Spreading kinetics of a Sn-30Bi-0.5Cu alloy on a Cu substrate

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The reactive wetting kinetics of a Sn-30Bi-0.5Cu Pb-free solder alloy on a Cu substrate was investigated by the sessile drop method from 493 to 623 K. The triple line frontier, characterized by the drop base radius R was recorded dynamically with a high resolution CCD using different spreading processes in an Ar-H₂ flow. We found a good agreement with the De Gennes model for the relationship between $\ln(dR/dt)$ and $\ln R$ for the spreading processes at 493 and 523 K. However, a significant deviation from the De Gennes model was found for the spreading processes at 548 and 623 K. Our experimental results show a complicated temperature effect on the spreading kinetics. Intermetallics at the Sn-30Bi-0.5Cu/Cu interface were identified as Cu₆Sn₅ adjacent to the solder and Cu₃Sn adjacent to the Cu substrate. The intermetallic compounds effectively enhanced the triple line mobility because of reaction product formation at the diffusion frontier.

molten metal and alloys, Pb-free solder, sessile drop method, kinetics, electronic materials

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In response to concerns over Pb, extensive investigations have been carried out over the last few years to find an acceptable Pb-free solder for various electronic attachment applications. A large number of Pb-free solder alloys have been proposed. The wetting of a solid by a melt and the subsequent interfacial reactions are essentially involved in a large number of processes such as coating and soldering [1–5]. Studying wetting behavior is important in the characterization of solder alloys and it provides basic physico-chemical data for the design and development of composite lead-free solder alloys [6–11]. However, systematic investigations into the wetting process of the ternary Sn-30Bi-0.5Cu lead-free solder alloy on different substrates are scarce. Cu is one of the most common substrates used in micro-electronic devices. Therefore, the general objective of this work is to better understand the wetting process of the Sn-30Bi-0.5Cu/Cu system.

1 Materials and methods

Sn-30Bi-0.5Cu (wt.%) alloy was prepared by induction melting the alloy powders in a medium-frequency induction furnace (WK-II, Beijing Wuke Photoelectric Technique Co., Ltd., Beijing, China) under an Ar (99.999%) atmosphere followed by casting into copper molds. The alloys were stirred in a quartz crucible for at least 15 min to obtain a homogeneous structure and composition before casting. The sample alloy with an approximate height of 4 mm was used for the wetting experiment and was cut from the as-cast rod that had a diameter of 5 mm. The oxygen-free Cu substrate that was used in the wetting process was cut into 20 mm × 20 mm × 2 mm pieces. Both the alloys and the substrates were polished with SiC paper with an abrasive number of up to 2000 and then cleaned ultrasonically.

Wetting experiments were performed by the sessile drop method in an Ar (99.999%)-H₂ (99.999%) flow, which has been described in more detail elsewhere [12,13]. The heat-

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ing rate was 20–30 K/min. When the temperature reached the desired value the temperature was kept stable for 30 min, i.e., the dwell time. The experimental conditions are summarized in Table 1. During the heating process the alloy melted *in situ* and formed a liquid drop. The profile of the molten drop was acquired dynamically with a high resolution CCD (Nikon D90, Nikon Corporation, Japan) aligned with the sample and a backlighting source. The experiments consist of monitoring the time-dependent variation of the contact angle θ , the drop base radius R and the drop height H .

2 Results and discussion

Changes in the molten drop's dimensions with time were investigated at different temperatures. Figure 1 shows representative photographs of the spreading process from experiment SBC-C4. In Figure 1, (a) is the original state of the Sn-30Bi-0.5Cu solder on the Cu substrate before melting while (b) is the solder on the Cu substrate at the very beginning of melting. The molten alloy formed a spherical droplet and the spreading velocity was relatively low as the solder began to melt while the shape of the droplet was relatively smooth at this initial contact stage, which is referred to as the incubation period. The second stage of the spreading process is referred to as the quasi-steady decreasing period during which the spreading velocity is relatively high as the spreading process expands. Figure 1(c)–(f) shows typical photographs of this period. The relatively high spreading velocity is due to the interfacial reaction between the solder and the substrate and the drop base radius R increases greatly during this period. The third and final stage

is referred to as the trend constant period during which the drop dimensions gradually become stable because of the constrained energetic equilibrium on the surface. Figure 1(g) is a typical stable state where the molten drop dimensions do not vary with time and the final spreading radius is reached.

Figure 2 shows the triple line frontier as characterized by the drop base radius R with time for the different processes. The drop base radius increases more sharply at a higher processing temperature. The final spreading radius increased significantly at a higher temperature. This phenomenon indicates that at higher temperature better wettability is obtained. This trend is consistent with that reported in [7,14].

The movement of the triple line was studied by the kinetics of the equivalent circular locus of points of the triple line as a function of time. The following equation was obtained by Hoffman [15] based on the amount of fluid flowing in a tube:

$$U = \frac{dR}{dt} \sim C(\sigma/\eta)\theta^m. \quad (1)$$

In eq. (1), R represents the instantaneous radius of the triple line of a sessile drop moving at a speed U and the triple line velocity is characterized by the viscosity μ and the surface tension σ . The assumed dynamic contact angle is $\theta(t)$ and C is a constant, $C = 0.02 \text{ rad}^{-3}$. The exponential m is 3 ± 0.5 .

Figure 3 shows the triple line velocity during the spreading processes of molten Sn-30Bi-0.5Cu on a Cu substrate. The variation in spreading velocity with time was observed to fluctuate for the different processes. The fluctuation in velocity can be explained by the formation of intermetallic compounds that promote spreading. The maximum velocity

Table 1 Experimental arrangement

Test no.	Temperature (K)	Solder	Substrate	Dwell time (min)	Atmosphere
SBC-C1	493	Sn-30Bi-0.5Cu	Cu	30	Ar-H ₂
SBC-C2	523	Sn-30Bi-0.5Cu	Cu	30	Ar-H ₂
SBC-C3	548	Sn-30Bi-0.5Cu	Cu	30	Ar-H ₂
SBC-C4	623	Sn-30Bi-0.5Cu	Cu	30	Ar-H ₂

Figure 1 Representative photographs from experiment SBC-C4 upon an increase in temperature and time. (a) Original state; (b) incubation period; (c)–(f) quasi-steady decreasing period; (g) equilibrium state.

Figure 2 R - t relationship during the spreading process of the molten Sn-30Bi-0.5Cu alloy on a Cu substrate.

Figure 3 Triple line velocity during the spreading process of the molten Sn-30Bi-0.5Cu alloy on a Cu substrate.

Figure 4 Relationship between $\ln(dR/dt)$ - $\ln R$ during the spreading process of the molten Sn-30Bi-0.5Cu alloy on a Cu substrate from experiments. (a), SBC-C1; (b), SBC-C2; (c), SBC-C3; (d), SBC-C4.

increases slightly with temperature, and this demonstrates that the mobility increased because the viscosity and surface tension both decreased with temperature. Comparative investigations into the spreading velocity of the four different processes at 493, 523, 548 and 623 K show that at higher temperature the mobility is higher especially for the spreading process of SBC-C4.

An analysis of the validity of the De Gennes model that was developed for inert wetting systems was carried out. According to De Gennes [16], eq. (1) can be used to study the quasi-equilibrium spreading process of a drop and the triple line mobility is given as:

$$dR/dt = (C\sigma/\eta)V^m R^{-3m}, \quad (2)$$

where V is the volume of the spreading drop. We found that when R is constant the increase in m will lead to a quicker decline in triple line mobility. Therefore, m is indicative of the spreading velocity.

The natural logarithm of eq. (2) is given as eq. (3) and an analysis was carried out using the linear regression method [17].

$$\ln(dR/dt) = a + b \ln(R), \quad (3)$$

where plot b is equal to $-3m$, a is equal to $\ln(C\sigma/\eta) + m \ln V$ and a is a constant for an inert system.

Figure 4 shows the relationship between $\ln(dR/dt)$ and $\ln R$ for the different spreading processes. In Figure 4(a) the initial stage of the spreading process has an irregular period and it is hard to determine the value of m whereas $\ln(dR/dt)$

and $\ln R$ are linearly plotted in the following period. The same trend is apparent in Figure 4(b) and (c). However, a larger deviation was found for the case shown in Figure 4(d). The value of m that was derived from plot b is listed in Table 2 for all the spreading processes.

For the spreading process of Sn-30Bi-0.5Cu on a Cu substrate, our experiments show that the value of m agrees well with the De Gennes model at 493 and 523 K since the value of m falls within 3 ± 0.5 as listed in Table 2. However m increases dramatically at 548 and 623 K, which is not consistent with the De Gennes model. Therefore, the increase in m indicates that the triple line mobility is faster at higher temperatures. Additionally, the decrease in the triple line mobility increases dramatically as the temperature increases.

For reactive wetting systems the spreading process usually occurs together with an extensive chemical reaction and this is accompanied by the formation of a new solid compound at the interface. The characteristics of the phase constitution near the interface of the Sn-30Bi-0.5Cu/Cu diffusion bonded joint was studied by scanning electron microscopy (SEM, SUPRATM 55, ZEISS, Germany). Figure 5(a) shows a back-scattered electronic image of the cross-section of the Sn-30Bi-0.5Cu/Cu interface of the solidified sample from experiment SBC-C2. An intermetallic compound exists at the interface over the entire contact area and its composition was analyzed using an electronic probe microscopic analyzer (EPMA, JEOL JXA-8100, JEOL Ltd., Japan). The scanning path is indicated in Figure 5(a) as a white arrow and the EPMA line scanning result shown in Figure 5(b) indicates that an obvious diffusion zone forms near the Sn-30Bi-0.5Cu/Cu interface as a result of the Cu-Sn interfacial reaction. The intermetallic compounds at the Sn-30Bi-0.5Cu/Cu interface were identified as Cu_6Sn_5 adjacent to the solder and Cu_3Sn adjacent to the Cu substrate. The intermetallic compounds were also detected at the triple line area of the solder/substrate. This favors an enhancement of the triple line mobility because of the reaction products that formed at the diffusion frontier.

3 Conclusions

The spreading kinetics of the Sn-30Bi-0.5Cu/Cu system was investigated by the sessile drop method from 493 to 623 K

Table 2 The value of m during the spreading process of the molten Sn-30Bi-0.5Cu alloy on a Cu substrate

Test no.	Temperature (K)	m
SBC-C1	493	3.20
SBC-C2	523	3.21
SBC-C3	548	3.96
SBC-C4	623	5.01
Model by De Gennes	—	3

Figure 5 (a) Back-scattered electronic image of the cross-section at the interface of Sn-30Bi-0.5Cu/Cu as detected by SEM. (b) EPMA line scanning result of the cross-section at the Sn-30Bi-0.5Cu/Cu interface.

and innovative results were obtained and are summarized as follows.

(1) Changes in molten drop dimensions with time were investigated at different temperatures. The whole spreading process can be divided into three stages: an incubation period, a quasi-steady decreasing period and a trend constant period. The molten alloy forms a spherical droplet and the spreading velocity is relatively low as the solder begins to melt and the shape of the droplet is relatively smooth during the first stage. The relatively high spreading velocity in the second period is attributed to an interfacial reaction between the solder and the substrate and, accordingly, the drop base radius R increases greatly. In the final stage, the drop dimension gradually reaches a stable state because of the constrained energetic equilibrium on the surface.

(2) Experimental results show good agreement with the De Gennes model for the relationship between $\ln(dR/dt)$ and $\ln R$ considering the spreading processes at 493 and 523 K. However, it deviates significantly from the De Gennes model for the spreading processes at 548 and 623 K. Our experimental results show a complicated temperature effect on the spreading kinetics for the Sn-30Bi-0.5Cu/Cu system.

(3) The intermetallics at the Sn-30Bi-0.5Cu/Cu interface were identified as Cu_6Sn_5 adjacent to the solder and Cu_3Sn adjacent to the Cu substrate. The intermetallic compounds can effectively enhance the triple line mobility because of reaction product formation at the triple line frontier.

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