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Understanding the Growth of Interfacial Reaction Product Layers between Dissimilar Materials

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When one starts to analyze the evolution of the interfacial reaction product layers between dissimilar materials it is often found out that as the number of interacting species grows, the complexity of the analysis increases extremely rapidly. It may even appear that the task is just too difficult to be completed. In this article we present the thermodynamic-kinetic method, which can be used to rationalize the evolution of interfacial reaction layers and bring back the physics to the analyses. The method is conceptually very simple. It combines energetics—what can happen—with kinetics—how fast things take place. Yet the method is flexible enough that it can utilize quantitative and qualitative data starting from the atomistic simulations up to the experiments carried out with bulk materials. Several examples about how to utilize this method in material scientific problems are given.

Keywords thermodynamics, phase diagrams, diffusion in solid state, intrinsic diffusion, physicochemical approach, thermodynamic-kinetic method

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1. BACKGROUND

Multimaterial structures are everywhere around us. A wide variety of devices are based on the utilization of properties that arise when two or more different materials meet. However, it is common knowledge that at this intermaterial region, in addition to the desired functions, problems also frequently appear, owing to the excess growth of intermediate reaction product layers, for instance. To optimize the desired interfacial properties and at the same time to minimize the possible problems related to these same interfaces is a challenge that is not easy to meet. While striving for this goal one needs fundamental understanding about the evolution of the interfacial area under various environmental conditions.

The thermodynamics of materials provides information about the stability of phases (e.g., phase diagrams) and on the driving forces for chemical reactions and diffusion processes (for example, molar Gibbs energy and activity diagrams). This information is valid even though complete phase equilibrium (global) is seldom met in practical applications. However, stable or metastable local equilibria are generally attained at interfaces, and this provides a feasible method—together with kinetic information—for analyzing the progress of interfacial reactions in various multimaterial systems.^{1–3} To further aid this task concepts like the “local nominal composition” (LNC) in the effective reaction region, which utilize both thermodynamic and kinetic data, have been developed.⁴

During recent years it has become feasible to utilize atomistic calculations to obtain either missing data, such as enthalpies of formations of compounds, for thermodynamic calculations or to predict structures and formation energies of metastable or even hypothetical structures. This has greatly broadened the scope of the energetic description of materials. Several examples where *ab initio* calculations have been used to obtain thermodynamic knowledge of the system exist in the literature.^{5–13}

When one attempts to take into account the time frame of the changes taking place in the system under investigation, kinetic analyses must be combined with energetics. Here, one typically introduces different types of diffusion parameters extracted from experiments carried out under various conditions. Unfortunately, the use of, for example, different

diffusion coefficients in the literature is often vague and even erroneous.¹⁴ As, for example, interdiffusion, intrinsic, and tracer diffusion coefficients represent different type of information, it is important to know what coefficient to use under which conditions. The available thermodynamic data can be utilized in the kinetic calculations to provide for example driving forces for diffusion of different species or to investigate changes in the intrinsic fluxes of the diffusing elements and so forth.^{2,3} Often, one is also interested in the atomistic mechanisms of diffusion in addition to the above mentioned phenomenological approach. Here, in addition to the more traditional thermodynamic data, atomistic simulations can provide valuable insight when various diffusion mechanism and formation energies of defects for instance are considered.¹⁵ Finally, it is to be noted that, although assessed thermodynamic data for practically all important binary systems and a few relevant ternary (or even quaternary) systems are available, the diffusion kinetic data, even in binary systems, are generally limited, especially at low ($T \leq 150^\circ\text{C}$) temperatures.

When one starts to analyze the evolution of interfacial region between dissimilar materials it is often found out that one needs to deal with a large number of special techniques and to master large quantities of data. It may appear that the task is just too formidable to be completed. In this review we will present the so called thermodynamic-kinetic method which is conceptually very simple. It combines energetics—what can happen—with kinetics—how fast things take place (Figure 1). However, it is flexible enough that it can incorporate data starting from the very detailed atomistic simulations ending up to results obtained from the experiments carried out with bulk materials. The method can be used as a guide for ones thinking even in the absence of any quantitative data. Further, it provides simple means to assess, for example, the effect of current flow on the evolution of interfacial reaction layer growth or how alloying elements may change the kinetics of phase growth kinetics.¹⁶

It is frequently found out that when dealing with diffusion in ternary or even higher-order systems the mathematics becomes very complicated and the physical picture of the phenomena

FIG. 1. Schematic presentation of the thermodynamic-kinetic method.

under investigation may be blurred or disappears totally.¹⁷ It will be shown below that the thermodynamic kinetic method can be used to greatly simplify the analyses and bring back the physics to the phenomena under investigation. Finally, as graphical methods are frequently used in the thermodynamic kinetic method it will be shown that a large amount of quantitative data can be condensed into relatively simple diagrams.

In this article we will first briefly describe the fundamentals of the energetics part of the method. We will also introduce several diagram types that are frequently used in the thermodynamic-kinetic analyses. Then the kinetics part is discussed and especially the various diffusion parameters are introduced in considerable detail. After that we proceed to the actual thermodynamic-kinetic method. We will explain the basic assumptions that must be made when the method is used and on what they are based on. We will then continue to present several examples how useful this method is before going into final conclusions and to pointing out some future directions how the method could be further improved.

2. THERMODYNAMIC EVALUATION OF PHASE EQUILIBRIA

In principle, the constituent atoms and the basic laws of physics determine the properties of any given material. Therefore, it should be possible to predict the properties of different materials by using only the composition as the input knowledge. The approach that tries to achieve this is commonly referred as first principles or ab initio calculations.¹⁸ During recent decades approaches based on the Density Functional Theory (DFT) have started to live up to the above discussed expectations.^{19–26} The success of the approach is due to its ability to make quantitative predictions about many material properties that would otherwise be hard or even impossible to access experimentally in the laboratory. However, there are still many issues related especially to the utilization of the output of the ab initio calculations in real material scientific problems. One approach is to use

ab initio results as input data for other more “macroscopic level” simulation tools such as the Computer Calculations of Phase Diagrams (CALPHAD) approach.²⁷ In addition, during recent years it has become possible to calculate so called ab initio phase diagrams^{28,29} that can then compared with the phase diagrams calculated with CALPHAD method. In this way, a direct link from atomic level information to the macroscopic thermodynamic data can be achieved.

The data that goes into the thermodynamic assessment of a given system include all kind of experimental and theoretical information, such as calorimetric data, activity values from electrochemical measurements, vapor pressure measurements, microstructural information and results from ab initio calculations,^{29,30} for instance. There are a wide variety of different mathematical models for various kinds of phases that can be used to represent the available thermodynamic data for a given phase.^{29,30} In this article, we will not consider these models or the actual assessment procedure in any detail, as there are several comprehensive treatments available for the interested reader.^{29,30} On the contrary, we will focus here on the utilization of this assessed thermodynamic data in the analyses of the evolution of the interfacial region between different materials as well as show examples of how to visualize the data obtained with relatively simple diagrams.

When the models for the phases to be considered are formulated and all the available experimental and theoretical data has been fitted into these, the phase equilibria are computed by summing up all the Gibbs (free) energies (see Note 1) of individual phases and then minimizing—according to the second law of thermodynamics—the total Gibbs energy of the n-component system at constant temperature and pressure:

$$G_{tot} = \sum_{\phi} \sum_i (\mu_i^{\phi} n_i^{\phi}) = \sum_{\phi} y^{\phi} \sum_{i=1}^n \left(x_i \mu_i^{\circ} + RT \sum_i x_i \ln x_i + G_m^E \right), \quad (1)$$

where y is the relative amount of a phase ϕ , R is the universal gas constant, T temperature (in Kelvin), and x_i is a mole fraction of a component i in the system. The parameters μ_i^ϕ in Equation (1) represent the partial molar Gibbs energies or chemical potentials of the pure components and are taken either from available databanks or from the literature. At this point it must be emphasized that as only relative values of thermodynamic functions can be determined, an agreed reference state has to be established for each element or species in order to make thermodynamic treatment quantitative. In principle, the choice of the reference state is arbitrary as long as the chosen state is used consistently throughout the analysis. The chosen state is then defined to be zero and all other possible states of the element are compared against the reference state to obtain their relative stabilities. It should be noted that there are often some uncertainties related to the usage of reference states in the literature^{2,3,30} and thus one must be careful when carrying out the assessment work.

The total Gibbs energy of the system can be expressed as a function of chemical potentials, which are related to the activities of the components as follows:

$$\mu_i^\phi \equiv \mu_i^0(T) + RT \ln a_i, \quad (2)$$

where $a_i = \gamma_i x_i$ and γ_i is the activity coefficient. It is the difference in the chemical potentials of individual elements inside and between different phases that will drive the diffusion of elements in a system under investigation.

2.1. Different Kind of Equilibria

The chemical potential (or activity) of a component i will have the same value in all the phases that are in complete mutual equilibrium, and therefore the driving force for its diffusion will vanish in the system. However, in the case of reactions between dissimilar materials the equilibrium is typically attained only at the interfaces and, even though the activity of a component has the same value at the interface, there are activity gradients in the adjoining phases. These gradients, together with diffusivities, determine the diffusion of components in various phases of the reaction region.

The equilibrium states to be considered within the framework of this review are: (i) complete thermodynamic equilibrium; (ii) local thermodynamic equilibrium; and (iii) metastable equilibrium. It is to be noted that partial equilibrium, in which only some of the components fulfill the equilibrium condition, is also possible.

(1) Complete Equilibrium. As stated above, when the system is in complete equilibrium its Gibbs free energy has reached its minimum value and then the system is in mechanical, thermal, and chemical equilibrium with its

surroundings:³¹

$$dG = 0 \text{ or } \mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\phi. \quad (3)$$

In other words, when complete equilibrium is obtained the activities of all components ($i=A, B, C, \dots$) are the same in all phases ($\alpha, \beta, \dots, \phi$) and there are no gradients inside the phases. Naturally, complete (or global) thermodynamic equilibrium is seldom met in practical applications.

(2) Local Equilibrium. Local equilibrium means that the equilibrium exists only at the interfaces between different phases present in the system. The thermodynamic functions are continuous across the interfaces and the interfacial compositions can be obtained from the equilibrium phase diagrams. Therefore, the local equilibrium at the interphase between the α -phase and β -phase can be defined as:³¹

$$\begin{aligned} \mu_i^\alpha &= \mu_i^\beta \\ \mu_i^\alpha &= {}^0\mu_i^\alpha + RT \ln a_i^\alpha = {}^0\mu_i^\alpha + RT \ln x_i^\alpha + RT \ln \gamma_i^\alpha \\ \mu_i^\beta &= {}^0\mu_i^\beta + RT \ln a_i^\beta = {}^0\mu_i^\beta + RT \ln x_i^\beta + RT \ln \gamma_i^\beta \end{aligned} \quad (4)$$

where ${}^0\mu_i$ is the chemical potential of pure i in the standard state, μ_i^j the chemical potential of component i in phase j , a_i^j the activity of component i in phase j , x_i^j the mole fraction of component i in phase j , γ_i^j the activity coefficient of component i in phase j , R is the gas constant, and T the temperature. The local equilibrium concept is especially important when analyzing the interphasial reactions based on the so-called diffusion couple approach.^{32–34} When local equilibrium can be assumed to be fulfilled in the system, the reaction products formed between components in a binary system can be predicted by using the relevant phase diagram. After annealing at a certain temperature for a sufficiently long time, all the thermodynamically stable phases of the system at that particular temperature (and only them) will exist as layers between the end members. According to the Gibbs phase rule, only single-phase regions can be formed and the interfaces between the phases have to be macroscopically planar under constant pressure and temperature. For example, when pure Cu is in contact with liquid Sn at 250°C the intermetallic compounds that are formed in the interphasial region can be derived from the phase diagram (see Figure 2, red contact line). From the critically assessed thermodynamic description of the system more information can be obtained by utilising the Gibbs free energy diagram (see Figure 3), where the molar Gibbs energy curves of the solution phases fcc (α), bct (β), and Liquid (Liq) are presented with solid green, blue, and red lines, respectively. The intermetallic compounds Cu_6Sn_5 (η) and Cu_3Sn (ϵ), which have a narrow homogeneity range, have been modeled as stoichiometric line compounds. Here we have defined the β -Sn with body centered tetragonal and α -Cu with face centered

FIG. 2. Binary Cu-Sn phase diagram showing the schematic reaction structure as well the two temperatures considered.

cubic structure as the reference states for the pure Sn and Cu, respectively. Thus, the stability of other structures in the system will be compared to the “zero-level” defined by the above reference states. The local equilibria at the interfaces I, II, and III, marked with dashed, dotted, and double-dashed lines, respectively, are: $\mu_{Sn}^{Liq} = \mu_{Sn}^{\eta}$ and $\mu_{Cu}^{Liq} = \mu_{Cu}^{\eta}$, $\mu_{Sn}^{\eta} = \mu_{Sn}^{\epsilon}$ and $\mu_{Cu}^{\eta} = \mu_{Cu}^{\epsilon}$, as well as $\mu_{Sn}^{\epsilon} = \mu_{Sn}^{\alpha}$ and $\mu_{Cu}^{\epsilon} = \mu_{Cu}^{\alpha}$.

FIG. 3. Gibbs energy diagram of the Cu-Sn system at 250°C.

Both intermetallic phases [$Cu_6Sn_5(\eta)$ and $Cu_3Sn(\epsilon)$] can be observed after 64 min annealing as shown in Figure 4a. It is to be noted that the local equilibrium between Sn and Cu is, naturally, a function of temperature. If the temperature is raised to 500°C (see Figure 2, dotted blue contact line), Cu_6Sn_5 is not stable anymore and liquid Sn comes into direct equilibrium with Cu_3Sn , which can also be experimentally verified (see Figure 4b and 4c). Another phase (δ) becomes stable and can be observed between Cu_3Sn and Cu. The Gibbs free energy diagram at 500°C for the Cu-Sn system is presented in Figure 5. In addition to the interfacial compositions (such as $x_{Cu}^{Liq|\epsilon}$ and $x_{Cu}^{\delta|\alpha}$), the driving forces for diffusion can also be obtained from the Gibbs energy diagram. For example, $\Delta_r G_{Cu}^I$ represents the driving force for a pure Cu atom to diffuse through the δ - and ϵ -phases to the liquid| ϵ -interface to react with Sn atom, as will be discussed later on.

(3) Metastable Equilibrium. Metastable equilibrium can be defined as a local minimum of the total Gibbs energy of the system. Therefore, in order to obtain the global stable equilibrium some activation (e.g., thermal energy) must be brought into the system. It is to be noted that metastable equilibrium can also be complete, local, or partial; out of these the local metastable equilibrium concept will be used frequently in the thermodynamic-kinetic method. Very often one or more intermetallic compounds, which should be thermodynamically stable at a particular temperature, are not observed between two materials and these interfaces are therefore in local metastable equilibrium. Another situation where it is commonly

FIG. 4. SEM micrographs from the Cu-Sn reaction structure (a) at 250°C, (b) 500°C, and (c) optical micrograph at 500°C.

FIG. 5. Gibbs energy diagram from Cu-Sn system at 500°C.

encountered is in rapid interfacial reactions when one of the reacting materials is in a liquid state. Then, during the few first seconds, the solid material is in local metastable equilibrium with the liquid containing dissolved atoms, before the intermetallic compound(s) is formed at the interface. This can also be analyzed with the help of Gibbs energy diagrams, as explained in the next section.

2.2. Different Thermodynamic Diagram Types

Here, we will present some of the thermodynamic property diagrams that are most frequently used in the context of thermodynamic-kinetic method. We will assume that the reader is familiar with the common temperature composition diagrams³⁵ and instead concentrate on other perhaps less familiar diagram types.

2.2.1. Molar Gibbs Energy Diagrams

The molar Gibbs energy diagrams are extremely useful for analyzing interfacial reactions. A detailed presentation about their properties, use and so forth can be found from Hillert.³⁰ In Figure 6 the molar Gibbs energy diagram for the binary system Cu-Sn at 235°C is shown. For instance, the common tangent between the curves g_{bin}^L and g^n gives the equilibrium solubility of Cu to a liquid solder (L), which is given as $^eX_{Cu}^L$. The equilibrium solubility is the amount of Cu that can be dissolved infinitely slowly to liquid solder before the η -phase comes into equilibrium with the liquid. The formation of the η -phase does not, however, occur with this composition, as the driving force is zero at this point (no supersaturation). In real cases the dissolution of Cu does not take place infinitely slow and, therefore, the equilibrium solubility is generally

FIG. 6. Gibbs energy diagram from Cu-Sn system at 235°C.

exceeded. The solubility of Cu does not increase infinitely, but there is an upper limit for its value and this can also be determined from Figure 6. When more and more Cu dissolves into liquid eventually a situation is faced where the dissolution of more Cu would lead to the precipitation of pure metallic Cu out of the supersaturated solder. This corresponds to the common tangent construction between the solder and pure Cu. The tangent point in the liquid curve at this metastable equilibrium gives the upper value of Cu that can be dissolved into liquid solder at any rate, i.e., the metastable solubility ${}^mX_{Cu}^L$. When this value has been reached, also the driving force for the formation of the η -phase has reached its maximum (shown in the diagram as $\Delta g^{L \rightarrow \eta}$ in Figure 6). Since the metastable solubility is directly related to the dissolution rate of a given metal to a solder in question, it provides important information about the formation of intermetallic compounds between different metals and solders. In many cases its value is about 2–3 times larger than the equilibrium solubility.²

The common tangent construction can be used to determine the driving forces for diffusion of Cu through Cu_3Sn and Sn

through Cu_6Sn_5 in Figure 6. $\Delta\mu_{Cu}^\epsilon$ is the chemical potential difference of Cu between interfaces Cu_3Sn/Cu and Cu_6Sn_5/Cu_3Sn , which drives the diffusion of Cu through Cu_3Sn and $\Delta\mu_{Sn}^\eta$ is the chemical potential difference of Sn between the interfaces Sn/Cu_6Sn_5 and Cu_6Sn_5/Cu_3Sn , which drives the diffusion of Sn through the Cu_6Sn_5 layer. It is easy to realize that changes in the stabilities of the η and ϵ phases (in their Gibbs free energy) will change the values of $\Delta\mu_{Sn}^\eta$ and $\Delta\mu_{Cu}^\epsilon$ and thus increase or decrease the driving forces for diffusion of components in the system. This is shown in Figure 7. It is to be noted that the Gibbs energy diagram in Figure 7 is not a binary one, but a vertical section from a ternary 3-dimensional Cu-Ni-Sn Gibbs energy diagram. It is to be noted that in ternary systems the tie-lines are not usually in the plane of the vertical sections.³⁵ Therefore, the free energy values must be obtained along the diffusion paths (following the tie-lines) as done here. More details about this procedure can be found for example from Laurila et al.² and Yu et al.³⁶ Sn is known to be the main diffusing species in Cu_6Sn_5 whereas Cu is the main diffusing species in Cu_3Sn .^{37,38} From Figure 7 one can see

FIG. 7. Superimposed Gibbs energy diagrams from Cu-Sn and Cu-Ni-Sn systems showing the changes in the driving forces for diffusion.

that when, for example, 10 at-% Ni is added to $(\text{Cu,Ni})_6\text{Sn}_5$ its stability will increase as already reported earlier³⁹ and also indicated by first-principle calculations.⁴⁰ This will have effect on the chemical potentials (and thereby activities) at the Sn/ $(\text{Cu,Ni})_6\text{Sn}_5$ and $\text{Cu}_3\text{Sn}/\text{Cu}$ interfaces in such a way that the driving force for example for Sn diffusion through $(\text{Cu,Ni})_6\text{Sn}_5$ increases from ΔG_{Sn} to ΔG_{Sn}^* (almost four times ΔG_{Sn}) whereas the driving force for diffusion of Cu through Cu_3Sn decreases from ΔG_{Cu} to ΔG_{Cu}^* (about $3/5 \Delta G_{\text{Cu}}$). From Figure 7 one can also reason that driving force for diffusion of Sn over Cu_3Sn decreases and diffusion of Cu through Cu_6Sn_5 increases in comparison to binary case. As the diffusion flux is linearly proportional to the driving force, the material flux can be expected to grow over (Cu_6Sn_5) and to decrease over Cu_3Sn . When combined with the diffusion kinetic data from the system³⁹ this information can be used to calculate changes in the intrinsic fluxes of Sn and Cu inside the intermetallic compounds for instance.

2.2.2. Activity Diagrams

The activity diagram shown in the right-hand side of Figure 8 is one form of many different types of stability diagrams. In such a diagram the thermodynamic potential of one of the components is plotted as a function of the relative atomic fractions of the other two components at constant temperature and pressure. The activity values which are needed in the construction of such a diagram can be obtained from the assessed thermodynamic data. When calculating the activities of the components, the activities of the stoichiometric compounds at equilibrium are regarded to be one. It should be noted that the precision of the calculations is very much dependent on the accuracy and consistency of the thermodynamic

data used. Therefore, great care should be exercised when using data from different sources.

The edges of the diagram shown in Figure 8 represent the binary systems (Sn-Bi, Sn-Pb, and Pb-Bi). The ternary phase relations are represented by the inside of the diagram. In activity diagrams the stoichiometric single-phase regions are represented as vertical lines, one phase regions with extensive solubility as well as two-phase regions as areas and three phase equilibria as horizontal lines. It should be noted that tie-lines are valid inside the two-phase regions also in these diagrams. The diffusion path (see below) should therefore cross the two phase regions along a tie-line, as will be discussed below. In Figure 8 the identical phase regions in the ternary isotherm and in the activity diagram at the same temperature are identified with the same color. The three-phase equilibria are shown as red triangles in the isothermal section and as red horizontal lines in the activity diagram. As will be explained later on, if one wants to investigate the odds of diffusion of certain elements in a given reaction layer structure in a ternary system, activity diagrams for all the elements must be calculated. For example, in Figure 9 the activity diagrams for all three species of the C-Si-Ta system are shown. Figure 10 shows the corresponding isothermal section. The activity diagrams provide useful information about the formation of the reaction layer sequence when used together with the isothermal sections as will be shown.

2.2.3. Diffusion Couples and the Diffusion Path

Despite the fact that diffusion kinetics is formally introduced in Section 3, we will here discuss about the extremely important related concepts of diffusion couple and diffusion path, as the latter especially is very much thermodynamic in

FIG. 8. Isothermal section from the Bi-Pb-Sn ternary system at 120°C and the corresponding activity diagram (showing the activity of Bi) at 120°C.

FIG. 9. Activity diagrams for Si, Ta, and C in the C-Si-Ta system at 800°C.

its origin. Generally, in a binary system the interaction between components and the resulting reaction products can be predicted by using the relevant phase diagram. After annealing at a certain temperature for sufficiently long time, all the thermodynamically stable phases of the system at that particular temperature (and only them), will exist as layers between the end members. According to the phase rule only single-phase homogeneous regions can be formed, the interfaces between various phases must be macroscopically planar, and the concentrations at the interfaces of various phases can be read from the phase diagram (Figure 11).

If certain phases are absent, it may be caused by nucleation problems or by the “kinetic” stability described later on and in Paul et al.⁴¹ In a case when there are no nucleation problems associated with the phase formation and the diffusion is the rate-limiting step, the phase sequence after the reaction is determined by the corresponding phase diagram. In principle, in a specific binary system one can also say something about the temporal evolution of the system, if the interdiffusion

coefficients (see Section 3) in all the appearing phases are known. However, when one is dealing with higher-order systems the prediction of the reaction layers becomes much more difficult. In a ternary system the additional degree of freedom enables also the formation of two-phase regions and curved interfaces. This means that theoretically many different phase sequences are possible and the final structure cannot be, in general, interpreted directly from the phase diagram. In addition, the concentration and activity gradients are not necessarily into the same direction as generally in the binary systems, thus enabling for example the so-called “up-hill” diffusion.

Phase transformation will be diffusion controlled when the mass transport through the bulk is the rate-limiting step. Then the boundary conditions governing the rate of diffusion can be evaluated by assuming that whenever two phases meet at the interface, their compositions right at the interface are very close to those required by the equilibrium, and the thermodynamic potentials are continuous across the interface. This is called the local equilibrium approximation,²⁹ as discussed

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FIG. 12. Examples of possible morphologies for the reaction layer in a diffusion couple X/C. The corresponding diffusion paths are plotted on the isotherms. (© Elsevier. Adapted with permission from Elsevier.³⁴ Permission to reuse must be obtained from the rightsholder.)

FIG. 13. Experimentally determined isothermal section and the calculated activity diagram at 1273 K. The contact line (C.L.) and the diffusion path are also superimposed onto both diagrams. τ is the ternary phase. (© Hanser Publications. Adapted with permission from Hanser Publications.⁴⁷ Permission to reuse must be obtained from the rightsholder.)

isothermal section from the Cr-Si-C system at 1273 K. The experimentally determined diffusion path is superimposed into the isothermal section and into the activity diagram. From Figure 13 it is evident that Cr moves along its decreasing activity in the experimentally observed reaction sequence $\text{SiC}/\tau/\text{Cr}_3\text{Si}/\text{Cr}_3\text{Si}+\text{Cr}_7\text{C}_3/\text{Cr}_7\text{C}_3/\text{Cr}_{23}\text{C}_6/\text{Cr}$. The phase sequence $\text{SiC}/\text{Cr}_3\text{C}_2/\tau/\text{CrSi}/\text{Cr}_5\text{Si}_3/\text{Cr}_3\text{Si}/\text{Cr}$, another example of a diffusion path that fulfills the mass-balance requirement, is impossible from the thermodynamic point of view, since Cr would have to diffuse against its own activity gradient inside the ternary phase τ to get from CrSi to Cr_3C_2 .

It should be noted that in thin film samples (as when working with very thin diffusion barriers) the assumption of local equilibrium, which is necessary for the above treatment, is not self-evident. The assumption of local equilibrium requires that reactions at the interfaces are fast enough so that all the atoms arriving in the reaction region are used immediately and the rate-determining step is diffusion, as discussed above. However, with very thin layers this requirement may not be always fulfilled. The reasons for this originate mainly from special conditions prevailing during thin film reactions: (a) relatively low reaction temperatures, (b) small dimensions, (c) high density of short-circuit diffusion paths, (d) relatively large stresses incorporated in thin films, (e) relatively high concentration of impurities, (f) metastable structures, (g) large gradients, and so on. These conditions mean at least that the complete thermodynamic equilibrium is practically never met in thin film systems. However, based on experimental results the local equilibrium is generally attained at interfaces quite rapidly and can still be expected to prevail in most cases.³³ Therefore, the procedure presented above provides a feasible analysis method also for studying thin film reactions. Finally, it must be emphasized that there is no fundamental difference between thin film and bulk diffusion couples, and the differences often observed (i.e., sequential vs. simultaneous phase formation) occur because of the structural features of thin film structures (see the list above).

3. KINETIC CONSIDERATIONS

The driving force for interdiffusion is the difference in concentration (or more precisely in chemical potential or activity). Typically, diffusion kinetic analyses are based on the standard solutions of Fick's laws under certain boundary conditions. In the case of the steady state materials flow, i.e., when the concentration remains constant with time, Fick's first law states that the flux of element i (J_i) is directly proportional to the product of the diffusion coefficient (D) and the concentration gradient of an element i :³²

$$J = -D \frac{\partial c}{\partial x}. \quad (11)$$

For non-steady state diffusion, in which the concentration varies with distance and time, Fick's second law is applied:³²

$$\frac{\partial c}{\partial t} = - \frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right). \quad (12)$$

Thus, at constant temperature the rate of change of concentration is equal to the diffusivity times the rate of change of the concentration gradient. The utilization of Equation (12) requires there to be a significant (measurable) composition difference within a phase. Then the diffusion coefficients can be obtained by using either Boltzmann-Matano or Sauer-Freise analysis.³² However, if the system includes phases that have narrow homogeneity ranges (like many intermetallic compounds in solder interconnections), the above-mentioned analyses are not applicable and the method derived by Wagner⁴⁸ needs to be used.

The total Gibbs energy of the system, as shown in Equation (1), can be expressed as a function of chemical potentials, which are related to the activities of the components as follows:²¹

$$\mu_i^\phi \equiv \mu_i^0(T) + RT \ln a_i. \quad (13)$$

Since the chemical potential of a component i will have the same value in all the equilibrated phases, the difference in activity of a component (i.e., the driving force for its diffusion) will vanish at equilibrium. In the case of local equilibrium there are concentration gradients in the adjoining phases, but due to the chemical interaction between component atoms the diffusion is not necessarily driven by these gradients. Instead, the difference in chemical potential is the real driving force for diffusion as already discussed. A fundamental condition is that no atom can diffuse intrinsically against its own activity gradient as discussed above and in van Loo.³⁴ If a maximum is found experimentally in the activity profile of a component it is caused by the intrinsic movement of the other components. This condition is used as a criteria when thermodynamic prerequisites for the diffusion of certain species in a given reaction sequence is rationalized with the help of activity diagrams (Figure 8). In addition, the thermodynamic data obtained from the simulations can be utilized also in quantitative diffusion flux calculations, as shown next.

The intrinsic flux of a component A in, for instance, an A-B binary alloy will be written in terms of gradient in chemical potential μ :

$$J_A = -B_A C_A \frac{\partial \mu_A}{\partial x}, \quad (14)$$

where B_A is called the atomic mobility of A. The chemical

potential of A, μ_A , can be written in terms of activity, a_A :

$$\mu_A = \mu_A^\theta + RT \ln a_A, \quad (15)$$

where μ_A^θ is the chemical potential at the chosen standard state ($T = 298$ K; $p^\theta = 1$ bar) in J/mol and R is the gas constant (8.3143 J/molK). Substituting Equation (15) in Equation (14) and knowing that $dN_A = (V_m^2/V_B) dC_A$ [48] and $C_A = N_A/V_m$ one can obtain:

$$J_A = -B_A RT \frac{V_m}{V_B} \left(\frac{\partial \ln a_A}{\partial \ln N_A} \right) \frac{dC_A}{dx}, \quad (16)$$

with $\frac{d \ln a_A}{d \ln N_A} = \frac{d \ln a_B}{d \ln N_B}$ being the *thermodynamic factor* (a_A and a_B are the chemical activities of components and mole fraction is now denoted by N_i). The standard state is generally the pure element (Raoultian) reference state. In a binary system there is only one thermodynamic factor, but this is not the case in ternary systems (Note 2). It should also be noted that even in a binary system the situation may become more complicated if the vacancies are not present in their equilibrium amount. In that case their chemical potential is no longer zero and the binary system turns effectively to a ternary one.

The mobility of A, B_A , can be experimentally determined from a tracer experiment. If one deposits an “infinitely” thin layer of a radioactive isotope of A on the surface of an homogeneous A-B alloy, the activity as a function of the distance in the diffusion direction after annealing can be measured using the sectioning technique. By applying the method of Gruzin,⁵⁰ in which it is assumed that the atoms A and isotopes A* move identically, a so-called *tracer diffusion coefficient* D_A^* can be derived. The Nernst-Einstein relation directly connects the tracer diffusion coefficient to the atomic mobility:

$$D_i^* = B_i RT. \quad (17)$$

When we now take Fick's law, Equations (16) and (17), we arrive at a general relation between the intrinsic and tracer diffusion coefficients:

$$D_A = D_A^* \frac{V_m}{V_B} \left(\frac{\partial \ln a_A}{\partial \ln N_A} \right). \quad (18)$$

If the pertinent thermodynamic data are available, Equation (18) allows the calculation of intrinsic diffusivities from tracer diffusion coefficients. At this point, it is appropriate to remember that when we have calculated the phase and stability diagrams for the system under investigation we have this thermodynamic data. In this way, we can utilize tracer diffusion coefficients that are available in the literature, which will greatly reduce the amount of experimental work necessary when phase growth behavior in specific system is investigated. It is to be noted here that for example when using marker

experiments to determine intrinsic diffusion coefficients (D_i 's) (needed in the thermodynamic-kinetic analysis) they can be only determined at the Kirkendall-plane (i.e., at one composition). Thus, for a phase with wide solubility range many diffusion couples and/or multifoil experiments should be carried out to determine the D_i 's over the appropriate concentration range. However, when thermodynamic assessment of the system is at hand the D_i 's can be calculated with the help of Equation (18).

It is often the case that the phase under investigation grows with very narrow homogeneity range following the phase diagram and it is not possible to determine the vanishingly small concentration gradient to calculate the interdiffusion coefficient. To circumvent this problem, Wagner²⁰ introduced the concept of integrated diffusion coefficient ($\tilde{D}_{int}$) and can be expressed in terms of composition of i as

$$\tilde{D}_{int} = \int_{N'_i}^{N''_i} \tilde{D} dN_i = \tilde{D} \Delta N_i \quad (19)$$

where $\tilde{D}$ (m^2/s) is the interdiffusion coefficient, N_i is the composition of I, and $\Delta N_i = N''_i - N'_i$ is the narrow homogeneity range of the product phase.

Further, interdiffusion coefficient, $\tilde{D}$ is related to the tracer diffusion coefficient of the species, D_A^* and D_B^* by

$$\tilde{D} = (N_A D_B^* + N_B D_A^*) W \left(\frac{d \ln a_B}{d \ln N_B} \right), \quad (20)$$

where N_A and N_B are the composition of A and B in the AB-phase, $\frac{d \ln a_B}{d \ln N_B}$ is the thermodynamic factor, a_B is the activity of the element B and W is the vacancy wind effect and can be in most cases considered as one.⁵⁰ By replacing Equation (20) in Equation (19) and following standard utilization of common tangent construction in Gibbs energy diagrams.^{30,51}

$$\begin{aligned} \tilde{D}_{int} &= \int_I^{II} (N_A D_B^* + N_B D_A^*) N_B d \ln a_B \\ &= (N_A D_B^* + N_B D_A^*) N_B [\ln a_B^{II} - \ln a_B^I], \end{aligned} \quad (21)$$

where I and II represents the interfaces from which the product phase grows.

Furthermore, following Equation (21) and from the standard thermodynamic relation, $\mu_B = \mu_B^\theta + RT \ln a_B$, we can

FIG. 14. Micrographs showing the microstructures and position of Kirkendall planes in different systems.

write as

$$\begin{aligned}\tilde{D}_{\text{int}} &= (N_A D_B^* + N_B D_A^*) \frac{N_B (\mu_B^{\text{II}} - \mu_B^{\text{I}})}{RT} \\ &= - (N_A D_B^* + N_B D_A^*) \frac{N_B \Delta_r G_B^o}{RT},\end{aligned}\quad (22)$$

where G_B is the free energy of pure B, μ_B is the chemical potential of B, and $\Delta_r G_B^o$ is the driving force for the diffusion of B. The values of $\Delta_r G_B^o$ under different ambient conditions can be calculated from the appropriate data.

3.1. A Physico-Chemical Approach to Explain the Morphological Evolution in an Interdiffusion Zone

In many cases a characteristic morphology develops in the product phase which grows by reactive diffusion. For example, microstructures from three incremental diffusion couples from Co-Si, Ni-Si and Ni-Al systems are shown in Figure 14. It can be seen that a duplex morphology is present always when there is a Kirkendall marker plane present inside a phase.

The experimental results shown above indicate that the mechanism of the phase layer growth depends on the properties of the interface where it grows. In reactive diffusion, the product phase layers are grown because of the chemical reactions of diffusing component at the interfaces. Thus, even though one can use the phenomenological approach outlined above to investigate the thickness evolution of growing reaction layers, the reactions at the reaction interfaces are important if morphological evolution in the interdiffusion zone is to be investigated. It is to be noted that the interfacial reactions are not typically the rate controlling process in the examples discussed below, since in these the diffusion of components through the product phase take much longer time than the reactions at the interface, especially after the initial steps of the phase growth. However, there are many examples, specifically in thin film condition, where the growth of the phase may be reaction controlled.³³ For the following examples (Chapter 5), we will always consider that diffusion is the rate

controlling process. The equivalence of the physicochemical approach and the phenomenological relations discussed above is shown in detail in the Appendix.

4. THERMODYNAMIC-KINETIC METHOD

In Sections 2 and 3 the two fundamental subjects, energetics, and kinetics that can be utilized to rationalize the phase growth were briefly introduced. If one considers the phenomena of phase growth at a very general level one can see that there are always two factors that are involved, namely the thermodynamic driving force ΔG and the kinetic “factor” K . Thus, the phase growth can be described as a product of the two contributing factors $\Delta G \times K$. When one looks at this very generic expression at least three different cases can be thought of: (i) very large driving force (ΔG), but very sluggish kinetics (K), which will lead to slow or no growth of the phase in question; (ii) very low driving force (ΔG) but very facile kinetics (K), which again can lead to slow or no growth; and (iii) both factors are large enough so that the phase growth will be feasible. Thus, even with these very elementary considerations it is evident that if one only looks at the energetic or kinetic part alone, severe errors may be induced to the analysis. This is the very core of the thermodynamic-kinetic method (Figure 1). It combines both aspects outlined in the above sections to a one method that can be used for many different applications, as will be shown in Section 5. In addition, the method enables one to use both quantitative thermodynamic and diffusion kinetic data by providing clear guidelines what thermodynamic quantities or which diffusion coefficients should be used, for instance. To provide here a few connections between thermodynamics and diffusion kinetics one can think of: (i) using driving forces for diffusion obtained from the Gibbs free energy diagrams to calculate integrated diffusion coefficient based on the tracer diffusion data (Equation (22)); (ii) utilize the activity data to calculate intrinsic diffusion coefficients; (iii) use of Gibbs energy diagrams to investigate the effect of alloying elements on the driving forces for diffusion; and (iv) use the physicochemical approach to rationalize how the

TABLE 1

The integrated diffusion coefficients, $\tilde{D}_{int}$, molar volumes, v_m of the Co-silicides and the ratio's of intrinsic fluxes of Si and Co, $V_{Co}D_{Si}/V_{Si}D_{Co}$ at 1100°C in different phases are listed

	Phase	
	Co ₂ Si	CoSi
$\tilde{D}_{int}[\text{m}^2/\text{s}]^*$	$(1.5 \pm 0.5) \times 10^{-14}$	$(4.6 \pm 0.3) \times 10^{-14}$
$\frac{D_{Si}^*}{D_{Co}^*} = \frac{V_{Co}D_{Si}}{V_{Si}D_{Co}}$	0.06 ± 0.025	35 ± 15
$v_m[\text{m}^3 \cdot \text{mole}^{-1}]$	6.56×10^{-6}	6.60×10^{-6}

*average values obtained from different diffusion couples

forementioned changes affect the reactions and dissociation at different interfaces and so forth. Some of the ways to use thermodynamic-kinetic method are shown in Section 5. It must be evident, however, that a large amount of other possibilities also exist.

5. EXAMPLES OF THE USE OF THERMODYNAMIC-KINETIC METHOD

In this section we will show several examples of how to utilize the above outlined thermodynamic-kinetic method in various ways to rationalize reactive phase growth in different systems.

5.1. Physicochemical Approach to Study Co-Si System

Because of the extensive data available, we consider the phase growth in Co-Si system. Similar method can be used also in other systems. The useful data at 1100°C are listed in

FIG. 15. Co-Si binary phase diagram. (© ASM International. Adapted with permission from ASM International.⁵² Permission to reuse must be obtained from the rightsholder.)

FIG. 16. Schematic diffusion couple Co/CoSi₂.

Table 1. At first, we consider a diffusion couple of Co/CoSi₂, in which, according to the phase diagram shown in Figure 15, two phases, Co₂Si and CoSi should grow in the interdiffusion zone.

Schematic diffusion couple is shown in Figure 16. As shown in the figure, it is necessary to consider the presence of a Kirkendall marker plane in both phases. In the following, we consider that the total fluxes of Co and Si atoms that cross the Kirkendall marker plane in the Co₂Si phase are $[m]_{Co}$ and $[n]_{Si}$, respectively. Similarly, the total flux of Co and Si that cross the Kirkendall marker plane in the CoSi phase are $[p]_{Co}$ and $[q]_{Si}$, respectively. Growth of the Co₂Si phase occurs at the interface I by the reaction Co with Si that has diffused through this phase after being released by dissociation from the interface II. At the interface II, the same phase grows owing to the dissociation of Si from the CoSi phase. At the same time, the phase also grows because of reaction between CoSi and diffusing Co that has been released from the interface I. Likewise, CoSi phase grows at the interface II because of dissociation of Co from the Co₂Si phase and reaction of diffusing Si with the same phase. The dissociated Co atoms subsequently diffuse through the CoSi product phase and react with the CoSi₂ phase to produce CoSi at the interface III. Si that reacts with the Co₂Si phase at the interface II originates from the dissociation of the CoSi₂ phase at the interface III. Thus, it is clear that phases Co₂Si and CoSi grow (i) by consuming the neighboring phase(s) and (ii) at the same time they get consumed because of the growth of the neighboring phase(s). Hence, the two phases do not grow independently in this reaction couple. This is the situation irrespectively of the number of phases growing in the reaction couple (as long as it is equal or larger than two).

In terms of reaction equations these can be written as:

At the interface I (Co/Co₂Si on the Co₂Si-side)

At the interface II (Co₂Si/CoSi on the Co₂Si-side)

At the interface II (Co₂Si/CoSi on the CoSi – side)

At the interface III (CoSi/CoSi₂ on the CoSi – side)

Therefore, $3n$ moles of Co₂Si phase is produced at the interface I. At the interface II, $(3m + 3n)$ moles of Co₂Si is produced and at the same time $(3p + 3q)$ moles gets consumed. At the same interface, at the other side, $(2p + 4q)$ moles of CoSi is produced and $(4m + 2n)$ moles get consumed. At the interface III, $(4p + 2q)$ moles of CoSi is produced:

$$\begin{aligned} v_m^{\text{Co}_{2/3}\text{Si}_{1/3}} \times 3n &= \Delta x_{\text{Co}_2\text{Si}}^I \\ v_m^{\text{Co}_{2/3}\text{Si}_{1/3}} \times (3m + 3n - 3p - 3q) &= \Delta x_{\text{Co}_2\text{Si}}^{II} \\ v_m^{\text{Co}_{1/2}\text{Si}_{1/2}} \times (2p + 4q - 4m - 2n) &= \Delta x_{\text{CoSi}}^{II} \\ v_m^{\text{Co}_{1/2}\text{Si}_{1/2}} \times (4p + 2q) &= \Delta x_{\text{CoSi}}^{III} \end{aligned} \quad (23a)$$

The integrated diffusion coefficients can be written as

$$\begin{aligned} \tilde{D}_{\text{int}}^{\text{Co}_2\text{Si}} &= \frac{v_m^{\text{Co}_2\text{Si}}}{2t} [N_{\text{Si}}^{\text{Co}_2\text{Si}} p + N_{\text{Co}}^{\text{Co}_2\text{Si}} q] (\Delta x_{\text{Co}_2\text{Si}}^I + \Delta x_{\text{Co}_2\text{Si}}^{II}) \\ \tilde{D}_{\text{int}}^{\text{CoSi}} &= \frac{v_m^{\text{CoSi}}}{2t} [N_{\text{Si}}^{\text{CoSi}} m + N_{\text{Co}}^{\text{CoSi}} n] (\Delta x_{\text{CoSi}}^{II} + \Delta x_{\text{CoSi}}^{III}). \end{aligned} \quad (23b)$$

The ratio of diffusivities can be written as

$$\begin{aligned} \left. \frac{D_{\text{Si}}^*}{D_{\text{Co}}^*} \right|_{\text{Co}_2\text{Si}} &= \frac{\bar{v}_{\text{Co}} D_{\text{Si}}}{\bar{v}_{\text{Si}} D_{\text{Co}}} \bigg|_{\text{Co}_2\text{Si}} = \frac{q}{p} \\ \left. \frac{D_{\text{Si}}^*}{D_{\text{Co}}^*} \right|_{\text{CoSi}} &= \frac{\bar{v}_{\text{Co}} D_{\text{Si}}}{\bar{v}_{\text{Si}} D_{\text{Co}}} \bigg|_{\text{CoSi}} = \frac{n}{m}. \end{aligned} \quad (23c)$$

Using the values of molar volumes, integrated diffusion coefficients and the ratio of the intrinsic or tracer diffusion coefficients, as listed in Table 1, we find the values as

$$\begin{aligned} \Delta x_{\text{Co}_2\text{Si}}^I &= 32 \mu\text{m}, \Delta x_{\text{Co}_2\text{Si}}^{II} = 133 \mu\text{m}, \Delta x_{\text{CoSi}}^{II} = 168.5 \mu\text{m}, \\ \Delta x_{\text{CoSi}}^{III} &= 294.5 \mu\text{m}, m = 26.8, n = 1.6, p = 0.6 \text{ and } q = 21.0, \\ &\text{mol/m}^2. \end{aligned}$$

One interesting fact that should be noted here is that the thicknesses of all the sublayers are positive. Thus, despite getting consumed by the neighboring phases at the interface II, the values $\Delta x_{\text{Co}_2\text{Si}}^{II}$ and $\Delta x_{\text{CoSi}}^{II}$ are still positive. This means both phases will have stable Kirkendall marker plane and

FIG. 17. Kirkendall velocity profile.

bifurcation of the Kirkendall marker plane is expected.⁵³ This can be shown with the Kirkendall velocity diagram construction. Velocity of the phases can be estimated as

$$\begin{aligned} V_m^{\text{Co}_2\text{Si}}(n - m) &= 2tv_K^{\text{Co}_2\text{Si}} = x_K^{\text{Co}_2\text{Si}} = -165.3 \mu\text{m} \\ V_m^{\text{CoSi}}(q - p) &= 2tv_K^{\text{CoSi}} = x_K^{\text{CoSi}} = 134.6 \mu\text{m}. \end{aligned}$$

Note that here we have assumed the partial molar volume of the component to be equal to the molar volume of the phase. It should be noted here that for the velocity diagram plot, we have not determined the initial contact plane, as this cannot be carried out properly in the present case. However, if the range of the y and x axes are kept the same, the straight

FIG. 18. Micrographs from the Co/CoSi₂ diffusion couple.

FIG. 19. SEM micrograph of the structure of the component used in the electromigration study.

line $2tv_K = x_K$ will have an angle of 45° . That means the straight line can be drawn from one corner of the diagram to another, as shown in Figure 17. The location of the initial contact plane is the position at which the line intersects $2tv = 0$. The points of intersection by the straight line $2tv_K = x_K$ and the line representing the marker velocity in a given phases indicate the location of the Kirkendall marker plane in that phase. Since we have considered the phases with an average composition, the velocity of the phase is drawn by the straight lines with slope of zero. The interdiffusion zone in the Co/CoSi₂ phase is shown in Figure 18. It can be seen that the thickness of the phase layers are similar within the range of experimental error. As estimated, both phases have the Kirkendall marker plane. The presence of duplex morphology is also evident in both phases indicating the location of the marker planes. Note here that there was very small dissolution of Si in the Co end member, which is neglected in this analysis. This result into minor error in the values estimated.

5.2. Effect of Electron Flux on the Growth of ϵ and η -Phases in Cu-Sn System

Let us build on the above discussion and consider the effect of additional driving forces, such as electric field, on the growth of interfacial phases. Figure 19 shows a cross-section of the component with the directions of the current and electron flux superimposed. The electron flux enters the component from the source contact and leaves from the drain contact. In the forthcoming analysis of the effect of the electron flow on the IMC growth only the PWB side is considered. This is because, at the component side, the presence of Ag finish will make the analysis less quantitative.

Figure 20 shows the interfacial microstructures from solder|PWB interfaces from the samples that have been annealed at 110°C for 750 h and both the drain as well as source contacts after 750 h of constant current stressing. Due to the relatively complex geometry of the interconnections and the differences in cross-sectional areas, the current crowding effects and thus the differences in current densities cannot be easily addressed. However, even if only the direction of the electron flux is taken into consideration, the marked differences in the total IMC growth kinetics as well as the relative thicknesses on the Cu₆Sn₅ and Cu₃Sn intermetallic compounds can be observed when these differences are compared with the results obtained using the diffusion couple experiments.⁵⁴ Closer examination of Table 2 and Figure 20 reveals that when the flow of electrons is towards the PWB, the η and ϵ layers are almost of the same thickness, whereas in the opposite situation the thickness of Cu₃Sn is drastically reduced.

From the results of the steady current experiments, it can be seen that in the drain contact the electron flux comes from the solder side to the interface. Thus, the PWB pad is acting as the anode, meaning that the Sn flux towards the PWB is increased in both IMC layers whereas the flux of Cu from the PWB is decreased, which, based on the experimental results, seems to favor the growth of Cu₃Sn. This can be analyzed in more detail with the help of Figure 21 and the following reaction equations.

5.3. The Reaction Scheme

5.3.1. The Reaction Scheme

The reactions occurring at different interfaces of the reaction couple, as shown in Figure 21, can be expressed as

TABLE 2
Thickness data of the intermetallic compounds grown at the interface

	Cu ₃ Sn	Cu ₆ Sn ₅	Cu ₆ Sn ₅ to Cu ₃ Sn ratio
No current	0.8 μm 0.093 mol/m ²	3 μm 0.283 mol/m ²	3.8
Constant current from PWB	2.1 μm 0.244 mol/m ²	2.3 μm 0.217 mol/m ²	1.1
Constant current from solder	0.9 μm (~ no change) 0.1 mol/m ²	3.8 μm 0.360 mol/m ²	4.2

FIG. 20. SEM micrograph showing how the interfacial reaction layer structure depends on the direction of the electron flux.

follows:

Interface I :

Interface II – Cu₃Sn side :

Interface II – Cu₆Sn₅ side :

Interface III :

FIG. 21. Schematic presentation of the interfacial reactions occurring in the reaction couple.

Here, p and q are the moles of Cu and Sn, respectively, transferred per unit area through the Cu_3Sn phase during the total diffusion time t . Similarly, r and s are the number of moles of Cu and Sn transported during interaction per unit area through the Cu_6Sn_5 -phase layer. From the equations written above, it is clear that at the interface II, not only $(\frac{20}{9}p + \frac{8}{3}q)$ moles of Cu_3Sn grow, but also $(\frac{20}{9}r + \frac{8}{3}s)$ moles get consumed because of the growth of the Cu_6Sn_5 phase. Similarly, $(\frac{11}{9}r + \frac{11}{3}s)$ moles of Cu_6Sn_5 grow at the same interface, but $(\frac{11}{9}p + \frac{11}{3}q)$ moles get consumed by the Cu_3Sn phase.

The thickness of the parts of the product phase layers resulting from the interfacial reactions given above can be expressed

TABLE 3
Summary of the experimental results

After soldering	Cu_6Sn_5 [μm]	Cu_3Sn [μm]	IMC tot [μm]
No current	1	0.1	1.1
Drain	1	0.1	1.1
Source	1	0.1	1.1
1500 cycles			
No current	1.8	1.4	3.2
Drain	2.4	1.2	3.6
Source	3.6	0.3	3.9
3000 cycles			
No current	1.9	1.9	3.8
Drain	2.7	1.7	4.2
Source	4.4	0.5	4.9

as

$$\begin{aligned}
 4q \times V_m^{Cu_3Sn} &= \Delta x_I^{K_1} \\
 \left(\frac{20}{9}p + \frac{8}{3}q - \frac{20}{9}r + \frac{8}{3}s \right) \times V_m^{Cu_3Sn} &= \Delta x_{II}^{K_1} \\
 \left(\frac{11}{9}r + \frac{11}{3}s - \frac{11}{9}p - \frac{11}{3}q \right) \times V_m^{Cu_6Sn_5} &= \Delta x_{II}^{K_2} \\
 \frac{11}{9}r \times V_m^{Cu_6Sn_5} &= \Delta x_{III}^{K_2}
 \end{aligned}$$

where $\Delta x_I^{K_1}$ and $\Delta x_{II}^{K_1}$ are the thicknesses of the sublayers in the Cu_3Sn phase. $\Delta x_{II}^{K_2}$ and $\Delta x_{III}^{K_2}$ are the thicknesses of sublayers in the Cu_6Sn_5 phase. The subscript K refers to the Kirkendall plane formed at the location where the two growth fronts (i.e., from the interfaces I and II) meet. The subscript 1 refers to Cu_3Sn and 2 to the Cu_6Sn_5 phase. In Table 3, the experimental results about the effect of the electron flow on the growth of the IMCs are presented in a different way. In addition to thickness, the amount of each phase has been tabulated in terms of mole/m² for the sake of discussion.

5.3.2. PWB as the Anode

Let us first consider that there is an equal increase in the flux of Sn and an equal decrease in the flux of Cu in both phases. First, the two cases will be addressed separately and then the combined effect of the changes in the Cu and Sn fluxes is addressed.

(1) Increase in the Sn flux through the phases. Owing to the diffusion of Sn, 4 parts (in terms of moles) of the Cu_3Sn product phase will grow at the interface I plus a further 8/3 parts at the interface II by consuming the Cu_6Sn_5 phase. On the other hand, 8/3 parts will get consumed because of the growth of the Cu_6Sn_5 phase at the interface II. *So in total there will be a net gain of 4 parts of the Cu_3Sn phase in this case.*

On the other hand, 11/3 parts of the Cu_6Sn_5 phase will grow at the interface II and the same amount will get consumed because of the growth of the Cu_3Sn phase at that interface. *So there should be no net change in the layer thickness of the Cu_6Sn_5 phase.*

(2) Decrease in the Cu flux through the phases. If the flow of Cu decreases at the same rate through both phases, there will be 20/9 parts (in terms of moles) less production of Cu_3Sn at the interface II. Further, because of the decreased diffusion rate of Cu through the Cu_6Sn_5 phase, there will be 20/9 less consumption of the Cu_3Sn phase at the interface II. *So there should be no net change in the layer thickness of the Cu_3Sn phase because of the flow of electrons from solder to the PWB.*

On the other hand, as a result of the lower production of the Cu_3Sn phase at the interface II, there will be 11/9 parts less consumption of the Cu_6Sn_5 phase at that interface. At the same time (because of the decreased flow rate of Cu through the Cu_6Sn_5 phase), there will 11/9 parts less production of the Cu_6Sn_5 phase due to the dissociation of the Cu_3Sn phase at the

interface II. Finally, there will be lower production of 11/6 parts of the Cu_6Sn_5 phase at the interface III. *So there should be a net loss in the thickness of the Cu_6Sn_5 phase compared to the situation when there is no flow of electrons.*

(3) Combined effect of Sn and Cu fluxes. Thus, if the Cu and Sn fluxes are affected similarly in both phases, then for every 4 parts of Cu_3Sn phase increase there will be a corresponding 11/6 parts decrease in the layer thickness of the Cu_6Sn_5 phase. This means that for a 1-part increase in the thickness of the Cu_3Sn phase there will be a corresponding 0.46 parts decrease in the thickness of the Cu_6Sn_5 phase. In our experimental results we actually get for a 0.151 parts (mol/m²) increase in the thickness of the Cu_3Sn phase a corresponding decrease of 0.066 parts in the Cu_6Sn_5 phase. This can be put another way: for a 1-part Cu_3Sn phase increase, we get 0.44 parts of decrease in the Cu_6Sn_5 phase. This is very close to the analysis presented above and can thus be taken to indicate that the components (Sn and Cu) are indeed affected in a similar fashion by the electron flow. To conclude, it is now self-evident that it is time to re-examine the assumption that Sn should be strongly affected by the electron flux owing to its higher effective valence (Z^*).

5.3.3. PWB as the Cathode

Again, we consider there to be an equal decrease of Sn flux and an increase of Cu in both phases. The good match between the analysis results based on this assumption with the experimental results, shown above, gives us further confidence that this approach is justified.

(1) Increase in Cu flux through the phases. When the amount of Cu_3Sn increases by 20/9 parts (in moles) by consuming the Cu_6Sn_5 phase at the interface II because of the increase of Cu flux, 20/9 parts of the same phase will get consumed because of the growth of the Cu_6Sn_5 phase at the same interface. So there will be no net gain or loss in the thickness of the Cu_3Sn phase because of the increase in the diffusion rate of Cu. Owing to the increase in the flow of Cu through the Cu_3Sn phase, the increased consumption of 11/9 of the Cu_6Sn_5 phase will occur at the interface II. However, at the same time, 11/9 parts of the same phase will grow by dissociation of the Cu_3Sn phase, because of the increase in flow of Cu through this phase. A further increase of 11/6 parts of the Cu_6Sn_5 phase will occur due to the increase in the flow of Cu through the η phase. *So there should be no net gain in the thickness of the Cu_3Sn phase, but a net gain of 11/6 parts in the thickness of the Cu_6Sn_5 phase.*

(2) Decrease in Sn flux through the phases. Owing to the decreased diffusion rate of Sn through the Cu_3Sn phase there will be a corresponding four parts decrease in the layer thickness. Similarly, there will be 8/3 parts less produced at the interface II caused by the dissociation of the Cu_6Sn_5 phase. Furthermore, because of the decreased diffusion rate of Sn through the Cu_6Sn_5 phase, the consumption of the same phase will be 8/3 parts less at the same interface. *So the net loss for the Cu_3Sn should be 4 parts.*

TABLE 4
Summary of the experimental and calculated results

PWB acting as:	Effect of electron flux				Theoretical result		Experimental result	
	Flux of Sn in Cu ₃ Sn	Flux of Cu in Cu ₃ Sn	Flux of Sn in Cu ₆ Sn ₅	Flux of Cu in Cu ₆ Sn ₅	Thickness of Cu ₃ Sn	Thickness of Cu ₆ Sn ₅	Thickness of Cu ₃ Sn	Thickness of Cu ₆ Sn ₅
Anode	↑	↓	↑	↓	↑	↓	↑	↓
Cathode	↓	↑	↓	↑	±0	↑	±0	↑

Because of the decrease of Sn flux through the Cu₆Sn₅ phase, there will be 11/3 parts less production of the phase at the interface II by consuming the Cu₃Sn phase. At the same time there will be 11/3 parts less consumption of the same phase because of the low diffusion rate of Sn through the Cu₃Sn phase. *So there should be no net gain in the Cu₆Sn₅ phase layer thickness because of low flux of Sn through both phases.*

(3) Combined effect of Sn and Cu fluxes. Hence, when we consider the increase in the flow of Cu and the corresponding decrease in the flow of Sn to occur equally through both phases, there will be a net gain of 11/6 parts in the thickness of Cu₆Sn₅ and a net decrease of four parts in the thickness of the Cu₃Sn phase. However, the diffusion rate of Sn is known to be small compared to Cu in the Cu₃Sn phase, as shown in the ratios of the tracer diffusion coefficients:³⁸

$$\left. \frac{D_{Cu}^*}{D_{Sn}^*} \right|_{Cu_3Sn} = \frac{p}{q} \approx 30$$

$$\left. \frac{D_{Cu}^*}{D_{Sn}^*} \right|_{Cu_6Sn_5} = \frac{r}{s} \approx 0.35.$$

Consequently, the role of Sn in this phase can be neglected—especially in this particular case as the diffusion of Sn is further hindered by the electron flux.

Overall, therefore, there should be an increase in the layer thickness of the Cu₆Sn₅ phase, which is what we see in the

experiment. The results from the above analysis and from the experiments are summarized in Table 4 below.

5.3.4. Combined Effect of Electrical and Chemical Potential Gradients

What if one would have Ni at the opposite (component) side of the interconnection in the case of PWB is acting as the cathode? In this case the effect of chemical driving force due to the presence of Ni will be superimposed on top of the effect of electrical potential. This issue will be discussed next.

First, let us consider the presence of only the chemical potential as the driving force. (i) We have shown above that the dissolution of Ni in Cu₆Sn₅ will increase the driving force for diffusion of Sn and Cu through η -layer significantly. If there is about 5 at-% of Ni in the (Cu,Ni)₆Sn₅ the diffusion flux driven by the chemical potential should increase over (Cu,Ni)₆Sn₅ and decrease over that of Cu₃Sn. (ii) As can be seen from Table 5, the stability of (Cu,Ni)₆Sn₅ with 5at.% Ni is significantly higher than that without Ni. This may significantly influence the interfacial reactions at interface II. Especially the decomposition of Cu₆Sn₅ should be hindered in the case of thermal annealing, owing to the higher stability of the (Cu,Ni)₆Sn₅ compound. This will again favor the growth of Cu₆Sn₅. (iii) From Table 5 it is seen that the chemical potential of Cu at the (Cu,Ni)₆Sn₅ interface with about 5 at.% Ni dissolved is markedly higher than that at the component side where there is, according to energy-dispersive X-ray spectroscopy (EDS) analysis, about 15 at.% Ni dissolved in the (Cu, Ni)₆Sn₅ compound. This difference in chemical potential (about 15%; see Table 5) provides another, significant, driving force for Cu to diffuse from the PWB-side Cu₆Sn₅/solder interface to the corresponding interface at the component side. Thus, it is expected that the amount of Cu₆Sn₅ produced in the reaction at interface III will be decreased. If one combines all the information given above it may be concluded that the presence of, for example, 5 at-% Ni in (Cu,Ni)₆Sn₅ compound will favor the growth of (Cu,Ni)₆Sn₅ and hinder the growth of Cu₃Sn.

Next, consider that the electron flux is added on top of the chemical potential difference. (i) The electron flux drives Cu to diffuse through, not only Cu₃Sn and Cu₆Sn₅ layers, but also through the solder interconnection to the component side. This

TABLE 5

Thermodynamic calculations showing the effect of dissolved Ni on the stabilities of Cu₃Sn and Cu₆Sn₅ and the values of chemical potential of Cu in equilibrium with (Cu,Ni)₆Sn₅ as a function of the Ni mole fraction in the IMC compound

x(Ni)	ΔG_m (Cu ₆ Sn ₅) (J/mol)	ΔG_m (Cu ₃ Sn) (J/mol)	μ_{Cu} (J/mol)
0	−6952	−8267	−12742
0.01	−7679	−8270	−12815
0.05	−10226	−8597	−13239
0.1	−13070	−8418	−14071
0.15	−15636	−8859	−15252

additional driving force for the Cu diffusion will influence the interfacial reactions especially at interface III. The experimental results indicate that it will decrease the growth of Cu_6Sn_5 with respect to the case when the electron flow is absent. This will be at least to some degree counterbalanced by the corresponding increase in the Cu flux through the Cu_6Sn_5 . (ii) The flux of Cu through the Cu_3Sn is increased due to the electron flow, but as at the same time the flux of Cu is increased in Cu_6Sn_5 also, the net effect is difficult to estimate. Based on the above shown results it appears that the thickness of Cu_3Sn should remain approximately unaffected by the current flow.

Now we will try to summarize the above analysis. The facts that: (a) Cu diffusion is accelerated through Cu_6Sn_5 both by electrical and chemical potential gradients, but that of Sn is reduced by electrical current, should end up favoring the growth of $(\text{Cu,Ni})_6\text{Sn}_5$ but slightly less than in the absence of electrical driving force; (b) the stability of $(\text{Cu,Ni})_6\text{Sn}_5$ is much higher than that of without Ni, so this should favor $(\text{Cu,Ni})_6\text{Sn}_5$ over Cu_3Sn irrespectively of the presence of electrical driving force; (c) the increase of the flux of Sn through $(\text{Cu,Ni})_6\text{Sn}_5$ is hindered by the presence of electric current thus slightly reducing the growth rate of η -phase when compared to the situation where there is no current present; and (d) the flux of Cu away from the Cu_6Sn_5 /solder interface is increased in both cases and is manifested as the decrease in growth of Cu_6Sn_5 or $(\text{Cu,Ni})_6\text{Sn}_5$ in both cases. The net result should be that when *both driving forces* are present the Cu_6Sn_5 should be somewhat *thinner* and the Cu_3Sn should be somewhat *thicker* in comparison to the case when there is *only chemical potential gradient* driving the diffusion (in the absence of electrical driving force).

5.4. Use of Stability Diagrams to Rationalize Reactions in the Cu-Si-Ta-O-C System

The current trend of scaling down the dimensions of integrated circuits in order to achieve better electrical performance places serious demands for materials used in silicon-based devices. In particular, thin film interconnections are becoming the limiting factor in determining performance and reliability of integrated circuits. The interconnection delay, usually defined as the RC -delay, where R is the resistance of the interconnection and C is the associated total capacitance, is one of the most important factors determining the device/circuit performance.⁵⁵ Reducing the RC -delay to lower than or equal to the device delay has become both a material and an interconnection design/architecture challenge. Aluminum has been the most widely used material for metallization in very-large-scale integration (VLSI) and ultralarge-scale integration (ULSI) circuits during the past decades. However, as critical dimensions of devices have approached submicron dimensions, reliability requirements have ruled out the possibility of using pure aluminum. In order to improve reliability,

alloys with several additives such as Si, Cu, Ti, Pd, Cr, Mg, and Mn, have been tested.⁵⁶ The improvement in the electromigration performance thus achieved remains to date limited and is offset by the corresponding increase in interconnection resistivity.⁵⁶

Hence, emphasis and burden have been placed on materials, e.g., switching from Al/W based metallizations to Cu-based interconnections. Unfortunately, the interaction between Si and Cu is rapid and detrimental to the electrical performance of Si even at temperatures below 473 K.^{57–59} Mobility of copper is also relatively fast in SiO_2 and many polymers used as dielectric layers.^{60,61} Moreover, copper corrodes easily upon exposure to moisture or oxygen and a technique to passivate the copper surface is essential for multilevel copper interconnection.⁶² Therefore, owing to these multiple material problems, it is necessary to implement a barrier layer into the Cu metallization scheme and to encapsulate copper conductors from all sides. In this respect, diffusion barriers in Cu metallizations differ from the ones used in Al metallizations, where a diffusion barrier is generally used only at one interface. The need to encapsulate Cu conductor imposes also boundary conditions for diffusion barrier thickness. Among the most promising candidates to be used for this purpose are tantalum-based alloys and binary tantalum nitrides and carbides.

FIG. 22. HREM micrograph from the amorphous $\text{Ta}[\text{O,C}]_x$ phase from the sample annealed at 600°C for 30 min. (© AIP. Adapted with permission from AIP.⁶³ Permission to reuse must be obtained from the rightsholder.)

FIG. 23. Isothermal section from the evaluated metastable ternary Ta-C-O phase diagram at 600°C under the external oxygen pressure of about 0.2×10^{-4} Pa. The tie-lines in the TaC-Ta₂O₅ two-phase region are shown in the diagram. The contact-line (C.L.) between the TaC film and oxygen indicating the initial unstable equilibrium as well as the approximate composition of the TaC[O]_{gb} are also shown. (© AIP. Adapted with permission from AIP.⁶³ Permission to reuse must be obtained from the rightsholder.)

5.4.1. Si/TaC/Cu System

In this investigation copper and tantalum carbide films were sputtered onto cleaned and oxide-stripped (100) n-type Si substrates in a dc/rf-magnetron sputtering system. The deposition of TaC was obtained from the TaC-target (hot-pressed, 6.2 wt-% of C, main impurity Nb $\sim$ 0.3 wt-%) in argon atmosphere. The pressure before the deposition runs was approximately 10^{-5} Pa. The thickness of the tantalum carbide layers was 70 nm. The copper films with thickness of 400 nm were subsequently sputter-deposited without breaking the vacuum. Details of the experimental set-up and analyses can be found from Laurila et al.^{63,64}

The as deposited and films annealed up to 550°C showed clearly discrete layers according to the RBS measurement.⁶⁴ After annealing at 600°C the RBS spectrum suggested that interdiffusion of Ta and Cu had taken place.⁶⁴ Investigations with transmission electron microscope (TEM) revealed that after annealing at 600°C the formation of an amorphous layer at the TaC/Cu interface took place (Figure 22). The composition of the layer was determined to be Ta with marked amounts of oxygen and carbon from the very thin foil (tens of

FIG. 24. HREM micrograph from the Si/TaC interface from the sample annealed at 600°C for 30 min.

nanometers thick) with the X-ray energy dispersive spectrometry (EDS) in the analytical TEM. Equally high amounts of oxygen and carbon were not detected from either side of the amorphous layer. The layer is most probably Ta[O,C]_x (i.e., metastable oxide) containing some carbon released from the partly dissociated TaC layer. The formation of the amorphous layer was most likely caused by the presence of oxygen in the films (mainly at the grain boundaries) and also because of the diffusion of extra oxygen to the films from the annealing environment. The reasons leading to the formation of the layer can be analyzed with the help of Figure 23 that shows the evaluated metastable ternary Ta-C-O phase diagram. The grounds for using the metastable phase diagram instead of the stable one have been previously discussed.⁶⁵ As the oxygen content of the TaC films is in the order of 1-2 at-%⁶⁵ the initial composition is inside the TaC-Ta₂O₅-graphite three-phase region. The initial situation, marked as a point on the contact line (C.L.) connecting the end members of the diffusion couple (1/2O₂/TaC) in the isothermal section (Figure 23), is highly unstable, since the oxygen inside the TaC film (most probably located mainly at grain boundaries) has been forced there during the sputter-deposition.

The solubility of Ta₂O₅ into TaC is not known, but it is not expected to be substantial at low temperatures. Thus, there must be a large driving force for the formation of Ta-oxide that is in fact more stable than TaC. When the TaC[O]_{gb} films are annealed at elevated temperatures, oxygen starts to dissolve into the TaC matrix, since the solubility is expected to increase as temperature is elevated. This will ultimately result in the formation of the stable Ta₂O₅ and graphite. However, the kinetics of the system inhibits the formation of stable Ta-oxide (and thereby also graphite, issue that will be addressed below) at this considerably low temperature and the metastable amorphous layer is formed instead. As the

FIG. 25. HREM micrograph from the Si/TaC interface from the sample annealed at 750°C for 30 min. Normal arrows indicate the crystalline phase and arrows with a line at their end indicate the amorphous phase.

solubilities of impurities to metastable amorphous phases are generally higher than into stable crystalline ones, the amorphous layer can be expected to act as a “drain” for the excess oxygen. At the Si/TaC interface formation of a very thin amorphous layer was observed after annealing at 600°C. Based on the high-resolution micrograph shown in Figure 24 the amorphous layer appears to be quite transparent to electrons and therefore consist of relatively light elements. It is expected that the layer is an amorphous mixture of silicon and oxygen. The reasons for this interpretation are as follows. First, the lower part of TaC film also contains some oxygen

incorporated during the deposition (as shown by EDS elemental mapping). Second, again oxygen has been forced into the TaC layer during processing and the thin film system is far away from equilibrium. As discussed above, the equilibrium solubility of Ta_2O_5 into TaC is not known, but it is not anticipated to be substantial and therefore segregation of oxygen to grain boundaries and interfaces can be expected.^{66,67}

This would lead to the accumulation of oxygen at the Si/TaC interface and consequently to the formation of the thin amorphous interphase. In order to verify the composition of the amorphous layer EDS analyses were carried out. However, as the thickness of the layer is very small (Figure 25) reliable chemical analysis was not possible.

It should be noted that no sputter cleaning was applied to the Si substrate before TaC film deposition and therefore the “diffuse” interface is not caused by processing. Further, the layer is not expected to be an artifact resulting from sample preparation owing to its visual appearance and moreover, due to effect of temperature to its thickness as will be discussed below. After annealing at 750°C the amorphous layer at Si/TaC interface is clearly thicker than after annealing at 600°C (Figure 25). However, the thickness was still so small that it was not possible to reliably analyze the composition of the layer. It is expected that the layer is a $\text{Si}[\text{O,C}]_x$ type layer, i.e., amorphous mixture of silicon, oxygen, and carbon and the growth of the layer is due to the stability of stable and metastable Ta-oxides with respect to TaC. In addition to the growth of the amorphous layer, a mixture of amorphous (arrows with a line in their head) and crystalline phases (normal arrows) can be seen inside TaC layer at 750°C (Figure 25). The thickness of this phase “mixture” is quite large (10 nm). Figure 26 indicates that the phase “mixture” may be growing at the expense

FIG. 26. Bright field TEM micrograph from the Si/TaC/Cu sample annealed at 750°C for 30 min.

FIG. 27. Bright field TEM micrograph from the Si/TaC/Cu sample annealed at 800°C for 30 min.

of TaC layer and thus some of the carbon dispersed inside the amorphous layer is anticipated to be expelled from the partly decomposed TaC layer. Furthermore, the micrograph indicates that there is a boundary between the phase mixture and TaC. This may be quite important from the mechanical point of view as can be seen from Figure 26 that shows lower magnification micrograph from the whole structure. The ruptured TaC film seen in the micrograph is actually composed of three different layers. From Figure 26 it appears that the bottom layer (the two-phase mixture shown with higher magnification in Figure 25) is still in contact with Si whereas the other two layers have been torn away during sample fabrication. The large Cu_3Si inclusion is also clearly visible on the right-hand side.

At 800°C the layered metallization structure is completely destroyed owing to the extensive interfacial reactions. TaC layer seen at 750°C has been completely consumed at 800°C . Instead, one can see the formation of uniform TaSi_2 layer as well as a layer of SiC (Figure 27). The formation of the mixture of amorphous and crystalline layers inside the TaC layer observed at 750°C is expected to be related to the formation of TaSi_2 and SiC layers seen in this micrograph. It is probable that the "mixed" layer acted at least partly as a "precursor" for the crystalline TaSi_2 and SiC layers. The large Cu_3Si "precipitates" seen already at 750°C are also clearly present. There is also considerable amount of oxygen distributed through the layer as shown by the elemental analyses with EDS. This indicates that the Si substrate has been oxidized after the rupture of the overlying films. The thermodynamically expected formation of graphite was not detected even at 800°C . It is anticipated that owing to the very difficult nucleation of graphite the carbon will stay dispersed inside the amorphous phase. There are many reasons for the difficult

nucleation of graphite. One probable reason is that the crystal structure is quite complex, and so nuclei do not form easily. Another reason may be that because the coordination number is small, the formation of graphite in a purely solid state system requires a considerable increase in volume. The strain energy involved in this process makes the nucleation of graphite more difficult, since the mechanical energy associated with the formation of graphite must be extracted from the available free energy driving the nucleation process, as discussed above. It is expected that in this system carbon, which is released from the partially decomposed TaC layer and incorporated into the growing amorphous $\text{Ta}[\text{O},\text{C}]_x$ layer, stabilizes the amorphous structure.

In order to analyze the phase formation at the Si/TaC interface, one should have a firm thermodynamic description available. In principle, to investigate the reactions in the present system, the thermodynamic description of the five-component Si-Ta-C-O-Cu system should be used, since both Cu and O influence the reactions at the Si/TaC interface. Unfortunately, there does not exist adequately reliable data on all the multicomponent systems required. Therefore, the reactions at the Si/TaC interfaces at 800°C are examined with the help of the assessed Si-Ta-C ternary phase diagram together with the calculated activity diagrams (Figures 28a and 28b), since they already provide a considerable amount of useful information about the interfacial reactions. The main goal is to evaluate the possible reaction sequence at the interface. Hence, the ternary Si-Ta-C phase diagram was evaluated from the assessed binary thermodynamic data,^{68–70} and is presented in Figure 28. The question of carbon solubility in Ta_5Si_3 , which is expected to be substantial based on the other Me_5Si_3 silicides (e.g., $\text{Ti}_5\text{Si}_3 \sim 10 \text{ at-}\%$),⁷¹ must be carefully considered in the Si-Ta-C system. However, owing to the

FIG. 28. Isothermal section and the corresponding activity diagram for Si from the C-Si-Ta system at 800°C .

lack of reliable ternary data in the literature, ternary solubility has not been incorporated. Possible ternary compounds have similarly been excluded from the diagrams. Assuming that the local equilibrium is achieved at the interfaces of the thin film system, it is possible to use phase diagrams coupled with certain kinetic rules to predict possible or at least to rule out impossible reaction sequences. First, the mass-balance requires that the diffusion path, which is a line in the ternary isotherm, representing the locus of the average compositions parallel to the original interface through the diffusion zone,³⁴ crosses the straight line connecting the end members of the diffusion couple at least once. Second, no element can diffuse *intrinsically* against its own activity gradient³⁴ (i.e., from a low chemical potential area to a high chemical potential area). If such is observed it is induced by the movement of other components.

From the phase diagram it is evident that the Si/TaC interface is not in equilibrium and driving force for the formation of additional phases between the substrate and the TaC layer therefore exists (Figure 28a). Although there exists a TaC + TaSi₂ two-phase region in the phase diagram (Figure 28a), SiC must be formed to incorporate the carbon released after the formation of TaSi₂ in the reaction between Si and TaC, because of the mass balance requirement. The formation of SiC and TaSi₂ was confirmed with TEM investigations and therefore gives support to the assessed phase diagram. As shown in Figure 27 the reacted structure consists of layers of SiC and TaSi₂ on top of the silicon substrate. The original TaC is completely consumed during the reaction, since no traces of it can be found at 800°C. The reaction structure seems to be Si, then a layer of SiC, on top of that a layer of TaSi₂ and finally on the top layer of TaC (i.e., Si/SiC/TaSi₂/TaC), in which the TaC is used completely to yield the final structure Si/SiC/TaSi₂. Silicon is expected to be the first species moving at this interface owing to the following reasons. First, Si has been found to be the mobile species during the formation of TaSi₂ that occurs around 650°C in the binary Ta-Si system by Si indiffusion whereas the movement of Ta has not been observed under similar conditions.⁷² Second, chemical bonding between Ta and C in the TaC compound is expected to be strong, and breaking of these bonds, which is required for the release and subsequent diffusion of Ta, would require large amounts of energy. Owing to the facts stated above, diffusion of tantalum or carbon in this system is not considered to be highly probable. Consequently, Si is anticipated to be the main diffusing species at the Si/TaC interface around 800°C.

Whether the above-presented phase formation sequence is thermodynamically possible, can be investigated with the help of Figure 28b. As can be seen from the calculated activity diagram, Si can move along its lowering activity gradient in the proposed reaction sequence and therefore diffusion of Si in this particular reaction sequence is allowed on thermodynamic grounds. The examinations of the calculated activity diagrams for carbon and tantalum do not restrict diffusion of

these elements in the suggested reaction sequence either (Figure 28b). However, as already discussed, carbon and tantalum are strongly bonded to each other in the TaC compound and are not expected to move easily. Therefore, the reaction most likely starts by Si indiffusion into TaC (most probably via grain boundaries). This is followed by the formation of TaSi₂, which then leads to the accompanied dissociation of TaC. The released carbon is then available for the formation of SiC in the reaction with Si. This mechanism will finally yield the experimentally observed structure Si/SiC/TaSi₂. Thus, carbon and tantalum would not have to move and undergo only local rearrangement. Almost identical behavior has been observed in a very similar NbC/Si diffusion couple.⁷³ It must be emphasized that in the present analysis diffusion of oxygen and copper and their influence on the interfacial reactions between Si and TaC have been ignored.

5.5. Understanding the Diffusion and Growth Behavior in Cu-Nb-Sn System

Nb-Ti is a widely used superconductor material. However, its use is limited to applications of magnetic field up to 8T.⁷⁴ At present, Nb₃Sn intermetallic compound with A15 structure is considered to be one of the most suitable superconductors for the applications where field requirements go beyond the limit of Nb-Ti superconductors. However, intermetallic compounds are in general brittle and cannot be drawn as wire. To circumvent this problem, different manufacturing technologies have been developed for Nb₃Sn, such as bronze method, internal tin process, powder metallurgy route, Jelly roll process, ECN technique, and so forth.^{74,75}

FIG. 29. Isothermal section from the Cu-Nb-Sn system at 700°C.

In the bronze method, several Nb rods are inserted inside Cu(Sn) bronze alloy and drawn as a multifilamentary wire. The product phase Nb_3Sn is grown during the subsequent annealing by solid state diffusion. The efficiency of a superconductor wire largely depends on the presence of microstructural defects, such as grain boundaries and Kirkendall pores, grain size distribution, possible layer thickness differences, the variation of chemical composition over the cross section^{75–79} and so on. Since the evolution of microstructure is determined by the thermodynamics and kinetics of the system, the combined thermodynamic-kinetic approach provides a feasible tool to rationalize the formation of the observed reaction structures. There are basically two fundamental questions concerning the growth of Nb_3Sn by the bronze technique.

1. Why Sn is the only diffusing species during the reaction?
2. Why there is such a drastic increase in the thickness of the Nb_3Sn grown under same conditions, when Sn content of the Cu(Sn) alloy is increased from 7 at-% to 8 at-%?

What has been stated earlier indicates the thermodynamic-kinetic approach can be utilized to find answers to the above two questions.

With the aim to calculate the thermodynamic parameters to understand the diffusion process, the ternary phase diagram of the Cu-Nb-Sn system was calculated with the help of the assessed data from Hamalainen et al.,⁸⁰ Toffolon et al.,⁸¹ and Shim et al.⁸² In these calculations, all intermetallic compounds were modeled as binary compounds, since dissolution of ternary elements were found to be negligible based on the available information. In addition, no ternary compounds are known to exist in the Cu-Nb-Sn system. Isothermal section

FIG. 30. Isothermal section from the Cu-Nb-Sn system at 700°C where ternary solubility to Nb_3Sn has been introduced.

FIG. 31. Changes in the driving forces for diffusion of different species as a function of Sn content.

calculated at 700°C is shown in Figure 29. It is in general consistent with the recent publication on the thermodynamic assessment of the Cu-Nb-Sn system,⁸² except for two details. First, in Shim et al.⁸² the Nb_6Sn_5 phase is stable already below 700°C, different from our calculations and results of Pan et al.⁸² Second, there is also some ternary solubility to both Nb_3Sn and Nb_6Sn_5 in the diagram by Li et al.⁸¹ However, as the most relevant equilibrium to our analysis is the three-phase triangle Cu-Nb₃Sn-Nb, the occurrence of Nb_6Sn_5 phase that establishes equilibrium with the liquid phase, has no effect on the equilibria between Nb_3Sn and Cu, β or γ phases, even if it is stable already at 700°C or below. We also induced ternary solubility to Nb_3Sn (up to 10 at-%) and it did not have any effect on the three-phase triangle of interest (Figure 30) and did not markedly influence the values of chemical potentials of the species. Thus, from our analysis point of view these minor differences can be disregarded.

With the same set of assessed thermodynamic data the values of driving forces for the diffusion (the difference in chemical potential between two moving interfaces, $\Delta\mu$ in the diffusion couple) of given species over Nb_3Sn layer at 700°C, 750°C, and 775°C, as a function of Sn content of 6, 7, and 8 at.% in Cu-Sn alloy were calculated. The results are tabulated in Figure 31. Following the data on driving force, it is clear that only the diffusion of Sn through the product layer is allowed from the thermodynamic point of view. If Nb or Cu would diffuse intrinsically they should move against their own activity gradient, which is not possible.³⁴ However, if we consider the possible atomic mechanism of diffusion, based on the structure of the Nb_3Sn , the diffusion of Nb should be much easier than diffusion of Sn.⁸⁴ However, as seen above, from the thermodynamic point of view there is no possibility for diffusion of Nb (and Cu) in Nb_3Sn in Nb/Cu(Sn) diffusion couple, as there exist no driving force. Thus, the only way for the

FIG. 32. Experimentally measured thickness of the Nb₃Sn phase with two different Cu(Sn) alloys.

product layer to grow is by diffusion of Sn. That is also the reason why the TiO₂ particles used as inert markers are found near the Cu(Sn)/Nb₃Sn interface. The fact that Sn must be the only *intrinsically* diffusing species in this reaction layer sequence, from the thermodynamic point of view, is evident also based on the isothermal section shown in Figure 29 which shows also the diffusion path for the reaction sequence under investigation. When we have a diffusion couple Cu(Sn)/Nb (the contact line connecting the end-members is drawn as dashed line) the diffusion path must proceed, as drawn in Figure 29. This is because of the requirement that the contact line between the end-members must be crossed at least once; otherwise, the mass balance would not be fulfilled.³⁴ Thus, as can be seen from the figure, the diffusion path must always start from the Cu(Sn) end *towards* the Cu corner (i.e., towards higher activity of Cu) and then go to Nb₃Sn and finally to Nb. This also means that there should not be Cu inside Nb₃Sn, as in order to get there, it would have to move against its own activity gradient.

Further from the experimental results, we have seen that there is considerable increase in the growth rate and decrease in activation energy just because of small increase in Sn content from 7 to 8 atomic percent in the Cu-Sn alloy. This can be rationalized by considering the changes in chemical potentials between the two interfaces in the diffusion couple owing to the change in the Sn content. For example at 775°C, the difference in the chemical potential of Sn changes from -14217 in Nb/(Cu-7at.%Sn) couple to -16008 J/mole in Nb/(Cu-8at.%Sn) at the same temperature (Figure 31). The change is around 12.5%. We can roughly consider that the flux of elements is linearly proportional to the driving force, if we neglect any other differences in the properties of the end members, which might be caused by the change in the Sn content. Thus, we can

estimate that the amount of Sn flux through the product layer (Nb₃Sn) will increase approximately by 12.5%. Further, since one mole of Sn produces four moles of the product layer, we can expect that there will be at least 50% increase in the layer thickness because of the change in Sn content from 7 to 8 at.%. The results presented in the Figure 32 are consistent with this calculation. So the increase in layer thickness because of such a small change in Sn content in the (Cu-Sn) alloy is expected from the thermodynamic point of view. Since the change in driving force plays an important role in the activation energy, the considerable change in activation energy because of the change in Sn content is also rational. Consequently, the high value of activation energy for the growth of

Note 1: By utilizing the Gibbs free energy all forms of work (excluding expansion work) can be taken into account - $(\Delta G)_{p,T} \geq w' = \Sigma \mu_i n_i + \gamma A + z F U + \dots$, where the first term is the chemical part, the second is the surface energy contribution, the third is the electrical component, etc. Thus, Gibbs energy gives the amount of maximum additional (non-expansion) work that the system can perform. For all spontaneous processes the change in Gibbs energy must be negative. It should also be noted that the temperature and pressure of the system do not have to be constant during the whole process. It is adequate that they are the same at the initial and final stages. An example is an exothermic reaction taking place at temperature T, where the reaction heat is transferred to the environment at the end of the reaction, thus making T_{initial} equal to T_{final}. This is, of course, a consequence of the fact that the Gibbs energy is a state function and its value is only dependent on the initial and final states, not the path between them.

Note 2: It is to be noted that in ternary systems there are more than one thermodynamic factor. In a binary system the Gibbs-Duhem Equation (will be derived in Section 1.16) gives

$$X_A d\mu_A + X_B d\mu_B = 0$$

and

$$X_A d\mu_A = RT(dX_A + X_A d \ln \gamma_A)$$

$$X_B d\mu_B = RT(dX_B + X_B d \ln \gamma_B)$$

In a binary system $X_A + X_B = 1$

and thus $dX_A + dX_B = 0$

which finally gives

$$X_A \left(\frac{d \ln \gamma_A}{dX_A} \right) = X_B \left(\frac{d \ln \gamma_B}{dX_B} \right)$$

or

$$\frac{d \ln a_A}{d \ln X_A} = \frac{d \ln a_B}{d \ln X_B}$$

In a ternary system Gibbs-Duhem equation is written as

$$X_A d\mu_A + X_B d\mu_B + X_C d\mu_C = 0$$

and it is immediately seen there must be more than one thermodynamic factor in a given ternary system. In fact, there are four factors of which three are independent.

Van Loo et al. derived³⁴ equations for the four thermodynamic factors in a ternary system as well as the relation between the three independent ones and the fourth which depends on the other three as follows:

$$\Theta_{11} = \left(\frac{d \ln a_1}{d \ln X_1} \right)_{p,T,X_2} \quad \Theta_{12} = \left(\frac{d \ln a_1}{d \ln X_2} \right)_{p,T,X_1}$$

$$\Theta_{21} = \left(\frac{d \ln a_2}{d \ln X_1} \right)_{p,T,X_2} \quad \Theta_{22} = \left(\frac{d \ln a_2}{d \ln X_2} \right)_{p,T,X_1}$$

$$\Theta_{23} = \frac{X_1}{(1-X_1)} \left[\frac{(1-X_2)}{X_2} \Theta_{12} + \Theta_{22} - \Theta_{11} \right]$$

Nb_3Sn is also reasonable, since the phase growth occurs by diffusion of Sn, which is heavily dependent on the concentrations of antisite defects and vacancies present in the structure.⁸³

6. CONCLUSIONS

It was shown above that the thermodynamic-kinetic method can be used to rationalize the evolution of interfacial reaction zone in a wide variety of different cases. The power of the method is clearly in its generality. Its use is not restricted to metal-metal reaction couples or even to inorganic materials. It can be as well used in biological applications, as long as there is adequate data available. Especially in the field of soft matter, the data is unfortunately often missing. However, even without actual data about the system under investigation, this method can be used as an aid for reasoning. We have thermodynamics that give us criteria what can happen. It does not contain any information about time frame of the change and thus must be combined with kinetics (i.e. diffusion fluxes and their calculations). These together give us the microstructure (that contain also defect structures), which in turn will dictate how the system (for example an interconnection) will behave under operational conditions. In order to know the morphology and distribution of phases in the microstructure experimental investigation is needed, for example by Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). It is argued that by using the method outlined above, it is possible to avoid the so called “trial-and-error” approach that easily leads to confusing and even completely erroneous results. Finally, the “rise” of atomistic simulation techniques will further strengthen this method by providing information that is hard or even impossible to access experimentally.

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APPENDIX

For the sake of simplicity let us consider a diffusion couple of α and γ phases in which a line compound β grows in an interdiffusion zone, as shown in Figure A1. The stoichiometric compositions of the α , β and γ phases are $A_{1-m}B_m$, $A_{1-n}B_n$, and $A_{1-p}B_p$, respectively. Suppose α is a A-rich and β is a B-rich phase. Therefore, as shown in the figure, A dissociates from the α phase at the interface I to produce the product β phase. The dissociated A then diffuse to the interface II and reacts with the γ phase to produce the β phase. At the same time, B dissociates from the γ phase at the interface II to produce the β phase. The dissociated B diffuse to the interface I to produce the β phase. Therefore, at both the interfaces the product phase β is grown by dissociation and reaction of components. $[du]_A$ mol/m² is the flux of component A crossed the Kirkendall marker plane in small time dt . Similarly the flux of component B that crosses the marker plane in that small time is $[dv]_A$ mol/m². The location of the marker plane in the interdiffusion zone is shown by filled circles and the location is denoted as x_K . It is evident that the part of the product phase that is grown on the left hand side of the marker plane does so because of reaction and dissociation at the interface I. On the other hand, the part of the phase on the right hand side of the product phase from the Kirkendall marker plane will grow because of the reaction and dissociation at the interface II. Therefore, we need to write the reaction and dissociation equations for the corresponding two different interfaces.

FIG. A1. Composition profile and schematic reaction couple α/γ .

Reaction and dissociation equations at the interface I:

$$\begin{aligned} \frac{n}{n-m} du A_{1-m} B_m (\alpha \text{ phase}) &\rightarrow du [A]_d \\ &+ \frac{m}{n-m} du A_{1-n} B_n (\beta \text{ phase}) \quad \text{dissociation of A} \\ \frac{1-n}{n-m} dv A_{1-m} B_m (\alpha \text{ phase}) &+ dv [B]_d \\ &\rightarrow \frac{1-m}{n-m} dv A_{1-n} B_n (\beta \text{ phase}) \quad \text{reaction of B} \end{aligned}$$

Reaction and dissociation equations at the interface II:

$$\begin{aligned} \frac{n}{p-n} du A_{1-p} B_p (\gamma \text{ phase}) &+ du [A]_d \\ &\rightarrow \frac{p}{p-n} du A_{1-n} B_n (\beta \text{ phase}) \quad \text{reaction of A} \\ \frac{1-n}{p-n} dv A_{1-p} B_p (\gamma \text{ phase}) &\rightarrow dv [B]_d \\ &+ \frac{1-p}{p-n} dv A_{1-n} B_n (\beta \text{ phase}) \quad \text{dissociation of A} \end{aligned}$$

The amount of the β phase produced at the interface I is $\frac{1}{n-m} [mdu + (1-m)dv]$ and at the interface II is $\frac{1}{p-n} [pdu + (1-p)dv]$ mol/m². Let us assume that the molar volume of the product β phase is v_m^β . Further, suppose the thicknesses of the phase layer grown from interface I and II in this small time dt are $dx^{I/K}$ and $dx^{K/III}$. Therefore, we can write

$$\frac{1}{n-m} [mdu + (1-m)dv] v_m = dx^{I/K} \quad (\text{A1a})$$

$$\frac{1}{p-n} [pdu + (1-p)dv] v_m = dx^{K/III}, \quad (\text{A2b})$$

where v_m is the molar volume of the product phase. Further, we can write for the left-, right-hand side of the end members, and the composition of the product phases as $m = N_B^-$, $p = N_B^+$ and $n = N_B$. Therefore, Equations (A1) can be rewritten as

$$N_B^- du + (1 - N_B^-) dv = \frac{N_B - N_B^-}{v_m} dx^{I/K} \quad (\text{A2a})$$

$$N_B^+ du + (1 - N_B^+) dv = \frac{N_B^+ - N_B}{v_m} dx^{K/III} \quad (\text{A2b})$$

If the flux of diffusing components A and B are 0 at time $t = 0$ and u and v after the annealing time, t , we can write the

Equations (A2) by integrating as

$$N_B^- \int_0^u du + (1 - N_B^-) \int_0^v dv = \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx \quad (\text{A3a})$$

$$N_B^- u + (1 - N_B^-) v = \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx$$

$$N_B^+ \int_0^u du + (1 - N_B^+) \int_0^v dv = \int_{x_K}^{x^+} \frac{N_B - N_B^-}{v_m} dx \quad (\text{A3b})$$

$$N_B^+ u + (1 - N_B^+) v = \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{v_m} dx.$$

Next, we would like to write the expressions separately for u and v . Multiplying Equation (A3a) by $(1 - N_B^+)$ and Equation (A3b) by $(1 - N_B^-)$ and then by subtracting, we get

$$\begin{aligned} &N_B^- (1 - N_B^+) u - N_B^+ (1 - N_B^-) v \\ &= (1 - N_B^+) \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx \\ &- (1 - N_B^-) \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{v_m} dx \\ &u = - \left[(1 - N_B^+) \int_{x^-}^{x_K} \frac{N_B - N_B^-}{N_B^+ - N_B^-} \frac{1}{v_m} dx \right. \\ &\quad \left. - (1 - N_B^-) \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{N_B^+ - N_B^-} \frac{1}{v_m} dx \right]. \end{aligned}$$

Introducing the variable $Y_B = \frac{N_B - N_B^-}{N_B^+ - N_B^-}$ such that $1 - Y_B = \frac{N_B^+ - N_B}{N_B^+ - N_B^-}$, we can write

$$\begin{aligned} u &= - \left[(1 - N_B^+) \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - (1 - N_B^-) \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx \right] \\ u &= - \left[N_B^+ \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx \right]. \end{aligned} \quad (\text{A4a})$$

Multiplying Equation (A4a) by N_B^- and Equation (A4b) by N_B^+ and then by subtracting, we get

$$\begin{aligned} & N_B^+ (1 - N_B^-)v - N_B^- (1 - N_B^+)v \\ & v = N_B^+ \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{v_m} dx \\ & v = N_B^+ \int_{x^-}^{x_K} \frac{N_B - N_B^-}{N_B^+ - N_B^-} \frac{1}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{N_B^+ - N_B^-} \frac{1}{v_m} dx \\ & v = N_B^+ \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx. \end{aligned} \quad (\text{A4b})$$

Next, it will be shown that the intrinsic flux (Equation 14) of A that is J_A and the intrinsic flux of B that is J_B can be related to u and v . While doing this the sign of flux of A should be taken as positive since it diffuses from left to right and the flux of B as negative since it diffuses from right to left. Further, as the intrinsic fluxes are inversely proportional to $t^{1/2}$ we can write:

$$u = \int_0^u du = \int_0^t J_A dt = \int_0^t \frac{k}{t^{1/2}} dt = \frac{kt^{1/2}}{1/2} = 2tJ_A = -2tD_A \frac{\partial C_A}{\partial x} \quad (\text{A5a})$$

$$v = \int_0^v dv = - \int_0^t J_B dt = - \int_0^t \frac{k}{t^{1/2}} dt = -2tJ_B = 2tD_B \frac{\partial C_B}{\partial x}, \quad (\text{A5b})$$

where k is the proportionality constant. Note here that $J_i = -D_i \frac{\partial C_i}{\partial x}$. From Equations (A4) and (A5), we can write

$$D_A = \frac{1}{2t} \left(\frac{\partial x}{\partial C_A} \right) \left[N_A^+ \int_{-\infty}^{x_K} \frac{Y}{v_m} dx - N_A^- \int_{x_K}^{+\infty} \frac{1 - Y}{v_m} dx \right] \quad (\text{A6a})$$

$$D_B = \frac{1}{2t} \left(\frac{\partial x}{\partial C_B} \right) \left[N_B^+ \int_{-\infty}^{x_K} \frac{Y}{v_m} dx - N_B^- \int_{x_K}^{+\infty} \frac{1 - Y}{v_m} dx \right] \quad (\text{A6b})$$

These are the relations developed by van Loo.³⁴

From the standard thermodynamic relations $\partial C_A = \left(\frac{V_B}{V_m^2} \right) \partial N_A$, $\partial C_B = \left(\frac{V_A}{V_m^2} \right) \partial N_B$ we can write the ratio of

intrinsic diffusion coefficients as

$$\frac{V_A D_B}{V_B D_A} = \frac{J_B}{J_A} = \frac{v}{u}. \quad (\text{A7a})$$

We can write this with respect to the ratio of tracer diffusion coefficients as

$$\frac{D_B^*}{D_A^*} = \frac{V_A D_B}{V_B D_A} = \frac{J_B}{J_A} = \frac{v}{u}. \quad (\text{A7b})$$

The relation between the interdiffusion coefficients and the intrinsic diffusion coefficients has been derived by Darken⁸⁵ as:

$$\tilde{D} = C_A V_A D_B + C_B V_B D_A \quad (\text{A8})$$

And, since $N_B + N_A = 1$, $C_i = \frac{N_i}{v_m}$, we can write the interdiffusion coefficients with respect to u and v with the help of Equation (A5) as

$$\tilde{D} = \frac{V_m}{2t} \frac{\partial x}{\partial N_B} [N_B u + N_A v]. \quad (\text{A9})$$

In the case of a compound with very narrow homogeneity range, since we cannot measure the composition profile, the integrated diffusion coefficient is used. With respect to u and v , we can express this as

$$\begin{aligned} \tilde{D}_{\text{int}}^\beta &= \int_{N_B^I}^{N_B^{II}} \tilde{D} dN_B = \int_{x_\beta^I}^{x_\beta^{II}} \frac{v_m}{2t} [N_B u + N_A v] dx \\ &= \frac{v_m^\beta}{2t} [N_B^\beta u + N_A^\beta v] \Delta x_\beta. \end{aligned} \quad (\text{A10})$$

As explained earlier, the unknown composition range of the β phase is $N_B^{II} - N_B^I$, the thickness of the phase layer is $\Delta x_\beta = x_\beta^{II} - x_\beta^I$. The average molar volume of the phase, v_m^β can be considered as constant and during a fixed annealing time of t fixed amount of fluxes u and v transfers through the Kirkendall marker plane. The values of u and v can be estimated from the composition profile using the relations expressed in Equations (A4a) and (A4b). It should be noted here that by replacing these relations in Equations (A9) and (A10), we can derive the same relations, for the interdiffusion coefficient and the integrated diffusion coefficient derived by Wagner.⁴⁷

The velocity of the marker plane can be estimated by

$$v_K = -(\bar{v}_A J_A + \bar{v}_B J_B).$$

Replacing Equation (A5) in the above equation, we get

$$v_K = - \left(\bar{v}_A \frac{u}{2t} - \bar{v}_B \frac{v}{2t} \right) = \frac{1}{2t} (\bar{v}_B v - \bar{v}_A u). \quad (\text{A11})$$

If the values of the partial molar volumes are not known, we consider $v_m = \bar{v}_A = \bar{v}_B$, where v_m is the molar volume of the

product phase. Therefore, we can write

$$x_K = 2tv_K = v_m(v - u). \quad (\text{A12})$$

From the above discussion it is clear that the phase layer grows by different mechanism at the two different interfaces. Based on this we can expect a duplex morphology separated

by a Kirkendall marker plane, as shown in Figure 14. The approach outlined above can perfectly well be extended to cases where more than one phase grows in a given system as will be shown in Section 5. Further, we have shown that there exist relations between the phenomenological diffusion theory and the physic-chemical approach. This ensures that we can extensively utilize thermodynamic data in both kinetic “approaches.”