Nucleation and Morphology of Cu$_6$Sn$_5$ Intermetallic at the Interface between Molten Sn-0.7Cu-0.2Cr Solder and Cu Substrate

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Abstract: The nucleation kinetics and morphology of Cu$_6$Sn$_5$ IMCs at the interface between a Sn-0.7Cu-0.2Cr solder and Cu substrate were investigated in this study. A Sn-0.7Cu solder was utilized as a reference to elucidate the impact of Cr addition. The mechanical properties of the solder joints were determined via ball-shear tests. Cu coupons were dipped in the molten solders for 1 and 3 s at 240–300 °C, and the morphological analyses were conducted via electron microscopy. Both the solders contained scallop-like Cu$_6$Sn$_5$ IMCs. The smallest Cu$_6$Sn$_5$ IMCs were observed at 260 °C in both the solders, and the particle size increased at 280 and 300 °C. The IMCs in the Sn-0.7Cu-0.2Cr solder were smaller and thinner than those in the Sn-0.7Cu solder at all the reaction temperatures. The thickness of the IMCs increased as the reaction temperature increased. Inverse C-type nucleation curves were obtained, and the maximum nucleation rate was observed at an intermediate temperature. The shear strengths of the Sn-0.7Cu-0.2Cr solder joints were higher than those of the Sn-0.7Cu solder joints. This study will facilitate the application of lead-free solders, such as Sn-0.7Cu-0.2Cr, in automotive electrical components.

Keywords: lead-free solder; intermetallic compound; dipping test; shear strength; nucleation kinetics

1. Introduction

Lead-free solders are utilized as the joint materials in automotive electrical components to comply with environmental regulations such as end-of-life vehicles (ELVs) and restriction of hazardous substances (RoHS) directives [1,2]. Sn reacts with the Cu substrates in lead-free solders to form a soldered joint [3,4]. A typical reflow process involves four steps, i.e., preheating, ramping, dipping, and cooling. The solder is not completely liquefied at the preheating stage. Therefore, the diffusion of Sn atoms from the solder to the Cu substrate is slow. The local concentration of the Cu atoms is higher than the concentration of the Sn atoms on the surface of the Cu substrate. This induces the formation of an extremely thin (few nm-thick) Cu$_3$Sn intermetallic compound (IMC) layer at the Cu interface. The liquid-solid-state diffusion is initiated between the Sn of the molten solder and the Cu substrate in the ramping step. This results in the intrusion of Sn atoms into the Cu substrate. Consequently, a thick Cu$_6$Sn$_5$ IMC layer is formed over the thin Cu$_3$Sn IMC layer. The IMC grains continue to grow in the dipping step which is performed at a temperature above the melting point of the solder. The Cu atoms are locally precipitated on top of the existing Cu$_6$Sn$_5$ IMC interface owing to their low-energy state in the cooling step [5–8]. The presence of thick IMCs induces the occurrence of brittle fractures under adverse thermal conditions during thermal aging and cycling. This failure is attributed to the differences in the thermal expansion coefficients of the material and substrate [9]. Therefore, the reaction for the initial formation of IMCs is an important step that controls the growth...
and morphology of the IMCs since the Sn/Cu reaction may occur in various environments. The reliability of automotive electrical components under high temperature, high humidity, and combined vibrations should be higher than that of other components. To address this challenge, the use of Sn-Ag-Cu, Sn-Ag, Sn-Au, Sn-Zn, and Sn-Cu solders as joint materials have been studied extensively. However, all these materials exhibit various drawbacks under the actual operating conditions. Sn-Ag-Cu alloys exhibit a low bonding strength and undergo creep under high-temperature conditions [10]. The use of metallic Au in Sn-Au alloys increases the cost of the raw materials. Sn-Zn alloys exhibit low wettability owing to their high susceptibility to oxidation [11,12]. The applications of Bi-based alloys are limited owing to the poor mechanical properties and low melting temperatures of these alloys [13]. Therefore, the eutectic Sn-0.7Cu solder has attracted significant attention for automotive electronic applications owing to its low cost and high drop reliability. However, the Sn-Cu solder also exhibits a severe limitation. The growth of IMCs at the Sn-Cu/Cu interface is substantially faster than that at the interfaces for other lead-free solders [14]. In recent years, several researchers have attempted to address this limitation by adding a low quantity of metals (e.g., Ni, Ag, Al, Co, or Cr) to the solder. Subsequently, they investigated the microstructure and mechanical properties of the solder. The addition of trace elements may decrease the diffusion rate of IMC by lowering the activity of Cu and Sn elements or blocking the diffusion path of atoms in a liquid-solid reaction state. Additionally, the mechanical strength may be improved by a composite microstructure close to the prediction of the dispersion reinforcement theory [15–20]. However, the impact of Cr addition to the commercial Sn-0.7Cu solder on the initial formation and growth of IMCs is unexplored. Therefore, the heterogeneous nucleation of IMCs and the mechanical properties at the interface in molten Sn-0.7Cu/Cu and Sn-0.7Cu-0.2Cr/Cu were investigated in this study. A Sn-0.7Cu-0.2Cr solder was fabricated to analyze the effect of Cr addition to Sn-0.7Cu/Cu. The effective nucleation rate of the IMCs at 240–300 °C, the average radius of the crystallites at each temperature, and the effect of the Cr addition on the nucleation rate and mechanical properties were investigated via a systematic experiment. The results revealed that the size and thickness of the Cu$_6$Sn$_5$ IMCs in the Sn-0.7Cu-0.2Cr solder were lower than those of the Cu$_6$Sn$_5$ IMCs in the Sn-0.7Cu solder. The shear strengths of the Sn-0.7Cu-0.2Cr solder joints were higher than those of the Sn-0.7Cu solder joints.

2. Materials and Methods

The effects of Cr addition to a Sn-0.7Cu solder on the nucleation and growth rate of Cu$_6$Sn$_5$ IMCs under various dipping times and temperatures were elucidated using a Sn-0.7Cu-0.2Cr solder. The experiments were also performed under the same conditions using a Sn-0.7Cu solder, and the results were compared. To measure the melting temperature levels of the two solders, differential scanning calorimetry (DSC) equipment (DSC-Q100, TA Inst., New Castle, DE, USA) was used. For testing, approximately 8 mg samples of both solder alloys were used. Measurement conditions were stabilized at 50 °C, then heated to 300 °C at a rate of 10 °C/min, and cooled at the same rate. The melting point of each solder was measured using the heat absorption and exothermic reaction characteristics based on the solder composition. The samples were fabricated by initially polishing the surface of a Cu coupon size (10 × 3 × 1 mm) to a 0.3 µm finish. Subsequently, the Cu coupon was cleaned with ethanol via ultrasonication. Thereafter, a rosin mildly activated (RMA)-type flux (CVP-390, Alpha Assembly Sol., South Plainfield, NJ, USA) was applied on the Cu surface. The samples were then dipped in a bath that contained 300 g of solder using a wetting balance tester (SWB-2, Malcom Co., Ltd., Tokyo, Japan). The schematic diagram of the dipping test, with the dipping conditions, is presented in Figure 1. The bath temperature was varied from 240 to 300 °C, and dipping was performed for 1 and 3 s at intervals of 10 °C. Subsequently, the samples were air cooled. After the molten solder reached the test temperature, it was maintained at this temperature for 10 min to reduce the temperature deviation. The solder in the bath was replaced after each test to prevent
changes in its composition. Afterwards, to observe the Cu₆Sn₅ IMCs, Sn was etched with the NH₄OH 3% + HCL 2% + C₂H₅OH 95% solution and its top view was observed using the field emission scanning electron microscope (FE-SEM; Inspect F, FEI Co. Hillsboro, OR, USA) and energy-dispersive spectroscopy (EDS; Superdry, Thermo Noran Inc., Waltham, MA, USA). In addition, the number of Cu₆Sn₅ grains per unit area and their average size were measured. Moreover, cross-sectional images of Cu₆Sn₅ IMC were observed using FE-SEM. The shape and microstructure of the Cr compound were observed using an electron probe micro-analyzer (EPMA; JXA-8530F, JEOL Ltd., Tokyo, Japan) and a transmission electron microscope (TEM; JEM-2100F, JEOL Ltd., Tokyo, Japan). A TEM lamella sample of a specific region containing a Cr compound was prepared via the in situ lift-out method using a focused ion beam (FIB, JIB-4500, JEOL Ltd., Tokyo, Japan). A FIB milled TEM lamella sample was mounted on the Cu grid. Prior to FIB milling, a 2 µm carbon layer was deposited on the cross-sectional sample surface. The Cr compound was analyzed via the TEM bright field (BF) image and selected area electron diffraction (SAED) pattern. To measure the shear strength of the solder joint over the bonding temperature and time, a 300 µm solder ball was bonded to the Cu coupon. Bonding was carried out for 1 and 3 s at reaction temperatures of 240, 260, 280, and 300 ºC. In this process, a RMA type flux was used to remove the oxide film of the Cu coupons. The schematic of the ball shear test setup is presented in Figure 2. The tests were conducted using a ball shear tester (Dage 4000 HS; Nordson Co., Aylesbury, Buckinghamshire, UK). The shear height for the test was 50 µm, while the shear speeds were 0.01 and 1 m/s. The shear force was estimated based on the average of at least 20 trials. The fracture surfaces after the shear test were observed using the FE-SEM.

![Figure 1](image1.png)

Figure 1. Schematic of the (a) dipping test and (b) ball shear test sample.

![Figure 2](image2.png)

Figure 2. Schematic of the ball shear test.
3. Results and Discussion

DSC results are shown in Figure 3. The measured melting temperatures of Sn-0.7Cu and Sn-0.7Cu-0.2Cr solders were 227.8 and 230.7 °C, respectively. The addition of Cr to Sn-0.7Cu solder increased the melting temperature by approximately 3 °C due to the reduced supercooling.

![DSC curve of Sn-0.7Cu and Sn-Cu-0.2Cr solders.](image)

Initially, Cu₆Sn₅ is precipitated at the interface between the solder and the Cu substrate in a Cu-Sn soldering system. Subsequently, Cu₅Sn is precipitated at the interface between Cu₆Sn₅ and the Cu substrate. The Cu–Sn phase diagram indicated the existence of the Cu₁₄Sn and Cu₁₀Sn₃ phases at temperatures exceeding those for the reflow process. Furthermore, the Cu₆Sn₅ and Cu₅Sn phases existed at <350 °C [21–23]. Figure 4 shows the SEM line scan images of the IMCs that were observed after immersing the Cu coupon in the Sn-0.7Cu-0.2Cr solder at 300 °C for 3 s. Scallop-like IMC layers were formed after the dipping test, and the EDS analysis confirmed the formation of the Cu₆Sn₅ IMC. The presence of Cu₅Sn was not detected via SEM owing to the low dipping time.

![Cross-sectional images and corresponding EDS line scanning results of the intermetallic compounds (IMCs) for 3 s of dipping at 300 °C at Sn-0.7Cu-0.2Cr/Cu: (a) SEM image and (b) EDS results.](image)

Figure 5 shows the cross-sectional images of the Cu coupons that were dipped in the Sn-0.7Cu and Sn-0.7Cu-0.2Cr solder ports for 1 and 3 s at 240–300 °C. Scallop-shaped Cu₆Sn₅ IMCs were observed in both solders. The size of the IMCs increased as the dipping time increased. The Cu₆Sn₅ IMCs were small and thin at the low reaction temperatures owing to the high nucleation rate. The size and thickness of the Cu₆Sn₅ IMCs increased as the temperature increased owing to the increase in the nucleus growth rate [24]. Fur-
Moreover, the IMCs in the Sn-0.7Cu-0.2Cr solder joint were smaller than the IMCs in the Sn-0.7Cu solder joint at all the reaction temperatures. The shape of the IMCs in both the solder joints transformed from scallop-like to round as the reaction temperature increased. The growth of these round IMCs was clearly observed at 3 s of dipping.

| 1 s dipping test                      | 3 s dipping test                      |
|--------------------------------------|--------------------------------------|
| **Sn-0.7Cu**                         | **Sn-0.7Cu-0.2Cr**                   |
| 240 °C                               | 240 °C                               |
| ![Cross-sectional images](image1)    | ![Cross-sectional images](image2)    |
| 260 °C                               | 260 °C                               |
| ![Cross-sectional images](image3)    | ![Cross-sectional images](image4)    |
| 280 °C                               | 280 °C                               |
| ![Cross-sectional images](image5)    | ![Cross-sectional images](image6)    |
| 300 °C                               | 300 °C                               |
| ![Cross-sectional images](image7)    | ![Cross-sectional images](image8)    |

Figure 5. Cross-sectional images of the Cu₆Sn₅ IMCs obtained after dipping the Cu coupon in Sn-0.7Cu and Sn-0.7Cu-0.2Cr solders at various reaction temperatures.

Figure 6 shows the IMC thicknesses at various reaction temperatures. The thicknesses were measured after dipping the Cu coupons in the Sn-0.7Cu and Sn-0.7Cu-0.2Cr solder ports for 1 and 3 s at 240–300 °C. The thickness of the IMCs increased as the solder temperature and the dipping time increased. The IMCs in the Sn-0.7Cu-0.2Cr solder were approximately 0.3 µm-thinner than those in the Sn-0.7Cu solder at all the reaction temperatures.

![Graph showing IMC thickness vs. reaction temperature](chart)

Figure 6. Thickness of the Cu₆Sn₅ IMCs at various reaction temperatures.

Figure 7 shows the Cu₆Sn₅ IMCs grain images observed after dipping the Cu coupon into the Sn-0.7Cu and Sn-0.7Cu-0.2Cr solders under various melting temperature conditions for 1 and 3 s. Thus, the changes in the joints with the variation in the solder composition, dipping temperature, and dipping time were analyzed. The sizes of the IMCs in both
solders decreased slightly as the temperature increased from 240 to 260 °C. The smallest IMCs were observed at 260 °C. The grain size of the IMCs increased as the temperature exceeded 260 °C. The IMC grains in the Sn-0.7Cu solder were larger than those in the Sn-0.7Cu-0.2Cr solder at all the reaction temperatures. The addition of Cr decreased the supercooling degree and promoted nucleation, thereby lowering the particle size [25]. The sizes of the Cu₆Sn₅ IMCs in both solders were higher when dipped for 3 s compared to those dipped for 1 s. Furthermore, the particle sizes of the Cu₆Sn₅ IMCs increased over time at the same temperature [26].

![Figure 7. Top view images of the Cu₆Sn₅ IMCs at various reaction temperatures at Sn-0.7Cu/Cu and Sn-0.7Cu-0.2Cr/Cu solders.](image)

Figure 7. Top view images of the Cu₆Sn₅ IMCs at various reaction temperatures at Sn-0.7Cu/Cu and Sn-0.7Cu-0.2Cr/Cu solders.

Figure 8 shows the number of Cu₆Sn₅ IMC grains per unit area (µm²) and the average particle size of the Cu₆Sn₅ IMCs formed at various reaction temperatures. The particle size of the IMCs decreased slightly as the temperature increased from 240 to 260 °C, irrespective of the dipping time and solder composition. The smallest Cu₆Sn₅ IMCs were observed at 260 °C. The size of the IMC grains increased as the temperature exceeded 260 °C. The particle size of the IMCs in the Sn-0.7 Cu solder was approximately 12% higher than that of the IMCs in the Sn-0.7Cu-0.2Cr solder. Furthermore, the particle sizes when the dipping time was 3 s were larger than they were when the dipping time was 1 s. The initial growth rate of the IMC particles was high. However, the growth rate decreased as the surface area of the unreacted copper decreased. The formation of IMCs between Sn and Cu also lowered the growth rate. The inverse C shapes of the obtained curves were consistent with the previous results of the nucleation theory [27].

![Figure 8. (a) Number of Cu₆Sn₅ IMC grains per unit area (µm²) and the (b) average radius of the Cu₆Sn₅ IMC grains, at various reaction temperatures.](image)
Figure 9 shows an EPMA mapping image for the samples that were dipped in the Sn-0.7Cu-0.2Cr solder at 300 °C for 3 s. The results revealed the presence of a Cr compound in the Sn-0.7Cu-0.2Cr solder. A high quantity of this compound was observed at the interface between the IMCs and the interior of the solder.

Figure 10a shows TEM and SAED pattern images of Cr compounds and interfacial Cu₆Sn₅ IMCs. The IMCs that were generated at the interface were identified as Cu₆Sn₅ using the SAED pattern (Figure 10b). No stable IMCs were detected in the Cr-Sn binary phase diagram. However, the presence of other metastable compounds was reported in previous studies [28,29]. The SAED patterns of the Cr-Sn compound in Figure 10c were consistent with the reported crystal structure of the orthogonal CrSn₂.

Figure 11 shows the diffusion behaviors of Cu and Sn in the Sn-0.7Cu/Cu and Sn-0.7Cu-0.2Cr/Cu systems. The Cu₆Sn₅ IMC was formed via the interdiffusion of Cu and Sn. The precipitation of additional elemental materials at the grain boundary impeded
the migration of Cu into the Sn matrix, thereby lowering the diffusion rate. The existence of the Cr or CrSn$_2$ IMCs at the interface suppressed the nucleation of the Cu$_6$Sn$_5$ IMCs. The CrSn$_2$ IMCs that were produced during the fabrication of the alloy were precipitated near the IMC layers and dispersed. Moreover, the existence of some products was detected at the Cu$_6$Sn$_5$ grain boundary [17]. These results suggested that the addition of Cr to the Sn-0.7Cu solder effectively prevented the increase in the thickness of the Cu$_6$Sn$_5$ IMCs.

![Figure 11. Schematic of the interdiffusion of Cu and Sn in the (a) Sn-0.7Cu/Cu and (b) Sn-0.7Cu-0.2Cr/Cu systems.](image)

The shear strengths of the solder joints, for different junction temperatures, dipping times, and solder compositions, are presented in Figure 12. The shear strength of the Sn-0.7Cu-0.2Cr solder joint was approximately 80 gf higher than that of the Sn-0.7Cu solder joint at the relatively low shear speed of 0.01 m/s, under all reaction temperatures. The shear strength of both solder joints at a dipping time of 1 s were slightly higher than those at a dipping time of 3 s. The deterioration inside the solder following the increase in the dipping duration resulted in the slight lowering of the shear strength. When the shear speed was high (1 m/s), the shear strength of the Sn-0.7Cu solder joint was higher than that of the Sn-0.7Cu-0.2Cr solder joint at low reaction temperatures. This was attributed to the slower growth of the IMCs in the Sn-0.7Cu-0.2Cr solder as compared to that of the IMCs in the Sn-0.7Cu solder at the low reaction temperatures. Consequently, the Sn-0.7Cu-0.2Cr solder joints were not robust under this condition. However, robust Sn-0.7Cu-0.2Cr solder joints were formed at the reaction temperatures above 260 °C. Therefore, the Sn-0.7Cu-0.2Cr and Sn-0.7Cu solder joints yielded similar shear strengths above 260 °C. The shear strength of the Sn-0.7Cu-0.2Cr solder joint was higher than that of the Sn-0.7Cu solder joint above 280 °C. This was due to the fact that the shape of the IMCs in the Sn-0.7Cu-0.2Cr solder joint was more scallop-like compared to that of the IMCs in the Sn-0.7Cu solder. The presence of these scallop-like IMCs resulted in the high shear strength of the Sn-0.7Cu-0.2Cr solder joint under the high-speed shear conditions. The increase in the shear strength following the increase in the shear speed was reported in previous studies [30,31].

![Figure 12. Shear strength of the solder joints at shear speeds of (a) 0.01 and (b) 1 m/s under various reaction temperatures.](image)
Figure 13 shows the tensile strength of Sn-0.7Cu and Sn-0.7Cu-0.2Cr solders. When Cr was added, the tensile strength increased by approximately 12%. This is believed to increase the tensile strength by acting as second-phase particles of CrSn$_2$ or Cr dispersed in the solder, thus blocking the propagation of cracks generated in the tensile strength test. Accordingly, the shear strength of Sn-0.7Cu-0.2Cr solder was higher than that of Sn-0.7Cu at a shear rate of 0.01 m/s.

![Figure 13. Tensile strength of Sn-0.7Cu and Sn-0.7Cu-0.2Cr solders.](image)

Figure 14 shows the fracture surfaces of the Sn-0.7Cu and Sn-0.7Cu-0.2Cr solders at various reaction temperatures. The ductile fracture occurred at the low shear rate of 0.01 m/s. When the shear rate was 1 m/s, a complex fracture with both ductile and brittle characteristics was observed. At low shear rates, all fractures are stress relieved by deformation inside the bulk solder, so the ductile fracture dominates. As the shear rate increases, a large amount of stress accumulates at the interface due to the rapid deformation inside the solder, causing breakage along the solder/IMC interface. The stress may be concentrated in the solder/IMC region due to the mismatch of the modulus of elasticity between the rough interface and the dissimilar material [32]. In general, in the thermal aging test or thermal cycle test, delamination occurs between heterogeneous IMCs or at the IMC/interface due to the excessive growth of IMCs and kirkendall voids [33–35]. In this study, the growth of Cu$_6$Sn$_5$ IMC increased as the dipping temperature and time increased. Accordingly, the brittle fracture rate increased.

![Figure 14. Fracture surfaces of the solder joints at dipping times of (a) 1 and (b) 3 s for different shear speeds under various reaction temperatures.](image)

Figure 15 shows the statistics of the fracture modes of the solder joints at shear speeds of 0.01 and 1 m/s. When the shear speed was 1 m/s, the brittle fracture rate in the Sn-0.7Cu solder was higher than that in the Sn-0.7Cu-0.2Cr solder. The brittle fracture rate in the Sn-0.7Cu-0.2Cr solder remained low owing to the relatively thin interfacial IMCs.
IMCs are typically fragile, and the increase in their thickness results in an increase in the number of brittle areas. Consequently, the fragility of IMCs increases with the increase in thickness [36]. The high shear strength of the Sn-0.7Cu-0.2Cr solder was attributed to the influence of the shear strength of the Cr or CrSn$_2$ compounds that existed inside and near the surface of the solder. It was concluded that the shear strengths of the Sn-0.7Cu-0.2Cr solder joints was significantly higher than those of the Sn-0.7Cu solder joints in this study.

Figure 15. Statistics of the fracture modes of the solder joints at shear speeds of (a,c) 0.01 and (b,d) 1 m/s.

4. Conclusions

The nucleation kinetics and growth rate of Cu$_6$Sn$_5$ IMCs in a Sn-0.7Cu-0.2Cr solder were investigated in this study. Additionally, the mechanical properties of the Sn-0.7Cu-0.2Cr solder joints were characterized. The study results are summarized as follows:

1. The samples revealed that the grain size of the Cu$_6$Sn$_5$ IMCs in both solders was minimum at 260 °C. The grain size increased as the temperature increased to 280 and 300 °C. The grain size of the Cu$_6$Sn$_5$ IMCs in the Sn-0.7Cu-0.2Cr solder was lower than that of Cu$_6$Sn$_5$ IMCs in the Sn-0.7Cu solder, at all dipping times and temperatures. The addition of Cr decreased the supercooling degree and promoted nucleation, thereby lowering the particle size.

2. The Sn-0.7Cu-0.2Cr solder/Cu joints suppressed IMC growth more effectively than the Sn-0.7Cu solder/Cu joints. This suppressed the interfacial IMC growth by interfering with the diffusion of Sn and Cu by CrSn$_2$ IMC present at the interface.

3. In the shear test, the fracture occurred inside the solder at low shear rates, and at high shear rates at the solder/IMC interface or IMC/substrate interface. The results of the low shear strength tests revealed that the shear strengths of the Sn-0.7Cu-0.2Cr solder joints were higher than those of the Sn-0.7Cu solder joints. The high shear strength of the Sn-0.7Cu-0.2Cr solder joints was attributed to the shear strength of the CrSn$_2$ compounds inside and near the surface of the solder. In the high-speed shear test, the brittle fracture increased as the thickness of IMC increased.

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