Design of Pb-free solders in electronic packaging by computational thermodynamics and kinetics

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Abstract: Computational thermodynamics and kinetics were used to design the Pb-free micro-solders for replacing the conventional Sn-Pb solders because of the health and environmental safety problem. On the basis of CALPHAD (Calculation of Phase Diagrams) method we can easily calculate properties such as the liquidus projection, isothermal and vertical sectional diagrams and phase fraction in multi-component system including Ag, Bi, Cu, In, Sb, Sn, Zn and Pb elements. In addition, other related information such as the surface tension, viscosity of the liquid phase and solidification simulation can also be obtained. DICTRA (Diffusion Controlled Transformation) software was used to simulate the interfacial reactions between substrate and Pb-free solders, which can easily give the information on the growth of intermetallic compounds and moving speed of interface between substrate and solders etc.

Key words: Pb-free solders; thermodynamic database; thermodynamic calculation; computational kinetics
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Recently very substantial efforts have been made to design Pb-free solders to replace Pb-Sn ones due to environmental and health hazards[1,2]. Many investigations have indicated that the needed Pb-free solders are likely to be multi-component alloys because the melting temperatures of binary candidates are either too high or too low and their mechanical properties may be improved by alloying. Therefore, alloy design is important for development of Pb-free soldering alloys.

Thermodynamics and kinetics of materials are an effective method for alloy design and have widely been used in development of new materials. For example, the CALPHAD method was widely used to calculate the phase diagram, phase fraction, melting temperature etc.[3], while DICTRA software is used to predict the diffusion behavior including the growth of intermediate compounds, the moving speed of interfacial boundary etc[4]. Such information will play an important role in the design of Pb-free solder and interfacial reaction between substrate and solders. This paper presents some examples to design Pb-free solders using computational thermodynamics and kinetics.

1 Method of calculation

1.1 Thermodynamic model

Based on the CALPHAD method, the Gibbs energy of the liquid and solid solution phases are described by the regular solution model. The Gibbs energies of intermetallic phases with a range of solubility are described by the sublattice model[5].

The surface tension in an A-B binary liquid alloy is expressed by considering the equilibrium between the bulk phase and surface phase, which is regarded as a hypothetical independent phase, as follows[6~8]:

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$$\sigma = \sigma_A + \frac{RT}{S_A}\ln\frac{1-x_B^S}{1-x_B^B} + \frac{1}{S_A}({}^{E}G_A^S(T,x_B^S) - {}^{E}G_A^P(T,x_B^B)) = \sigma_B + \frac{RT}{S_B}\ln\frac{x_B^S}{x_B^B} + \frac{1}{S_B}({}^{E}G_B^S(T,x_B^S) - {}^{E}G_B^P(T,x_B^B))$$

where R is the molar gas constant, T is the thermodynamic temperature, σ_i is the surface tension of pure liquid, and S_i is the molar surface area in a monolayer of pure liquid.

The excess term in the surface phase, ${}^{E}G_A^S(T,x_B^S)$, can be obtained from ${}^{E}G_A^S(T,x_B^S) = 0.83\,{}^{E}G_A^P(T,x_B^S)$ · ${}^{E}G_A^P(T,x_B^S)$ can be directly obtained from the thermodynamic database.

Seetharaman *et al*[9]. proposed the equation for the viscosity of liquid alloys as follows:

$$\eta = 39.9\times10^{-11}\frac{\rho}{M}\exp\left(\frac{\Delta G^*}{RT}\right) \quad (1)$$

where ΔG^* is the activation energy of the alloy, which can be obtained from the thermodynamic database. ρ is the density of liquid alloy, M is the molar mass of liquid alloy.

1.2 Kinetic model

The diffusion flux of the specie B in a multi-component system is given by

$$J_B = -c_B M_B\frac{\partial\mu_B}{\partial z} = -M_B RT\Phi\frac{\partial c_B}{\partial z} \quad (2)$$

where $\Phi\left(=\frac{\partial\mu_B}{\partial c_B}\frac{c_B}{RT}\right)$ is the thermodynamic factor, which can obtained from thermodynamic database developed by the present authors[10]. R is the molar gas constant, and M_B is the atomic mobility, which is given by

$$M_B = \exp\left(\frac{-\Delta G_B^*}{RT}\right)\frac{1}{RT} \quad (3)$$

where $\Delta G_B^* = (Q_B - RTM_B^0)$ is a composition dependent property of the specie B. It is worthwhile to point out that ΔG_B^* contains both the diffusion activation enthalpy (Q_B) and the logarithm of the frequency factor (M_B^0). In the spirit of CALPHAD approach, the composition dependence of both Q_B and M_B^0 is expressed by a Redlich-Kister polynomials[11]. Both Q_B and M_B^0 are optimized based on the experimental data of various diffusion coefficients in the present work.

2 Design of micro-soldering alloy using thermodynamics

Computational thermodynamics can provide much information on the design of the micro-soldering materials in the multi-component system. A thermodynamic tool for designing for Pb-free solders has been developed by the present authors[10], which can provide much information such as stable and metastable equilibria, thermodynamic properties, and physical properties, as shown in Fig. 1. As an example, the calculated results of the Sn-Ag-Cu base alloys, which are promising candidates for Pb-free solders, are presented here.

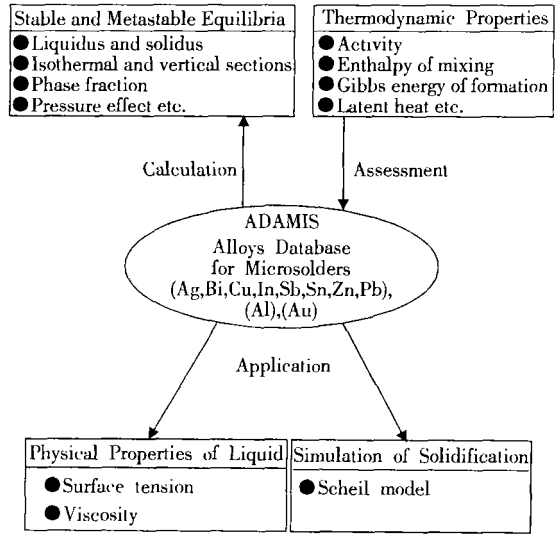

Fig 1　Outline of CALPHAD method

Figure 2 shows the calculated liquidus surface of the Sn-Ag-Cu system, from which the primary crystal and solidification temperature at any composition of alloys can be determined. In addition, the invariant reactions in the whole composition region can be obtained. It is indicated that there are four peritectic reactions and one eutectic reaction in this system.

In the practical solidification process, non-equilibrium rather than equilibrium solidification is often observed and is easily simulated by the Scheil model. The solidification of Sn-2.0Ag-0.5Cu-7.5Bi alloy was simulated and the results are shown in Fig. 3. The solidification starts with the primary crystals of the η phase; it proceeds substantially, however, with the growth of β Sn at the beginning. After commencement of the crystallization of the Ag_3Sn phase, the liquid phase would disappear at 177.9 ℃ under the equilibrium solidification condition.

The surface tension and viscosity of the liquid phase are very relevant to the soldering process. From the calculated results of the effect of alloying elements on surface tension and viscosity of the ternary eutectic alloy in the Sn-Ag-Cu system it can be known that the surface ten-

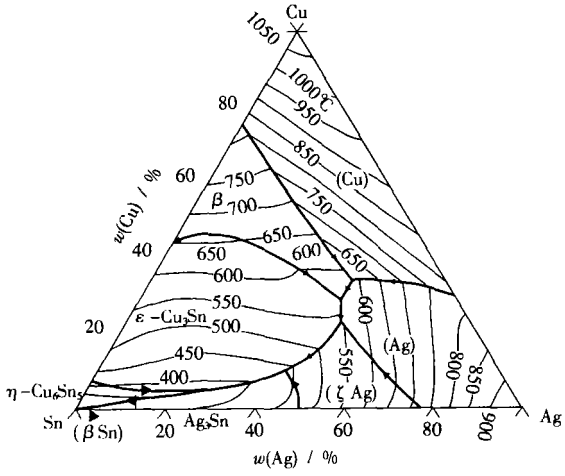

Fig 2 Calculated liquidus projection in the Sn-Ag-Cu system

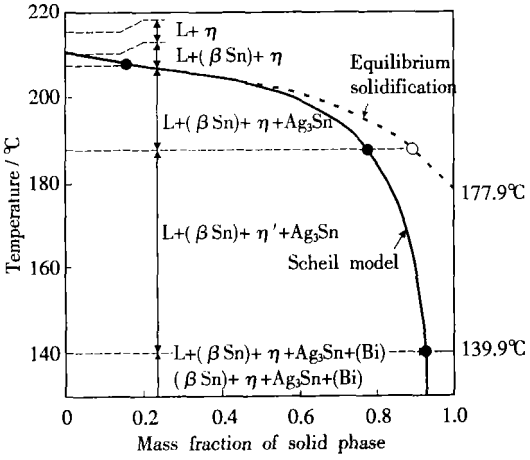

Fig 3 Solidification simulations of the Sn-2.0Ag-0.5Cu-7.5Bi alloy

sion is higher than, due to the addition of Zn, but lower than, due to the addition of Sb, that of the ternary eutectic alloy. The viscosity is slightly lower than that of the ternary eutectic alloy due to the addition of elements Bi, In, Sb and Zn.

3 Design of micro-soldering alloys using kinetics

The interfacial reaction between substrate and solders is important for the reliability of semiconductor electronic packaging. Now we consider a simple example using simulation of diffusion by DICTRA software. If diffusion couple Cu(solid)/Sn(liquid) is treated at 250 ℃ for different time, ε and η intermetallic compounds should form and grow during diffusion process, according to phase diagram of the Cu-Sn system.

Here we firstly consider the dissolution behavior of Cu at the beginning step of diffusion. Figure 4 (a) shows the dissolution of Cu during 500 s at 250 ℃, where the concentration of Cu increases in liquid Sn, and almost reaches the equilibrium composition when time is about 500 s. Figure 4 (b) gives the position and moving speed of the fcc/liq interfacial boundary.

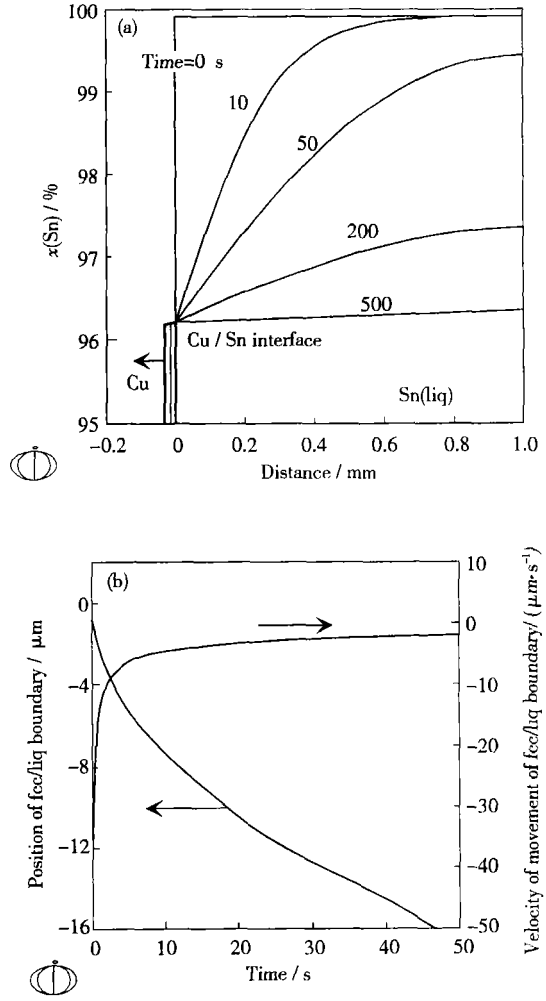

Fig 4 Calculated results of dissolution behavior of Cu in molten Sn. (a) the change of concentration in liquid phase; (b) velocity of movement and position of fcc/liquid boundary

It is seen that Cu/Sn boundary moves at the larger negative speed at the beginning of diffusion, which means this boundary moves into Cu side, e.g. Cu dissolves into liquid Sn. With increasing of time, the speed of Cu dissolution decreases.

With increasing of time, ε and η phases will form and grow. Figure 5 shows the simulation of diffusion couple of Cu/Sn including ε and η phases at 250 ℃, in which the growth of ε and η

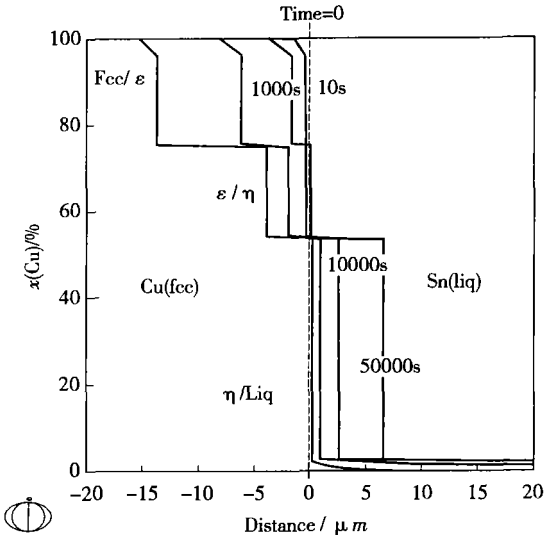

Fig 5　Calculated diffusion behavior in the Cu/ Sn diffusion couple

phases can be calculated. From the calculated results, we know that with the increasing of time the Cu/ ε and ε/ η phase boundaries move into the Cu side, while the η/ Sn(liq) boundary moves into Sn side, which is in agreement with the experimental results. In addition, the calculated growth layers of ε and η phases are also good in agreement with our experimental results[12]. These results indicate that simulation of diffusion using DICTRA can predict the interfacial reactions between Cu substrate and Pb-free solders.

4 Summary

The computational thermodynamics and kinetics have been used in design of the melting temperature of alloys, composition, microstructure, surface tension and viscosity of liquid phase, as well as the diffusion behavior. Examples have been given to demonstrate the great utility of these methods for designing Pb-free solders used in microelectronic package.

Acknowledgement

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Recent papers in Thermodynamics and kinetics of materials and metallurgical processes, alternative Iron making routes, process optimization. Papers. People.Â Keywords â€" CAPEX estimates, PMBookÂ®, Interface Risks, Front End Loading, GCC, Process Design, casting, refining of Silicon, HC FeCr, Turnkey, Package Based, Feasibility. Save to Library. Download. The Pb-rich phase particles coarsened more quickly in samples made at the two fastest cooling rates. There was little Pb-rich phase particle coarsening at 25 and 55 Â°C for all annealing times. Coarsening rate kinetics were examined specifically for the 10 and 100 Â°C/min data using the expression Atnexp[â^'Î"H/RT].Â 23Machlin, E.: An Introduction to Aspects of Thermodynamics and Kinetics Relevant to Materials Science (Giro Press, Croton-on-Hudson, NY, 1999) pp. 299â€"308.Google Scholar. Full text views. Full text views reflects PDF downloads, PDFs sent to Google Drive, Dropbox and Kindle and HTML full text views.Â Computational modeling of phase separation and coarsening in solder alloys. International Journal of Solids and Structures, Vol. 49, Issue. 13, p. 1557. The present thermodynamic database can provide much information such as stable and metastable phase equilibria, phase fraction, liquidus projection and various thermodynamic quantities and so on, which is expected to play an important role in the design of copper base alloys. q 2004 Elsevier Ltd. All rights reserved.Â In particular, Cu base alloys with high performance are required in the field of electronic materials, such as substrate and lead frame in the printed board, interconnection and so on, because the electronic packaging has a tendency to miniaturization [1,2]. In addition, Pb-free micro-soldering alloys to replace conventional Pb Sn alloys have been designed and developed to meet the requirements. Pb-free solders cannot fully meet the requirements for applications in electronic packaging, additional alloying elements are added to improve the performance of these alloys. Thus, ternary and even quaternary Pb-free solders have been developed [5-7], such as Sn-Ag-Cu, Sn-Ag-Bi, and Sn-Zn-Bi solder. However, the knowledge base on Sn-Pb solders gained by experience is not directly applicable to lead-free solders.Â 3. Nano-composite solders. As electronic devices continue to become lighter and thinner, they require much smaller solder joints and fine-pitch interconnections for microelectronic packaging. For example, portable electronic devices, such as portable computers and mobile phones, have become thinner and smaller while adding more complicated functions.