Structural Analysis of Three-Component Nanoparticles of Sn-58Bi and Cu Wires Prepared by Pulsed Wire Discharge

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Abstract: We used Sn-58Bi and Cu wires to investigate the effects of variable conditions (such as pressure and wire diameter) on the formation of three-component nanoparticles. In the synthesis of the three-component nanoparticles, pulsed wire discharge was used to sublimate the wires. In this system, the K factor is described as E_c/E_s, where E_c and E_s are respectively the applied energy and the sublimation energy of the system. Experiments were conducted in a N₂ atmosphere using the following parameters: voltage of 6 kV, pressure of 50–100 kPa, and Cu wire diameters of 0.1 and 0.2 mm. X-ray diffraction and field emission scanning electron microscopy were employed for structural analysis, particle size distribution analysis, collection rate, and composition studies of the nanoparticles.

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1. INTRODUCTION

With the continuing trend of miniaturization and weight reduction of electronic products, modern electronic packaging technology has received increased research attention [1,2]. Traditionally, Pb solders have been employed in chip packaging, but due to the global environmental issues associated with the toxicity of Pb, its use has been increasingly discouraged. Instead, Pb-free solders such as Sn-Ag-Cu or Sn-Cu solder systems have been widely studied as alternative electronics packaging materials [3–9]. The Sn-3.5Ag-0.5Cu composition, which is often used in current industrial processes, has a melting point of 217 °C. In order to ensure sufficient wettability, reaction characteristics, and reliable yield, it is necessary to apply a temperature profile of 250 °C or more when examining such solders [10,11]. However, at temperatures above 250 °C, the substrate materials deteriorate and an excessive intermetallic compound layer can occur at the solder joint, which adversely affects mechanical reliability. Therefore, a low melting point is necessary for the research and development of such solders.

With Sn-58Bi solders, it is possible to significantly lower the processing temperature because it has a low melting point (139 °C) compared to Sn-Ag-Cu based solders. Furthermore, recent studies of Sn-58Bi solders have revealed their relatively high strength values compared to Sn-Ag-Cu and Sn-Pb solders [12,13]. In previous reports, Sn-58Bi solder alloys undergoing tensile tests have shown relatively high intensity values compared to other solder alloys; this indicates that brittleness is high, and fracturing has been observed during plastic deformation or elastic deformation [14,15]. The plastic deformation of Sn-58Bi solder can be improved by reducing the deformation rate. When the solder joints are only under the influence of stresses originating from differences in the thermal expansion coefficients at the solder joint, they exhibit good reliability, but they exhibit poor reliability when subjected to sudden physical impacts. In addition, the melting point of Sn-58Bi is 139 °C, at which temperature the reliability of the solder joint is rapidly reduced. Therefore, changes in the physical properties of Sn-Bi solders are very important [16–18].

Various methods for improving the physical properties of solder material have been studied. One such method involves the synthesis of nanoparticles using pulsed wire discharges (PWD) [19–21]. When the solder material is nano-sized, the
Table 1. Experimental parameters used in this study.

<table>
<thead>
<tr>
<th>Wire</th>
<th>Diameters, d/mm</th>
<th>Sn-58Bi</th>
<th>0.1 mm Cu</th>
<th>0.2 mm Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>32</td>
<td>0.5</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>of wire</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sublimation energy</td>
<td>89.74</td>
<td>13.93</td>
<td>55.72</td>
<td></td>
</tr>
<tr>
<td>of the wire, Es/J</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacitance of capacitor, C/μF</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charging Voltage, Vc/kV</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charging energy, Ec/J</td>
<td>540</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative energy, K (=Ec/Es)</td>
<td>- 5.21 3.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmosphere gas</td>
<td>N2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure of atmosphere gas, Pa/kPa</td>
<td>50, 100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of the pulsed wire discharge setup.

surface energy at the interface increases, allowing the sintering temperature to be reduced. Furthermore, by using nanomaterials this method makes it possible to improve the solder’s physical properties without including a third element or requiring an increase in the intermetallic compound (IMC) growth [22,23].

The solubility of Cu is extremely low in Sn-58Bi, but in the case of eutectic Sn-3.5Ag, the solubility of Cu increases, and at a high reflow temperature the Sn reacts very quickly with Cu to form a large amount of IMC. However, the amount of added Cu determines the type and the growth rate of the IMC [24]. Adding Cu to Sn-58Bi solders can improve the mechanical properties of those solder joints. In addition, the strength of the Sn-58Bi solder joints with added Cu is comparable to the strength of Sn-Pb joints, owing to the structural reinforcement provided by the IMCs.

A certain amount of Cu can form Cu6Sn5, but as mentioned elsewhere, the solubility of Cu is not suitable for this purpose. Due to the fact that the solder material produced by PWD is

nanoscale in size (which overcomes several material limitations), it is possible to synthesize a variety of component systems in this fashion. In this study, we have attempted to overcome the limitations of Sn-58Bi solder materials by using nanoparticles and experiments were also performed to synthesize Cu wires with Sn-58Bi.

2. EXPERIMENTAL PROCEDURES

Figure 1 shows a detailed view of a PWD device, where reactions were carried out with wires on both ends of the electrodes under an applied voltage. Experiments were carried out by installing wires of Sn-58Bi (0.5 mm) and Cu (0.1 and 0.2 mm; Nilaco, 99.9%), with lengths of 32 mm. The produced nanoparticles were gathered by a filter installed in the device. After the wires were set, the internal pressure in the device was maintained at a vacuum pressure < 50 Pa in order to prevent oxidation. To synthesize the nanoparticles, N2 gas was used to fill the chamber, at two different pressures of 50 and 100 kPa. The capacitance (C) and voltage (V) used to synthesize the two types of wire were 30 μF and 6 kV respectively, and the stored energy, Ec was determined using Equation (1).

\[ E_c = \frac{1}{2} CV^2 \]  

The experimental conditions are shown in Table 1. The sublimation energy required for 0.5 mm Sn-58Bi and 0.1 mm and 0.2 mm Cu wires was calculated using the heat capacity and the melting point of each material, and the value of K was determined accordingly. In order to determine the
Table 2. Physical properties of each wire

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Volume (mm³)</th>
<th>Weight (g)</th>
<th>Cu amounts in Sn-58Bi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-58Bi</td>
<td>7.53</td>
<td>6.28</td>
<td>0.0473</td>
<td></td>
</tr>
<tr>
<td>Cu (0.1 mm)</td>
<td>8.96</td>
<td>0.251</td>
<td>0.00225</td>
<td>4.5</td>
</tr>
<tr>
<td>Cu (0.2 mm)</td>
<td>8.96</td>
<td>1.005</td>
<td>0.00900</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Fig. 3. Liquidus projection with isotherms of the Bi-Cu-Sn system (left) and Sn-rich region (right).

particle size, field emission scanning electron microscopy (FESEM; Zeiss SUPRA25) and particle size analysis (Zetasizer Nano S90, Malvern) were employed. X-ray diffraction studies (XRD; Rigaku RINT 2500HF) were carried out to analyze the structures of the nanoparticles.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the synthesized nanoparticles. In the current experiments, the ratios of Cu in the Sn-58Bi wires for the 0.1 and 0.2 mm Cu wires were 4.5 and 15.9 wt%, respectively (Table 2). The XRD patterns of all the specimens showed standard Sn and Bi peaks. However, while small peaks corresponding to copper-tin compounds (Cu₆₂₆Sn₅; DB: 00-004-0673, Cu₆.8Sn; DB: 00-031-0487) were observed in the XRD pattern of the nanoparticles with 0.2 mm Cu wire, they were not observed in the case of the 0.1 mm Cu wire.

When a large amount of energy is momentarily applied to a Cu wire, it reacts favorably with Sn to form a Cu₆Sn₅ phase. However, in order to make this process feasible, a certain amount of Cu is necessary to precipitate Cu₆Sn₅, as shown in Fig. 3 [25-27]. However, the synthesized sample composition in this study was above the solubility line of Cu₆Sn₅, indicating that a different behavior is involved when using PWD. One possible explanation for this phenomenon may be the high energy momentarily applied to sublimate the solid. The weight ratio in the case of 0.2 mm Cu wire was 15.9 wt%, but the peaks of the Cu₃Sn and Cu phases do not appear in the XRD data.

Another possibility is the shift of the liquidus curve. According to Fig. 3, it is possible to synthesis Cu₆Sn₅ with only a small amount of Cu. Commonly, when a liquid is cooled down there are many possible reaction sites, but in PWD, there are fewer reaction sites, because PWD applies the electric energy for only a very short time. Therefore, when there is Cu, there are fewer sites to react with Sn to form IMC. This confirms that the instantaneous energy provided to the Cu wire aids in the reaction with Sn-58Bi, resulting in nanosized IMCs.

The size analysis of the synthesized nanoparticles is shown in Fig. 4. Smaller particles were formed at 50 kPa, and the size distribution of the particles became more uniform at 100 kPa. These results are consistent with the results published by Suematsu [28]. The addition of the Cu wire does not have a significant effect on the particle size distribution. As shown in the Sn-Bi-Cu phase diagram in Fig. 3, a weight percentage of 15 or more is required for the formation of copper-tin compounds when using a 0.2 mm Cu wire. Figures 5 and 6
show SEM images and the energy dispersive X-ray analysis of the nanoparticles, respectively, which further confirm the size and distribution of these particles and allow us to verify our initial synthesis plans.

The sublimation energy of each substance is calculated from the integral value of temperature vs. heat capacity, using the Shomate Equation [29]

\[
C_p = A + B * t + C * t^2 + D * t^3 + \frac{E}{t^2}
\]  

where \(C_p\) is the heat capacity, \(t\) is the temperature (K)/1000 and \(A, B, C, D\) and \(E\) are constants. The calculated values of the sublimation energies of each element are as follows: Sn = 23.64 J/mm\(^3\), Bi = 11.11 J/mm\(^3\) and Cu = 55.43 J/mm\(^3\). The calculated sublimation energy values were all slightly smaller than the applied energy, which allowed the Sn-58Bi and Cu wires to be easily sublimated. Although the expected Cu contents were 4.5 and 15.9 wt\%, the real content of Cu was 2.54–10.64 wt\%. This was caused by the differences between the sublimation energies of each wire (14.29 J/mm\(^3\) for Sn-58Bi wire and 55.43 J/mm\(^3\) for the Cu wire). These sublimation energies also depend on the volume of each wire, which were 6.28 mm\(^3\) for the Sn-58Bi 0.2512 mm\(^3\) for the 0.1 mm Cu wire and 1.0048 mm\(^3\) for the 0.2 mm Cu wire.

These data demonstrate that when the Cu wire contents are reduced, most of the energy becomes concentrated on the Sn-58Bi wire, which has a low sublimation energy. Regardless of the Cu\(_6\)Sn\(_5\) and Cu\(_3\)Sn phases present, the Cu compound was anteriorly sublimated, and Sn reacted with a small amount of sublimated Cu when using the 0.1 mm Cu wire. When the 0.2 mm Cu wire was used, the Cu contents increased sharply, decreasing the energy absorbed by the Sn-Bi wire, resulting in IMC formation.

4. CONCLUSIONS

In this paper, three-component nanoparticles were synthesized using Sn-58Bi and Cu wires. We controlled the Cu wire contents to determine the solubility of Cu with the Sn-58Bi wire using PWD. Theoretically, in the Sn-Bi-Cu phase diagram, a small amount of Cu reacts with Sn to form the IMC. When a lesser amount of Cu wire was sublimated with the Sn-58Bi wire, most of the energy was absorbed by the Sn-58Bi wire and not enough energy was available to sublimate Cu to react with Sn and form the IMC. When the Cu content exceeds a certain amount, it absorbs a sufficient amount of energy to react with Sn to form a Cu IMC and Cu precipitates.
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REFERENCES