The electrochemical behaviors, microstructures, and corroded products of Sn-9Zn-xAg lead-free solders were investigated in this study. The 63Sn-37Pb and Sn-3.5Ag solder alloys were also tested for comparison. The Sn-3.5Ag solder alloy had a higher equilibrium potential (\(-0.44\) V\textsubscript{SCE}\)) than the ones of 63Sn-37Pb (\(-1.10\) V\textsubscript{SCE}\) and Sn-9Zn (\(-1.43\) V\textsubscript{SCE}\)). The Ag addition enhanced the corrosion resistance of the Sn-9Zn solder alloy. Passivation behavior occurred in the solder alloys used in this study except the 63Sn-37Pb one. X-ray diffraction patterns showed that the Zn segregated in the Sn-9Zn solder alloy as solidified, but it dissolved when 0.5 wt % Ag was added to the solder alloy. The Ag\(_2\)Zn\(_3\) and Ag\(_5\)Zn\(_8\) were found in the Sn-9Zn-1.5Ag solder alloy but they were substituted by the Ag\(_3\)Sn when the Ag content in the solder alloy was above 2.5 wt %. However, they were the initial sites for pits formation. The corroded product of SnCl\(_2\) was observed in all solder alloys tested. In addition, the ZnCl\(_2\), ZnO, and SnO were observed in the Sn-9Zn-1.5Ag solder alloys.


Experimental

The 63Sn-37Pb and Sn-3.5Ag solder alloys used in this study were commercial products with purity of 99.9%. The Sn-9Zn-xAg solder alloys were melted in our laboratory with pure metals (purity of 99.9%), which are degreased and deoxidized in 5 wt % NaOH and 5 vol % HCl solutions, respectively, then added with Ag contents of 0, 0.5, 1.5, 2.5, and 3.5 wt %, respectively. Afterward, they were melted at 600°C and stirred to homogenize.

The solder alloys were cast in a metal mold with a diam of 3 cm at 250°C and cooled in air, the microstructure was observed with a scanning electron microscope (SEM, JXA-840, JEOL, Japan) and the chemical composition of the intermetallic compounds (IMCs) was determined with an energy dispersive spectrometer (EDS, AN10000/85S, LINKS, England). An X-ray diffractometer (XRD, D-MAXIIIB, Rigaku, Japan) was used to identify the structure of the solder alloy. The corroded products were identified with X-ray diffraction (XRD, D-MAXIIIB, Rigaku, Japan) and energy dispersive spectrometry (EDS, AN10000/85S, LINKS, England).

Figure 1. Schematic diagram of the electrochemical instrument.

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2 Many factors have to be considered for developing a new lead-free solder, such as wettability, melting point, solder joint reliability, and corrosion resistance. The Sn-9Zn solder alloy is a promising free solder, such as wettability, melting point, excellent wettability on substrate, and suitable mechanical properties. But it will be limited to use after 2006 because of its toxicity. Therefore, it is an urgent mission to develop a suitable lead-free solder for using in practice.

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the IMCs formed in the solder matrix at a scanning rate of 4°/s for 2 ~
0 from 20 to 80°.

The samples were cut to a size of 1 × 1 cm and attached to a
plastic-wrapped Cu wire by carbon adhesive tape, and then mounted
in epoxy. Before the electrochemical test, the sample was ground
with sandpapers to expose the fresh surface. The electrochemical
test was conducted according to the Japanese International Standard
(JIS G 0579). A potentiostat (model 273, EG&G, USA) with soft-
ware was utilized to determine the overpotential of the solder alloys,
the schematic diagram of the electrochemical instrument is shown in
Fig. 1.12 A 3.5 wt % NaCl solution (Wako Pure Chemical Industries,
Ltd., 99.5% purity, Osaka, Japan) was used as a test medium, and
deaerated by N2 with purity of 99.9% for 30 min before test. The
sample was then connected to the cell as shown in Fig. 1, 12 in which
a Pt-coated Ti net was used as an counter electrode and the reference
electrode was a saturated calomel electrode (SCE) with a stable
potential of 0.244 V in a saturated KCl solution. The sample was
cathodically treated at 2.5 to 0.5 V SCE at a sweeping rate of 1 mV/s.

After salt spraying, the corroded products on the sample surface
were removed with sandpapers and the clean samples were adhered
to an Al stud with diams of 0.27 cm (0.106 in) and the strength of
epoxy on the Al stud was 70 MPa. The pull-off tester as shown in
Fig. 2 applied the force to the Al stud at 89.0 N/s and stopped automatically when the Al stud separated from the sample. The adhesion strength of the solder alloy/Cu interface was recorded
on a computer.

Results and Discussion

Electrochemical behaviors of the solder alloys.—Figure 3 shows
the polarization curves of the four eutectic solder alloys used in this
study and the results are listed in Table I. The equilibrium potentials
of the Sn-3.5Ag and 63Sn-37Pb solder alloys are −0.44 and −1.10
V SCE, respectively, indicating that the Sn-3.5Ag solder alloy has a
corrosion resistance of the Sn-3.5Ag and 63Sn-37Pb solder alloys, exhibiting that the
maximum current density of the Sn-3.5Ag and 63Sn-37Pb solder alloys, exhibiting that the
Sn-9Zn solder alloy is more inferior than the Sn-9Zn-0.5Ag solder alloys. Besides, the maximum
current density of the Sn-9Zn solder alloy is 1.07 × 10⁻¹ A/cm²,

Table I. The electrochemical properties of the eutectic solder alloys used.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( E_c ) (V)</th>
<th>( E_p ) (V)</th>
<th>( I_p ) (A/cm²)</th>
<th>( E_{max} ) (V)</th>
<th>( I_{max} ) (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63Sn-37Pb</td>
<td>−1.10</td>
<td>−1.10</td>
<td>−1.04</td>
<td>−1.11 × 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>Sn-3.5Ag</td>
<td>−0.44</td>
<td>−0.11 to 0.23</td>
<td>3.02 × 10⁻¹</td>
<td>−0.23</td>
<td>7.52 × 10⁻¹</td>
</tr>
<tr>
<td>Sn-9Zn</td>
<td>−1.43</td>
<td>−0.82 to −0.43</td>
<td>1.09 × 10⁻¹</td>
<td>−0.22</td>
<td>1.07 × 10⁻¹</td>
</tr>
<tr>
<td>Sn-9Zn-0.5Ag</td>
<td>−1.07</td>
<td>−0.05 to 0.39</td>
<td>3.92 × 10⁻¹</td>
<td>−0.21</td>
<td>8.54 × 10⁻¹</td>
</tr>
</tbody>
</table>

\( E_c \) : corrosion potential of solder alloy, \( E_p \) : passivation range of solder alloy, \( I_p \) : current density of solder alloy in passivation, \( E_{max} \) : potential for the maximum current density, and \( I_{max} \) : maximum corrosion current density.
The Sn-3.5Ag solder alloy is composed of Sn-rich phase and which is much higher than that of 7.52 × 10⁻³ and 1.11 × 10⁻³ A/cm² for the Sn-3.5Ag and 63Sn-37Pb solder alloys, respectively, showing that the Sn-9Zn solder alloy has a higher corrosion rate.

Lin and Shih¹³ have shown that the current density efficiency of a sacrificial Al anode is dependent on its microstructure. The Ag has a low solubility in Sn even at the eutectic point, hence, the Ag₈Sn is formed at the solder alloy containing Ag contents above 0.1 wt %.¹⁴ The Sn-3.5Ag solder alloy is composed of Sn-rich phase and Ag₈Sn with a lamellar structure.¹⁶ The 63Sn-37Pb solder alloy also has a lamellar structure, but it is composed of Sn-rich phase and Pb-rich phase due to the high solubility of Pb in Sn.¹⁷ The structure of the Sn-9Zn solder alloy is broken Zn lamellar rods dispersed in the Sn matrix because Zn has a low solubility in Sn and segregates as solidified.

Nisancioglu¹⁸ has reported that the IMCs formation is an important factor in the susceptibility of Al alloys to pitting and other forms of localized corrosion. Because IMCs are more noble than the matrix and deteriorate the corrosion resistance they play a role of cathode and the matrix undergoes anodic dissolution, leading to a localized cell. The similar reaction also occurs in the Sn-3.5Ag solder alloy, in which the Ag₈Sn is a cathode and Sn matrix plays as an anode, showing that the Sn/Ag₈Sn interface is the initial site of corrosion because of the largest potential difference. But the quantity of Ag₈Sn in the Sn-3.5Ag solder alloy is much lower than Pb in the 63Sn-37Pb and Zn in the Sn-9Zn solder alloys, hence the Sn-3.5Ag solder alloy shows a higher equilibrium potential than the others.

On the other hand, IMC is not found in the 63Sn-37Pb and Sn-9Zn solder alloys, the initial corrosion site could be at the interface of two different phases. The potentials of anodic reactions for the solders elements are listed in Table II, which indicates that the potentials of anodic reaction for Sn, Zn and Pb are −0.136, −0.763, and −0.126, respectively.¹⁹ The potential difference of the Sn-rich and Pb-rich phases in the 63Sn-37Pb solder alloy is much lower than that of the Sn-rich and Zn-rich phases in the Sn-9Zn and that of the Sn/Ag₈Sn interface in the Sn-3.5Ag solder alloy, therefore a lower corrosion current density is obtained.

From Fig. 3, a passivation reaction is not found for the 63Sn-37Pb solder alloy, which shows that the corrosion current density increases with the applied potential when it exceeds the equilibrium potential. However, the Sn-3.5Ag and Sn-9Zn solder alloys are passive in a range from −0.11 to 0.23 V_SCE and from −0.82 to −0.43 V_SCE, respectively. The passivation current densities of the Sn-3.5Ag and Sn-9Zn solder alloys are 3.02 × 10⁻³ and 1.09 × 10⁻³ A/cm², respectively, showing that the Sn-3.5Ag solder alloy has a wider passivation range and a lower passivation current density than the Sn-9Zn solder alloy.

The equilibrium potential of the Sn-9Zn solder alloy is enhanced from −1.43 to −1.07 V_SCE when 0.5 wt % Ag is added to the solder alloy. Lin et al. have exhibited that the equilibrium potential of the Sn-Zn-Al solder alloy is in the range of −1.35 to −1.25 V_SCE, showing that the addition of Ag is more efficient than Al in enhancing the corrosion resistance of the Sn-9Zn solder alloy. The Sn-9Zn-0.5Ag solder alloy has a passivation range of −0.05 to −0.39 V_SCE and a corrosion current density and passivation current density of 8.54 × 10⁻² and 3.92 × 10⁻³ A/cm², respectively, showing that the corrosion resistance of the Sn-9Zn-0.5Ag solder alloy is superior than that of the Sn-9Zn solder alloy and is comparable to the Sn-3.5Ag solder alloy.

The polarization curves of the other Sn-9Zn-xAg solder alloys (x ≥ 1.5 wt %) are shown in Fig. 4 and the results are summarized in Table III. The equilibrium potential decreases from −1.07 to −1.37 V_SCE with increasing the Ag content in the solder alloy from 0.5 to 1.5 wt %, showing that the corrosion resistance of the Sn-9Zn-1.5Ag solder alloy is inferior than that of the Sn-9Zn-0.5Ag solder alloy. On the other hand, two corrosion reactions (marked as 1 and 2 in Fig. 4) are found in the Sn-9Zn-1.5Ag solder alloy as indicated at potentials of −2.36 and −2.05 V_SCE, which are due to, respectively, the dissolution of the AgZn₁ and Ag₃Zn₅ IMCs. The potentials have been identified as a pitting potential for the sample.

| Table III. The electrochemical properties of the non-eutectic solder alloys used. |
|---------------------------------|----------|------------|----------------|----------------|----------------|
| Materials | E_corr (V) | E_pass (V) | I_max (A/cm²) | E_max (V) | I_max (A/cm²) |
| Sn-9Zn-1.5Ag | −1.37 | −0.06 ~ 0.27 | 4.98 × 10⁻³ | −0.27 | 8.57 × 10⁻² |
| Sn-9Zn-2.5Ag | −1.04 | −0.72 ~ 0.49 | 2.16 × 10⁻³ | −0.23 | 7.52 × 10⁻² |
| Sn-9Zn-3.5Ag | −0.51 | −0.13 ~ 0.08 | 6.92 × 10⁻³ | −0.25 | 9.48 × 10⁻² |

E_corr: corrosion potential of solder alloy, E_pass: passivation range of solder alloy, I_max: current density of solder alloy in passivation, E_max: potential for the maximum current density, I_max: maximum corrosion current density.
owing to a great number of active sites as reported by Barbucci et al.\textsuperscript{20} The local dissolution also has been observed in aluminum alloy and stainless steel due to the dealloying and Cr-depletion zone formation, respectively, which is caused by the IMCs formation.\textsuperscript{21,22} Song et al.\textsuperscript{23} have demonstrated that the AgZn\textsubscript{3} and Ag\textsubscript{5}Zn\textsubscript{8} were found in the Sn-9Zn-xAg solder alloys. Hence the corrosion reaction of the Sn-9Zn-1.5Ag solder alloy should be also caused by the IMCs formation and the corrosion mechanism is discussed in the section on the role of intermetallic compounds in corrosion.

Figure 5 shows the relationship between the equilibrium potential vs. the Ag content for the Sn-9Zn-xAg solder alloy, exhibiting that the equilibrium potential increases to -1.04 V\textsubscript{SCE} when the Ag addition in the solder alloy is 2.5 wt \%. It indicates that the corrosion resistance of the Sn-9Zn-xAg solder alloys is enhanced again. A highest corrosion potential of -0.51 V\textsubscript{SCE} is obtained for the Sn-9Zn-3.5Ag solder alloy, which is close to that of the Sn-3.5Ag solder alloy (-0.44 V\textsubscript{SCE}) and an excellent corrosion resistance is obtained.

Microstructure of the solder alloys.—The XRD pattern of the Sn-3.5Ag solder alloy is shown in Fig. 6a, which exhibits that the Sn-3.5Ag solder alloy is composed of Sn-rich phase and Ag\textsubscript{3}Sn, agreeing with the results of previous reports.\textsuperscript{15,16} Fig. 6b shows the XRD pattern of the 63Sn-37Pb solder alloy, which indicates that the Sn-rich phase and Pb-rich phase are in the solder matrix without any IMC because of the high solubility of Pb in Sn.

In the XRD patterns of the Sn-9Zn-xAg solder alloys (x \leq 1.5 wt \%) as shown in Fig. 6c, the reflection peaks of the Sn-rich phase and Zn-rich phase are found in the Sn-9Zn solder alloy due to the segregation of Zn as solidified. However, the peak of the Zn-rich phase disappears when the Ag addition in the solder alloy is 0.5 wt \%, there is not any IMC found in the solder matrix, either. The results show that the Ag addition increases the solubility of Zn in Sn and the Ag also dissolves in the Sn matrix. Two Ag-Zn IMCs, namely AgZn\textsubscript{3} and Ag\textsubscript{5}Zn\textsubscript{8} are found in the Sn-9Zn-1.5Ag solder alloy, due to that the Ag addition of 1.5 wt \% exceeds the solubility
of Ag in Sn,\textsuperscript{14} leading to the compounds formation because Ag has a higher affinity with Zn than Sn. A similar result was also reported by Song \textit{et al.}\textsuperscript{23}

Figure 6(d) exhibits the XRD patterns of the Sn-9Zn-\(x\)Ag solder alloys (\(x \geq 2.5\) wt %), which shows that the AgZn\(_3\) remains in the Sn-9Zn-2.5Ag solder alloy but the Ag\(_5\)Zn\(_8\) is substituted by the AgZn IMC. Moreover, the AgZn\(_3\) is also replaced by AgZn with increasing the Ag addition in the solder alloy to 3.5 wt %. The phenomenon is resulted from the macrosegregation as solidified due to the different densities of Sn, Zn and Ag of 7.30, 7.14 and 10.15 g/cm\(^3\), respectively. Part of Ag atoms react with Zn to form the AgZn, the residual ones segregate in the bottom of ingot, and react with Sn matrix to form the Ag\(_3\)Sn.

The microstructure of the Sn-9Zn-1.5Ag solder alloy is shown in Fig. 7(a), which indicates that a dark second phase is formed in the solder matrix. The EDS analysis as shown in Fig. 7b indicates that the second phase is Ag-Zn compound with an atomic ratio of 1:3, indicating that the second phase is AgZn\(_3\) agreeing with the result of XRD pattern. Fig. 7c shows the Zn mapping analysis of the AgZn\(_3\), which indicates that the Zn atoms in the solder alloy are consumed to form the AgZn\(_3\).

When the Ag content in solder alloy increases to 2.5 wt %, the Ag\(_3\)Sn with particle size of 1 \(\mu\)m is formed in the solder matrix, as shown in Fig. 8a, which agrees with the result obtained from the XRD pattern shown in Fig. 6c. Fig. 8b shows the microstructure of the Sn-9Zn-3.5Ag solder alloy, in which more Ag\(_3\)Sn particles as confirmed by an EDS analysis in Fig. 8c are found in the solder matrix. Besides, another Ag-Zn compound with chemical composition of 48.72Ag-52.28Zn (in atom %) is also observed, which has a larger particle size than the Ag\(_3\)Sn and could be the AgZn compound detected in the XRD pattern (Fig. 6d).

Corroded products on the solder surface.—Figure 9a shows the surface morphology of the 63Sn-37Pb solder alloy after electrochemical experiment, in which the small particles with size of 5 \(\mu\)m are the corroded product and determined as SnCl\(_2\). The larger par-
articles with size of 30 μm are determined as chloride, showing that the Cl\(^-\) ions adsorbed on the surface of the 63Sn-37Pb solder alloy. The adsorption of aggressive Cl\(^-\) ions into the faults of the protective film and their penetration and accumulation in these imperfections are considered as one of the factors initiating the corrosion.\(^{24,25}\)

The sheet-shaped corroded product on the Sn-3.5Ag solder alloy shown in Fig. 9b is determined as SnCl\(_2\). Lin and Liu\(^4\) have demonstrated that the corroded products on the XSn-9(5Al-Zn)-YIn solder alloys were ZnO and SnO\(_2\), showing that the corroded products on the Zn-free solder alloys and Zn-contained solder alloy are very different.

The corroded surface morphology of the Sn-9Zn solder alloy as shown in Fig. 10a exhibits that a pit is formed in the Sn-9Zn solder alloy and the corroded products of SnCl\(_2\) and SnO are found. Another hairy product as shown in Fig. 10b is found in the pit and determined as ZnO. The O\(_2\) comes from the electrolysis of H\(_2\)O, which is trapped in the pit and reacts with Zn\(^{2+}\). Figure 10c shows the corroded surface morphology of the Sn-9Zn-0.5Ag solder alloy, in which a pit is also observed, indicating that the Sn-9Zn series solder alloy is sensitive to pitting corrosion. The corroded products of SnO and ZnO are perceived on the Sn-9Zn-0.5Ag solder alloy as shown in Fig. 10d.

Figure 11a is the corroded surface morphology of the Sn-9Zn-1.5Ag solder alloy, in which some narrow but deep pits are found. The formation of the pits is due to the dissolution of the Ag\(_2\)Zn\(_6\) and Ag\(_2\)Zn\(_8\) during electrochemical experiment. The corroded products as shown in Fig. 11b are also determined as ZnO and SnCl\(_2\).

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**Figure 9.** Surface morphologies of the (a) 63Sn-37Pb and (b) Sn-3.5Ag solder alloys after electrochemical experiment.

**Figure 10.** Surface morphologies of (a) the Sn-9Zn solder alloy after electrochemical experiment and (b) the hairy product on the Sn-9Zn solder alloy, (c) the corroded surface of the Sn-9Zn-0.5Ag solder alloy and (d) the corroded products on the Sn-9Zn-0.5Ag surface.
The role of intermetallic compounds in corrosion.—From the Pb-Sn binary phase diagram, Pb and Sn have a high solubility to each other and the 63Sn-37Pb solder alloy has been reported being composed of the lamellar Sn rich and Pb-rich phases. On the other hand, Pb has a higher equilibrium potential than Sn, hence the Cl\textsuperscript- ions tend to react with Sn to form the SnCl\textsubscript{2}. The oxygen produced at the anode in an electrolysis reaction is deoxygenated by N\textsubscript{2}, hence there is not any oxide found. The IMCs formation affects the corrosion resistance of materials significantly, such as phase in stainless steels and S phase (Al\textsubscript{2}CuMg) in aluminum alloys. The phase in stainless steels is a Cr-rich phase, which causes a Cr-depletion zone around it. In a corrosion reaction, the phase is a cathode and the Cr-depletion zone is an anode, hence the Cr-depletion zone is the initial site of pitting corrosion. However, The S phase appears to be active with respect to the Al alloy matrix, it prefers to dissolve in a corrosion reaction and causes the pits formation as reported by Buchheit et al.

The XRD pattern of the Sn-3.5Ag solder alloy after electrochemical experiment shown in Fig. 12a indicates that the Ag\textsubscript{3}Sn IMC is retained after test and the corroded product is SnCl\textsubscript{2}. The result shows that the Ag\textsubscript{3}Sn is more noble relatively to the Sn matrix, it does not dissolve during the test but acts as a cathode. On the other hand, the Sn matrix is an anode in the electrochemical reaction, which reacts with Cl\textsuperscript- to form the SnCl\textsubscript{2}, agreeing with the SEM observation as shown in Fig. 9b. The compound of SnCl\textsubscript{2} has been reported being quite soluble in aqueous solution however, it also has been observed in the Sn-Zn-Al solder alloy. Windholz et al. have been reported that the SnCl\textsubscript{2} is able to absorb O\textsubscript{2} from air to form insoluble oxychloride. Hence the SnCl\textsubscript{2} found in this study should be some oxychlorides. Figure 12b is the XRD pattern of the Sn-9Zn-1.5Ag solder alloy after electrochemical test, showing the corroded products of SnCl\textsubscript{2}, ZnCl\textsubscript{2}, and ZnO. The product of ZnCl\textsubscript{2} has been found in the Sn-9Zn solder alloy after corrosion test by Vincent and Richards. Besides, ZnO is the most stable product in the Zn\textsuperscript{2}/H\textsubscript{2}O system. The peaks of IMCs of AgZn\textsubscript{3} and Ag\textsubscript{5}Zn\textsubscript{8} disappear, indicating that they dissolve in the corrosion reaction at the potentials of −2.36 and −2.05 V\textsubscript{SCE} as shown in Fig. 4. Hence the AgZn\textsubscript{3} and Ag\textsubscript{5}Zn\textsubscript{8} IMCs appear to be active with respect to the Sn matrix and are the initial sites for pits formation as shown in Fig. 11a, they play the same role as the S phase in the aluminum alloy 2024-T321 and the corrosion resistance of the Sn-9Zn-1.5Ag solder alloy is deteriorated.
Conclusions

The results of this study are summarized as follows:

1. The Sn-3.5Ag solder alloy had a better corrosion resistance than the 63Sn-37Pb and Sn-9Zn-3.5Ag solder alloys in a 3.5 wt % NaCl solution. But the 63Sn-37Pb solder alloy had a lower current density due to the lower potential difference.

2. The Ag addition enhanced the corrosion resistance of the Sn-9Zn solder alloy, when the Ag addition increased to 3.5 wt %.

3. The corrosion product on the surfaces of the 63Sn-37Pb and Sn-3.5Ag solder alloys was SnCl₂. Besides, the SnO and ZnO were also observed on the surface of the Sn-9Zn-3.5Ag solder alloys.

4. The pits formation on the surface of the Sn-9Zn and Sn-9Zn-0.5Ag solder alloys was due to the dissolution of Zn-rich phase. But for the Sn-9Zn-1.5Ag solder alloy it was caused by the dissolution of the AgZn₁ and Ag₅Zn₈ IMCs.

5. The Sn-9Zn-3.5Ag solder alloy offered a better salt spraying resistance than that of Sn-9Zn after aging and salt spraying for 48 h.

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