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Time-dependent Microstructural and Compositional Changes at The Interfaces between Materials in Electronics

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Abstract

Combined thermodynamic and kinetic models and concepts were presented for the better understanding, prediction and control of the time-dependent microstructural and compositional changes caused by diffusion, dissolution and chemical reaction processes at the interfaces between different materials. The chemical compatibility of the multitude of materials used in high-density electronics interconnections is increasingly important with decreasing solder volumes and thinner metallization layers, but needs also to be considered in the kinetically constrained local edge regions of the joints in conventional surface mount assemblies. The thermodynamic assessment of the joining or bonding system combined with the introduced qualitative kinetic understanding and models can indeed be used to improve the design and production of electronics devices. However, the presence of liquid phase, irregularities such as grain boundaries as well as the lack of kinetic and thermodynamic data and realistic kinetic software cause practical limitations to the extensive modelling concept.

Preface

This thesis has been carried out at the Department of Electrical and Communications Engineering of the Helsinki University of Technology. I'm most grateful to my supervisor Professor Jorma Kivilahti, not only for his sound guidance, support and time, but also for introducing me to the world of materials, interconnection technologies and electronics manufacturing. His continuous reminding of the practical constrains and the applicability of this work prepared me for the practical soldering problems that I have encountered later on.

Professor Frans van Loo from the Eindhoven University of Technology, I warmly thank for the guidance, support and the exiting discussions on the diffusion kinetics issues and problems. His enthusiasm and expertise really inspired my young scientific mind.

I want to thank all the people in the Laboratory of Solid State Chemistry and Material Science in Technical University of Eindhoven where I stayed for over 2.5 years. Especially I would like to mention John, Marco, Slobodan, Jan and Sasha not only as colleagues but also as friends. I want also to thank everybody in the Laboratory of Electronics Production Technology, and there, especially Vesa Vuorinen for his great help in the practical work for this thesis. The financial support from the Academy of Finland is greatly acknowledged.

I want with this thesis to honor the memory of my father and greatly thank my mother for her continuous support and love. Special thanks go also to Turon Toverit including O'No for all those moments of fun and off-laboratory activities.

Finally I want to express my humble gratitude to my wife Anna for the endless love and support. No words will ever be enough to thank her properly. And last, huge hugs for our lovely little Sofia for not eating or tearing apart the final manuscript of this thesis.

Oulu, October 2000

Kari Rönkä

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Publication I. K.J. Rönkä, A.A. Kodentsov, P.J.J. van Loon, J.K. Kivilahti, and F.J.J. van Loo, "Thermodynamic and Kinetic Study of Diffusion Paths in the System Cu-Fe-Ni", *Metallurgical and Materials Transactions A.* **27A** (1996) pp. 2229-38.

Publication II. K.J. Rönkä, F.J.J. van Loo, and J.K. Kivilahti, "Thermodynamic and Kinetic Study of Diffusion Paths in the System Cu-Ag-Zn", *Zeitschrift für Metallkunde,* **88**(1) (1997) pp.9-13.

Publication III. K.J. Rönkä, F.J.J. van Loo, and J.K. Kivilahti, "The Local Nominal Composition - Useful Concept for Microjoining and Interconnection Applications", *Scripta Materialia*, **37**(10) (1997) pp. 1575-81.

Publication IV. K. J. Rönkä, F. J. J. van Loo, and J. K. Kivilahti, "A Diffusion-Kinetic Model for Predicting Solder/Conductor Interactions in High Density Interconnections", *Metallurgical and Materials Transactions A*, **29A** (1998) pp. 2951 – 56.

The research program has been planned by the author together with the co-authors (J.K. and F.vL). The kinetic models were developed and the combined thermodynamic and kinetic calculations were carried out by the author. The experimental work and the microstructural characterisations were performed out in co-operation with the co-authors and the laboratory personnel except Publication II that was carried out fully by the author. The small volume effect (SVE) was originally introduced and thermodynamic descriptions were provided by the co-author (J.K). The author wrote the manuscripts which have been discussed in details with the co-authors.

Chapter 1

Introduction

Advanced high density interconnection and packaging applications in electronics require novel joining and bonding technologies such as Flip Chip bonding, Tape Automated Bonding (TAB), wire bonding, adhesives joining and transfusion bonding. The application of any of these bare chip mounting technologies as well as more conventional through hole or surface mount technologies in the industrial electronics manufacturing utilises several joining and bonding operations for assembling components on printed wiring boards being composed of multicomponent and multiphase materials.

The primary joining and bonding techniques used in electronics manufacturing are soldering, brazing, diffusion bonding and adhesive joining [1]. In soldering, two base materials, typically metals or metal coatings on metallic or non-metallic substrates are joined by employing a third, “filler” metal or alloy with the melting temperatures distinctly lower than those of the substrates. The brazing differs from the soldering by higher melting temperatures of the filler alloys which are in brazing above and in soldering below about 450 ºC. On the other hand, the diffusion bonding is a solid state operation where the bonding temperatures do not exceed the melting points of the materials to be joined, and therefore, the formation of the bond is notably based on the chemical diffusion of the component atoms across the joint interface. Adhesive joining is becoming more popular in electronics manufacturing. In addition to environmental issues there are several benefits provided by thermosetting or thermoplastic polymers that adhere to the mating surfaces with physical forces. Thus, it differs from other conventional techniques by producing- generally at relatively low temperatures - electrical or insulating contacts without chemical reactions.

The production and performance of reliable, cost-efficient high density fine-pitch electronics is not only limited by the development of very-large-scale integrated (VLSI) circuits but also by the quality of the interconnections between components and subsystems of the devices. The

quality of solder joint is dependent, firstly, on the wettability of the surfaces to be joined during the soldering operations and, secondly, on the subsequent ability of the joint to retain it's performance. In use the joint or contact regions are under continuous microstructural and/or compositional evolution including several kinetic processes. In diffusion bonding no intermetallic compounds are typically formed at the joint interface, and therefore, the bonding operation involves only solid state diffusion across the joint interface at a relatively high temperature. On the other hand, the typical soldering or brazing systems involve also the formation and growth of intermetallic compounds at a conductor/filler (solder or braze) interface or between metallizations. Despite the short time interval that the conductor metal or substrate to be joined are in contact with the molten solders or brazes during the industrial soldering or brazing operations, marked dissolution of materials into liquid fillers will occur causing a subsequently fast formation of intermetallic compound(s) at the liquid filler/substrate interface. These processes are expected to have important role in determining the wettability of the substrate materials by the liquid fillers. On the other hand, the ability of the joint to retain it’s electrical and mechanical performance during the long-time use of the assembly/device, especially at elevated temperatures being as high as 150 °C, or even higher in harsh automotive and avionics application environments, is remarkably endangered due to the growth of typically brittle intermetallic compounds at the solder/substrate interface.

Likewise, continuous miniaturisation of electronic devices increases the importance of the understanding and control of the physical and the chemical compatibility between materials in order to design and produce electrically and mechanically reliable high-density interconnections. Due to the so-called Small Volume Effect (SVE) one or more of the interconnection elements, either by diffusing, dissolving into and/or by reacting with the mating materials in the solder, metallization and substrate, can be consumed entirely during the joining operation or in the use of the assemblies leading to marked changes in the microstructures and the mechanical properties of the joints [2]. Therefore, also the physical and chemical properties of the solder joints and other interconnections are notably altered tending to decrease the overall reliability of the electronic device. The changes will occur faster as the relative solder volumes and the thicknesses of the metallization layers in the assembly decrease and the operational temperatures increase.

The Small Volume Effect increases the reliability risks and requirements for new high-density assemblies [2, 3]. The requirements vary significantly depending on the business segments such as computers, telecommunications, low-cost portables or automotive applications, with diverse operating environments and lifetime expectations. The reliability tests and analysis of the new high-density packaging and interconnection technologies have become an essential verification step in the electronics industry. The long time required for the careful reliability testing is, however, in contradiction with the increasing time-to-market requirements for the new products and, therefore, more attention has been paid to the reliability modelling. The reliable thermomechanical modelling requires knowledge of the material parameters of all different microstructures and compositions existing in the joint during the whole operational time of the assembly at different conditions.

The employment of a combined thermodynamic and diffusion kinetic approach, together with detailed microanalysis techniques, is necessary to obtain better understanding, and so, the control of the time-dependence of the microstructural and/or compositional changes caused by the diffusion, dissolution, and chemical reaction processes at the interfaces between different materials. The equilibrium phase diagrams of the systems provide useful information about the stability of the phases (i.e. microstructure), i.e. what phases can be energetically present in the joint region, as well as the driving forces for dissolution, intermetallic formation and diffusion processes. However, the thermodynamic data of the system need to be combined with the kinetic information in order to provide the knowledge of both the possible sequence of the events in the interconnection or joint region and how they depend on time. Due to the extreme complexity of the typical problems encountered in the actual interconnection and microjoining applications, the combined thermodynamic and diffusion kinetic approach was to be first developed in relatively simple model systems and then applied to the soldering applications that are more interesting from the electronics manufacturing point of view.

Chapter 2

Thermodynamic modelling

The thermodynamics of materials provide fundamental information on the phases (or microstructures) that can be energetically present or formed in a system at a certain temperature and pressure. It provides also driving forces for chemical reactions and diffusion processes. Meanwhile, kinetics tells us how fast these changes in the microstructure or composition can happen. In this chapter some basics of the thermodynamic modelling relevant to this work are introduced.

The thermodynamic software and databanks have significantly been developed during the last decade and several software packages are now commercially available [4, 5, 6, 7]. Thermodynamic assessment of a system provides a wide range of thermodynamic properties, as well as all stable and metastable phase equilibria as a function of temperature and pressure. The thermodynamic assessment is mostly used to present the isothermal cross sections revealing the stability regions of each phase present in the system. However, valuable additional information can be obtained, for example, from activity diagrams or from liquidus surfaces. It should be noted that the isothermal sections of phase diagrams or activity diagrams represent phase relations in heterogeneous systems. The complete equilibrium is never achieved in the interconnection or joining applications, where the contact regions are under continuous microstructural and/or compositional evolution. However, the binary or ternary phase diagrams can be utilised to determine the phases that are in local - stable or metastable - equilibrium with each other at the phase interfaces.

The most sophisticated thermodynamic software and databanks are based on the CALPHAD (CALculation of PHAse Diagrams) method [8]. The basic idea is to derive analytical expressions for the free energy functions of all phases by matching the best possible agreement between the experimental and calculated quantities with adjustable model parameters. Therefore, all relevant measured phase diagrams and experimental thermochemical data can be used for the assessment in a consistent manner. The total Gibbs energy of the system is expressed as a function of chemical potentials, μ_i^ϕ, which are related to the activity of the components as follows [9]

$$\mu_i^{\phi} = \mu_i^0(T) + RT\ln a_i = \mu_i^0(T) + RT\ln \gamma_i N_i \qquad (1)$$

where a_i is the activity of component i in a phase, N_i is a mole (or atomic) fraction of a component i, γ_i is the activity coefficient of the component i, R is the gas constant, and T is the absolute temperature. For an ideal solution, γ_i equals to 1 and the activity equals to the atomic fraction. However, for most real systems the activity deviates from the ideal behaviour because different kinds of atoms in the solution influence each other by attractive or repulsive mutual interactions. The value of the activity depends on the choice of the Reference State. Generally, the most stable phase at the desired temperature and pressure is chosen, and so, the activity of component i changes between 0 and 1 in that phase. The parameter μ_i^0 represents the partial molar Gibbs energy (chemical potential) of a pure component and is available in the SGTE databank [10, 11] and in literature. By summing up all the Gibbs (free) energies of individual phases (i.e. solutions and compounds), G_m^{ϕ}, the phase equilibria in the system can be computed by minimising, according to the second law of thermodynamics, the total Gibbs energy of n-component system (sum of all components in all phases) at constant temperature and as

$$G_{tot} = \sum_{\phi}\sum_{i}\left(\mu_i^{\phi} n_i^{\phi}\right) = \sum_{\phi} y^{\phi} \sum_{i=1}^{n}\left(N_i\mu_i^0 + RT\sum_{i}^{n} N_i \ln N_i + G_m^E\right) \qquad (2)$$

where y is the number of the moles of a phase ϕ (solution or compound). The phase diagram is obtained by finding the lowest common tangent planes to the functions, and so, finding the phase boundaries with equal chemical potentials for each component. The excess molar Gibbs energy, G_m^E, is generally presented by the Redlich-Kister-type polynomials [12], which take into account all attractive or repulsive interactions between the component atoms in each phase. This form is generally used to represent the binary contributions to the thermodynamic properties of higher-order systems. The excess part of the molar Gibbs free energy is presented then as

$$G_m^E = N_1 N_2 \sum_{k=0}^{n} L_{12}^k (N_1 - N_2)^k \qquad (3)$$

where L^k_{12} is the binary interaction parameter for a phase. The great advantage of this approach is, that it allows fitting of experimental data from many sources in a single consistent manner, and

the phase equilibria or thermodynamic properties can be calculated for such compositions and temperatures where no data were originally available.

Most of the solder/conductor systems include binary intermetallic compounds with a narrow region of homogeneity. Even though these “line compounds” have very small variations in concentration across the phase, there can still be large variations in chemical potential, and thus, in activities. Solution phases, either solid or liquid, require additional data on the interactions between different component atoms, presented in the excess molar Gibbs energy term. Generally, the thermodynamic descriptions are first developed for the three binary systems, and the ternary system is then described by extrapolating the binary solution phase energies by methods such as the one of Muggianu [13]. However, additional ternary parameters in some of the solution phases of the system may be needed for a better fit with the experimental ternary diagram.

Once the parameters in each phase are known, it is possible to calculate not only the stable, but also the metastable phase equilibria, as a function of the temperature and pressure. This is of a great importance in understanding, for example, the dissolution of a conductor metal into molten solders, as well as the formation of intermetallic compounds at the solder/substrate interface, as it has been discussed in Publications III - IV. It should be noted, however, that generally the thermodynamic functions have been optimised only to achieve a satisfactory fit between the experimental and calculated stable diagrams. Therefore, to obtain more realistic metastable solubilities and phase equilibria, the solder-substrate systems need to be re-optimised in a self-consistent manner; for example, so that the phase is weakly metastable as possible without altering the phase boundaries in the stable phase diagram.

In a binary system the chemical potentials of the components in a phase can be obtained from the intersects of the tangent of the Gibbs energy curve with the vertical axes, as it has been illustrated in Figure 1. In the two-phase regions the chemical potential of each component is equal in both solid solutions ($\mu_A^\alpha = \mu_A^\beta$ and $\mu_B^\alpha = \mu_B^\beta$) and so, the common tangent of the Gibbs energy curves determines the solubility of each component in each phase. In a ternary system, the phase equilibria are obtained by common tangent planes of Gibbs energy surfaces.

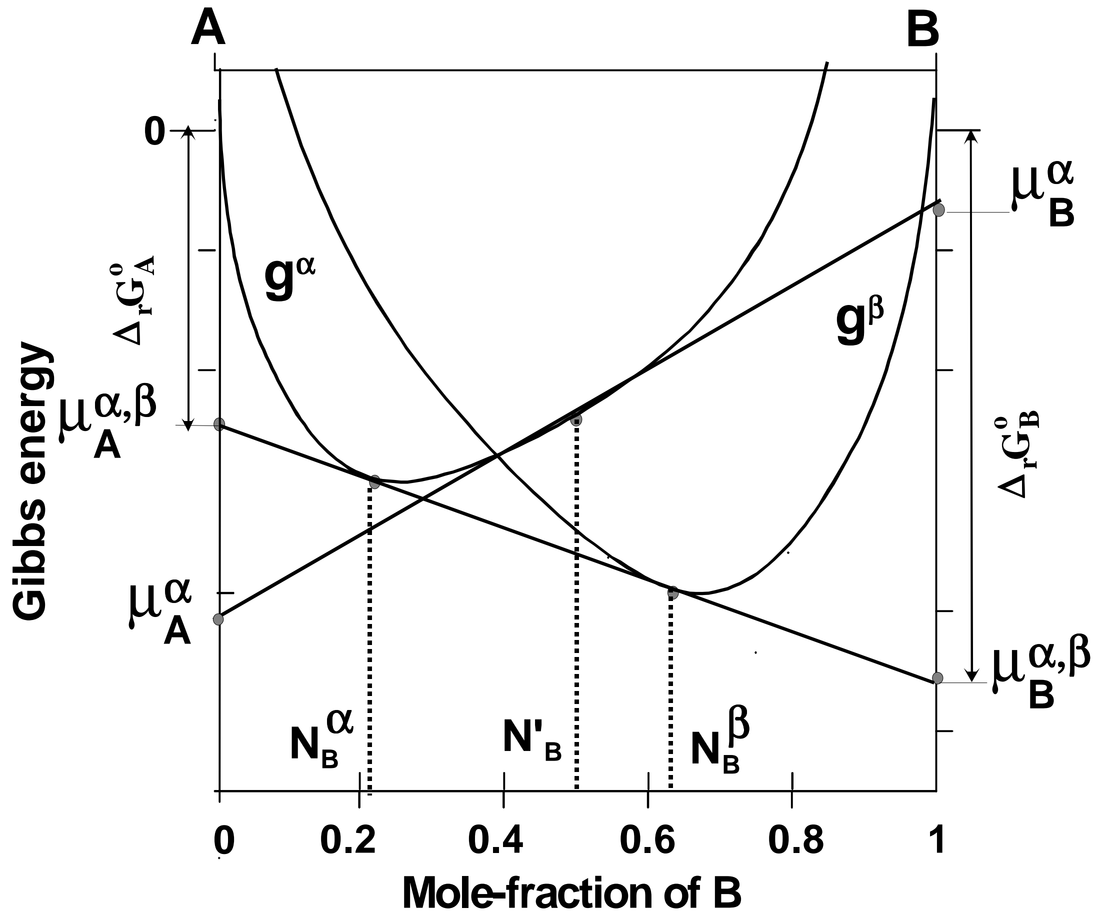


Fig 1. Gibbs energy of two solid solutions α and β as a function of mole (or atomic) fraction of component B in binary AB system. With any composition, e.g. N'_B, the chemical potentials of both components can be obtained in each phase by a tangent of the Gibbs energy curve. It should be noted, that in the steep parts of the Gibbs energy curve, a large change of chemical potential over a small concentration range is observed. The α and β phases are in equilibrium with the compositions N_B^{α} and N_B^{β}, determined by the common tangent construction.

The importance of the phase diagrams, especially when combined with the kinetic information, has been emphasised throughout this thesis. Various binary and ternary phase diagrams have been used for obtaining the phase relations and tie-line information in all the publications. In addition, the thermodynamic assessments have been used for obtaining various data, such as driving forces for dissolution, formation and growth of intermetallic compounds and chemical diffusion, the stability of intermetallics, the activities of the components, as well as both stable and metastable solubility of the conductor metal into the molten solders.

Even though significant amount of relevant metallurgical and electrochemical data are available in various databanks and in the literature [10, 11, 14, 15], in most cases the solder-substrate systems have been studied only empirically. The assessed thermodynamic descriptions of various binary and ternary systems used in this thesis are the following: 1. Cu-Fe-Ni, 2. Cu-Ag-Zn, 3. Cu-Sn-Bi-Zn, 4. Cu-Sn-Bi(Pb), 5. (Cu, Ni, Au, Ag, Pd)-Sn-(Bi, Pb), have been discussed in details in each publication. An extensive collection of thermodynamic assessments relevant in interconnection and packaging applications has been compiled by Kivilahti [16]. Moreover, assessments of several additional binary and ternary systems relevant in soldering applications and evaluation of new lead-free solders can be found in literature [17, 18, 19, 20, 21, 22].

Chapter 3

Kinetic modelling

The joining of dissimilar materials involves several kinetic processes, such as dissolution of conductor metal into the molten solder or braze, layer growth of intermetallic compounds, and chemical solid state diffusion. Generally, these kinetic processes quicken as the operating temperature increases. In the diffusion bonding, the joint between materials is essentially formed due to the solid state diffusion of the component atoms across the interface at a relatively high temperature. The joint formation depends, therefore, on the joining temperature and time, the mutual solubilities, and the diffusion rates of the diffusing components. On the other hand, during the soldering operations at low temperatures, the solid state diffusion in the typical conductor materials, such as copper and nickel, is very slow and can be neglected. However, the growth kinetics of reaction layers, formed between the conductor material and the reactive component in the solder, is in many cases controlled by the solid state diffusion of the component through these layers during several months and years of storage and the use of the assemblies. Notably, this is the case in the harsh environments, such as in the automotive and avionics applications where the operational temperature during the use can rise up to 150 °C. Also in telecommunication and portable products, the miniaturisation of the assemblies together with the increasing power consumption of the integrated circuits causes localised thermal management concerns. The solid state diffusion is also important in the thin metallization layers common used, for example, in Flip Chip interconnections.

In this chapter, the basic solid state diffusion kinetic functions and terms, relevant in this thesis, will be introduced.

3.1 Diffusion in multicomponent metallic systems

According to the Fick's first law [23], the flux of a diffusing particle, J (mol $m^{-2}s^{-1}$), is proportional to the concentration gradient of the substance

$$J_i = -D\frac{\partial c_i}{\partial x} \qquad (4)$$

where c is the concentration (mol m^{-3}), D is the diffusion coefficient (m^2 s^{-1}), and x is the space coordinate. Since the motion of different atoms in an organised lattice is relative, the chemical diffusion in the solids has to be fixed to a certain frame of reference. Most commonly the *interdiffusion* flux equations are used, related to the Matano frame of reference fixed to the ends of the sample. In this frame of reference, the sum of the interdiffusion fluxes of all components is zero. The so called Matano plane can be constructed by dividing the diffusion areas in the concentration profile, i.e. across this plane an equal amount of each component has arrived one side than has left another side. The interdiffusion coefficient, $\tilde{D}$, can be seen as a measure of mixing rate during the interdiffusion in a diffusion couple and it depends on the concentration.

In the Kirkendall frame of reference, the relative motion of atoms can be fixed to the mobile lattice sites. It is related to the Kirkendall plane that actually coincides with the original interface prior to the heat treatment. The location of this interface is of importance because it gives information on the relative diffusivities of the elements. In order to make the Kirkendall plane visible, inert markers placed at the original contact interface can be used, but sometimes “natural” markers can be found. The *intrinsic diffusion* fluxes represent the individual movements of the atoms, and so, the sum of the intrinsic diffusion fluxes at each section of the diffusion couple is not zero. There exists a net flux of atoms in one direction, which is balanced by the movement of vacancies to the opposite direction in order to conserve the lattice sites [24]. The vacancies must be created in certain parts of the sample (sources) and annihilated in other parts (sinks) of the diffusion couple. Generally this creation and annihilation of vacancies occurs at the surfaces, grain boundaries, or at the dislocations. However, in some cases due to the unequal diffusivities, the vacancies can be pilled up in one part of the diffusion couple leading to a nucleation and growth of the, so called, Kirkendall voids [24, 25]. They can lead to the damage of the joint such as in the case of the bonding of gold wires to aluminium metallization layers [26].

The relationship between the interdiffusion flux, $\tilde{J}_i$, and the intrinsic diffusion flux, $J_{i'}$, for a component i is given by [27]

$$\tilde{J}_i = J_i + c_i v^{K/M} = J_i - N_i \sum_{i=1}^{n} J_i \qquad (5)$$

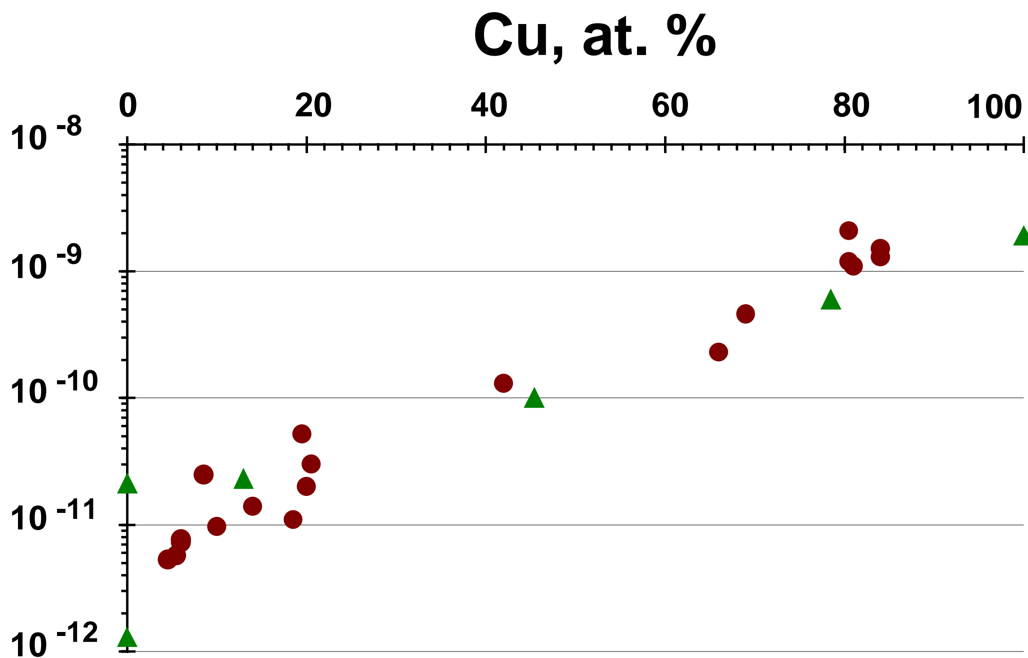
where $v^{K/M}$ is the relative velocity between the Kirkendall and Matano frames and N_i is the atomic fraction of component i. When inert markers have been placed at the original interface and observed after annealing, the term $v^{K/M}$ can be calculated from the experimental Kirkendall shift. The intrinsic diffusion flux J_i [mol m^{-2} s^{-1}], related to the Kirkendall frame of reference, can be written as [28]

$$J_i = -\frac{c_i D_i^*}{RT}\frac{\partial \mu_i}{\partial x} = -\frac{D_i^*}{V^m}\frac{N_i}{a_i}\frac{\partial a_i}{\partial x} \qquad (6)$$

where μ_i is the chemical potential of component i, a_i is the activity, D^*_A is the tracer diffusion coefficient [m^2 s^{-1}], R is the gas constant [J $mol^{-1}K^{-1}$], T is the temperature [K], and V^m is the molar volume [m^3/ mole of atoms], generally assumed to be constant. Knowing the activities of components as a function of composition and temperature, it is possible to use in the diffusion analysis, the gradients of chemical potentials, which are known to be the real driving forces for diffusion processes. Therefore, Eq. (6) can be taken as a basic equation for combining the thermodynamics and diffusion kinetics. It essentially shows that the diffusion flux of a component depends both on the driving force and the mobility of the component. Due to the lack of sufficient driving force, the flux is unavoidably small independent of the mobility, while even with very large driving force, the flux can be small if the component is essentially immobile. On the other hand, the relative movement of other components needs to be also considered, as has been discussed later in this chapter and in Publications I-II. The same consideration can be applied to other kinetic processes as well.

Different kinds of diffusion coefficients can be found in literature. The interdiffusion coefficient, $\tilde{D}$, can be easily determined from the binary diffusion couples using the Matano-Boltzmann analysis [29]. However, it does not give information on the relative diffusivities of the components. Even though the interdiffusion coefficient is a function of composition, in the commonly published diffusion analysis, they have been considered as constants in order to use analytical solutions and to avoid other practical difficulties in the analysis. In ternary diffusion couples, there are already four independent interdiffusion coefficients to be determined which is

only possible at the intersection points of two independent concentration profiles. On the other hand, the intrinsic diffusion coefficients, D_i, can be obtained from binary system only when the experimental Kirkendall shift is known from the inert marker experiments, and even then, only at the composition at the Kirkendall plane. Therefore, the most convenient choice for the independent parameter for the kinetic databanks is the tracer diffusion coefficient, D^*_i, which describes the motion of isotope A^* atoms in the solution phase or intermetallic compound of a certain composition. Alternatively the mobility, M_i which is related to the tracer diffusion coefficients ($D^*_A = M_i RT$), can be used. All these diffusivities are strongly dependent on temperature, which is typically expressed with an Arrhenius plot, ln (D/D_0) vs. 1/T. The mobility of each component depends strongly on the composition of the alloy as can be seen in Figure 2



from Publication I. Some alloying elements increase the mobility while others decrease them, as was discussed in Publications I-II.

Fig. 2. The tracer diffusion coefficients of copper (circles) as a function of the atomic fraction of copper calculated at the intersection points at 1000 °C. The literature data in binary Cu-Ni and Fe-Ni alloys [30] have been calculated from Arrhenius plots and are presented as triangles. The values in the binary Fe-Ni system are shown on the axis, $N_{Cu} \rightarrow 0$. The highest values are in pure nickel and the lowest in pure iron.

The tracer diffusion coefficients are usually determined by isotope experiments. However, a method to calculate the three tracer diffusion coefficients at the intersection points of diffusion paths in a substitutional ternary metal system has been presented in Publication I and further applied in Publication II. Using the thermodynamic data available, an experimental composition profile can be converted to a profile of activity or chemical potential. Therefore, at the intersection point of two independent diffusion profiles, the four interdiffusion coefficients and the three tracer diffusion coefficients can be calculated as a function of composition at the particular temperature.

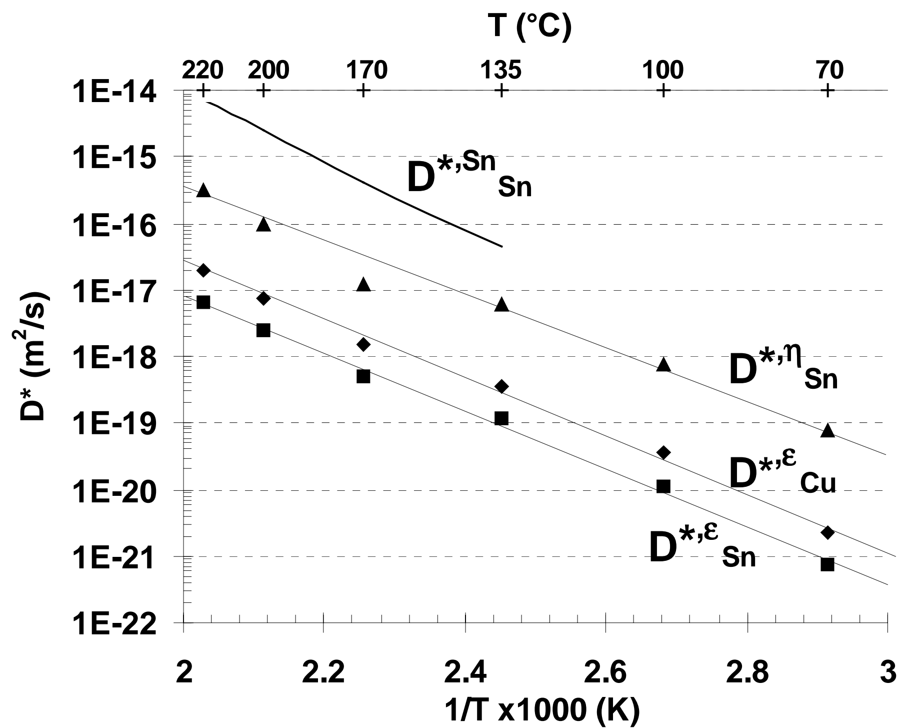


Fig. 3. Arrhenius plots of the mobilities of Sn and Cu in the η- and ε- phase in relation to the mobility of Sn in pure tin [1].

For phases which have a narrow homogeneity range, i.e. line compounds, the concentration gradient in the phase approaches zero. This makes the determination of the interdiffusion coefficients inaccurate or even impossible. Wagner has introduced the integrated diffusion coefficient, D_{Int}, which is the binary interdiffusion coefficient, $\tilde{D}$, integrated over its (unknown) limits of homogeneity [31]. In Publication IV, a kinetic model to calculate the intermetallic layer growth rate using the integrated diffusion coefficients has been presented for a substrate/solder-system and demonstrated with the help of the ternary Cu/SnBi system. A method for the determination of the mobility of tin and copper in the Cu_6Sn_5 (η) and Cu_3Sn (ε)

intermetallic compounds from the experimental binary Sn-Cu diffusion couple is also shown as can be seen in Figure 3. This is of great importance since the mobility of each diffusing component in the intermetallics are material constants at constant temperature and they can be used with various solder compositions as long as the intermetallics remain relatively pure binary phases.

3.2 Prediction of diffusion paths and layer sequence

The prediction of diffusion-controlled transformations in the joint region is very much connected to the understanding of the diffusion path through the joint. The diffusion path is defined as the set of the average compositions, measured in a plane parallel to the original interface going from one terminal (or starting) material to the other [32]. Both qualitative and quantitative models for predicting the diffusion paths in binary and multicomponent systems have been suggested by several authors [27, 28, 33, 34, 35, 36, 37, 38, 39, 40]. However, especially in multicomponent systems, this task is very difficult.

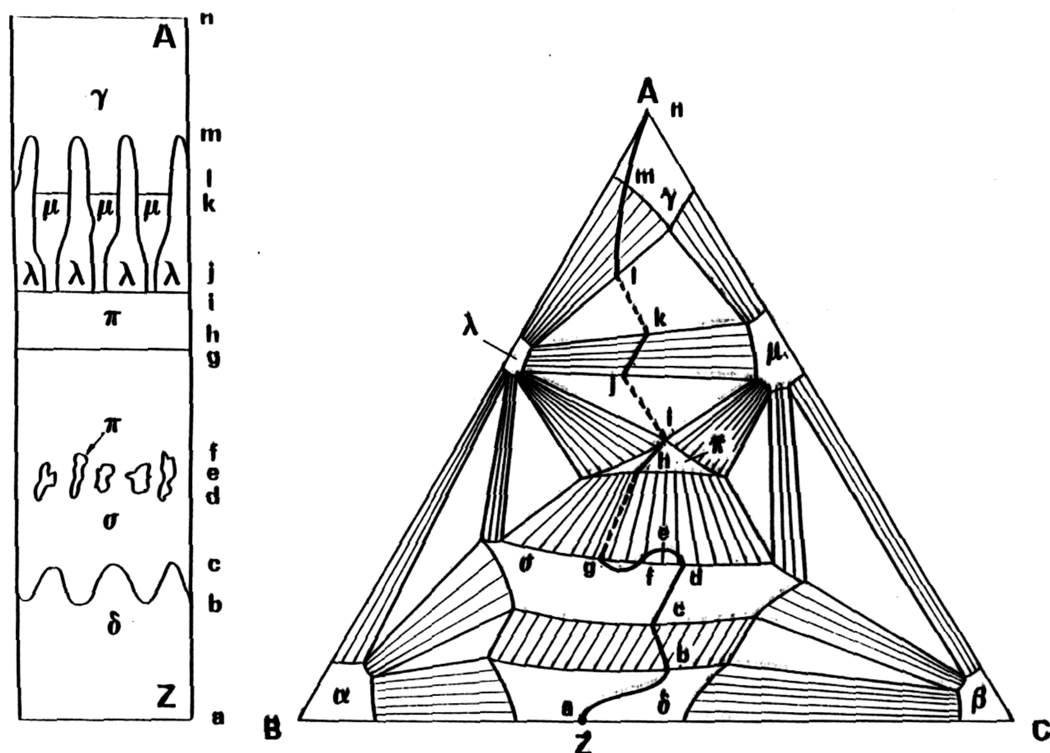


Fig. 4. Possible morphologies for the reaction layer in a schematic diffusion couple A/50%B-50%C. The corresponding diffusion path is plotted on the ternary isothermal cross section.

When two metals or alloys are brought into a contact at elevated temperatures, interdiffusion as well as possible nucleation and growth of intermetallic compounds can occur. According to the phase rule, the reaction products will, in multiphase binary systems, always be formed in layers bounded by planar interfaces. The phase diagram of the binary system determines the number and the composition of the phases formed between the end members of the diffusion couple, provided that no nucleation problems occur. The thicknesses of the layers of the various phases are not interrelated but they depend on the values of the diffusion coefficients in each phase. In a ternary system, however, the diffusion path cannot be predicted simply from the phase diagram alone since an infinite number of possible diffusion paths are available, and therefore, kinetic information of the system is required. In ternary systems, non-planar interfaces are also possible because of the extra degree of freedom as can be seen in Figure 4

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According to Kirkaldy and Brown [41], given a specific semi-infinite ternary diffusion couple, there is only one diffusion path at constant temperature and pressure. However, when one of the terminal alloys has a limited volume, this statement is not true anymore, since the composition of the terminal alloy can change due to the diffusion or chemical reaction. In time, this can even lead to the total disappearance of the terminal phase. Kirkaldy et al. [41] have given a number of rules concerning the course of the diffusion path. The main constrain is the mass-conservation law: no material can be lost or created, provided that the system do not contain very volatile components. This forces the diffusion path to cross at least once the straight connection line between the starting material compositions in a ternary phase diagram at a constant temperature (i.e. between A and Z in Figure 4). This also means that the thickness of the various layers are interrelated since the total layer thickness and the morphology is dependent on the rate limiting phase. In many cases, the diffusion path goes through several phases and the concentration profile is discontinuous. When the two phases are in equilibrium the chemical potentials of each component are equal in both phases at the planar interface, and so, the diffusion path follows a specific tie-line in the two-phase region. If the diffusion path crosses the tie-lines, the interface is not straight any more, but wavy, while when the diffusion path goes through three-phase regions, a solution phase with precipitates can be found in the diffusion couple.

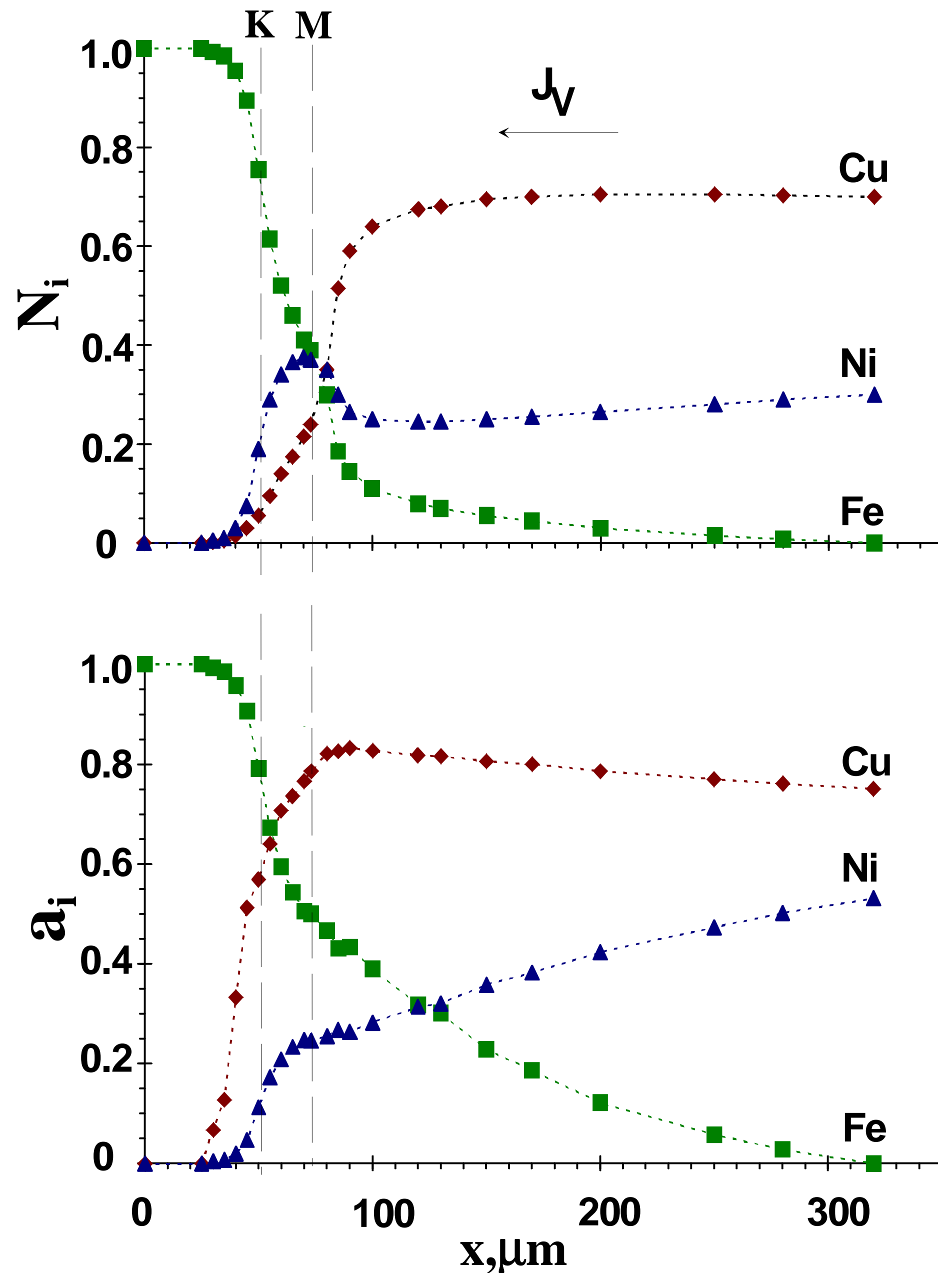


Fig. 5. The concentration profiles (above) and the activity profiles (below) in the diffusion couple Fe vs. 70Cu-30Ni, annealed 100 hours at 1000 °C. Notice the strong "up-hill" diffusion of nickel against it's own concentration gradient. The activity curve instead goes "correctly" downwards. In the copper-rich alloy a "pile-up" of both concentration and activity of copper is observed. The vacancy flux goes from right to left. The letters K and M indicate the positions of Kirkendall and Matano planes.

Van Loo et al. [42] have presented a model based on the slope of the tie-lines in the ternary phase diagram which allows a prediction of the initial layer sequence, or at least to exclude other types of sequences of the reaction products. The essential statement valid, generally in multicomponent

metal systems is, that no element will intrinsically diffuse into the direction where its own activity will be raised. This means that in the experiments where the atoms appear to diffuse upwards their own activity gradient, this is in fact caused by the mobility of the other components. When experimentally determined concentration-penetration (N_i - x) -curves are converted into (μ_i -x) or (a_i - x) –curves, it is possible that extrema in these curves will be found leading to the so called "up-hill "diffusion behaviour, as has been demonstrated in Figure 5 from Publication I. According to Eq. (6) the intrinsic flux, J_i, is positive on one side and negative on other side of this extremum, but it is dependent on the other fluxes. The independent intrinsic flux, J'_i, defined by van Loo [27], is however, always directed from the higher activity of a component in one end-member to the lower activity in the other end-member.

The growth of intermetallic compounds can be controlled by either diffusion through one of the phases or by the interfacial reaction kinetics. If the volume diffusion is the rate-limiting step of the diffusion process, the layer thickness and annealing time are related through the parabolic growth. Irregularities, such as an oxide film at the interface, act like a diffusion barrier causing an incubation time before the regular diffusion process sets in. On the other hand, the reaction between elements to form a new compound may be the rate-limiting step and the layer grows linearly with time. But as the layer thickness increases it takes more time for the reactants to diffuse to the interface and the diffusion eventually becomes rate limiting. In the case of fast grain-boundary diffusion, a significant deviation from the parabolic layer growth is also encountered.

Analytical methods to calculate diffusion paths and other diffusion properties can be used only when the interdiffusion coefficients are assumed to be constants. Many equations and solutions available in the literature [28, 33, 34, 35, 36] are based on the use of error-functions. The assumption of constant interdiffusion coefficients is generally reasonable only in the diffusion couples with a relatively small composition difference between the terminal alloys. Solutions based on error-functions produce symmetric concentration profiles on both sides of the Matano-plane unless modified mathematical models are used, for example, as done by van Loo [27] and Morral [37, 38]. Therefore, for a realistic diffusion analysis, numerical simulations of diffusion transformations in multicomponent alloys are needed [39, 40, 43], especially in the diffusion couples with concentration dependent diffusion coefficients and/or large concentration differences. However, if the composition dependence of the diffusion

coefficients are known together with the thermodynamic assessment of the system, the actual diffusion paths can be calculated, provided that a proper diffusion kinetic software is available.

3.3 Numerical modelling of diffusion controlled transformations

Beside the software development, establishment of relevant kinetic database is needed. Anderson and Ågren have introduced a presentation of the experimental data on multicomponent diffusion in alloys [44]. The diffusion coefficients are obtained as a product of thermodynamic and kinetic factors. The thermodynamic factor is essentially the second derivatives of the molar Gibbs energy with respect to the concentrations and it is known if the system has been thermodynamically assessed. The kinetic factors contain the mobilities of each component and may be evaluated from the diffusion data when the thermodynamic factor is known [45]. The composition dependence of the mobility can be presented with the Redlich-Kister expansion (in analogy to thermodynamic functions) including the linear combination of the mobility in pure elements and the binary and ternary interactions in the solution phases and intermetallics.

The possibility of making thermodynamic assessments of systems by combining all kind of thermodynamic data has decreased remarkably the amount of experiments needed to verify the phase diagrams of the system as well as to apply them for technological problems. The thermodynamic-diffusion kinetic modelling becomes more important also in the interconnection and packaging applications, and eventually, it is of great interest to combine it with other simulation and modelling software and databases, such as those existing for thermal and electrical design and the FEM based stress analysis and thermomechanical modelling.

Generally the kinetic data available [30] exist in many different forms including interdiffusion, intrinsic diffusion or tracer diffusion coefficients, and their concentration dependence is known mainly only in binary solid solutions. So, the importance of the mobility (tracer diffusion coefficients) data becomes evident and methods to calculate them from normal diffusion couple experiments, such as presented in Publication I and IV, can be of great help. However, due to the fact that the practical kinetic problems contain severe irregularities, which cause a huge challenge for the software development, the amount of relevant reliable diffusion data is more limited than the one in thermodynamics. In many cases exact calculations are not possible to carry out because of the lack of the necessary data. Therefore, qualitative considerations of the

multiphase diffusion and the possible diffusion paths, such as reviewed in Refs. [32, 41, 42, 46], remain important also in future.

3.4 Kinetic modelling of the solder-substrate systems

Only very limited amount of diffusion kinetic models for solder-substrate interactions are available in the literature [2, 47, 48, 49]. These models are mainly developed for studying the intermetallic layer growth of intermetallics at low temperatures during ageing where normal volume diffusion in solid state is assumed. Typically these models are applied only to binary cases [47, 48] and do not take the thermodynamics of the systems into account. Some trials have been done to include the liquid phase into the analysis [2]. Only planar interfaces between phases can be dealt with which is, however, very seldom the case when liquid phase is involved. The diffusion in the liquid is generally so fast that the composition remains more or less uniform throughout the whole solder volume and the diffusion coefficients in liquids for various components do not considerably differ from each other.

The grain boundaries and other irregularities in the lattice provide faster diffusivity paths for the components than those by the volume diffusion in bulk. This is of great importance, for example, in the thin coatings or metallizations where the average grain size can be in the order of microns. The short circuit diffusion also accelerates the growth kinetics of the reaction layers, and therefore, in a way or another it should be taken into account in reliable diffusion analysis.

The modelling of the dissolution of conductor metal or metal finish into the molten solder is also becoming more important. A kinetic model to calculate dissolution rates in a binary case, represented by Boettinger et el. [20], can be also applied to ternary systems (see Figure 7 later in thesis). According to the model, the dissolution rate is essentially dependent only on the metastable solubility of the conductor metal in the molten solder, which can be determined when the thermodynamic assessment of the system is known. However, the knowledge of the stable phase diagram of a solder/conductor system is in many cases adequate to determine the relative qualitative dissolution rates as a function of temperature and solder composition despite the limited kinetic data.

Chapter 4

Solder-Substrate Interactions and The Small Volume Effect

A successful soldering process requires a solder-substrate-flux system in which the different materials are chemically compatible both with each other and with the specified soldering atmosphere and temperature profile. The chemical compatibility of different materials is strongly dependent on the solder-substrate interactions, such as the dissolution of conductor metal into molten solders and the formation of intermetallic compounds at the solder-substrate interface. These interactions strongly determine the wetting properties of the system as well as the microstructure and the morphology of the soldered joint. They have a pronounced impact on the physical and chemical properties, and finally, on the overall reliability of the assembly. With decreasing solder volumes used in high-density electronics interconnections, it is ever more likely that an excessive fraction of the solder filler and/or the adjacent metallization will partake the chemical reactions. This so-called Small Volume Effect (SVE) does not operate only in advanced interconnection techniques with the small total solder volumes or thin metallization layers. On the contrary, similar consequences can also be encountered in kinetically constrained local edge regions (tip or meniscus) of large total solder volumes e.g. in the surface mount assemblies, or when due to the limited solid state diffusion the reactive component of the solid solder alloy is consumed only in the vicinity of the reaction layers giving rise to a depleted zone from this reactive component (e.g. tin).

In the conventional industrial soldering operations, the joint regions are for a relatively short time at elevated temperatures and only from few seconds to a couple of minutes in the liquid state, when the component leads and contact pads (conductor metal or metallization) on the substrate to be joined are in contact with molten solders. Despite the short time interval, marked dissolution of materials into liquid solders will occur following by a fast formation of intermetallic compound(s) at the liquid solder/substrate interfaces, as has been discussed in Publications III-IV. On the other hand, the intermetallic compounds nucleate and grow at the solder/conductor interface and/or between the different metallization layers, also in the solid state during the other manufacturing steps, the storage, and the service lifetime of the joint. Thus, in all these cases, one or more of the interconnecting elements, either by diffusion,

dissolution, and/or reacting with the mating materials in the joint region, can be entirely consumed due to the SVE during the operational time of the device [2].

In the following, some background knowledge and empirical results on wetting, dissolution, and intermetallic layer growth have been presented and discussed together with the SVE consideration and other results of this thesis. More detailed review can be found e.g. in References [20, 50, 51].

4.1 Wetting

The joint reliability is associated with the wettability of the surfaces to be joined and the joint's subsequent ability to retain its performance. The wettability is a complex phenomenon and it dependents on substrate, solder composition, impurities, soldering atmosphere, flux, pre-tinning type and thickness, storage conditions and time as well as on reflow conditions. There must be an adequate thermodynamic driving force to provide fast wetting at the solder/conductor interface while the kinetics of the wetting must be such to enable the bond to be formed in the relatively short time available in the manufacturing process. Although wetting is essential for the successful soldering process, the correlation between the quantitative measures of wettability and soldering performance is inadequate in practice, even for the most commonly used eutectic Sn-Pb solder alloy [50]. The current lack of fundamental understanding of the thermodynamics and kinetics of the wetting process inhibits also the prediction and interpretation of the behaviour of new lead-free solder alloys in electronics products and manufacturing processes [20,51].

Wettable materials, such as Cu, Ni, and their alloys, are common conductor materials. When clean, these surfaces are readily wetted by the common solders using mild fluxes, but become increasingly difficult to wet as they oxidise or contaminate. Thin layer of Au, Pt, Pd or fusible solder coatings are commonly plated on the conductor materials to maintain the wettability during storage. When using fusible materials, e.g. the eutectic Sn-Pb alloy, the coating must be sufficiently thick to retain the solderability for an appropriate shelf time prior to soldering, because of the continuous growth of infusible intermetallic compounds at the coating/substrate interface [52].

It is evident that the fluxes used in soldering processes play an important role in determining good wettability [53, 54, 55, 56]. Fluxes are used primarily to improve the wetting properties of the solder-substrate system by removing oxides and other surface contamination as well as preventing the re-oxidation. On the other hand, the good overall component solderability allows the use of less active fluxes, water-soluble fluxes, or even fluxless soldering.

In the case of an inert system where no dissolution or chemical reaction can occur, the wetting is controlled by the surface energy imbalance only, as

$$F = \sigma_{SV} - (\sigma_{SL} \pm \sigma_{LV} \cos\theta), \quad (7)$$

where $\sigma_{SV}, \sigma_{SL}, \sigma_{LV}$ are the solid-vapour (or flux), solid-liquid and liquid-vapour (flux) surface energies and θ is the contact angle. Additionally the dissolution of conductor metal or metal finish and chemical reactions between the conductor metal and the reactive component(s) of the solder can affect the wetting process.

Several solderability test methods are used in electronics [57], but the wetting balance measurement technique has been the most useful tool for investigating the soldering properties of various combinations of solders, fluxes, and surfaces since it can provide information of both the extent and speed of wetting [58]. The extent of wetting is an equilibrium case dependent on the surface and interfacial energies involved at the liquid/solid interface. The speed of wetting is governed by the ability of the heat source to supply heat, the efficacy of the flux, the viscosity of the solder, and the dissolution and chemical reactions occurring at the interface. However, more work need to be done in order to achieve consistent correlation between the wetting force tests and the practical wetting process, e.g. of the ever smaller surface mount components during reflow soldering.

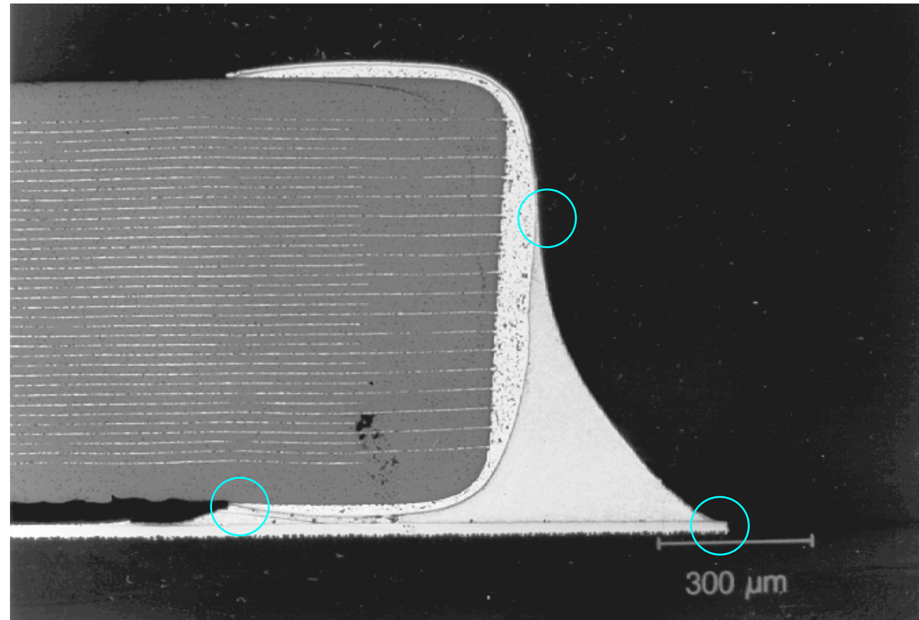


Fig. 6. The kinetically constrained regions in the solder joint between a surface mount component lead and a solder land on a printed wiring board [59].

The wetting/spreading process occurs essentially in the local edge regions of the molten solder, e.g. in the wetting tip of a spreading solder droplet or in a rising solder meniscus. In these kinetically constrained regions, the conductor metal or metal finish is in contact with only a limited solder volume in an otherwise bulky solder joint (see Fig.6 [59]). The initiation of solder spreading depends on the heat flow and the melting of the solder. Subsequent solder spreading involves motion of fluid within the droplet being dependent on the viscosity of the liquid solder and the kinetics of the moving contact line [20]. Usually the wetting analysis has been based on the interfacial energy imbalance neglecting the role of the chemical reactions at the solder/substrate interface. It has been suggested, that the chemical reaction decreases the interfacial tension at the solid/liquid interface and so, the driving force for wetting in Eq. (7) at the early stage of the spreading process increases [52, 60, 61]. Any of these considerations is not yet confirmed by quantitative experimental results and the role of the intermetallic formation in the wetting kinetics is still unclear. Based on the observations in this thesis, the role of the dissolution is suggested to be as essential for good wetting in the solder/conductor systems as the formation of intermetallic compounds.

In the advancing wetting tip at the oxide-free conductor/solder interface, the dissolution of the conductor metal (and/or surface finish) into the molten solder precedes the formation of the

intermetallic compounds since the supersaturation of the solder at the solder/substrate interface is needed [20]. Since there is a direct contact between the conductor metal and the solder for some time, metastable solubilities have to be studied, as has been discussed in Publications III-IV. The composition of the solder alloy in the vicinity of the wetting tip can be different from the rest of the solder volume affecting essentially the surface energy and viscosity of the solder as well as the thermodynamic and kinetic properties. The compositional changes of the solder alloy can originate from the dissolving conductor metal and/or metal finish or from the chemical reactions with the conductor metal.

The surrounding atmosphere as well as the alloying elements, impurities, and dissolved conductor metals or metal finishes will affect the liquid surface energy, σ_{LV}, of the solder/vapour interface. The additions of Pb, Bi, and Sb into the pure molten tin are known to decrease the liquid surface energy, σ_{LV}, of Sn/vapour interface, while additions of Ag and Cu increase it [62, 63]. The interfacial energies for several pure metals are increasing in a following order: Bi, Pb, Sn, Zn, Ag, Au, Cu, Ni, and Pt [64, 65, 66]. Accordingly, it is likely that also dissolved Au, Ni, and Pt could increase the liquid surface tension of the pure liquid tin solder. It is interesting to note, that this order is almost the same as the decreasing dissolution rates found both by calculations in this work and in literature [67] (see Figure 7). Small impurity additions could also have effect on the overall wetting behaviour [53, 56, 68]. The effect on small addition of Zn, Ag, Cu, In, Sb, and Bi into the eutectic Sn-Bi and Sn-Ag solders at 165 and 200 °C were studied in reference [56], but no remarkable changes on the wetting angles were observed. Generally, the addition of Cu and Sb had a positive effect, and Zn and In a negative effect on the wetting angle. On the other hand, when 1 wt-% of zinc is added, the wetting angle increased remarkably at the temperature of 250 °C using RMA flux [56]. This effect of the added zinc has been explained later by Kivilahti [2].

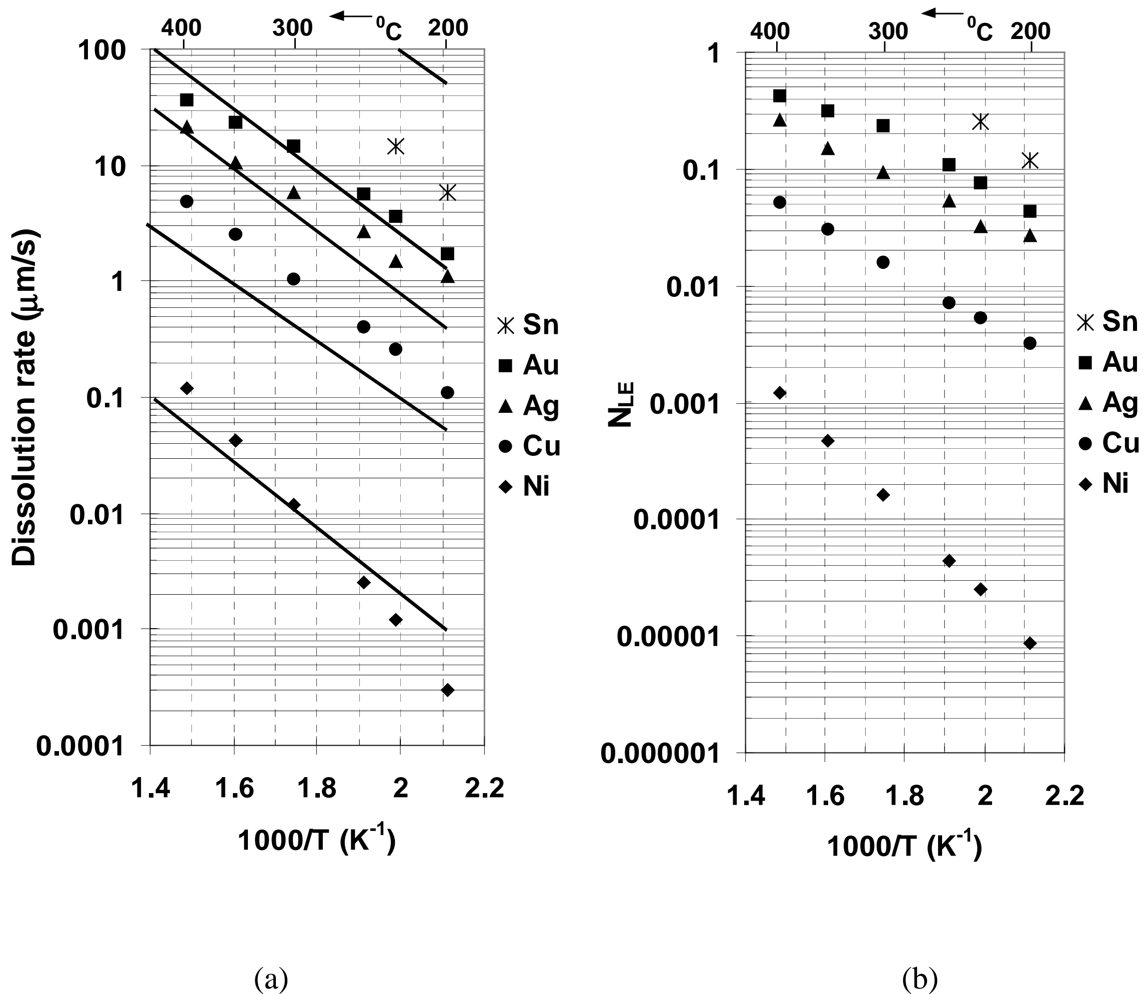
The wetting properties of a solder-substrate system are strongly dependent on the composition of both solder and the substrate. One comparison between the most typical elements used in various binary, ternary and quaternary solder alloys was done by Humpston and Jacobson based on the ability of the solder to promote solder spreading on gold, copper, and tin substrates in various conditions [69]. They found a ranking order of Sn > Pb > Ag > In > Bi. However, with other fluxes used also other results have been reported [70].

Lead-bearing solders comprise the largest group of alloys used in electronic products. In order to remove Pb from solders, component leads and printed wiring board finishes, a better understanding of the role of Pb in soldering needs to be achieved. For this reason, both the lead-free solder alloys and the Sn-Pb solders are still extensively studied. The performance of the SnBi and SnAg solders, as well as some ternary and quaternary combinations with Sn, Bi, Ag, and In, has been shown to be adequate for the surface mount applications using the present (Sn-Pb) paste technology [71] although the wetting properties of these alloys are weaker. However, the implementation of the lead-free solders has been slow in the electronics industry due to the remarkable additional work and costs caused by the changes and potential risks in manufacturing processes, reliability, component availability and costs in comparison to the attainable competitive advantages. The eutectic Sn-Bi solder alloy has been studied extensively as a potential replacement for Sn-Pb solder and it has had also an important role in this thesis. In many respects the behaviour of the eutectic Sn-Bi solder has been quite comparable to the eutectic Sn-Pb solder, but for example, the formation of a pure Bi-layer between the solder and Cu-Sn intermetallics will be a serious hazard for the overall reliability of the assembly. At this moment, the most promising replacements of the lead-bearing solder alloys are SnAg-based alloys, although the relatively high melting point of around 220 ºC complicates its adoption to the present electronics manufacturing processes.

4.2 Dissolution of conductor metal

The experimental diffusion rate data of typical conductor metals and metallizations found in the literature are quite limited. The dissolution rates of several metals into the eutectic Sn-Pb solder have been investigated experimentally by Bader [72] and a ranking order of Ni, Pt, Pd, Cu, Ag and Au was found, nickel being the slowest and gold the fastest. The same ranking order has been found for 5Sn-95Pb (wt-%)and 5In-2.5Ag-92.5Pb (wt-%) solders [73]. Boettinger at al [20] have presented a simple kinetic model to estimate the dissolution rate of copper into pure molten tin. This model was further modified and applied to ternary systems used in soldering applications in this thesis work (unpublished results). According to the model, dissolution rate depends essentially on the metastable solubility of the conductor metal in the molten solder, and therefore, the dissolution rate of various conductor metals into different solders can be estimated as a function of composition and temperature provided that the kinetic data and the thermodynamic assessment of the system with reliable metastable

solubilities are available. However, presently the metastable solubilities can not be calculated accurately enough because the thermodynamic functions are optimised to fit the experimental data in the stable region, which tends to give too large values for the metastable solubility [16]. Therefore, the stable equilibrium solubilities have been used in these calculations.

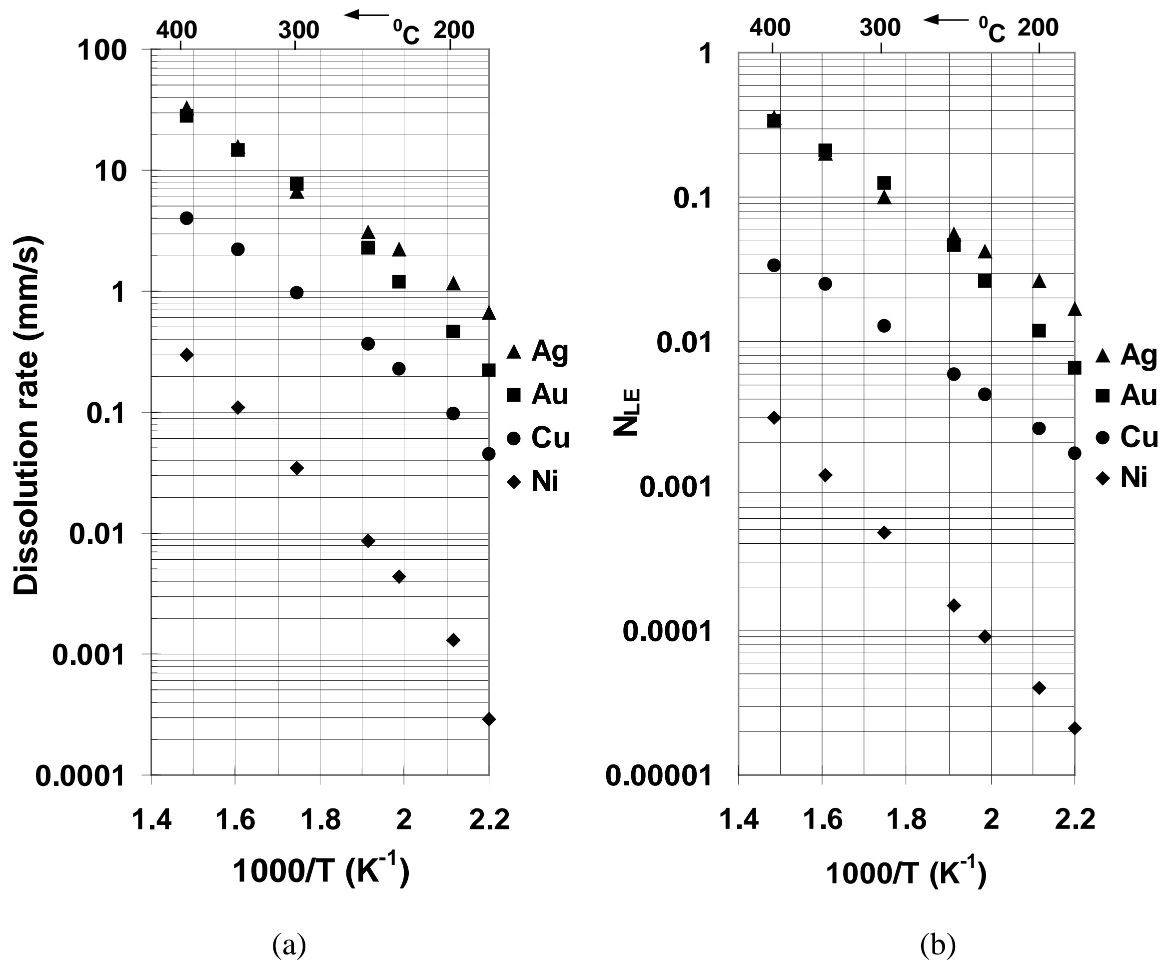


(a) (b)

Fig. 7. (a) The calculated dissolution rates and (b) the maximum stable solubilities (the compositions are in atomic percents) of tin, gold, silver, copper and nickel into the eutectic Sn26Pb solder as a function of temperature compared with the literature data (solid lines) [67].

The experimental dissolution rates presented by Klein Wassink [67] were verified with the model calculations (see Figure 7), and a similar diagram for the eutectic Sn-Bi solder was constructed in Fig 8. The results show that the dissolution rates indeed depend strongly on the solubility of the conductor metal into the molten solder. The solubility, and therefore, the dissolution rate increases as the temperature increases. Similarly, the solubility of the conductor metal into the molten solder depends on the solder composition that should affect also the diffusion rates. Thus for many purposes, the knowledge of the phase diagram of a

solder/conductor system is adequate for determining the qualitative or relative dissolution rates as a function of temperature and solder composition despite the limited kinetic data available.



(a) (b)

Fig. 8. (a) The calculated dissolution rates and (b) the maximum stable solubilities (the compositions are in atomic percents) of silver, gold, copper and nickel into the eutectic Sn43Bi solder as a function of temperature compared with the literature data (solid lines) [67].

Additions of Ag or Cu into the Sn-Pb solder alloys help to decrease the dissolution rates of Ag and Cu [74]. Okamoto and Yasuda [75] have shown that, for Cu, the initial dissolution into molten Sn40Pb (wt-%) solder is rapid until Cu has saturated the solder and then dissolution slows dramatically. Thermodynamically this is obvious since the driving force for the dissolution is very large for the very first copper atoms but vanishes when the equilibrium is attained.

Based on the results in this work and in literature, it has been concluded that the dissolution of the conductor metal or metal finish (essentially in the wetting tip) can stop or be substantially reduced by a) saturation of the molten solder by the dissolving metal, b) formation of

intermetallic compound(s) or c) when the surface energy balance has been attained in the cases where no intermetallic compounds are formed (e.g. pure tin vs. SnPb solder). It should be noted, that in the first two cases, the driving force for dissolution is vanished or remarkably reduced, while in the last case there is still driving force left. The possible connection between the dissolution and surface energy balance is, however, not yet properly understood and would require more detailed experimental and theoretical considerations.

4.3 Phase formation and intermetallic layer growth

The substrate and solder materials used in electronics assemblies are typically chosen by considering the requirements of design and manufacturability. They include solderability and reliability issues as well as electrical, mechanical and thermal characteristics of the materials to be joined. In the systems of particular interest in electronics, the intermetallic compounds are formed almost always at the interface between typical conductor metal or metal finish (Cu, Ni, Au, Pd ...) and the active component in the solder (mainly either Sn or In).

The interface reaction at the wettable solder-substrate interface is generally essential for a strong bonding. On the other hand, the intermetallic layer can be a source of mechanical weakness in the soldered joints due to the thermal expansion coefficient mismatch and the brittle nature of intermetallic compounds. Moreover, they may lead to a loss of solderability through excessive growth during storage. During the service time the intermetallic compound layers may grow in the solid state to significant thicknesses (>20 μm) depending on the kinetics of growth for the particular solder-substrate system and the service conditions (cumulative temperature and time), and may so, cause delayed and unpredicted reliability problems.

Wettable materials, such as Cu and Ni and their alloys, are common conductor materials. Copper forms two intermetallics, η-Cu_6Sn_5 (adjacent to solder) and ε-Cu_3Sn (adjacent to copper), with tin-based solders (Sn-Pb, Sn-Ag and Sn-Bi) at typical soldering temperatures. Essentially only the η-phase forms into the liquid when copper conductors are soldered with Sn-Pb or Sn-Bi solders, while both phases grows at the solid state during ageing at lower temperature. However, with low Sn-content solders only the ε-phase can be formed due to the thermodynamic reasons. The critical composition in which the equilibrium between the ε-phase

and liquid solder is achieved depends also on temperature, and for example, in case of Sn-Bi solder it moves towards high tin contents as temperature rises. It can be calculated as a function of temperature when the ternary thermodynamic assessment is known [16], as presented in Publication III.

In the solid state, the growth of Cu-Sn intermetallics is about 40 μm in a year at 170 °C, about 7 μm at 100 °C, and 1 μm at room temperature [76]. Normally the growth of η-phase dominates at lower temperatures, while at higher temperatures the ε-layer grows much thicker [77]. The growth rate of the intermetallic layers is related to the diffusion rate of the reactants to and/or through the existing layer. The growth rate is initially much higher when the solder is molten because a near complete mixing in liquid ensures that Sn is readily available. The growth rate of Cu-Sn intermetallics depends also on the solder composition. With tin-lead solders the maximum growth rate has been observed near the eutectic composition at 170 °C [78]. The alloying of Cu substrate generally slows down the layer growth of Cu-Sn intermetallics [51].

The growth rates for stable Ni-Sn intermetallics compounds (mainly Ni_3Sn_4) are much lower than those for Cu-Sn intermetallics both in the liquid and solid state [70,79]. For example at room temperature, the Cu-Sn compounds grow 20 times faster than the Ag-Sn compounds and 120 times faster than the Ni-Sn compounds [51]. However, fast growth of a metastable plate-like intermetallic compound, $NiSn_3$, is a potential cause for long-term solderability degradation. The $NiSn_3$ transforms rapidly into stable intermetallics and free tin at temperatures above the tin melting point [80]. Therefore, the solderability of matte tin plating over nickel underplating, stored at room temperature or slightly above, deteriorates after a relatively short time. The addition of 10 wt-% of Pb greatly reduces $NiSn_3$ growth, and the addition of 40 wt-% Pb practically eliminates it [80].

When studying experimentally the effect of fast formation of the intermetallic compounds between the conductor metal and the molten tin-lead solder, the dissolution of copper or nickel as a conductor metal is essentially stopped after the formation of intermetallic layers Cu_6Sn_5 and Ni_3Sn_4. When the Cu_6Sn_5-layer is formed, the driving force for the dissolution of Cu disappears since a local stable equilibrium between the Cu_6Sn_5 intermetallic compound and molten solder is achieved.

Noble metals including gold, palladium and platinum are used as surface finish on assembly parts [81] since they are resistant to ambient atmospheres and solvents used for degreasing. Gold is indeed widely used in soldering applications [82]. Gold reacts with tin-based solder forming a $AuSn_4$ layer adjacent to the solder having generally a linear growth kinetics. However, adjacent to the molten solder $AuSn_4$ intermetallic compound is commonly observed to form during solidification [51], which can explain the continuous dissolution of gold in tin-based solders until the whole gold finish has been dissolved. Also, the lead-rich matrix phase containing the $AuSn_4$ crystals support this assumption. Gold is highly soluble in most common solders and the resulting alloying alters their metallurgical and physical characteristics [80, 83, 84, 85]. An exception to this trend is provided by some of the indium-based solders. These alloys react with gold to form a layer of the $AuIn_2$ intermetallic compound [82]. Once established, the $AuIn_2$ layer tends to inhibit further dissolution of the gold layer into the molten solder. In general the gold dissolution into the indium-based solder In-50Pb (wt-%) is much smaller than into the eutectic Sn-Pb solders [83] due to the clearly smaller solubility of Au. Also palladium is highly resistant to oxidation and easily wetted by solders [81 above]. Tin-lead solder reacts readily with palladium forming typically $PdSn_4$ intermetallic compound. This reaction goes on until the intermetallic compound formation has consumed all the solder or the palladium substrate [86].

Intermetallic layers at the solder/conductor metal interface form and thicken relatively rapidly during the initial soldering despite the short bonding times, since the temperature is relatively high and the solder is molten. It has been discussed in Publication III-IV, that the nucleation and growth mechanisms need to be different from those operating in the solid state in order to explain the fast formation of the initial layer of a significant thickness and the special morphology of these layers. Due to the dissolution, the composition of the conductor metal reaches the metastable solubility limit at the solid/liquid interface. This maximum metastable solubility is larger than the stable one and it limits the amount of the conductor metal that can be dissolved before the formation of the intermetallic compound. Due to this supersaturation, the melting point of the liquid enriched by the conductor metal rises leading to a formation of the intermetallic compound. It should be also noted that the thickness of the solidified reaction layer depends – due to the mass balance reasons - on the amount of the conductor metal needed

in the intermetallic compound. In the case of gold or palladium, only 20 atomic percents is needed while for copper the amount is 55 atomic percents.

4.4. Microstructural and compositional changes in the soldered joints

With decreasing solder volumes and metallization thicknesses used in high density electronics interconnections it is ever more likely that an excessive fraction of the reactive component(s) of solder filler and/or the adjacent metallization will partake the chemical reactions needed for reliable bonding. When the reactions consume only the solvent of a solder alloy, i.e. in most cases Sn, the original microstructure of the solder alloy may change drastically which will reduce the reliability of the soldered joints. Similar consequences of the miniaturisation can be encountered also in the local tip regions of larger solder volumes, e.g. in the surface mount assemblies, or when, due to a limited solid state diffusion, the reactive component of solid solder alloy is consumed only in the vicinity of the reaction layers which give rise to a depleted zone from this reactive element. In the following some of these possible microstructural and compositional changes in soldered joints and the applicability of the combined thermodynamic and kinetic models and concepts introduced in this thesis have been discussed.

4.4.1. Critical thickness of conductor metal, finish or metallization layer

A typical flip-chip metallurgy between bump and chips metallizations or pads consists of several thin (0.1 - 3 μm) metal or alloy layers. Copper can be used as a solderable adhesion layer providing proper wetting by the melting tin-based solder bump. The Cu_6Sn_5 and Cu_3Sn intermetallics grow in solid state between the tin-based solder bump and the copper metallization during the use of the assembly. In Publication IV the diffusion model was introduced and applied also to calculate the minimum thickness of the copper metallization layer needed so that it is not totally consumed by reacting with a pure solid tin solder bump. According to the calculations at the temperature of 100 °C the thicknesses of the consumed copper metallizations are 1.2 and 3.8 μm after 1 000 and 10000 hours, respectively. At room temperature the layer growth of the intermetallics is so slow that after 10 000 hours only a 0.3 μm thick layer of copper is totally consumed. In addition to the long-term growth, a relatively thick layer of Cu_6Sn_5 intermetallic can be formed already during the bonding and the required

thickness of the copper metallization needs to be between 5 to 10 µm in order to guarantee reliable functioning flip-chip interconnections in high-temperature applications. However, these thick copper metallizations can cause other manufacturing problems and, therefore, other solutions such as nickel or copper-nickel alloys are needed.

The diffusion model introduced in Publication IV is mostly applicable in the binary cases, such as above, but it can give realistic results also in ternary solder/conductor systems as long as tin (or other reactive element) is readily available at the solder/intermetallics interface. However, it has been observed experimentally in the Cu/SnBi system that tin is first consumed near the solder/intermetallics interface and a layer enriched in bismuth is formed between the intermetallics and solder as has been discussed in Publication III. This Bi-layer acts as a diffusion barrier and hinders the further growth of the intermetallic layers.

In similar manner, a critical thickness or a storage time of e.g. a solderable SnPb finish on component leads could be estimated based on the solid state growth of the intermetallic compounds. When the whole SnPb finish has been consumed the intermetallic compound adjacent to the solder is exposed to air and oxidised leading to a deterioration of the solderability of the component lead [52, 87].

On the other hand, a conductor metal, metal finish or metallization layer can be totally consumed by dissolution into molten solders. As it has been discussed in chapter 4.2, the dissolution rates of several conductor metals or metal finishes, and so, the critical thicknesses of these layers can be estimated with the simple kinetic model. The consumption of the whole metallization layer can be harmful like in the case of solderable adhesion layers such as Cu and Ni, or desired, like in the case of e.g. Au or Pd coatings that prevent the oxidation of the adhesion layer.

4.4.2. Decomposition of the original solder into a mixture of intermetallics and non-reactive components

Due to excessive reactions between the chemically active components of solder alloy and the conductor metal (or it's metal finish), the phase structure (or microstructure) of small solder joints or kinetically constrained edge regions of bulky joints can decompose into the mixture of intermetallics and nonreactive components [2,3]. This has been most pronouncedly observed in adhesive joining where the whole solder mass takes part in the intermetallic reactions between the small solder particles in the conductive adhesives and the metallization (mainly Cu or Ni/Au), and transforms into the matrix of various intermetallics already during the solder reflow as can be seen in the case of eutectic Sn-Bi solder in Figure 9 [88].

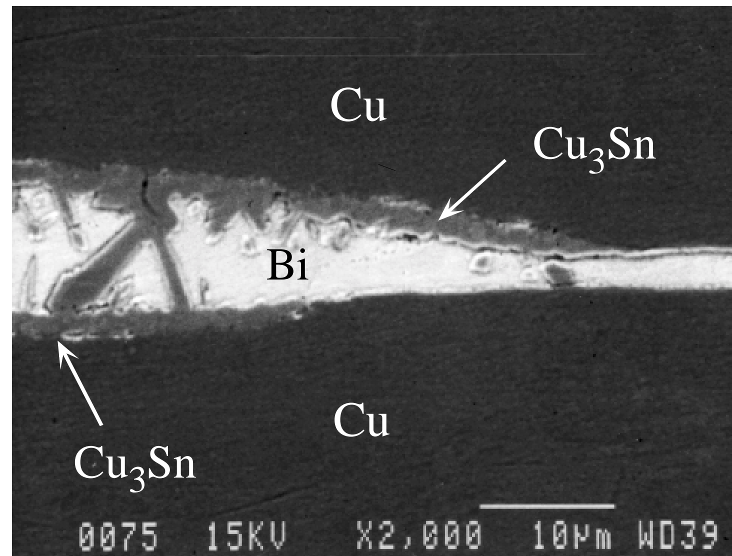


Fig.9. Cross-section of a microjoint bonded at 180 °C for 1 min. with a thin layer of the eutectic SnBi alloy. Disintegration of the eutectic structure between Cu metallizations. The once formed Cu_6Sn_5 layer has been transformed into a Cu_3Sn –phase, and a pure Bi layer has formed due to the consumption of tin from the solder.

In Publication III, a concept “Local Nominal Composition” (LNC) in the effective joint or contact region has been used to explain and model the microstructural and compositional changes in the solder/conductor systems such as in Figure 9. The LNC calculations involve the use of combined thermodynamic and kinetic approach. The LNC will chance with time giving information which phases are present in the effective joint region at each temperature and time, provided that the thermodynamic and kinetic properties of the system are known. In Figure 10, calculations of the intermetallics layer growth and LNC in the Cu/SnBi system introduced in Publication IV have been presented showing disappearance of already formed phases and appearance of new ones. However, for a more quantitative prediction of the time-dependence of these events a better estimation of the intermetallics layer growth into the liquid solder is still needed than what the solid-state diffusion model provides, as has been discussed in chapter 4.3 and Publications III –IV.

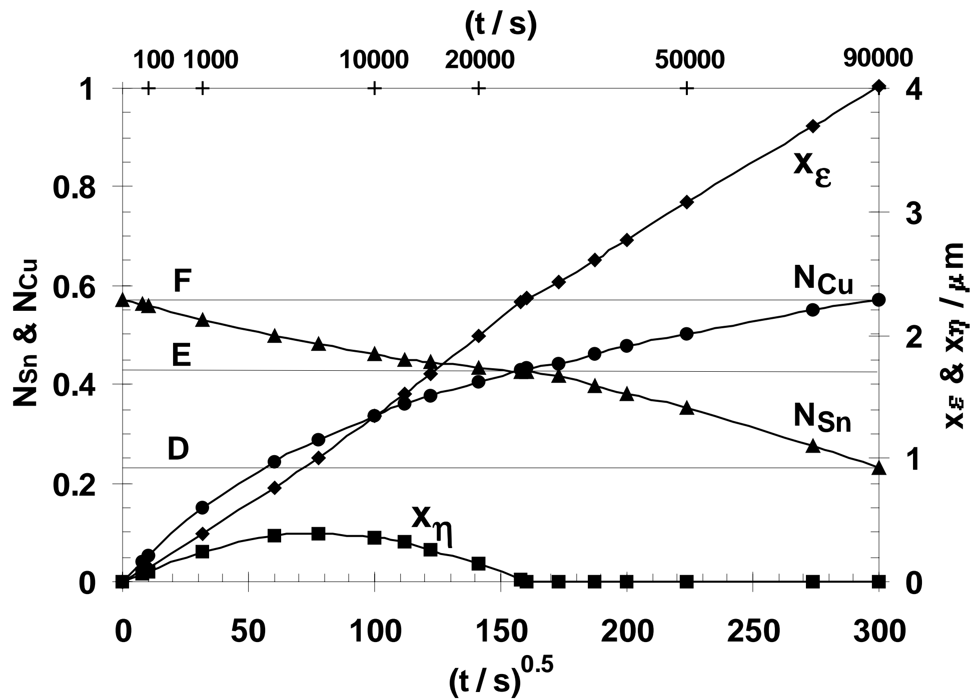


Fig. 10. Growth of the η(Cu_6Sn_5)- and ε (Cu_3Sn)-phases, the local nominal composition ${}^{L}N_C$ (copper content with fixed ratio of tin and bismuth) and the tin content of the liquid solder, N_{Sn}, as a function of time in the Cu *vs.* eutectic Sn43Bi solder system at 220 °C. In the calculations the original thickness of the liquid was taken as 5 μm (per conductor interface). The lines D, E and F correspond ${}^{L}N_C$ values in the moments when η-phase starts disappearing, η-phase has totally disappeared and a pure Bi –layer has formed, respectively (see also the isothermal cross-section of the Cu-Sn-Bi system in Fig 1 in Publication IV).

4.4.3. Formation of a depleted zone

In a binary solder/conductor system, such as Sn-Cu, Sn is readily available to the chemical reaction with Cu leading to the formation and growth of Cu_6Sn_5 and Cu_3Sn intermetallic compounds. In ternary (or higher order) solder/conductor systems where the third element (typically Pb or Bi) is not reactive, the reactive component of solid solder alloy (typically Sn or In) is consumed mainly in the vicinity of the reaction layers which give rise to a depleted zone from this reactive element. This depleted zone can be seen as a pure Bi or Pb layer between the intermetallic layer and the coarsened eutectic structure of the in the SnPb or SnBi solder. The atoms of the reactive element need to diffuse in solid state an increasing distance through the growing depleted zone leading to the retardation of the growth of the intermetallic compounds.

This is even more pronounced if the diffusivity of the reactive element atoms in the depleted zone is lower than in the original eutectic solder alloy. The Sn-depleted zone can also change the mechanical properties, and so the reliability, of the joint.

4.4.4. Change of the phase equilibrium due the change in temperature or composition

Other types of microstructural transformations in the solder/conductor system are also possible since the phase equilibria depend on the temperature and the composition of the solder alloy and conductor metal (or alloy), as have been discussed in Publication III in Cu/SnBi system. The phase equilibria and the layer sequence formed during soldering or bonding operation can be different than what exist at low temperatures. If the adjacent phases are not in local equilibrium with each other anymore at the changed temperature there is a thermodynamic driving force for the transformation of the phases according to the new phase equilibria. These possible changes can be predicted when the thermodynamic assessment of the system is known in function of temperature. How fast these transformations occur depends on the kinetic constrains and can be a matter of months or years in solid state at low temperature or from seconds to minutes in liquid state. Similar transformations due to the changed solder composition in Cu/SnBi systems have been discussed in Publication III.

Chapter 5

Summary of the Thesis

This thesis, “Time-Dependent Microstructural and Compositional Changes at the Interfaces between Materials in Electronics”, consists of four publications. The objective of the thesis was to use the combined thermodynamic and diffusion kinetic approach together with detailed experimental microanalysis techniques to obtain better understanding and control of the time-dependence of the microstructural and/or compositional changes caused by diffusion, dissolution, and chemical reaction processes at the interfaces between materials in electronics. This is of increasing importance in developing interconnection and packaging technologies, especially in microelectronics, where a multitude of materials is used in ever more diminutive amounts, e.g. thinner diffusion barriers or adhesion layers, coated overlayers and smaller solder joint volumes. Due to the Small Volume Effect (SVE) the reliability risks and the requirements for the new high density assemblies are continuously increasing. This consideration should not be limited only to the bare chip attachment and other advanced interconnection and joining techniques. Similar consequences can be encountered also in the kinetically constrained local (tip) regions of large solder volumes, e.g. in the surface mount assemblies, or when, due to a limited solid state diffusion, the reactive component of solid solder alloy is consumed only in the vicinity of the reaction layers. This is especially important due to the current tendency to introduce more environmentally friendly products, which require the adoption of new materials and the adjustment of the manufacturing processes. In order to have tools needed for the predictions and control of the structural and compositional time-depended changes in practical microjoining applications, several combined thermodynamic and kinetic models were introduced in Publications I-IV. Likewise a new concept Local Nominal Composition (LNC) in the effective joint region was introduced and applied in Publication III.

The combined thermodynamic and diffusion kinetic approach has not been applied often to ternary or multicomponent systems, especially to those relevant to interconnection and packaging applications. On the other hand, the available thermodynamic and, especially, kinetic

data have been very limited. Therefore, due to the complexity of the practical joining and bonding systems this thesis was started with a more general study of the possibilities and the limitations of the combined thermodynamic and solid state diffusion kinetic approach in the experimentally and thermodynamically relatively simple ternary model systems, Cu-Fe-Ni and Cu-Ag-Zn. The introduced concept and results obtained in these systems are primarily applicable to the metallization systems where the materials to be joined typically have relatively large solubility regions, and no intermetallic compounds are formed at the joint interface.

In Publication I entitled, “Thermodynamic and Kinetic Study of Diffusion Paths in the System Cu-Fe-Ni”, the basic concept to predict diffusion paths was introduced. It was shown, that by knowing the thermodynamic description of a multicomponent system the experimental concentration profile can be converted into a corresponding activity profile giving the possibility to obtain the activity gradients, which are the real driving forces for the chemical diffusion process. A diffusion kinetic model for calculating the tracer diffusion coefficients (mobilities) of each diffusing component at the intersection points of the diffusion paths in a ternary metallic system with large solubility regions was introduced and a good consistency with the literature data was obtained. The importance of the model lies in the possibility to generate new diffusion rate/mobility data, essential for the predictive modelling, by using a diffusion couple technique.

In Publication II entitled, “Thermodynamic and Kinetic Study of Diffusion Paths in the System Cu-Ag-Zn”, the ideas of Publication I were applied to technologically more interesting and, thermodynamically and kinetically more difficult Cu-Ag-Zn system. The kinetic connection between the solid-solid and solid-vapour-solid type of diffusion couples was shown, demonstrating that practically immobile component can have an activity gradient, sometimes even with a maximum, in a depth profile because of the relative movement of the other components. These findings emphasise the importance of the knowledge of the thermodynamic data and phase diagrams of the studied system, since the actual diffusion paths can in many cases be qualitatively estimated by knowing the driving forces for the chemical diffusion even with limited kinetic data. It became obvious that while the solubility regions of the solid solution phases become smaller, the diffusion kinetic model presented in Publication I was not

adequate, and more simple model had to be constructed for calculating the growth kinetics of intermetallic compounds in practical solder applications.

In Publication III entitled, “The Local Nominal Composition - Useful Concept for Microjoining and Interconnection Applications”, the concept of the *Local Nominal Composition (LNC)* in the effective joint region was introduced. It can be used to design e.g. the interconnection and microjoining metallurgy with a limited amount of filler alloy, or the extent of dissolution of a component into liquids, or chemical reactions between thin metal overlayers. It provides information about the phases that are present in the joint region with time, and thereby, combines the kinetics with the phase diagram information. The microstructural and/or compositional evolution in the joint region can be better understood and controlled by utilising both stable and metastable phase diagrams and stability diagrams. With the help of the LNC concept the experimentally found structural changes and transformations in the Cu/SnBi solder/conductor system were clarified.

On the other hand, the approach of Publication I and II needed to be chanced to model the layer growth of intermetallic compounds at the solder/conductor interface in typical soldering and brazing systems. In Publication IV entitled, ”A Diffusion Kinetic Model for Predicting Solder/Conductor Interactions in High Density Interconnections”, a model for calculating the layer growth of Cu_3Sn and Cu_6Sn_5 intermetallic compounds by using the integrated diffusion coefficients and tracer diffusion coefficients, was introduced and exemplified with a relatively simple ternary conductor/solder system, Cu/SnBi, which is interesting for the lead-free soldering applications. The advantage of the model, as compared with the employment of the interdiffusion fluxes, is the possibility to use the tracer diffusion coefficients (mobilities) and, in certain cases, also the integrated diffusion coefficients as material constants. So, by determining them experimentally in one case, they can be used together with the available thermodynamic data in other cases. When liquid phase is involved, some modifications in the model are, however, needed for more realistic prediction of the layer growth of the intermetallics. Another model for calculating the tracer diffusion coefficients (mobility) of Sn and Cu in the Cu_6Sn_5 and Cu_3Sn intermetallics from the binary Sn-Cu diffusion couples was also presented and shown to be in good agreement with the experimental data.

The effect of the dissolution of conductor metal or metal finish into molten solders and the fast formation of intermetallic compounds during the first few seconds of soldering operation was examined also in this thesis. The dissolution rates of several conductor metals into the molten eutectic 74Sn26Pb and 57Sn43Bi solders were calculated in different temperatures using a simple combined thermodynamic and kinetic model. The results showed that the dissolution rate strongly correlates with the solubility of the conductor metal in the molten solder at different temperatures and solder compositions. Therefore, knowing the phase diagram of a solder/conductor system can in many cases be adequate for determining the relative dissolution rates as a function of temperature and solder composition despite of the limited kinetic data available. It was emphasised that SVE considerations should not be restricted only to advanced microjoining methods, e.g. Flip Chip bonding or anisotropically conductive adhesives with small total volumes and thin metallization layers, but also in the conventional soldering applications in the kinetically constrained local edge regions (wetting tips or solder meniscus) at a solder/conductor metal or metal finish interface. It was pointed out that the dissolution could be as essential for the good wetting in solder/conductor systems as the intermetallic compound formation. It was also concluded that the dissolution of the conductor metal or metal finish (essentially in the wetting tip) can stop or be dramatically reduced by a) saturation of the molten solder by the dissolving metal, b) formation of intermetallic compound(s) or c) when the surface energy balance has been attained in the cases where no intermetallic compounds are formed.

Based on the results in this thesis, it is also evident that for more realistic predictions, the fast formation and growth of intermetallic layers and phase transformations into the liquid solder need to be taken into account by some means in future. Also, the lack of both kinetic and thermodynamic data and realistic kinetic software brings practical limitations for the modelling concept. On the other hand, these limitations will emphasise the great importance of the fundamental knowledge of the phase diagrams and the other thermodynamic data of the solder/conductor systems combined with the qualitative kinetic understanding and models.

As the final conclusion, at least the following four factors should be remembered when dealing with microstructural and compositional changes in joining applications: driving force, kinetic factors, material availability and the relative movement of other material components. First of all, without driving force not much change or movement can occur even though the kinetic

factors are high. Secondly, it should be checked if the variation of the kinetic factors within the system is considerable, e.g. many decades in some solid state diffusion cases, or the same order of magnitude, as it typically happens in some dissolution cases. In the first case, more accurate knowledge of the kinetic constrains is needed, while in the latter case, the knowledge of the relative differences of the driving forces is adequate for qualitative conclusions. Moreover, the availability of material constituents can vary with time, and therefore, it can become a rate-limiting step for e.g. a chemical reaction at the joint interface. Finally in the multicomponent systems, the relative movement of other components needs also to be taken into account, such is the case for example in the up-hill diffusion cases.

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