Difference Between Various Sn/Ag/Cu Solder Compositions

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About Nihon Almit Co., Ltd.

- Founded: 1956

- Leading manufacturer in Japan for solder products.
- First manufacturer in the world to produce aluminum solder.
- SnPb products adopted and used by NASA for space shuttle project.

- Customers:
  Automotive: Honda / Hyundai / Mitsubishi / Nissan / Toyota / Volvo
  Non-Automotive: Ericsson / Hitachi / LG / NEC / Panasonic / Philips / Pioneer / Samsung / Sanyo / Sharp / Siemens / Sony
1.1 Overview

The use of lead is being banned to help preserve the environment, and the traditionally used Sn-Pb solder is being restricted (RoHS etc.) From reliability standpoints, Sn/Ag/Cu alloys has been chosen as the replacement for Sn-Pb solder. However, there is no industry standard on which alloy to chose among the various Sn/Ag/Cu alloys available in the market.

- Sn + 3.9% Ag + 0.6% Cu (iNEMI recommended)
- Sn + 3.5% Ag + 0.7% Cu
- Sn + 3.0% Ag + 0.5% Cu (JEITA recommended)

Purpose of this test
- To determine the difference in performance and reliability among the various Sn/Ag/Cu alloys, and find out which alloy will be best suited for various applications, especially under harsh environmental conditions.
1.2 Lead-free Progress for Automotive

2005-2006: Continue evaluation

2005: Start use for new designs
2006: Start low volume production
2008: Start mass-production / eliminate SnPb solder

Note: The above information is a summary of various manufacturer’s schedules. Actual schedule and procedures will vary by company.
2. Evaluation Points

1) Tensile Strength / Elongation / Yield Point
2) Young’s Modulus / Poisson’s Ratio
3) Thermal Conductivity (at 60 °C) / Specific Gravity
4) Specific Heat
5) Coefficient of Thermal Expansion / Thermal Expansion ratio
6) Visual Appearance (Whitening phenomenon)

Note: number of samples tested (n) = 3 of each alloy for tests 1-5
2. Test Samples

• Composition of test samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Sn-3.9Ag-0.6Cu (SAC396)</td>
<td>iNEMI recommended</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Sn-3.5Ag-0.7Cu (SAC357)</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>Sn-3.0Ag-0.5Cu (SAC305)</td>
<td>JEITA recommended</td>
</tr>
<tr>
<td>Reference</td>
<td>63Sn-37Pb</td>
<td>Eutectic Solder</td>
</tr>
</tbody>
</table>
2.1 Tensile Strength

Test Method: Tensile Strength Measurement eqp.
Test Specimen: Shown below

Diameter: 10mm
Length: 50mm
Parallel: 60mm
R: 15

Test environment: 25 °C
Pull Speed: 10mm/min

Before

After

Test Equipment
(Shimadzu)

Mechanical Properties
2.2 Young’s Modulus / Poisson’s Ratio

Test Method: Ultrasonic

ie) Calculate the Young’s Modulus and Poisson’s Ratio from the speed that the ultrasonics travel through the metal

Test Specimen: 20mm sq, t=10mm
Test Environment: 25 °C

Results:

Young’s modulus = sonic speed x (density)^2
2.3 Thermal Conductivity / Specific Gravity

Test Method: Laser Flash Method
ie) Apply laser beam to test specimen, measure the calories and time from the back side, and calculate the specific gravity and thermal conductivity.

Test Specimen: 10mm diameter / t = 2mm
Test Environment: 25°C / 60% RH / vacuum

Test Results

Thermal conductivity = specific heat x heat diffusion x specific gravity

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>Thermal Conductivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.9Ag-0.6Cu</td>
<td>7.4</td>
<td>61.1</td>
</tr>
<tr>
<td>Sn-3.5Ag-0.7Cu</td>
<td>7.4</td>
<td>62.1</td>
</tr>
<tr>
<td>Sn-3.0Ag-0.5Cu</td>
<td>7.4</td>
<td>63.2</td>
</tr>
<tr>
<td>63Sn-37Pb</td>
<td>8.4</td>
<td>52.8</td>
</tr>
</tbody>
</table>

Thermal Conductivity Measurement eqp.
(Ulvac-Rico Inc.)
2.4 Specific Heat

Test Method: Insulating Continuous Method
ie) Measure the temp difference between the specimen and the insulated container, and calculate the specific heat

Test Specimen: 10mm dia x t=2mm
Test Environment: 25 C

Test Results:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Specific Heat (J/g K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.9Ag-0.6Cu</td>
<td>0.22</td>
</tr>
<tr>
<td>Sn-3.5Ag-0.7Cu</td>
<td>0.22</td>
</tr>
<tr>
<td>Sn-3.0Ag-0.5Cu</td>
<td>0.23</td>
</tr>
<tr>
<td>63Sn-37Pb</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Outline of test equipment

Test equipment (Ulvac-Rico)
2.5 Coefficient of Thermal Expansion (CTE)

Test Method: Heat Expansion Measurement

ie) The metal expansion transferred from the measurement stick to the pressure reader will be transferred to voltage and recorded.

Test Specimen: 4mm × 4mm × t=10mm

Test Environment: 20-60°C / 20-100°C

Test Results:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Coefficient of Expansion (10^-6/K) 20-60°C</th>
<th>Coefficient of Expansion (10^-6/K) 20-100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.9Ag-0.6Cu</td>
<td>21.4</td>
<td>21.8</td>
</tr>
<tr>
<td>Sn-3.5Ag-0.7Cu</td>
<td>21.5</td>
<td>21.7</td>
</tr>
<tr>
<td>Sn-3.0Ag-0.5Cu</td>
<td>21.6</td>
<td>21.6</td>
</tr>
<tr>
<td>63Sn-37Pb</td>
<td>21.6</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Outline of equipment
(Alvac-Rico)
### 2.6 Test Results

#### Chart 2. Mechanical Properties Test Results (n=3)

<table>
<thead>
<tr>
<th></th>
<th>Sn-3.9Ag-0.6Cu</th>
<th>Sn-3.5Ag-0.7Cu</th>
<th>Sn-3.0Ag-0.5Cu</th>
<th>63Sn-37Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus Temp C</td>
<td>218</td>
<td>218</td>
<td>220</td>
<td>183</td>
</tr>
<tr>
<td>Solidus Temp C</td>
<td>217</td>
<td>217</td>
<td>217</td>
<td>183</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>43.7</td>
<td>44.0</td>
<td>41.1</td>
<td>34.7</td>
</tr>
<tr>
<td>Yield Point (MPa)</td>
<td>31.3</td>
<td>35.0</td>
<td>34.2</td>
<td>28.4</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>40.6</td>
<td>43.4</td>
<td>41.0</td>
<td>91.2</td>
</tr>
<tr>
<td>Coefficient of Work Hardening</td>
<td>0.083</td>
<td>0.056</td>
<td>0.040</td>
<td>0.032</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>52</td>
<td>51</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.35</td>
<td>0.36</td>
<td>0.36</td>
<td>0.37</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>7.4</td>
<td>7.4</td>
<td>7.4</td>
<td>8.4</td>
</tr>
<tr>
<td>Specific Heat (J/g K)</td>
<td>0.22</td>
<td>0.22</td>
<td>0.23</td>
<td>0.18</td>
</tr>
<tr>
<td>Thermal Conductivity (%) 25C</td>
<td>61.1</td>
<td>62.1</td>
<td>63.2</td>
<td>52.8</td>
</tr>
<tr>
<td>Thermal Conductivity (%) 60C</td>
<td>0.085</td>
<td>0.086</td>
<td>---</td>
<td>0.086</td>
</tr>
<tr>
<td>Thermal Conductivity (%) 100C</td>
<td>0.174</td>
<td>0.173</td>
<td>0.173</td>
<td>0.173</td>
</tr>
<tr>
<td>CTE (10^-6/K)</td>
<td><strong>20-60C</strong></td>
<td><strong>21.4</strong></td>
<td><strong>21.5</strong></td>
<td><strong>21.6</strong></td>
</tr>
<tr>
<td></td>
<td><strong>20-100C</strong></td>
<td><strong>21.8</strong></td>
<td><strong>21.7</strong></td>
<td><strong>21.6</strong></td>
</tr>
</tbody>
</table>
2.7 Observations

- The 3 various SAC alloys perform similarly with only a nominal variation level, and there seems to be no difference among the various alloy’s mechanical properties.

Ref. SAC vs. Sn63

<table>
<thead>
<tr>
<th></th>
<th>SAC</th>
<th>Sn63</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Yield Point</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Elongation</td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>CTE</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>
2.8.1 Visual Appearance and Whitening Phenomenon

63Sn-37Pb  Sn-3.5Ag-0.7Cu

Whitening phenomenon occurs when Beta Sn forms peaks and Sn-Ag-Cu forms valleys in the SAC alloys.
Deep valleys may cause Hot-Tear, which is different from cracking.
2.8.2 Difference between “Hot-tear” and “Crack”

Beta Sn
Sn-Ag-Cu
Deep Valley = Hot Tear

<Condition>
Alloy : SAC305
After 1000 Temp Cycle

Crack
2.8.3 Whitening Ratio Test Method

Heat at 300 °C

Cooling

Ni Plate

SnAg solder alloy

Whitening Ratio = $\frac{S_w}{S_m}$
2.8.4. Cooling Speed and Whitening Ratio

Solidify at 0 °C  Solidify at 100 °C  Solidify at 200 °C
Observations:

- Whitening most occurs at 1% Ag content solders, and gradually reduces to 0 at 4% Ag content.

- Faster cooling speed helps reduce the whitening, and no whitening is observed with cooling on ice.
3. Evaluation Points

Test after 1,000 / 3,000 temperature cycles at -40 / +125 Deg C

1) Shear Strength Test
2) Visual Analysis
3) Cross Section Analysis
4) EPMA Analysis
3. Test Specimen

Flux: Almit TM-HP (12% flux content)
PCB: Single sided glass epoxy 100 x 100 x 1.6mm
PCB Surface Finish: no plating (Cu land)

Component: 2125 Chip Condenser (Sn plated)
Reflow conditions: See chart / air atmosphere
3. Heat Cycle Testing

Heat Cycle Test

Specimen

Tester (Kato)

Temperature: -40 / +125°C
Transfer time: 20 Min
Dwell time: 30 Min
Test at initial / 1000 cycles / 3000 cycles

Shear strength test

Check impact on joint strength

Tacking Tester
(Aiko Engineering)

Cross section analysis

Check impact on molecule structure

EPMA (JEOL)
Reliability Tests

3.1 Shear Testing

Speed: 12mm / min
Environment: 25 C
d number of tests = 5
Initial / 1000 cycles: Break at component side (solder itself is intact)
3000 cycles: Break at component and solder.

=> No significant variance among the alloys.
### 3.2. Visual Appearance

<table>
<thead>
<tr>
<th>cycles</th>
<th>Sn-3.9Ag-0.6Cu</th>
<th>Sn-3.5Ag-0.5Cu</th>
<th>Sn-3.0Ag-0.5Cu</th>
<th>63Sn-37Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>1000</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>3000</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>
3.2. Observation from Visual Appearance

- 0 cycles
  All SAC alloys show a white streak (whitening phenomenon)
- 1000 cycles
  Discoloration (not corrosion) of the flux is observed. No surface changes or cracks observed.
- 3000 cycles
  Wrinkles on the surface become more prominent. No cracks observed.
### 3.3.1 Cross Section Analysis (SEM x350)

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Sn-3.9Ag-0.6Cu</th>
<th>Sn-3.5Ag-0.5Cu</th>
<th>Sn-3.0Ag-0.5Cu</th>
<th>63Sn-37Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>1000</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>3000</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- **0 Cycles**: No visible cracks or voids.
- **1000 Cycles**: Appearance of voids in Sn-3.9Ag-0.6Cu and Sn-3.5Ag-0.5Cu.
- **3000 Cycles**: Visible cracks in Sn-3.9Ag-0.6Cu, Sn-3.5Ag-0.5Cu, and Sn-3.0Ag-0.5Cu, with more pronounced changes in 63Sn-37Pb.
3.3.2 Crack Analysis @ 3000 cycles

Sn-3.9Ag-0.6Cu

Sn-3.5Ag-0.7Cu

Sn-3.0Ag-0.5Cu

63Sn-37Pb

In all SAC alloys, cracks are coming in from under the component, which is normally considered the weakest point.
3.3.3 Observation from Cross Section

1000 cycles
SAC: Growth of inter-metallic layer thickness.
   Growth of inter-metallic structure (Ag3Sn / Cu6Sn5 etc.) within the solder.
   No noticeable difference
   The void observed in SAC396 is not related to heat cycle
SnPb: Increase of grain size / Pb rich layer near inter-metallic layer.
Notes:
- Growth of inter-metallic layer is normally considered to weaken the joint strength.
- The inter-metallic structure / grain size change / is not at a level to affect the joint strength.
- Surface roughness is most likely due to the polishing for the cross section analysis.

3000 cycles
Cracks observed in all of the SAC and SnPb solders, primarily from under the component.
Further growth of inter-metallic layer thickness, inter-metallic structure observed.
Reliability Tests

### 3.4.1 EPMA Analysis (Sn)

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Sn-3.9Ag-0.6Cu</th>
<th>Sn-3.5Ag-0.5Cu</th>
<th>Sn-3.0Ag-0.5Cu</th>
<th>63Sn-37Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="#" alt="Image 1" /></td>
<td><img src="#" alt="Image 2" /></td>
<td><img src="#" alt="Image 3" /></td>
<td><img src="#" alt="Image 4" /></td>
</tr>
<tr>
<td>1000</td>
<td><img src="#" alt="Image 5" /></td>
<td><img src="#" alt="Image 6" /></td>
<td><img src="#" alt="Image 7" /></td>
<td><img src="#" alt="Image 8" /></td>
</tr>
<tr>
<td>3000</td>
<td><img src="#" alt="Image 9" /></td>
<td><img src="#" alt="Image 10" /></td>
<td><img src="#" alt="Image 11" /></td>
<td><img src="#" alt="Image 12" /></td>
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</tbody>
</table>
### Reliability Tests

#### 3.4.2 EPMA Analysis (Ag)

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Sn-3.9Ag-0.6Cu</th>
<th>Sn-3.5Ag-0.5Cu</th>
<th>Sn-3.0Ag-0.5Cu</th>
<th>63Sn-37Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td>Not applicable</td>
</tr>
<tr>
<td>1000</td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td>Not applicable</td>
</tr>
<tr>
<td>3000</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
<td>Not applicable</td>
</tr>
</tbody>
</table>
## Reliability Tests

### 3.4.3 EPMA Analysis (Cu)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Sn-3.9Ag-0.6Cu</th>
<th>Sn-3.5Ag-0.5Cu</th>
<th>Sn-3.0Ag-0.5Cu</th>
<th>63Sn-37Pb</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>1000</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
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<tr>
<td>3000</td>
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<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Reliability Tests

3.4.4 Observation from EPMA

<Sn>
- 1000 cycles
  SAC: No significant change / SnPb: Increase of grain size
- 3000 cycles
  No significant difference from 1000 cycles
=> No difference among the 3 SAC alloys / SnPb: Further increase of grain size

<Ag=Ag3Sn>
- 1000 cycles
  The network-like structure seen prior to heat cycling (Ag3Sn) has collapsed.
- 3000 cycles
  The Ag(Ag3Sn) forms individual particles.
=> No difference among the 3 SAC alloys

<Cu>
- 1000 cycles
  Growth of inter-metallic layer (Cu3Sn / Cu6Sn5) observed.
  Growth of inter-metallic structure of Cu6Sn5 observed throughout the solder.
- 3000 cycles
  Further growth of inter-metallic layer, and structure of Cu6Sn5.
=> No difference among the 3 SAC alloys

<Point>
Collapse of Ag (Ag3Sn) network-like structure is the most prominent from EPMA test.
4.1. Conclusion

• No significant difference has been observed among the 3 SAC alloys for mechanical properties.

• No significant difference has been observed among the 3 SAC alloys regarding joint strength or metallic structure after 3000 temperature cycles. (Cracks were observed in the solder, but effect on Joint “Shear” strength was minimal, and all alloys showed similar structure changes.)

• Higher Ag content material (Sn+3.9%Ag+0.6%Cu) will help reduce the occurrence of the whitening phenomenon, and will reduce the Hot-tear on the solder surface. The correlation of Hot-tear to reliability was not observed during this study (SMT), but depending on where the Hot-tear is located, it may possibly become an entry point for larger cracks in the solder surface.

**Points for alloy selection**

• Lower Ag content material will have the lowest price. (Sn+3.0%Ag+Cu0.5%)
• Higher Ag content material will help to reduce the whitening phenomenon occurrence (Sn+3.9%Ag+Cu0.6%).
4.2 Other Comments

- The metal alloy itself is basically the same among solder manufacturers.

=> Flux will be the factor to differentiate good and bad solder products.

- Selection Points
  - Cored Solder Wire: Spattering / Wetting
  - Solder Paste: Printing / Wetting / Voids
4.3.1 Flux Differences

Paste visual appearance after 24 hours continuous printing. Paste on right is ‘dry’ so powder oxidises heavily causing poor soldering.

Void results after reflow due to poor paste flux stability/powder oxidation.

Good anti-voiding performance if paste flux is stable
Paste wettability. Solder on left has fully covered component termination but the paste on the right has not fully wet to component termination. This poor wetting will affect the solder joint reliability. Manufacturers must strive for the best wetting possible when using lead free solder as full pad/component termination wetting will indicate a reliable solder joint.

Exposed component termination = poor wetting.
Thank You!

For any questions please contact
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