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Andriy M. Gusak, Oleksii Yu. Liashenko, Fiqiri Hodaj

MODELS OF PHASE FORMATION, GROWTH AND COMPETITION IN SOLDERING - SOME NEW RESULTS

Simple phenomenological models of formation, competition and growth of the intermediate Cu-Sn phases during soldering are presented. The first attempt to estimate the width of liquid channels between scallops of Cu_6Sn_5 phase is suggested. Also, an attempt to take into account the change of scallops shape (aspect ratio) with modeling of the Cu_6Sn_5 growth is made.

Keywords: diffusion, intermetallics, growth kinetics, tin-based solders, grain boundary wetting.

Introduction

Soldering is and in future will remain an important technological process in microelectronics and in other fields [1-2]. Solders are, as a rule, eutectic tin-based alloys containing lead, bismuth, silver, copper etc.

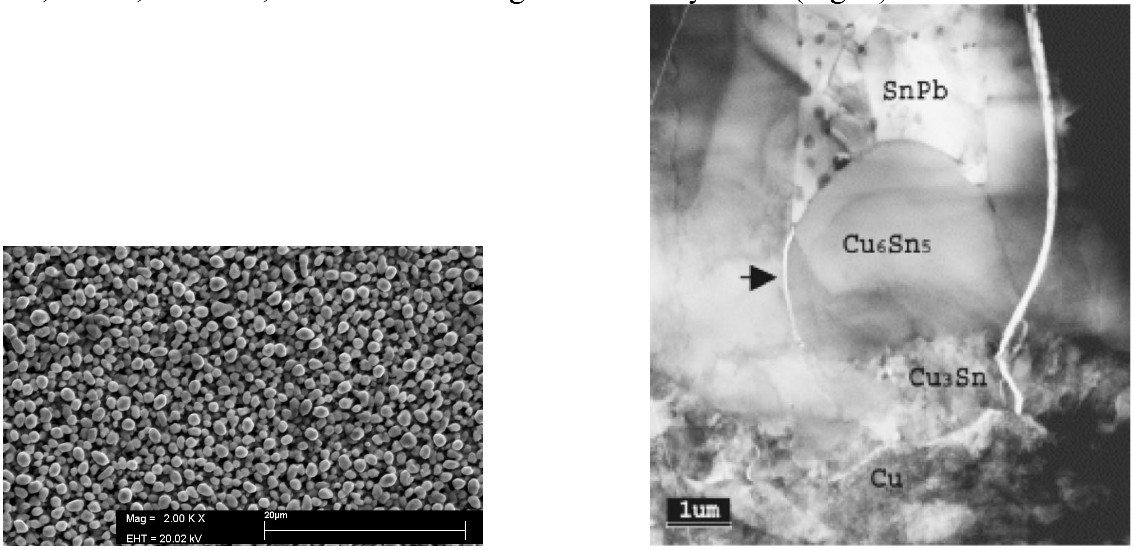
Most widespread is soldering of copper or nickel. Typical soldering of copper consists of (1) eutectic melting (reflow) of solder bump and (2) formation and growth of one or two intermetallics, η – phase Cu_6Sn_5 and ε – phase Cu_3Sn [3-9]. Mechanical bonding is provided mainly by η - phase, which has peculiar morphology – scallops of individual grains separated by some boundaries, nature of which is still under discussion – liquid channels of molten solder [8-10], prewetted grain boundaries [11], ordinary grain boundaries [12, 13]

Contrary to solid state aging at temperatures 200^0C and lower, when both phases grow simultaneously and demonstrate similar growth rates, in reaction with liquid solder the growth of η – phase proceeds much faster than that of ε – phase. On the other hand, presence and growth of ε – phase is very important since just in this phase the Kirkendall voiding takes place due to much higher diffusivity of copper than that of tin in this phase. Voiding deteriorates the solder contact and finally leads to its failure.

Investigation of reactions between Cu (or Ni) and molten solder have proved that the growth of intermetallic is accompanied by diffusion coarsening. A classical coarsening is a stage that follows nucleation and growth when the total volume of the new phase is practically maximal and the substance just undergoes diffusion redistributions between the particles. The driving force of classical coarsening is the reduction of the interface area or surface energy. Therefore, the total area of the surface of new phase is reduced. Investigation of surface reactions between molten solder and metal has shown that ripening of scallop-type intermetallide phase at the surface proceeds simultaneously with scallop growth. Since the volume of intermediate phase increases with time, the type of coarsening is referred to as non-conservative. The driving force of this process is the increase of free energy of intermediate phase growth.

Assuming scallops to have a hemispherical shape (which appears to be realistic until the reaction zone becomes about 10 microns thick and if composition of liquid solder is close to eutectic), we consider the total area of the intermediate phase as not changing with time in the process of growth. The scallop growth is observed at the reaction between eutectic solder SnPb and Cu, and also between Pb-free solders (for example, SnAg) and Cu, and between pure tin and copper. It was experimentally shown that as the layers of reaction products grow the ripening of scallops takes place, the corresponding model that describes this phenomenon was proposed as well. In [8] Gusak and Tu proposed the kinetic theory for the new type of coarsening grounding upon (a) conservation of the interface area at increasing volume and (b) dominating role of channels between the scallops. This phenomenon was called a flux-driven ripening (FDR).

Solder reactions typically occur at 200-250°C, lasting anywhere from a few seconds to several minutes. In case of pure Sn or Cu the reaction temperature is typically around 250°C. In these reactions, Cu_3Sn i Cu_6Sn_5 intermetallic compounds (IMCs) are formed at the interfaces. The Cu_6Sn_5 is the dominant growth phase and has scallop-type morphology. The size of the scallops can grow to several microns in diameter after a few minutes of reaction at 200°C between eutectic SnPb and Cu. The radius of scallops was found to obey an approximately $t^{1/3}$ dependence of growth. The number of scallops decreases at an approximately $t^{-2/3}$ dependence. The activation energy of the growth, measured from the growth rates occurring from 200 to 240°C during the reaction between eutectic SnPb and Cu, is about 0.2–0.3 eV/atom. On the other hand, the Cu_3Sn is a thin layer and its growth is very slow. Liquid channels between the scallops remain during the whole process the morphology of scallops and channels is thermodynamically stable at the presence of molten solder. Indeed, the molten eutectic solder SnPb quickly wets the grain boundaries of Cu_6Sn_5. The channels serve as fast diffusion paths supplying copper to the molten solder and activating the scallop growth. According to the data of scanning electron microscopy, the channels are less than 20 nm wide, which, however, exceeds the usual grain boundary width (Fig. 1).



a b

Fig. 1. Scallop-like morphology of Cu_6Sn_5 during wetting reactions between molten eutectic SnPb solder and Cu: (a) – top view of Cu_6Sn_5 scallops after 1 minute reflow at 200°C; (b) – cross-sectional image of Cu_6Sn_5 scallops after 10 minute reflow at 200°C (channels indicated by arrows). Figure 1b is taken by one of authors from his paper [8].

Aim of this paper is to present the simple models of phase formation and competition during soldering.

Basic approximations

The scallops have a shape of a hemisphere (Fig. 2). Designating the area between the scallops and copper as S^{total}, take into account that the total surface area between hemispherical scallops and molten solder is equal to double S^{total}:

$$S^{scallops/melt} = \sum_{i=1}^{N} 2\pi R_i^2 = 2\cdot\sum \pi R_i^2 = 2S^{total} = const$$

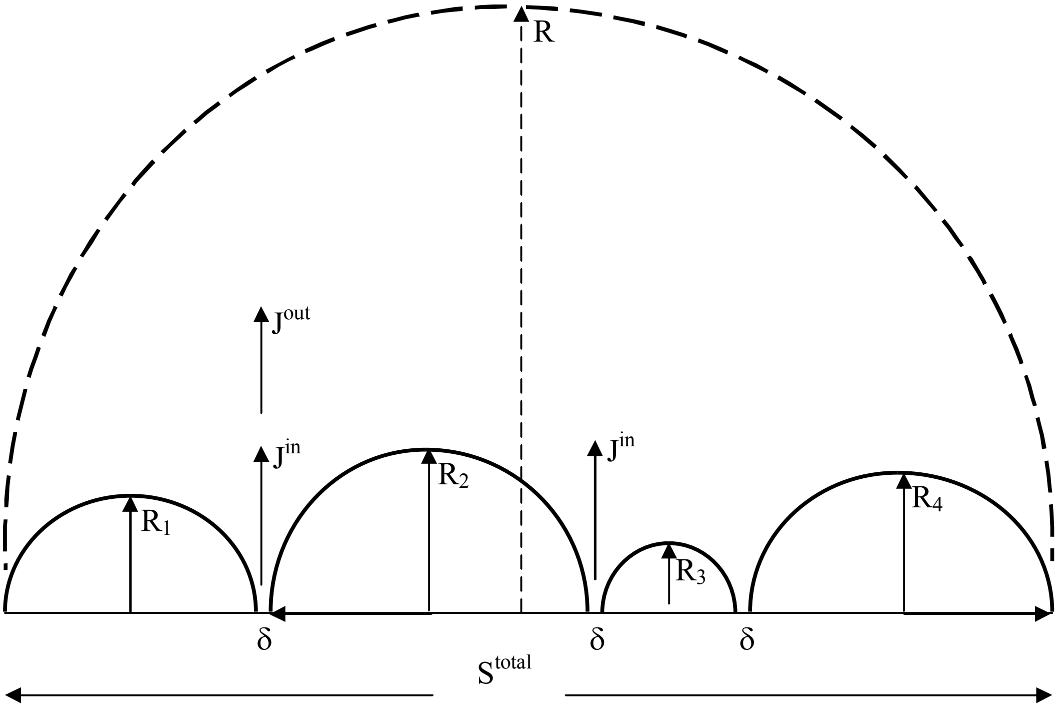


Fig. 2. Schematic diagram of the cross section of an array of scallops on Cu. J_{in} is an in-flux of copper directed from the substrate into the melt via channels (serving for the growth of scallops), J_{out} is an out-flux of copper which was not used for building up the intermetallic compound. For small solder bumps this out-flux quickly tends to zero after their saturation. Thus, while the phase growth contributes into the total volume increase, the total area of scallops doesn't change.

Alternatively, Schmitz et al suggested [11] that channels are not totally liquid but instead they are the grooves, transforming (near the substrate) into prewetted grain boundaries of Cu_6Sn_5 phase (also with high permittivity for copper). Last observations of John-ook Suh and K.N.Tu [10] demonstrate that actually the situation might be intermediate: crystallographic orientation of the Cu_6Sn_5 scallops is not fully chaotic. There exist some agglomerates of scallops, within which orientations are close, but misorientation between agglomerates is far from being close. Since the wetting condition depends on the grainboundary tension, and this tension depends on misorientation, one can expect that the grainboundaries between scallops of the same agglomerate are not wetted, but boundaries between agglomerates (with large misorientations) are wetted by liquid solder and are transformed into liquid channels.

All copper coming from the substrate is utilized for scallop growth, so one may neglect the out-flux of copper from the ripening region into the volume. It is fair for at least small solder bumps, since, say, a 100-micron bump becomes saturated with copper in 10 seconds.

Interfacial diffusion of copper along the scallop/copper interface is not a rate-limiting factor.

Since a growth of a scallop must occur at the expense of its neighbors, it is a ripening process. In this process, there are two important constraints. The first (geometrical) constraint is that the interface of the reaction is constant. The second is a conservation of mass, in which all the in-flux of Cu is consumed by scallop growth.

Simple model for monosize hemispheres

Strictly speaking, the monosize distribution is not compatible with scallop growth since scallop growth is competitive and realized by growth of some scallops due to the shrinkage of neighboring scallops. Therefore, the initial monosize distribution should be inevitably transformed into a widersized distribution. Yet, the monosize approximation is good for a rough estimate of average values.

According to the first constraint that the interface between the scallops and Cu be occupied completely by scallops except the thin channels, we have

$$N\pi R^2 \cong S^{total} = const, \tag{1}$$

where N is the number of scallops. The free surface (the cross-sectional area of channels at the bottom) for the supply of Cu from the substrate is

$$S^{free} = N 2\pi R \frac{\delta}{2} = \frac{\delta}{R} S^{total}, \tag{2}$$

where δ is the channel width. So the free surface decreases during the scallop growth as $1/R$. The volume of the reaction product of IMC scallops is equal to

$$V_i = N\frac{2\pi}{3}R^3 = \frac{2}{3}S^{total}R. \tag{3}$$

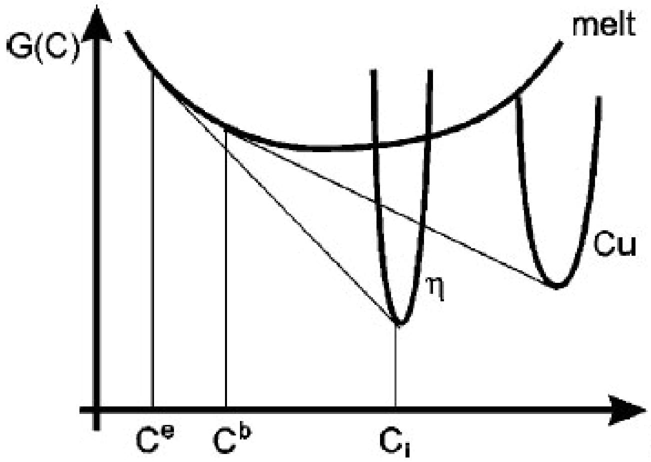


Fig. 3. Schematic dependence of the Gibbs free energy vs composition. The Cu quasiequilibrium concentration in the melt in the vicinity of the substrate (C^b), in the intermetallic compound Cu_6Sn_5 or η phase (C_i), and in the melt for stable equilibrium with planar η phase (C^e).

According to the second constraint that all influx of Cu atoms from the substrate is consumed by growing IMC scallops due to conservation of mass, we have

$$n_i C_i \frac{dV_i}{dt} = J^{in} S^{free}. \tag{4}$$

Here n_i is atomic density in IMC's, i.e., the number of atoms per unit volume, and C_i is atomic fraction of Cu in IMC's, which is 6/11 in Cu_6Sn_5. The influx is taken approximately as

$$J^{in} = -nD\frac{\left(C^e + \frac{\alpha}{R}\right) - C^b}{R}, \tag{5}$$

where n is the atomic density or number of atoms per unit volume in the melt or molten solder, $\alpha = C^e 2\gamma\Omega / R_G T$ in which γ is the isotropic surface tension at the IMC/melt interface, Ω is the molar volume, R_G is the gas constant, and T is the temperature. C^e is the equilibrium concentration (atomic fraction) of copper in solder at the planar interface between Cu_6Sn_5 and molten solder; C^b is equilibrium concentration of Cu in molten solder at the interface between substrate and solder at the channel's bottom (see Fig. 2). In our case $2\gamma\Omega / R_G T \approx 4.4 \cdot 10^{-7}$ cm and $C^e \approx 0.003$. We consider the case when $\alpha / R << C^b - C^e$, so that

$$J^{in} \cong nD\frac{C^b - C^e}{R}. \tag{6}$$

Then, substituting Eqs. (6), (2), and (3) into the balance equation (4), one obtains

$$n_i C_i \frac{2}{3} S^{total} \frac{dR}{dt} = nD\frac{C^b - C_e}{R}\left(\frac{\delta}{R} S^{total}\right), \tag{7}$$

which immediately gives

$$R^3 = kt, \tag{8a}$$

$$k = \frac{9}{2}\frac{n}{n^i}\frac{D\left(C^b - C^e\right)\delta}{C_i}. \tag{8b}$$

Note that the surface tension is absent in the expression for the rate constant, despite the ‘‘ripeninglike’’ time law.

If we take $n/n_i \approx 1,\ C_i = \frac{6}{11},\ D \approx 10^{-9}\, m^2/s,\ \delta \approx 10^{-8}\, m$, and $C^b - C^e \approx 0.01$, where the concentration C^b is taken for equilibrium of melt with the Cu_3Sn phase, the rate constant $k \approx 8\cdot 10^{-19}\, m^3/s$. For example, for annealing time t=300 s, it gives $R \approx 6\cdot 10^{-6}\, m$, which agrees very well with experimental data.

According to the approximate equation (8a) and geometrical constraint (1), the number of scallops should depend on time as $t^{-2/3}$, as observed experimentally. It seems astonishing that such a naive and simple model can fit the experimental data very well. The reason for this is an incoming flux being a rate-controlling step, determining the ripening rate during FDR.

We can understand now the crucial difference between the classical coarsening described by LSW theory and the flux-driven ripening described here. In the former the phase volume is almost constant at a sufficiently long time, and it is simply redistributed between grains. The driving force is a decrease of Gibbs free energy due to the decrease of total surface of the phase. In our case the surface is constant (the total surface of hemispheres). Indeed,

$$S^{scallops/melt} = N 2\pi R^2 = 2S^{total} = const. \tag{9}$$

Thus, in our case, the constant interfacial area is a constraint of the reaction. The driving force is the gain of Gibbs free energy from the increase of phase volume. This increase is possible owing to ‘‘influx’’ of Cu from the substrate. Therefore, we have flux-driven ripening in open systems. We should note that, of course, we are not the first to treat ripening in open systems. Slezov [14] treated ripening of voids by taking into account the vacancy flux moving towards the external boundaries in the theory of caking. Yet in that case there were no two-dimensional constraints, and the coarsening, even in nonhomogeneous conditions, proceeded due to a decrease of surface energy.

Evidently, the monosize model is oversimplified, since the growth of scallops cannot proceed without the shrinking of neighboring scallops. Thus, we should take the size distribution into account. This was accurately done in [8], and we will not repeat it here.

Model for simultaneous growth of two phases during soldering

In the case of solid-state aging (simultaneous growth of both phase layers between sold copper and tin, the growth kinetics is well described by the set of ordinary differential equations for two thicknesses [15]:

$$\frac{d\Delta X_\eta}{dt} = \frac{1}{C_\varepsilon - C_\eta}\left(\frac{C_\varepsilon}{C_\eta}\frac{D_\eta \Delta C_\eta}{\Delta X_\eta} - \frac{D_\varepsilon \Delta C_\varepsilon}{\Delta X_\varepsilon}\right) \tag{10.a}$$

$$\frac{d\Delta X_{\varepsilon}}{dt}=\frac{1}{C_{\varepsilon}-C_{\eta}}\left(-\frac{D_{\eta}\Delta C_{\eta}}{\Delta X_{\eta}}+\frac{1-C_{\eta}}{1-C_{\varepsilon}}\frac{D_{\varepsilon}\Delta C_{\varepsilon}}{\Delta X_{\varepsilon}}\right) \tag{10.b}$$

The main differences for soldering (in comparison with solid state aging) can be reduced to two issues:

1. Wagner integrated diffusivity of eta-phase is changed by the product $\frac{\delta D_{Cu}^{melt}}{R}\left(C^{l/\varepsilon}-C^{l/\eta}\right)$, where $C^{l/\varepsilon}, C^{l/\eta}$ - tin concentrations (mole fractions) of the melt in local equilibrium with epsilon-phase (at the bottom of the channel) and with eta-phase, R is a grain lateral size of eta-phase (in the model – radius of semispherical scallop).
2. Lateral size R of the grain is approximately equal or proportional to eta-phase thickness H (with constant in time aspect ratio), meaning that the phase growth proceeds simultaneously with lateral grain coarsening.

Then the basic kinetic equations for simultaneous growth of both phases are:

$$\begin{aligned}
&\left(1-C_{\varepsilon}\right)\frac{\mathrm{d}x^{Cu/\varepsilon}}{\mathrm{d}t}=\frac{\tilde{D}^{(\varepsilon)}\Delta C_{\varepsilon}^{eq}}{\Delta x_{\varepsilon}}\\
&\left(C_{\varepsilon}-C_{\eta}\right)\frac{\mathrm{d}x^{\varepsilon/\eta}}{\mathrm{d}t}=\frac{\delta D_{Cu}^{melt}}{H^{2}}\left(C^{l/\varepsilon}-C^{l/\eta}\right)-\frac{\tilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{\Delta x_{\varepsilon}}\\
&\left(C_{\eta}-0\right)\frac{\mathrm{d}x^{\eta/Sn}}{\mathrm{d}t}=-\frac{\delta D_{Cu}^{melt}}{H^{2}}\left(C^{l/\varepsilon}-C^{l/\eta}\right)
\end{aligned} \tag{11}$$

Equations for phase thicknesses are:

$$\left(C_{\eta}-0\right)\frac{\mathrm{d}H}{\mathrm{d}t}=\left(\frac{1}{C_{\eta}}+\frac{1}{C_{\varepsilon}-C_{\eta}}\right)\frac{\delta D_{Cu}^{melt}}{H^{2}}\left(C^{l/\varepsilon}-C^{l/\eta}\right)-\frac{1}{C_{\varepsilon}-C_{\eta}}\frac{\tilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{\Delta x_{\varepsilon}} \tag{12a}$$

$$\frac{\mathrm{d}\Delta x_{\varepsilon}}{\mathrm{d}t}=\left(\frac{1}{C_{\varepsilon}-C_{\eta}}+\frac{1}{1-C_{\varepsilon}}\right)\frac{\tilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{\Delta x_{\varepsilon}}-\frac{\delta D_{Cu}^{melt}}{\left(C_{\varepsilon}-C_{\eta}\right)H^{2}}\left(C^{l/\eta}-C^{l/\varepsilon}\right) \tag{12b}$$

From experiment we know that epsilon-phase during soldering grows slowly.
Let us use a steady-state approximation for the epsilon phase:

$$\begin{aligned}
&\left(\frac{1}{C_{\varepsilon}-C_{\eta}}+\frac{1}{1-C_{\varepsilon}}\right)\frac{\tilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{\Delta x_{\varepsilon}}-\frac{\delta D_{Cu}^{melt}}{\left(C_{\varepsilon}-C_{\eta}\right)H^{2}}\left(C^{l/\eta}-C^{l/\varepsilon}\right)\approx 0\Rightarrow\\
&\Rightarrow\frac{\tilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{\Delta x_{\varepsilon}}\approx\frac{C_{\varepsilon}}{C_{\eta}}\frac{\delta D_{Cu}^{melt}}{H^{2}}\left(C^{l/\eta}-C^{l/\varepsilon}\right)
\end{aligned} \tag{13}$$

Then, substituting eq. (13) into eq. (12a), one obtains

$$\frac{\mathrm{d}H}{\mathrm{d}t}\approx\frac{1}{C_{\eta}\left(1-C_{\eta}\right)}\frac{\delta D_{Cu}^{melt}}{H^{2}}\left(C^{l/\varepsilon}-C^{l/\eta}\right) \tag{14}$$

Simple integration gives

$$H^{at\,Cu\,substrate}=R=\left(\frac{3\delta D_{Cu}^{melt}}{C_{\eta}\left(1-C_{\eta}\right)}\left(C^{l/\varepsilon}-C^{l/\eta}\right)t\right)^{1/3}. \tag{15}$$

Cu_3Sn suppression criterion

Formation and growth of η-Cu_6Sn_5 and ε-Cu_3Sn IMCs greatly affects the physical properties and especially the mechanical properties of the joints. Indeed, because of the inherent brittle nature and the tendency to generate structural defects [16], very thick IMC layer at the solder/Cu interface may degrade the reliability of solder joints. Numerous studies indicated that excessive growth of IMCs may promote the brittle failure through weakening the solder joint strength, and hence affect the long term solder joint reliability [17].

Moreover, studies of intermetallic formation between Cu and Sn-based solders have shown that micro-voids can form at the Cu-Cu_3Sn interface and in the Cu_3Sn layer during annealing and aging of solder joints [18, 19]. Development of such micro-voids in one of the solder joints is shown in Fig. 4.

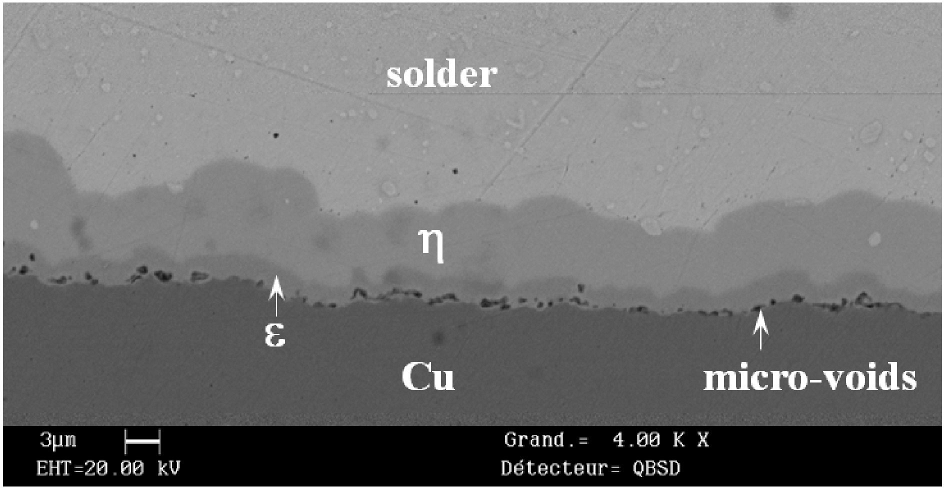


Fig.4. SEM micrographs of copper/solder interface showing voiding after annealing. Micro-voids developed at Cu/ε-Cu_3Sn interface and in the ε-Cu_3Sn layer during annealing of solder joint at 180°C for 7 days.

Given the fact that these Kirkendall voids are reported as a damaging factor leading to the weakening of the joint, initiating failures notably during thermal aging, it would be advisable to avoid their formation. It is very important to underline that in almost all studies, the Kirkendall voids formed in Sn based solders/Cu substrate system is related to the formation of the ε-Cu_3Sn compound.

In the case of solid state interactions between Sn-based solders and Cu substrate, the thickness of ε-Cu_3Sn layer is comparable to that of η-Cu_6Sn_5 phase [20, 21].

On the contrary, in liquid Sn-based solder/Cu systems the thickness of Cu_3Sn phase is much lower than that of Cu_6Sn_5 phase [22]. This last observation is due to the fact that during the reaction between molten solder and copper, the growth of Cu_6Sn_5 scallops takes place at the solder/metal interface by rapid liquid state diffusion through nanometric liquid channels between Cu_6Sn_5 scallops, leading thus to a rapid growth rate of this phase. Moreover, it is generally accepted that the first phase that forms and grows at the liquid solder/Cu interface is η-Cu_6Sn_5 phase and it is only afterwards that the growth of the ε-Cu_3Sn phase occurs at Cu/Cu_6Sn_5 interface. However, the conditions under which the ε-Cu_3Sn phase starts to grow are not well known. We think that the growth conditions of the ε-Cu_3Sn are strongly related to the mass flux balance at Cu/Cu_6Sn_5 interface and so to the thickness of the first η phase growing at this interface. In [23] we tried to evaluate, from thermodynamic and kinetic considerations, the average thickness of the η-Cu_6Sn_5 phase above which ε-Cu_3Sn starts to grow as a continuous layer at Cu/Cu_6Sn_5 interface during liquid Sn/solid Cu interaction.

In our case diffusion through the Cu/Cu_3Sn interface is not a growth rate controlling process. As a first approximation, we assume that liquid channels with average thickness δ exist between the mono-sized hemispherical scallops (with radius R) of growing η-Cu_6Sn_5 phase (see Fig.5). Also we assume that ε-phase layer of some minimal constant thickness l_{cr} (say l_{cr} = 2 nm) has just formed by nucleation and lateral growth and now is trying to grow normally between η-phase and Cu. It seems physically evident that ε-phase (as any other phase) cannot be thinner than, say, one nanometer (due to nucleation issues or/and due to existence of minimal size of elementary cell with the structure of Cu_3Sn_1.

Here we shall not discuss the details of nucleation and lateral growth of ε-phase since the voiding in this phase seems to become a problem only after formation of continuous layer. All what we need now at what conditions the minimally possible layer of this phase is stopped to be kinetically suppressed by the fast-growing η-phase?

We want to evaluate the crossover scallop size $R = R^*$ of η-phase at which ε-phase layer will start to grow.

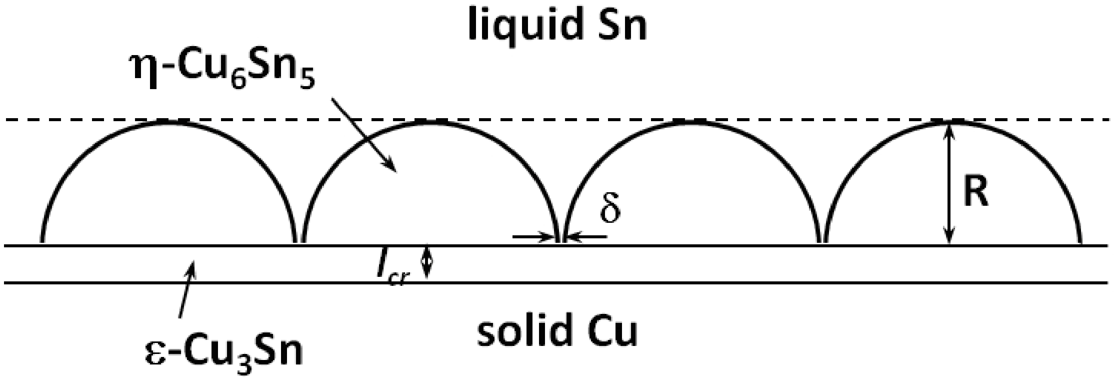


Fig. 5. Model system.

We assume that the liquid is homogeneous in concentration and already saturated by copper for $x > R$ and a constant concentration gradient exists in the liquid phase (channels) from the top of the eta/liquid interface to the epsilon/liquid interface at the bottom of channels (see Fig. 6).

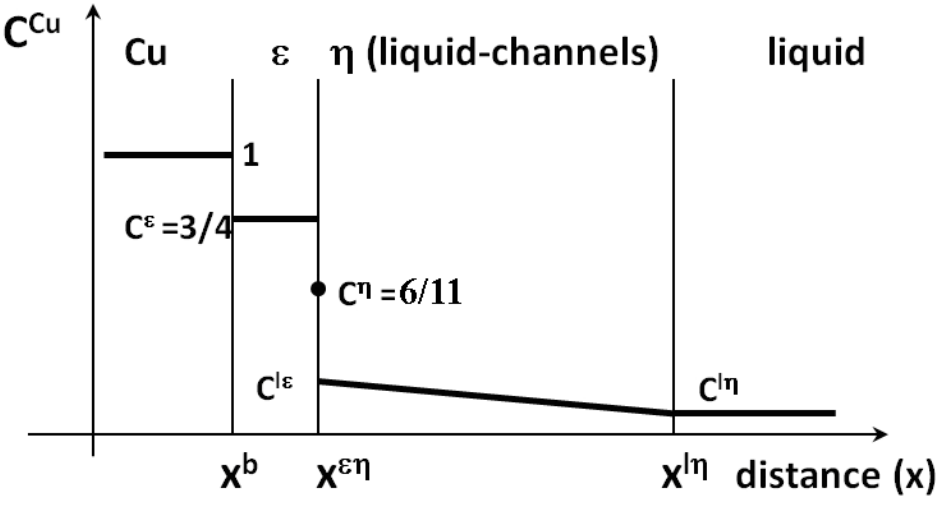


Fig. 6 Schematic presentation of variation of Cu concentration through the solid Cu/liquid Sn system.

For the fluxes of Cu atoms through both intermetallic phases (evidently, through ε-phase layer and liquid channels) we can use the following expressions:

$$\Omega J^{(\varepsilon)} = \frac{\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{l_{cr}^{\varepsilon}}, \tag{16a}$$

$$\Omega J^{(\eta)} = D_{Cu}^{melt}\frac{c^{l/\varepsilon}-c^{l/\eta}}{R}\frac{S^{free}}{S^{total}} = \frac{\delta}{R^2}D_{Cu}^{melt}\left(c^{l/\varepsilon}-c^{l/\eta}\right), \tag{16b}$$

here $\widetilde{D}^{(\varepsilon)}$ is the interdiffusion coefficient in ε – phase, D_{Cu}^{melt} is the diffusion coefficient of Cu in liquid Sn-Cu solution, $c^{l/\varepsilon}$ and $c^{l/\eta}$ are the equilibrium concentration of Cu at the liquid/ε – phase and liquid/η – phase interface correspondingly (see Fig.7).

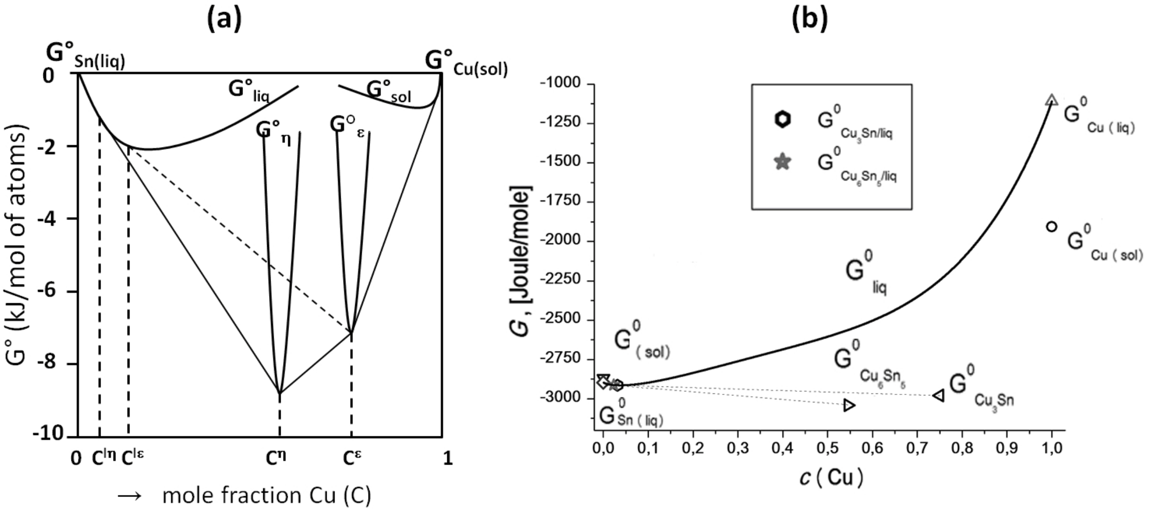


Fig. 7. Gibbs free energy formation of (Cu,Sn) liquid phase and Cu_3Sn and Cu_6Sn_5 compounds (reference states were *G–HSER*: FCC_A1 (Cu), BCT_A5 (Sn)) [24]

At that, both planar solid interfaces Cu/ε, ε/η and averaged nonplanar (scallop-like) interface η/melt will shift accordingly to the growth laws of eqs (11).

Eventually, the growth rate of ε-phase layer could be found as the difference in the velocities of two interfaces ($\frac{d\Delta x^{\varepsilon}}{dt} = \frac{dx^{\varepsilon/\eta}}{dt} - \frac{dx^{Cu/\varepsilon}}{dt}$):

$$\frac{d\Delta x^{\varepsilon}}{dt}\Big|_{l_{cr}} = \left(\frac{1}{c^{\varepsilon}-c^{\eta}} + \frac{1}{1-c^{\varepsilon}}\right)\frac{\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{l_{cr}^{\varepsilon}} - \frac{1}{c^{\varepsilon}-c^{\eta}}\frac{\delta D_{Cu}^{melt}}{R^2}\left(c^{l/\varepsilon}-c^{l/\eta}\right), \tag{17}$$

Finally, growth condition of the ε-phase layer:

$$\frac{1}{R^2}\frac{1}{c^{\varepsilon}-c^{\eta}}\delta D_{Cu}^{melt}\left(c^{l/\varepsilon}-c^{l/\eta}\right) < \frac{1-c^{\eta}}{\left(c^{\varepsilon}-c^{\eta}\right)\left(1-c^{\varepsilon}\right)}\frac{\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}{l_{cr}^{\varepsilon}}, \tag{18}$$

$$R > R^{*} = \sqrt{\frac{\left(c^{l/\varepsilon}-c^{l/\eta}\right)\left(1-c^{\varepsilon}\right)}{1-c^{\eta}}\frac{D_{Cu}^{melt}}{\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}}\delta\cdot l_{cr}^{\varepsilon}}. \tag{19}$$

For estimation of exact values we need to find values of $c^{l/\varepsilon}$, $c^{l/\eta}$, D_{Cu}^{melt} and $\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}$. It is generally accepted that $D_{Cu}^{melt} = 10^{-9}\,m^2/s$.

In their recent work Paul et al. [20] measured experimentally the value of integrated diffusion coefficients for ε-phase (the product $\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq}$) in the range 498 – 623 K. At 523 K:

$$\widetilde{D}^{(\varepsilon)}\Delta c_{\varepsilon}^{eq} = 0.87\times 10^{-16}\frac{m^2}{s}.$$

To find equilibrium concentration of Cu at the liquid/ε – phase and liquid/η – phase interface we used CALPHAD data to build the G_l(c) dependence (in J/mole) on the Fig.7 in the form of *G–HSER* [23].

At $T = 523$ K we found

$$G^{\eta} = -30412.3 J/mole,$$

$$G^{\varepsilon} = -29784.2 J/mole.$$

By simple calculation using common tangent rule (see Fig. 7b) we found the values $c^{l/\varepsilon} = 0.03152$ and $c^{l/\eta} = 0.02277$.

After substitution of all parameters into Eq. (6) we can build the dependence $R^*(\delta)$ (see Fig.8). According to Jong-Ook Suh et al.[10] the width of the channel was estimated to be 2.54 nm which gives the value $R^* = 0.553$ μm.

In principle, details of the channel parameters should be found from the conditions of optimal non-equilibrium steady-state wetting in open system under competition between tendency to complete wetting and tendency to transform the liquid channel into intermetallic phase by reaction. We hope to solve this problem elsewhere.

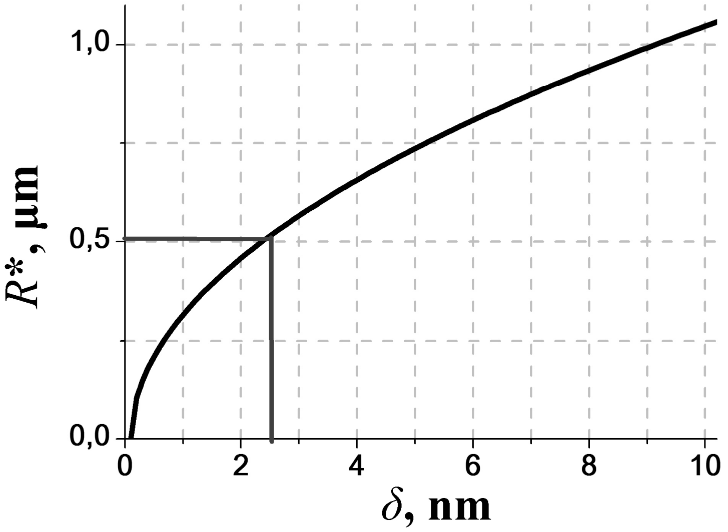


Fig.8. Dependence of the scallop mean radius R^* on the the width of the liquid channels δ

So, our crude evaluations predict that ε-phase layer can overcome suppression by η-phase after mean size of scallops exceeds about 1 micron. Immediately after this we can expect beginning of voiding due to the difference of mobilities in ε-phase.

Theoretical Prediction of the Liquid Channel Width in Soldering Reactions of Copper

Formation of the scallop-like η-phase Cu_6Sn_5 during reaction of copper substrate with liquid tin-based solder (with a little higher than eutectic one) proceeds much (by several orders of magnitude) faster than the same phase growth in reaction with solid solder under temperature just a little lower than eutectic one. It cannot be related to the temperature dependence of diffusion in intermetallic compound. Instead, it is related to the easy-diffusion paths emerging between neighboring scallops, which let copper intensively diffuse into the melt and there to react with tin at the scallop/liquid interfaces. To the best of our knowledge, there are 3 ways of interpreting the easy-diffusion paths in the mentioned system:

1. According to [1,2,8-10], paths are just liquid channels formed due to full wetting of inter-scallop boundaries by liquid solder, so that grain-boundary tension between two neighboring grains of compound is larger than two interface tensions between scallop and liquid solder:

$$\gamma_{\eta\eta} > 2\gamma_{\eta/l}. \tag{20}$$

In this case the liquid channels are formed towards the very bottom of scallops – towards the copper substrate (at first) and later towards the layer of ε-phase Cu_3Sn.

2. According to [11], wetting of grain-boundaries by the liquid solder is not full: $\gamma_{\eta\eta} < 2\gamma_{\eta/l}$. In this case the easy paths are the grooved grainboundaries between scallops.

3. There is also a compromise possibility [10]: scallops growing at the base of the same copper grain, have close orientations, so that grain boundaries between them have low tension, condition (2) is satisfied; on the other hand the scallops growing at different (neighboring) grains, have large misorientations, grain-boundaries between them have high tension, they are wetted by liquid solder, condition (1) is satisfied.

Cases (1) and (3) mean the existence of the liquid channels. As shown in [8], the growth and coarsening kinetics of soldering reaction is determined, first of all, by the width of these channels. To measure this width (may be, a few nanometers) directly, in situ, under condition of molten solder, seems to be not possible. After freezing the morphology changes (no full wetting anymore).

Thus, it is of major importance to make some reasonable theoretical predictions for the width of channels. Obviously, it cannot be too big, since there is a driving force of reaction which will lead to filling the existing gap by the η-phase growing grains. On the other hand, it cannot be zero because then two compound/liquid interfaces will convert into one grain-boundary between two solid grains, then the energy will increase due to condition (20)

Let us consider the channel of some width δ dividing the two parallel walls of η-compound grains, based on the substrate of ε-phase. In this configuration the bottom of the channel presents the contact of liquid tin-based solution and ε-phase, so that in usual free contact one might expect emergence of η-phase. Yet, in our case it should mean simultaneously the change of surface energy. It means that we actually have the nucleation problem – competition of bulk and surface terms. The only peculiarity is that the nucleus now is the island of η-phase containing grain-boundary instead of two preexisting η-phase/liquid interfaces.

Nucleation can be "homogeneous" ("kissing" of grains somewhere at arbitrary point contact of two walls – disk of η-phase) and "heterogeneous" – emerging of η-phase island (semi-cylindrical or rectangular "sheet" of η-phase) at the base of ε-phase bottom. The second possibility seems to be more probable due to presence of copper necessary to form "sheet" of η-phase from the tin-based liquid.

For simplicity consider semi-disc of radius R and thickness δ at the bottom of the channel. Semi-disc consists of two semi-discs of some thicknesses δ_1, δ_2, $\delta_1 + \delta_2 = \delta$, being the "continuations" of the two neighboring grains. Exact position of grain-boundary (and related ratio δ_1 / δ_2 does not influence the energy and therefore is not important).

The change of Gibbs free energy due to formation of semi-disc is equal to

$$\Delta G(R,\delta) = \left(-\frac{\Delta g_{\varepsilon+solder\to\eta}}{\Omega}\right)\cdot\delta\cdot\frac{1}{2}\pi R^2 + \left(\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}\right)\cdot\frac{1}{2}\pi R^2 \\ +\gamma_{\eta/liquid}\cdot\pi R\cdot\delta + \left(\gamma_{\eta/\varepsilon} - \gamma_{\varepsilon/liquid}\right)\cdot 2R\cdot\delta \qquad (21)$$

The first term is a “bulk” one. The second term corresponds to change from two solid/liquid interfaces to one grain-boundary. The third term corresponds to side semicircle. The last, fourth term, corresponds to change of bottom rectangular side interface from liquid/epsilon to eta/epsilon.

As usual in nucleation problems, let us unite terms with squared radius and with linear radius:

$$\Delta G(R,\delta) = \left(\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid} - \frac{\Delta g_{\varepsilon+solder\to\eta}}{\Omega}\delta\right)\cdot\frac{1}{2}\pi R^2 \\ +\left(\frac{\pi}{2}\gamma_{\eta/liquid} + \gamma_{\eta/\varepsilon} - \gamma_{\varepsilon/liquid}\right)\cdot\delta\cdot 2R \qquad (22)$$

One can easily see that the R-dependence of Gibbs free energy can

(1) can have typical barrier type at $\delta > \frac{\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}}{\Delta g_{\varepsilon+solder\to\eta}}\Omega$

or

(2) can be monotonically increasing at $\delta < \frac{\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}}{\Delta g_{\varepsilon+solder\to\eta}}\Omega$.

Thus, there exists some “critical” channel width, UNDER WHICH further filling of the liquid channel by eta-phase is IMPOSSIBLE.

$$\delta^* = \frac{\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}}{\Delta g_{\varepsilon+solder\to\eta}}\Omega \qquad (23)$$

If $\delta > \delta^*$ then nucleation is not even needed, and channel will proceed becoming narrower by normal movement of walls till the width reaches the mentioned critical value.

Thus, our simple model PREDICTS the operating width of the liquid channels.

Possibility to take into account the aspect ratio evolution of scallops

In model approximations the scallops of Cu_6Sn_5 phase have the parallelepiped shape with changing aspect ratio (see fig. 9).

Chemical potentials of top and side facets are defined as:

$$\mu_1 = \mu_{\eta/l} + \frac{p+q}{q}2\gamma\Omega\left(\frac{1}{H_i} + \frac{1}{a_i}\right), \\ \mu_2 = \mu_{\eta/l} + \frac{p+q}{q}\frac{4\gamma\Omega}{a_i} \qquad (24)$$

there $\mu_{\eta/l}$ is the volume chemical potential, p and q are the mass parts of tin and copper, Ω is the atomic volume, γ is the surface energy, H_i is the height of i-scallop, a_i – is the width of the top facet of the *i*-scallop.

In the mean-field approximation the velocity of normal and lateral growth of scallops is defined as the product of Onsager effective coefficient and the difference between mean chemical potential of liquid phase, which surrounds the scallop and the chemical potential of the growing facet. Thereby, lateral and normal growth velocities are defined as:

$$\frac{da_i}{dt} = L \cdot \left\{ \bar{\mu} - \left(\mu_{\eta/l} + \frac{p+q}{q} 2\gamma\Omega \left(\frac{1}{H_i} + \frac{1}{a_i} \right) \right) \right\}$$
$$\frac{dH_i}{dt} = L \cdot \left\{ \bar{\mu} - \left(\mu_{\eta/l} + \frac{p+q}{q} \frac{4\gamma\Omega}{a_i} \right) \right\} \qquad (25\text{ a,b})$$

where L is the Onsager effective coefficient.

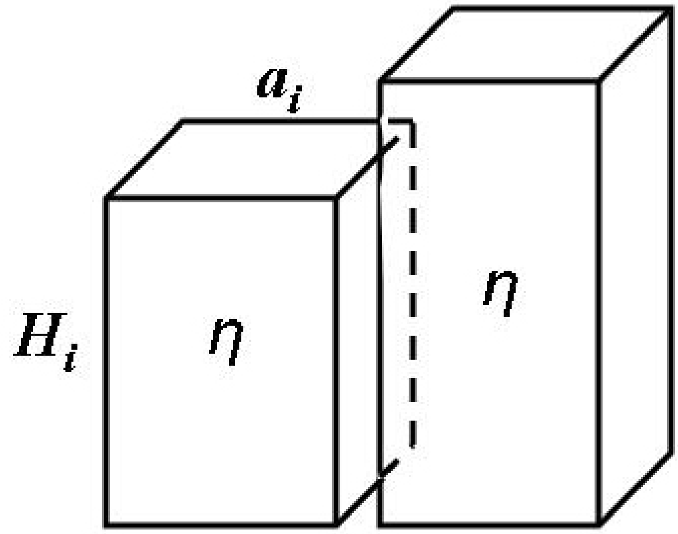


Fig. 9. The model approximation for the scallop shape.

We use two conservation laws:

Conservation of total area of the top facets: $\sum_i a_i \frac{da_i}{dt} = 0$ (26)

1) Conservation of total mass: $\frac{q}{p+q} \sum_i \frac{dV_i}{dt} = \frac{q}{p+q} \sum_i \left(a_i^2 \frac{dH_i}{dt} + 2a_i H_i \frac{da_i}{dt} \right)$ (27)

The total flux of copper atoms is defined as:

$$J_{tot} = \frac{1}{\Omega} \sum_i \left(2a_i \delta \frac{\bar{c}_{Cu} D^{melt}}{kT} \frac{\mu_{\varepsilon/l} - \bar{\mu}}{H_i} \right), \qquad (28)$$

there δ^{ef} is the effective liquid channel width, $\bar{c}_{Cu}$ is the equilibrium concentration of copper in liquid phase, k is the Bolzman constant, T is the temperature. The whole flux of copper atoms is consumed for the growth of scallops, thereby with use of eq. (26) we derive:

$$\sum_i \left(2a_i \delta \frac{\bar{c}_{Cu} D^{melt}}{kT} \frac{\mu_{\varepsilon/l} - \bar{\mu}}{H_i} \right) = \frac{q}{p+q} \sum_i \left(a_i^2 \frac{dH_i}{dt} + 2a_i H_i \frac{da_i}{dt} \right), \qquad (29)$$

We substitute eq.(25a,b) in the equation (29):

$$\left(\mu_{\varepsilon/l} - \bar{\mu} \right) 2\delta \frac{\bar{c}_{Cu} D^{melt}}{kT} \sum_i \frac{a_i}{H_i} = \frac{q}{p+q} \sum_i a_i^2 L \left[\bar{\mu} - \mu_{\eta/l} + \frac{p+q}{q} \frac{4\gamma\Omega}{a_i} \right] +$$
$$\frac{q}{p+q} \sum_i 2a_i H_i L \left[\bar{\mu} - \mu_{\eta/l} + \frac{p+q}{q} 2\gamma\Omega \left(\frac{1}{H_i} + \frac{1}{a_i} \right) \right],$$

so that

$$
\begin{gathered}
\left(\mu_{\varepsilon/l}-\bar{\mu}\right)2\delta\frac{\bar{c}_{Cu}D^{melt}}{kT}\sum_i\frac{a_i}{H_i}= \\
\left(\bar{\mu}-\mu_{\eta/l}\right)L\frac{q}{p+q}\left(\sum_i\left(a_i^2+2H_ia_i\right)+4\gamma\Omega L\sum_i\left(a_i\right)+4\gamma\Omega L\sum_i\left(a_i+H_i\right)\right)
\end{gathered}
\qquad (30)
$$

If we take that the average number of scallops is *MM* then we can write down:

$$
\begin{aligned}
&\sum_i\frac{a_i}{H_i}=MM\left\langle\frac{a}{H}\right\rangle \\
&\sum_i\left(a_i^2+2H_ia_i\right)=MM\left(\left\langle a^2\right\rangle+2\left\langle Ha\right\rangle\right) \\
&\sum_i\left(a_i\right)=MM\left\langle a\right\rangle \\
&\sum_i\left(a_i+H_i\right)=MM\left\langle a+H\right\rangle
\end{aligned}
\qquad (31a,b,c,d)
$$

Then, after simple but long algebra, we derive the final formulas for the lateral and normal growth velocity of scallops:

$$
\begin{aligned}
\frac{da_i}{dt}&=L\cdot\frac{p+q}{q}\frac{2\gamma\Omega}{\langle a\rangle}\left\{\left\langle\frac{a}{H}\right\rangle+1-\frac{\langle a\rangle}{H_i}-\frac{\langle a\rangle}{a_i}\right\} \\
\frac{dH_i}{dt}&=L\cdot\frac{p+q}{q}\frac{2\gamma\Omega}{\langle a\rangle}\left\{\left\langle\frac{a}{H}\right\rangle+1-\frac{2\langle a\rangle}{a_i}\right\}
\end{aligned}
\qquad (32a,b)
$$

Results of simulations of the scallop growth and redistribution by solving numerically the equations (32) are following:

The distribution of the lateral sizes a is well fitted well by the Weibull distribution with parameters $a_{\text{weibull}}=5{,}26\cdot10^{-7}$ and $b_{\text{weibull}}=3{,}36$.

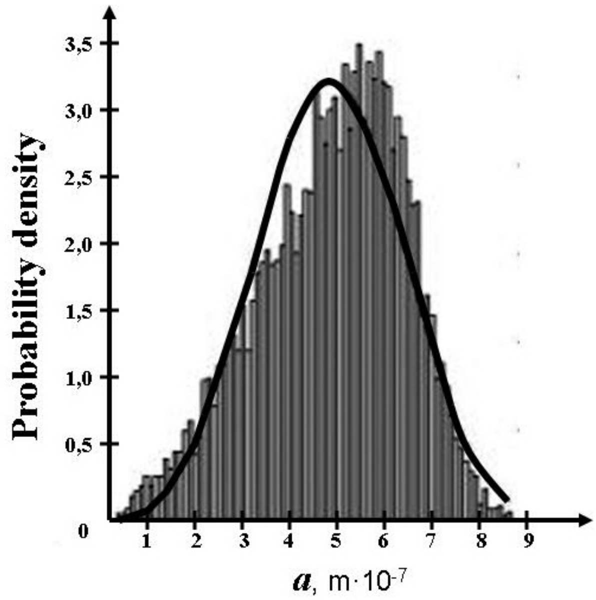


Fig. 10. The distribution of the shape parameter fitted by Weibull distribution.

Summary

Growth kinetics of intermediate phases during soldering is described by equations (13-15). Criteria of epsilon-phase growth after initial suppression by eta-phase is described by eq. (19). Optimal width of liquid channels between scallops of eta-phase can be rougly estimated by eq. (23). Self-consistent description of growth kinetics, aspect ratio and size distribution of scallops is given by the set of equations (32)

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Анотація. ***А.М. Гусак, О.Ю. Ляшенко, Ф. Одаж. Моделі формування, росту і конкуренції фаз у процесі пайки – деякі нові результати.*** *У роботі представлені прості феноменологічні моделі формування, конкуренції та росту проміжних фаз у процесі пайки. Була зроблена перша спроба оцінити ширину рідких каналів між зернами фази* Cu_6Sn_5*. Також було побудовано модель росту фази* Cu_6Sn_5*, враховуючи зміну форми зерен (параметру форми).*

Ключові слова: дифузія, проміжні фази, кінетика росту, люті на основі олова, змочування границь зерен.

Аннотация. ***А.М. Гусак, О.Ю. Ляшенко, Ф. Одаж. Модели формирования, роста и конкуренции фаз в процессе пайки – некоторые новые результаты.*** *В работе представлены простые феноменологические модели формирования, конкуренции и роста промежуточных фаз в процессе пайки. Была предпринята первая попытка оценить ширину жидких каналов между зернами фазы* Cu_6Sn_5*. Также была построена модель роста фазы* Cu_6Sn_5 *с учетом изменения формы зерен (параметра формы).*

Ключевые слова: диффузия, промежуточные фазы, кинетика роста, припои на основе олова, смачивание границ зерен.

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