

Understanding of void formation in Cu/Sn-Sn/Cu system during transient liquid phase bonding process through diffusion modeling

Sylvie Bourdineaud-Bordère, Emilien Feuillet, Jean-Luc Diot, Renaud de Langlade, Jean-François Silvain

► To cite this version:

Sylvie Bourdineaud-Bordère, Emilien Feuillet, Jean-Luc Diot, Renaud de Langlade, Jean-François Silvain. Understanding of void formation in Cu/Sn-Sn/Cu system during transient liquid phase bonding process through diffusion modeling. Metallurgical and Materials Transactions B, 2018, 49 (6), pp.3343-3356. 10.1007/s11663-018-1391-8. hal-01945557

HAL Id: hal-01945557 https://hal.science/hal-01945557

Submitted on 2 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1	Understanding of void formation in Cu/Sn-Sn/Cu system during Transient Liquid Phase
2	Bonding process through diffusion modeling.
3	
4	Sylvie Bordère ^a , Emilien Feuillet ^b , Jean-Luc Diot ^c , Renaud de Langlade ^c , Jean-François Silvain ^{a,*}
5	
6	^a CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
7	^b Innoptics, rue François Mitterrand, 33400 TALENCE (France)
8	^c Composite Innovation, 2 allée du Doyen Brus, 33600 PESSAC (France)
9	
10	*Corresponding author : Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB-CNRS, 87
11	Avenue du Dr A. Schweitzer, F-33608 PESSAC Cedex, France.
12	Phone : +33 (0)5 40 00 84 37
13	Email address : jean-francois.silvain@icmcb.cnrs.fr
14	
15	Abstract
16	Transient Liquid Phase (TPL) bounding of Sn foil sandwiched between two Cu foils involves, in the
17	temperature range above the melting point of Sn (232°C) and below 350°C, the formation and the growth
18	of two intermetallic compounds (IMCs) Cu ₆ Sn ₅ and Cu ₃ Sn and mostly unintended micro-pores. The
19	present study aims to analyze the mechanism of void development during the soldering process through
20	an experimental and modeling approach of diffusion controlled IMC transformation. This modeling
21	couples the diffusion process and the interface motion with the volume shrinkage induced by the
22	difference of partial molar volumes of atoms between each phase. We also consider two types of inter-

28 For Cu₆Sn₅ intermetallic two mechanisms are considered, volume diffusion and grain boundary

diffusion transports: i) inter-diffusion based on the exchange of Cu and Sn-atoms and ii) inter-diffusion

of Sn atoms with vacancies allowing Kirkendall void formation. The simulations of IMC growth

performed corresponds to a sequence of planar phase layers, where the distinctive scallop morphology

of the Cu₆Sn₅ layer is described through an analytical function allowing to quantify the grain boundary

diffusion pathway. We take into account of the volume diffusion mechanism for Cu₃Sn intermetallic.

23

24

25

26

diffusion, limited by grain growth. The simulations of IMC growth kinetics, for different transport
scenarios, are compared to the experimental evolving morphologies to determine the most likely
mechanism of micro-void formation.

32

Keywords: Transient liquid phase bounding; Intermetallics; Cu-Sn; Diffusion; void formation and
 growth; Simulations.

35

361. Introduction

The current trend of power electronic modules towards higher power densities and higher junction temperatures requires the development of new interconnect technologies that are able to withstand cyclic thermomechanical stresses at temperatures higher than 200°C. Indeed, classical packaging technologies, such as soft soldering and wire bonding, are the limiting factors for better performance of power modules [1].

42 One promising interconnect technology for high temperature applications is the Transient Liquid Phase Bonding (TLPB) process [2]. This technique relies on the formation of intermetallic compounds (IMCs) 43 as a bonding medium involving a liquid phase which is progressively consumed. The process employs 44 45 a binary system consisting of two metals (or metal alloy) with different melting points: a low-melting point interlayer, such as tin (Sn), sandwiched between two high-melting point substrates, such as copper 46 47 (Cu). The choice of the Cu-Sn system was motivated first by the widespread use of Cu-metal in 48 electronic packaging, in particular as metallization layers on ceramic substrates, and secondly by the 49 low melting point (232°C) of Sn-metal, together with its ability to form IMCs with Cu, and its low cost. 50 Upon heating to typical bonding temperature, just above Sn melting point, the Cu substrates react with the liquid Sn trough inter-diffusion. According to the Cu-Sn phase diagram [3,4], two IMCs, Cu_6Sn_5 and 51 52 Cu₃Sn, form and grow through isothermal condition. The goal of the process is to entirely transform the Sn interlayer into the Cu-rich IMC, Cu₃Sn. This phase is thermodynamically stable up to 350°C and has 53 a re-melting temperature (676°C) much higher than the process temperature. 54

55 The growth kinetics and the evolving morphologies of the IMCs during TLP soldering are highly dependent on the process parameters: heating rate and bonding temperature, compressive stress for layer 56 57 contact [5] and initial thickness of the Sn foil [6]. Nevertheless, within the bonding temperature range 58 $[240^{\circ}\text{C}-280^{\circ}\text{C}]$ the following growth sequence was observed. The Cu₆Sn₅-phase growth dominates, that of the Cu₃Sn-phase, in the early stages of the process. It is only when the Sn liquid phase is entirely 59 consumed that the Cu_3Sn layer grows at the expense of the previously formed Cu_6Sn_5 -layer. Moreover, 60 61 the Cu₆Sn₅-layer does not grow in a flat but rather in a rough way associated with a rounded grains 62 morphology called scallops [7]. High coarsening rate gives rise to some large Cu_6Sn_5 scallops on the 63 two opposite diffusion front which quickly impinge before the complete transformation of Sn into IMCs [2]. Such early scallop impingement is expected to be the necessary condition for the formation of voids 64 in the bond mid plane during TLP bounding [8]. The presence of such voids decreases the IMC bonds 65 reliability as well as their thermal and mechanical properties, and should be therefore limited as much 66 67 as possible. Many experimental studies have so focused on the way to inhibit the development of microvoids. They have shown that favorable conditions are high bonding temperature, high heating rate [5], 68 69 low Sn foil thickness [6] and high contact pressure [5]. Simulation works of Park and coworkers also investigated the microstructure evolution during TLP bonding process using the multi-phase field 70 71 modeling together with thermodynamics and kinetics databases (CALPHAD) [9-11]. They provide, 72 through the variation of the model parameters and experimental comparisons, a valuable insight into the 73 kinetic growth of the IMC layers, the morphological evolution and especially the parameter conditions 74 for high interface roughness that is one of the key points for further voids development. Nevertheless, 75 these simulation works do not account for the mechanism of the pore formation which remains a 76 challenge for the complete understanding of IMC bounding mechanism. Some authors have suggested, 77 through the studies of TLP bonding of equivalent Ag/Sn/Ag [12] and Ni/Sn/Ni [13] sandwich structures that the observed void formation is due to the difference in molar volume between the initial reacting 78 phases and IMC products leading to volume shrinkage. Similarly, the molar volume properties of the 79 Cu_6Sn_5 -phase, $Cu_{(s)}$ and $Sn_{(1)}$ -reactants give rise to about 8.5% [14] of volume shrinkage. So, when the 80 Cu_6Sn_5 -scallops on the two opposite layers impinge, the reaction progress within a fixed $Sn_{(1)}$ volume 81 allowing the pore formation. The pore volume is thus expected to be lower than 8.5% of the overall 82

83 Cu₆Sn₅ volume, the later the scallop impingement occurs the lower the volume fraction of the pores formed. Therefore, volume shrinkage seems to underestimate the large pore volume observed which can 84 85 reach the high value of 25 % of the IMC layer [5]. Other type of voids, due to Kirkendall effect [15], can also form in the IMC layers. Their formation is the result of the difference between the diffusion 86 rates of Cu and Sn which is counterbalanced by the transport of atomic vacancies [16-17]. The 87 aggregation of vacancies generates Kirkendall voids inside the compound behind the migration of the 88 89 atoms which diffuse faster. For the Cu₃Sn layer, the intrinsic diffusion coefficient of Cu-atoms is shown 90 to be much larger than the Sn atom one, with a ratio around 7 at 150°C [16] and 30 at 200°C [18]. This 91 difference in diffusion coefficient confirmed that Kirkendall voids are present at the Cu₃Sn/Cu interface 92 under the Sn melting point [16-17]. For the Cu_6Sn_5 -layer, some controversy about whether the Cu-atoms diffuse faster or not exists. As it is generally held, the diffusion rate of Cu-atoms was determined to be 93 greater than that of Sn atoms in some studies [19-20] whereas it was found lower in other [18]. In the 94 95 case where Sn-atoms diffuse faster than Cu-atoms in the Cu₆Sn₅ layer, Kirkendall voids may also form in the Cu₆Sn₅ interlayer, but the question remains whether such mechanism would account for such 96 97 micro-void formation.

98 The complete understanding of the mechanism of the pore formation during IMC bounding still remains 99 a challenge. In this paper, our main objective is to get an insight of pore formation through a modeling 100 approach of diffusion controlled phase growth involving different mass transport mechanisms and 101 volume shrinkage inherent to the difference of the Cu and Sn partial molar volumes between each 102 involving phases.

103 In a first step, we will reinvestigate bonding tests for experimental parameters favoring the development 104 of macro-voids to easily compare the remaining $Sn_{(1)}$ volume at the Cu_6Sn_5 scallop impingement with 105 that of micro-voids. In a second step, 1D-simulations of the evolution of phase volume fractions and 106 pore volume fraction will be performed by considering, i) inter-diffusion of Sn atoms with Cu atoms or 107 vacancies, ii) partial molar volume induced shrinkage, iii) volume diffusion or grain boundary diffusion 108 as limiting transport processes. The comparison between experimental and numerical results, will allow us to determine the most likely mechanisms for IMC growth and macro-void formation during TLB 109 110 process.

112 **2- Experimental part**

113 **2.1 Formation of IMC joint**

The formation of a joint entirely composed of intermetallic compounds (IMC), which shows a higher 114 thermal cycling reliability than the reference SnAgCu solder alloys, using the Transient Liquid Phase 115 Bonding process (TLPB) based on the copper-tin binary system, has already been described by several 116 117 authors [2, 8, 21-24]. Figure 1 shows the binary Cu-Sn phase diagram (Fig. 1f) and the different steps linked with this IMC joint formation (Fig. 1a to 1e). In the first step, the system is heated at 250°C, just 118 above the melting temperature of Sn (232°C), leading to a complete wetting of the Cu substrate by the 119 120 liquid Sn (Fig. 1a) and spontaneous dissolution of the Cu substrate inside the liquid Sn leading to a supersaturated Sn liquid phase. In the second step, dissolution of part the Cu substrate continue and 121 122 nucleation of the first Cu_6Sn_5 intermetallic germs (η phase) begun (Fig. 1b). Then, the isotherm 123 solidification of the IMC joint, at 250°C, start associated with the growth of Cu₆Sn₅ intermetallic with 124 3D column like shape, also called scallops, (Fig. 1 c) and the growth of 2D Cu₃Sn one (ϵ phase) [25]. The chemical reaction ($6 \text{ Cu} + 5 \text{ Sn} \rightarrow \text{Cu}_6 \text{Sn}_5$) end when all the liquid Sn is transformed to solid Cu₆Sn₅ 125 126 (Fig. 1 d). Finally, transformation of Cu_6Sn_5 to Cu_3Sn continues up to a complete consumption of Cu_6Sn_5 127 intermetallic (Fig. 1e).

128 (Fig. 1e).



Figure 1: Different steps of the IMC report using TLPB based on Cu-Sn system. a) Fusion of the Sn filler metal (liquid Sn in blue color), b) Dissolution of part of the Cu substrate inside liquid Sn and nucleation of first Cu₆Sn₅ germs, c) Growth of both Cu₆Sn₅ and Cu₃Sn IMCs and consumption of remaining liquid Sn d) Complete consumption of liquid Sn and solidification of the IMC joint, e) Homogenization of the joint toward the most stable Cu₃Sn intermetallic, f) Cu-Sn binary phase diagram (Reprinted from reference [3]).

137 2.2 Evolution of the IMC morphology, chemical composition and volume fraction with holding 138 time

However, in that theoretical process, porosity is not considered which is not exactly the case for a real IMC joint. A specific experimental apparatus has been used for the formation of the IMC joints. It is composed of a hermetic metallic chamber with 2 heating plates separately controlled with 2 temperature regulators. Temperature is measured with 2 k thermocouples. The pressure is applied with the lower plate using a hydraulic system. The chamber is working under secondary vacuum (10⁻³ mbar). After surface cleaning using hydrochloric acid (5%), Copper substrates are coated with Sn thin film using conventional PVD system.

Figure 2 shows the evolution of a real IMC joint for a fixed temperature and pressure and for different 146 147 holding time. For a holding time of 0 min and for a process temperature (250° C) above the melting 148 temperature of Sn (232°C), the dissolution of Cu inside Sn (red arrows) is associated with a 3-149 dimensional (3D) growth of Cu-Sn intermetallic (mainly Cu₆Sn₅ one) at the Cu-Sn interface (Fig. 2a). At the same holding stage (0 min) the composition of the Cu-Sn reaction zone has been analyzed using 150 line profile Auger electron spectroscopy (Fig. 2b). The line profile clearly shows the Cu substrate, the 151 152 Cu-Sn reaction zone composed of the 2 intermetallics Cu₃Sn and Cu₆Sn₅. For a holding time of 5 min, 153 the growth of 3D Cu₆Sn₅ intermetallic and 2D Cu₃Sn one is clearly shown (Fig. 2c). Continuous precipitation of Cu₆Sn₅ at the surface of the 3D Cu₆Sn₅ hemispheric intermetallics (green arrows in Fig. 154 2c) induces the vertical growth of the intermetallics (blue arrow in Fig. 2c) up to a contact green dashed 155 line Fig. 2d) and chemical link between 2 facing hemispherical Cu_6Sn_5 scallops (labeled (1) and (2) in 156 157 Fig. 2d) growing from both Cu substrate. At that stage, the thickness of the IMC joint become fixed and lateral growth (for example blue arrows in Fig. 2d) of the intermetallic take place up to a complete 158 159 consumption of the liquid Sn (Fig. 2f). Up to a complete consumption of liquid Sn, the growth kinetic of the Cu₃Sn intermetallic is very slow and, for our system, it thickness is smaller than 1 µm. When the 160 161 the liquid Sn is completely consumed (Fig. 2f), one can observe two sorts of pores in the Cu_6Sn_5 IMC; 162 small ones located near the Cu₃Sn IMC, and large ones which can fill nearly all the gap between the 2 Cu₃Sn IMC layers. We can suppose that the pores are initially formed in the liquid channel near the 163 Cu₆Sn₅-Sn interface, as observed in Fig 2e (blue arrow). Some of the pores are then trapped within the 164 Cu₆Sn₅ IMC during IMC growth (green arrows in Fig. 2e) and the others can growth toward the liquid 165 166 phases (white arrows) to formed large porosities.





168 Figure 2: Experimental formation of Cu-Sn IMC joint for different holding time for a 5 KPa pressure

and a holding temperature of 250°C. a) SEM micrograph at 0 min, b) AES line profile at 0 min, c) SEM

- 170 micrograph at 15 min, d) SEM micrograph at 30 min, e) SEM micrograph at 45 min, f) SEM micrograph
- 171 at after complete reaction of liquid Sn (2 hours)
- 172 Color scale (a-e) (darker to lighter gray): Cu substrate; Cu₃Sn; Cu₆Sn₅, Sn
- 173 Color scale (f) (darker to lighter gray): Cu substrate; Cu₃Sn; Cu₆Sn₅
- 174

175 2.3 Evolution of the IMC morphology and chemical composition with holding temperature

Figure 3 shows the evolution of IMC Cu-Sn joints for pressure and holding time of report of 5 KPa and 176 120 min respectively and for 3 holding temperature (250°C, 270°C and 300°C). On that figure, for a 177 same initial Sn thickness (thin fil close to 20 µm), the thickness of the IMC joints decreases when the 178 179 holding temperature increases. This behavior is linked with the decrease of the viscosity of the liquid Sn with the temperature and the ejection of part of the liquid Sn due to the 5 KPa pressure used. It can be 180 observed that large pores are present in the middle of the joint whatever the holding temperature even 181 182 when all the Cu₆Sn₅ phase has been transformed into Cu₃Sn (Fig. 3c). Therefore, the volume fraction of porosity can vary from 10 to 20% depending on the elaboration condition and on the volume fraction of 183 184 the IMCS in the joint.

Finally, the increase of diffusion fluxes with the temperature induces an increase of the Cu_3Sn intermetallic growth. At 300°C, all the Cu_6Sn_5 intermetallic is transformed to Cu_3Sn one after just 2 hours (Fig. 3c). The two sorts of voids, previously observed in the Cu_6Sn_5 IMC (Fig. 2e), still remain for this equilibrium microstructure: large pores in the middle of the Cu_3Sn joint and smaller ones closer to the Cu_3Sn/Cu interface. Such groups of pores were already observed for this end state [26].



191 Figure 3: Evolution of the IMC morphology and chemical composition with holding temperature
192 (pressure of 5 KPa and holding time of 120 min): a) 250°C, b) 270°C and c) 300°C

- 193 Color scale (a-c) (darker to lighter gray): Cu substrate; Cu₃Sn; Cu₆Sn₅
- 194

190

195 3 – Modelling of the formation of the Cu/Sn-based solder joint

3.1 Description of the physical equations

197 The formation of the Cu₆Sn₅ and Cu₃Sn IMCs in the Cu-Sn solder are considered to evolve through 198 diffusion controlled phase changes. This is described by equations based on inter-diffusion of Sn and 199 Cu-atoms. It means that to any Cu-flux, a strictly opposite Sn-flux is involved. In this diffusion 200 modeling, we chose to only describe the Sn flux. The governing equation of the Sn flux $\mathbf{J}_{Sn}^{i}(X,t)$ 201 within each involved phase i (i=1,...4), at each time t and position \mathbf{X} of the system, is based on the first 202 Fick's diffusion law written as:

203
$$\mathbf{J}_{Sn}^{i}(\mathbf{X},t) = -D^{i}(\mathbf{X},t) \nabla C_{Sn}^{i}(\mathbf{X},t) .$$
(1)

Here, $D^{i}(\mathbf{X},t)$ and $C^{i}_{Sn}(\mathbf{X},t)$ are respectively the inter-diffusion coefficient of the Cu/Sn-couple and the Sn-molar concentrations relative to the *i*-phase, at the position **X** and the evolution time *t*. For non-stationary diffusion regime, mass conservation requires the use of the second Fick's law writtenas:

208
$$\nabla \cdot \mathbf{J}_{Sn}^{i}(\mathbf{X},t) = -\frac{\partial}{\partial t} C_{sn}^{i}(\mathbf{X},t)$$
 (2)

Moreover, when the flux balance at the interface I_i between two adjacent *i* and *i*+1 phases is non-zero, the Sn-molar concentrations $C_{Sn}^i(\mathbf{X}_{I_i},t)$ and $C_{Sn}^{i+1}(\mathbf{X}_{I_i},t)$ at the I_i -interface are kept consistent with thermodynamics by interface displacement. The normal displacement rate of a point of the interface positioned at $\mathbf{X}_{I_i}(t)$ is defined at time *t* as:

213
$$\frac{dX_{I_i}(t)}{dt} = \frac{\left(\mathbf{J}_{Sn}^{i}(\mathbf{X}_{I_i}, t) - \mathbf{J}_{Sn}^{i+1}(\mathbf{X}_{I_i}, t)\right) \cdot \mathbf{n}}{\left(C_{Sn}^{i}(\mathbf{X}_{I_i}, t) - C_{Sn}^{i+1}(\mathbf{X}_{I_i}, t)\right)}$$
(3)

The difference between the Cu and Sn-partial molar volumes, of the phase *i*-phase $(\overline{V}_{cu}^{i} \text{ and } \overline{V}_{Sn}^{i})$ and that of the *i*+1-phase $(\overline{V}_{cu}^{i+1} \text{ and } \overline{V}_{Sn}^{i+1})$, induces additional normal displacement of the *I_i*-interface to relax the elastic strain within the phase transition area. This displacement, $dX_{I_i}^{R_1}$, is written through two equivalent equations involving either the *i*-phase (Eq. (4a)) or the *i*+1-phase (Eq. (4b)).

$$\frac{dX_{I_{i}}^{R_{1}}(t)}{dt} = \left(\mathbf{J}_{Sn}^{i}(\mathbf{X}_{I_{i}},t) - C_{Sn}^{i}(\mathbf{X}_{I_{i}},t)\frac{dX_{I_{i}}(t)}{dt}\right) \left(\overline{V}_{Sn}^{i+1} - \overline{V}_{Sn}^{i}\right) \\
+ \left(\mathbf{J}_{Cu}^{i}(\mathbf{X}_{I_{i}},t) - C_{Cu}^{i}(\mathbf{X}_{I_{i}},t)\frac{dX_{I_{i}}(t)}{dt}\right) \left(\overline{V}_{Cu}^{i+1} - \overline{V}_{Cu}^{i}\right) \\
\frac{dX_{I_{i}}^{R_{1}}(t)}{dt} = \left(\mathbf{J}_{Sn}^{i+1}(\mathbf{X}_{I_{i}},t) - C_{Sn}^{i+1}(\mathbf{X}_{I_{i}},t)\frac{dX_{I_{i}}(t)}{dt}\right) \left(\overline{V}_{Sn}^{i+1} - \overline{V}_{Sn}^{i}\right)$$
(4a)

219

$$+ \left(\mathbf{J}_{Cu}^{i+1}(\mathbf{X}_{I_i}, t) - C_{Cu}^{i+1}(\mathbf{X}_{I_i}, t) \frac{dX_{I_i}(t)}{dt} \right) \left(\overline{V}_{Cu}^{i+1} - \overline{V}_{Cu}^{i} \right)$$

$$(4b)$$

220

If this displacement allows relaxing locally the elastic strain within the phase transformation area, it nevertheless induces elastic strain within the neighboring phases, depending on their elastic properties and on the boundary conditions of the mechanical problem. This second step of elastic strain energy relaxation potentially involves the normal displacement $dX_{I_i}^{R_2}$ of the entire interface I_i of the system. The complete modeling equations of this second step of elastic strain relaxation is complex and is not described in this paper.

Note that the displacements $dX_{I_i}^{R_1}(t)$ and $dX_{I_i}^{R_2}(t)$ of the I_i -interfaces during time interval dt, implies an advection along the displacement field of the molar concentrations $C_{Sn}^i(\mathbf{X}, t + dt)$ previously determined from the diffusion equation solving.

230

231 **3.2** Numerical procedure for the one-dimensional problem

3.2.1 Description of the one-dimensional system

The complex growing morphology of the Cu₆Sn₅ and Cu₃Sn layers in the Sn based solder-Cu system is 233 reduced to a one-dimensional problem of a succession of planar layers of surface S (Fig. 4). Such planar 234 235 geometry has been considered for analytical models of intermetallic layer growth, which nevertheless 236 need numerical approaches to be solved [14, 27]. Here, the possible development of a vapor phase as 237 well as the description of the morphology evolution through an analytical function (see paragraph 3.2.2.) 238 make that diffusion equations are solved numerically using time-step procedure. Each layer is indexed 239 in agreement with the experimental phase sequence. Note that the vapor phase in not indexed. The constant dimension of the system implies that the scalar position X_{I_0} and X_{I_L} are fixed. The X_{I_0} -240 position is a cut-off point within the large width of the $Cu_{(s)}$ -phase and the $X_{I_{I}}$ - position is a symmetry 241 point allowing to represent the two layers of the overall experimental system (Fig. 4). The thickness of 242 each layer at time t can thus be determined from the position on the X-axis of the interfaces $Cu_{(s)}$ - Cu_3Sn 243 $(I_1), Cu_3Sn-Cu_6Sn_5 (I_2), Cu_6Sn_5-Sn_{(1)} (I_3) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ and } Sn_{(1)}-Sn_{(v)} (I_4) \text{ noted as } X_{I_1}(t), X_{I_2}(t), X_{I_3}(t) \text{ noted } Sn_{(1)}-Sn_{(1)} (I_4) \text{ n$ 244 $X_{L}(t)$, respectively (Fig. 4). 245

The Sn molar concentrations $C_{Sn}^{i}(I_{i})$ and $C_{Sn}^{i+1}(I_{i})$ at the *I_i*-interface (*i*=1,3) (Fig. 4) correspond to the local equilibrium values and are thus constant during phase transformations. They are determined from the Sn molar fractions $x_{Sn}^{i}(I_{i})$ and $x_{Sn}^{i+1}(I_{i})$ relative to the Cu-Sn phase diagram [3] for the temperature of 250 °C, and from the partial molar volumes of Cu (\overline{V}_{cu}^{i}) and Sn (\overline{V}_{sn}^{i}) relative to the *i*-phase. They can be expressed through the following equation.

251
$$C_{Sn}^{i}(I_{j}) = \frac{x_{sn}^{i}(I_{j})}{x_{sn}^{i}(I_{j})\overline{V}_{sn}^{i} + (1 - x_{sn}^{i}(I_{j}))\overline{V}_{Cu}^{i}}; i = j, j+1; j = 1,3$$
(5)



252

Figure 4: One-dimensional problem of the Cu₆Sn₅ and Cu₃Sn layers in the Sn based solder-Cu system using linear profile of Sn molar concentrations $C_{Sn}^{i}(X,t)$ within each phase *i*.

255

The values of the Sn-molar fractions $x_{Sn}^{i}(I_{j})$ $(j=i-1; i=2, 4; j \le 3)$ are indicated in table 1 and the partial molar volumes \overline{V}_{cu}^{i} and \overline{V}_{sn}^{i} (i = 1, 4) in table 2. For solving the diffusion problem, we have made the following assumptions illustrated in figure 4: i) Cu_(s) phase (i=1) is considered Sn saturated $C_{Sn}^{1}(I_{1}) = C_{Sn}^{1}(I_{0})$ near the I_{I} -interface i.e. within the width $[X_{I_{0}}, X_{I_{1}}(t)]$. This assumption has low impact on the evolution of the phase volume fractions since the two conditions, $J_{Sn}^{1}(X,t) = 0$ and $x_{Sn}^{1}(I_{1}) = 0.022 \approx 0$ are compatible with a very low diffusion coefficient which is more than nine order of magnitude lower than the diffusion coefficient

263 of the others involved phases (see Table 2).

264 ii) Sn-molar concentration $C_{Sn}^{i}(X,t)$ within the IMCs Cu₃Sn (*i*=2) and Cu₆Sn₅ (*i*=3) are 265 linear from the molar concentration $C_{Sn}^{i}(I_{i-1})$ to $C_{Sn}^{i}(I_{i})$ at the interfaces I_{i-1} and I_{i} , respectively. 266 iii) Sn₍₁₎-phase is considered Cu-saturated $C_{Sn}^{4}(I_{4}) = C_{Sn}^{4}(I_{3})$ (Fig. 4).

267

iv) Inter-diffusion coefficient $D^{i}(X,t)$ characterizing the *i*-phase is assumed independent of the Sn molar concentration. The constant values of inter-diffusion coefficients D^{i} are indicated in table 2.

270

269

268

Interface	Cu _(s) -Cu ₃ Sn		Cu ₃ Sn-Cu ₆ Sn ₅		Cu_6Sn_5 - $Sn_{(l)}$	
Sn molar	$x_{Sn}^1(I_1)$	$x_{Sn}^2(I_1)$	$x_{Sn}^2(I_2)$	$x_{Sn}^3(I_2)$	$x_{Sn}^3(I_3)$	$x_{Sn}^4(I_3)$
fraction	2.2	23.6	24.7	44.5	45.4	97.8

Table 1: Sn-molar fractions at the different interfaces involved in the Cu-Sn system with reference to the phase diagram for a temperature of 250 °C [3].

2	7	1
2	1	т

Phase <i>i</i>	$Cu_{(s)}$ (<i>i</i> = 1)	$Cu_3Sn (i = 2)$	$Cu_6Sn_5 (i=3)$	$Sn_{(1)}$ (<i>i</i> = 4)
Sn partial molar volume \overline{V}_{Sn}^{i} (cm ³ /mol)	16.3 ^b	15.9ª	15.9ª	17.0 ^b
Cu partial molar volume \overline{V}_{Cu}^{i} (cm ³ /mol)	7.1°	6.2ª	6.2ª	7,3°
Inter-diffusion coefficient D^i (m ² /s)	1.0x10 ^{-22e}	3.6x10 ^{-15d}	7.6x10 ^{-15d}	2.0x10 ^{-9f}

Table 2: Partial molar volumes of Sn and Cu-atoms and inter-diffusion coefficients for the phases involved in the Sn-based solder/Cu system: ^adeduced from the lattice parameter data available in the literature [28]; ^bdeduced from the density of liquid tin at 250°C [29] and from the 3% variation for the liquid/solid transition as determined in [30] for the Cu_(s)-phase; ^cdeduced from the density of copper at 250°C and from the extrapolation at 250°C of the linear variation of liquid copper density for the Sn_(l)-phase [31]; ^dcalculated at 250°C from Arrhenius equation defined in [14]. They are close to that we can obtain from other references [32-33]; ^ecalculated at 250°C from Arrhenius equation defined in [35].

3.2.2 Morphology function for Cu₆Sn₅-layer

The distinctive scalloped morphology of the Cu₆Sn₅-layer is described by the hexagonal-base/spherical-cap geometric model of Schaefer et al. [25] (Fig. 5a). In this model, each scallop corresponds to a grain and each grain is characterized by uniform evolving morphology and grain size. The molten channel connected to grain boundaries is here represented leading to a shortened average diffusion distance along these grain boundaries (d_{GB}) in comparison with the volume diffusion distance similar to the average thickness (d_L) (Fig. 5b). The effective area available for grain boundary diffusion represents a small fraction (f) of the layer surface. Assuming hexagonal grains with diagonal size, d, and constant width distance δ , this fraction was defined as [25]:









286 b)

Figure 5: Geometric model for the microstructure of the Cu₆Sn₅-layer described in [25]. (a), top view of the layer showing grain size *d* and grain boundary width δ . (b), cross section corresponding to the dashed line in (a) showing the average layer thickness d_L and the average grain boundary length d_{GB} .

290 → Sn-fluxes in the bulk and along grain boundaries of the Cu₆Sn₅-layer and along the Cu₃Sn/Cu₆Sn₅ 291 interface

292 \rightarrow Reverse Cu-fluxes of equal intensity in the case of inter-diffusion

293

294 **3.2.3** Solving procedure for volume and grain boundary inter-diffusion and volume shrinkage

In the following, only the Sn fluxes are solved since inter-diffusion mass transport means that to any Sn fluxes is associated reverse Cu fluxes of equal intensity. So, when it is not specified, the term "flux" is always related to Sn flux. The one-dimensional system approximation reduces the fluxes to be perpendicular to the layer. The total flux $J_{Sn}^{i}(X,t)$ through each phase (i = 1, 4) corresponds to the contribution of volume flux $J_{Sn/Vol}^{i}(X,t)$ and grain boundary flux $J_{Sn/GB}^{4}(X,t)$ through the relation below.

301
$$J_{Sn}^{i}(X,t) = J_{Sn/Vol}^{i}(X,t) + J_{Sn/GB}^{i}(X,t)$$
(7)

302 The total fluxes at the interfaces I_{i-1} and I_i relative to the *i*-phase written as $J_{Sn}^i(X_{I_{i-1}},t)$ and 303 $J_{Sn}^i(X_{I_i},t)$ respectively, are determined using the following assumptions.

No fluxes are involved through the Cu_(s)-phase (negligible diffusion) and Sn_(l)-phase (saturated
 solution):

306
$$J_{S_n}^1(X_{I_0},t) = J_{S_n}^1(X_{I_1},t) = 0 \text{ and } J_{S_n}^4(X_{I_3},t) = J_{S_n}^4(X_{I_4},t) = 0$$

Volume diffusion is the predominant mechanism within the Cu₃Sn-phase [2, 5, 20, 26]; molar
 concentration profile (Fig. 4) at time *t* gives using Eq. (1),

309
$$J_{Sn}^{2}(X_{I_{1}},t) = J_{Sn}^{2}(X_{I_{2}},t) = J_{Sn/vol}^{2}(X,t) = -D^{2} \frac{C_{Sn}^{2}(I_{2}) - C_{Sn}^{2}(I_{1})}{(X_{I_{2}}(t) - X_{I_{1}}(t))}.$$

Grain boundary diffusion is considered to be competitive with volume diffusion within the
 Cu₆Sn₅-scalloped phase [2, 18]. Grain boundary flux is characterized by:

312
$$J_{Sn/GB}^{3}(X,t) = -f D_{GB}^{3} \frac{C_{Sn}^{3}(I_{3}) - C_{Sn}^{3}(I_{2})}{d_{GB}}, \text{ where } D_{GB}^{3} \text{ is the grain boundary inter-diffusion}$$

313 coefficient.

314 Moreover, assuming that:

315 i) Scallop shape remains constant during layer growth we have, 316 $d_{GB} = R \times d_L = R \times (X_{I_3}(t) - X_{I_2}(t))$, with *R* constant;

317 ii) Scallops are equiaxed during layer growth, we have $d = X_{I_3}(t) - X_{I_2}(t)$ which 318 corresponds to a grain coarsening process;

319 iii) Grain boundary diffusion constant
$$D_{GB}^3$$
 is proportional to the volume diffusion constant
320 through the relation, $D_{GB}^3 = R_D \times D^3$;

321 We finally have:

$$J_{Sn}^{3}(X_{I_{3}},t) = J_{Sn}^{3}(X_{I_{2}},t) = J_{Sn}^{3}(X,t)$$

$$= -D^{3}\left((1-f) + \frac{\delta R_{D}}{\sqrt{3} R(X_{I_{3}}(t) - X_{I_{2}}(t))}\right) \frac{C_{Sn}^{3}(I_{3}) - C_{Sn}^{3}(I_{2})}{X_{I_{2}}(t) - X_{I_{3}}(t)}$$
(8)

330

Then, the flux balance at the interfaces I_i (i=1, 3) allows calculating the I_i -interface displacement 323 $\Delta X_{I_i}(t)$ during the time increment Δt using Eq. (3) and the interface fluxes just defined: 324

325
$$\Delta X_{I_i}(t) = \frac{\left(J_{S_n}^i(X_{I_i}, t) - J_{S_n}^{i+1}(X_{I_i}, t)\right) \Delta t}{C_{S_n}^i(I_i) - C_{S_n}^{i+1}(I_i)}$$
(9)

The flux values $J_{Sn}^1(X_{I_0},t) = J_{Sn}^4(X_{I_4},t) = 0$, together with the boundary conditions we considered, 326

327
$$\frac{\partial C_{sn}^{i}(X,t)}{\partial X} \bigg|_{X_{I_{j}}} = 0, \text{ for } j = 0 \text{ and } j = 4.$$
(10)

328 induce that the molar concentrations, at the two boundaries, remain constant with time, $C_{Sn}^{1}(I_{0}, t + \Delta t) = C_{Sn}^{1}(I_{0}, t) = C_{Sn}^{1}(I_{0})$ and $C_{Sn}^{4}(I_{4}, t + \Delta t) = C_{Sn}^{4}(I_{4}, t) = C_{Sn}^{4}(I_{4})$. 329

Since the molar concentration profiles (Fig. 4) induce stationary diffusion regimes $(\nabla \mathbf{J}_{Sn}^{i}(X,t)=0)$, no $C_{Sn}^{i}(X,t)$ -variation is thus induced during time increment Δt (Eq. (2)) within the *i*-phase width 331 $]X_{I_{i-1}}(t), X_{I_i}(t)[$. The concentration profiles at time $t + \Delta t$ are thus simply updated assuming linear 332 *X*-dependence of the $C_{Sn}^{i}(X, t + \Delta t)$ -molar concentration within the width $[X_{I_{i-1}}(t + \Delta t), X_{I_i}(t + \Delta t)]$ 333 from $C_{Sn}^{i}(I_{i-1})$ to $C_{Sn}^{i}(I_{i})$ values. 334

In a last step, we evaluate the elastic strain relaxation induced by the difference of Sn and Cu partial 335 molar volumes from one phase to the other. The values of the Sn and Cu partial molar volumes (Table 336 337 2) show that elastic strains are not involved during transformation at the $Cu_3Sn-Cu_6Sn_5$ interface since the partial molar volumes are similar within the Cu_3Sn and Cu_6Sn_5 phases. Just the opposite is the 338 339 difference in partial molar volumes of the Cu_(s) and Cu₃Sn phases on one part and that of Cu₆Sn₅ and 340 $Sn_{(1)}$ phases on the other part, which will induce tensile elastic strains during phase transformation at the 341 $Cu_{(s)}$ - Cu_3Sn and Cu_6Sn_5 - $Sn_{(1)}$ interface respectively.

342 The displacement $\Delta X_{I_3}^{R_1}(t)$, at time t of the I₃-interface, induced by elastic relaxation of the transformed

343 zone
$$\Delta X_{I_3}(t)$$
 gives, using Eq. (4b) with $J_{Sn}^4(X_{I_3},t) = J_{Cu}^4(X_{I_3},t) = 0$:

$$344 \qquad \Delta X_{I_3}^{R_1}(t) = -\left(C_{Sn}^4(I_3)\frac{\Delta X_{I_3}(t)}{\Delta t}\right)\left(\overline{V}_{Sn}^4 - \overline{V}_{Sn}^3\right)\Delta t - \left(C_{Cu}^4(I_3)\frac{\Delta X_{I_3}(t)}{\Delta t}\right)\left(\overline{V}_{Cu}^4 - \overline{V}_{Cu}^4\right)\Delta t . \tag{11}$$

The displacement $\Delta X_{I_3}^{R_1}(t)$ of the I_3 interface Cu₆Sn₅-Sn₍₁₎ necessarily induces tensile elastic strain within the Sn_(liq) phase. Closed boundary condition, at the I_L -interface of symmetry, together with fixed X_{I_L} -position of this interface, makes that the liquid phase can relax through the formation of a vapor phase involving the displacement $\Delta X_{I_4}^{R_2}(t)$ of the I_4 -interface. Complete liquid phase relaxation leads to $\Delta X_{I_4}^{R_2}(t) = \Delta X_{I_3}^{R_1}(t)$.

Similarly, the displacement $\Delta X_{I_1}^{R_1}(t)$ of the I_1 -interface induces tensile elastic strain within the Cu_(s)-phase that we can expect to be negligible in consistency with the large dimension of the experimental Cu_(s)-phase. Open boundary condition at the cut-off I_0 -interface makes that an input of Cu_(s)-phase amount at constant $C_{Sn}^1(I_0)$ -concentration equivalent to the length $\Delta X_{I_0}^{R_2}(t) = \Delta X_{I_1}^{R_2}(t)$ allows to obtain a zero-strain condition within this Cu_(s) phase.

355

Finally, when elastic strain relaxation is considered, the position $X_{I_i}(t + \Delta t)$ of the I_i -interface (*i*=1,4) at time $t + \Delta t$ can be calculated from the position of the interface at time *t* through the equation:

358
$$X_{I_i}(t + \Delta t) = X_{I_i}(t) + \Delta X_{I_i}(t) + \Delta X_{I_i}^{R_1}(t) + \Delta X_{I_i}^{R_2}(t).$$
(12)

359

360 3.2.4- Solving procedure for Sn/vacancies inter-diffusion within the Cu₆Sn₅-phase

The diffusion process involving interface movement is described by equations based on inter-diffusion of Sn and Cu atoms. Here, we describe another mechanism where the Sn atoms diffuse through reverse flux of vacancies within the Cu_6Sn_5 -phase only (Fig. 6). The three entities, Sn and Cu atoms and vacancies are thus considered in this mechanism. The solving methodology is done in four steps: 365 • As a first step, the Sn-fluxes, at the interfaces I_3 and I_2 , relative to the Cu₆Sn₅ phase, are defined 366 assuming competitive grain boundary and volume inter-diffusion Sn atoms and vacancies. Equation (8) 367 is also here considered but using the volume inter-diffusion coefficient of Sn/vacancy couple $D_{Sn/L}^3$.

368 The decrease of the Sn concentration at the I_3 -interface is associated to an increase of vacancy 369 concentration. This mechanism is supposed to be counterbalanced, for interface equilibrium, by a supply 370 of Sn atoms from the Sn₍₁₎ phase (Figure 6). It gives:

371
$$J_{Sn/L}^4(X_{I_3},t) = J_{Sn/L}^3(X_{I_3},t).$$
 (13)

Similarly, the increase of the Sn concentration, at the I_2 -interface, is counterbalanced by depletion of Sn atoms passing within the Cu₃Sn-phase (Figure 6). It gives:

374
$$J_{Sn/L}^2(X_{I_2},t) = J_{Sn/L}^3(X_{I_2},t)$$
 (14)



375

Figure 6: Schematic illustration of the mechanism of Sn/vacancy inter-diffusion within the Cu₆Sn₅-phase involving Cu₆Sn₅-growth at the interfaces I_3 and I_2 together with displacements of the I_1 and I_4 interfaces. The I_4 interface displacement induces pore formation.

the interfaces I_2 and I_3 , respectively assuming that the partial volume change from \overline{V}_{Sn}^4 to \overline{V}_{Sn}^3 takes place before the Sn transport through the I_3 -interface.

384

380

381

385 • The second step of the procedure is related to the stress relaxation induced by the depletion and the 386 excess of the Sn atoms within the Sn₍₁₎ phase and the Cu₃Sn-phase, respectively. The tensile stress, 387 induced by the depletion of the Sn atoms within the Sn₍₁₎ phase (*i*=4), can relax through the I_4 -interface 388 displacement $\Delta X_{I_4}^{R/L}$ during time increment Δt . It is defined as follows.

389
$$\Delta X_{I_4}^{R/L}(t) = J_{Sn/L}^4(X_{I_3}, t) \times \overline{V}_{Sn}^4 \times \Delta t$$
(15)

The compressive stress, induces by the excess of Sn atoms within the Cu₃Sn-phase (*i*=2), can potentially relax through both Cu₆Sn₅ phase and Cu_(s)-phase. Nevertheless, in the case where the Cu₆Sn₅-phase is bridging the two IMCs layers, the relaxation through the Cu_(s) phase can be favored expecting negligible strain because of the large dimension of this Cu_(s) phase compared to that of the Cu₆Sn₅-phase. This relaxation thus involved a displacement $\Delta X_{I_1}^{R/L}$ of the I_1 -interface during time increment Δt defined as:

396
$$\Delta X_{I_1}^{R/L}(t) = J_{Sn/L}^2(X_{I_1}, t) \times \overline{V}_{Sn}^2 \times \Delta t .$$
 (16)

The open boundary condition, at the cut-off I_0 -interface, makes that an output of $\operatorname{Cu}_{(s)}$ -phase amount at constant $x_{Sn}^1(I_0)$ -fraction equivalent to the length $\Delta X_{I_0}^{R/L} = \Delta X_{I_1}^{R/L}$ allows obtaining a zero strain within this $\operatorname{Cu}_{(s)}$ -phase.

400

401 • The third step of the procedure is related to the displacements of the interfaces I_3 and I_2 induced by 402 the phase transformations within the Sn₍₁₎ and Cu₃Sn phases. The $\Delta X_{I_3}^L(t)$ -displacement, induced by the 403 precipitation of the Cu₆Sn_{4.99} compound (stoichiometry defined in relation with the molar fraction 404 $x_{Sn}^{3}(I_{3})$) at the I_{3} -interface from the Sn under saturated solution, is determined through the relation:

405
$$\Delta X_{I_3}^{L}(t) = X_{I_4}(t) + \Delta X_{I_4}^{R/L}(t) - X_{I_3}(t) - \frac{\left(6N_{Sn}^4(t) - 4.99N_{Cu}^4(t)\right) \times V_a^4(I_3)}{6C_{Sn}^4(I_3) - 4.99C_{Cu}^4(I_3)},$$
(17)

406 where $N_{Sn}^4(t)$ and $N_{Cu}^4(t)$ are the initial Sn and Cu molar quantities per unit area defined as follows.

407
$$N_{Sn}^{4}(t) = C_{Sn}^{4}(I_{3}) \times \left(X_{I_{4}}(t) - X_{I_{3}}(t)\right) + J_{Sn/L}^{4}(X_{I_{3}}, t) \times \Delta t$$
(18)

408
$$N_{Cu}^4(t) = C_{Sn}^4(I_3) \times \left(X_{I_4}(t) - X_{I_3}(t)\right)$$
 (19)

Similarly, we calculate the $\Delta X_{I_2}^{L}(t)$ -displacement of the I_2 -interface relative to the growth of the Cu₆Sn_{4.81} compound (stoichiometry defined in relation with the molar fraction $x_{Sn}^{3}(I_2)$) at the I_2 interface from the Sn over-saturated solution through the relation,

412
$$\Delta X_{I_2}^{L}(t) = X_{I_2}(t) - (X_{I_1}(t) + \Delta X_{I_1}^{R/L}(t)) - \frac{\left(6N_{sn}^2(t) - 4.81N_{Cu}^2(t)\right) \times V_a^2(I_2)}{6C_{sn}^3(I_2) - 4.81C_{Cu}^3(I_2)},$$
(20)

413 where the initial Sn and Cu molar quantities per unit area, $N_{Sn}^2(t)$ and $N_{Cu}^2(t)$ within the Cu₃Sn phase 414 are defined as follows.

415
$$N_{Sn}^{2}(t) = \frac{C_{Sn}^{2}(I_{2}) + C_{Sn}^{2}(I_{1})}{2} \left(X_{I_{2}}(t) - X_{I_{1}}(t) \right) - J_{Sn/L}^{2}(X_{I_{2}}, t) \times \Delta t$$
(21)

416
$$N_{Cu}^{2}(t) = \frac{C_{Cu}^{2}(I_{2}) + C_{Cu}^{2}(I_{1})}{2} \left(X_{I_{2}}(t) - X_{I_{1}}(t) \right)$$
(22)

417

418 • The fourth step of the procedure is to calculate the additional displacements of the I_3 and I_4 -interfaces 419 induced by the change of partial molar volumes of Sn and Cu-atoms during precipitation (Eq. (4b)). 420 These displacements are here written as:

421
$$\Delta X_{I_4}^{R_2/L} = \Delta X_{I_3}^{R_1/L} = -\left(\frac{x_{Sn}^4(I_3)}{V_a^4(I_3)}(\overline{V}_{Sn}^4 - \overline{V}_{Sn}^3) - \frac{(1 - x_{Sn}^4(I_3))}{V_a^4(I_3)}(\overline{V}_{Cu}^4 - \overline{V}_{Cu}^3)\right)\Delta X_{I_3}^L$$
(23)

423 Finally, the position $X_{I_i}(t + \Delta t)$ of the I_i -interface (i=1,4) at time $t + \Delta t$ can be calculated from the

424 position of the interface $X_{I_i}(t)$ at time *t* through the equation:

425
$$X_{I_i}(t + \Delta t) = X_{I_i}(t) + \Delta X_{I_i}^{R/L}(t) + \Delta X_{I_i}^{L}(t) + \Delta X_{I_i}^{R_1/L}(t) + \Delta X_{I_i}^{R_2/L}(t).$$

426

427 4. Simulation results and discussion

As we have seen, the IMC growth is the result of numerous reactions, kinetic and thermodynamic processes which for most of them superimpose. In this part we will discuss, in the light of experimental results, the modeling results of IMC growth based on different assumptions of diffusion mechanisms in order to propose a realistic scenario for IMC and micro-void formation.

432 • It is shown the simulations of IMC growth until the Sn liquid phase is consumed for different assumptions of diffusion mechanisms through the Cu_6Sn_5 layer. Volume diffusion is supposed to be the 433 predominant mechanism within the Cu₃Sn-phase. The initial layer thicknesses of each involved phases 434 are the average ones that we have measured from our experiments just after the heating rate (250° C). 435 436 They are the result of the fast precipitation of the Cu_6Sn_5 -phase from the Cu-oversaturated $Sn_{(1)}$ -solution. 437 The phase growth evolutions were calculated from the concentration profile drawn in figure 4 and using the inter-diffusion coefficients and the partial volumes of Cu and Sn-atoms indicated in Table 2. In these 438 calculations, we take account of the elastic strain relaxation induced by the difference between the Cu 439 and Sn partial molar volumes from the liquid phase to the IMC phases for one part, and from the Cu_(s) 440 441 phase to the IMC phases on the other part. The shrinkage relative to this relaxation at the Cu₃Sn-Cu_(s) interface and through the Cu_(s)-phase is counterbalanced by the contact pressure used. No pore space 442 can thus develop at the Cu_(s)-boundary. The shrinkage $\Delta X_{I_4}^{R_2}(t) = \Delta X_{I_3}^{R_1}(t)$, relative to the relaxation at 443 the Cu₆Sn₅-Sn₍₁₎ interface through the Sn₍₁₎ phase (see paragraph 3.2.3) is shown in Fig. 7a and Fig. 7b 444 between the dashed line (system symmetry) and the $Sn_{(1)}$ -phase. The total displacement 445 $\Delta X_{I_4}^{R2}(t) + \Delta X_{I_4}^{R/L}(t)$ involving the additional displacement $\Delta X_{I_4}^{R/L}$ of the *I*₄-interface, due to the 446 447 depletion of the Sn atoms within the $Sn_{(1)}$ phase (*i*=4), (which could be also considered as vacancy 448 aggregation), is shown in Fig. 7c.

Before the impingement of the two opposite layers, the development of the pore space is counterbalanced by the contact pressure. After the Cu_6Sn_5 -scallop impingement, which constrains the reaction to take place into a fixed volume, the shrinkage leads to void formation until the consumption of the $Sn_{(1)}$ phase. This void is drawn in red in figure 7. We expect, in the light of experiments, that impingement occurs for similar thicknesses (6 µm) of Cu_6Sn_5 and $Sn_{(1)}$ layers.



455

454



458 l





462 d)

Figure 7: Evolution of the interface displacements and void formation involved in the Cu/Sn-based solder joint for different mass transport scenarios taking account for volume shrinkage induced by the difference of Cu and Sn-partial molar volumes between each phase. Inter-diffusion of Cu and Sn-atoms is considered except for the simulation case (d). The bulk Cu and Sn-inter-diffusion coefficients as well as the partial molar volumes of Cu and Sn-atoms relative to each involved phase are indicated in table 2.

469

470 4.1- Interface evolution controlled by volume diffusion through the Cu₆Sn₅-layer

We show in figure 7a the modelling of the IMC growth in the Sn-based solder/Cu system until the Sn_(l)phase is consumed.

473 First of all, we compare our results of phase change evolution with that reported in reference [33] in which similar constants to ours was considered: same atomic molar volume V_a^i for each *i*-phase; close 474 ratio of inter-diffusion coefficient of Cu₆Sn₅ phase to that of Cu₃Sn one ($D^3/D^2 = 2.4$ for the present 475 work and $D^3/D^2 = 2.1$ in reference [33]). In the modeling study of reference [33], the authors solved 476 the same one-dimensional diffusion problem, with real molar volumes for the different phases, and 477 478 quantified the pore volume formation. They used a fixed grid discretization allows to deal with more 479 realistic molar fraction profiles than those here considered. Nevertheless, the present simplified profiles 480 give rise to consistent results with regards to: i) the evolving ratio of the thickness of the Cu₃Sn-layer to that of Cu₆Sn₅, ii) the nearly constant position of the Cu₃Sn/Cu₆Sn₅ interface during phase change and 481 iii) the non-dimensional time $t \times D^3/e^2 \approx 11$ for the Cu₆Sn₅ phase to reach the thickness $e = 10 \,\mu\text{m}$. 482 The comparison of the simulated results with experiment ones, for IMC growths, shows that the elapse 483 484 time for the $Sn_{(1)}$ -phase to be consumed is largely overestimated in the modeling (about twenty times greater), and that the experimental inhibition of the Cu_3Sn phase growth is not matched. This suggests 485 that the Cu and Sn fluxes arriving at the Cu₃Sn-Cu₆Sn₅ interface from the Cu₆Sn₅-phase i.e. $J_{Sn}^3(X_{I_2},t)$ 486 487 , should be greater to inhibit the Cu_3Sn -phase growth and to accelerate the overall phase change kinetics. 488 Therefore, the dominant kinetic mechanism is supposed to be different from simple volume diffusion in the Cu_0Sn_5 phase in agreement with many experimental and modeling results [2, 18]. 489 490 The void formation after the impingement of the two opposite layers corresponds to about 2.5 % of the

- 491 total IMC and void layer (red zone in Figure 7a).
- 492

493 4.2- Interface evolution with competitive grain boundary diffusion limited by coarsening through 494 the Cu₆Sn₅ phase

The competition between volume diffusion and grain boundary, limited by grain coarsening, is modeled using Eq. (8). The Cu₆Sn₅ grain size d (Fig. 5) will here be greater than 1 µm, during the overall growth, implying negligible grain boundary fraction $f \approx 0$ Eq. (6). The value we take for the grain boundary 498 factor $\frac{\delta R_D}{\sqrt{3} R} = 5.8 \times 10^{-5}$ in Eq. (8) is realistic since it corresponds to grain boundary width $\delta = 1 \text{ nm}$

499 [36], grain boundary to volume diffusion coefficient ratio $R_D = \frac{D_{GB}^3}{D^3} = 10^4$ [37], and grain boundary

500 length to layer thickness ratio $R = \frac{d_{GB}}{d_L} = 0.1$. These values agree with experimental analysis. The

501 grain boundary diffusion mechanism predominates when $\frac{\delta R_D}{\sqrt{3} R \left(X_{I_3}(t) - X_{I_2}(t) \right)} > 1$ (see Eq. (8)),

leading to a Cu₆Sn₅ layer thickness $d_L = (X_{I_3}(t) - X_{I_2}(t))$ lower than 58 µm. Since it is the case for the present system dimensions, grain boundary mechanism is the one which predominates during the diffusion process through the Cu₆Sn₅ layer. This condition is consistent with kinetics studies that have shown that Cu₆Sn₅ growth is dominated by grain boundary diffusion limited by coarsening [2, 18].

506

The IMC growth modeled with such predominant grain boundary diffusion mechanism is shown in figure 7b. The main point that we can notice is that the grain boundary mechanism allows to model the inhibition of the Cu₃Sn-growth through larger $J_{Sn}^3(X_{I_2},t)$ -flux at the Cu₆Sn₅-Cu₃Sn interface compared to that involved for volume diffusion only as previously shown in figure 7a. The inhibition of the Cu₃Sn growth reduces with time as the grain boundary flux decreases consequently to the grain coarsening process. In fact, the ratio of the grain boundary flux to volume flux is 58 (*d*=1 µm) for the initial time and decreases to about 4.5 (*d* = 13 µm) for the end time.

If grain boundary diffusion allows to well model the inhibition of Cu_6Sn_5 -growth with process time of the order of magnitude of experimental one, this mechanism nevertheless still fails in representing the large pore space obtained when the $Sn_{(1)}$ phase is entirely consumed. The fraction of void is like that obtained when the volume diffusion is the only mechanism involved (see for comparison figure 7a).

518 Similarly to the previous modelling case based on volume diffusion mechanism, only (see for 519 comparison figure 7a) the pore volume which develops after the Cu_6Sn_5 bridge formation (visualized in 520 red) reaches about 2.5% of the total IMCs and void layer at the end of the process. This pore volume is the result of volume shrinkage induced by the difference in partial molar volume of atoms between the reacting phases and the IMCs that we account for in this model. More precisely, the pore formation is induced by the partial molar volume change of Sn at the $Cu_6Sn_5/Sn_{(1)}$ interface. The effect of partial molar volume change of Cu atoms at the Cu_3Sn/Cu interface does not contribute to the pore formation since the Cu substrates are free in the perpendicular direction.

- 526
- 527

4.3- Additional mechanism involving inter-diffusion of Sn/vacancies couple within the Cu₆Sn₅
phase.

The use of inter-diffusion coefficient is just like to any Sn fluxes, is associated with reverse Cu-fluxes 530 of equal intensity. The intrinsic diffusion coefficient of Cu and Sn-atoms relative to the Cu₆Sn₅-phase, 531 respectively D_{Cu}^3 and D_{Sn}^3 , are thus hidden through this apparent inter-diffusion coefficient written as, 532 D^3 . In presence of vacancies and when one component diffuses faster than the others, Kirkendall voids 533 534 can form behind the migration of the atoms which diffuse faster. Here, in the case of the Cu and Sn-535 based solder, voids are in the middle of the Cu₆Sn₅-interlayer sustaining our hypothesis of Sn-atoms as the faster diffusing components, as was shown in some studies [18, 32]. The inter-diffusion of Sn atoms 536 with vacancies is modeled through equations described in paragraph 3.2.4. Same predominant grain 537 boundary diffusion limited by grain growth was considered using Eq. (8) and similar values for the δ , 538 R_D , R-constants as previously defined in paragraph 4.2. We also assumed that Sn/vacancy inter-diffusion 539 coefficient $D_{Sn/L}^3$ is twice greater than the Sn/Cu inter-diffusion coefficient D^3 ($D_{Sn/L}^3 = 2D^3$). In this 540 condition, 1/3 of the diffusion within the Cu₆Sn₅-phase is devoted to the Sn and Cu inter-diffusion and 541 542 2/3 to the Sn/vacancy one.

543 IMC growth modeled with such additional Sn/vacancy inter-diffusion with predominant grain boundary 544 diffusion through the Cu_6Sn_5 phase, is shown in figure 7c. First, we can notice that the formation of the 545 void space from the impingement time is largely amplified. This void space, drawn in red, reaches 14 % 546 of the total IMC and void layer which is close to experimental data. Note that the volume shrinkage participates to only 18% of the void volume formation. The remaining 82% of the void is the result of the IMC preferential growth towards the $Cu_{(s)}$ -phase which is correlated to the aggregation of vacancies interlayer. Secondly, we can notice that the inhibition of the Cu₃Sn growth, when grain boundary diffusion is active (paragraph 4.3.2), remains and is even enhanced with Sn/vacancy inter-diffusion. The total IMC/void thickness, close to 20 µm, is consistent with the experimental dimension of this layer.

Therefore, we can confirm that the large void formation can be explained by greater $Sn_{(1)}$ fluxes than Cu₍₁₎ fluxes through the Cu₆Sn₅ phase which are mainly located along the grain boundaries. This agrees with the conclusions of other papers [25, 32] which state that the accumulation of Sn atoms at the Cu₆Sn₅ boundary is the driving force for IMC growth. In these conditions, the reaction, 2 Cu₃Sn + 3 Sn \rightarrow Cu₆Sn₅, at the Cu₆Sn₅-Cu₃Sn interface, is favored instead of the Cu₆Sn₅ precipitation at the Cu₆Sn₅-Sn₍₁₎ interface.

This is also in agreement with large void formation in the Cu_6Sn_5 -phase induced by electro-migration which enhances the diffusion of Sn atoms compared to that of Cu atoms at a temperature below the melting point [38].

561

562 **4.4. Final step up to the equilibrium state**

Further interface evolution, at 250°C, when the Sn_(l)-phase is consumed, is shown in Fig. 7d. The initial phase-thicknesses are that obtained at the end time of figure 7c for the case where Sn/vacancy interdiffusion is considered. The calculation was done from the concentration profile within the Cu₃Sn-phase drawn in figure 4 except for the Cu₆Sn₅ layer where the Sn molar concentration is now taken constant $C_{Sn}^4(X,t) = C_{Sn}^4(I_3)$ since it is bounded by Cu₃Sn-Cu₆Sn₅ interfaces only. No mass transport within the Cu₆Sn₅-phase is thus involved during this last step. No shrinkage relative to the liquid/solid phase change has to be considered.

570 The modeling results clearly show the growth of the Cu_3Sn layer at the expense of Cu_6Sn_5 layer in 571 agreement with experimental results, the pore volume remaining constant. It finally represents around 572 10 % of the Cu_3Sn -layer thickness. Simulation kinetics show that the time to reach the final stable state, 573 where the Cu_6Sn_5 IMC is entirely consumed, is very long at 250°C (about 140 h). Same order of magnitude was predicted for the phase-field simulations of Park et al [10] for T=260°C and similar initial Sn layer thickness (25 μ m). These results suggested that the dominant kinetic mechanism in the Cu₃Sn phase is bulk diffusion [2, 5, 11, 20, 26].

577

578 5. Conclusion

The growth and the morphology of the Cu₃Sn and Cu₆Sn₅ phases, during the TPL bounding of Cu-Sn-579 Cu sandwich structures, was investigated through both experimental and modeling approaches. The 580 581 experiments were carried out with process parameters favoring void formation (temperatures of 250 °C, 270 °C, 300 °C, pressure loading of 5 kPa, Sn foil thickness of 10 µm) allowing to clearly exhibit the 582 key role of the scallop-type morphology of the Cu₆Sn₅ intermetallic. This morphology favored early 583 impingement and constrained, from that time, the Cu₆Sn₅ growth evolve into a fixed and large volume 584 of $Sn_{(1)}$ phase. The pore formation is shown to start from that impingement time near the Cu₃Sn IMC in 585 between 2 Cu₆Sn₅ scallops and to grow until the Sn₍₁₎ phase is totally consumed. The volume fraction of 586 587 pores, inside the IMC layer, is ranging from 10 % to 20%. The growth of the Cu₃Sn phase is shown to 588 be inhibited until the complete consumption of the $Sn_{(1)}$ phase and to evolve from that time with a planar 589 surface.

The modeling of the IMC growth was based on i) the diffusion mass transport as limiting process, ii) 590 591 the rate of interface displacement depending on the local equilibrium at the interface and finally iii) the 592 shrinkage induced by the difference of partial molar volumes of atoms between the $Cu_{(s)}$ and $Sn_{(l)}$ phases 593 and the IMCs. The simulations were reduced to a 1D-problem corresponding to the experimental 594 sequence of phase layers and including the potential development of a void space. The evolution of the 595 IMC growth was simulated, assuming saturations of the $Cu_{(s)}$ and $Sn_{(l)}$ solutions, from the experimental 596 IMC thicknesses (average layer thickness for Cu_6Sn_5) analyzed for 250°C temperature and 0 min holding 597 time up to the final equilibrium state corresponding to a complete transformation of Cu_6Sn_5 to Cu_3Sn . 598 Several mass transport scenarios have been simulated depending on i) the type of inter-diffusions, 599 (exchange between Cu and Sn atoms and/or exchange between Sn atoms and vacancies) and ii) the type 600 of diffusion mechanisms (volume diffusion for both IMC layers or volume diffusion for Cu₃Sn layer and boundary diffusion limited by grain growth for Cu₆Sn₅ layer). Within this 1D solving procedure, the latter diffusion mechanism was modeled through the introduction of an analytic function in the flux equation. This function tries to describe the scallop morphology of the Cu₆Sn₅ layer, with time through the ratio of the grain boundary length to the grain size (R = 0.1), assuming equiaxed grains. Realistic values of the other function parameters were taken, $\delta = 1$ nm for the grain boundary width and $R_D = 10^5$ for the ratio of grain boundary diffusion coefficient to volume diffusion coefficient.

607 The comparisons of simulation and experimental results have shown that:

608 i) The inter-diffusion of Cu and Sn atoms, along the shortened grain boundaries of Cu_6Sn_5 layer, 609 enhanced the displacement rate of the $Cu_3Sn-Cu_6Sn_5$ interface in the direction of Cu_3Sn phase compared 610 to volume diffusion. This behavior induced the observed growth inhibition of that latter IMC.

ii) The formation of micro-pores, inside the interlayer, is mainly driven by the inter-diffusion of 611 612 Sn atoms with vacancies along the Cu_6Sn_5 grain boundaries and not to the volume shrinkage induced by 613 the difference of partial molar volumes of atoms between each phase. When 2/3 of the diffusion is devoted to the Sn and vacancies inter-diffusion and 1/3 to the Sn and Cu one, void space, inside the IMC 614 layer, reach 14% of volume fraction. This value closely matches the experimental analyzed values. This 615 616 mechanism of Kirkendall pore formation requires that Sn atoms diffuse faster that Cu ones through 617 Cu₆Sn₅ layer, which tends to favor the growth of Cu₆Sn₅ IMC towards the Cu_(s) phase rather the Sn_(l) 618 one.

620 5. References

- 621 [1] P. Beckedahl, Power Electron. Europe, 2011, 5, 23 (http://www.power-
- 622 mag.com/pdf/issuearchive/47.pdf)
- 623 [2] J.F. Li, P.A. Agyakwa, C.M. Johnson, Acta Mater., 2011, 59, 1198
- [3] T.B. Massalski, Binary alloy phase diagrams. (ASM Int. Materials Park, Ohio, 1990), pp. 1481-
- **625** 1483
- 626 [4] S. Fürtauer, D. Li, D. Cupid, H. Flandorfer, Intermetallics, 2013, 34, 142
- 627 [5] C. Flötgen, M. Pawlak, E. Pabo, Microsyst. Technol., 2014, 20, 653
- 628 [6] W.-L. Chui, C.-M. Liu, Y.-S. Haung, C. Chen, Appl. Phys. Lett., 2014, 104, 171902
- 629 [7] D. Ma, W.D. Wang, S.K. Lahiri, J. Appl. Phys., 2002, 91, 3312
- 630 [8] N.S. Bosco, F.W. Zok, Acta Mater., 2004, 52, 2965
- 631 [9] M.S. Park, R. Arróyave, Acta Mater., 2012, 60, 923
- 632 [10] M.S. Park, S.L. Gibbons, R. Arróyave, Acta Mater., 2012, 60, 6278
- 633 [11] M.S. Park, S.L. Gibbons, R. Arróyave, Microelectron. Reliab., 2014, 54, 1401
- 634 [12] H. Shao, A. Wu, Y. Bao, Y. Zhao, G. Zou, Mater. Sc. Eng. A, 2017, 680, 221
- [13] H.Y. Chuang, T.L. Yang, M.S. Kuo, Y.J. Chen, J.J. Yu, C.C. Li, C.R. Kao, IEEE Trans. Device
- 636 Mater. Reliab., 2012, **12**, 233
- 637 [14] Z. Mei, A.J. Sunwoo, J.W. Morris, Metall. Trans. A, 1992, 23, 857
- 638 [15] E. Kirkendall, Trans. AIME, 1947, 147, 104
- 639 [16] F. Gao, J. Qu, Mater. Lett., 2012, 73, 92
- 640 [17] M. O, G. Vakanas, N. Moelans, M. Kajihara, W. Zhang, Microelectron. Eng., 2014, 120, 133
- 641 [18] A. Paul, C. Ghosh, W.J. Boettinger, Metall. Mater. Trans. A, 2011, 42A, 952
- 642 [19] K.N. Tu, R.D. Thompson, Acta Metall., 1982, **30**, 947
- [20] S. Kumar, C.A. Handwerker, M.A. Dayananda, J. Phase Equilib. Diff., 2011, 32, 309
- 644 [21] D.S. Duvall, W.A. Owczarsk, D.F. Paulonis, Weld. J., 1974, 53, 203
- 645 [22] L. Bernstein, J. Electrochem. Soc., 1966, 113, 1282
- 646 [23] I. Tuah-Poku, M. Dollar, T.B. Massalski, Metall. Trans. A, 1988, **19A**, 675
- 647 [24] G.O. Cook, C.D. Sorensen, J. Mater. Sc., 2011, 46, 5305

- 648 [25] M. Schaefer, R.A. Fournelle, J. Liang, J. Electron. Mater., 1998, 27, 1167
- [26] B. Dimcic, R. Labie, J. De Messemaeker, K. Vanstreels, K. Croes, B. Verlinden, I. De Wolf,
- 650 Microelectron. Reliab., 2012, **52**, 1971
- 651 [27] K.L. Erickson, P.L. Hopkins, P.T. Vianco, J. Electron. Mater., 1994, 23, 729
- [28] P. Villars, L.D. Calvert, Pearson's handbook of Crystallographic Data for intermetallic Phases
- 653 (ASM, Metals Park, Ohio, 1985), pp. 2030
- 654 [29] B. Alchagirov, A.M. Chochaeva, High Temp., 2000, 38, 48
- 655 [30] M. Raessi, J. Mostaghimi, Numer. Heat Tr. Part B, 2005, 47, 507
- 656 [31] J.A. Cahill, A.D. Kirshenbaum, J. Phys. Chem., 1962, 66, 1080
- 657 [32] M. Onishi, H. Fujibuchi, Trans. JIM, 1975, 16, 539
- 658 [33] J.F. Li, P.A. Agyakwa, C.M. Johnson, Intermetallics, 2013, 40, 50
- 659 [34] K. Hoshino, Y. Iijima, K. Hirano, Trans JIM, 1980, 21, 674
- 660 [35] C.A. Ma, R.A. Swalin, Acta Metall., 1960, 8, 388
- 661 [36] D. Prokoshkina, V.A. Esin, G. Wilde, S.V. Divinski, Acta Mater., 2013, 61, 5188
- 662 [37] Y. Zhou, T.H. North, Acta Metall. Mater., 1994, 42, 1025
- 663 [38] R. An, Y. Tian, R. Zhang, J. Mater. Sci.: Mater. Electron., 2015, 26, 2674

666 Table

667

Table 1: Sn-molar fractions at the different interfaces involved in the Cu-Sn system with reference to
the phase diagram for a temperature of 250 °C [3].

670

Interface	Interface Cu _(s) -Cu ₃ Sn Cu ₃		Cu ₃ Sn-	Cu ₆ Sn ₅	Cu ₆ Sn ₅ -Sn _(l)	
Sn molar	$x_{Sn}^1(I_1)$	$x_{Sn}^2(I_1)$	$x_{Sn}^2(I_2)$	$x_{Sn}^3(I_2)$	$x_{Sn}^3(I_3)$	$x_{Sn}^4(I_3)$
fraction	2.2	23.6	24.7	44.5	45.4	97.8

671 Table 2: Partial molar volumes of Sn and Cu-atoms and inter-diffusion coefficients for the phases 672 involved in the Sn-based solder/Cu system: adeduced from the lattice parameter data available in the literature [28]; ^bdeduced from the density of liquid tin at 250°C [29] and from the 3% variation for the 673 674 liquid/solid transition as determined in [30] for the Cu_(s)-phase; ^cdeduced from the density of copper at 675 250°C and from the extrapolation at 250°C of the linear variation of liquid copper density for the Sn()phase [31]; ^dcalculated at 250°C from Arrhenius equation defined in [14]. They are close to that we can 676 obtain from other references [32-33]; ecalculated at 250°C from Arrhenius equation defined for 2% of 677 Sn in [34]; ^fclose to Sn₍₁₎ self-diffusion coefficient [35]. 678

Phase <i>i</i>	$Cu_{(s)}$ (<i>i</i> = 1)	$Cu_3Sn (i=2)$	$\mathrm{Cu}_6\mathrm{Sn}_5\ (i=3)$	$Sn_{(1)} (i = 4)$
Sn partial molar volume \overline{V}_{Sn}^{i} (cm ³ /mol)	16.3 ^b	15.9ª	15.9ª	17.0 ^b
Cu partial molar volume \overline{V}_{Cu}^i (cm ³ /mol)	7.1°	6.2ª	6.2ª	7,3°
Inter-diffusion coefficient D^i (m ² /s)	1.0x10 ^{-22e}	3.6x10 ^{-15d}	7.6x10 ^{-15d}	2.0x10 ^{-9f}

679

681 **Figure captions**

682

Figure 1: Different steps of the IMC report using TLPB based on Cu-Sn system. a) Fusion of the Sn 683 684 filler metal (liquid Sn in blue color), b) Dissolution of part of the Cu substrate inside liquid Sn and 685 nucleation of first Cu₆Sn₅ germs, c) Growth of both Cu₆Sn₅ and Cu₃Sn IMCs and consumption of 686 remaining liquid Sn d) Complete consumption of liquid Sn and solidification of the IMC joint, e) Homogenization of the joint toward the most stable Cu₃Sn intermetallic, f) Cu-Sn binary phase 687 diagram (Reprinted from reference [3]). 688 689 Figure 2: Experimental formation of Cu-Sn IMC joint for different holding time for a 5 KPa pressure 690 691 and a holding temperature of 250°C. a) SEM micrograph at 0 min, b) AES line profile at 0 min, c) SEM 692 micrograph at 15 min, d) SEM micrograph at 30 min, e) SEM micrograph at 45 min, f) SEM micrograph 693 at after complete reaction of liquid Sn (2 hours) 694 Color scale (a-e) (darker to lighter gray): Cu substrate; Cu₃Sn; Cu₆Sn₅, Sn Color scale (f) (darker to lighter gray): Cu substrate; Cu₃Sn; Cu₆Sn₅ 695 696 697 Figure 3: Evolution of the IMC morphology and chemical composition with holding temperature 698 (pressure of 5 KPa and holding time of 120 min): a) 250°C, b) 270°C and c) 300°C 699 Color scale (a-c) (darker to lighter gray): Cu substrate; Cu₃Sn; Cu₆Sn₅ 700 701 Figure 4: One-dimensional problem of the Cu₆Sn₅ and Cu₃Sn layers in the Sn based solder-Cu system using linear profile of Sn molar concentrations $C_{Sn}^{i}(X,t)$ within each phase *i*. 702 703 704 Figure 5: Geometric model for the microstructure of the Cu_0Sn_5 -layer described in [25]. (a), top view of 705 the layer showing grain size d and grain boundary width δ . (b), cross section corresponding to the dashed line in (a) showing the average layer thickness d_L and the average grain boundary length d_{GB} . 706

- 707 \rightarrow Sn-fluxes in the bulk and along grain boundaries of the Cu₆Sn₅-layer and along the Cu₃Sn/Cu₆Sn₅ 708 interface
- 709 \rightarrow Reverse Cu-fluxes of equal intensity in the case of inter-diffusion
- 710

Figure 6: Schematic illustration of the mechanism of Sn/vacancy inter-diffusion within the Cu₆Sn₅-phase involving Cu₆Sn₅-growth at the interfaces I_3 and I_2 together with displacements of the I_1 and I_4 interfaces. The I_4 interface displacement induces pore formation.

Figure 7: Evolution of the interface displacements and void formation involved in the Cu/Sn-based solder joint for different mass transport scenarios taking account for volume shrinkage induced by the difference of Cu and Sn-partial molar volumes between each phase. Inter-diffusion of Cu and Sn-atoms is considered except for the simulation case (d). The bulk Cu and Sn-inter-diffusion coefficients as well as the partial molar volumes of Cu and Sn-atoms relative to each involved phase are indicated in table 2.

(a), volume diffusion mechanism within both IMCs; (b) diffusion mechanism through the volume for Cu₃Sn and along the grain boundaries including grain growth for Cu₆Sn₅; (c), same diffusion mechanisms as in case (b) with 2/3 of the inter-diffusion devoted to the Sn/vacancy-exchange and 1/3to the Sn and Cu one; (d) last step after the Sn₍₁₎-phase is consumed leading to the final stable state.