Effect of Strain-Enhanced Microstructural Coarsening on the Cyclic Strain-Hardening Exponent of Sn–Ag–Cu Joints

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The effects of temperature and strain-enhanced coarsening of intermetallic compounds (IMCs) on the cyclic strain-hardening exponent of Sn–Ag–Cu microsolder joints were investigated. The effect of temperature on the exponent is described by the Arrhenius function, and the cyclic strain-hardening exponent is proportional to the reciprocal square root of the average radius of the IMCs. Ag₃Sn and Cu₆Sn₅ IMCs coarsened with time, temperature, and inelastic strain. In the growth process with time and temperature, the phase-size exponent and activation energy for a Sn–Ag–Cu microsolder joint were ~3 and 50 kJ/mol, respectively. Ag₃Sn and Cu₆Sn₅ growth with isothermal aging was controlled by the diffusion of Ag and Cu in the Sn matrix. In addition, the strain-enhanced coarsening of the IMCs can be described by the growth model with consideration of isothermal aging and inelastic strain-enhanced growth. Therefore, the cyclic strain-hardening exponent decreases with temperature, and the strain-enhanced coarsening of IMCs can be described by the reciprocal square root of the average radius of the IMCs and the strain-enhanced growth model.

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1. Introduction

Solder joints in large scale integrated (LSI) devices are constantly subjected to temperature variation and consequent thermal fatigue due to the differences in thermal expansion coefficients. Therefore, an understanding of the low-cycle fatigue properties of a solder joint is essential.¹–³ The Norris–Landzberg model shown in eq. (1) is used to predict the thermal fatigue life of solder joints.⁴

\[ N_f = C \cdot f^k \cdot \Delta \varepsilon_{in}^{-1/\alpha} \cdot \exp \left( \frac{Q_1}{RT} \right) \]  
(1)

In this equation, \( N_f \) is the fatigue life, \( C \) is the fatigue ductility coefficient, \( f \) is the frequency, \( k \) is the frequency exponent, \( \Delta \varepsilon_{in} \) is the equivalent inelastic strain range, \( \alpha \) is the fatigue ductility exponent, \( Q_1 \) is the activation energy, \( R \) is the gas constant, and \( T \) is the maximum temperature in thermal condition. In the Norris–Landzberg model (eq. (1)), the fatigue ductility exponent, \( \alpha \), is constant regardless of the frequency, \( f \), and temperature, \( T \). However, in our recent studies, the fatigue ductility exponent was affected by the temperature and holding time of the low-cycle fatigue properties of a Sn–Ag (3.0 mass%)–Cu (0.5 mass%) (Sn–Ag–Cu) microsolder joint specimen that simulated an actual solder joint. Accordingly, the fatigue ductility exponent in Coffin-Manson’s law (eq. (2)) for Sn–Ag–Cu microsolder joints can be represented by eq. (3).⁵,⁶

\[ \Delta \varepsilon_{in} \cdot N_f^\alpha = C \]  
(2)

\[ \alpha = \frac{0.6}{n' + 1} \]  
(3)

In these equations, \( \Delta \varepsilon_{in} \) is the equivalent inelastic strain range, \( N_f \) is the fatigue life, \( \alpha \) is the fatigue ductility exponent, \( C \) is the fatigue ductility coefficient, and \( n' \) is the cyclic strain-hardening exponent, which reflects the dynamic work-hardening properties. In eq. (3), the cyclic strain-hardening exponent determines the fatigue ductility exponent for the Sn–Ag–Cu microsolder joint. Since the cyclic strain-hardening exponent, which reflects the dynamic work-hardening properties, may depend on the temperature and microstructure, the effect of environmental factors, such as temperature and holding time, on the low-cycle fatigue properties of Sn–Ag–Cu solder joints were described using the cyclic strain-hardening exponent; this differs from the Norris–Landzberg model. Therefore, to understand the effect of environmental factors on the low-cycle fatigue properties of Sn–Ag–Cu solder joints, investigations of the effect of temperature and the microstructure on the cyclic strain-hardening exponent are necessary.

For a Sn–Ag–Cu alloy with fine intermetallic compound particles of Ag₃Sn and Cu₆Sn₅ dispersed in the matrix, the cyclic strain-hardening exponent was expected to depend on the temperature and size of the intermetallic compounds.⁵ Hence, in order to model the effect of the environment on the low-cycle fatigue properties of Sn–Ag–Cu solder joints, clarification of the effect of temperature and the microstructure on the cyclic strain-hardening exponent under high-temperature fatigue conditions was needed. In particular, since IMCs in solder joints coarsen due to temperature and strain loading under thermal cycling conditions, understanding the influence of temperature and strain-enhanced coarsening of IMCs on the cyclic strain-hardening exponent for Sn–Ag–Cu microsolder joints is necessary. However, it has yet to be elucidated.

In this study, the effect of temperature and strain-enhanced coarsening of IMCs on the cyclic strain-hardening exponent of Sn–Ag–Cu microsolder joint specimens is investigated.
2. Experimental Procedure

2.1 Microsolder joint specimens and aging conditions

The microsolder joint specimen used in this study comprised two chrome-coated Cu rods connected with a solder ball, as shown in Fig. 1.7,8) The solder alloy in this study was Sn–Ag (3.0 mass%)–Cu (0.5 mass%). The rods were soldered at 518 K using a rosin mildly activated (RMA)-type flux then held for 30 s under ambient conditions. Figure 2 shows the scanning electron micrograph of the initial microstructure of the Sn–Ag–Cu microsolder joint. The microstructure consists of β-Sn dendrites and a fine eutectic microstructure with intermetallic Ag3Sn and Cu6Sn5 and Sn.9,10) To coarsen the IMCs in the matrix, the microsolder joint was aged at 348 and 398 K for 17 h, 6 days, 19 days, 46 days and 90 days.

2.2 Mechanical testing machine

A micromechanical testing machine was used to examine the mechanical properties.11) This machine employs a piezo-stage actuator with a displacement enlargement mechanism; the maximum stroke is ±250 µm and the maximum load is ±40 N. The displacement was measured using an electrical capacitance displacement sensor (displacement resolution: 0.01 µm) positioned at the end of the specimen-fixing jig, and the actuator was controlled by the values measured by the displacement sensor. The specimen-fixing jig was heated by a ceramic heater placed at the bottom of the jig; the temperature was monitored to remain within ±2 K by a thermocouple attached to the specimen.

2.3 Obtaining the cyclic strain-hardening exponent

The cyclic strain-hardening exponent was obtained from the cyclic stress-inelastic strain curve, which was generated by connecting the tips of several stable stress-inelastic strain hysteresis loops.12) The relationship of the cyclic stress-inelastic strain curve is as follows:

\[
\sigma = A_1 \cdot \varepsilon_{\text{in}}^{n'}, \tag{4}
\]

where \(\sigma\) is the stress, \(A_1\) is the constant, \(\varepsilon_{\text{in}}\) is the inelastic strain, and \(n'\) is the cyclic strain-hardening exponent. The cyclic stress-inelastic strain curve was obtained using the multi-step method,12) which enables several points from the same specimen at different strains to be obtained.5 The stress-inelastic strain curve was calculated from the apparent stress and inelastic strain considering the rigidity of the testing machine based on the load-displacement hysteresis loop that was obtained from shear fatigue testing of the microsolder joint. Then, the cyclic strain-hardening exponent was determined from eq. (4) by fitting the apparent stress-inelastic strain curve using a non-linear least-squares method. The displacement ranges for the multi-step method were 4, 6, 8, 10, 12 and 14 µm, and the testing temperature was the same as the aging temperature.

2.4 Mechanical fatigue testing and finite element analysis

To examine the strain-enhanced growth of IMCs, isothermal low-cycle shear fatigue testing was performed on the microsolder joint specimen and the microstructures were observed. A displacement-controlled low-cycle shear fatigue test was performed at 398 K. The control waveform was a symmetrical trapezoidal wave (ramp rate: 5 µm/s); a displacement hold time of 120 s was imposed for every maximum and minimum displacement. The displacement ranges were 7, 8 and 9 µm, and the testing times were 8, 20 and 55 h. The equivalent inelastic strain range was calculated via finite element analysis (FEA). In FEA, the model is a half model with the symmetry of the specimen shape, as shown in Fig. 3, and the equivalent inelastic strain range is obtained from the mean value of the crack initiation region. An elasto-plasto-creep analysis was performed on ANSYS ver. 11.0 using a hexahedral element with eight nodes (SOLID185). The plastic constitutive equation was a two straight-line approximation-type kinematic hardening rule, and the creep property was described by Norton’s law.5) The material constant was obtained from the shear and stress relaxation testing of the Sn–Ag–Cu microsolder joint specimen.5)
2.5 Microstructural observations

The microstructures were observed using a scanning electron microscope (SEM). The specimens were prepared by mechanical polishing with SiC polishing paper and diamond paste and further polishing using a colloidal silica suspension liquid to remove the layers that were damaged during mechanical polishing.

3. Results

3.1 Influence of temperature and average radii of the intermetallic compounds on the cyclic strain-hardening exponent

The effects of temperature and the average radii of the IMCs on the cyclic strain-hardening exponent of the Sn–Ag–Cu microsolder joint were examined. Figure 4 shows the relationship between the stress and inelastic strain, which was obtained using the multi-step method of specimen aging for 46 days at 348 and 398 K; this provides an example of how the cyclic strain-hardening exponent is determined. If, according to Ashby’s proposal,\textsuperscript{13} the strength properties of metals are assumed to be proportional to the reciprocal square root of the average radii of the IMCs, the cyclic strain-hardening exponent with consideration of the thermal activation process for dispersion-hardening alloys is expected to obey the following equation:

\[ n' = A_2 \exp \left( \frac{Q_2}{RT} \right) \sqrt{\frac{1}{r}}, \]  

where \( n' \) is the cyclic strain-hardening exponent, \( A_2 \) is a constant, \( Q_2 \) is the activation energy, \( R \) is the gas constant, \( T \) is the temperature, and \( r \) is the average radius of Ag\(_3\)Sn and Cu\(_6\)Sn\(_5\). The relationship between the cyclic strain-hardening exponent and the average radius of the IMCs for the isothermally aged Sn–Ag–Cu microsolder joint specimen was determined using eq. (5). Figure 5 shows the influence of temperature and the size of IMCs on the cyclic strain-hardening exponent. The vertical axis indicates the cyclic strain-hardening exponent with the Arrhenius term, and the horizontal axis indicates the average IMC radius of the isothermally aged microsolder joint specimen, which was the mean value of the Ag\(_3\)Sn and Cu\(_6\)Sn\(_5\) particle radii in the matrix. At 398 and 348 K, although the data is somewhat dispersed, the slopes of the lines were approximately 0.5, and the effects of temperature and the average radius on the cyclic strain-hardening exponent can be described by eq. (5) (Fig. 5). The activation energy was calculated to be 6 kJ/mol using the best-fit method.\textsuperscript{16} Since the decrease in the cyclic strain-hardening exponent with increasing temperature is attributed to diffusion at higher temperatures, the activation energy may correlate with the energy of volume diffusion for \( \beta \)-Sn (\(~100\) kJ/mol) or creep for Sn–Ag–Cu (\(~50–120\) kJ/mol).\textsuperscript{16,17} However, the activation energy calculated using eq. (5) was approximately 1/20 the energy of volume diffusion for \( \beta \)-Sn. Also, in the case of polycrystalline Al,
the activation energy upon strain hardening was lower than the energy of lattice diffusion for pure Al.\textsuperscript{18} The physical background for this data has yet to be elucidated.

3.2 Influence of temperature and inelastic strain on coarsening of the intermetallic compounds

The effects of temperature, time, and equivalent inelastic strain range on the average radius of IMCs in a Sn–Ag–Cu microsolder joint were examined. According to the reports on Sn–Ag solder alloys published by Dutta\textit{ et al.}, the effects of temperature, time, and inelastic strain on the coarsening of IMCs can be described using the following equation:\textsuperscript{14,15}

\[
 r_{\text{growth}}^m = K \exp\left(\frac{-Q_3}{RT}\right)t + K \exp\left(\frac{-Q_3}{RT}\right)2N\varepsilon_{\text{in-total}}. \quad (6)
\]

Where \( r_{\text{growth}}^m \) is the growth increment of the average radius of IMCs, \( m \) is the phase size exponent, \( K \) is a constant, \( Q_3 \) is the activation energy, \( R \) is the gas constant, \( T \) is the temperature, \( N \) is the constant that represents strain-enhanced aging, and \( \varepsilon_{\text{in-total}} \) is the accumulated equivalent inelastic strain. In this equation, the first and second terms on the right side indicate isothermal aging and strain-enhanced growth, respectively. Equation (6) can be rewritten as eq. (7) when the coarsening of IMCs by strain-enhanced growth does not occur (i.e., \( \varepsilon_{\text{in-total}} \) in eq. (6) is equal to zero).

\[
 r_{\text{growth}}^m = K \exp\left(\frac{-Q_3}{RT}\right)t. \quad (7)
\]

Equation (7) shows the relationship between the growth increment of the average radius of the IMCs due to isothermal aging and aging time. The SEM image of the microstructures of a specimen that was isothermally aged at 398 K for 19 and 46 days are shown in Fig. 6; the Ag\textsubscript{3}Sn and Cu\textsubscript{6}Sn\textsubscript{5} in the matrix show evident coarsening, and the IMCs in the specimen that was aged for 46 days are significantly larger. Figure 7 shows the relationship between the average particle radius of the IMCs at 348 and 398 K and the aging time for isothermally aged specimens. Although some data dispersion is observed, the relationships between the average particle radius and the aging time at each temperature obey eq. (7). The slope of the line in Fig. 7 is approximately 0.33, and the activation energy is 50 kJ/mol.

By only considering the strain-enhanced growth of the IMCs, eq. (6) can be rewritten to eq. (8).

\[
 r_{\text{growth}}^m = K \exp\left(\frac{-Q_3}{RT}\right)t = K \exp\left(\frac{-Q_3}{RT}\right)\varepsilon_{\text{in-total}} \cdot 2N. \quad (8)
\]

The left side of eq. (8) pertains only to the strain-enhanced growth increment. Figure 8 shows the SEM image of the microstructure of a specimen that was fatigue-tested with a displacement range of 8 µm at 398 K for 19 h. From Fig. 8, it is evident that the coarsening of IMCs in isothermally aged specimens under strain occurred much earlier than in isothermally aged specimens without strain loading. This suggests that the growth of IMCs is hastened by strain loading as well as increased temperature and time. Figure 9 shows the relationship between the growth increment during strain-enhanced growth and the accumulated equivalent inelastic strain for an isothermally aged mechanical fatigue-tested specimen; the strain was calculated to be the equivalent inelastic strain during a cycle multiplied by the number of cycles for fatigue testing. From Fig. 9, it is evident that the strain-enhanced growth increment of the IMCs essentially conformed to eq. (8), and that the constant representing strain-enhanced aging, \( N \), is 15 000. The effects

![Fig. 6 SEM micrograph of the microstructure of a Sn–Ag–Cu joint (a) isothermally aged for 19 days at 398 K and (b) isothermally aged for 46 days at 398 K.](image)

![Fig. 7 Relationship between the average particle radius and aging time at each temperature for an isothermally aged Sn–Ag–Cu joint.](image)

![Fig. 8 SEM image of the microstructure of a specimen that was mechanical fatigue-tested with a displacement range of 8 µm at 398 K for 19 h.](image)

![Fig. 9 Relationship between the growth increment during strain-enhanced growth and the accumulated equivalent inelastic strain for an isothermally aged mechanical fatigue-tested specimen.](image)
of temperature, time, and inelastic strain on the coarsening of IMCs in Sn–Ag–Cu microsolder joints are represented by the strain-enhanced growth model shown in eq. (8). The above experiments demonstrate that the influence of temperature, time, and equivalent inelastic strain on the cyclic strain-hardening exponent of a Sn–Ag–Cu microsolder joint can be described using eqs. (5) and (6) from the perspective of the average IMC particle radius and its growth model.

4. Discussion

From Fig. 7, the phase-size exponent, which was determined from the slope of the line, and activation energy for the isothermal aging of Ag3Sn and Cu6Sn5 intermetallic compounds in a Sn–Ag–Cu microsolder joint were determined to be ~3 (~1/0.33) and 50 kJ/mol, respectively. The growth law for the IMCs may be estimated from the phase-size exponent and the activation energy. The growth exponent, $m$, is indicative for the growth/coarsening mechanism. Grain-boundary diffusion controlled growth corresponds to an $m$ value equal to 4, and volume diffusion-controlled growth is indicated by an $m$ value equal to 3. In addition, the activation energy is related to the energy of the volume diffusion of Sn and the diffusion of Ag and Cu in the Sn matrix. Table 1 shows the activation energy of the diffusion of Ag, Cu and Sn in the Sn matrix; the activation energy measured in this study was close to the energies of diffusion of Ag and Cu in the Sn matrix. Since the activation energy was measured from the growth increments of Ag3Sn and Cu6Sn5 without distinguishing between the composites, it is suggested that the diffusion of Ag and Cu in the Sn matrix is dominant for the isothermal aging of Ag3Sn and Cu6Sn5 in the Sn–Ag–Cu microsolder joint.

It was also revealed that the cyclic strain-hardening exponent that represents the low-cycle fatigue property was governed by the average particle radius of the IMCs. Also, the IMCs in the Sn–Ag–Cu microsolder joint were coarsened by temperature, time, and inelastic strain. This suggests that the IMCs in Sn–Ag–Cu solder joints in LSI packages are coarsened by environmental temperature, electronics operating time, and inelastic strain resulting from differences in the thermal expansion coefficients of components; the fatigue ductility exponent for the joint increases due to the average radius increment of the IMCs. This trend clearly differs from the Norris–Landzberg model used for the prediction of the thermal life of solder joints. To predict the lifetime with a high degree of accuracy, the effect of the coarsening of IMCs on the low-cycle fatigue properties of Sn–Ag–Cu solder joint must be considered.

5. Conclusions

The cyclic strain-hardening exponent for a Sn–Ag (3.0 mass%–Cu (0.5 mass%) microsolder joint is proportional to the reciprocal square root of the average radius of the IMCs, and the effect of temperature on the exponent can be described by the Arrhenius function. The Ag3Sn and Cu6Sn5 IMCs coarsened with time, temperature, and inelastic strain. In the growth process characterized by time and temperature, the phase-size exponent and activation energy for the Sn–Ag–Cu microsolder joint were ~3 and 50 kJ/mol, respectively. From the perspective of the phase-size exponent and activation energy, the Ag3Sn and Cu6Sn5 growth during isothermal aging was controlled by the diffusion of Ag and Cu in the Sn matrix. In addition, the strain-enhanced coarsening of the IMCs can be described by the growth model with consideration of isothermal aging and inelastic strain-enhanced growth. Therefore, the cyclic strain-hardening exponent decreased with temperature and the strain-enhanced coarsening of the IMCs and can be described by the reciprocal square root of the average radius of the IMCs and the strain-enhanced growth model.
These results indicate that the coarsening of IMCs in Sn–Ag–Cu solder joints for LSI packages under thermal cycling was affected by environmental temperature, operation time of electronics, and inelastic strain resulting from differences in the thermal expansion coefficients of components; therefore, the fatigue ductility exponent representing the low-cycle fatigue property increased with increasing average IMC radius. This trend clearly differs from the Norris–Landzberg model, which is used for standard thermal life prediction of solder joints.

REFERENCES