Strain Rate Dependence on Nanoindentation Responses of Interfacial Intermetallic Compounds in Electronic Solder Joints with Cu and Ag Substrates

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This study evaluated mechanical behavior of the intermetallic compounds (IMCs) formed at the interfaces between potential Pb-free solders (Sn-Ag-Cu and Sn-Zn) and the wires of Cu and Ag under different loading rates. Compared to Ag based IMCs, Cu based IMCs were harder and stiffer, but less strain rate sensitive. The morphology of the indent impression was found depending on the ratio of the modulus to hardness, and the crystal structure of the IMCs. \[\text{DOI: 10.2320/matertrans.M2009016}\]

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1. Introduction

In view of the recent technological as well as legislative developments, more reliability challenges are encountered at all interconnection levels in electronic applications. With respect to portable electronic items, which may experience accidental shock loadings, a fundamental understanding of the mechanical behaviors of the interconnections under different strain rates is crucial. For that reason, strain rate effect on the strength of Pb-free solder materials has been investigated. It seems that the strain rate sensitivities of solders with various compositions do not differ too much, however, at high strain rate regimes ($50 \text{s}^{-1}$), the strain rate sensitivity is about two times higher than that at low strain rates ($0.05 \text{s}^{-1}$).\textsuperscript{1)} Instead of solder bulk, fracturing of solder joints subjected to drop impact generally occurs at brittle IMCs at the interface.\textsuperscript{2,3)} In order to increase the reliability of solder interconnections, this study aims to study the mechanical behavior of IMCs at the interfaces between Pb-free solders (Sn-Ag-Cu and Sn-Zn) and common electronic substrates, Cu and Ag using nanoindentation. The effect of strain rate on the mechanical properties is the main concern.

2. Experiments

The solders used in this study were Sn-3 mass\%Ag-0.5 mass\%Cu (referred as SAC) and Sn-8.6 mass\%Zn (referred as SZ). The solders were placed in a quartz tube and then soaked in an oil bath at 250°C. Cu and Ag wires with diameter of 1 mm were used. The metallic wires were sequentially degreased in NaOH solution, deoxygened in HNO\textsubscript{3} and dipped in a dimethylammonium chloride (DMAHCl) solution before soldering. The fluxed specimen was soaked in the isothermal solder liquid for a desired duration ($20\sim60 \text{min}$) to obtain IMC layers with enough thickness for nanoindentation testing.

The reacted specimens were mounted with epoxy resin and then polished. Interfacial IMCs of the specimens was investigated by optical microscopy (OM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

The mechanical properties of the intermetallic layers at the interface between the solder and the wire were investigated by means of nanoindentation (MTS Nano Indenter XP) with a Berkovich tip (tip radius 20 nm). The indentations were made along the lateral direction of IMC layers. A continuous stiffness measurement (CSM) technique was used during indentation. A purely isotropic silica standard was used to calibrate the system. The indenter was pressed into the specimen up to 800 nm. The load-displacement data obtained were analyzed using the method of Oliver and Pharr\textsuperscript{4)} to determine the hardness and the elastic modulus as a function of the displacement of the indenter. Each datum was the average of at least 10 tests.

To obtain the strain rate sensitivity, constrain strain rate testing was performed using CSM mode. The indent strain rate, $\dot{\varepsilon}$, defined as the indenter displacement velocity divided by the plastic depth,\textsuperscript{5)} was kept at $3 \times 10^{-4}$, $10^{-2}$ and $10^{-1} \text{s}^{-1}$:

$$\dot{\varepsilon} = \frac{dh}{dt} \frac{1}{h(t)} \tag{1}$$

where $h$ is indent depth and $t$ is time.

The strain rate sensitivity $m$ was defined as

$$m = \frac{d \ln H}{d \ln \dot{\varepsilon}} \tag{2}$$

where $H$ is the hardness measured at different strain rates.

3. Results and Discussion

Table 1 lists the interfacial IMCs examined in this study and also the corresponding lattice structures. According to the EDS results and previous investigations,\textsuperscript{6,7)} Cu based IMCs included Cu$_x$Sn, Cu$_x$Sn$_5$ and Cu$_x$Zn$_8$, while Ag based IMCs were Ag$_3$Sn, AgZn and Ag$_5$Zn$_8$. Cu$_6$Sn$_5$ had a monoclinic structure at room temperature and both the
Cu$_3$Sn and Ag$_3$Sn were orthorhombic. All the Zn containing IMCs were with cubic structure. Representative nanoindentation load (L)-displacement (D) curves of the IMCs under a strain rate of 0.01/s are illustrated in Fig. 1. With respect to Cu based IMCs, the L-D curves upon loading exhibit a more or less serrated flow. The degree for serration in decreasing order is Cu$_6$Sn$_5$, Cu$_5$Zn$_8$, and Cu$_3$Sn with a smooth L-D curve (Fig. 1(a)). Likewise, the L-D curves of the Ag based compounds show similar serrate features (Fig. 1(b)). Among these, the loading segment of Ag$_3$Sn was not that steep and had several stair-like steps on it.

The average hardness and elastic modulus measured at different strain rates, calculated from the data within the steady stage, the selected depth from 200 to 300 nm, are listed in Table 2 and Fig. 2. It is found that the hardness and Young’s modulus values of Cu based IMCs (Cu$_6$Sn$_5$, Cu$_5$Sn, and Cu$_3$Sn) are higher than the Ag-based. All the IMCs became hardened and stiffer with an acceleration in strain rate. Using eq. (2), the strain rate sensitivity ($m$) could be obtained as 0.082, 0.083, 0.091, 0.112, 0.093 and 0.109, respectively for Cu$_6$Sn$_5$, Cu$_5$Sn, Cu$_3$Sn, Ag$_3$Sn, AgZn and Ag$_5$Zn$_8$ (listed in Table 1). Figure 3 illustrates that the $m$ value was the function of the hardness of IMCs material, indicating that soft Ag based IMCs exhibited a greater degree of hardening compared with hard Cu based IMCs.

The indent morphologies of the IMCs showed no significant change with increasing the strain rate. As illustrated in Fig. 4(a), only Cu$_3$Sn has a perfect indented impression with no inhomogeneous plastic deformation feature (crack, pile-up, or sink-in). No apparent pile-up and sink-in could be observed at the indent edges of Cu$_6$Sn$_5$, Fig. 4(b). Serious cracking initiated from the indent corners, presumably due to its poor fracture toughness (KIC = 0.91 MPa m$^{1/2}$ estimated in this study). In addition, the local pile-up on the lower edge of the indent in Fig. 4(b) was quite sharp and might be caused by local cracking.

Table 1 The $E/H$ ($E$: elastic modulus, $H$: hardness) and crystal structure for each phase.\textsuperscript{8)}

<table>
<thead>
<tr>
<th>Structure</th>
<th>m</th>
<th>Indent morphology</th>
<th>$E/H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_6$Sn$_5$</td>
<td>Monoclinic</td>
<td>cracking at corners</td>
<td>18.7</td>
</tr>
<tr>
<td>Cu$_5$Sn</td>
<td>Orthorhombic</td>
<td>perfect indent</td>
<td>25.4</td>
</tr>
<tr>
<td>Cu$_3$Sn</td>
<td>Orthorhombic</td>
<td>pile up</td>
<td>29.5</td>
</tr>
<tr>
<td>Cu$_5$Zn$_8$</td>
<td>Cubic</td>
<td>pile up</td>
<td>36.7</td>
</tr>
<tr>
<td>Ag$_3$Sn</td>
<td>Orthorhombic</td>
<td>sink in</td>
<td>33.1</td>
</tr>
<tr>
<td>AgZn</td>
<td>Cubic</td>
<td>pile up</td>
<td>36.7</td>
</tr>
<tr>
<td>Ag$_5$Zn$_8$</td>
<td>Cubic</td>
<td>pile up</td>
<td>29.4</td>
</tr>
</tbody>
</table>

Fig. 1 Load versus displacement curves for nanoindentation testing of different interfacial IMCs: (a) Cu based, and (b) Ag based.

Fig. 2 Mechanical properties of IMCs as the function of strain rate strain rates: (a) hardness and (b) elastic modulus.
Pile-ups took place in the indents of AgZn, Ag₅Zn₈ and Cu₃Sn (as the example of AgZn shown in Fig. 4(c)), while indentation sink-in was observed in Ag₅Sn (Fig. 4(d)). All those inhomogeneous plastic deformations caused the serrate flow on the L-D curves. According to the work of Hay and Pharr,⁹ the degree of pile up or sink-in can be interpreted by the ratio of the Young’s modulus to yield strength \( \frac{E}{\sigma_y} \) and also the work hardening ability. If we replace \( \frac{E}{\sigma_y} \) by \( H \), it is true that with an increase in \( E = H \) the relative elastic recovery becomes less.¹⁰,¹¹) and results in a greater degree of plastic deformation. If the \( E = H \) values given in Table 1 are combined with the crystal structure, it can be inferred that high \( E = H \) value, as well as a cubic structure, contributes to a high degree of plasticity and thus pile-up at the indent edges.

Table 2 Nanoindentation data under different strain rate conditions.

<table>
<thead>
<tr>
<th></th>
<th>( 3 \times 10^{-4} ) s⁻¹</th>
<th>( 10^{-3} ) s⁻¹</th>
<th>( 10^{-1} ) s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( H ) (GPa)</td>
<td>( E ) (GPa)</td>
<td>( H ) (GPa)</td>
</tr>
<tr>
<td>Cu₂Sn₁</td>
<td>5.2 ± 0.15</td>
<td>110 ± 3.1</td>
<td>7.3 ± 0.08</td>
</tr>
<tr>
<td>Cu₃Sn</td>
<td>5.1 ± 0.06</td>
<td>140 ± 2.1</td>
<td>7.2 ± 0.21</td>
</tr>
<tr>
<td>Cu₃Zn₈</td>
<td>4.9 ± 0.02</td>
<td>170 ± 2.2</td>
<td>6.9 ± 0.09</td>
</tr>
<tr>
<td>Ag₅Sn</td>
<td>1.7 ± 0.12</td>
<td>72 ± 4.12</td>
<td>2.8 ± 0.12</td>
</tr>
<tr>
<td>AgZn</td>
<td>2.3 ± 0.26</td>
<td>96 ± 2.11</td>
<td>3.4 ± 0.08</td>
</tr>
<tr>
<td>Ag₅Zn₈</td>
<td>3.0 ± 0.12</td>
<td>97 ± 2.68</td>
<td>4.8 ± 0.15</td>
</tr>
</tbody>
</table>

Fig. 3 Relationship between the strain rate sensitivity (m) and hardness of the IMCs under \( 10^{-1} \) s⁻¹.

Fig. 4 SEM images of the indents: (a) Cu₂Sn under \( 10^{-2} \) s⁻¹, (b) Cu₃Sn₂ under \( 10^{-2} \) s⁻¹ (the cracks are indicated by the arrows), (c) AgZn under \( 10^{-2} \) s⁻¹ (the pile-ups are indicated by the arrows), and (d) Ag₅Sn under \( 3 \times 10^{-4} \) s⁻¹. The red triangles indicate perfect indentation impressions.
In conclusion, it was demonstrated that the hardness and modulus of Cu based IMCs were significantly higher than those of Ag based IMCs. Observation on the characterization of indentation marks of Cu$_6$Sn$_5$ revealed large cracks initiated from the indent tips implying the brittle nature and inferior fracture toughness of this compound. Pile-ups took place in indents of AgZn, Ag$_5$Zn$_8$ and Cu$_5$Zn$_8$, while indentation sink-in was observed in Ag$_3$Sn. This was closely related to the degree of plastic deformation which could be evaluated by $E/H$ value. With an acceleration of strain rate, the hardness and modulus of all the IMCs increased. It was also found that, with increasing strain rate, soft Ag based IMCs exhibited a greater degree of hardening (strain rate sensitivity exponent ($m$)) compared with hard Cu based IMCs.

Acknowledgements

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