Effects of Heat Treatment on Corrosion Resistance in Tin-Nickel Alloy Films Formed by Thermal Diffusion

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Introduction

Tin-nickel alloy films show excellent corrosion resistance and have been used in decorative plating. These films are currently fabricated from tin-nickel alloy plating baths, but this requires that anode dissolution and the tin-to-nickel concentration ratio be controlled.

Forming alloy films by heating plating following double plating of tin and nickel on steel enables the usual single metal plating bath to be used with conventional bath control.

Few papers have studied the properties of tin-nickel alloy films formed by thermal diffusion, although studies have been done on intermetallic tin-nickel compounds formed when nickel plating was used as a diffusion barrier to prevent interdiffusion between copper substrates and the tin plating layer to improve the solderability of copper substrates.

We have already reported the crystal structure, contact resistance, and hardness of tin-nickel alloy films formed on copper substrates by thermal diffusion. This letter covers the effects of heat-treatment temperature and time on corrosion resistance in tin-nickel alloy films formed by thermal diffusion.

Experiments

Bright nickel and tin plating baths were the same as previously reported, but nickel plating was applied at a current density of 30mA/cm². Steel was used as the substrate. After 10μm thick nickel was plated on steel, 0.05 μm thick tin was plated on top of that. The resulting samples were heated at 160-200°C for 4-24 hours in a drying oven to form alloy films.

Patterns of tin/nickel double plating film were measured using an X-ray diffractometer (θ-2θ) with Cu Kα radiation (40kV, 100mA).

A CASS test was made to estimate the corrosion resistance of films. Corrosion resistance after 4-12 hours was represented by a rating number referencing the standard figure.

Results and Discussion

X-ray diffraction patterns of tin/nickel double films showed diffraction lines corresponding to tin and unknown peaks which appeared without heat-treatment (Fig. 1). According to reports by J. Haimovich on X-ray diffraction patterns in NiSn₃ formed on tin/nickel double film, unknown peaks correspond to NiSn. Intermetallic NiSn₃ is metastable and not shown in the equilibrium-phase diagram.

In heat-treatment at 200°C for 4 hours, diffrac-

Fig. 1 Effects of heat-treatment time on X-ray diffraction patterns in tin/nickel double plating films.
Sample : Sn 0.05 μm, Ni 10 μm
Heat-treatment : 200°C, 4h, 24h
tion lines corresponding to tin disappeared and those for intermetallic Ni$_2$Sn$_4$ and Ni$_3$Sn appeared.

In CASS test results (Table 1), the corrosion resistance values of films heat-treated at 160°C for 4 hours were similar to those for films heat-treated for 24 hours, while the corrosion resistance was enhanced with increased temperature (except for films heat-treated at 200°C for 4 hours) and increased heat-treatment time.

The results of X-ray diffraction patterns suggested that corrosion resistance was enhanced by the formation of intermetallic tin-nickel compounds. Enhancement due to increased temperature and treatment time was thought to be related to the tin-nickel alloy layer thickness.

This, however, requires separate investigation.

In photographs of films after the CASS test (12h) with heat-treatment at 200°C for 24 hours, Table 1 indicates that sample B (Fig. 2), which was heat-treated, was more corrosion-resistant than sample A, which was not. The white rust observed on the surface of sample A was not observed on sample B. Sample B resembled slightly pink stainless steel. The X-ray diffraction patterns (Fig. 1) suggested that this white rust resulted in the tin layer on the surface of samples.

**Table 1** CASS test results.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Testing time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>4</td>
<td>9.3</td>
</tr>
<tr>
<td>160</td>
<td>24</td>
<td>9.4</td>
</tr>
<tr>
<td>180</td>
<td>4</td>
<td>9.4</td>
</tr>
<tr>
<td>180</td>
<td>24</td>
<td>9.8</td>
</tr>
<tr>
<td>200</td>
<td>4</td>
<td>9.3</td>
</tr>
<tr>
<td>300</td>
<td>24</td>
<td>9.8</td>
</tr>
</tbody>
</table>

*As-plated* | 9.5 | 8.5 | 7.5 |

**Conclusions**

After 10 μm thick nickel was plated on steel and 0.05 μm thick tin was plated on top of that, the corrosion resistance of double plating films was enhanced by heat-treatment at 200°C for 24 hours. Increased temperature and heat-treatment time appeared to be the mechanism of this enhancement.

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**References**

1) D. E. Lay; *Plat. and Surf. Fin.*, 75, 26 (Jul. 1988)