Solder Alloy Evolution and Development

Presented by Timothy O’Neill, Technical Marketing Manager, AIM

SMTA Boston
November 4, 2018
A Brief Review of Electronic Solders
1960’s to 2006

- Tin/Lead (Sn/Pb) Solder was universal.
- Sn60/Pb40 in early versions – migrating to Sn63/Pb37
- Some applications (<5%) required Sn/Ag or Pb > 85%
- 2006 RoHS 1 banned lead in EU – 10 year phase in – categorical exemptions.
- SAC Alloys SAC305, SAC387 evolved a de facto standards (iNEMI, ITRI recommendations)
## SAC Alloy Characteristics

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>RoHS Compliant</td>
<td>Melt Temperature</td>
</tr>
<tr>
<td>Compatible With Other Materials (Pb)</td>
<td>Equipment compatibility</td>
</tr>
<tr>
<td>Acceptable Reliability</td>
<td>Aesthetic issue</td>
</tr>
<tr>
<td>Good Soldering Performance</td>
<td>Cost</td>
</tr>
<tr>
<td></td>
<td>Drop-Shock – Thermal Cycling</td>
</tr>
</tbody>
</table>
SAC Alloy Acceptance

SAC305 was an acceptable Sn/Pb alternative, but the drawbacks had assemblers and solder manufacturers seeking alternatives.

SN100C, SACX, K100LD, 995, SACM, INNOLOT, SACM, SAC0105, Sn97/Cu3 to name a few.

The alloy market continues to fragment/diversify and niche/designer alloys are becoming more commonplace.
Comparison of SAC Alloys to Novel Alloys

- Degradation of mechanical performance with aging
- Tin whisker growth
- Low drop/shock performance due to large $\text{Ag}_3\text{Sn}$ platelets (high-silver SAC)
- High cost of Ag
Degradation of Mechanical Performance with Aging

**Tension Test**

- SAC305 (As cast)
- SAC305 (Aged 18hr at 150C)

**Creep**

- σ=25MPa, RT
- AS cast, SAC305
- Aged, SAC305

**Hardness**

- SAC305
  - As cast
  - Aged (24 hr@150°C)
Tin Whisker Formation with SAC305
Large IMC Plates in SAC Alloys with >3% Ag

Optical micrograph of free-standing Sn3.8-Ag0.7-Cu solder alloy showing a large Ag₃Sn primary precipitate.

To avoid detrimental effect of Ag₃Sn plates Ag content should be kept low.

K. Zeng et al, 2012
Large IMC Plates in High Ag-SAC

Cu substrate

primary Cu₆Sn₅

primary Ag₃Sn-plates

J. Keller et al, Acta Mat. 2011
Pb-Free Alloy Alternatives
The Next Wave

• RoHS2/ReCAST will be fully implemented in July 2019 – essentially eliminating lead (Pb) from electronics manufacturing.

• Bismuth can be reconsidered as an element in electronics solders

Bismuth in Electronic Solders

- Lowers Melting Temperature
- Improves Mechanical Properties*
- CANNOT Be Exposed to Tin/Lead

*In controlled amount
Pb-Free Alloy Alternatives
The Next Wave

Bismuth

- One of lowest thermal and electrical conductivity of all metals
- Denser in liquid form than solid
- Expands on solidification
- Most naturally diamagnetic element
Sn-Bi

![Graph showing the relationship between Bi content and tensile properties, as well as changes in melting temperature with varying Bi content.](image)
Pb-Free Alloy Alternatives
The Next Wave

Micro-Alloy Elements – Sb, In, Ge, Ni, Mg etc.

Trace amounts of alloying elements can increase desirable properties and minimize undesirable traits in alloy combinations.
Sn-X

X =

- Bi
- Ag
- Cu
- Sb
- Ni
Sn-Cu

Sn-xCu

Tensile properties vs Cu content (wt%)

- Strength (MPa)
- Elongation (%)

Pure Sn

Sn-0.7Cu

Phase diagram of Sn-Cu alloy

© 2018 AIM Solder
Sn-Ag

**Graph:**
- **Y-axis**: Tensile properties (MPa)
- **X-axis**: Ag content (wt%)
- **Data Points**:
  - Strength (MPa) marked with black circles.
  - Elongation (%) marked with red triangles.

**Sn-3.5Ag**
- Kerr & Chawla, 2004

**Phase Diagram**
- Liquid phase
- Sn-Ag phase
- Sn3Ag phase
- Ag3Sn phase

**Sn-3.8Ag-0.7Cu**
- F. Mutuku, et al, 2017
Sn-Ni

Aging @150 °C

Aging 20 days @150 °C
## Summary

<table>
<thead>
<tr>
<th>Elements</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength</td>
</tr>
<tr>
<td>Bi</td>
<td>⬆ (≤3wt%)</td>
</tr>
<tr>
<td>Ag</td>
<td>⬆</td>
</tr>
<tr>
<td>Sb</td>
<td>⬆</td>
</tr>
<tr>
<td></td>
<td>(&gt;3wt%) ↓</td>
</tr>
<tr>
<td>Cu</td>
<td>⬆</td>
</tr>
<tr>
<td></td>
<td>(&gt;3wt%) ↑</td>
</tr>
<tr>
<td>Ni</td>
<td>suppresses Cu₃Sn growth, improves fluidity</td>
</tr>
</tbody>
</table>

*Strong (⬆⬇), fair (⬆⬇), weak (⬇⬆)
A Comparison Between Properties of SAC305, NA2 and NA6
## Physical & Mechanical Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melting Properties</strong></td>
<td></td>
</tr>
<tr>
<td>NA2</td>
<td>210°C with a range of 2 degree undercooling</td>
</tr>
<tr>
<td>SAC305</td>
<td>217°C with a range of 20 degrees undercooling</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td></td>
</tr>
<tr>
<td>NA2</td>
<td>29/HV</td>
</tr>
<tr>
<td>SAC305</td>
<td>14/HV</td>
</tr>
<tr>
<td><strong>Tensile Strength (aged 150°C for 24 hours)</strong></td>
<td></td>
</tr>
<tr>
<td>NA2</td>
<td>86 MPa</td>
</tr>
<tr>
<td>SAC305</td>
<td>34 MPa</td>
</tr>
<tr>
<td><strong>Microstructure Analysis (aged 150°C for 24 hours)</strong></td>
<td></td>
</tr>
</tbody>
</table>

**150° for 24 hours**
## Physical & Mechanical Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NA6</td>
</tr>
<tr>
<td>Melting point</td>
<td>208-216°C</td>
</tr>
<tr>
<td>Hardness</td>
<td>24/HV</td>
</tr>
<tr>
<td>Tensile Strength (aged 24hrs @ 150°C)</td>
<td>80 MPa</td>
</tr>
<tr>
<td>Kinetics of IMC Growth (740hrs @ 150°C)</td>
<td>13.5 µm</td>
</tr>
<tr>
<td>Microstructure Analysis (aged)</td>
<td>![Image](SU3500 20.0kV x2.00k BSE-COMP 20.0µm)</td>
</tr>
<tr>
<td>150°C for 24 hours</td>
<td></td>
</tr>
</tbody>
</table>
Wetting Balance Behavior

Test condition:
- Test piece: Copper plate (thickness: 0.5mm, width: 6mm, length: 25mm)
- Immersion speed & depth: 20mm/s & 6mm
- Flux: NC265, T=265°C
- Data are average of 3 tests

Wetting performance of three alloys are comparable. Visual appearance of SAC305 and NA6 surface is slightly smoother than NA2.
Thermal Behavior
(melting temperature)

- SAC305
- NA6
- NA2
Kinetics of Intermetallic Growth (IMC) at $150^\circ\text{C}$

| SAC305 / 480hr@150C | NA6 / 480hr@150C | NA2 / 480hr@150C |
Tension Test

Tension test performed per (ASTM E8/E8M-11)
- Samples aged 24hrs at 150°C
- Cross head speed: 2 mm/min

NA6 and NA2 show much higher strength as compared with SAC305. Elongation of NA2 is higher than NA6 and slightly lower than SAC305.
Microstructure Comparison After High Temperature Aging 24h @150° C

Microstructure of NA6 & NA2 remains stable vs. SAC305.
Humidity 85%, $T = 60^\circ C$, $t = 3100$ hr

The coated wire was stressed by making a “U-shaped” bend to 90 degrees.
Thermal Cycling Test Results
Thermal Cycle Testing Scope

- DfR Solutions performed thermal cycling experiments on test coupons assembled with three different solder alloys
  - SAC305 and three alternative Pb-free solders (NA6, NA2 & IN1)
- Sufficient time to failure data was obtained from three different package styles
  - LED, MLF and Resistor
  - Other packages tested had insufficient failure data or failure data that was suspect
- Both alternative Pb-free solders demonstrated improvement in thermal cycle lifetime over SAC305
Thermal Cycle Testing Samples

Eight boards were assembled for each solder alloy. Data derived from highlighted components.

Data provided by: DfR Solutions
NA6
Thermal Cycle Test Results

Thermal Cycling - SAC305 Vs. NA2
(SAC305 Baseline of 1.0)

SAC305 is better than or equal to NA2.
REL22 is twice as durable as SAC305.
NA2 No Clean Solder Paste For LED Applications
Commercial applications of high-power LEDs have dramatically increased over the last several years because of LEDs’ high reliability, long lifetime and energy savings potential.

LED-based luminaires are increasingly required to meet the reliability standards and ENERGY STAR® requirements for long-term lumen maintenance.

Solder joint failure has been documented as a reliability concern.

Images courtesy of CREE
NA2 Solder Paste for LED

LED Technology is evolving putting more demands on solder interconnection. Earlier LED were limited by materials used in their construction. Modern high power LED have case temperatures in excess of 120°C.

At temperature less than 85°C, the IMC layer grows very slowly, whereas at 120°C the IMC layer thickens quickly creating brittle crack propagation sites.
NA2 Solder Paste for LED

Intermetallic Layer Growth after Temperature Exposure
NA2 Solder Paste for LED

Coefficients of Thermal Expansion (CTE):

- AlN Substrate: $4.5 \times 10^{-6}/^\circ C$
- Al (MCPCB): $23 \times 10^{-6}/^\circ C$

During LED operation (heating and cooling), the differences in the coefficients of thermal expansion between the LED substrate and the PC board cause stress on the solder joints as the materials expand and contract.

Data Supplied by CREE
Originally presented at LED A.R.T. Symposium
NA2 Solder Paste for LED

Thermal cycle per IPC-SM-785

-40°C to 125°C / 15 minute dwells / 20°C per min ramp

SAC305 Failed after 600 cycles

NA2 Survived 2000+ Cycles

Data Supplied by CREE
Originally presented at LED A.R.T. Symposium
No Clean Solder Paste Test Data
Drop-in for SAC305
BGA and QFN Voiding

Improved BGA Voiding with NA2

QFN Voiding Lower with NA2

NA2 vs. SAC305 No Clean Paste
X-Ray BTC Void Comparison

Competitor
SAC305

M8
NA2

NA2 reduces voids.
## Summary

<table>
<thead>
<tr>
<th>Property</th>
<th>SAC305</th>
<th>NA6</th>
<th>NA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Temperature</td>
<td>217-219°C</td>
<td>208-216°C</td>
<td>210-212°C</td>
</tr>
<tr>
<td>Wetting Performance</td>
<td>Good</td>
<td>Good</td>
<td>Best</td>
</tr>
<tr>
<td>Thermal Fatigue Performance</td>
<td>Poor</td>
<td>Good</td>
<td>Best</td>
</tr>
<tr>
<td>Drop Shock Performance</td>
<td>Poor</td>
<td>Good</td>
<td>Best</td>
</tr>
<tr>
<td>Mechanical Strength</td>
<td>Good*</td>
<td>Good</td>
<td>Best</td>
</tr>
<tr>
<td>Significant degradation over time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermetallic Performance</td>
<td>Good</td>
<td>Better</td>
<td>Best</td>
</tr>
<tr>
<td>Thermal Cycling Performance</td>
<td>Poor</td>
<td>Better</td>
<td>Best</td>
</tr>
</tbody>
</table>
An Introduction to Low Temperature Solder Alloys

Motivation for Low Temperature Reflow

Energy and Emissions Reductions
- CO$_2$ Emissions Reduced
- Electricity Consumption Reduced. Thousands Saved per Oven per Year.

Reduced Temperatures Process and Materials
- Substrate Warping Reduced
- Component Warping Reduced
- Reduced Material Costs
- Thinner Substrates and Components
An Introduction to Low Temperature Solder Alloys

Material And Process Benefits

Reduced Temperatures Process and Materials

• Substrate Warping Reduced
• Component Warping Reduced
• Reduced Material Costs

225° C

183° C
An Introduction to Low Temperature Solder Alloys

Material And Process Benefits

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Melt Point °C</th>
<th>Δ SAC305 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn42/Bi5 8</td>
<td>138°C</td>
<td>-79</td>
</tr>
<tr>
<td>Sn42/Bi57/Ag1</td>
<td>138-140°C</td>
<td>-78</td>
</tr>
<tr>
<td>SAC305</td>
<td>217-219°C</td>
<td>0</td>
</tr>
<tr>
<td>SnCu</td>
<td>227°C</td>
<td>+10</td>
</tr>
</tbody>
</table>

The addition of silver improves mechanical properties.
An Introduction to Low Temperature Solder Alloys

Material Concerns

• High bismuth alloys are harder, but more brittle than SAC and Sn/Pb alloys they replace.
• The addition of silver improves mechanical properties, but they will not equal the performance of SAC and Sn/Pb for thermal cycling, thermal and mechanical shock.
• The addition of alloy dopants such as copper and nickel and grain refiners including cobalt and antimony can decrease brittleness.
• Intense development efforts to improve high bismuth alloys is underway.
Takeaways

- Electronics are becoming more dense and more powerful. Heat is a byproduct, adversely impacting SAC alloys.
- Electronics are being used in more harsh environments with greater reliance on their performance.
- The alloys used in electronics fragmented with the implementation of RoHS.
- Fragmentation continues with “niche or designer” alloys gaining popularity.
- Bismuth is now available as an element for electronics solders.
- New generation alloys are more reliable than SAC305 with few processing drawbacks.
Thank You

Solder plus Support

www.aimsolder.com    info@aimsolder.com