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THE LOCAL NOMINAL COMPOSITION-USEFUL CONCEPT FOR MICROJOINING AND INTERCONNECTION APPLICATIONS

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Introduction

Thermodynamics of materials provide fundamental information on the stability of the phases (and microstructures) as well as on the driving forces of chemical reactions and diffusion processes. Therefore, this is of great importance for developing interconnection and joining technologies, especially in microelectronics where a multitude of dissimilar materials is used in diminutive amounts. Likewise, the thermodynamics provide phase diagrams that also contain information on metastable equilibria—usually not available in experimentally determined equilibrium diagrams. The complete phase equilibrium is never reached in joining or interconnection applications since the joint or contact regions are under continuous microstructural evolution. The local equilibrium is, however, generally attained at interfaces. Thus, the tie-lines of binary or ternary phase diagrams as well as the stability diagrams can be employed for determining the phases that can be in *local* stable or metastable equilibrium with each other.

On the other hand, for predicting the actual diffusion paths in ternary or multicomponent systems kinetic data are also needed. In fact, the phase diagrams provide an efficient method for designing reliable microjoining and interconnection materials and processes, especially when they can be combined with kinetic information. This approach is becoming even more important in the future, when thinner diffusion barriers or adhesion layers, coated overlayers and smaller solder joint volumes will be encountered in very high density electronic assemblies. For this purpose a special concept of the “local nominal composition” (LNC) in the effective joint region is introduced in this paper. Essentially, this combines the thermodynamic and diffusion-kinetic approaches and can be used for predicting possible microstructures that evolve in microjoints and in thin material layers as a function of time (1).

Local Nominal Composition

The nominal composition of an equilibrium system is defined as the average (global) composition of the whole system which remains constant with time-provided, of course, that the system does not contain very volatile components. For example, in a binary alloy system containing two equilibrated phases, the nominal composition of the system is represented in the phase diagram as a point in one of the tie-lines of the two-phase region, where there is no degree of freedom at constant temperature and pressure.

Since in microjoining and interconnection applications the equilibria are attained only at the interfaces, the nominal composition can be defined only locally in an effective joint or contact region (Fig. 1), where the concentrations (and other properties) of the components differ from those of the original contact materials. When a “filler” material is used for joining, the initial joint or contact region equals that of the filler, and it can be liquid as in soldering or brazing or solid as in diffusion bonding or in layered metallizations. Likewise, the materials to be joined can be different. Even though the evaluation of the local nominal composition in such a general case is more complicated than, for example, in most soldering or brazing applications, the approach is in principle the same. Thus, the LNC approach is applied herein to one of the most interesting conductor-solder systems in a high-density electronics assembly, namely the Cu-SnBi system.

Under typical soldering conditions (i.e. temperature and time), the diffusion of the components of liquid filler material into the original solid contact materials, e.g. conductor metals, is generally very slow and can therefore be ignored. In the beginning of soldering processes, the effective joint region corresponds to the original volume of the filler material (F), and it enlarges when the conductor metal enters it by dissolution and/or by chemical reactions. It is essential that the amount of filler material, i.e. the number of moles of all components in the filler as well as their ratios, does not change with time in the effective joint region. Therefore, the local nominal composition of the effective joint region, LNC, is located on the *connection line* (CL) between the original solder composition and that of the conductor metal—for example, as in the eutectic solder/conductor system in Fig. 2(a). Thus, the LNC, being defined as the number of moles of the conductor or substrate divided by the total number of moles of all the components ($i = 1$ to n) in all phases ($\phi = 1$ to v) in the effective joint volume, can be evaluated with the help of the following equation

$$N_C^L = \frac{\sum_{\phi=1}^v n_C^\phi}{\sum_{i=1}^n \sum_{\phi=1}^v n_i^\phi} = \frac{\sum_{\phi=1}^v \left(\frac{a^\phi}{a^\phi + b^\phi} \right) \Delta z^\phi}{\sum_{\phi=1}^v \frac{\Delta z^\phi}{V_m^\phi}} \tag{1}$$

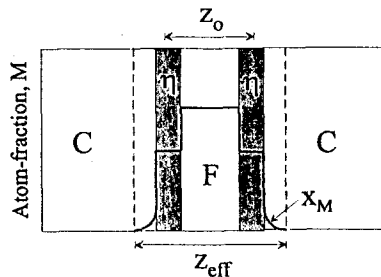


Figure 1. Schematic representation of the effective joint region.

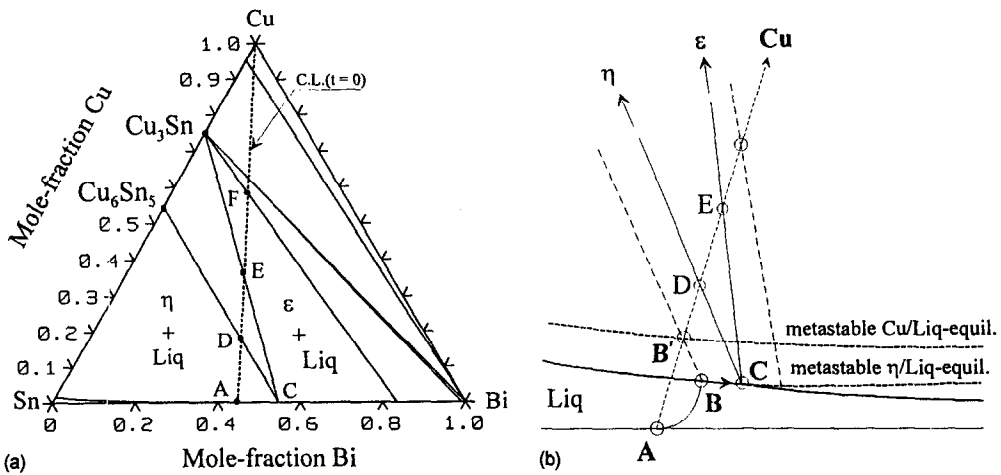


Figure 2. (a) The isothermal section of the Cu-Sn-Bi system at 235°C (3). Note the connection line (C.L.). (b) Enlarged section of the Cu-Sn-Bi phase diagram near the tip of the Liq-Cu₆Sn₅-(h)-Cu₃Sn (e) triangle.

with the fixed ratio of filler components (e.g. with the fixed Sn-to-Bi ratio along the connection line in Fig. 2(a)). Since the contact area remains generally unchanged, the effective joint volume can be obtained with the help of the effective joint thickness, z_{eff} . Then, the local nominal composition can be expressed by the layer thickness, Δz_i , of the intermetallic compounds, A_aB_b , and/or solution phases with the respective molar volumes V_m . The LNC corresponds to the relative amount of the incoming contact material, and the rate of change of the LNC can be evaluated only by applying the combined thermodynamic-kinetic approach shown analytically elsewhere (2). On the other hand, the LNC can be useful also qualitatively in several applications, such as in high-density electronics packaging, where conductor metals saturating rapidly throughout ever smaller solder volumes react with solute or solvent metals, for example, during the conventional reflow-soldering. In this case the LNC indicates the phases existing in microjoints without special knowledge of the kinetics, as will be illustrated later. Similar drastic microstructural and compositional changes can occur in the tip of the solder meniscus or tail of the solder fillet around component leads, where filler material exists locally in small volumes or thin layers.

In order to predict the onset of possible reaction products as well as the driving forces of the dissolution and reaction processes, both stable and metastable phase equilibria need to be known. It is emphasized here that special care must be taken when metastable equilibria in the thermodynamically assessed systems are considered. Generally, the functions describing the Gibbs energies of individual phases have been optimized to achieve a satisfactory fit between the experimentally determined and calculated (stable) phase diagrams based on the available thermodynamic data. So, there seems to be a trend that the solution phases, in particular, become much too stable in their (extrapolated) metastable regions. In order to obtain more realistic metastable solubilities and phase equilibria, the relevant thermodynamic systems need to be re-optimized in a self-consistent way; for instance, using the criterion that the degree of metastability of a solution phase is made in the optimization procedure as low as possible while ensuring that the experimentally confirmed phase diagram remains unaltered.

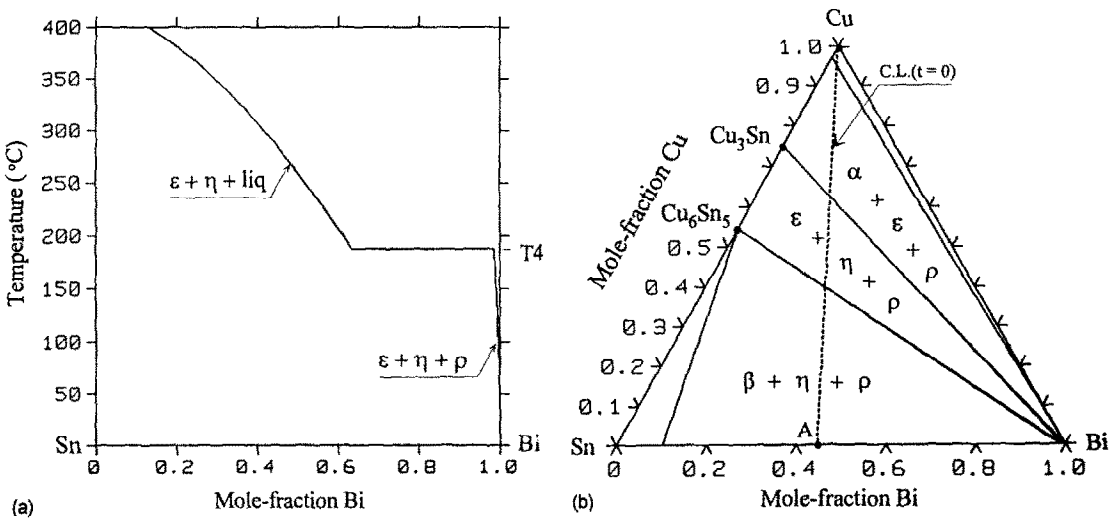


Figure 3. (a) Location of apex C of the three-phase triangle at different temperatures in the CuSnBi system (3). (b) The isothermal section of the Cu-Sn-Bi system at 125°C (3).

Results and Discussion

In this paper the concept of local nominal composition is exemplified using a microjoining process where Cu conductors are soldered together with the eutectic SnBi alloy. The assessed ternary phase diagram of the system is shown in Figs. 2(a) and 2(b), where Cu, Sn and Bi are the conductor metal, the reactive component and the inert component of the solder, respectively. It should be noticed, however, that the concept of the local nominal composition can be applied to other interesting soldering or interconnection systems as well.



(a)



(b)

Figure 4. (a) Cross-section of a microjoint bonded at 180°C for 1 min. with a thin layer of the eutectic SnBi alloy. Disintegration of the eutectic structure between Cu metallisations. (b) Cross-section of the joint area bonded at 300°C for 100 min. showing that a layer of pure Bi is formed during cooling between the 40Sn60Bi (at-%) solder and Cu₃Sn on Cu.

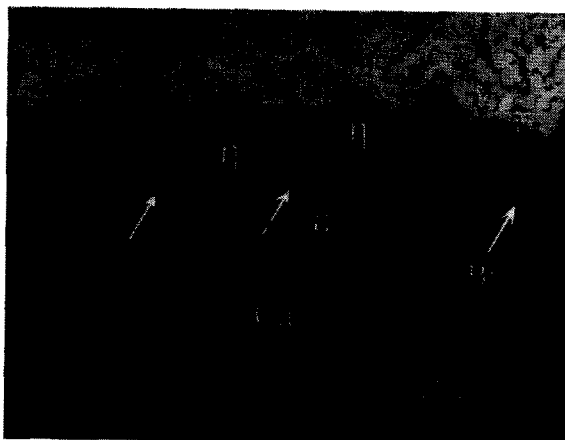


Figure 5. Transformation of the η -phase into the ϵ -phase after 100 seconds' immersion into the 30Sn70Bi (at-%) solder at 235°C. Note the Bi-rich phase (arrows) between the intermetallics.

Firstly, a pure copper conductor is in contact with the liquid solder at its original solder composition corresponding to point A in Figs. 2(a) and 2(b). Then, the effective joint volume (or thickness) consists only of the liquid and now the local nominal composition corresponds to that of the original solder. Immediately after the first contact Cu dissolves rapidly into the molten solder until it has reached the *metastable solubility* limit B' at the liquid/copper interface (Fig. 2(b)).

This maximum attainable supersaturation of copper in the liquid is essential for the formation of the Cu_6Sn_5 intermetallic 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 whole solder volume in conventional reflow-soldering processes and, therefore, the composition of solder will change from point A to B while the local nominal composition point moves from A to point B'. With larger solder volumes the supersaturation occurs only locally at the liquid/Cu interface. The formation of intermetallics like η - Cu_6Sn_5 or ϵ - Cu_3Sn directly from the Sn-based liquid alloy is so fast that mechanisms other than those in the solid state must operate (4). It is suggested here that a thin layer of the Cu_6Sn_5 (or Cu_3Sn) is formed rapidly by heterogeneous precipitation from the supersaturated melt at the Cu/liquid interface. As the Sn is consumed from the solder by the growth of the Cu_6Sn_5 phase, the solder composition moves from B towards point C along the liquidus while the local nominal composition moves along the contact line from B' towards point D. It should be noted, however, that the ϵ - η -liquid three-phase equilibrium point C moves towards the tin-rich corner in the Cu-Sn-Bi phase diagram when the soldering temperature is raised, as illustrated in Fig. 3(a). Therefore, at higher temperatures or at higher Bi-content (i.e. at the right side of point C in Fig. 2(b)) the ϵ -phase will form directly between copper and liquid Sn-Bi solder.

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

It has been shown experimentally in Fig. 4(a) that the once formed η -layer will transform into the ϵ -phase and a pure Bi layer is formed during the bonding operation. When the η -phase continues to grow, the composition of the solder passes point C following the metastable η /liquid solubility line. After point C the η -phase becomes too metastable compared with the ϵ -phase, and this initiates the fast

transformation of the η -phase into the ε -phase with the help of the liquid. When the transformation is completed the local nominal composition has passed point E. After the consumption of the η -phase, the ε -phase continues to grow, while the LNC moves along the connection line in the ($\varepsilon + \text{Liq}$) phase region, where the corresponding tie-lines fix the liquid composition. Eventually the ($\varepsilon - \text{Liq} - \text{Bi}$)-triangle is reached and pure solid bismuth becomes stable following the disappearance of the liquid phase as shown also in Fig. 4(a).

The fast transformation of the η -phase into the ε -phase has been verified by growing first thick layers of the η -phase (about 20 μm) and the ε -phase (about 8 μm) on copper wires by immersing the copper wires into the Sn35Bi (at-%) solder bath at 235°C for 100 hours. Immediately after this, the copper wires were transferred into the Sn70Bi (at-%) solder bath of the same temperature. With the higher Bi composition the liquid is not in equilibrium with the η -phase and, therefore, the liquid penetrates along the grain boundaries of the η -phase into the η/ε -interface already during 10 seconds' immersion. As shown in Fig. 5, the liquid is at the η/ε -interface within 100 seconds, and the η -phase has transformed into the ε -phase completely within 300 seconds. It should be noted that the newly formed ε -phase retains the original morphology of the η -phase, while the liquid dissolves the extra tin released in the transformation.

The above description deals with small solder volumes or thin solder layers, but brittle Bi-enriched layers can form at the solder/ η or solder/ ε interfaces also in the case of larger solder volumes either during cooling, as illustrated in Fig. 4(b), or during solid-state ageing as also reported in the literature (5). During the bonding operation the intermetallic compound (either η and/or ε -phase) will grow to a certain thickness, and it continues to grow at lower temperatures as well during testing or in use of the assembly. In the solid state the intermetallic growth consumes tin, however, essentially near the solder/ η or solder/ ε interface and, thus, a layer enriched in Bi is formed. This layer sequence is, in fact, evident on the basis of the mass-balance requirement. The further growth of the intermetallics is considerably retarded or even halted, since the additional tin has to diffuse through a more or less continuous Bi layer.

Other types of microstructural transformations are also possible due to the different phase equilibria at different temperatures. When joining Cu conductors with SnBi or SnPb solders, the ε -layer forms next to the solder alloy during the bonding either owing to the transformation discussed above or as an initial layer. However, after the bonding when the solder joint has cooled down, say, to a temperature of 125°C, the LNC located inside the ($\beta + \eta + \rho$) triangle. Fig. 3(b) shows the local stable equilibrium between the η -phase, the Sn-rich solution phase (β) and Bi-rich phase (ρ) of the solidified filler alloy. Therefore, the η -layer is expected to form between the ε -phase and the solder alloy during the usage of the soldered assembly.

Conclusions

The local nominal composition of the effective joint region is a useful concept for designing, e.g., interconnection and microjoining metallurgies with a limited amount of filler alloy, or the extent of dissolution of a conductor metal into liquids or chemical reactions between thin metal overlayers. It provides useful information on the microstructures (phases and their compositions) present in the joint region with time, and thereby it combines kinetic information with thermodynamic information. Microstructural evolution of the joint regions between dissimilar materials can be better understood and controlled by utilizing stable and metastable phase diagrams and the stability diagrams that give the driving forces for kinetically feasible phase transformations together with the mass-balance requirement.

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