

# A Diffusion-Kinetic Model for Predicting Solder/Conductor Interactions in High Density Interconnections

K.J. RÖNKÄ, F.J.J. VAN LOO, and J.K. KIVILAHTI

A combined thermodynamic and diffusion-kinetic approach is very viable for developing microjoining and interconnection materials and processes, in particular, whenever thinner metallizations, coated overlayers, or smaller solder-joint volumes are encountered in very high density electronics. A diffusion-kinetic model based on the utilization of integrated diffusion coefficients and mobilities is introduced and discussed for calculating the layer growth of intermetallic compounds between metal conductors and tin-based solders and is exemplified with a relatively simple ternary Cu/SnBi system. The model has also been used for calculating the local nominal composition of the effective joint or contact region. Moreover, the mobilities of Sn and Cu in  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  intermetallic compounds are determined, and the role of both stable and metastable phase diagrams is discussed in predicting the appearance of possible reaction products as well as the driving forces for the dissolution, diffusion, and precipitation processes.

## I. INTRODUCTION

JOINING dissimilar materials involves different bonding techniques, such as diffusion bonding, brazing, and soldering. The prediction and control of the microstructural and compositional changes in the joint region are not only important during these bonding operations but also during testing and in use of the assemblies. This is most pronounced in the advanced microjoining technologies, such as Flip Chip, that provide high-density/fine-pitch interconnections, where increasing joint densities (finer pitch) are associated with decreasing solder-joint volumes and thinner metallization layers. One or more of the interconnection elements, either by diffusing, by dissolving into, and/or by reacting with the mating materials in the solder, bump, metallizations, and substrate, can be entirely consumed during a joining operation or in use of the assemblies, which leads to marked changes in the microstructures. Accordingly, it is evident that more emphasis has to be placed on better understanding and control of the energetics and kinetics of the intermaterial dissolution and the diffusion and reaction processes.

Long-term microstructural changes, including the *solid-state* nucleation and growth of intermetallic compounds, occur during solid-state diffusion bonding or between the metallization layers, for example, in the Flip-Chip bonding. This also occurs, regardless of the joining technique, during cycling testing and when using the electronic assemblies at elevated temperatures, which can be as high as 150 °C in harsh automotive and avionics application environments. In conventional industrial soldering or brazing operations, the joint regions spend a relatively short time at elevated temperatures and only a few seconds in the *liquid state*, where

the conductor metal or substrate to be joined is in contact with molten solders or brazes. Despite the short time interval, marked dissolution of the materials into the liquid fillers will occur, causing a subsequently fast precipitation of intermetallic compound(s) at the liquid filler/substrate interfaces.<sup>[1,2,3]</sup> Thus, the dissolution and precipitation processes are expected to play an important role in determining the wetting of the materials to be joined by the liquid fillers.<sup>[3]</sup>

In diffusion bonding, the materials to be joined typically have relatively large solubility regions, and no intermetallic compounds are formed at the joint interface. The bonding operation involves only solid-state diffusion across the joint interface, and therefore, the combined thermodynamic-diffusion kinetic approach can be based on the diffusion flux equations with concentration gradients or, preferably, gradients of chemical potentials (activities).<sup>[4]</sup> On the other hand, in the applications encountered in microelectronics assemblies, the typical soldering or brazing systems contain intermetallic compounds whose growth kinetics need to be modeled. However, the determination of the interdiffusion coefficients in the intermetallics with a narrow homogeneity region is inaccurate or even impossible when the concentration gradients in the intermetallics approach zero such that their applicability is impaired. Therefore, the growth kinetics of the intermetallics must be calculated by some other means. In this work, this has been done using the integrated diffusion coefficients introduced by Wagner.<sup>[5]</sup>

The integrated diffusion coefficients and the tracer diffusion coefficients are inter-related. Mobilities are material constants, so, when they are determined, for example, in a binary system, they can be applied for calculating the layer growth rates of the same intermetallic compounds in a ternary case provided that the thermodynamics of the system are known and the intermetallics remain relatively pure binary phases. This provides the possibility of applying Wagner's concept also in the ternary conductor/solder systems, where the solder is in a liquid state. Therefore, one aim of this article is to study the applicability of a solid-state diffusion model based on parabolic layer growth of the intermetallic compounds for predicting the structural/com-

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K.J. RÖNKÄ, Design Manager, is with Interconnection Technology, Nokia Telecommunications, Fixed Access Systems, Operations, 90831 Haukipudas, Finland. F.J.J. VAN LOO, Professor, is with the Laboratory for Solid State and Materials Science, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands. J.K. KIVILAHTI, Professor, is with the Laboratory of Electronics Production Technology, Helsinki University of Technology, 02015 TKK, Finland.

Manuscript submitted July 15, 1997.

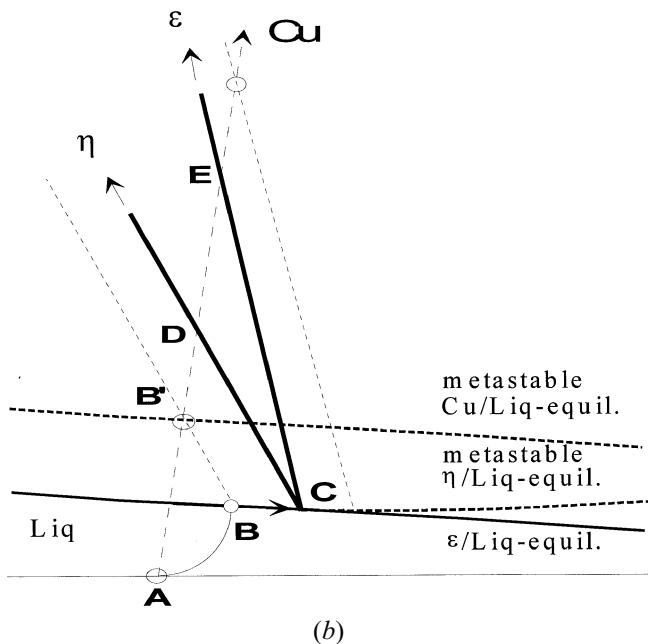
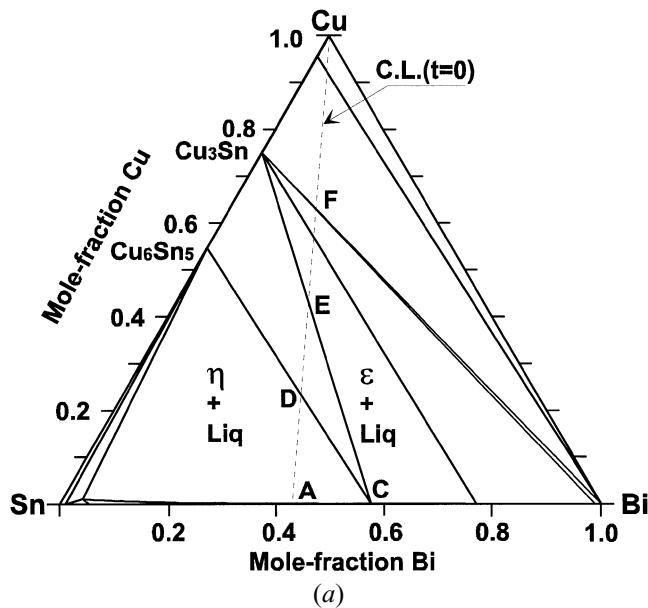


Fig. 1—(a) The isothermal section of the Cu-Sn-Bi system at 220 °C.<sup>[6]</sup> Note the connection line (C.L.). (b) Enlarged section of the Cu-Sn-Bi phase diagram near the tip of the liquid-Cu<sub>6</sub>Sn<sub>5</sub> (η) - Cu<sub>3</sub>Sn (ε) triangle.

positional changes between conductor metals and molten solders during the soldering operation. Moreover, the model has been used for calculating the “local nominal composition” (LNC) of the effective joint region and is compared with the experimental observations presented in earlier articles.<sup>[1,2]</sup>

## II. MODELING THE GROWTH KINETICS OF INTERMETALLICS WITH THE INTEGRATED DIFFUSION COEFFICIENT APPROACH

In order to calculate the LNC of the effective joint region, say, in a solder/conductor system, the growth kinetics of the reaction layers have to be known. In this work, the growth rates are evaluated by using the model based on the

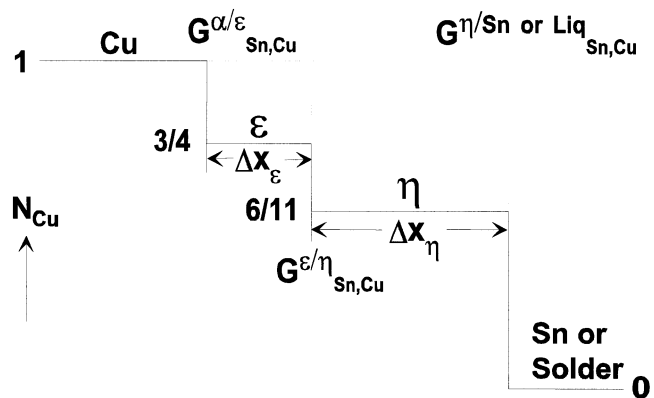


Fig. 2—Schematic concentration profile of Cu/Sn or Sn-base solder diffusion couple showing the formation of Cu<sub>3</sub>Sn (ε) and Cu<sub>6</sub>Sn<sub>5</sub> (η) intermetallics.

integrated diffusion coefficient approach.<sup>[5]</sup> After presenting the model, it is applied herein to relatively simple binary Cu-Sn and ternary Cu-Sn-Bi systems. In the ternary example, which is also presented in Figure 1, Cu, Sn, and Bi are the conductor, the reactive component, and the inert component of the solder alloy, respectively. It should be noticed, however, that the following presentation can be applied equally well to other interesting solder/conductor or interconnection systems. As an example, the minimum thickness of the copper metallization used as a solderable layer under the tin solder bump in the Flip-Chip interconnection has been estimated during use of the assembly.

Wagner has introduced the integrated diffusion coefficient  $\bar{D}_{int}$  as the binary interdiffusion coefficient,  $\bar{D}$ , integrated over its (unknown) limits of homogeneity.<sup>[5]</sup> A general form for the integrated diffusion coefficient can be written as follows:

$$D_{int}^{(i)} = \frac{(N^{(i)} - N^-)(N^+ - N^{(i)}) (\Delta x^{(i)})^2}{(N_i^+ - N_i^-) 2t} + \frac{\Delta x^{(i)}}{2t} \left[ \frac{(N^+ - N^{(i)}) \sum_{v=2}^{v=i-1} \frac{V_m^{(v)}}{V_m} (N^v - N^-) \Delta x^{(v)} + (N^{(i)} - N^-) \sum_{v=i+1}^{v=n-1} \frac{V_m^{(v)}}{V_m} (N^v - N^+) \Delta x^{(v)}}{N^+ - N^-} \right] \quad [1]$$

where  $t$  is the annealing time,  $\Delta x$  the layer thickness,  $V_m$  the molar volume of phase  $i$  ( $i = 1$  to  $n$ ), and  $N_i^-$  and  $N_i^+$  the atomic fractions of component  $i$  of the terminal phases of the diffusion couple (Figure 2). The homogeneity ranges of the Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> intermetallics, as determined experimentally with the scanning electron microscopy/electron probe micro-analysis technique, are 1.5 and 1.0 at. pct, respectively,<sup>[1]</sup> and so the employment of Wagner’s treatment is justified. In the model, the growth of the solid intermetallics is assumed to occur in the same way in both the solid/solid and liquid/solid diffusion couples, parabolically with time. Hence, in the  $\eta$  phase, only tin diffuses, while in the  $\epsilon$  phase, both tin and copper are the diffusing components.<sup>[7]</sup>

The equilibrium solubility of copper in the eutectic solder exemplified in this study is very small (0.5 at. pct at 220 °C), and the diffusion of the components of the solder material into original conductor metals is generally very slow under typical soldering conditions (i.e. temperature and time) and can be ignored. Based on Eq. [1], the following

expression for the integrated diffusion coefficients in the  $\varepsilon$ -Cu<sub>3</sub>Sn and  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> intermetallics can be written as

$$\begin{cases} D_{\text{int}}^{\varepsilon} = \frac{3}{16} \frac{\Delta x_{\varepsilon}^2}{2t} + \frac{3}{22} \frac{V_m^{\varepsilon}}{V_m^{\eta}} \frac{\Delta x_{\varepsilon} \Delta x_{\eta}}{2t} \\ D_{\text{int}}^{\eta} = \frac{30}{121} \frac{\Delta x_{\eta}^2}{2t} + \frac{3}{22} \frac{V_m^{\eta}}{V_m^{\varepsilon}} \frac{\Delta x_{\varepsilon} \Delta x_{\eta}}{2t} \end{cases} \quad [2a,b]$$

The simplest way to determine the integrated diffusion coefficient is to anneal the diffusion couples between copper and pure tin for a fixed time and measure the layer thickness of the intermetallic compounds. In a binary system, the integrated diffusion coefficient is a material constant at constant temperature, but in multicomponent systems, this is not necessarily valid anymore. Therefore, in order to use the data from binary diffusion couples in a ternary case, the tracer diffusion coefficients  $D_i^*$ —related to the mobility  $\beta_i$  by the relation  $D_i^* = \beta_i RT$ —need to be solved as real material constants. Based on the procedure introduced by Gülpén *et al.*<sup>[8,9]</sup> for partial diffusion couples, the following expressions are derived:

$$\begin{cases} D_{\text{int}}^{\varepsilon} = -(N_{\text{Sn}}^{\varepsilon} D_{\text{Cu}}^{*,\varepsilon} + N_{\text{Cu}}^{\varepsilon} D_{\text{Sn}}^{*,\varepsilon}) \frac{N_{\text{Cu}}^{\varepsilon} \Delta_r G_{\text{Cu}}^{\circ}(\varepsilon)}{RT} \\ D_{\text{int}}^{\eta} = -N_{\text{Cu}}^{\eta} D_{\text{Sn}}^{*,\eta} \frac{N_{\text{Sn}}^{\eta} \Delta_r G_{\text{Sn}}^{\circ}(\eta)}{RT} \end{cases} \quad [3a,b]$$

where  $N_i$  is the atomic fraction of a component  $i$ ,  $D_i^*$  is the tracer diffusion coefficient of Sn and Cu in the  $\varepsilon$  and  $\eta$  phases, and  $\Delta_r G_i^{\circ}$  is the standard molar Gibbs energy of reaction. The evaluation of  $\Delta_r G_{\text{Sn}}^{\circ}(\eta)$  and  $\Delta_r G_{\text{Cu}}^{\circ}(\varepsilon)$  has been exemplified in the ternary Cu-Sn-Bi system at 235 °C (just above the melting point of pure tin for the reason of simplicity) in Figure 3. The ratio of the intrinsic diffusion coefficients of Cu and Sn in the  $\varepsilon$  phase is constant in the temperature range from 180 °C to 250 °C:<sup>[7]</sup>

$$\frac{\bar{V}_{\text{Sn}}}{\bar{V}_{\text{Cu}}} \frac{D_{\text{Cu}}}{D_{\text{Sn}}} = \frac{D_{\text{Cu}}^*}{D_{\text{Sn}}^*} = 3 \quad [4]$$

with which the tracer diffusion coefficients can be solved as

$$\begin{cases} D_{\text{Cu}}^{*,\varepsilon} = -\frac{8}{3} D_{\text{int}}^{\varepsilon} \frac{RT}{\Delta_r G_{\text{Cu}}^{\circ}(\varepsilon)} \\ D_{\text{Sn}}^{*,\varepsilon} = -\frac{8}{9} D_{\text{int}}^{\varepsilon} \frac{RT}{\Delta_r G_{\text{Cu}}^{\circ}(\varepsilon)} \\ D_{\text{Sn}}^{*,\eta} = -\frac{121}{30} D_{\text{int}}^{\eta} \frac{RT}{\Delta_r G_{\text{Sn}}^{\circ}(\eta)} \end{cases} \quad [5a,b,c]$$

where the integrated diffusion coefficients are determined experimentally using Eq. [2a,b] and

$$\begin{cases} \Delta_r G_{\text{Cu}}^{\circ}(\varepsilon) = RT[\ln a_{\text{Cu}}^{\eta/\varepsilon} - \ln a_{\text{Cu}}^{\text{Cu}/\varepsilon}] \\ \Delta_r G_{\text{Sn}}^{\circ}(\eta) = RT[\ln a_{\text{Sn}}^{\varepsilon/\eta} - \ln a_{\text{Sn}}^{\eta/\text{Sn or liq}}] \end{cases} \quad [6a,b]$$

corresponding to the activity difference of copper and tin across the  $\varepsilon$  and  $\eta$  phases calculated using the thermodynamic data available. The values  $a_{\text{Cu}}^{\eta/\varepsilon}$ ,  $a_{\text{Cu}}^{\text{Cu}/\varepsilon}$ , and  $a_{\text{Sn}}^{\varepsilon/\eta}$  can be found from the binary Cu-Sn data, whereas the value of  $a_{\text{Sn}}^{\eta/\text{Sn or liq}}$  (which changes with the Sn-Bi ratio in solder and,

therefore, with time) can be found from the ternary Cu-Sn-Bi data. The ternary Cu-Sn-Bi system was critically assessed by optimizing the available thermodynamic data together with the experimental composition of the liquid ternary phase at different temperatures while in equilibrium with both intermetallics.<sup>[6]</sup>

The mass balance needs to be obeyed throughout the analysis, and by using the Matano analysis, the following relation in the ternary case for the tin content in the solder,  $N_{\text{Sn}}$ , can be obtained:

$$\left( \frac{1}{4} \frac{\Delta x_{\varepsilon}}{V_m^{\varepsilon}} + \frac{5}{11} \frac{\Delta x_{\eta}}{V_m^{\eta}} \right) (1 - N_{\text{Sn}}) = (N_{\text{Sn}}^0 - N_{\text{Sn}}) \frac{\Delta x_{\text{liq}}^0}{V_m^{\text{liq}}} \quad [7]$$

where the  $N_{\text{Sn}}^0$  is the tin content and  $\Delta x_{\text{liq}}^0$  the thickness of the original solder. Knowing the tracer diffusion coefficients in the intermetallics and the thermodynamics of the ternary Cu-Sn-Bi system at each temperature, the growth rates of the intermetallic layers between the copper and Sn-Bi solder can be calculated. In the case of small solder volumes or thin metallizations, the solder markedly enriches in bismuth since only tin is consumed in the intermetallics reactions. Therefore, the integrated diffusion coefficients, layer growth, and local nominal composition need to be iterated at each time-step from Eqs. [2], [3], [6], and [7].

When the composition of the liquid solder has passed the apex C of the three-phase ( $\varepsilon$ - $\eta$ -liquid) triangle (Figure 1(a)), the activities of tin and copper are equal at both sides of the  $\eta$  phase and then the driving force for the growth of the  $\eta$  phase has disappeared. At the right-hand side of point C, the  $\varepsilon$  phase in direct contact with the liquid solder has reached a local stable equilibrium, while the  $\eta$  phase has become metastable. Now, the driving force  $\Delta_r G_{\text{Cu}}^{\circ}(\varepsilon)$  is dependent on the solder composition. When only the  $\varepsilon$  phase is growing ( $\Delta x_{\eta} = 0$ ), Eqs. [2], [3], [6], and [7] become simpler.

### III. RESULTS AND DISCUSSION

#### A. Binary Solid-Solid Systems

The tracer diffusion coefficient (or mobility) of Sn and Cu in the  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> and  $\varepsilon$ -Cu<sub>3</sub>Sn intermetallic compounds was calculated at different temperatures using Eqs. [4] through [6]. The calculations are based on experimentally determined layer thicknesses of the intermetallics grown between copper and pure tin in solid-state diffusion couples.<sup>[7,10–12]</sup> In those cases where only the total layer thickness was reported, the calculated ratio of the  $\varepsilon$  phase to the  $\eta$  phase thickness vs temperature was applied.<sup>[10]</sup> The temperature dependence of the mobilities is presented as the Arrhenius plot in Figure 4 and compared with the tracer diffusion coefficient of tin in pure tin.<sup>[13]</sup> As expected, tin moves slower in the intermetallics than in pure tin but much faster than in pure copper. The diffusion is clearly faster in the  $\eta$  phase than in the  $\varepsilon$  phase. The mobility ratio of Sn-to-Cu in the  $\varepsilon$  phase is assumed to be constant in the temperature range considered, in parallel to Eq. [4]. Since the mobilities are material constants, they can be used in any solder system where the Cu<sub>6</sub>Sn<sub>5</sub> and/or Cu<sub>3</sub>Sn intermetallics are formed by the solid-state diffusion process.

The results presented in Figure 4 can be compared with

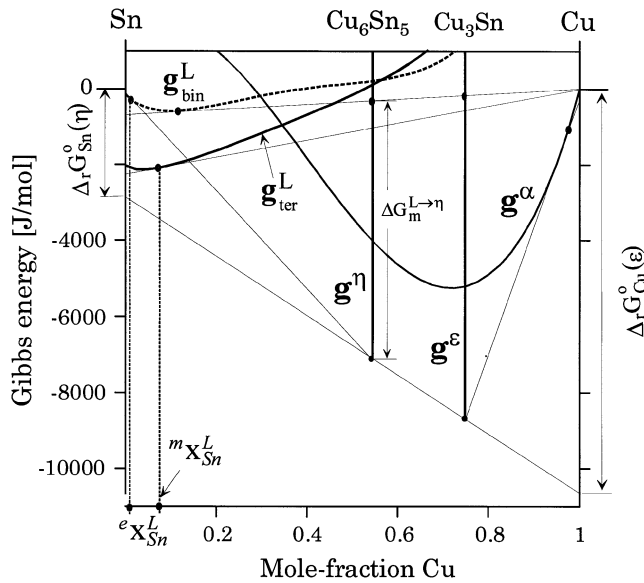


Fig. 3—The Gibbs energy diagram for Cu-Sn system at 235 °C showing the Gibbs energy of reaction for  $\epsilon$  and  $\eta$  phases.<sup>[6]</sup>

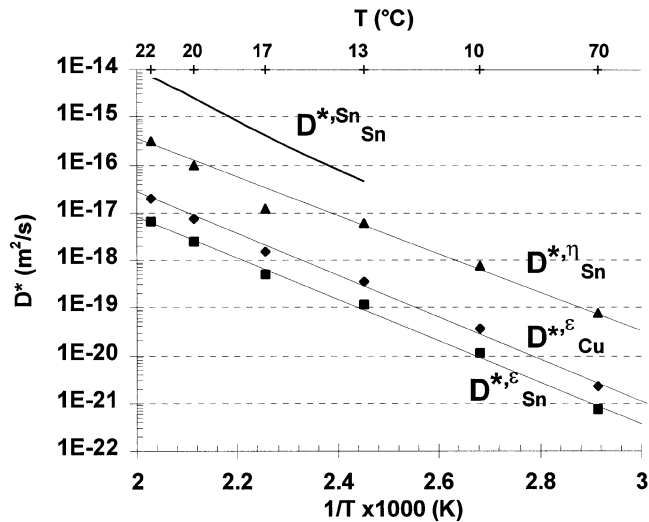


Fig. 4—Arrhenius plots of the mobilities of Sn and Cu in the  $\eta$  and  $\epsilon$  phases in relation to the mobility of Sn in pure tin.<sup>[13]</sup>

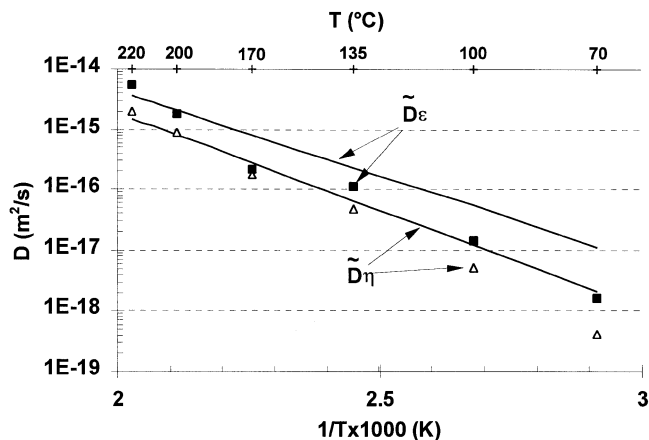


Fig. 5—Calculated binary interdiffusion coefficients in the  $\epsilon$  and  $\eta$  phases (data points) and the experimental fit over the temperature range of 190 °C to 220 °C (continuous line).<sup>[10]</sup>

the available interdiffusion data<sup>[10]</sup> by applying Darken's equation<sup>[14]</sup> in the  $\eta$  and  $\epsilon$  intermetallics and by ignoring the volume effects as follows:

$$\tilde{D} = (N_{\text{Sn}}D_{\text{Cu}}^* + N_{\text{Cu}}D_{\text{Sn}}^*) \left( 1 + \frac{\Delta \ln \gamma_i}{\Delta \ln N_i} \right) \quad [8]$$

where  $\tilde{D}$  is the interdiffusion coefficient in the  $\eta$  or  $\epsilon$  phase and  $\gamma_i$  is the activity coefficient of tin or copper, which can be calculated if the thermodynamic data on the system are known. The term in the second set of parentheses is the thermodynamic factor, averaged by taking the differences of  $\ln \gamma_i$  and  $\ln N_i$  at the phase interfaces.

As can be seen in Figure 5, at higher temperatures, the calculated results agree very well with the Arrhenius expression suggested to fit the experimental results in the temperature range of 190 °C to 220 °C,<sup>[10]</sup> while at lower temperatures, the calculated values are somewhat lower. It should be noted that the thermodynamic factor for the  $\epsilon$  phase varies from 130 to 230 and for the  $\eta$  phase from 30 to 40 depending on the temperature, and therefore, the interdiffusion coefficients are considerably higher than the mobilities.

A typical Flip-Chip metallurgy between bump and chips metallizations or pads consists of several thin (0.1 to 3  $\mu\text{m}$ ) metal or alloy layers. Copper can be used as a solderable adhesion layer providing proper wetting by the melting tin-based solder bump. The  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  intermetallics grow in solid state between the tin-based solder bump and the copper metallization during testing and use of the assembly. The diffusion model introduced previously was applied to calculate the minimum thickness of the copper metallization needed to prevent the total consumption of the copper metallization by reacting with a pure solid tin solder bump. In some harsh automotive and avionics application environments, the temperature of the assembly can rise up to 150 °C when, according to the calculations, a 4.5- $\mu\text{m}$ -thick copper metallization is already consumed after 1000 hours of use, while after 10,000 hours, the corresponding thickness is 14  $\mu\text{m}$ . In several applications, a temperature of 100 °C is typically reached when the thicknesses of the consumed copper metallizations are 1.2 and 3.8  $\mu\text{m}$  after 1000 and 10,000 hours, respectively. At room temperature, however, the layer growth of the intermetallics is so slow that after 10,000 hours, only a 0.3- $\mu\text{m}$ -thick layer of copper is totally consumed. Since in addition a relatively thick layer of  $\text{Cu}_6\text{Sn}_5$  intermetallic can be formed already during bonding, the required thickness of the copper metallization needs to be between 5 and 10  $\mu\text{m}$  in order to guarantee reliable functioning Flip-Chip interconnections in high-temperature applications. However, these thick copper metallizations can cause other manufacturing problems, and therefore, other solutions, such as nickel or copper-nickel alloys, are needed together with pure tin solder bumps.

### B. Ternary Solid-Solid Systems

At low temperatures when the microstructural changes in the joints are studied during testing or in use of the assembly, the diffusion model gives realistic results as long as the tin is readily available at the solder/intermetallics interface. It has been observed experimentally, however, that since the tin is first consumed near the solder/intermetallics

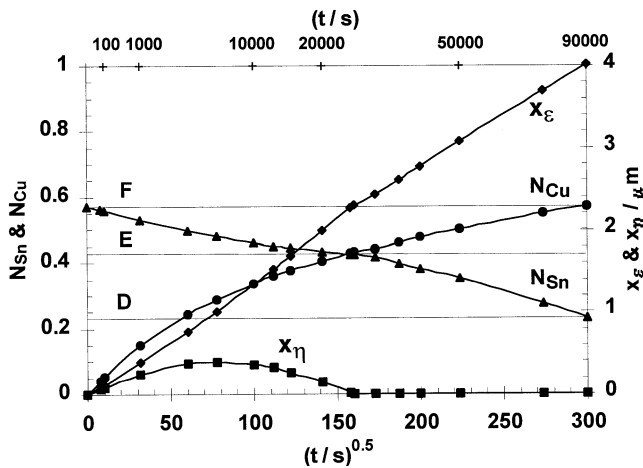


Fig. 6—Growth of the  $\eta$  and  $\varepsilon$  phases, the local nominal composition  ${}^L N_{Cu}$  (copper content with fixed ratio of tin and bismuth), and the tin content of the liquid solder,  $N_{Sn}$ , as a function of time in the Cu vs eutectic Sn43Bi solder system at 220 °C. The letters D, E, and F correspond  ${}^L N_{Cu}$ , as shown in Fig. 1(a).

interface, a layer enriched in bismuth is formed between the intermetallics and solder.<sup>[2,15]</sup> This mechanically brittle layer acts as a diffusion barrier and hinders the further growth of the intermetallic layers, thus, significantly reducing the reliability of the solder joint.

### C. Ternary Solid-Liquid Systems

The layer growth rate and the local nominal composition in the Cu-Sn43Bi system are illustrated in Figure 6. In the calculations, the original thickness of the liquid was taken as 5  $\mu\text{m}$  (per conductor interface). In the beginning of the joining, both the  $\eta$  and  $\varepsilon$  phases grow parabolically and the LNC (*i.e.*, the copper content,  $N_{Cu}$ , in the effective joint region) increases between points A and E in Figure 1. As the composition of the whole solder volume moves from B toward point C, the growth rate of the  $\eta$  phase decreases. Since the  $\varepsilon$  phase grows at the expense of the  $\eta$  phase, the decomposition rate of the  $\eta$  phase exceeds its growing rate and the  $\eta$  phase starts to disappear. At point C, the  $\eta$  layer has been consumed totally, while the LNC has reached point E. After this, the  $\varepsilon$  phase will grow slightly slower, and finally, the ( $\varepsilon$ -liquid-Bi) triangle is reached and a pure bismuth layer is formed. The LNC has concurrently reached point F.

It is obvious, however, that in the case of the liquid phase, the experimental growth rate of the intermetallics as well as the rate of the transformation of the  $\eta$  phase into the  $\varepsilon$  phase is much too high to agree with the results of the model calculations based on the solid-state diffusion,<sup>[2,3]</sup> and so, other mechanisms must operate. It has been shown that a thin layer of the solid  $\text{Cu}_6\text{Sn}_5$  (or  $\text{Cu}_3\text{Sn}$ ) is formed rapidly by the heterogeneous nucleation (or precipitation) from the supersaturated melt at the Cu/liquid interface.<sup>[1,2]</sup> For example, when a copper wire is immersed into the eutectic SnPb solder at 230 °C, a 0.5- $\mu\text{m}$ -thick layer of  $\eta$  phase was formed on the copper already after 10 seconds' immersion, and it continued to grow up to 1  $\mu\text{m}$  after 100 seconds. In the case of palladium, the layer thicknesses of a  $\text{PdSn}_4$  phase after 10 and 100 seconds' immersion were 4 and 40  $\mu\text{m}$ , respectively.<sup>[3]</sup>

First, the nucleation mechanism at the liquid/solid interface is different than at the solid/solid interface. Immediately after the first contact, Cu dissolves rapidly into the liquid solder until it has reached the *metastable solubility* limit B' at the liquid/copper interface (Figure 1(b)). This is also seen from Figure 3, where the common tangent between pure Cu and the  $g_{\text{ter}}^L$  curve gives the metastable solubility,  ${}^m N_{Cu}^L$ . This maximum attainable supersaturation of copper in the liquid (and the related driving force  $\Delta G_m^{L \rightarrow \eta}$ ) is essential for the formation of the  $\text{Cu}_6\text{Sn}_5$  phase, which comes into *local stable* equilibrium with the liquid of composition B at the phase boundary. When the solder volume is small enough, the maximum supersaturation of Cu is reached rapidly throughout the solder, and therefore, the composition of the liquid will change from point A to B, while the LNC moves from A to point B'. With larger solder volumes, the supersaturation occurs only locally at the liquid/Cu interface.

On the other hand, when the initial layer of  $\eta$  phase is formed, the supersaturation of Sn in the Cu-rich solution ( $\alpha$ ) is needed for the nucleation of the  $\varepsilon$  phase at the Cu/ $\eta$  interface. The diffusion of tin and/or other solder elements in solid Cu (or Ni, Au, Pd, . . .) is very slow considering the time and temperatures generally used for soldering in electronics, and especially when comparing with the dissolution rate of Cu into the molten solder. Therefore, the formation of the  $\varepsilon$  phase between the solid phases occurs probably much later than the precipitation of the  $\eta$  phase, and so, there will be a metastable local equilibrium at the Cu/ $\eta$  interface for some time.

When the composition of the solder passes point C following the metastable  $\eta$ /liquid solubility line, the  $\eta$  phase becomes too metastable in relation to the  $\varepsilon$  phase. It has been verified experimentally that since the liquid is no longer in equilibrium with the  $\eta$  phase, it starts to penetrate into the  $\eta/\varepsilon$  interface along the grain boundaries of the  $\eta$  phase initiating the fast transformation of the  $\eta$  phase into  $\varepsilon$  phase.<sup>[2]</sup> Therefore, for more realistic predictions of the structural/compositional changes in the joint region, this fast transformation and the faster layer growth rate of intermetallics into the liquid should be taken into account by some means.

## IV. CONCLUSIONS

A model for calculating the layer growth of the  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  intermetallics by using integrated diffusion coefficients and tracer diffusion coefficients was introduced and applied to a relatively simple Cu/SnBi system. The tracer diffusion coefficients (mobilities) of Sn and Cu in the  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  intermetallics were determined and shown to be in good agreement with the experimental interdiffusion coefficients. The advantage of the model compared with the employment of interdiffusion fluxes is the possibility of using the tracer diffusion coefficients (mobilities) and, in certain cases, also the integrated diffusion coefficients as material constants and so by determining them experimentally in one case to use them together with the available thermodynamic data in another case. The calculations of the layer growth of the  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  intermetallics in solid state give realistic results, and the model was successfully applied to estimate the minimum thickness

of a copper metallization adjacent to a solid tin solder bump during use of the Flip-Chip bonded assembly. When liquid phase is involved, some modifications are needed for more realistic predictions of the layer growth of the intermetallics. The local nominal composition of the effective joint region has been demonstrated to be a useful concept for combining the thermodynamics and diffusion kinetics of a solder/substrate system with a limited amount of solder alloy.

#### ACKNOWLEDGMENTS

We are grateful to Mr. Vesa Vuorinen for his valuable assistance. This work was financially supported by the Academy of Finland.

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