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Phase Field Modeling of Ghost Diffusion in Sn-Ag-Cu Solder Joints

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***Abstract* — In this paper, we have introduced a phase field modeling technique to simulate ghost diffusion phenomena of intermetallic compounds in a bulk mettalic matrix phase. We used Zenner-Frank phase field approach to define free energy density functional which is to be evolved using Chan-Hilliard and Alan-Chan equations to simulate time evolution of the precipitates. We verified our simulation results with intermetallic compound growth of Sn-Ag-Cu solder joints in isothermal aging process attributing to the diffusion of Ag_3Sn intermetallic compound. Herewith we present that Zenner-Frank model demonstrates sound validity and provides a best understanding of such phenomena.**

***Keywords* — Ghost Diffusion, Microstructure Evolution, Phase Field Modeling, Precipitate Growth, Zenner-Frank Phase Field Model.**

I. INTRODUCTION

Phase field modeling (PFM) is an important simulation tool to understand phase transformation processes in materials. PFM has been utilized to study solid-state phase transformations, precipitate growth, grain growth, solidification and melting and as well phase transformations due to an external field (uniaxial stress, hydrostatic pressure etc.) [1], [2]. In addition, PFM facilitate in describing phase change mechanisms using a theoretical framework where, availability of experimental data can be challenging [3]. PFM integrates all shortcomings of Fick's diffusion laws [4], [5] taking free energy as a driving parameter into account. In addition to the entire dependence of composition in Fick's diffusion, PFM rely on chemical potential, where, non-conventional diffusion phenomenon can be successfully addressed [6].

Application of PFM for studying various phase change and evolution of microstructure are ubiquitous in literature. The main foundation in developing a phase field model is to obtain a unique free energy density functional (FDF) addressing underlying phenomena of the specific process. The FDF is then evolved using phase field equations (Chan-Hilliard and Alan-Cahn) to identify the behavior of the phase changing system [1]. Contributions to FDF can be generalized to two categories based on chemical and external contributions. Chemical contributions are mainly based on free energy of the atomic system associated from the chemical structure and temperature. External contributions can be considered as additional free energy supplied to the system due to an external stimuli (stress, heat etc.) [1]. To extract few previous works performed on PFM on multiple engineering areas, Mukherjee *et al*. [1] performed PFM to study the behavior of precipitates subjected to uniaxial stress. They have added an additional term to FDF addressing the contribution to free energy from uniaxial stress. Weerasekera and Abdulla [7] studied Cu depletion effect in Sn-Ag-Cu solder joints using Zenner-Frank (ZF) phase field kinetics. They were abe to simulate Cu precipitate depletion effect in solder joints which are grown in a bulk Sn matrix phase. Ohno *et al*. [2] performed PFM for understanding transformation kinetics of welding of steel which can be mainly attributed to melting and solidification. They have used Kurz-Giovanola-Trivedi (KGT) model to modify the FDF according to the underlying process. Yang *et al*. [8] performed PFM on electron powder bed fusion process. They approached by defining the FDF based on powder scale thermal fluid flow (TFF) model to describe the phenomena. Finally, Sweidan *et al*. [9] performed studies in phase change phenomena in thermal energy storage application using PFM. In their study, they have uniquely developed FDFs based on theory of microscopic porous media for the evolution of phase change system [9]. In conclusion, PFM as a modeling method can be highly beneficial and also benifitted for many phase change processes. At present, PFM has contributed to studies in thermal energy storage [10], conventional welding processes [2], additive manufacturing processes [11] micro-nano scale heat transfer [12] and as well as in evaluating

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special functional properties [13] of materials and many solid state phase transformation [14]–[16] problems.

Through this work, we present another application of PFM to identify diffusion of intermetallic (IMC) precipitates due to isothermal aging. We model this phenomena by validating simulation results with isothermal aging of Sn-Ag-Cu (SAC) solder joints focusing on the growth of IMC layers demonstrating ghost type of diffusion. From our experiments, we observed that Ag in the Sn matrix of the solder joint has been transported towards the main IMC layer which was produced in the process of solder-joint and Cu bonding. We were able to successfully model this phenomena using the Zenner-Frank (ZF) phase field model only with considering the chemical contributions to FDF as discussed in this work [1], [17]. In addition, this work also served as a direct experimental verification of ZF PFM model which is challanging to observe in many direct experimental analysis [1].

II. Experiemntal Analysis and Observation of Ghost Diffusion

We have obtained SAC solder joints manufactured by CISCO corporation. The solder joints were made from the initial composition of SAC305 which contain compositions of Sn – 96.5%, Cu – 0.5% and rest with Ag. We have sliced the joints initially from an ultra-precision diamond saw (PACE Technologies – PICO 155P) and obtained scanning electron micrographs (SEM) as in Fig. 1. SEM image identifies the Cu precipitates which are initially distributed in the Sn matrix. However, SEM image was not capable of identifying Ag as a constituent.

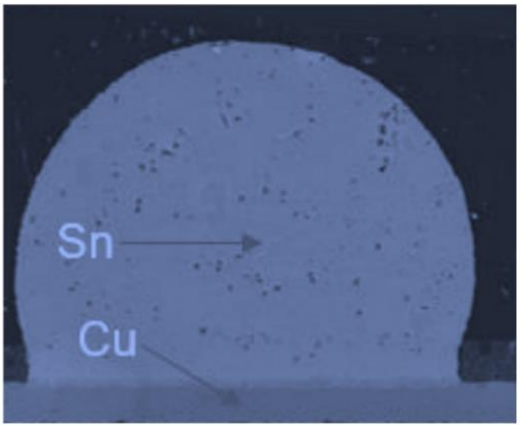

Fig. 1. SEM image of a dissected SAC solder joint and identification of Sn and Cu constituents.

We have isothermally aged a batch of solder joints for discrete time periods of 50, 100, 250 and 500 hrs using a convection oven (Thermo Scientific – Precision Gravity Convection - PR305225G). Isothermally aged solder joint samples were then cut through the center line from the ultra - precision diamond saw. We have performed electron backscatter diffraction (EBSD) on cut solder joint samples using EBSD module attached to TESCAN VEGA scanning electron microscope. EBSD images are resolved by the standard world EBSD data base for target constituents of Ag and Cu. Fig. 2 shows the EBSD images of isothermally aged samples which are resolved for Ag and Cu.

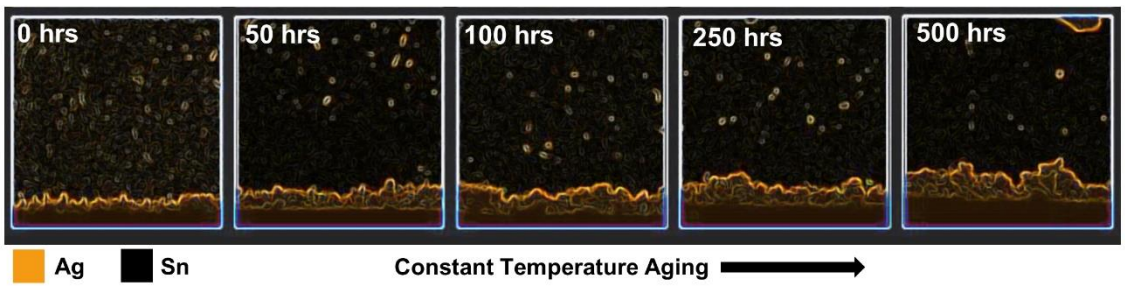

Fig. 2. Isothermal aging process of the solder joint up to 500hrs. Observation of the growth of Ag_3Sn IMC compound due to interstellar diffusion where distribution of Ag_3Sn and Cu_6Sn_5 precipitates can be attributed to Ag and Sn contours respectively.

The IMC compounds that are generated as a byproduct of Ag-Sn bonding at the soldering process can be attributed to Ag_3Sn and identified in the bottom regions which show concentrated Ag. However, it is observable that more Ag_3Sn precipitates are initially scattered in Sn matrix as shown in Fig. 2, before

isothermal aging, due to the soldering process. We observe that growth of the IMC Ag_3Sn layer while in subsequent aging process and reduction in Ag_3Sn precipitates scattered in the Sn matrix. From this result, it is observed that Ag as a constituent is attracted towards the Ag rich region provided by Ag_3Sn IMC compound. Such phenomena can be successfully attributed to uphill diffusion process which can be mainly described using phase field approaches as discussed in upcoming section. The main reason for uphill diffusion is the overcoming of the free energy barrier from one phase to another due to thermal energy provided in the isothermal aging process [18].

III. Phase Field Model

We present the PFM model to simulate and analyze the uphill diffusion process observed in experimental results as below. Here with we incorporate Zenner-Frank (ZF) phase field model as presented by Mukherjee *et al*. [1] and Roy and Gururajan [17] which is soundly demonstrated for precipitate growth and solid state transport phenomena. ZF model is developed based on Cahn-Hilliard equation to evolve the conserved order parameter which is the composition (c). Secondly, Alan-Chan equation is used for evolving non-conserved order parameter which is the phase of the constituents (η). Chan-Hilliard equation differs from conventional Fick's diffusion equation mainly due to the incorporation of atomic mobility (M) and chemical potential (μ) where gradient effects are attributed to chemical potential instead of the composition. Incorporation of the chemical potential facilitate to observe the uphill diffusion phenomena contrary to Fick's diffusion.

As the initial step in developing phase field model, Cahn-Hilliard equation can be given as:

$$\frac{\partial c}{\partial t} = M\nabla^2\left(\frac{\partial (F/N)}{\partial c}\right) \tag{1}$$

where, F/N is the free energy density functional normalized per atom (Where N is the number of atoms per unit volume in the system) which only accounts the chemical contribution [1]. Similarly, Alan-Cahn equation takes the form:

$$\frac{\partial \eta}{\partial t} = -L\left(\frac{\partial (F/N)}{\partial \eta}\right) \tag{2}$$

where, L is the interface mobility considered for microstructure (phase) order parameter. Free energy density functional (F/N) for ZF model can be given as:

$$\frac{F}{N} = \int \left\{ f(c,\eta) + k_c(\nabla c)^2 + k_\eta(\nabla \eta)^2 \right\}. dV \tag{3}$$

where, $f(c,\eta)$ is the bulk free energy of the system and k_c is the gradient energy coefficient for composition which is different from the diffusion coefficient applied in Fick's law. k_η is the gradient energy coefficient in microstructure order parameter which is unique for the system. The bulk free energy density function can be written using the dual minimum approach using Wang function $W(\eta)$ as [1]:

$$f(c,\eta) = f^m(c)(1 - W(\eta)) + f^p(c)W(\eta) + P\eta^2(1-\eta)^2 \tag{4}$$

With P as a constant, $f^m(c)$ represents the free energy of the bulk phase (matrix) and $f^p(c)$ represents the free energy of the precipitate phase. $f^m(c)$ and $f^p(c)$ are modeled simply using quadratic functions to implement the effect of double well potential and subsequent spinodal decomposition as, $f^m(c) = Ac^2$ and $f^p(c) = B(1-c)^2$ [1]. To implement F/N in Chan-Hilliard and Alan-Cahn equations, derivatives with respect to c and η of F/N can be given as:

$$\frac{\partial (F/N)}{\partial c} = \frac{\partial f(c,\eta)}{\partial c} - 2k_c\nabla^2 c \tag{5}$$

$$\frac{\partial (F/N)}{\partial \eta} = \frac{\partial f(c,\eta)}{\partial \eta} - 2k_\eta\nabla^2 \eta \tag{6}$$

In similar fashion, derivatives of free energy density function with respect to c and η can be given as:

$$h_c = \frac{\partial f(c,\eta)}{\partial c} = 2Ac(1 - W(\eta)) - 2B(1-c)W(\eta) \tag{7}$$

$$h_c = \frac{\partial f(c,\eta)}{\partial c} = 2Ac(1 - W(\eta)) - 2B(1 - c)W(\eta) \quad (8)$$

$$h_\eta = \frac{\partial f(c,\eta)}{\partial \eta} = 2Ac^2W(\eta) - B(1 - c)^2W'(\eta) + 2P\eta(1 - \eta)(1 - 2\eta) \quad (9)$$

where, Wang function, $W(\eta)$ and it's derivative $W'(\eta)$ can be obtained according to:

$$W(\eta) = \begin{cases} 0 & \text{If } \eta < 0 \\ \eta^3(10 - 15\eta + 6\eta^2) & \text{If } 0 \le \eta \le 1 \\ 1 & \text{If } \eta > 1 \end{cases}$$

$$W'(\eta) = \begin{cases} 0 & \text{If } \eta < 0 \\ 3\eta^2(10 - 15\eta - 16\eta^2) + \eta^3(12\eta - 15) & \text{If } 0 \le \eta \le 1 \\ 0 & \text{If } \eta > 1 \end{cases}$$

We have developed a code using MATLAB software incorporating Fast Fourier Transform with periodic boundary conditions. In the model, we considered compositions of Ag and Sn where, Ag based precipitates, which is in Ag_3Sn form, dispersed in Sn matrix. Therefore, composition as the conserved order parameter is evolved based on Ag. Secondly microstructure or phase order parameter is attributed to microstructure of Ag_3Sn which is dispersed in Cu_6Sn_5 where Sn is the rich compound as presented in experimental EBSD images.

We considered all diffusion parameters (M, L, k_c, k_η, A, B and P) to unity since values of these constants do not adhere with the qualitative simulation results. Secondly, we considered composition and microstructure order parameter in normalized form within 0 to 1. However, we have relaxed the order parameter (η) to evolve greater than 1 since it was initially considered as non-conserving.

An initial composition and microstructure distributions were produced like the EBSD image in Fig. 2 (0h) as shown in Fig. 3a and Fig. 4a. We applied c and η distributions in the bottom area near to 1, in the initial distribution. Rest of the matrix is filled with random distribution of c and η varying from 0-1. This arrangement was evolved in time with a nondimensionalized time step value of 0.5 up to 125 steps where stability of the order parameters is reached.

IV. Results and Discussion

Fig. 3 shows the time evolution of composition and Fig. 4 shows the evolution of microstructure order parameter. It is evident that experimental observation is demonstrated in the phase field model showing the growth of the IMC precipitate while reducing Ag_3Sn precipitates dispersed in the Sn matrix. Precipitates located far away from the IMC layer performed a ghost transport reaching to the IMC layer traveling through the Sn matrix. Another significance of the simulation is that the composition order parameter is automatically conserved without imposing any restrictions to control the order of magnitude. However, microstructure order parameter has evolved greater than 1 demonstrating its non-conserved behavior. This effect takes place due to the Gibbs-Thompson effect as described elsewhere [17]. In addition to IMC layer growth, multiple precipitates are grown independently in the Sn matrix with initial precipitates which have demonstrated low free energy that can be similarly observed in experimental results. Fig. 5 shows another clear view of the evolution of the IMC growth front.

We attribute the behavior of scattered Ag precipitates in the middle of the Sn matrix as a ghost transport occurring similar to a warmic diffusion, following the uphill diffusion path to coalasse with high composition areas. The main driving force of the mechanism is the supply of thermal energy in an isothermal process that allows to overcome the free energy barrier for greater existence of Ag_3Sn phase. Since we observed the diffusion phenomena without an external contribution to the FDF, we can reasonably predict that ghost transport can still occur in Sn-Ag-Cu solder joint even at ambient temperatures within a sufficiently long time period. As a pratical concern, such transport of Ag in the Sn matrix may reduce the strength of solder joint and requires further studies to analyze its effects.

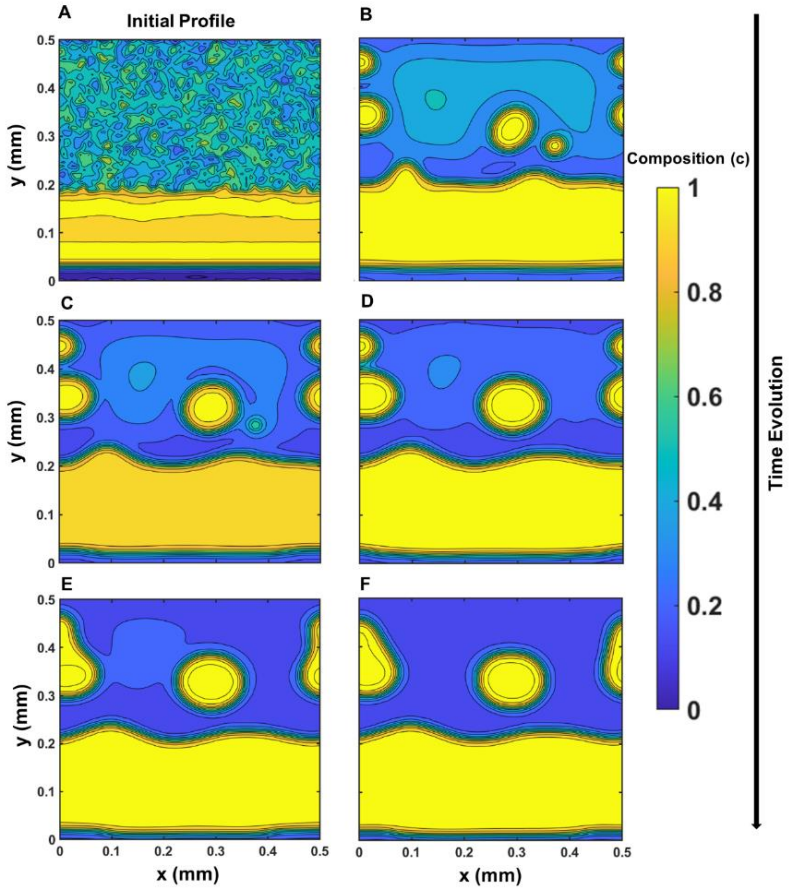

Fig. 3. Evolution of composition of Ag and Cu under transient simulation. Superscripts A to F represent subsequent time evolved composition (c).

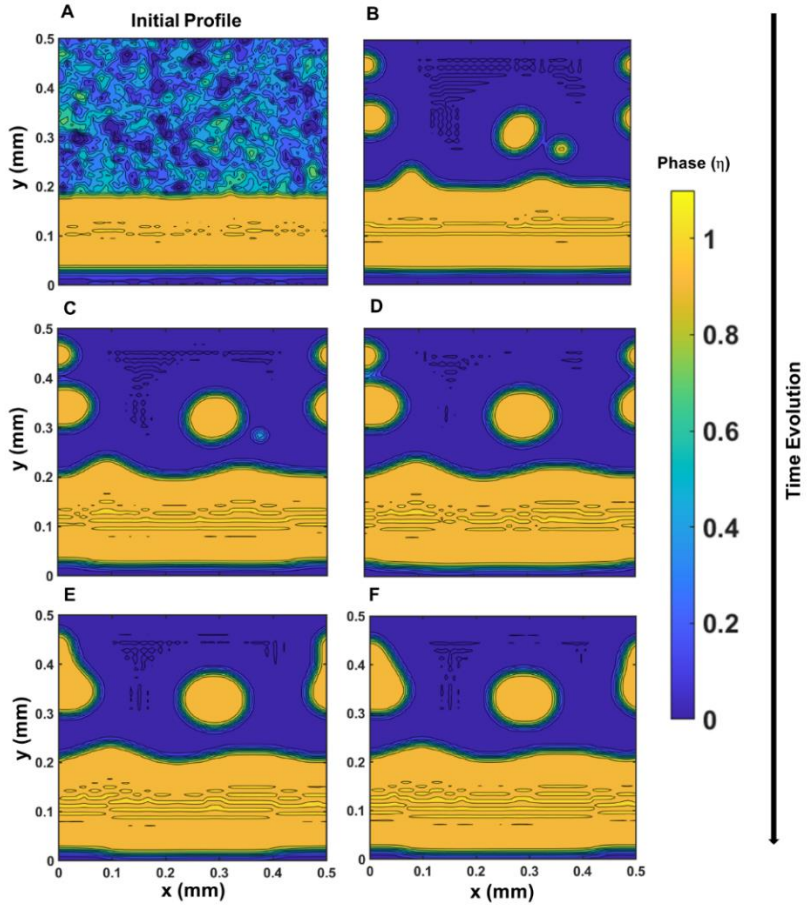

Fig. 4. Evolution of microstructure of Ag_3Sn and Cu_6Sn_5 precipitates under transient simulation. Superscripts A to F represent subsequent time evolved order parameter (η).

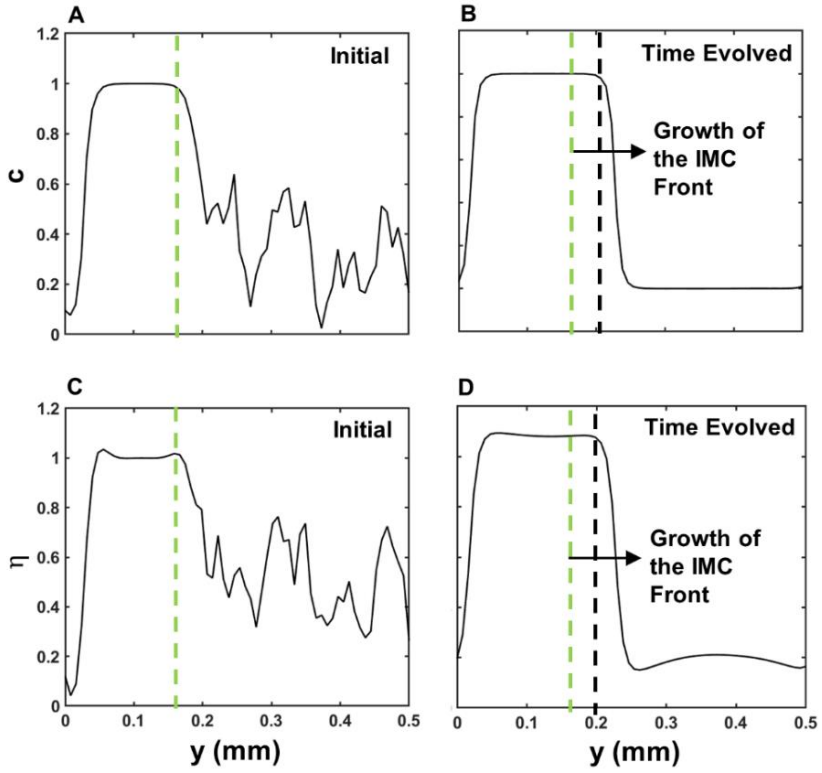

Fig. 5. Identifying growth of the IMC front due to ghost diffusion phenomena (A-B). Evolution of the IMC layer based the composition growth front, (C-D). Evolution of the IMC layer based on microstructure order parameter growth front.

V. Conclusion

In this work, we have introduced the ZF phase field model to simulate and identify the underlying phenomena of ghost transport process of precipitates which demonstrate uphill diffusion. We have justified this process comparing with experimental micrographs of isothermally aged solder joints where growth of Ag_3Sn IMC layer while depletion of Ag in the Sn matrix. Here with we conclude that ZF model can be an ideal candidate for simulating such processes in various phase change applications without accounting external contributions to free energy. In addition to understanding the phenomena, this work also verifies the accuracy of ZF model for precipitate growth processes.

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Conflict of Interest

Authors declare that they do not have any conflict of interest.

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