

INTERMETALLICS FORMATION AND GROWTH AT THE INTERFACE OF TIN-BASED SOLDER ALLOYS AND COPPER SUBSTRATES

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ABSTRACT

Increasing concerns regarding environmental contamination is driving the soldering research community to develop lead-free solder alloys. Previous studies have shown that Sn-based alloys such as Sn-3.5Ag, Sn-0.7Cu, Sn-9Zn, and Sn-3.2Ag-0.8Cu have promising mechanical properties, and can be considered as serious candidates to replace the Sn-Pb alloy. However, for joint life and reliability predictions, information about the interaction between these alloys and the most used substrates is needed. In that sense, the formation and growth of intermetallic compounds at the interface between the Cu-plated substrates and Sn-3.5Ag, Sn-0.7Cu, Sn-3.2Ag-0.8Cu, and Sn-9Zn have been studied.

Coupons of joints prepared with each solder alloy on a Cu-plated circuit board were subjected to thermal aging test for 20, 100, 200, 500 hours at 70, 100 and 150 degrees Celsius. Each sample was analyzed using metallographic techniques, light microscopy, SEM and EDS. The results indicate that the formation of intermetallic layers is a diffusion-controlled process. The thickness of the intermetallic compounds increased with increasing aging temperature and time. The Sn-3.5Ag alloy showed the smallest intermetallic growth and the Sn-9Zn alloy the highest. The results also suggest that at shorter aging times the chemical reaction between the substrate and the solder alloys result in the formation of small number of nucleation sites of intermetallic compounds.

INTRODUCTION

Lead-based solder alloys have been the joining material used for many years in electronic packaging. However, increasing concerns about the health and environmental hazards of lead drove the research community to find replacement solder alloys for the tin-lead alloys. The newly developed alloys must have mechanical, thermal, chemical, and electronic properties similar or better than the eutectic tin-lead alloy.

Despite that the mechanical properties of alloys Sn-3.5Ag, Sn-0.7Cu, Sn-9Zn, and Sn-3.2Ag-0.8Cu are promising,[1] there are still other properties that need to be studied. This is the case of the formation and growth of intermetallic compounds between the substrate material and the solder alloy. It is known that these layers of intermetallic compounds are usually deleterious to joint reliability.[2] They are usually brittle and if present in large amounts at the solder/substrate interface, they may reduce the lifetime of the joints. In order to predict the extent of the effect of the intermetallic compounds between the substrate and the newly developed solder alloys, a more extensive study must be conducted. This work characterizes the formation and growth of intermetallic compounds between copper substrates and the Sn-3.5Ag, Sn-0.7Cu, Sn-9Zn, and Sn-3.2Ag-0.8Cu solder alloys.

EXPERIMENTAL PROCEDURE

The experimental program consists of three parts: the production of copper/solder joints, the thermal aging tests, and the metallographic and microstructural characterization.

Production of Cu/solder joints

Two materials were used for the production of joints. One of them was a commercial Cu-plated printed circuit board (PCB). Copper was chosen as the substrate material because of its compatibility with the solder-joint systems, its frequent use in the electronics industry and its relatively low cost. The other material was one of the four lead-free solder alloys under investigation: Sn-3.2Ag-0.8Cu, Sn-3.5Ag, Sn-0.7Cu, and Sn-9Zn. Their respective melting temperatures are 217°C, 221°C, 227°C, and 198°C.

The substrates for all the coupons were cut into pieces of 25.4 x 25.4 mm (1x1 in.). The Cu surface was cleaned with a water-based solution of ammonium hydroxide, trisodium phosphate and sodium tetraborate pentahydrate (M-prep neutralizer). After letting the Cu surface dry for a few seconds, a solution of water-based phosphoric acid (M-prep conditioner) was applied. These solutions removed any impurities, dirt, and oxide layers present on the surface, and promoted wetting. Next, the molten solder alloy at 50°C above its melting temperature, would be deposited on the substrate and cooled in air to ambient temperature. In the case of alloy Sn-9Zn, the copper surface was prepared using commercial zinc chloride and ammonium chloride based paste, which provided better wetting than the phosphoric acid-based solution chosen for the other three solder alloys.

Thermal aging test

The thermal aging test of the Cu/solder joint coupons was done using furnaces with temperatures controlled to $\pm 1^\circ\text{C}$. To avoid oxidation during thermal aging, a continuous flow of industrial argon gas was provided to the furnaces. The Cu/solder joints were thermally aged at 70, 100 and 150 °C, and for 20, 100, 200 and 500 hours. The specimens were water-quenched as they were removed from the furnaces.

Metallographic characterization

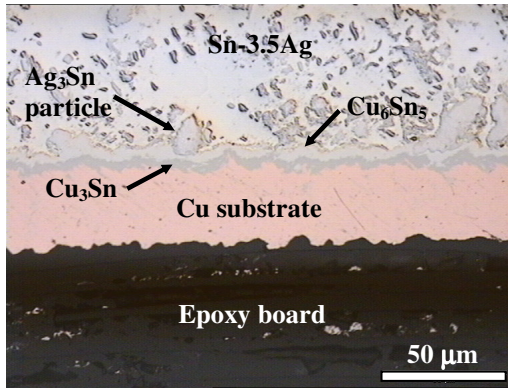
The samples were cut in half and cold mounted using epoxy for metallographic analysis. The reason for using cold mounting instead of hot mounting is that cold mounting undergoes a lower curing temperature. The mounted samples were ground and polished using standard metallographic techniques, first to 0.5 μm with diamond slurry, and then to 0.05 μm using colloidal silica. Polishing the samples in a vibratory machine with colloidal silica resulted in a good etched surface. The samples were examined using light microscopy, scanning electron microscope (SEM), and energy dispersive spectroscopy (EDS). Quantitative measurements of the intermetallic compounds were made using a digital image analysis system.

RESULTS AND DISCUSSION

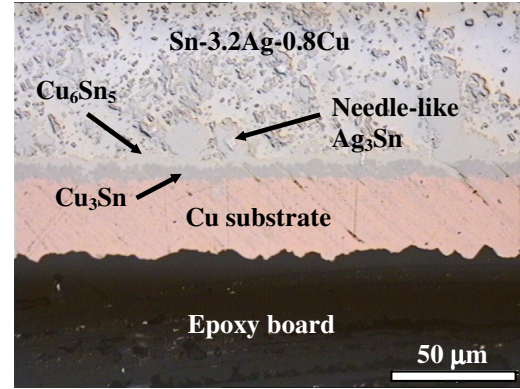
Cu/solder interface

The Cu/solder interface after thermal aging was found to be very different from the interface before the thermal test. Before, the most noticeable features of the interface were the epoxy board, the copper substrate, and the solder. Only at high magnifications can very small amounts of Cu_6Sn_5 be found at the Cu/solder interface.[3] After the thermal aging test, the appearance of the microstructure at the Cu/solder interface changed significantly. Evidence of the changes is shown in Figure 1 in the micrographs of the Cu/Solder interface at 150°C for 500 hours. Beginning from the bottom, in Figures 1(a), (b) and (c), the visible layers are the epoxy board, the copper substrate, the intermetallic compounds (IMCs) Cu_3Sn and Cu_6Sn_5 , and finally the solder matrix. It was observed that the layer of Cu_3Sn forms at the Cu/solder interface, and the layer of Cu_6Sn_5 on top of Cu_3Sn . This sequence is true for the three material systems, Cu/Sn-3.2Ag-0.8Cu, Cu/Sn-3.5Ag, and Cu/Sn-0.7Cu. In the case of Cu/Sn-3.5Ag, a few small particles of Ag_3Sn can also be observed at the Cu_6Sn_5 /Sn-3.5Ag interface. Different from the previous joint systems, the Cu/Sn-9Zn system displays only one intermetallic layer, Cu_5Zn_8 . The intermetallic compounds were identified using electron diffraction spectroscopy (EDS) analysis.

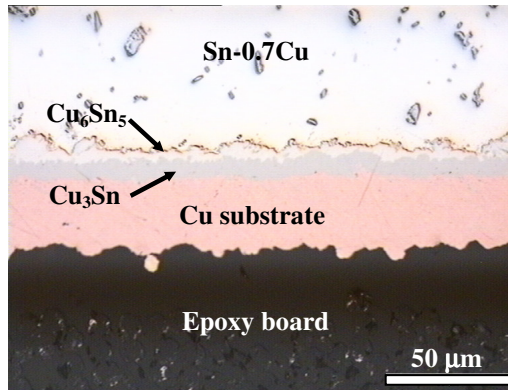
Evidence of morphological differences at the interface of the two IMCs was determined. The $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ interface was observed to be irregular.[4] The variation in thickness of the Cu_3Sn intermetallic layer was not as drastic as the thickness of the Cu_6Sn_5 intermetallic layer. In the case of the Cu_6Sn_5 /solder-matrix, the interface is more irregular, with localized developments of elongated, needle-like, or elongated scalloped structures, growing far into the solder matrix.



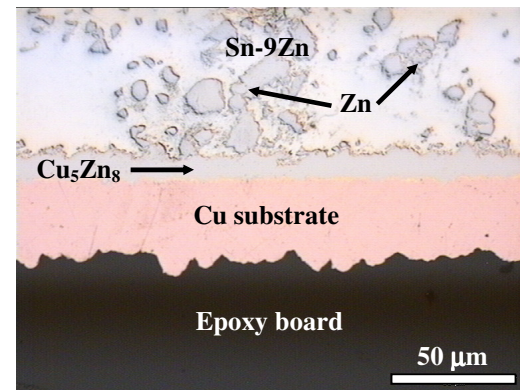
(a)



(b)



(c)



(d)

Figure 1. Micrographs of the Cu/solder interfaces at 150°C for 500 hours, for the four material systems, indicating their respective intermetallic layers, (a) Cu/Sn-3.5Ag, (b) Cu/Sn-3.8Ag-0.8Cu, (c) Cu/Sn-0.7Cu, and (d) Cu/Sn-9Zn.

In the case of the Cu/Sn-3.5Ag system, the morphology of the Cu_6Sn_5 layer is significantly different from that of Cu_3Sn . Figure 2(a) clearly exhibits the irregular interface of the Cu_6Sn_5 intermetallic, protruding into the solder matrix. Some areas of this interface (growth front) develop into elongated, needle-like morphologies such as the one shown in Figure 2(a). In other areas, the initiation of the needle-like morphologies, “A”, and the formation of the scalloped structures, “B”, are observed, Figure 2(a). In addition, Ag_3Sn is found in the form of small particles at the Cu_6Sn_5 /solder interface. It is plausible that these small particles of Ag_3Sn interrupt the fast growth of the Cu_6Sn_5 layer. The growth front of the Cu_3Sn layer is not as irregular as that of the Cu_6Sn_5 . For better visual clarification of the micrograph in Figure 2(a), the Cu_3Sn growth front is outlined with a dash-dotted line, and the copper surface with a dashed line. It seems that the irregularity of the Cu_3Sn layer depends more on the original surface of the copper substrate.

In the case of the Cu/Sn-3.2Ag-0.8Cu and Cu/Sn-0.7Cu, the interface of the Cu_6Sn_5 is smoother than that observed in the Cu/Sn-3.5Ag system. Evidence of this observation can be found in the Figure 2(b) and (c). Figure 2(b) displays the Cu/Sn-3.2Ag-0.8Cu interface. The most noticeable feature of this interface is that the Cu_6Sn_5

growth front is irregular but does not have sharp features as in the previous case of Cu/Sn-3.5Ag. For example, the needle-like and scalloped structures are not present here. The Cu_3Sn growth front is also irregular. In the case of the Cu/Sn-0.7Cu interface shown in Figure 2(c), the irregularity of the Cu_6Sn_5 growth front is more than in the case of the Cu/Sn-3.2Ag-0.8Cu. This interface also exhibits small pieces of Cu_6Sn_5 (~1 to 2 microns in size) detached from the Cu_6Sn_5 layer, but they do not seem to grow far into the solder matrix. Again, the Cu_3Sn growth front exhibits irregular characteristics.

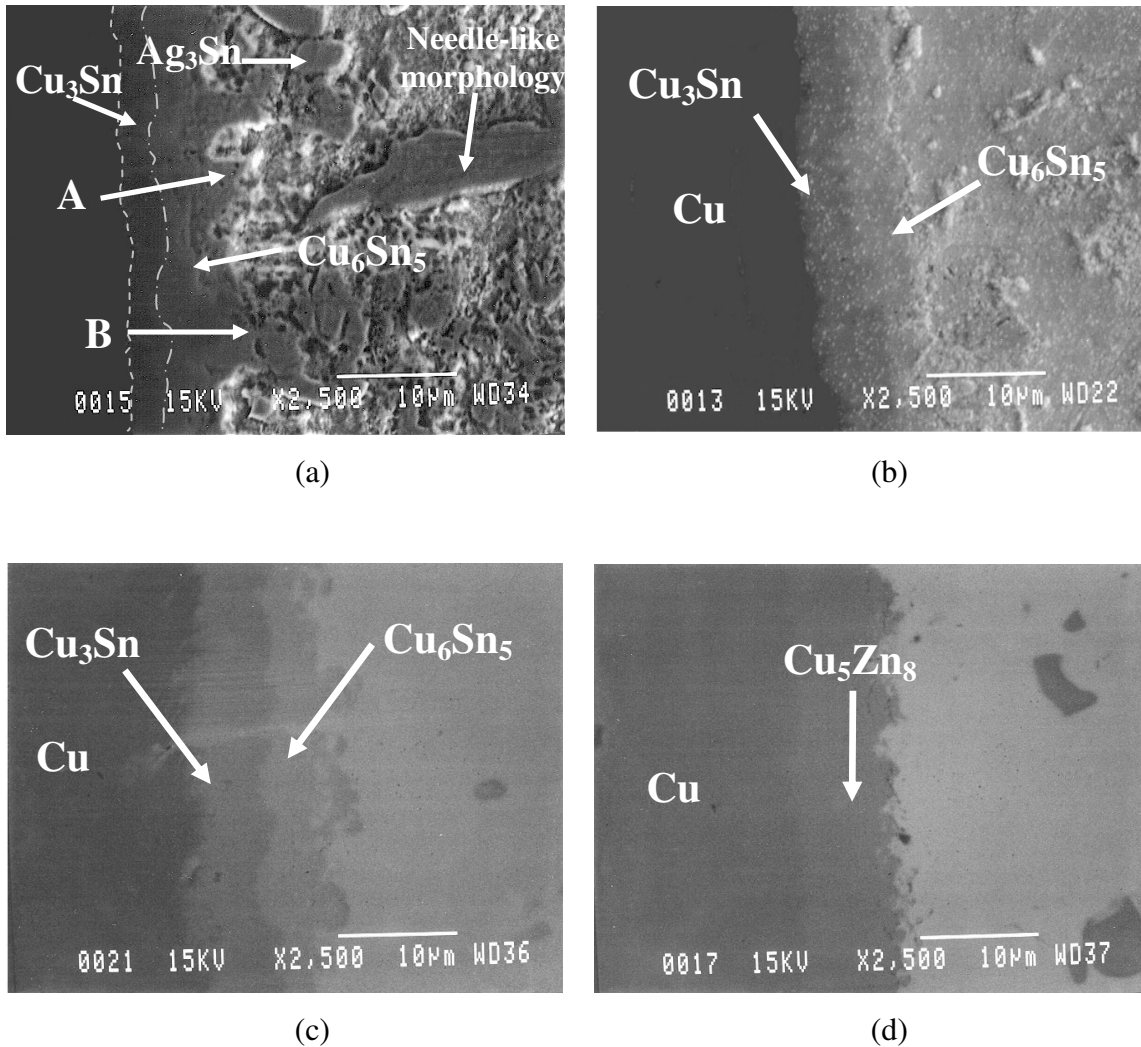


Figure 2. SEI image of the (a) Cu/Sn-3.5Ag interface, (b) Cu/Sn-3.2Ag-0.8Cu interface. BEI image of the (c) Cu/Sn-0.7Cu interface, and (d) Cu/Sn-9Zn interface.

The most significant difference between the Cu/Sn-9Zn interface and the interfaces of the other three systems is that the Cu/Sn-9Z interface exhibits only one intermetallic layer, which was identified as Cu_5Zn_8 . The growth front of this layer, as seen in Figure 2(d), is irregular, finely jagged, but does not present sharp irregularities as in the case of the Cu/Sn-3.5Ag.

Kinetics of intermetallic growth

The growth kinetics of the IMCs as a function of aging time and temperature was analyzed by measuring the thickness of the IMC layers. Individual Cu_3Sn and Cu_6Sn_5 layers and combined ($\text{Cu}_3\text{Sn} + \text{Cu}_6\text{Sn}_5$) IMC thickness were determined. The total intermetallic layer thickness at the highest aging temperature 150°C , for 500 hours in the four material systems were found to be the following: $13.3\ \mu\text{m}$ for Cu/Sn-3.5Ag, $13.6\ \mu\text{m}$ for Cu/Sn-3.2Ag-0.8Cu, $14.1\ \mu\text{m}$ for Cu/Sn-0.7Cu, and $19.1\ \mu\text{m}$ for the Cu/Sn-9Zn alloy.

A simple parabolic, diffusion-controlled growth model, represented by equation (1), was assumed in the analysis of these experiments.

$$X = (kt)^{1/2} \quad (1)$$

X is the thickness of the intermetallic layer, k the growth constant, and t the time. The observed total IMC thickness and time relationships at 70°C , 100°C and 150°C , shown in Figures 3(a), (b) and (c) respectively, were found to obey the parabolic relationship assumed previously. The slopes of the lines in Figure 3 indicate the rate of IMC growth; therefore, as the temperature increased, the rate of IMC layer growth increased. At the three temperatures, the alloy Sn-9Zn grows at the fastest rate. Alloy Sn-3.5Ag grows at the slowest rate at 70°C and 100°C , and alloy Sn-3.2Ag-0.8Cu at 150°C .

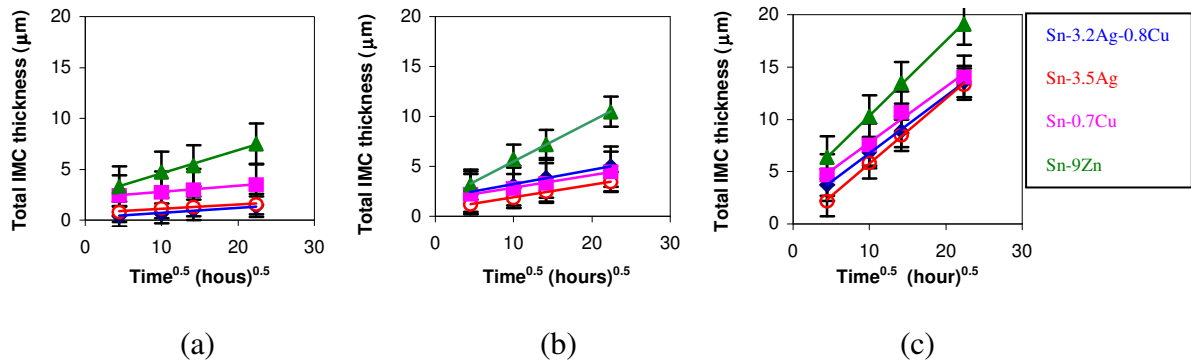


Figure 3. Total IMC growth ($\text{Cu}_3\text{Sn} + \text{Cu}_6\text{Sn}_5$) at the Cu/solder interface at three temperatures, (a) 70°C , (b) 100°C , and (c) 150°C .

Similar analysis was done with the individual IMCs in each Cu/solder system. The general observation is that their growth also obeys the parabolic growth as in the case of the growth of the total IMC. Figure 4 shows how the individual IMCs grow with time. In the case of the Cu/Sn-3.2Ag-0.8Cu joint system, shown in Figure 4(a), the Cu_6Sn_5 intermetallic compound grows at a faster rate than Cu_3Sn . This may be due to the availability of reactants (Cu and Sn atoms) at the interface to form Cu_6Sn_5 . In contrast, to form Cu_3Sn , Sn atoms need to diffuse through the Cu_6Sn_5 layer to react with the Cu atoms from the substrate.[5] At shorter aging times, the amount of Cu_3Sn is slightly higher than Cu_6Sn_5 , which suggests that at the time of solder deposition, this alloy actually forms more Cu_3Sn than Cu_6Sn_5 . However, at aging times approximately 150

hours, this behavior reverses. In the case of the Cu/Sn-3.5Ag system, shown in Figure 5(b), the Cu_6Sn_5 layer grows at a faster rate than the Cu_3Sn layer. This characteristic is expected for similar reasons as in the case of the Cu/Sn-3.2Ag-0.8Cu system. In addition, Cu_3Sn does not grow as fast as in the previous case because less Sn atoms are available since Sn is reacting with Ag to form Ag_3Sn at the Cu_6Sn_5 growth front. In the case of the Cu/Sn-0.7Cu system shown in Figure 5(c), Cu_3Sn exists in higher amounts but grows at approximately the same rate than Cu_6Sn_5 . The Cu_3Sn layer grows because no Ag_3Sn is formed in this system. More Sn atoms can migrate through the Cu_6Sn_5 layer to form Cu_3Sn . In the case of the Cu/Sn-9Zn system, only Cu_5Zn_8 forms. Therefore, Cu_5Zn_8 is considered as the total IMC layer.

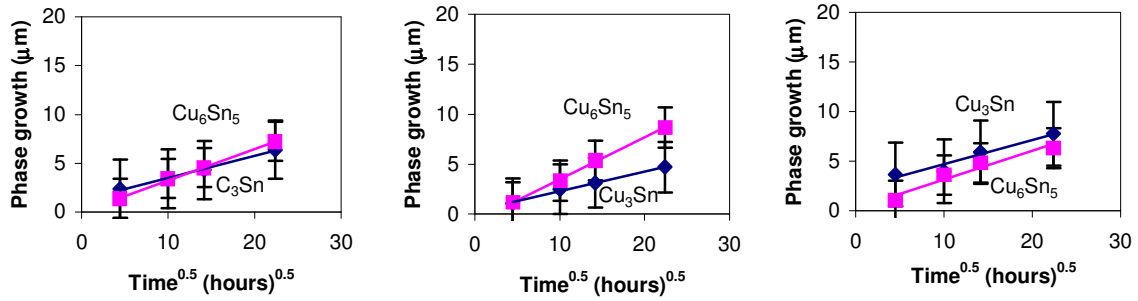


Figure 4. Individual IMC layers growth in the (a) Cu/Sn-3.2Ag-0.8Cu, (b) Cu/Sn-3.5Ag, and (c) Cu/Sn-0.7Cu solder joint systems.

The constant k in Equation (1) was determined from the slopes of the lines in the IMC thickness versus $\text{time}^{0.5}$ plots. Using the Arrhenius equation below,

$$k = k_o \exp\left(\frac{-Q}{RT}\right) \quad (2)$$

where k_o is the pre-exponential term, Q the activation energy, R the gas constant and T , the absolute temperature, the $\log k$ versus $(1/T)$ plots for the individual phases and for the total IMC can be made. Both Figures 5(a) and (b) are for the Cu/Sn-3.5Ag system. The slopes of the lines in Figure 5(a) suggest higher activation energy Cu_6Sn_5 formation than for Cu_3Sn . The line on Figure 5(b) corresponds to the combination of the two intermetallic phases in one layer. As expected, its slope suggests intermediate activation energy value.

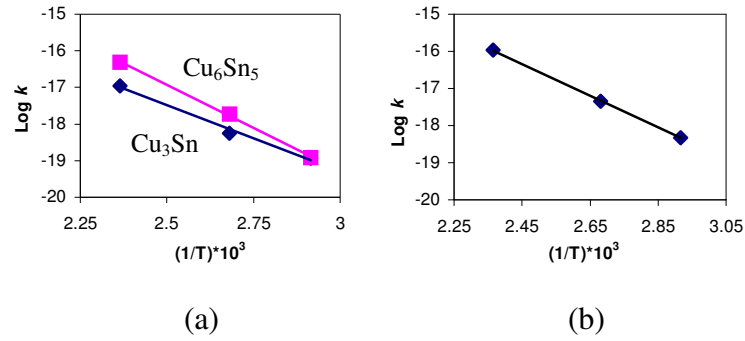


Figure 5. Growth rate constant data for the (a) individual Cu_3Sn and Cu_6Sn_5 IMCs plotted to determine the activation energy Q , and (b) total IMC ($\text{Cu}_3\text{Sn} + \text{Cu}_6\text{Sn}_5$) plotted to determine the activation energy Q , for the total IMC growth in the Cu/Sn-3.5Ag solder joint system.

The activation energies, Q , were calculated from the slope of the Arrhenius plot using a regression model. As the activation energy of a specific intermetallic compound increases, the formation and growth of this compound is more difficult. On the other hand, low activation energies indicate easier IMC formation and growth. The results of the activation energies for the total IMC thickness and for the individual phases for the four solder alloys are presented in Table 1. The activation energy data for the Cu/Sn-3.5Ag and Cu/Sn-0.7Cu joint systems are in good agreement with previous studies found in the literature.[3] [5] In the case of the Cu/Sn-3.2Ag-0.8Cu and Cu/Sn-9Zn joint systems, no comparison data were found.

Table 1. Activation energies, Q , determined experimentally for the total and individual IMCs in the Cu/Sn-3.8Ag-0.8Cu, Cu/Sn-3.5Ag, Cu/Sn-0.7Cu, and Cu/Sn-9Zn joint systems.

ALLOY	IMC	Q (kJ/mol)	Q (eV/atom)
Sn-3.2Ag-0.8Cu	Total	70.9	0.74
	Cu_3Sn	69.2	0.72
	Cu_6Sn_5	72.2	0.75
Sn-3.5Ag	Total	81.6	0.85
	Cu_3Sn	69.2	0.72
	Cu_6Sn_5	90.0	0.93
Sn-0.7Cu	Total	65.5	0.68
	Cu_3Sn	59.2	0.61
	Cu_6Sn_5	72.2	0.75
Sn-9Zn	Cu_5Zn_8	33.8	0.35

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Two intermetallic compounds are formed at the interface of the Cu/Sn-3.2Ag-0.8Cu, Cu/Sn-3.5Ag, and Cu/Sn-0.7Cu joint systems. These are Cu_3Sn and Cu_6Sn_5 . In the Cu/Sn-9Zn joint system, only Cu_5Zn_8 is formed.
2. The interfaces of all the intermetallic compounds were irregular. However, the Cu_3Sn intermetallic layer growth front was less irregular than of the Cu_6Sn_5 . The Cu_6Sn_5 /Sn-3.5Ag interface was the most irregular, with needle-like structures growing towards the solder matrix. Small Ag_3Sn intermetallic particles were found at this interface.
3. It was determined that the three intermetallic layers grow by thermal activation in a parabolic manner. The intermetallic compound thickness and the activation energies for the total IMC in the four systems were the following: 13.3 μm and 0.85 eV/atom for Cu/Sn-3.5Ag, 13.6 μm and 0.74 eV/atom for Cu/Sn-3.2Ag-0.8Cu, 14.1 μm and 0.68 eV/atom for Cu/Sn-0.7 Cu, and 19.1 μm and 0.35 eV/atom for the Cu/Sn-9Zn alloy.

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