Sn–Cu Alloy Electrodeposition and Its Connecting Reliability for Automotive Connectors*1

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The electrodeposition behavior of Sn–Cu alloys in a sulfate solution containing three additives, cresol sulfonic acid, benzal acetone, and nonionic alkyl polyethylene glycol ether surfactant, was investigated potentiostatically between +0.3 and −0.7 V vs. NHE at 298 K. The contact resistance of the alloys deposited on a Cu connector was evaluated. Cu in the alloys behaved as a more noble metal than did Sn, thus showing the typical feature of regular-type codeposition. In solutions containing additives, the difference in deposition potential between Cu and Sn decreased because Cu deposition was significantly suppressed by the additives. The alloys deposited in solutions containing additives exhibited smooth surfaces and were composed of Cu, Sn, Cu6Sn5, and Cu3Sn phases in accordance with the equilibrium phase diagram of a binary Cu–Sn system. The contact resistance of the alloys increased by heating at 433 K, thus indicating that connecting reliability did not improve by plating the stable metallic compound Cu6Sn5. The connecting reliability of a connector after abrasion was higher in deposited alloy films than in Sn reflow plating. [doi:10.2320/matertrans.M2011022]

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1. Introduction

Sn or Au electrodeposition is typically performed on Cu substrate to improve the connection reliability for automotive connectors. However, in Sn deposition, Sn and Cu from the substrate are likely to diffuse and form an intermetallic compound at the connector surface at high operating temperatures, thus causing the pure Sn of the top layer to disappear and connection reliability to decrease significantly. Although by Au deposition, high connection reliability can be achieved even at high operating temperatures, the application is expensive.

Future automotive connectors must be capable of handling high current needed for hybrid car motors, and thus, the control of the heat resistance of deposited films is important. In this study, deposition of the stable intermetallic compounds of Cu–Sn alloys on Cu substrate to prevent diffusion of Sn and Cu was investigated. The equilibrium phase diagram of the binary Sn–Cu system suggests the existence of stable phases of the intermetallic compounds (Cu6Sn5) and (Cu6Sn5). The connection reliability of Sn plating decreases because Cu6Sn5 forms at the surface. However, by Cu–Sn alloy deposition, the connection reliability is expected to increase with the formation of stable Cu6Sn5, and the formation of Cu6Sn5 is decreased by suppressing diffusion of Cu and Sn.

A large difference exists between the standard single electrode potentials of Cu (+0.337 V relative to a normal hydrogen electrode, NHE) and Sn (−0.136 V). Therefore, Sn–Cu alloy deposition has generally been performed in a solution containing cyanide ions, which form a stable complex with Cu2+ ions. However, since cyanogens are toxic, we investigate the more environmentally acceptable path of Sn–Cu alloy deposition in sulfate solution. Cresol sulfonic acid, benzal acetone, and nonionic alkyl polyethylene glycol ether surfactant were added to the electrolyte as leveling agents for the deposits. Sn–Cu alloy deposition was conducted on a Cu connector under plating conditions to produce a smooth surface, and connection reliability was evaluated before and after heating and abrasion. Cross sections of deposited Sn–Cu alloy before and after heating were observed by focused ion beam (FIB) microscopy, and alloy composition was analyzed by energy dispersive X-ray spectroscopy (EDS).

2. Experimental

Table 1 lists the compositions of the experimental electrolytic solutions and electrolysis conditions. The electrolytic solutions were prepared by dissolving reagent grade SnSO4 (0.28 mol/L), CuSO4 (0.24 mol/L, 0.012 mol/L for deposits of Cu content 10 mass% once), H2SO4 (1.0 mol/L), CH3C4H4(OH)SO3H (0.053 mol/L), C6H5CH-CHCOCH3 (0.0021 mol/L), and C12H25O(CH2CH2O)23 (2.0 g/L, hereafter termed Brij R35) in distilled and deionized water. Electrodeposition was performed in unagitated solution under coulometric (1.0 × 105 C/m2) and potentiostatic (+0.3 to −0.7 V vs. NHE) conditions at 298 K. Polarization curves were typically measured by the potential sweep method, which involves polarizing the electrode from a less noble potential toward a more noble potential direction at 0.5 mV/s. Nickel and platinum sheets (1 cm × 2 cm) were used as the cathode and anode, respectively. Cathode deposits were dissolved using nitric acid.

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Table 1 Electrolysis conditions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>0.24</td>
</tr>
<tr>
<td>SnSO₄</td>
<td>0.28</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>1.0</td>
</tr>
<tr>
<td>CH₃COOH(SO₄)₂·H₂O</td>
<td>0.053</td>
</tr>
<tr>
<td>C₆H₅CH(COCH₃)₂</td>
<td>0.0021</td>
</tr>
<tr>
<td>C₁₂H₂O₆(CH₂COOH)₂·3H₂O</td>
<td>2.0</td>
</tr>
<tr>
<td>Bath composition</td>
<td></td>
</tr>
<tr>
<td>Operating conditions</td>
<td></td>
</tr>
<tr>
<td>Cathode potential (V vs. NHE)</td>
<td>0.3−0.7</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298</td>
</tr>
<tr>
<td>Operating conditions</td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>Ni(1 × 2 cm²)</td>
</tr>
<tr>
<td>Anode</td>
<td>Pt(1 × 2 cm²)</td>
</tr>
<tr>
<td>Quiescent bath</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Deposition behavior of Sn–Cu alloy

Figure 2 shows total polarization curves measured by the potential sweep method for Sn–Cu alloy deposition in sulfate solution. In additive-free solution, current density increases rapidly at about +0.28 and −0.2 V; quantitative analysis reveals that the rapid increases in current density at 0.28 V and −0.2 V was attributed to the beginning of Cu and Sn depositions, respectively. In additive-free solution, Cu and Sn begin their deposition with little polarization because their standard single electrode potentials, +0.337 and −0.136 V, respectively, reflect their significantly different deposition potentials. Addition of cresol sulfonic acid, benzal acetone, or Brij R₃₅ suppresses Cu deposition at about +0.28 V. Particularly, a solution containing the above three types of additives together enhances the suppression of Cu deposition. In Sn deposition, the current density oscillates greatly at about −0.2 V of beginning of the deposition in solution containing Brij R₃₅, and greatly decreases once despite the cathode potential is shifted to the less noble direction. This indicates the suppression effect of Brij R₃₅ on the Sn deposition at the initial stage. High-frequency vibration of the power supply resulting from adsorption of Brij R₃₅ possibly causes the current-density oscillation at about −0.2 V. The difference in deposition potential between Cu and Sn is larger in additive-free solution than in solution containing the additives, because of significant suppression of Cu deposition. Alloys deposited in the solution containing the three types of additives are found to be superior in appearance; therefore, all electrodepositions described below were conducted in the solution containing the three additives.

Figure 3 shows the current efficiencies of Sn and Cu for Sn–Cu alloy deposition. At potentials more noble than −0.2 V, Cu efficiency reaches a maximum of about 100%. At about −0.2 V, Sn efficiency begins to increase, whereas Cu efficiency decreases gradually, and the current density oscillates significantly (Fig. 2), corresponding to the beginning of Sn deposition. The total current efficiency of Sn and Cu deposition is ≥85% at all potential regions studied.

Figure 4 shows the relationship between cathode potential and Cu content in deposited Sn–Cu alloys. The dotted line
indicates the composition reference line (CRL) of Cu, where the mass percentage composition of Cu in the deposit equals the metal percentage of Cu in the solution. Only Cu is deposited at potentials more noble than $-0.15 \text{ V}$. When the potential is shifted to less noble than $-0.15 \text{ V}$, the Cu content in the deposit decreases rapidly. When the potential is further shifted to $-0.7 \text{ V}$, the Cu content gradually decreases toward CRL. This behavior can be explained by considering Brenner’s classification of alloy electrodeposition, in which the electrodeposition is divided into five types based on the codeposition behavior of each constituent metal. In regular deposition, which is one of the five types, the more noble one of the two metals in the deposit varies in relative content as follows: (1) at lower current densities, only the more noble metal deposits; (2) as the current density increases to the diffusion-limiting value, the content decreases hyperbolically; and (3) as the current density increases further and approaches the diffusion-limiting value of the less noble metal, the content gradually decreases toward CRL. Since the current density for metal deposition increases as the cathode potential shifts toward the less noble direction, the cathode-potential dependence of Cu content in the deposit (Fig. 4) exhibits the characteristics of regular deposition. That is, Cu behaves as the more noble metal that codeposits with Sn in regular deposition.

3.2 Surface morphology of deposited Sn–Cu alloys

Figure 5 shows the surface morphology of Sn–Cu alloys deposited in a sulfate solution. Deposits of Cu content 87 and 75 mass% display slight asperity, while those of Cu content 33 and 10 mass% have smooth surfaces. The surface morphology of the alloys is mostly smooth, probably because of the leveling effect of the additives.

Figure 6 shows XRD patterns of Sn–Cu alloys deposited in a sulfate solution. At Cu content 87 and 75 mass%, the diffraction peaks indicate the presence of an intermetallic compound of $\text{Cu}_3\text{Sn}$ and $\text{Cu}_6\text{Sn}_5$. Cu and Ni resulting from the substrate. At Cu content 33 mass%, the main peaks of an intermetallic compound of $\text{Cu}_6\text{Sn}_5$ and other peaks of Sn are observed. At Cu content 10 mass%, the peaks of $\text{Cu}_6\text{Sn}_5$ decrease and those of Sn increase correspondingly.

Figure 7 shows the equilibrium phase diagram of the Cu–Sn binary system. The phases of $\delta(\text{Cu}_3\text{Sn})$ and $\eta(\text{Cu}_6\text{Sn}_5)$ are stable at Cu content 62 and 39 mass%, respectively. The mixed phase of $\text{Cu}_3\text{Sn}$ and Cu is stable at Cu content $>65 \text{ mass%}$; the mixed phase of $\text{Cu}_6\text{Sn}_5$ and Sn is stable at Cu content $<39 \text{ mass%}$. The constituent phase of deposits in this study shown in Fig. 6 corresponds approximately to the stable Cu–Sn phase in Fig. 7. However, at Cu content 87 and 75 mass%, $\text{Cu}_6\text{Sn}_5$ is evident in the deposits, contrary to the expectation based on the equilibrium phase diagram.
3.3 Connection reliability of deposited Sn–Cu alloys

Figure 8 shows the plots of contact resistance of Sn–Cu alloys of various composition deposited in a sulfate solution. Contact resistance, which was evaluated before heating and after heating at 433 K for 120 h, decreases abruptly with load. Before heating, in the region of loading <10 N, contact resistance of Cu content ≥33 mass% is high but for Cu content 10 mass%, it is almost the same as for reflow Sn produced by a commercial production line. After heating, contact resistance of all alloys is higher than before heating. In particular, for high Cu content of 87 and 75 mass%, the phase of the alloy is mainly Cu₃Sn and Cu and contact resistance is significantly higher after heating; for low Cu content of ≤33 mass%, the phase of the alloy is mixed Cu₆Sn₅ and Sn and contact resistance is relatively less higher after heating. Thus, alloying with Cu does not improve heat resistance. Among deposited Sn–Cu alloys with heating, the contact resistance of deposits consisting of mixed phase of Cu₃Sn and Cu was higher, while that of the mixed phase of Cu₆Sn₅ and Sn decreased with increasing the ratio of Sn phase.

Figure 9 denotes the plots of contact resistance of deposited Sn–Cu alloys of Cu content 33 and 10 mass% as a function of duration of heating at 433 K. Both alloys consist of the mixed phase of Cu₆Sn₅ and Sn and exhibit comparatively low contact resistance after heating. For Cu content 33 mass%, with a higher Cu₆Sn₅ ratio, contact resistance increases significantly with heating duration. For Cu content 10 mass%, with a higher Sn ratio, contact resistance increases gradually with heating duration.

Figure 10 shows plots of contact resistance and friction coefficient of deposited Sn–Cu alloys as a function of the number of sliding cycles during abrasion. The contact resistance of reflow Sn plating, which was initially about 1 mΩ, increases at 40 cycles (denoted by the circle); it decreases at 700 cycles, and again increases distinctly at 1000 cycles.

Fig. 6 X-ray diffraction patterns of deposited Sn–Cu alloys with various compositions.

Fig. 7 Equilibrium phase diagram of Cu–Sn binary system.

Fig. 8 Contact resistance of Sn–Cu alloys with various compositions deposited from sulfate solution. (Sn–Cu alloy: 4 μm, Reflow Sn: 1 μm).
cycles. The increase in contact resistance at 40 cycles can be attributed to accumulation of Sn powder consisting of Sn oxide from abrasion of the Sn plating, the decrease at 700 cycles is due to exposure of the Cu substrate, and the abrupt increase at 1000 cycles is due to the accumulation of Cu oxide powder resulting from abrasion of the Cu substrate.\(^3\)-\(^5\)

The friction coefficient of Sn plating increases gradually with cycle number. The contact resistance of deposited Sn–Cu alloy increases at 200 cycles for all alloy compositions. The extent of increase in contact resistance is smaller in Cu content 33 mass% than for 10 mass%. This is due to a decrease in the buildup of abraded Sn–Cu powder, because the deposit of Cu content 33 mass% is composed of an intermetallic compound of Cu\(_6\)Sn\(_5\), which has a high hardness value. The friction coefficient of deposited Sn–Cu alloy is almost identical to that of reflow Sn plating. Examination of the contact resistance for 100 sliding cycles shows that the connection reliability of deposited Sn–Cu alloy is better than that of reflow Sn plating, particularly at Cu content of 33 mass%.

3.4 Alloying behavior of deposited Sn–Cu alloy with heating

The cross sections of deposited Sn–Cu alloy before and after heating were observed by FIB microscopy. Alloy composition was then analyzed by EDS to determine the remarkable increase in contact resistance after heating.

Figure 11 shows the SIM images of the cross sections of Cu content 33 mass% deposits before and after heating at 433 K for 120 h. Before heating, the deposit is mainly composed of the intermetallic compound Cu\(_6\)Sn\(_5\). During heating, it separates into two phases, which EDS analysis revealed as the intermetallic compounds Cu\(_6\)Sn\(_5\) and Cu\(_3\)Sn.

Figure 12 shows the composition profiles in the thickness direction of Cu content 33 mass% deposits before heating and after heating at 433 K for 60, 120, and 240 h. Before heating, the deposit is mainly composed of the intermetallic compound Cu\(_6\)Sn\(_5\). During heating, alloys of specific compositions are formed in the thickness direction of the deposit. While increasing the heating duration, Cu\(_3\)Sn is formed in the substrate direction and the thickness of the upper layer of Cu\(_6\)Sn\(_5\) decreases correspondingly. Between durations 60 and 240 h, the thickness of the Cu\(_3\)Sn layer increases from 2 to 4 \(\mu\)m, indicating that growth rate is proportional to the square root of heating duration. Particle diffusion in a homogeneous, semi-infinite medium is known to be proportional to \((D t)^{1/2}\), where \(D\) is the diffusion coefficient and \(t\) is the heating duration.\(^{16}\) In this study, the thickness of the Cu\(_3\)Sn layer is proportional to the square root of heating duration, thus satisfying the diffusion equation in a semi-infinite medium.

The Sn–10 mass% Cu alloy was deposited on the deposit of Sn–33 mass% Cu to investigate the alloying behavior of Sn–Cu alloy during heating. Figure 13 shows the composition profiles in the thickness direction of deposited double layer of Sn–10 mass% Cu/Sn–33 mass% Cu alloys before heating and after heating at 433 K for 60, 120, and 240 h. With increasing heating duration, the thickness of the upper layer of Sn–10 mass% Cu decreases because of diffusion of Cu. At a duration of 120 h, the upper layer disappears and is replaced by Cu\(_6\)Sn\(_5\), and Cu\(_3\)Sn is formed in the substrate direction. At \(\geq 120\) h, the thickness of the Cu\(_3\)Sn layer increases by diffusion of Cu into the Cu\(_6\)Sn\(_5\) layer. The SIM images of the cross sections of the double layer reveal that the Sn–10 mass% Cu layer disappears and the Cu\(_3\)Sn layer grows thicker with increasing heating.
duration. At durations of 120 and 240 h, voids are observed in the $\text{Cu}_6\text{Sn}_5$ phase.

Figure 14 shows the SEM images of deposited Sn–Cu alloy after heating at 433 K for 360 h. Voids are present in alloys of Cu content 33 and 11 mass%. The densities of Cu, Sn, $\text{Cu}_6\text{Sn}_5$, and $\text{Cu}_3\text{Sn}$ are 8.92, 7.31, 8.31, and 11.3 g/cm$^3$, respectively, and hence the formation of $\text{Cu}_3\text{Sn}$ by alloying Cu and Sn decreases the volume of deposits. The presence of voids after heating seems to be because of decrease in deposit volume by the formation of $\text{Cu}_3\text{Sn}$.

Even when stable $\text{Cu}_6\text{Sn}_5$ is formed by alloy deposition, diffusion of Cu and Sn cannot be suppressed during heating. As a result, $\text{Cu}_3\text{Sn}$ forms the top layer of the deposit, resulting in increase in contact resistance. However, the connection reliability of deposited Sn–Cu alloys after abrasion is better than that of reflow Sn plating, because of the high degree of hardness of the intermetallic compound.
4. Conclusion

The electrodeposition behavior of Sn–Cu alloys in a sulfate solution was investigated, and the contact resistance of the alloys deposited on a Cu connector was evaluated. Cu in the alloys behaved as a more noble metal than did Sn, thus exhibiting typical regular-type codeposition. Best appearance were obtained for deposition in solution containing three additives, cresol sulfonic acid, benzal acetone, and nonionic alkyl polyethylene glycol ether surfactant. In this additive-containing solution, the following was observed: (1) the difference in deposition potential between Cu and Sn became small because Cu deposition was significantly suppressed by the additives; (2) the deposited alloys had smooth surfaces; and (3) the deposited alloys were composed of Cu, Sn, Cu₆Sn₅, and Cu₃Sn phases in accordance with the equilibrium phase diagram of the binary Cu–Sn system. The contact resistance of the deposited alloys increased by heating at 433 K. Thus, connecting reliability exhibited no improvement when plated with the stable metallic compound Cu₆Sn₅. The connecting reliability of a connector after abrasion was higher in deposited alloy films than in reflow Sn plating.

Acknowledgments

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REFERENCES