CALPHAD coupled phase-field simulation of microstructural evolution during active metal brazing with Ag-Cu-Sn-Ti alloy

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In this study, a new CALPHAD database of Ag-Cu-Sn-Ti system has been proposed, followed by a phase-field simulation to predict the solidification microstructure of the quaternary alloy during active metal brazing that joins copper circuits and Si_3N_4 substrates. From the CALPHAD coupled phase-field simulation, it was revealed that melting of copper circuit and a reaction of Ti with Si_3N_4 substrate decreases the amount of primary Sn_3Ti_5, resulting in an increased Sn concentration within Ag-Cu-Sn-Ti liquid and thus a lowering of the temperature at which solidification of the brazing metal is completed. Therefore, the developed phase-field program of our own coding can successfully clarify the effect of copper circuit melting and Ti depletion during active metal brazing, which cannot be experimentally monitored.

Keywords: *Phase-field method, CALPHAD, Ag-Cu-Sn-Ti, Active metal brazing, Solidification*

1. Introduction

Power semiconductor modules are utilized in power electronics such as controlling motors in electric vehicles. The modules consist of active metal brazed (AMB) ceramic substrates for ensuring electrical insulation and thermal dissipation, and Si_3N_4 and Ag-Cu-Sn-Ti alloy are typical examples of the substrate material and brazing metal. In electric industries, the AMB process to joint Si_3N_4 substrates with copper circuits is empirically conducted although the depletion of active Ti within Ag-Cu-Sn-Ti liquid occurs as a result of $9Ti+Si_3N_4 \rightarrow 4TiN+Ti_5Si_3$ reaction. In this study, a new CALPHAD database of Ag-Cu-Sn-Ti system has been proposed, followed by a phase-field simulation to predict the solidification microstructure of the brazing alloy taking the Ti depletion into account.

2. Theory

The total picture of active metal brazing of Si_3N_4 with Ag-Cu-Sn-Ti alloy obviously requires Ag-Cu-Sn-Ti-Si-N thermodynamic database, but in this study only Ag-Cu-Sn-Ti and Ti-Si-N systems were utilized for correlating Ti depletion within Ag-Cu-Sn-Ti liquid with the formation of TiN and Ti_5Si_3 through the difference of their chemical potentials of Ti. This is because, at present, the senary and its partial systems have not yet been evaluated and furthermore, the phase-field model dramatically increases calculation time as the number of components in a multi-component alloy increases.

For the Ag-Cu-Sn-Ti system, a multi-phase field model[1)] described by the following equation was used.

$$\frac{\partial \phi^i}{\partial t} = -\frac{2}{N}\sum_{j=1}^{N} M^{ij}\left[\sum_{k=1}^{N}\left\{\left(W^{ik}-W^{jk}\right)\phi^k + \frac{1}{2}\left(\left(a^{ik}\right)^2-\left(a^{jk}\right)^2\right)\nabla^2\phi^k\right\} - \frac{8}{\pi}\Delta G^{ij}\right] \quad (1)$$

Here, ϕ, N, M, W, a, and ΔG are the phase-field variable, the number of phases, phase-field mobility, height of double obstacle potential, gradient coefficient and interface driving force for phase transformation, respectively. Multiphase and multicomponent diffusion was calculated using the following equation;

$$\frac{\partial c_j}{\partial t} = \nabla \cdot \sum_{i=1}^{N} D^i \phi^i \nabla c_j^i \quad (2)$$

where c_j is concentration of component j. D^i, c^i_j are diffusion coefficient and concentration of phase i, respectively.

Interfacial migration was not considered at the interface between the ceramic and brazing metal. However, mass transfer of Ti was taken into consideration. Given that atoms diffuse much faster in the molten metal than in the ceramic substrate, Ti concentration at the interface between the brazing metal and ceramics was regarded as homogeneous along the horizontal direction. By using the representative concentration in the horizontal direction, one-dimensional diffusion equation was solved on the ceramic side.

The local equilibrium condition must be solved to find the concentration of each phase; nevertheless, such a convergence calculation is very time-consuming. Therefore, we have proposed a new model that can solve the local equilibrium condition without iterative calculations. This model considers the component exchange between phases as in the case of phase-field model with finite interface dissipation[2)]. Defining dc_i as the amount of exchange of component i between phase α and phase β, dc_i can be calculated by the following simultaneously equations;

$$\begin{cases} \sum_{k=1}^{\infty}\frac{1}{k!}\left(dc_1\frac{\partial}{\partial dc_1}+\cdots+dc_n\frac{\partial}{\partial dc_n}\right)\left(\frac{\partial f^\alpha}{\partial dc_1^\alpha}-\frac{\partial f^\beta}{\partial dc_1^\beta}\right)=0 \\ \vdots \\ \sum_{k=1}^{\infty}\frac{1}{k!}\left(dc_1\frac{\partial}{\partial dc_1}+\cdots+dc_n\frac{\partial}{\partial dc_n}\right)\left(\frac{\partial f^\alpha}{\partial dc_n^\alpha}-\frac{\partial f^\beta}{\partial dc_n^\beta}\right)=0 \end{cases} \quad (3)$$

where f^i is free energy of phase i. This equation was derived under the constraint that the difference of chemical potentials between phase α and phase β becomes zero. In numerical calculations, the terms higher than the second order as well as cross-terms were neglected. Defining c^i_{new} as the phase concentration in each phase after calculating concentration field and phase field equations, then it can be expressed as;

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$$c_{new}^{\alpha} = \frac{\left(\sum_{i=1}^{N} \phi^i c^i + \nabla \cdot \sum_{i=1}^{N} D^i \phi^i \nabla c^i + \nabla \cdot J^{at} - \sum_{i=1}^{N} \phi_{new}^i \left(c^i - K_{i\alpha} c^{\alpha}\right)\right)}{\sum_{i=1}^{N} K_{i\alpha} \phi_{new}^i} \quad (4)$$

where J^{at} is antitrapping current which counterbalances the solute trapping effect[3]. This equation was derived from a condition that the partition coefficient is constant and total concentration is conserved. The partition coefficient K was calculated in the same manner as in Eiken's multibinary extrapolation[4].

Nuclei must be artificially introduced because the phase-field model is inherently incompatible with thermally activated processes. Therefore, a nucleation model based on thermal fluctuations[5] was used to reduce factitiousness.

As an initial condition, a brazing metal with a composition of Ag-28Cu-5Sn-2Ti (in mass%) was placed between pure copper circuit and pure Si_3N_4 substrate , as illustrated in Figure 1. The brazing metal was assumed to be in equilibrium at 1060K, and Sn_3Ti_5 was arbitrarily distributed with the equilibrium amount. This system was held at 1060 K for 1 h and then cooled to the temperature at which solidification is completed (T_{finish}) at a cooling rate of 1 K/s.

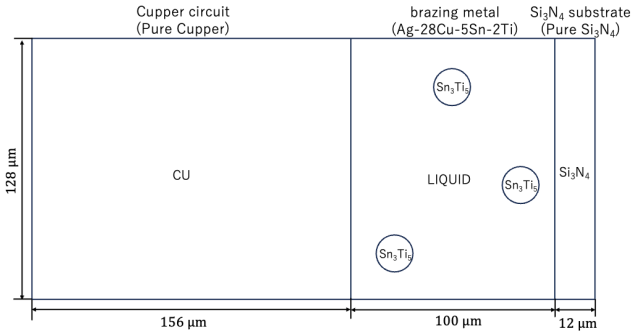

Figure 1 Initial condition of the developed simulation model.

3. Results and discussion

When the system was held at 1060 K, copper circuit first melted and then Ag, Sn and Ti diffused into the copper circuit. Ti was also depleted by the reaction with Si_3N_4. When the cooling process began, furthermore, Cu rich phase started to crystallize, followed by the nucleation of Ag rich phase because Ag was concentrated at the growing Cu rich phase/liquid interfaces. Subsequently, Cu rich phase and Ag rich phase formed a lamellar structure, and the final solidification position was observed on in vicinity of the Si_3N_4 substrate.

To clarify the relationship between brazing conditions (brazing time and brazing temperature) and T_{finish}, furthermore, Scheil solidification calculation was performed for each brazing condition. The results showed that the longer the brazing time and the lower the brazing temperature, the lower the T_{finish}. It was found that the depletion of Ti and melting of copper circuit reduce the fraction of Sn_3Ti_5 in the system, causing an increase in Sn concentration within the brazing alloy liquid, resulting in the lowering of T_{finish}.

References

1) J. Tiaden, B. Nestler, H. J. Diepers and I. Steinbach, Phys. D, 115 (1998) 73-86
2) I. Steinbach, L. Zhang, M. Plapp, Acta. Mater. 60(2012), 2689
3) B. Echebarria, A. Karma, M. Plapp, R. Folch, Phys. Rev. E. 70 (2004), 51
4) J. Eiken, B. Böttger, I. Steinbach, Phys. Rev. E 73 (2006) 066122
5) M. Ode, I. Ohnuma, Computational Materials Science 194 (2021) 110448