^0C and 220^0C (Figure 16a).

The same trend in the phase competition is supported by the results of T.Y. Lee et al. [31]. Authors performed experiments with electroplated Cu UBM with thickness of 15 µm. The solder balls used in this study with diameter of approx. 100 µm were reflowed for 1 min above the melting temperature of the used solder with a peak temperature 240^0C. Solders used in the study were eutectic SnPb, Sn-3.5Ag, Sn-3.8Ag-0.7Cu and Sn-0.7Cu. The annealing time varied from 0 (just reflow) to 1500 hours and the annealing temperatures were 125, 150 and 170^0C. In all cases the growth rate of the η-Cu_6Sn_5 phase was higher than the one of the ε-Cu_3Sn phase.

Nevertheless, R. Labie et al. [32] report the faster growth of the Cu_3Sn phase at late stage of reaction (annealing time more then 70 hours) at 125^0C (see Figure 16b). The principal difference from experiment held in [30] are the use of the thin electroplated Cu UBM (5 µm) as well as thin layer of the Sn-bump (40 µm height). It should be noticed that to reach bonding before solid state annealing [32], the Cu/Sn couple was reflowed for 40s at 260^0C. This results in the thick initial IMC layer of η-Cu_6Sn_5 phase (Figure 16b). Basically, the total thickness of the IMCs layers increase due to the increase of the ε-Cu_3Sn phase thickness that obeys square root law and, evidentially, growth by the diffusion controlled mechanism.
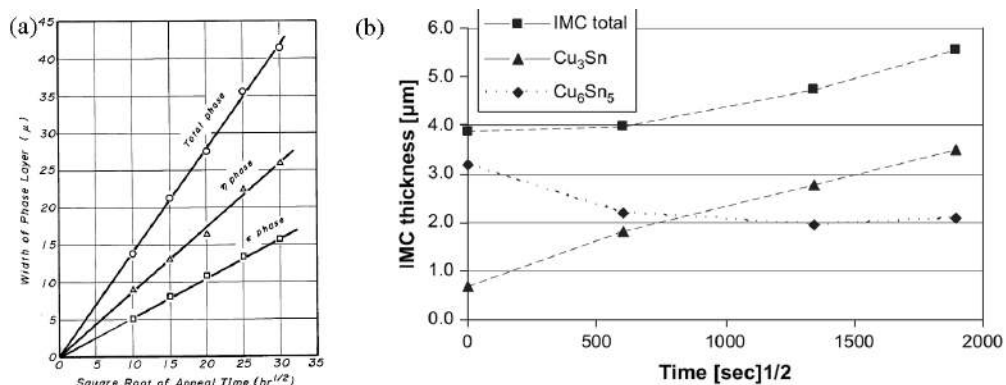

Figure 16. a – change of the intermetallic layer thickness with a time of reaction during reaction in Cu/Sn couple at 220^0C [30]; b – change of the thickness for each individual IMC phase and total IMC change with time in Cu-Sn couple annealed at 125^0C [32].

In their experiments with electroplated Cu and Sn film W.M. Tang et al. [28] measured the thickening kinetics of the individual IMC. Annealing was held at 150, 200 and 225^0C. Authors report that the η-Cu_6Sn_5 phase grows faster only at 150^0C. Reported growth constants are higher for the Cu_3Sn phase at 200 and 225 ^{0}C (see Figure 17).
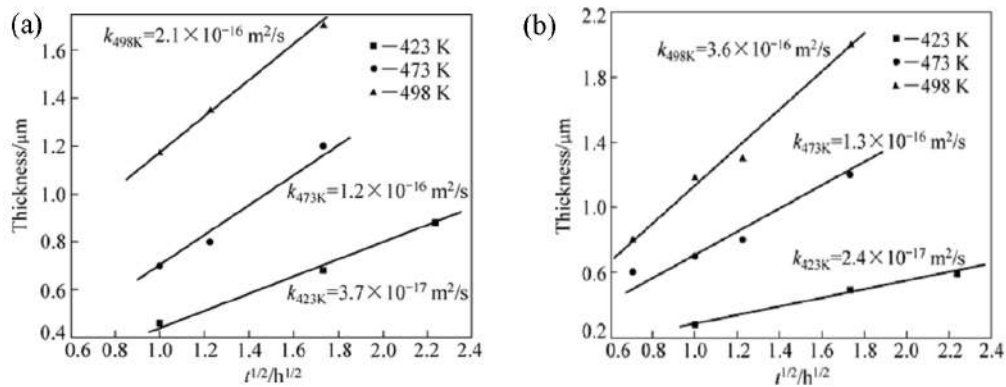
Figure 17. Average thickness of the η-Cu_6Sn_5 phase (a) and ε-Cu_3Sn phase (b) versus square root of time for Cu-Sn couple annealed at 150, 200 and 225^{0}C [28].

P. T. Vianco et al. [33] also measured the total mean thickness of the reaction layers formed between copper and tin or between copper and alloy as a function of the temperature of the solid state aging. The experiments were performed at various temperatures from 70^{0}C to 250^{0}C with aging time up to 400 days. It should be noticed that in the case of Cu/Sn couple the growth is slightly more expressive than in the case of Cu/SnAg couple. Like in previous cases, the growth kinetics obeys parabolic law. The activation energy of the reaction layer growth (ε + η) was determined: $Q_{ε+η}$(Cu/Sn) =43kJ·mole^{-1}; $Q_{ε+η}$(Cu/SnAg) =50kJ·mole^{-1}. The growth rates of both IMC in Cu/Sn couple were almost equal at 135, 170 and 205^{0}C, the Cu_3Sn layer comprised 0.4-0.6 fraction of the total IMC thicknesses.

In their experiments C. Yu et al. [34] were investigating solid state reaction between Cu foils (thickness 0.1 mm) with three types of the solders: pure Sn, Sn-0.7Cu and Sn-3.5Ag. The isothermal ageing was held at 150^{0}C and 180^{0}C. The initial contact was realized by reflow at 260^{0}C for 60s. Such relatively high reflow temperature resulted in thick η-Cu_6Sn_5 layer with thickness of 2-3μm. Only in the case of Cu/Sn-3.5Ag and Cu/Sn-0.7Cu couples the η-Cu_6Sn_5 continued to grow during isothermal annealing at 150^{0}C and 180^{0}C up to 700 hours surpassing the growth of the ε-Cu_3Sn layer. In the case of Cu/pure Sn couple the growth of the η-Cu_6Sn_5 layer was frozen, only the initial scallop-like interface was flattened. The parabolic growth of the ε-Cu_3Sn layer proceeded up to the thickness comparable with one of the η-Cu_6Sn_5 layer at 150^{0}C and 180^{0}C (see Figure 18).
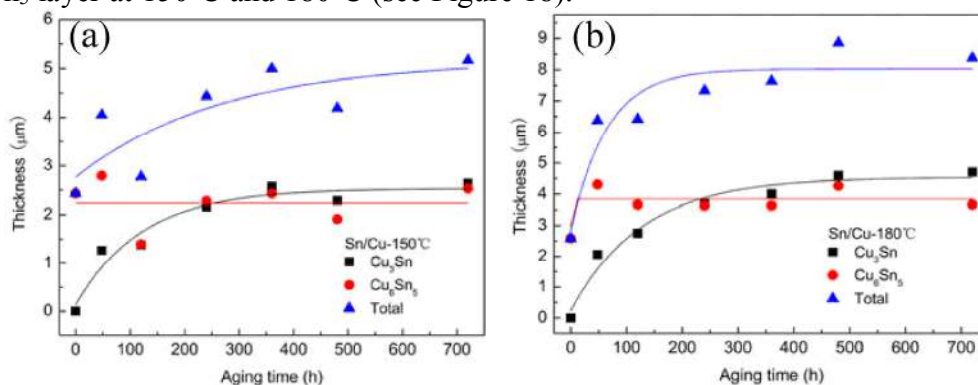

Figure 18. η-Cu_6Sn_5 phase, ε-Cu_3Sn phase and total IMC average thickness versus time for Cu-Sn couple annealed at a – 150^{0}C and b – 180^{0}C [34].

Kirkendall voids during solid-state reactions

The reason of voiding is the difference of diffusion fluxes of Cu an Sn atoms during solid-state aging or operation heating [2]. The formation of voids is strongly connected with formation of the ε-Cu_3Sn layer during reaction between Cu and Sn. As the Cu_3Sn forms the flux of vacancies emerges in the direction of the Cu substrate and the lack of the sinks results

in the voids formation. It should be emphasized that in common soldering reaction the formation of voids is strongly linked with formation or later stages of growth of the ε-Cu_3Sn layer. Therefore, the factors that can influence the formation, suppression or growth of the ε-Cu_3Sn layer are of great interest.

It is still under discussion how to choose correctly the proper substrate or electrolyte for the electroplating of the Cu pads in order to eliminate the formation of the Frenkel voids. For example, in literature there is a discussion whether the Frenkel voids are formed on the bulky polycrystalline Cu substrates or electroplated foils.

W. Yang et al [35] report the formation of the Frenkel voids in the Cu_3Sn layer during reaction in the electrodeposited Cu/Sn-Ag solder couple for 3 days at 190^0C (Figure 19a). It is important to notice that when the Cu pad was rolled no voids were detected even after 12 days of annealing at the same temperature (Figure 19b). It means that mechanical treatment of the UBM can influence the important reliability issue.
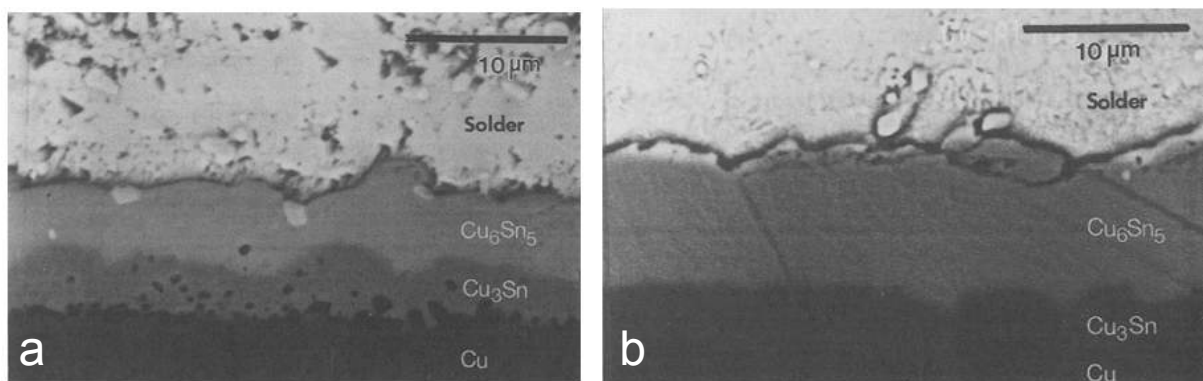

Figure 19. SEM images of electroplated Cu/Sn-Ag couple after 3 days annealing at 190^0C (a) and rolled Cu/Sn-Ag after 12 days annealing at 190^0C (b) [35].

A. Paul reports the formation [29] of the Kirkendall voids after reaction in the polycrystalline Cu/Sn couple at relatively high temperature of 215^0C as for the solid-state aging. The annealing time was 225 hours (see Figure 15).

K. Zeng et al. [36] reports the formation of the Kirkendall voids just after reflow between electroplated Cu and Sn-Pb solder (see Figure 20a). The reflow peak temperature was given to be 220^0C but the reflow time wasn't specified. The density of voids increases drastically after 3 days annealing at 150^0C (see Figure 20b).
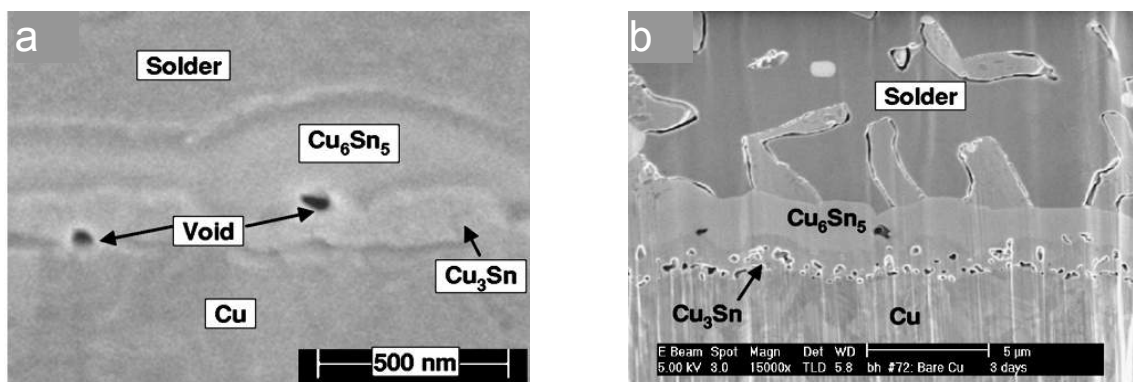

Figure 20. FIB images of the: a – just reflowed electroplated Cu/SnPb joint; b – annealed at 150^0C for 3 days [36].

V. Vuorinen et al. have studied the influence of the Cu purity on the voiding [37]. He demonstrated the absence of the voids for the case when the very pure polycrystalline Cu was

used (99.99%) for reaction with Sn (99.95%) at 125^0C for 3500 hours (Figure 21a). The excessive voiding appeared when the Cu was substituted by Cu(Ni) alloy with a composition 99.0Cu1.0Ni and annealed under the same conditions (Figure 21b). The important result was achieved when the composition of the Ni in the Cu(Ni) alloy was increased to 10% and no voids were detected (Figure 21c).
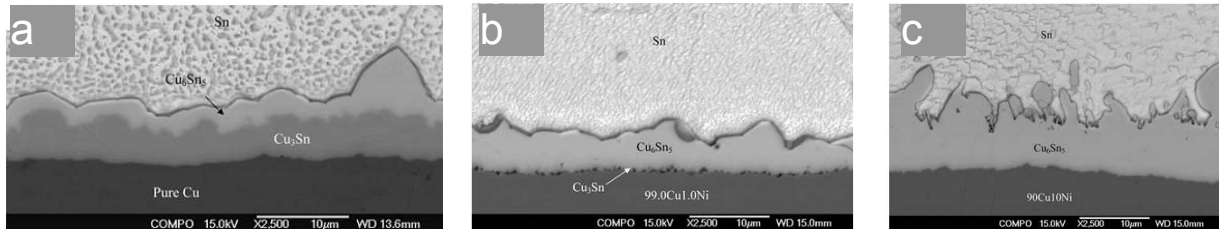
Figure 21. SEM images of the samples annealed for 3500 hours at 125^0C. The samples were: a – pure Cu/Sn couple; b – 99.0Cu1.0Ni/Sn couple; c – 90.0Cu10.0Ni/Sn couple [37].

The use of the nano-twinned Cu as UBM is believed to eliminate the formation of the Kirkendall voids. The H.Y. Hsiao et al. [38] have tested the densely packed [111] nanotwined Cu for UBM. The thickness of the Cu layer was 20 μm and it was annealed in the sandwich structure with Sn3.5Ag at 150^0C for 1000 hours. No Kirkendall voids were detected (see Figure 22a), what is believed to happen because of the existence of the numerous vacancy sinks between nano-twinned Cu grains. The same kind of the substrate material was tested by W.L. Chiu et al. [39] in the reaction with pure molten Sn at 260^0C. The authors also investigated the sandwich structure and achieved the complete transformation of the solder bulk to the Cu_3Sn IMC in 24 hours (Figure 22b). No voids were detected as well.
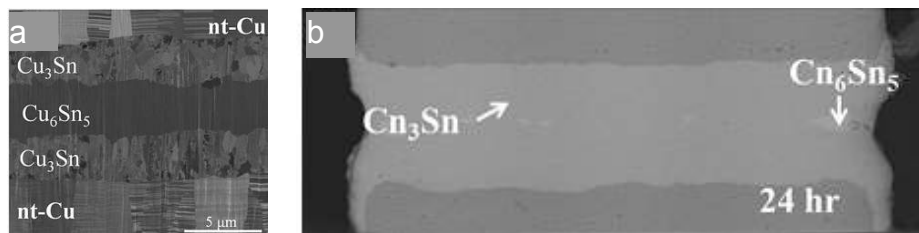
Figure 22. a – nt-Cu/Sn3.5Ag couple annealed for 1000 hours at 150^0C; b – nt-Cu/Sn couple annealed for 24 hous at 260^0C [38].

Modeling of the phase growth and competition during solid-state reactions

Nowadays, the standard model of the phase growth kinetics is well established [6]. For the late stages of the solid state reaction, when the sufficient amount of reagents is present, the phase layer growth obeys well-known parabolic law. Nevertheless, from 1970's the microelectronic industry provided new problems by operating with thin films. It was found that the intermediate phases could be suppressed partially or completely. Most successful theories of this type belong to U.Gesele and K.N.Tu [40] and A. M. Gusak and K.P. Gurov [41]. Nucleation issues, in terms of standard nucleation approach, but in application to solid state reactions, have been discussed by F.d'Heurle in 1986 [42].

Let's review the general case of the growth of two phases between two insoluble components. It can be done by considering the flux balance at three emerging interfaces (see Figure 23a). The concentration profile of such system is given on Figure 23b.
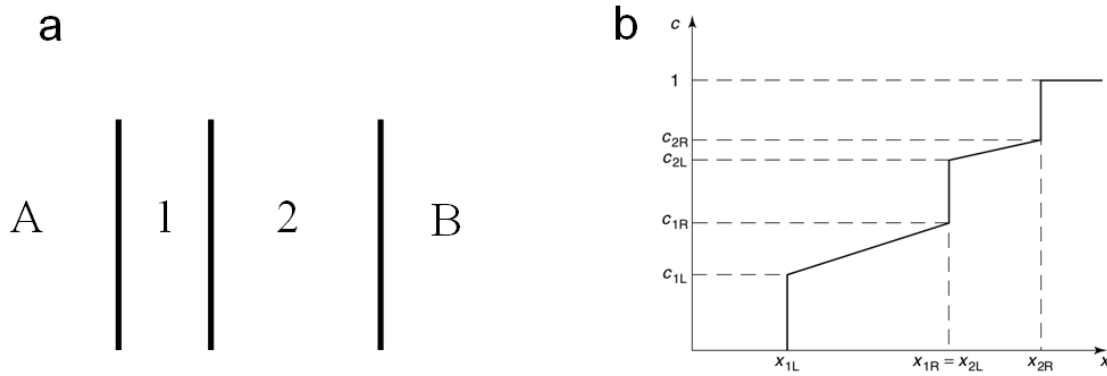
Figure 23. a – the principal scheme of the reaction couple A/B with formation of two intermediate phases 1 and 2 and b – the concentration profile of the system.

Let us consider the case when the growth of the phases is controlled by the bulk diffusion through the growing intermediate phases. The equations of flux balance at the interfaces can be written as:

$$\left(1-c_{2R}\right)\frac{dx_{2R}}{dt}=\frac{D_2\Delta c_2}{\Delta x_2},$$
$$\left(c_{2L}-c_{2R}\right)\frac{dx_{2L}}{dt}=-\frac{D_2\Delta c_2}{\Delta x_2}+\frac{D_1\Delta c_1}{\Delta x_1}, \qquad (7)$$
$$\left(c_{1L}-0\right)\frac{dx_{1L}}{dt}=-\frac{D_1\Delta c_1}{\Delta x_1},$$

where c_{1L}, c_{2L}, c_{1R} and c_{2R} are equilibrium concentration at different interfaces; x_{1L}, x_{2L}, x_{1R} and x_{2R} are interface positions; $D_1\Delta c_1$ and $D_2\Delta c_2$ are Wagner's integrated coefficient [43] in intermediate phases.

The system of differential equations for phase thicknesses could be obtained easily as:

$$\frac{d\Delta x_1}{dt}=a_{11}\frac{D_1\Delta c_1}{\Delta x_1}+a_{12}\frac{D_2\Delta c_2}{\Delta x_2},$$
$$\frac{d\Delta x_2}{dt}=a_{21}\frac{D_1\Delta c_1}{\Delta x_1}+a_{22}\frac{D_2\Delta c_2}{\Delta x_2}. \qquad (8)$$

Here

$$a_{ik}=\begin{pmatrix}\dfrac{c_2}{c_1} & -1 \\ -1 & \dfrac{1-c_1}{1-c_2}\end{pmatrix}\dfrac{1}{c_2-c_1}.$$

It can be found by direct substitution that that system has parabolic solutions

$$\Delta x_1=k_1 t^{1/2} \text{ and } \Delta x_2=k_2 t^{1/2}, \qquad (9)$$

where k_1 and k_2 are growth constants.

In fact, there a lot of real systems in which the one phase can have much lower diffusion permeability than another one. Mathematical condition reads as $D_2\Delta c_2 << D_1\Delta c_1$ in this case. The system controls the necessary flux of atoms to build the fast growing phase 1 by keeping the thickness of the phase 2 very small. It means that $\frac{d\Delta x_2}{dt}\approx 0$ and that the thickness of that thin phase can be derived from (2) as:

$$\Delta x_2 \approx \Delta x_1 \frac{1-c_1}{1-c_2} \frac{D_2 \Delta c_2}{D_1 \Delta c_1} \qquad (10)$$

Hence, the growth of the fast growing phase can derived as:

$$\frac{\mathrm{d}\Delta x_1}{\mathrm{d}t} = \frac{1}{c_1(1-c_1)} \frac{D_1 \Delta c_1}{\Delta x_1}. \qquad (11)$$

Therefore, Eq.(5) shows that the growth rate of the dominant phase 1 is not depending on the thickness of the suppressed phase 2. The η-phase grows like the single phase to be present in the interfacial zone. Its growth kinetics follows the parabolic regime.

Summary

The growth of the intermetallic phases is well studied experimentally during the late stages of reaction between solid copper and tin-based solder. The FDR model can be used for the description of the growth during conventional reflow process when the time of reaction with liquid solder is not exceeding couple of minutes. Nevertheless, the recent results show that the growth kinetics models should be reviewed for the initial stage of reaction (time of reaction is less than 10 s) as well as during the late stages of reaction (time > 30 min). The suppression criterion of the ε-phase growth is well defined and says that the phase starts to grow simultaneously with η-phase when the average thickness of the later exceeds 1 micrometer.

During solid-state reaction the intermetallic phases grow following parabolic law of growth. The growth process can be described well by existing models of phase during solid state reactions. However, the the ambiguity of experimental results in the growth competition during the late stages of the solid state ageing, when the the dominant phase is not clearly identified should be studied in details. The special effort should be made to reveal factors affecting voiding at the interface as fas as this problems affects significantly the reliability of the solder joints.

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Анотація. *О.Ю. Ляшенко. Особливості зародкоутворення і росту проміжних фаз при паянні: протиречиві експериментальні дані і останні досягнення в моделюванні.* В даній роботі приведено огляд робіт по дослідженню процесу реакційної взаємодії між оловом чи люттю на основі олова (як в твердому так і в рідкому стані) і твердою міддю. В більшості робіт показано, що під час оплавлення (англ. *reflow*) проміжна η-фаза (Cu_6Sn_5) утворюється першою і росте швидко. Порядок зародкоутворення і кінетика росту проміжних фаз залежать від пересичення міддю рідкої краплини олова. Швидкість зняття цього пересичення може також впливати на кінетику росту фаз. Під час оплавлення, η-фаза (Cu_6Sn_5) росте відповідно до відомого закону з показником росту 1/3 (режим росту контрольований інтерфейсом), або відповідно до закону з показником росту 1/2 (режим росту контрольований об'ємною дифузією), але також росте відповідно і до інших законів росту. Приведено огляд робіт, що описують ефективні моделі пригнічення і росту фаз. Кінетика росту, морфологія проміжних фаз під час старіння в твердому стані, а також пороутворення в об'ємі проміжних фаз залежить від структури мідної підкладки.

Ключові слова: пайка, зародкоутворення, ріст, конкуренція фаз, надійність.

Аннотация. *А.Ю. Ляшенко. Особенности зародышеобразования и роста промежуточных фаз при пайке: противоречивые экспериментальные данные и последние достижения в моделировании.* В роботе приведено обзор работ по исследованию процесса реакционного взаимодействия между оловом или пропоем на основании олова (как в твердом, так и в жидком состоянии) и твердой медью. В большинстве работ показано, что во время оплавления (англ. *reflow*) промежуточная η-фаза (Cu_6Sn_5) возникает первой и быстро растет. Порядок зародышеобразования и кинетика роста промежуточных фаз зависит от перенасыщения медью жидкой капли олова. Скорость снятия этого перенасыщения может также влиять на кинетику роста фаз. Во время оплавления η-фаза (Cu_6Sn_5) растет согласно известному закону с показателем роста 1/3 (режим роста контролированный интерфейсом), или согласно закону роста с показателем роста 1/2 (режим роста, контролированный объемной диффузией), но также растет согласно и другим законам роста. Приведено обзор работ, которые описывают эффективные модели подавления и роста фаз. Кинетика роста, морфология промежуточных фаз во время твердотельного старения, а также порообразование в объеме промежуточных фаз зависит от структуры медной подложки.

Ключевые слова: пайка, зародышеобразование, рост, конкуренция фаз, надежность.