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MODEL OF POROUS Cu_3Sn FORMATION BY THE FLUX-DRIVEN CELLULAR PRECIPITATION

Just discovered new morphology formation (porous Cu_3Sn with lamellar structure) is discussed. Several possible explanations are compared. The most reasonable seems to be an explanation by the new-developed theory of Flux-Driven Precipitation in open system. Simple formulae for prediction of the lamellar structure parameters and of the propagation velocity are obtained and compared with experiment. Comparison seems to be quite reasonable.

Keywords: sold state reaction, diffusion, void, phase competition, soldering.

Introduction

Phase transformations in materials are very well studied by now for the case of closed systems. In closed system any phase transformation is a part of evolution path to equilibrium. Closed system means homogeneous stationary external conditions. Standard examples are:

1. Isolated system - constant energy E and no diffusion contacts. Then evolution means entropy S tending to maximum.
2. System within thermal bath with fixed temperature T and volume V . Then evolution means Helmholtz free energy $F=E-TS$ tending to minimum.
3. System within thermal bath with fixed temperature and pressure. Then evolution means Gibbs free energy $G=E+pV-TS$ tending to minimum.

Yet, very often the phase transformations proceed in open systems. We call a system open if it exists in inhomogeneous external conditions. Such conditions (for example, external gradient of temperature or gradient of chemical potential) just make it impossible for system to reach any equilibrium. Open systems usually stay under in-going and/or outgoing fluxes of matter or/and energy and entropy.

List of open systems is long. We will concentrate here on the phase transformations under external fluxes of matter. The most known example is contact zone of diffusion couple during reactive diffusion. Chemists treat reactive diffusion as a chain of chemical reactions at moving interfaces of growing compounds layers, which (layers) serve as the diffusion barriers while providing atoms to interfaces [1]. For physicists reactive diffusion is actually the chain of phase transformations in the open system under gradients of chemical potentials and corresponding concentrations inside, and under in-going and out-going fluxes through the boundaries of this open system [2]. Typically, phase transformations in closed system consist of three main stages of nucleation, growth and coarsening (ripening) [3]. It is very intriguing how can the "openness" of the system influence (in our case – external fluxes) the mentioned three stages. In 2002 the theory of Flux-Driven Ripening (FDR) was proposed ([4]), based on the case of Cu_6Sn_5 -scallop growth during solid Cu - molten solder reaction. One of the interesting issues of this process appeared to be the simultaneous growth and ripening of scallops. Another interesting issue was the time behavior of interface area in such open system – instead of decreasing it tends to constant value. Instead, the total volume of the new phase does not tend to constant but grows unlimitedly. In 2003 the idea of FDR was generalized on the theory of Flux-Driven Grain Growth (FDGG) – [5]. Here also the total area of all grain boundaries remains constant during the bamboo-structured thin-film growth due to lateral grain growth. In 2011 the theory of Flux-Driven Nucleation (FDN) of the intermediate

phases and of voids at the moving interphase interfaces was formulated [6]. In this theory, the drift term in Fokker-Planck equation for the random walk of nuclei in the size space contains two terms – first term is traditional and proportional to the derivative of Gibbs free energy over nucleus size; second term is determined by the divergence of in- and out-going fluxes at the nucleation site. This second term may lead to kinetic suppression of some intermediate phases.

The above mentioned stages of phase transformations, both for closed and for open systems, are typical for the process controlled by bulk diffusion. It is well-known that at relatively low temperatures, when the bulk diffusion is frozen and grain boundary or interface diffusion is not frozen, nature finds the way to decompose the thermodynamically unstable system. This low-temperature process is usually called cellular decomposition (if initial and resulting phases are solid solutions) or eutectoid transformation (if initial and resulting phases are compounds or pure materials). The understanding and theory of this process, as alternative to bulk diffusion mechanism, was developed by Turnbull [7], Hillert [8] and John Cahn [9]. Recently, it was discovered that similar process can proceed in open system under condition of outgoing fluxes [10]. Namely, as we will see below, the components in this process are not just redistributed along the moving interface (as in normal cellular precipitation in closed system), but one of components is “sucked out” outside from the moving interface through the just formed lamellar structure. Therefore, it seems natural to develop the Cahn’s theory into the Theory of Flux-Driven Cellular Precipitation (or Flux-Driven Eutectoid Transformation).

Let “i” be a binary compound with narrow range of homogeneity. Let by some reason (selective oxidation, surface diffusion to external sink, radiation influence,...) some number of atoms of one of the components (B) is extracted leaving vacancies behind. Let the vacancy sinks at dislocations be not too efficient – it means that the time of relaxation of the vacancy concentration to the equilibrium level may be longer than the time of new structure nucleation. As a result, compound will find itself simultaneously (1) supersaturated with vacancies and (2) depleted with B (or supersaturated with A) – deviated from stoichiometry. First reason should lead to void nucleation. Second reason should lead to precipitation (nucleation) of the phase “j”, “next” in direction of decreasing B (richer in A). For example, let us consider compound Cu_6Sn_5 , from which some part of Sn atoms is sucked out by fast surface diffusion of tin to react with copper. If compound Cu_6Sn_5 loses Sn, it becomes supersaturated by copper, therefore it should precipitate the particles of the phase nearest at the phase diagram from the copper side. This phase is Cu_3Sn_1 – so, the Cu_3Sn_1 particles should precipitate. On the other hand, if extraction of tin is related to formation of extra vacancies, they should gather into voids. Thus, compound Cu_6Sn_5 should simultaneously demonstrate the precipitation of Cu_3Sn_1 phase and of voids. If the sucking out of B continues, then both voids and precipitates of new phase should grow along the outgoing flux of B.

So, on one hand, our work is just some modification of the classical Turnbull’s and Cahn’s approach to eutectoid transformation for the case of open decomposing system. Main difference is the change of boundary conditions due to existence of outgoing flux. The other peculiarity is that one of the emerging phases is just “emptiness” (hollow channels). Actually, we observe decomposition of the pseudoternary system copper-tin-vacancies under external outflux of tin. On the other hand, this paper has practical aim - to understand and describe the recently discovered new morphology of the intermetallic Cu_3Sn_1 .

At first (in Section II), we will review shortly the main experimental observations. Then, in (Section III) we will present the discussion of possible reasons of newly discovered morphology, then follow the basic equations and boundary conditions of the Flux-Driven Precipitation theory (Section IV). In Section V we will discuss the results.

Main experimental observations

It is well-known that the growth of Cu₃Sn₁ phase layer in the process of reactive diffusion between Cu and Sn or between copper and Cu₆Sn₅-phase leads to formation of Kirkendall voids in the vicinity of Cu/Cu₃Sn₁ moving interface [11]. It happens (1) because copper is the main diffusant across growing Cu₃Sn₁ phase layer, generating the back flux of vacancies to the Cu₃Sn₁/Cu interface and (2) because the vacancy sinks at dislocations near interface work not properly, enabling supersaturation by vacancies and voids formation. Recently, nanotwinned copper was used to form the contact with solder [11]. In this case voiding can be almost suppressed, due to numerous vacancy sinks at the twin boundaries. Our present paper is NOT about the Kirkendall voids formation at the interface Cu/Cu₃Sn during reactive growth of Cu₃Sn phase. This effect is known and, in principle, its nature and kinetics are clear. Instead, our paper is about the process which starts LATER: Imagine the layer of tin-based solder (with thickness 15-30 microns) between two copper rods. If solder is molten, its reaction with copper goes very fast and in about one minute all solder is consumed by the fast growing phase Cu₆Sn₅. If annealing continues, after this the solid state aging of the sandwich Cu-Cu₆Sn₅-Cu leads to the growth of two thin Cu₃Sn₁ layers. They grow normally up to several microns thickness each. If copper is not nanotwinned, simultaneously with growth the chain of Kirkendall voids along both Cu/Cu₃Sn₁ interfaces appears. After this the new phenomenon starts: one can observe formation of much more porous Cu₃Sn₁ with different morphology. This morphology resembles the picture of cellular precipitation, or, even more, eutectoid decomposition with essential difference – the second phase in lamellar structure is here just “emptiness” (net of interconnected voids – empty channels).

According to experimental data [10], region of such porous structure inside starts from the sides and propagates in almost steady-state regime until full disappearance of Cu₆Sn₅. Clearly, tin is going out due to some driving force. Most probably, it is a driving force of Cu₃Sn₁ formation at the SIDES of sample due to surface diffusion of tin to the side walls of copper rods. It looks like the presence of underfill somehow (for example, by wetting) helps tin to approach the side walls of copper rods, but the full picture is not yet clear in this respect. One thing is clear – some reason is sucking out tin via the sides of remaining Cu₆Sn₅ layer.

First, we consider shortly the list of possible explanations of the above described phenomenon.

Analysis of possible reasons of new morphology

In this Section we analyze three explanations of the porous compound formation and demonstrate that only one of them (the last one) has chances to be reasonable.

Is it possible that Cu₆Sn₅ is, first, decomposed into Cu₃Sn₁ and Sn which later diffuses out leaving the empty channels?

Here we shortly analyze the possibility of decomposition reaction



Figures 1a and 1b below show the Gibbs free energies (from left to right) of (1) pure copper, (2) Cu₃Sn₁ phase, (3) Cu₆Sn₅ phase and (4a) liquid solution of copper in tin or (4b) just pure solid tin (in which copper is almost insoluble).

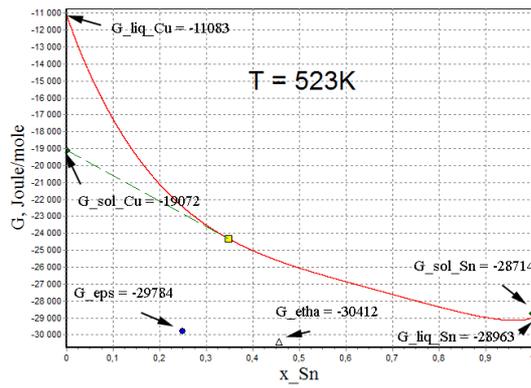


Fig. 1a. Gibbs free energies for for phases at 523 K (liquid tin).

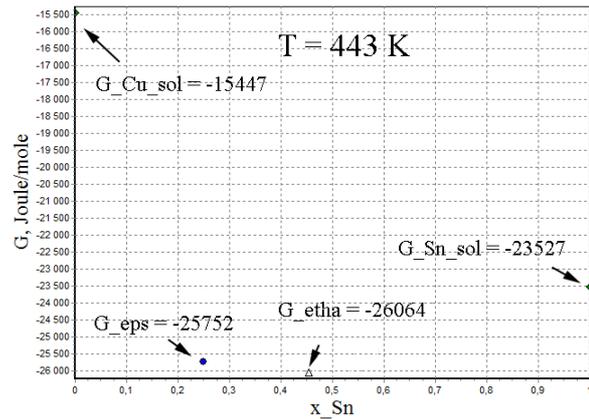


Fig. 1b. Gibbs free energies of initial components and of two intermediate phases at 423 K (solid tin).

We can see that in both cases (523 K and 423 K) the decomposition of Cu_6Sn_5 into Cu_3Sn_1 and tin is thermodynamically unfavorable – point of Cu_6Sn_5 is situated BELOW the common tangent of Cu_3Sn_1 and Sn. The EXTENT of this “unfavorableness” is rather small, especially at 523 K (Fig. 1a). Indeed, the driving force of Cu_6Sn_5 formation (instead of decomposition) from Cu_3Sn_1 plus Sn is

$$\begin{aligned} \Delta g_{\text{Cu}_3\text{Sn}_1+\text{Sn}\rightarrow\text{Cu}_6\text{Sn}_5} &= \\ &= \frac{1}{6.02 \cdot 10^{23}} \left(\frac{(-29784) \cdot (1 - 5/11) + (-28963) \cdot (5/11 - 1/4)}{1 - 1/4} - (-30412) \right) = \quad (2) \\ &= 1.42 \cdot 10^{-21} \text{ J / atom}, \end{aligned}$$

which is indeed rather small. For example, such driving force can change sign (making the decomposition favorable) under compression with pressure larger than

$$p > \frac{\Delta g}{\Omega(\eta)} \approx \frac{1.42 \cdot 10^{-21} \text{ J / atom}}{1.80 \cdot 10^{-29} \frac{\text{m}^3}{\text{atom}}} = 0.79 \cdot 10^8 \text{ Pa} \approx 780 \text{ atm}.$$

So far we can not see the physical reason for such compressive stress, since the change of molar volumes seems to lead to tension instead of compression. So, most probably, direct decomposition of Cu_6Sn_5 into Cu_3Sn_1 plus pure Sn is not favorable.

Yet, one can imagine the reaction



as consisting of the following two steps:



During the first step 3 moles of tin atoms may be deducted from one mole of Cu_6Sn_5 -phase not in the form of bulk tin phase (which is thermodynamically unfavorable, as we have just demonstrated above), but in the form of surface atoms at the free surface of Cu_3Sn_1 phase in the hollow channels. This possibility will be treated in subsection III-3.

Tensile stresses accumulation during the growth of continuous Cu₃Sn₁ layer in reaction of Cu with Cu₆Sn₅.

Another typical argument in discussing voiding or other morphological changes (well known since discussions around Kirkendall experimental study of interdiffusion), is a non-conservation of volume during reaction or/and diffusion.

Indeed, let us evaluate the change of volume in reaction $9\text{Cu} + \text{Cu}_6\text{Sn}_5 \rightarrow 5\text{Cu}_3\text{Sn}_1$.

Molar volume of Cu₃Sn₁ phase is $V^{\text{molar}}(\varepsilon \equiv \text{Cu}_3\text{Sn}_1) = 35.01 \frac{\text{cm}^3}{\text{mole}}$.

Atomic volume of Cu₃Sn₁ is

$$\Omega(\varepsilon \equiv \text{Cu}_3\text{Sn}_1) = \frac{35.01 \cdot 10^{-6} \text{ m}^3 / \text{mole}}{4 \cdot 6.02 \cdot 10^{23} \text{ atoms / mole}} \cong 1.46 \cdot 10^{-29} \frac{\text{m}^3}{\text{atom}}$$

Molar volume of Cu₆Sn₅ phase is $V^{\text{molar}}(\eta \equiv \text{Cu}_6\text{Sn}_5) = 118.72 \frac{\text{cm}^3}{\text{mole}}$.

Atomic volume of Cu₆Sn₅ is

$$\Omega(\eta \equiv \text{Cu}_6\text{Sn}_5) = \frac{118.72 \cdot 10^{-6} \text{ m}^3 / \text{mole}}{11 \cdot 6.02 \cdot 10^{23} \text{ atoms / mole}} \cong 1.80 \cdot 10^{-29} \frac{\text{m}^3}{\text{atom}}$$

Molar volume of Cu is $V^{\text{molar}}(\text{Cu}) = 7.16 \frac{\text{cm}^3}{\text{mole}}$.

Atomic volume of Cu is $\Omega(\text{Cu}) = \frac{7.16 \cdot 10^{-6} \text{ m}^3 / \text{mole}}{1 \cdot 6.02 \cdot 10^{23} \text{ atoms / mole}} \cong 1.19 \cdot 10^{-29} \frac{\text{m}^3}{\text{atom}}$

Reaction of Cu₃Sn₁ formation from Cu reaction with Cu₆Sn₅ is:



Total volume of the Left-Hand Side is

$$9 \cdot \Omega(\text{Cu}) + 11 \cdot \Omega(\eta) = 9 \cdot 1.19 \cdot 10^{-29} \text{ m}^3 + 11 \cdot 1.80 \cdot 10^{-29} \text{ m}^3 \cong 30.51 \cdot 10^{-29} \text{ m}^3$$

Total volume of the Right-Hand Side is

$$5 \cdot 4 \cdot \Omega(\varepsilon) = 5 \cdot 4 \cdot 1.46 \cdot 10^{-29} \text{ m}^3 \cong 29.20 \cdot 10^{-29} \text{ m}^3$$

Change of volume per atom is negative and equal to

$$\Delta\Omega(\text{per atom}) = \frac{29.20 - 30.51}{20} \cdot 10^{-29} \text{ m}^3 = -0.655 \cdot 10^{-30} \text{ m}^3.$$

$$\frac{\Delta\Omega}{\Omega(\varepsilon)} = \frac{-0.655 \cdot 10^{-30} \text{ m}^3}{1.46 \cdot 10^{-29} \text{ m}^3} \approx -0.045.$$

Even if all this volume change would go to void formation, the void fraction would not exceed 4.5 percents, which is clearly much less than we observe in the porous zone. Thus, the volume change cannot explain the observed amount of voids in porous Cu₃Sn₁. (Instead, voids formation can be explained by the extraction of tin atoms from Cu₆Sn₅ – see next section)

In case of rigidly constrained sides of the sample or in case of spherical (closed) geometry the volume change of minus 4.5 percents would mean significant tensile stresses – of a few gigapascals. As mentioned above, such tensile stresses cannot provide the observed amount of porosity but they can make initial nucleation of voids much easier.

Flux-driven simultaneous precipitation of Cu₃Sn₁ and voids

Currently we can see only one reasonable explanation of the two morphologies of Cu₃Sn₁ – (1) continuous layer of Cu₃Sn₁ with Kirkendall voids near the interface with copper, and (2) porous Cu₃Sn₁ with set of elongated voids everywhere. (We believe that this set of voids forms the percolating cluster making possible the migration of tin along the surfaces of voids to react with copper sides.)

Our main assumption is that in the bulk the main diffusant is copper, but at the free surface of intermetallics (and may be as well as on Cu₆Sn₅/Cu₃Sn₁ interface) the main diffusant is tin. For simplicity we will assume that the surface diffusion of tin not just faster but much faster than the surface diffusion of copper. Tin, of course, is not lost - it goes rapidly to the external (side) surface of copper inducing the reaction with copper and formation of additional side layer of intermetallic.

Due to the side out-diffusion of tin the phase Cu₆Sn₅ is gradually converted into two-phase zone – colonies of the lamellar structures – Cu₃Sn₁ layer of some width *a* is followed by empty channel of width *b* and this a+b structure is periodically repeated.

We can evaluate the volume fractions $a/(a+b)$ and $b/(a+b)$ of crystalline Cu₃Sn₁ and of voids as follows: $Cu_6Sn_5 - 3Sn \rightarrow 2Cu_3Sn_1$.

If 3 moles of tin go away by side surface diffusion, then molar volume 118.72 cm³ of Cu₆Sn₅ converts into two molar volumes of Cu₃Sn₁: $2 \cdot 35.01 \text{ cm}^3 = 70.02 \text{ cm}^3$.

The rest is empty (void): $118.72 - 2 \cdot 35.01$.

Thus, void fraction should be (if one neglects the relaxation effects)

$b/(a+b) = 1 - 70.02/118.72 = 0.41$. Respectively, $a/(a+b) = 0.59$.

So, if the volume of tin which has gone, is not relaxed, then the porous Cu₃Sn₁ should contain about 40 percents voids.

Note that if all atomic volumes would be equal, then the ratio *b/a* would be different – it would be 3/8: Cu₆Sn₅ has 11 atoms, 3 atoms of Sn go and are replaced by 3 vacancies, 8 atoms go for construction of 2 molecules of Cu₃Sn₁. So, void is a place of 3 atoms which had been sucked out, 2Cu₃Sn₁ is a new phase volume, containing 8 atoms. If all atomic volumes are assumed the same, then the ratio must be

$$b/a = 3/8. \tag{7}$$

Everywhere below we will use THIS approximation.

Kinetic model of the eutectoid-like porous zone formation in open system

In the following, we will concentrate on the behavior and conservation of tin, but it is impossible to describe the growth inside layer of empty channel without account of copper diffusion along the moving interface, “leaving place” for empty channels

So far we will treat the channels as planar and interface as planar as well – we will take it as a constraint. Later we will think about, say, sinusoidal planar shape, introducing at least one additional parameter of optimization.

Let *V* be the velocity, with which the interface between Cu₆Sn₅ and lamellar structure “Cu₃Sn₁ + lamellar voids” moves from the initial side inside the remaining phase Cu₆Sn₅.

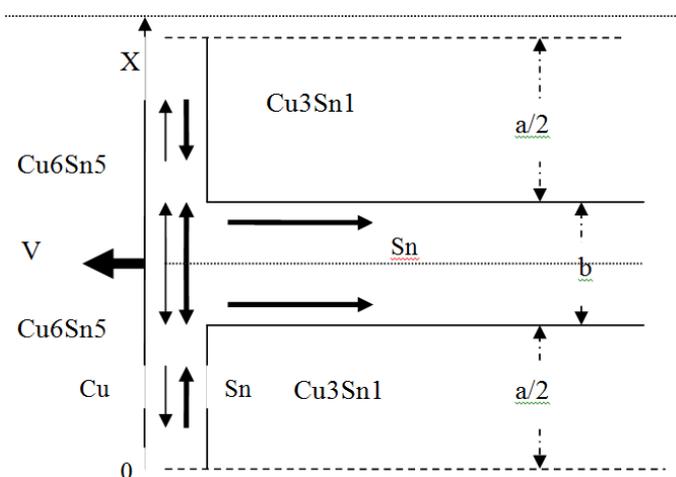


Fig.2. Scheme of lamellar zone formation by out-diffusion of tin.

In our model tin at first migrates to the surfaces of hollow channels (“corridors”) (I) via interface of length a between Cu_6Sn_5 and Cu_3Sn_1 phases, and also (II) via interface of length b between Cu_6Sn_5 and a hollow “corridor”. After this tin migrates along the walls of corridor to react with copper. Nucleation of such kind of structure will be considered elsewhere. Here we make a model only for the growth stage.

It is important to understand what are the directions and magnitudes of Cu interface fluxes, in respect to Sn fluxes. Let us make the simple calculation (assuming all atomic volumes the same): One mole of Cu_6Sn_5 loses 3 moles of Sn and is converted into 2 moles of Cu_3Sn_1 and void (“3 moles of vacancies”). Let us divide one mole of Cu_6Sn_5 into two parts: “left” contains $8/11$ mole of Cu_6Sn_5 and is followed by two moles of Cu_3Sn_1 . “Right” part contains $3/11$ mole of Cu_6Sn_5 and is followed by Void (empty channel). (See Fig.3)

It means that $8/11 \cdot 6 = 48/11$ moles of Cu atoms are converted into 6 moles of Cu atoms, and for this the left side should get (by interface diffusion) $6 - 48/11 = 18/11$ moles of copper atoms. To the opposite, $8/11 \cdot 5 = 40/11$ moles of tin atoms are converted into 2 moles of Sn atoms, and for this the same left part should give out $40/11 - 2 = 18/11$ moles of Sn atoms. Thus, the “left” part just exchanges $18/11$ moles of Sn atoms to the same quantity of Cu atoms.

The “right” part gives out both copper and tin – $18/11$ moles of copper and $15/11$ moles of tin, which fully corresponds to the stoichiometry of Cu_6Sn_5 phase. Thus, in the “right” part of interface the fluxes of copper and tin are not opposite, but instead codirected, and their ratio corresponds to the ratio of molar fractions. (Fig.3)

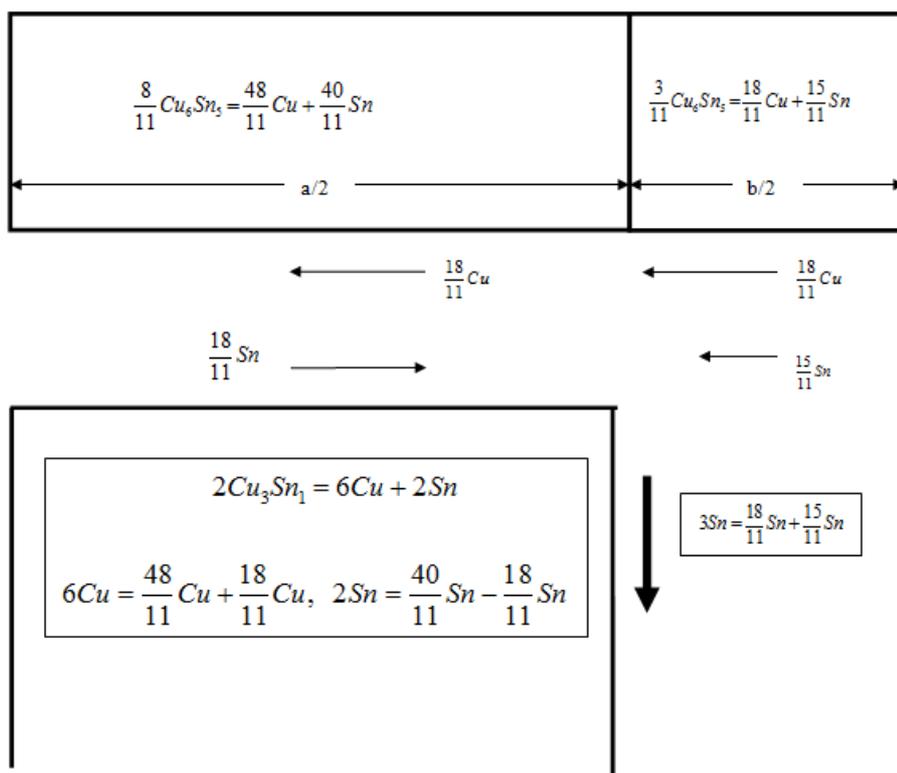
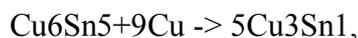


Fig.3. Scheme of components redistribution along the interface in FDP.

Now we should understand what are the driving forces generating the flux directions shown at Fig. 5. For tin the driving force seems evident – it is a low tin chemical potential after interaction with side copper - in other words, it is the driving force of already mentioned reaction



which in this case is realized by interface and then by surface diffusion of tin. In the “left” part of Fig.4 the copper flux along interface just must be opposite and equal by absolute value

to the tin flux along the same interface (to provide conservation of volume, if one neglects the difference of atomic volumes). Equality of absolute magnitudes and opposite directions of Cu and tin interface fluxes in the “left” part - along the η/ε interphase interface can be realized by various mechanisms (interface Kirkendall effect, interfacial backstress (“osmotic pressure”), but here we will not go into details.

In the “right” part the fluxes should be co-directed and proportional to stoichiometric fractions, to provide the full disappearance of material ahead of the propagating void channel. Thermodynamic reason is following: sucking out of tin from Cu_6Sn_5 decreases its concentration in this compound and, simultaneously, increases the concentration of copper, which means also increase of copper chemical potential. So, copper migrates along the slope of its chemical potential, to the edge of void channel.

We will formulate and solve equations of tin diffusion along the two interfaces – $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}_1$ (“left” part) and $\text{Cu}_6\text{Sn}_5/\text{void}$ (“right” part)

I. $|y| < a/2$. Diffusion of tin along interface $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}_1$ – “left” part

Diffusion of tin along the moving interface in its own reference frame with account of side fluxes is described very similar to the diffusion at the moving front of cellular precipitation.

$$\frac{\partial n_{\text{Sn}}^{\text{int}\eta/\varepsilon}}{\partial t} = D_{\text{Sn}}^{\text{int}\eta/\varepsilon} \frac{\partial^2 n_{\text{Sn}}^{\text{int}\eta/\varepsilon}}{\partial y^2} + \frac{V}{\delta} (n^\eta C_{\text{Sn}}^\eta - n_{\text{Sn}}^{\text{int}\eta/\varepsilon}(y)). \quad (8)$$

As usual, further we assume the steady-state approximation:

$$D_{\text{Sn}}^{\text{int}\eta/\varepsilon} \frac{\partial^2 n_{\text{Sn}}^{\text{int}\eta/\varepsilon}}{\partial y^2} \approx \frac{V}{\delta} (n_{\text{Sn}}^{\text{int}\eta/\varepsilon}(y) - n^\eta C_{\text{Sn}}^\eta). \quad (9)$$

If y is counted from the center of interval a , then the solution should be symmetric:

$$n_{\text{Sn}}^{\text{int}\eta/\varepsilon}(y) = A_L \cdot \cosh\left(\frac{y}{\lambda_L}\right) + B_L \quad (10)$$

$$\lambda_L = \sqrt{\frac{D_{\text{Sn}}^{\text{int}\eta/\varepsilon} \delta}{V}}$$

Constant A_L can be found from the conservation condition for tin in an a -band:

$$-D_{\text{Sn}}^{\text{int}\eta/\varepsilon} \frac{\partial n_{\text{Sn}}^{\text{int}\eta/\varepsilon}}{\partial y} \Big|_{y=a/2} \cdot \delta \cdot W \cdot t = (n^\eta C_{\text{Sn}}^\eta - n^\varepsilon C_{\text{Sn}}^\varepsilon) V t \frac{a}{2} W, \quad (11)$$

Or

$$-\frac{A_L}{\lambda_L} \cdot \sinh\frac{a}{2\lambda_L} = \frac{Va}{2D_{\text{Sn}}^{\eta/\varepsilon} \delta} (n^\eta C_{\text{Sn}}^\eta - n^\varepsilon C_{\text{Sn}}^\varepsilon),$$

so that

$$A_L = -\frac{(a/2\lambda_L)}{\sinh(a/2\lambda_L)} (n^\eta C_{\text{Sn}}^\eta - n^\varepsilon C_{\text{Sn}}^\varepsilon). \quad (12)$$

It is also natural to suppose that at the center of the future Cu_3Sn ($y=0$) the concentration should coincide with concentration of Cu_6Sn_5 . This condition gives us the second constant B_L :

$$n^\eta C_{\text{Sn}}^\eta = A_L \cdot \cosh\left(\frac{0}{\lambda_L}\right) + B_L = A_L + B_L \Rightarrow B_L = n^\eta C_{\text{Sn}}^\eta - A_L \quad (13)$$

II. $a/2 < |y| < a/2 + b$, $\left| y - \frac{a+b}{2} \right| < \frac{b}{2}$. Diffusion of tin along Cu6Sn5/void interface.

Diffusion of tin along the moving interface in its own reference frame with account of side fluxes is described very similar to the diffusion at the moving front of cellular precipitation.

$$\frac{\partial n_{Sn}^{int\eta/void}}{\partial t} = D_{Sn}^{int\eta/void} \frac{\partial^2 n_{Sn}^{int\eta/void}}{\partial y^2} + \frac{V}{\delta} (n^\eta C_{Sn}^\eta - n_{Sn}^{int\eta/void}(y)). \quad (14)$$

Steady-state approximation:

$$D_{Sn}^{int\eta/void} \frac{\partial^2 n_{Sn}^{int\eta/void}}{\partial y^2} \approx \frac{V}{\delta} (n_{Sn}^{int\eta/void}(y) - n^\eta C_{Sn}^\eta). \quad (15)$$

If y is counted from the center of interval b , then the solution should be symmetric:

$$n_{Sn}^{int\eta/void}(y) = A_R \cdot \cosh\left(\frac{y}{\lambda_R}\right) + B_R, \quad (16)$$

$$\lambda_R = \sqrt{\frac{D_{Sn}^{int\eta/void} \delta}{V}}$$

Constant A_R can be found from the conservation condition for tin in a b -band:

$$-D_{Sn}^{int\eta/void} \frac{\partial n_{Sn}^{int\eta/void}}{\partial y} \Big|_{y=(a+b)/2+b/2} \cdot \delta \cdot W \cdot t = (n^\eta C_{Sn}^\eta - 0) V t \frac{b}{2} W, \quad (17)$$

so that

$$A_R = -\frac{(b/2\lambda_R)}{\sinh(b/2\lambda_R)} (n^\eta C_{Sn}^\eta). \quad (18)$$

It is also natural to suppose that at the center of the future void ($y=(a+b)/2$) the concentration should coincide with concentration of Cu6Sn5. This condition gives us the second constant B_R :

$$n^\eta C_{Sn}^\eta = A_R \cdot \cosh\left(\frac{0}{\lambda}\right) + B_R = A_R + B_R \Rightarrow B_R = n^\eta C_{Sn}^\eta - A_R \quad (19)$$

One more natural condition should be the continuity of tin concentration along interface, including the border between “left” and “right” parts:

$$A_L \cdot \cosh\left(\frac{a}{2\lambda_L}\right) + B_L = A_R \cdot \cosh\left(\frac{b}{2\lambda_R}\right) + B_R$$

or

$$A_L \cdot \left(\cosh\left(\frac{a}{2\lambda_L}\right) - 1 \right) = A_R \cdot \left(\cosh\left(\frac{b}{2\lambda_R}\right) - 1 \right), \quad (20)$$

or

$$\frac{(a/2\lambda_L)}{\sinh(a/2\lambda_L)} (n^\eta C_{Sn}^\eta - n^\varepsilon C_{Sn}^\varepsilon) \cdot \left(\cosh\left(\frac{a}{2\lambda_L}\right) - 1 \right) = \frac{(b/2\lambda_R)}{\sinh(b/2\lambda_R)} (n^\eta C_{Sn}^\eta) \cdot \left(\cosh\left(\frac{b}{2\lambda_R}\right) - 1 \right). \quad (21)$$

We already know that, assuming approximately all atomic volumes be the same, the ration b/a in our case should be equal $3/8$, we can express b in terms of a in eq. (21) and get one transcendent algebraic equation for one unknown a :

$$\frac{\sinh\left(\frac{3}{8}a/2\lambda_R\right) \cosh\left(\frac{a}{2\lambda_L}\right) - 1}{\sinh(a/2\lambda_L) \cosh\left(\frac{3}{8} \frac{a}{2\lambda_R}\right) - 1} = \frac{n^\eta C_{Sn}^\eta}{n^\eta C_{Sn}^\eta - n^\varepsilon C_{Sn}^\varepsilon}. \quad (22)$$

Taking approximately $n^\eta \approx n^\varepsilon$ (since in this Section we already assumed all atomic volumes the same) and introducing nondimensional unknown and nondimensional parameter

$$x \equiv \frac{a}{2\lambda_L}, \quad p \equiv \frac{3}{8} \frac{\lambda_L}{\lambda_R} = \frac{3}{8} \sqrt{\frac{D^{\text{int}\eta/\varepsilon}}{D^{\text{int}\eta/\text{vacuum}}}}, \quad (23)$$

one gets the final equation

$$\frac{\sinh(px) \cosh(x) - 1}{\sinh(x) \cosh(px) - 1} = \frac{C_{Sn}^\eta}{C_{Sn}^\eta - C_{Sn}^\varepsilon} = \frac{20}{9}. \quad (24)$$

In case $p \equiv \frac{3}{8}$, $\left(\frac{D^{\text{int}\eta/\varepsilon}}{D^{\text{int}\eta/\text{vacuum}}} = 1\right)$ eq. (24) has numerical solution $x \approx 1.9$,

so that

$$a \approx 2 \cdot 1.9 \lambda_L = 3.8 \sqrt{\frac{D^{\text{int}\eta/\varepsilon} \delta}{V}} \approx 3.8 \sqrt{\frac{10^{-13} \frac{m^2}{s} 10^{-9} m}{10^{-9} \frac{m}{s}}} \approx 1.3 \cdot 10^{-6} m, \quad (25)$$

$$b = \frac{3}{8} a \approx 0.43 \cdot 10^{-6} m.$$

Here we took (so far) the velocity from experimental observations, but very soon below we will be able to estimate it theoretically (and it will indeed match this order of magnitude).

If one looks at the experimental pictures, our rough estimations look very reasonable.

Now comes the main question – how to find the velocity V of moving transformation front?

In the classic works on cellular precipitation in closed system this question (conjugate with question of optimal period of lamellar structure) is difficult and leads to using of semiempirical principle of the maximum release rate of Gibbs free energy or to similar hypotheses. In our case of open system it is much easier to answer this question than in the classic discontinuous precipitation theory. Reason is that in our case the transformation is complete. And velocity is not chosen by the system among a variety of possibilities, but instead is determined unambiguously by the external driving force, sucking out tin and generating the precipitation process.

The total out-flux of tin from the square area $W \cdot W$ is equal to

$$\begin{aligned} J_{Sn}^{\text{total}} &\approx \frac{W}{a+b} \cdot W \cdot \delta \cdot \left(-D_{Sn}^{\text{int}\eta/\varepsilon} \frac{\partial n_{Sn}^{\text{int}\eta/\varepsilon}}{\partial y} \Big|_{y=a/2} - D_{Sn}^{\text{int}\eta/\text{void}} \frac{\partial n_{Sn}^{\text{int}\eta/\text{void}}}{\partial y} \Big|_{y=(a+b)/2+b/2} \right) = \\ &\approx \frac{W^2 V}{a+b} \cdot \left(a(n^\eta C_{Sn}^\eta - n^\varepsilon C_{Sn}^\varepsilon) + b(n^\eta C_{Sn}^\eta - 0) \right) = \\ &= W^2 V \cdot \left(n^\eta C_{Sn}^\eta - \frac{a}{a+b} n^\varepsilon C_{Sn}^\varepsilon \right) \approx n W^2 V \cdot \left(\frac{5}{11} - \frac{8}{11} \frac{1}{4} \right) = \frac{3}{11} n W^2 V. \end{aligned} \quad (26)$$

To estimate the velocity of transformation front, one should equalize the just evaluated total flux through some square area $W \cdot W$ of the side surface of decomposing alloy to the total diffusion side flux through both sides of each of $W/(a+b)$ lamellae. Total flux has the structure

of product of the mobility D/kT , thermodynamic driving force, effective area of the easy diffusion paths via the net of free surfaces of the lamellar structure:

$$J_{Sn}^{total} \sim 2 \frac{W}{a+b} nW \delta \frac{(D_{Sn}^{surf})^* \Delta g}{l kT} \sim \frac{3}{11} nW^2 V. \quad (27)$$

Thus,

$$V \sim \frac{22}{3} \frac{\delta (D_{Sn}^{surf})^* \Delta g}{l(a+b) kT} \sim 7 \frac{\delta}{l(a+b)} (D_{Sn}^{surf})^* \frac{\Delta g}{kT}. \quad (28)$$

Eq.(28) so far cannot be used for direct estimation of velocity V since lamellar sizes a and b also depend on V . Therefore let us substitute eq. (25) into eq. (28):

$$V \sim 7 \frac{\delta}{l \cdot 3.8 \sqrt{\frac{D^{int\eta/\varepsilon} \delta}{V} \frac{11}{8}}} (D_{Sn}^{surf})^* \frac{\Delta g}{kT} \approx \sqrt{V} \cdot \frac{1.4}{l} \sqrt{\frac{\delta}{D^{int\eta/\varepsilon}}} (D_{Sn}^{surf})^* \frac{\Delta g}{kT},$$

so that

$$V \sim 2 \frac{\delta (D_{Sn}^{surf})^*}{l^2 D^{int\eta/\varepsilon}} \left(\frac{\Delta g}{kT} \right)^2. \quad (29)$$

Eq. (29) is our theoretical prediction of the precipitation front velocity V .

Driving force per atom of Cu_3Sn_1 formation from Cu and Cu_6Sn_5 (see Fig.1) is about $\Delta g \approx 0.75 \cdot 10^{-20} J$, $\frac{\Delta g}{kT} \approx 1$ at $T = 523K$

We take characteristic width of porous zone and distance from it to Cu as about 50 microns.

Let us try to evaluate the surface diffusivity of tin at the surface of Cu_3Sn_1 using the empirical rule $(D^{surf})^* \sim 10^{-4} \frac{m^2}{s} \cdot \exp\left(-8.9 \frac{T^{melt}}{T}\right)$.

According to equilibrium phase diagram, phase Cu_3Sn_1 decomposes before reaching melting but not far from it at temperature about 950K

Thus, $(D^{surf})^* \sim 10^{-4} \frac{m^2}{s} \cdot \exp\left(-8.9 \frac{950}{523}\right) \sim 10^{-11} \frac{m^2}{s}$. It is 100 times less than for diffusion in melt but ten times larger than the bulk diffusion before melting.

If one takes $(D_{Sn}^{surf})^* \sim 10^{-11} \frac{m^2}{s}$, then $V \sim 2 \frac{10^{-9} (10^{-11})^2}{(5 \cdot 10^{-5})^2 10^{-13}} \cdot 1 \sim 0.8 \cdot 10^{-9} \frac{m}{s}$

15 hours of annealing after start of pores formation may give the thickness of porous layer about $L = Vt \sim 8 \cdot 10^{-10} \frac{m}{s} \cdot 0.5 \cdot 10^5 s = 40 \cdot 10^{-6} m = 40 \text{ microns}$

That is also very reasonable correspondence to experimental picture.

Summary

We suggest the new mechanism of the recently discovered new morphology – porous Cu_3Sn compound with lamellar structure of crystalline and void phases. We treat this process as flux-driven discontinuous decomposition $Cu_6Sn_5 - 3Cu \rightarrow 2Cu_3Sn_1 + \text{Voids}$, generated by the outflux of tin from the system by surface diffusion along external surface and along the percolating net of new-born empty channels. New theory gives the reasonable predictions of lamellar structure sizes (eq. (25)) and of propagation velocity (eq. 29).

The nucleation of porous zone and corresponding delay of formation will be discussed elsewhere.

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Анотація. Обговорюється нещодавно відкрита нова морфологія (пориста фаза Cu₃Sn з ламелярною структурою). Порівнюються кілька можливих пояснень. Найбільш правдоподібним здається пояснення через спеціально розвинуту теорію індукованого потоками виділення у відкритих системах. Отримані і порівняні з експериментом прості формули для параметрів ламелярної структури і швидкості поширення ламелярної структури в період її росту. Порівняння з експериментом видається цілком задовільним.

Ключові слова: твердофазна реакція, дифузія, пора, конкуренція фаз, пайка.

Аннотация. Обсуждается недавно открытая новая морфология (пористая фаза Cu₃Sn с ламелярной структурой). Сравниваются несколько возможных объяснений. Наиболее правдоподобным кажется объяснение через специально развитую теорию индуцированного потоками выделения в открытых системах. Получены и сравниваются с экспериментом простые формулы для параметров ламелярного

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

Ключевые слова: твердофазная реакция, диффузия, пора, конкуренция фаз, пайка.

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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