Low and Medium Melting Temperature Solders

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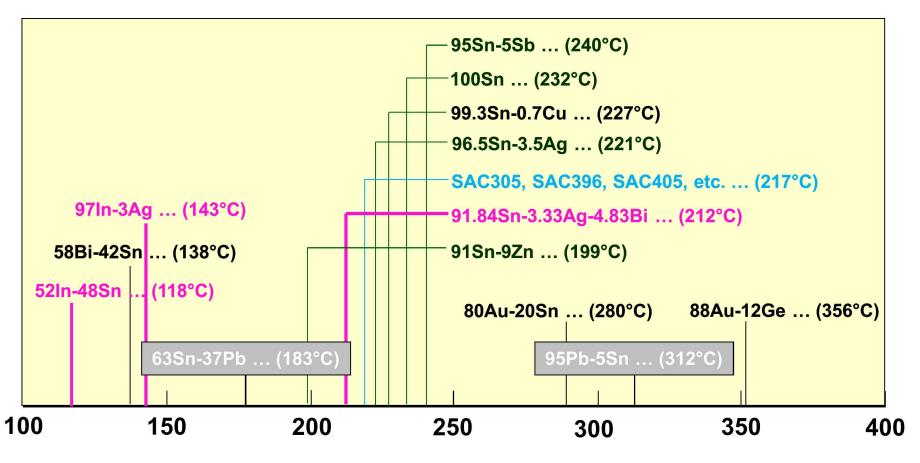


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Materials – Alloy Compositions

◆ The definition of low, medium, and high melting temperature solder has evolved over the history of Pb-free solders : 1986 – present.



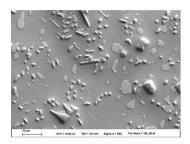
Liquidus Temperature °C

Outline

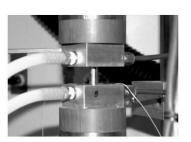
- "Traditional" Low Melting Temperature Solders
 - 97In-3Ag (wt.%), 58Bi-42Sn, 52In-48Sn

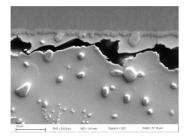


- "Current" Medium Melting Temperature Solders
 - 91.84Sn-3.33Ag-4.83Bi
 - Sn-Ag-Bi-X-Y-Z-etc.
- "Novel" Medium Melting Temperature Solders
 - 66Sn-5.0Ag-10Bi-5.0Au-10In-4.0Cu $(T_s = 178^{\circ}C)$



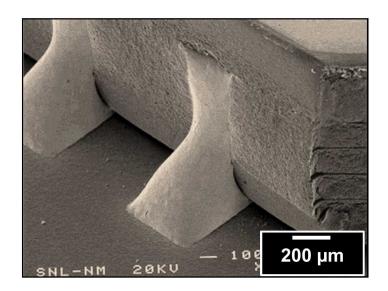
- Focus topics:
 - O Physical metallurgy
 - Mechanical metallurgy
 - Thermal mechanical fatigue (TMF)





Mechanical Metallurgy

◆ At room temperature, solder alloys are performing at temperatures that are equivalent to conditions in the combustion chamber of an operating jet engine !!!

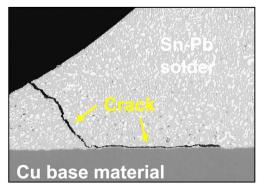




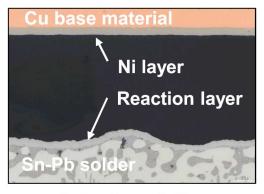
It's HOT ... even when it's not ...

Mechanical Metallurgy

- Traditionally, base materials were stronger than Sn-Pb solders.
 - Solder joint failures occurred in the filler metal or at an interface.

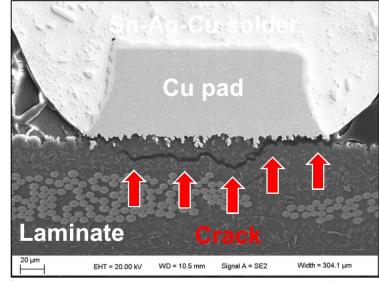


Solder (bulk) failure



Interface failure

- However, high strength solders can "push" the failure into printed circuit board (PCB) or component structures.
 - As the strength of the solder increases, so does the risk of this "collateral damage."



The three "traditional," low-temperature eutectic solders are:

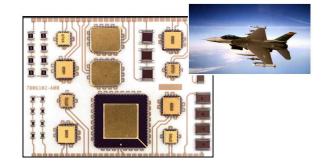
• 52In-48Sn (wt.%):
$$T_s = T_l = 118$$
°C

• 97In-3Ag:
$$T_s = T_1 = 143$$
°C

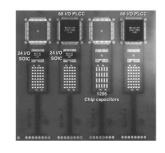
• 58Bi-42Sn: $T_s = T_l = 138^{\circ}C$

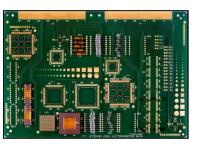


◆ The In-Sn and In-Ag alloys are used in opto-electronics components and hybrid microcircuit (HMC) products.



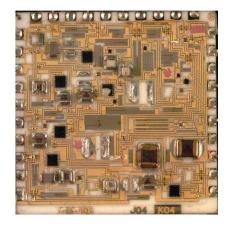
The In-Sn and Bi-Sn alloys were evaluated for solder joints on organic laminate, printed circuit board (PCB) test vehicles of 1990's technologies.



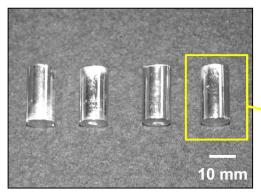


The 97In-3Ag and 58In-42Sn were suitable replacements for Pb- and Cd-containing solders used on hybrid microcircuit (HMC) products.

| Established alloys | Replacement alloys |
|--------------------|--------------------|
| In-Pb-Ag → ■ | → In-Ag |
| • In-Sn-Pb-Cd = | → → In-Sn |



 Modeling and test programs examined both time-independent and time-dependent mechanical properties of In-Ag and In-Sn.



Test specimens

Upper platen

Temperature control

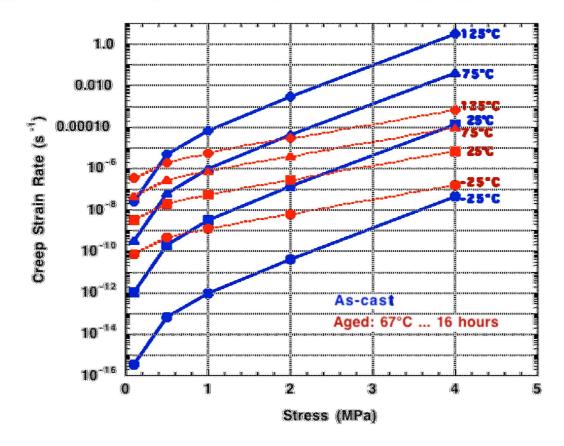
Jines Lower platen

Stress-strain, In-Ag (25°C)

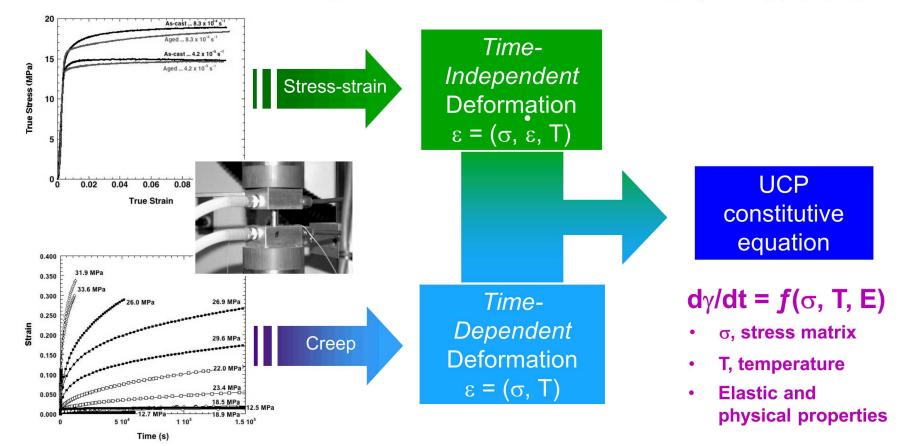
P. Vianco, et al., J. Mater Sci. (2006)

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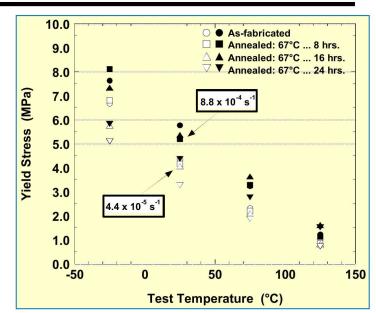
- As the solidus temperature decreases, mechanical properties can change significantly at seemingly innocuous temperatures.
 - The eutectic 97In-3Ag alloy ($T_s = T_l = 143^{\circ}$ C) experiences orders-of-magnitude changes to creep rate after aging at 67°C for 16 hours.

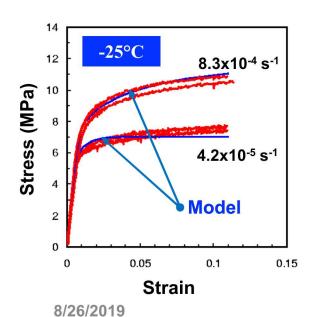


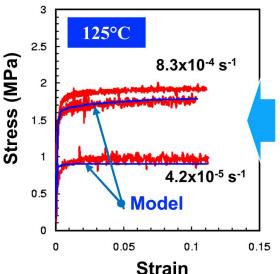
- The computational modeling approach was used, which was based upon the unified creep-plasticity (UCP) equation.
 - Combine time-independent and time-dependent deformation behaviors into a single UCP constitutive equation; $d\gamma/dt = f(\sigma, T, E)$.

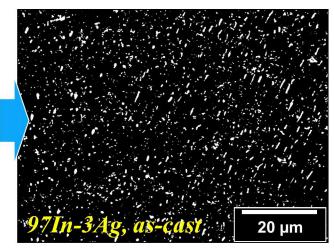


- In-Ag solder: The time-independent deformation curves were also used to validate the UCP equation.
 - The stress-strain curves provided a first-level validation of the model.
 - The microstructure/mechanical properties relationship is not always well-understood for these solders.





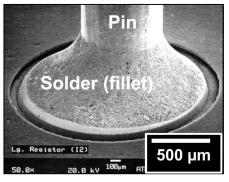


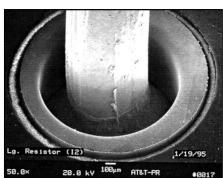


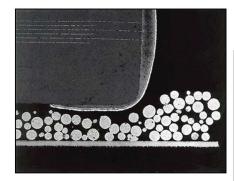
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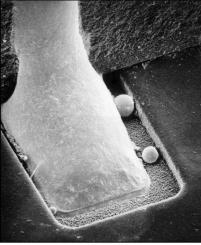
Solderability controls the final joint geometry (fillet size, voids, etc.), which in turn, affects long-term reliability.

58Bi-42Sn



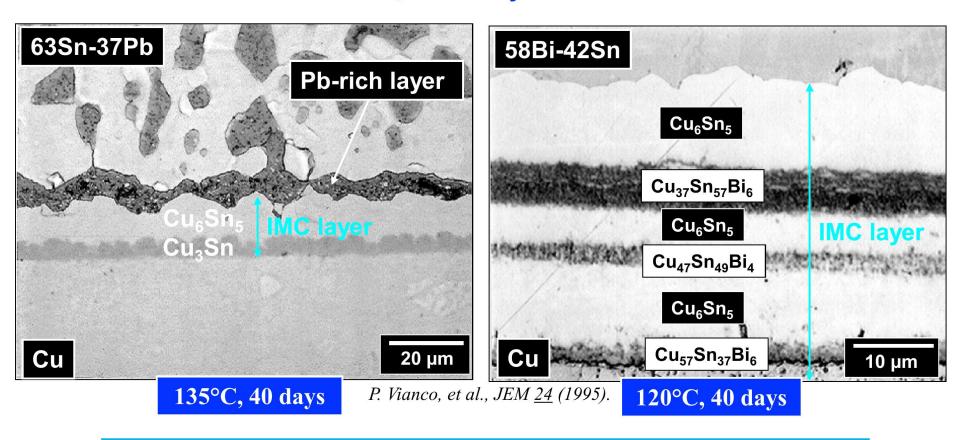






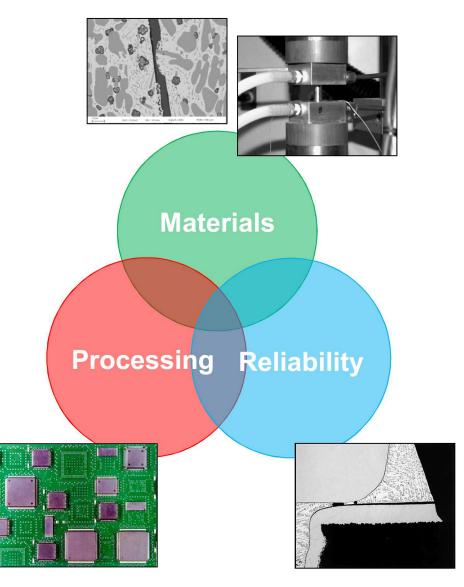
- In this instance, the flux did not activate at the low soldering process temperature – 160°C.
- The adoption of the Sn-Ag-Cu alloys further curtailed the impetus for suppliers to develop low-temperature fluxes.

- The interface reactions were documented for the Sn-Bi alloy on Cu.
 - Elements in the solder, which are rejected by the interface reaction, form a layered microstructure.

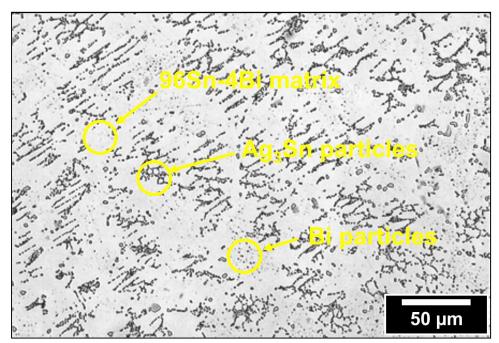


Layered interfaces create paths of easy crack propagation.

- Materials
 - Alloy microstructure
 - Mechanical performance
- Processing
 - Solderability performance
 - Pb-contamination effects
- Reliability
 - Interface reactions
 - Solder joint fatigue
 - Pb-contamination effects
- Summary



The as-cast microstructure is shown below for the 91.84Sn-3.33Ag-4.83Bi (T_s - 212°C) alloy:

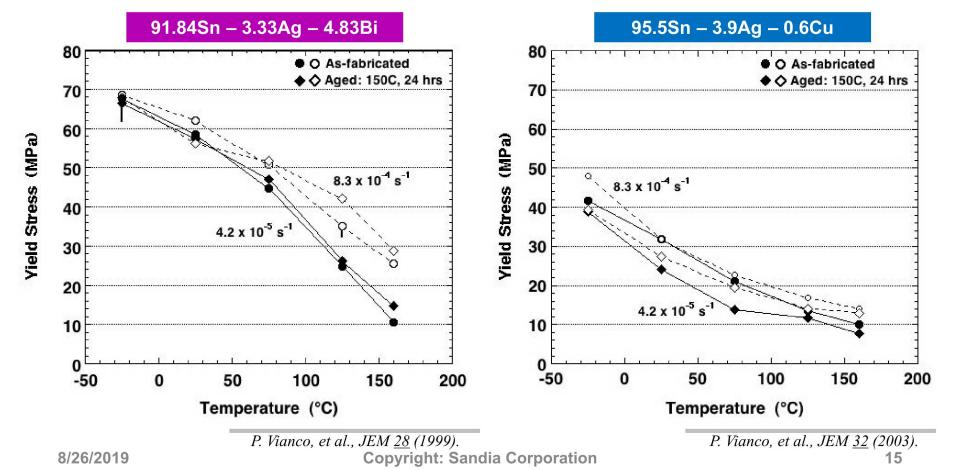


P. Vianco, et al., JEM <u>28</u> (1999).

- This solder was engineered to have the same strengthening mechanisms that are found in high-performance alloys:
 - Precipitation hardening
 - Solution strengthening

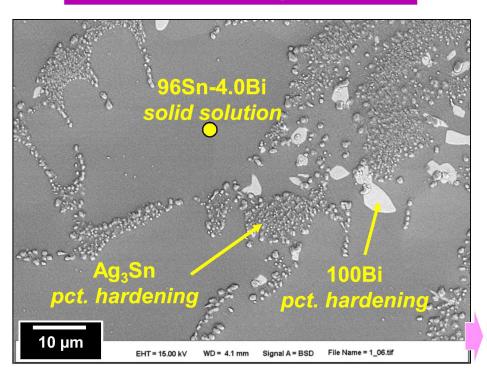
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- The improved strength of Sn-Ag-Bi is evidenced by its yield stress properties when compared to those of the SAC396 alloy.
 - The Sn-Ag-Bi maintains a higher strength over temperature and shows little sensitivity to aging (125°C or 150°C, 24 hours).

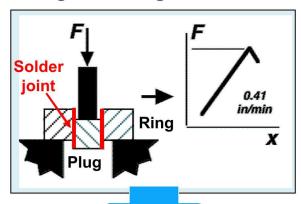


- The solder is tested in joint configurations to include the effects of gap thickness and (area) footprint on mechanical performance.
 - The ring-and-plug shear test provides a method to measure the shear strength of Sn-Ag-Bi solder joints.

91.84Sn - 3.33Ag - 4.83Bi

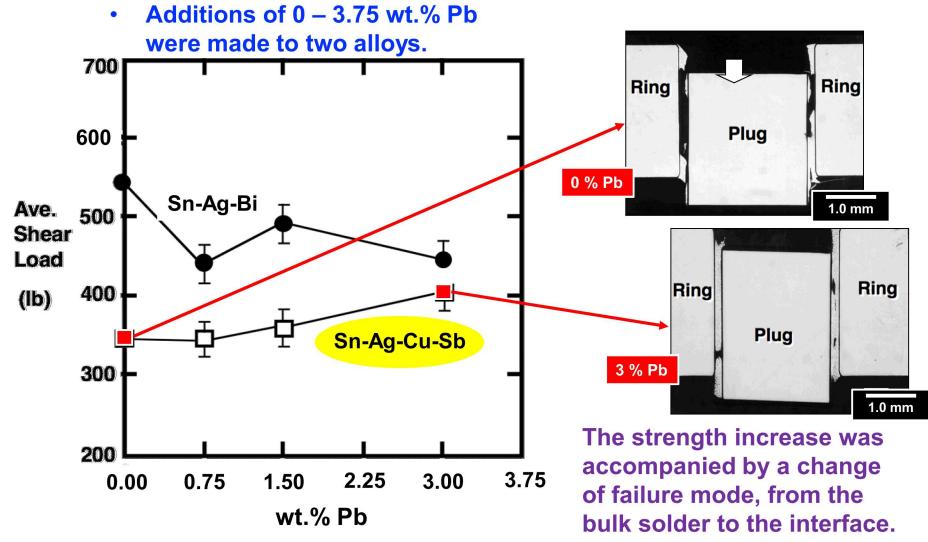


Ring-and-Plug Shear Test

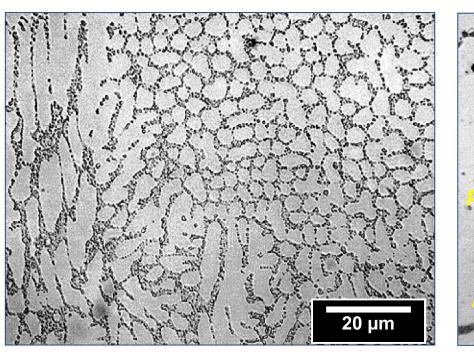


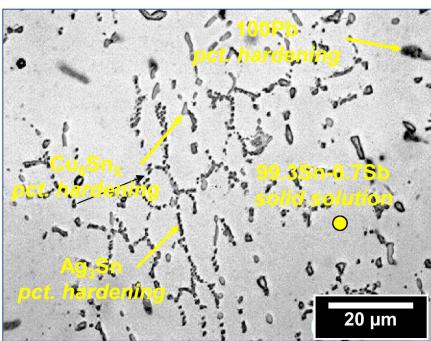
| <u>Solder</u> | Stress (psi) | | |
|---------------|--------------|--|--|
| Sn-Pb | 5840 | | |
| Sn-Ag | 7970 | | |
| Sn-Ag-Bi | 11800 | | |

Alloy additions affect the mechanical properties of the solder.



 Sn-Ag-Cu-Sb: The addition of Pb broke up the Ag₃Sn particle network, thereby enhancing the precipitation hardening effect.

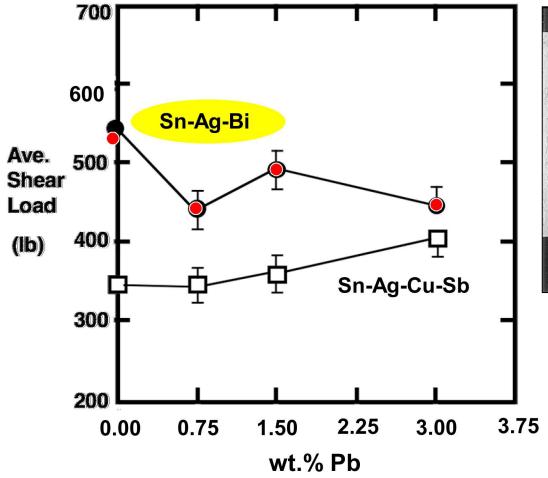


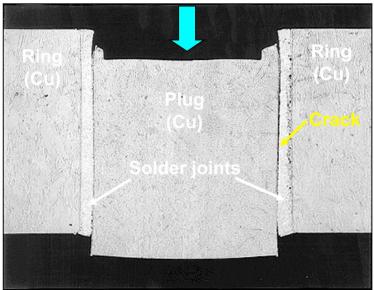


0.00 % Pb

3.00 % Pb

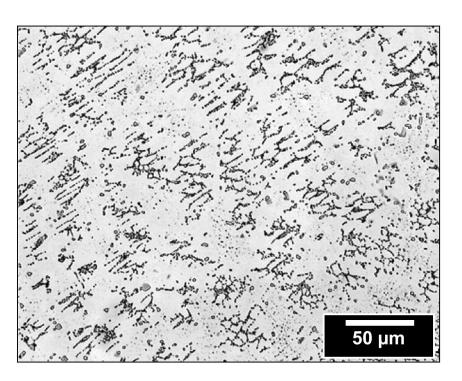
 Sn-Ag-Bi: The fracture path remained along the solder/base material interface for all Pb additions.

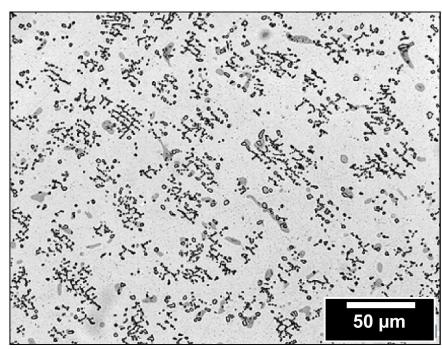




The nominal strength remained greater than the ≈ 400 lb. level above which failure occurs typically at the interface.

Microstructural effect: The Pb additions did not alter the microstructure on the large size scale.



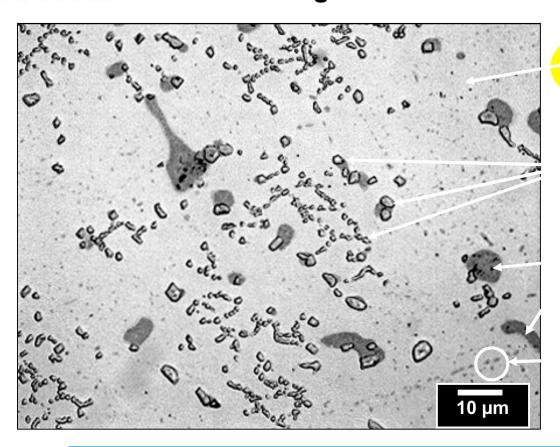


0.00 % Pb

3.00 % Pb

On the other hand ...

 ... The Pb additions altered the small-scale phase distributions within the Sn-Ag-Bi microstructure.



96.5Sn-3.5Bi Solid solution

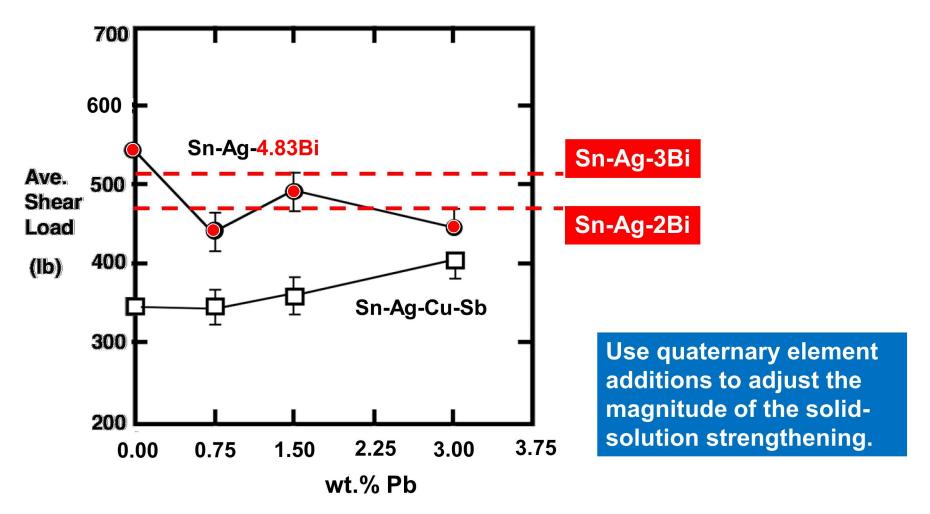
Ag₃Sn

64Pb-33Bi-3Sn

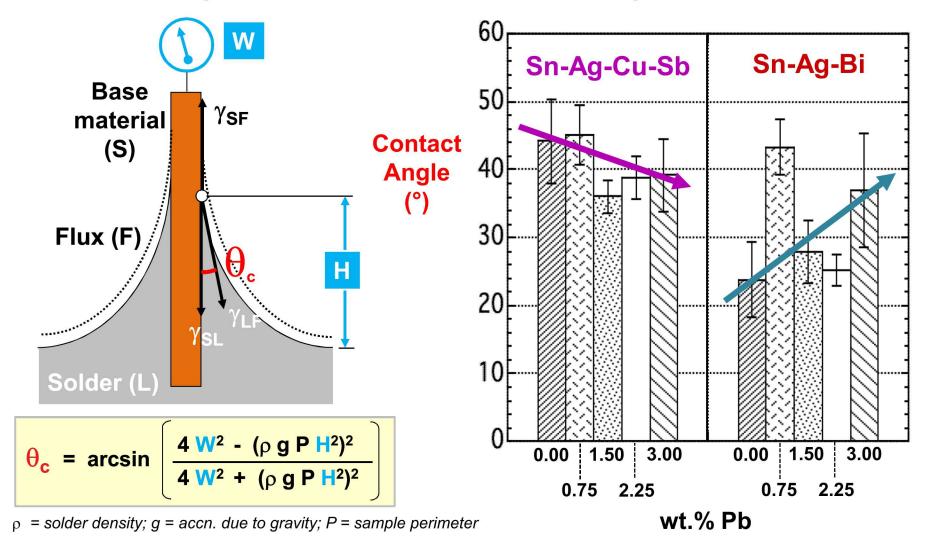
63Sn-24Pb-13Bi

The Pb scavenged Bi from the matrix phase, thus reducing the solid-solution strengthening effect.

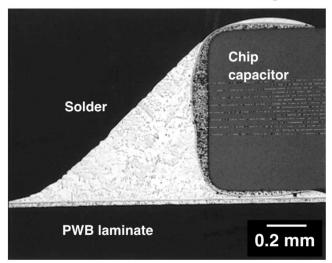
Ring-and-plug shear tests performed on Sn-Ag-XBi
 (X = 2, 3 wt.%) confirmed a similar drop of strength.

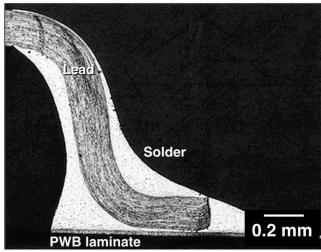


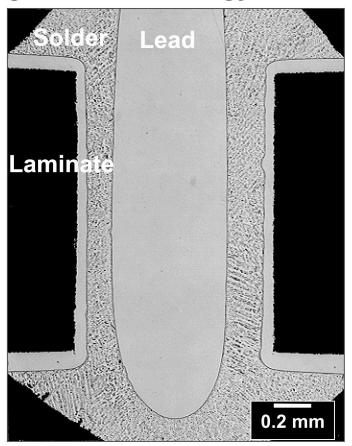
Careful ... alloy additions also affect solderability.



 Overall, the processibility of the Sn-Ag-Bi alloy was observed to be excellent for fine-pitch SMT and through-hole technology.

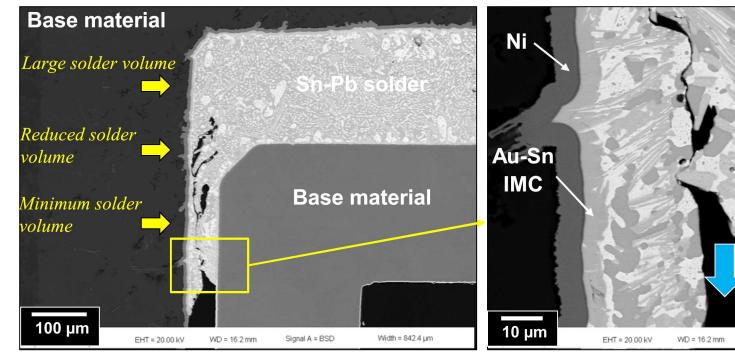


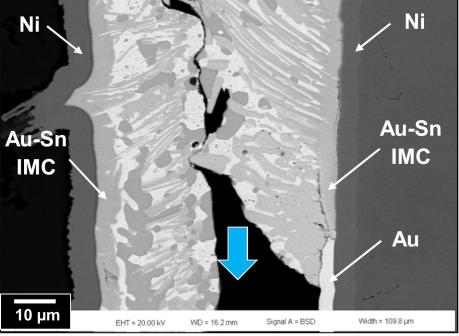




The Sn-Ag-Bi alloy exhibits excellent capillary actions

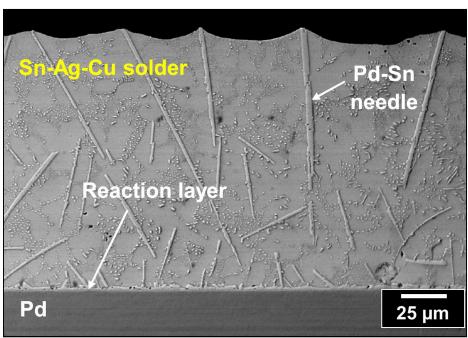
- There is a shortage of data describing the liquid-state interactions between Sn-Ag-Bi solder and new surface finishes (e.g., ENEPIG).
 - Increasing the solidus temperature (T_s) and/or liquidus temperature (T_I) can lead to constitutional solidification.



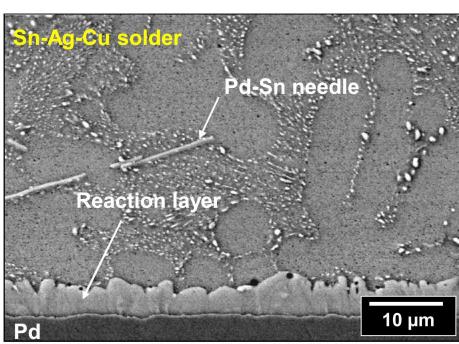


Higher solder strengths amplify the brittle failure of solder.

- Also, base material dissolution has not been documented for the Sn-Ag-Bi alloy. Reliability impacts may include:
 - Changes to the solder's bulk mechanical properties
 - Properties of the interface reaction layer e.g., use of ENEPIG finish



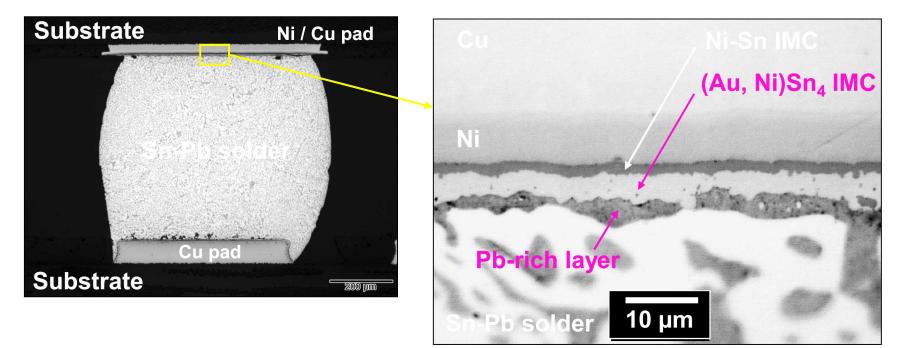
Sn-Ag-Cu, 350°C, 5s



Sn-Ag-Cu: 290°C, 5s

A database must be developed of these fundamental properties.

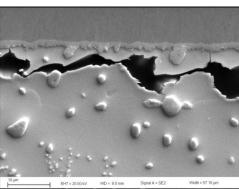
- Solid-state interactions have not been fully vetted between Sn-Ag-Bi solder and alternative surface finishes.
 - Long-term reliability effects: "return-of-Au" phenomenon.

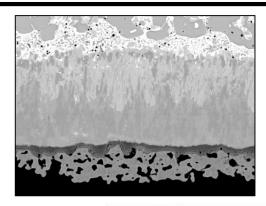


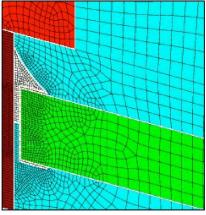
The (Au, Ni)Sn₄ IMC layer and Pb-rich layer negatively impact shock and thermal cycling reliabilities, respectively.

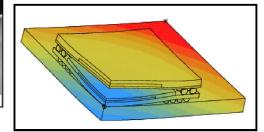
- Reliability
- Static properties
 - Interface reactions (solid-state)
 - Monotonic strength
- Cyclic (fatigue) properties
 - Empirical studies
 - Computational modeling



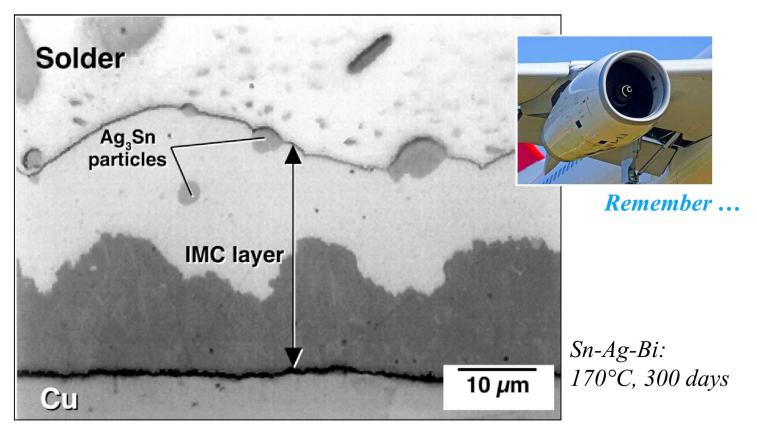




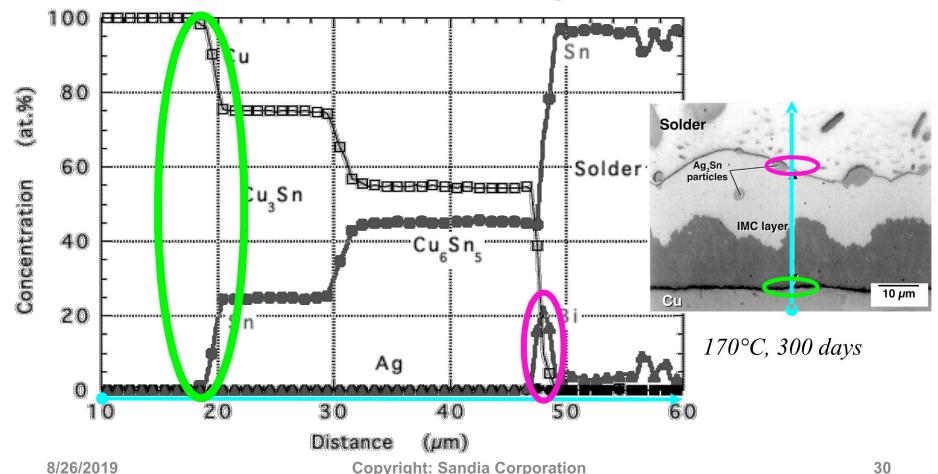




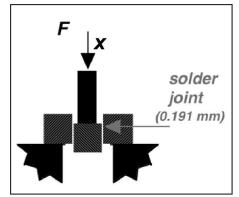
- After solidification, solid-state reactions continue to take place at the solder / base material interface:
 - Interfaces are non-equilibrium structures
 - Solid-state diffusion readily occurs in the solder.



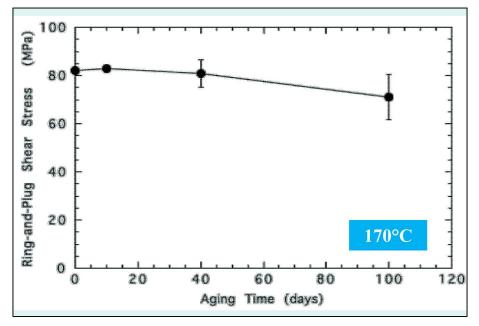
- The Sn-Ag-Bi / Cu interface microstructure was documented following solid-state aging.
 - Limited Bi accumulation was observed along the IMC/solder interface; none was observed along the IMC/Cu interface.

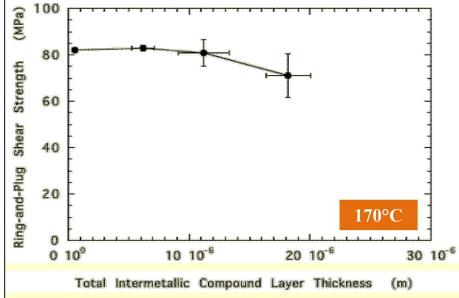


- ◆ The effect of solid-state IMC layer growth on joint strength was examined for Sn-Ag-Bi/Cu couples using the ring-and-plug shear test.
 - Isothermal aging did not cause a significant shear strength loss to the solder joints.
 - Moreover, the development of the IMC layer caused a small strength loss, but only when the IMC thickness exceeded ≈10 µm.

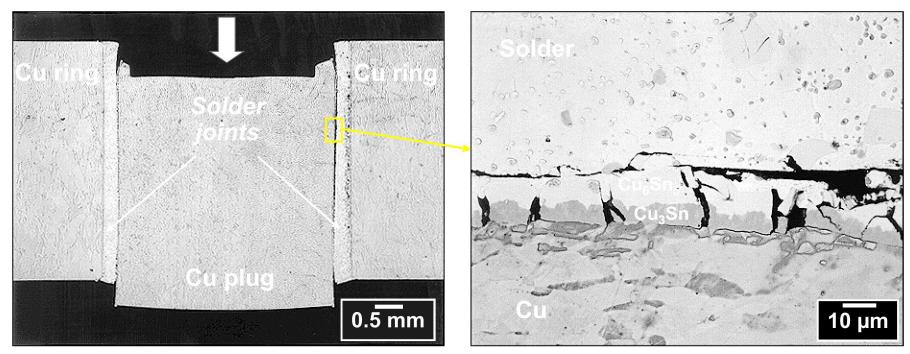


Ring-and-plug shear test



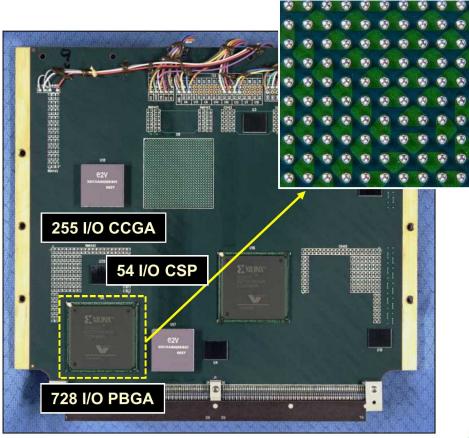


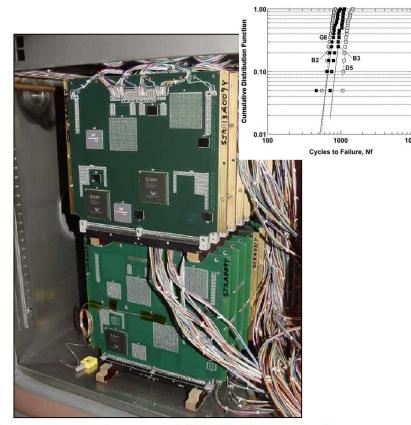
- The strength study included a failure mode analysis.
 - The crack path followed the IMC/solder interface, which is often the case at this displacement rate.
 - However, the concurrent presence of cracks in the IMC layer implies that Bi at the IMC/solder interface did not, itself, reduce solder joint strength.



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◆ Temperature cycling data per IPC 9701 data are being developed at the present time for assessing thermal mechanical fatigue (TMF) of Sn-Ag-Bi and Sn-Ag-Bi-X-Y-Z solder interconnections.





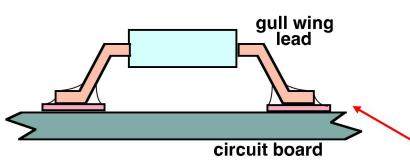
Event detection and Weibull statistics

- The most extensive database developed for the Sn-Ag-Bi solder has come from the Honeywell-Celestica study.
 - "Reliability Screening of Lower Melting Point Pb-free Alloys Containing Bi," J. Juarez, et al, APEX 2014
- The test vehicle included a variety of present-day packaging technologies as well as ENIG, ENEPIG, and OSP surface finishes.

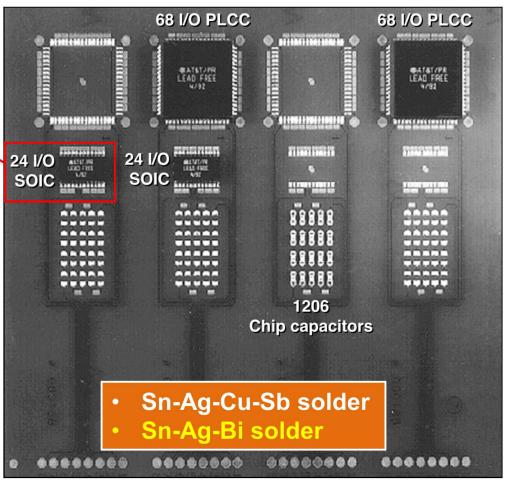
| I/O Count/ Package | Dimensions | Pitch | Lead Finish | Ball Composition |
|-----------------------|------------------|---------|--------------------|---------------------|
| 20 /SO | 6.35 X 12.70 mm | 1.27 mm | SnPb and Matte Tin | |
| 40 /SOJ | 10.16 X 25.40 mm | 1.27 mm | SnPb and Matte Tin | |
| 48 /SOP | 5.08 X 15.24 mm | 0.50 mm | SnPb and Matte Tin | |
| 54 /TSSOP | 10.16 X 21.59 mm | 0.64 mm | SnPb and Matte Tin | |
| 84 /PLCC | 29.21 X 29.21 mm | 1.27 mm | SnPb and Matte Tin | |
| 240/ PQFP | 31.75 X 31.75 mm | 0.50 mm | SnPb and Matte Tin | |
| 289 /BGA | 17.15 X 17.15 mm | 1.02 mm | | SnPb and SAC 305 |
| 352 /BGA | 35.56 X 35.56 mm | 1.27 mm | | SnPb and SAC 305 |
| 1156/ BGA | 34.93 X 34.93 | 1.02 mm | | SnPb and SAC 305 |

The Sn-Ag-Bi solder joints completed 3010 temperature cycles of -55°C/125°C without an electrical failure.

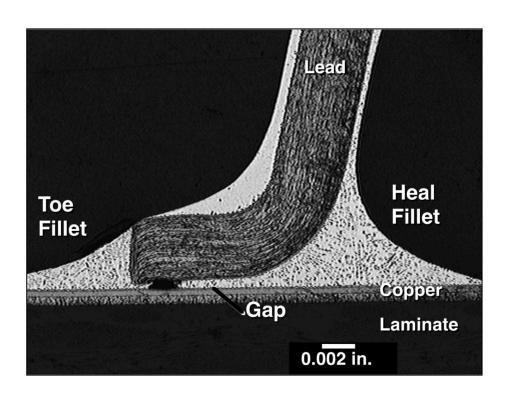
 Insight was provided into the temperature cycling performance of this alloy by means of early, Pb contamination studies.

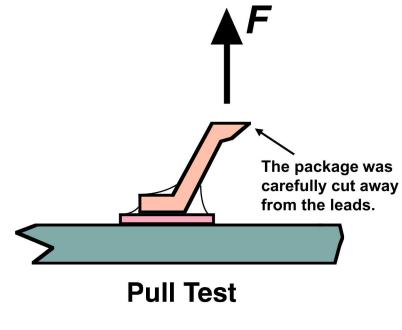


- Temperature cycling:
 - 0°C 100°C
 - 15 min hold times
 - 20°C/min ramp rates
- Measurement points;
 - 0 (as-fabricated), 2608, 5068, and 10,106 cycles



- Visual inspection and metallographic cross sections confirmed the excellent solderability of the test vehicle joints.
- ♦ The molded package was cut from the leads and the latter were then subjected to a pull test. The metric was the maximum force.





Cross-head speed 9 mm/min

The table shows the effect of thermal cycling on maximum force.

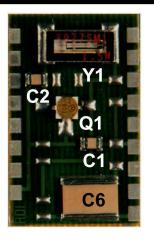
| | Sn-Ag-Cu-Sb | | Sn - Ag - Bi | | | |
|----------------|----------------------|--------------------|--------------------|---------------------|--------------------|--------------------|
| Thermal cycles | Sn-Pb/Sn-Pb (lb) | Sn-Pb/OSP (lb) | Sn/OSP (lb) | Sn-Pb/Sn-Pb (lb) | Sn-Pb/OSP (lb) | Sn/OSP (lb) |
| 0 | 5.42 <u>+</u> 0.32(| 5.47 <u>+</u> 0.53 | 5.81 <u>+</u> 0.59 | ***** | 2.75 <u>+</u> 0.61 | 5.31 <u>+</u> 0.67 |
| 2602 | 4.79 <u>+</u> 0.79 | 5.57 <u>+</u> 0.52 | 4.22 <u>+</u> 0.55 | ***** | ***** | ***** |
| 5068 | 4.77 <u>+</u> 0.82 | 4.71 <u>+</u> 0.38 | 4.05 <u>+</u> 0.99 | ***** | ***** | ***** |
| 10,106 | 4.24 <u>+</u> 0.43 (| 4.91 <u>+</u> 0.68 | 4.56 <u>+</u> 0.67 | ***** | 3.13 <u>+</u> 1.24 | 5.34 <u>+</u> 0.74 |
| | Δ= | -10% | -22% | Δ= | +13% | +1% |

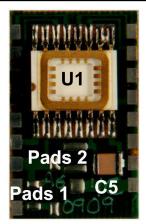
- Pull strength of the Sn-Ag-Cu-Sb is affected by thermal cycling.
- Although the Sn-Ag-Bi pull strengths were decreased by Pb additions, in either this condition or Pb-free, the pull strength is stable against thermal mechanical fatigue (TMF) effects.

- A large-pitch, surface mount test vehicle was used to assess both the processibility and long-term reliability of Pb-free solder joints:
 - 91.84Sn-3.33Ag-4.83Bi
 - 96.5Sn-3.5Ag
 - **63Sn-37Pb** (control)
 - Acceleratated aging environments:

| Cycling | Shock | | |
|--------------------------|----------------------------|--|--|
| (1) Limits: -55°C, 115°C | (1) Limits: -40°C, 115°C | | |
| (2) Ramp: 4°C/min | (2) Ramp: liquid-to-liquid | | |
| (3) Hold time: 30 min. | (3) Hold time: 15 min. | | |
| (4) 300 cycles | (4) 400 cycles | | |
| | | | |

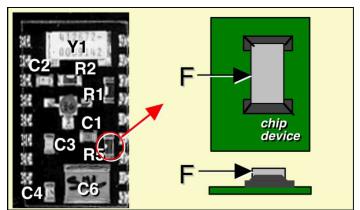
- · Mechanical (shear strength) testing:
 - (1) C1, C2, C3, C4, C5, and C6 were tested
 - (2) R1, R2, R3, R4, and R5 were tested
 - (3) Y1 package was tested.
 - (4) Test speed: 10 mm/min



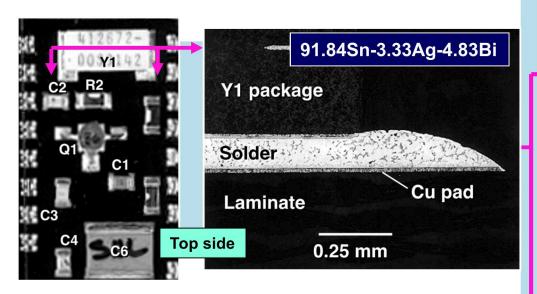


Ni-Pd Finish

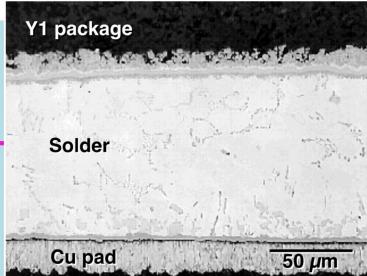
"1 oz." copper 3.8 μ electroless Ni 0.51 μ electroless Pd

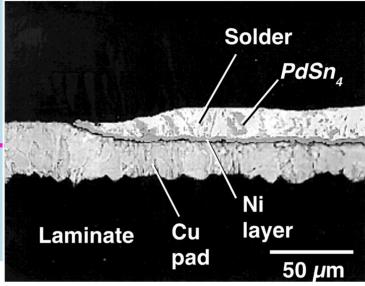


This examination focuses on the Sn-Ag-Bi solder joints:

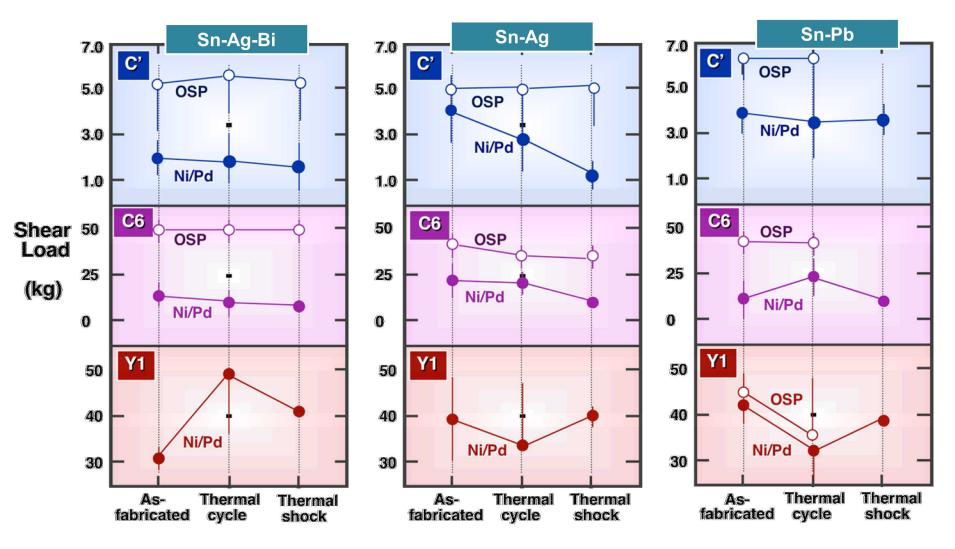


- Observations critical to the use of ENEPIG and ENIG surface finishes:
 - The Pd layer fully was dissolved into the solder, forming PdSn₄ particles.
 - Ni dissolution was reduced with the Sn-Ag-Bi alloy vs. Sn-Ag or Sn-Pb.

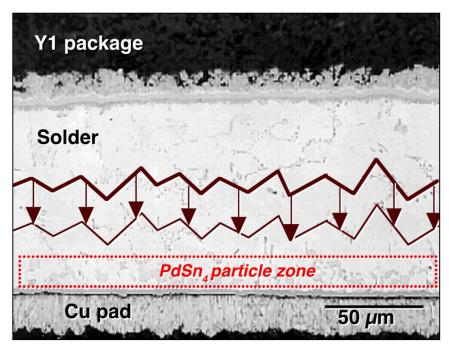




A reduced shear strength was observed with Ni/Pd finish.

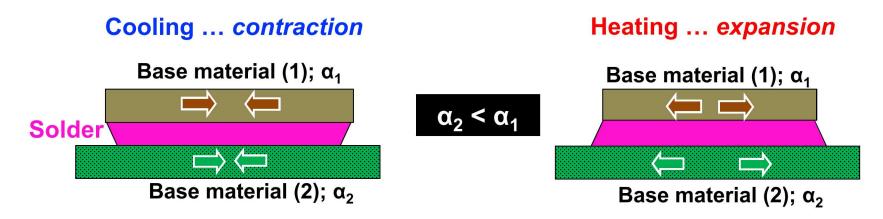


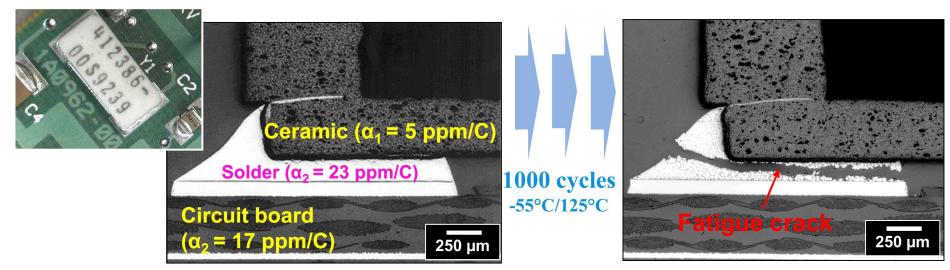
- A scenario was developed to explain the reduced strength of the solder joints made to the Ni/Pd finish.
- The higher intrinsic strength of the Sn-Ag-Bi alloy, and to a lesser extent, the Sn-Ag solder, forced the crack path closer to the solder/Cu pad interface.
- The concentration of PdSn₄ particles near that interface locally reduced solder ductility.



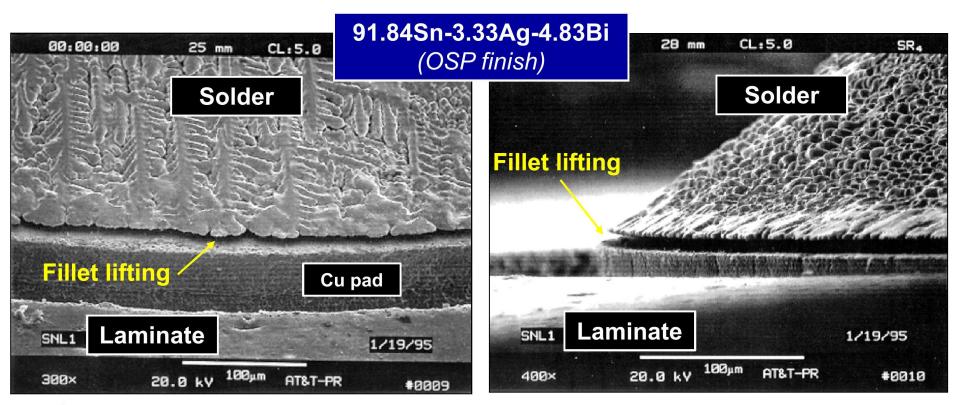
The higher strength of the Sn-Ag-Bi solder caused the joints to have an increased sensitivity to small microstructure changes, including a loss of ductility generated by surface finishes.

 Failure mode analysis has only recently begun development for the thermal mechanical fatigue (TMF) failure of Sn-Ag-Bi solder joints.



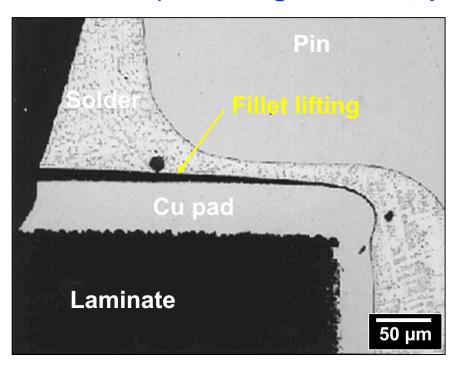


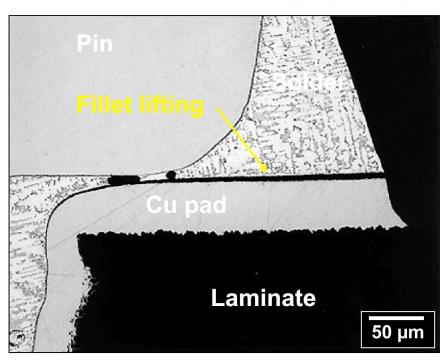
- Fillet lifting was pronounced in the Sn-Ag-Bi through-hole joints.
 - This phenomenon is observed with other solders, but not with the same prevalence.



Fillet lifting is very likely to appear in current through-hole joints.

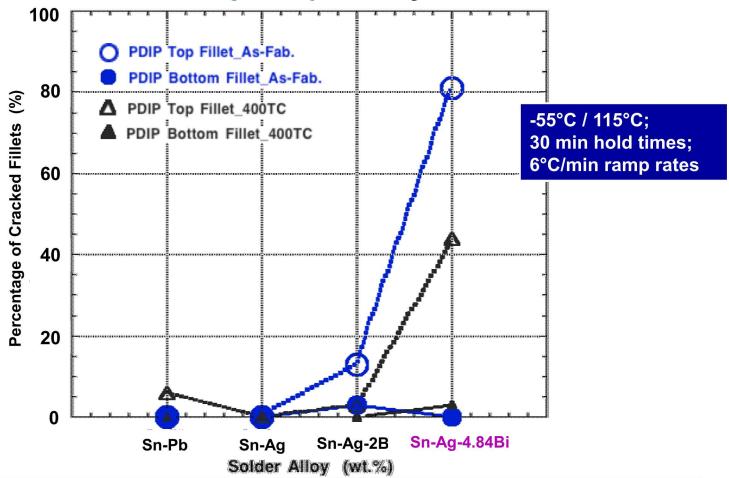
- Fillet lifting was characterized for a variety of joint geometries.
 - Example: Sn-Ag-Bi solder; plastic, dual in-line package (PDIP).





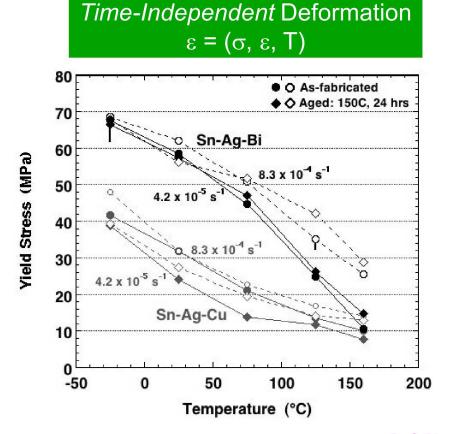
- Fillet lifting was observed on the component side.
- Fillet lifting was not observed on the bottom side.
- Cracks progressed around the knee, and arrested, there.
- Damage to the circuit board (Cu pad) was absent.

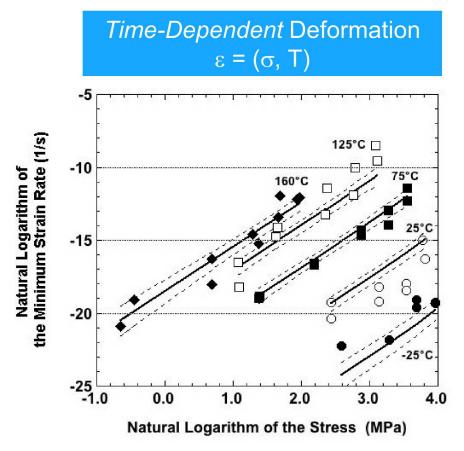
Fillet lifting did not increase with temperature cycling, which reduced the reliability risk posed by its occurrence.



Anticipate fillet lifting on jumper wires and connector pins.

 Both time-independent (stress-strain) and time-dependent (creep) data are being compiled to build the UCP computational model.



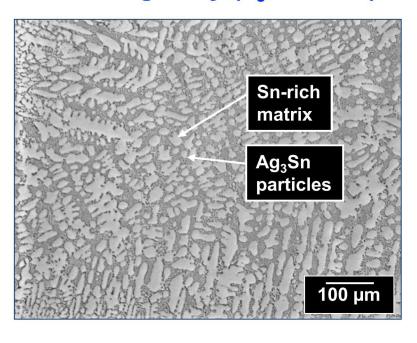


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 $d\gamma/dt = f(\sigma, T, E)$ σ , stress matrix; T, temperature; elastic and physical properties

Objective: "Develop a Pb-free solder having solidus and liquidus temperatures close to the 183°C eutectic temperature of 63Sn-37Pb."

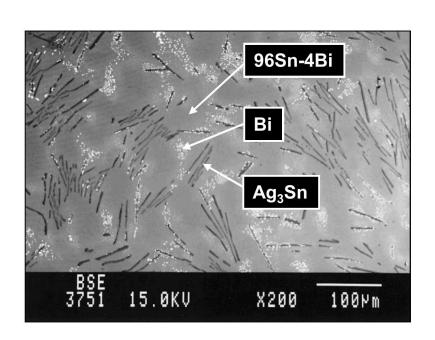
The starting point was the eutectic 96.5Sn-3.5Ag alloy (T_e = 221°C).

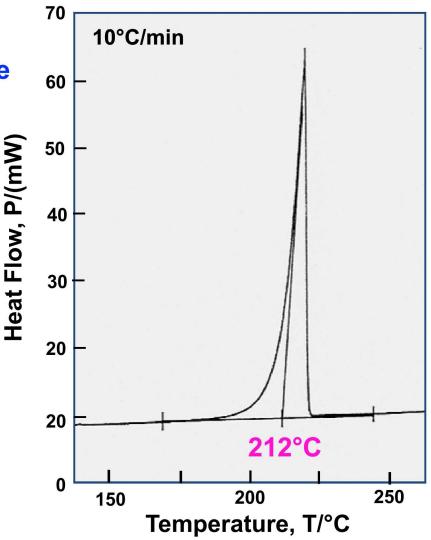


120 10°C/min 100 Heat Flow, P/(mW) 80 60 40 20 221°C 250 200 150 Temperature, T/°C

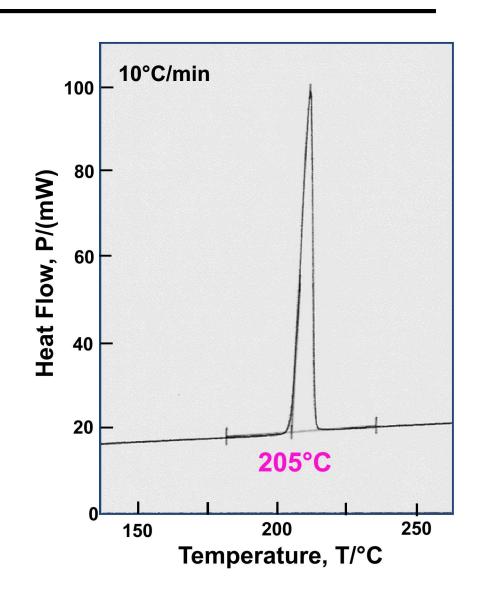
P. Vianco, et al., Mater. Trans of JIM (2004)

An extensive development effort led to the 91.84Sn-3.33Ag-4.83Bi alloy having a solidus temperature of 212°C (△H = 55 J/g).

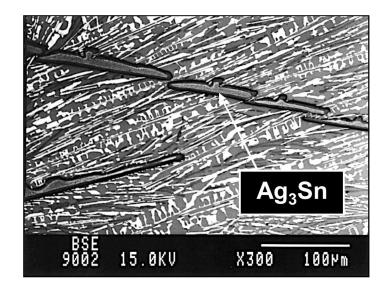


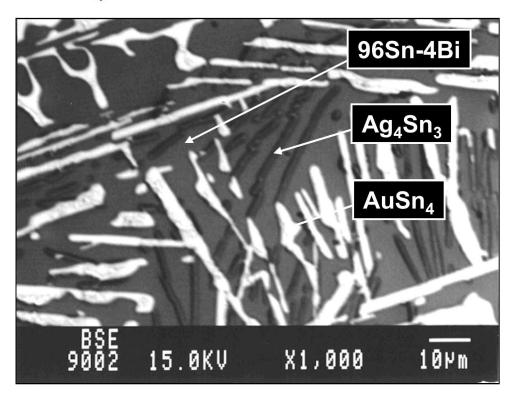


- Two ternary alloys were developed that confirmed the effectiveness of gold (Au) as a melting point depressant.
- The 86.4Sn-5.1Ag-8.5Au was developed from this precept:
 - 95% confidence intervals (mass%) were: Sn, 1.5;
 Ag, 0.33; and Au, 0.06
 - $T_s = 205$ °C; $\triangle H = 55 \text{ J/g}$
- The very sharp peak implies that: T_1 T_s is less than 5°C.

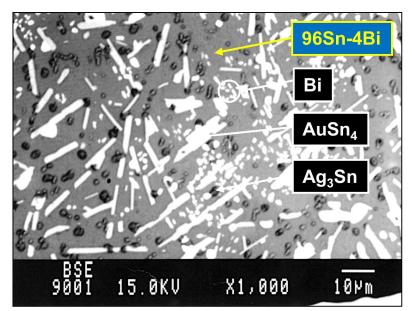


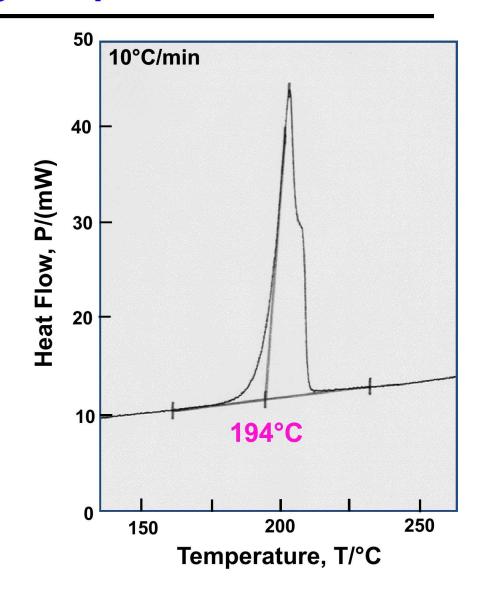
- The 86.4Sn-5.1Ag-8.5Au microstructure was comprised of a solid-solution (matrix) phase, 96Sn-4Bi, and three particle phases:
 - Ag₃Sn
 - Ag₄Sn₃
 - AuSn₄



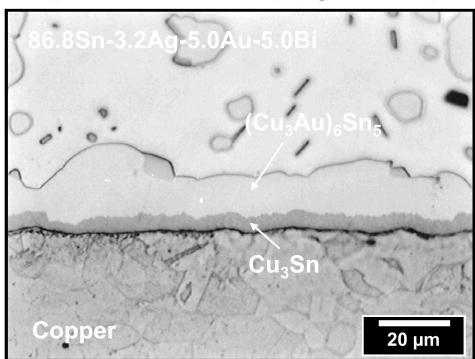


- The 86.8Sn-3.2Ag-5.0Au-5.0Bi exhibited a shoulder that is indicative of a liquidus point of ≈ 204°C.
 - $T_s = 194$ °C; $\Delta H = 53 \text{ J/g}$
 - Besides the particle phase, the matrix phase was a solid solution: 96Sn-4Bi.





◆ An extensive analysis was performed on the 86.8Sn-3.2Ag-5.0Au-5.0Bi alloy (T_s = 194°C).



Aged: 170°C, 100 days

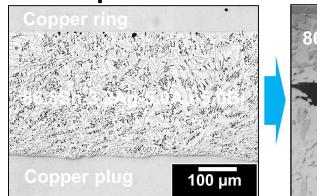
- The complexity of the solder composition did not alter intermetallic compound (IMC) layer development along the Sn-Ag-Au-Bi/Cu interface vis-à-vis other high-Sn solders.
 - The rate kinetics were similar to the Sn-Ag, 100Sn, etc. solders.

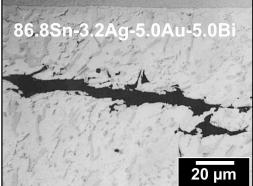
Ring-and-plug mechanical testing was performed using the 86.8Sn-3.2Ag-5.0Au-5.0Bi alloy (T_s = 194°C).

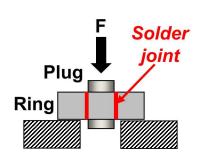
| Solder alloy (mass%) | Ring-in-plug shear strength | | |
|---|------------------------------|--------------------------------------|---|
| 87.5Sn-5.0Bi-7.5Au 86.8Sn-3.2Ag-5.0Bi-5.0Au* | 80 ± 2 (MPa) 84 ± 2 (MPa) | 11,600 ± 300 psi 12,200 ± 300 psi | _ |
| 96.5Sn-3.5Ag | 55 ± 1 (MPa) | 8,000 ± 100 psi | |
| 60Sn-40Pb | 40 ± 2 (MPa) | 5,800 ± 300 psi | |
| 91.84Sn-3.33Ag-4.83Bi | 80 ± 10 (MPa) | 11,600 ± 300 psi | |

*The ring-and-plug shear strength of the Sn-Ag-Bi-Au alloy remains as the highest value recorded of any solder alloy.

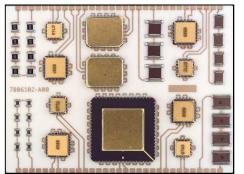
The fracture path remained in the solder, not at the interface.



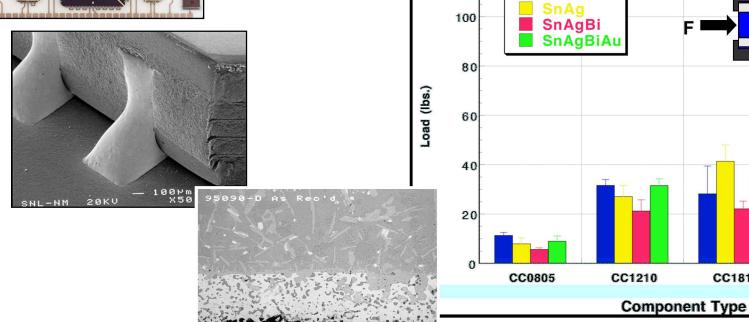




Hybrid microcircuit (HMC) test vehicles were made with this solder, expecting reduced scavenging of Au- and Ag-based thick films.



The shear strength of the chip capacitor solder joints did not reflect the ring-and-plug (Cu) shear strengths because failure occurred in the capacitor structure.

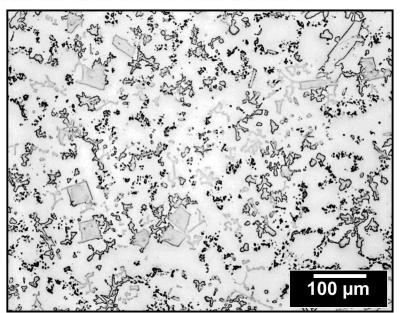


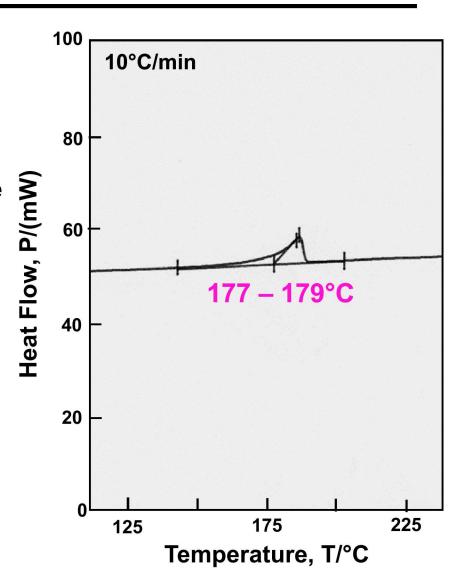
CC1825

CC1810

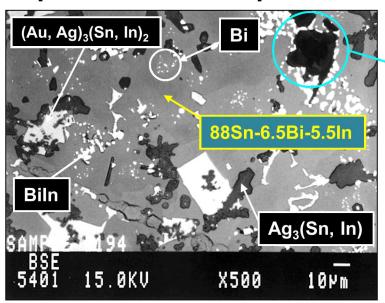
♦ 66Sn-5.0Ag-10Bi-5Au-10In-4.0Cu had a solidus temperature that was in the range of 177-179°C and △H = 31 J/g.

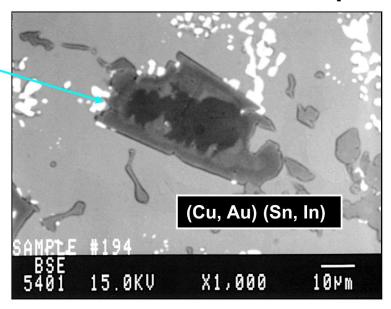
Although complicated, the particle phases were uniformly distributed within the microstructure.





The 66Sn-5.0Ag-10Bi-5Au-10ln-4.0Cu microstructure was comprised of several particles and a 88Sn-6.5Bi-5.5ln matrix phase.





Solderability:

"... pretty good"

| Solder alloy (mass%) | Contact angle (°) | Solder-flux interfacial tension (dynes/cm) |
|-------------------------------------|-------------------|--|
| 66Sn-5.0Ag-10Bi-5.0Au 10In-4.0Cu | 34.2 <u>+</u> 0.7 | 418 <u>+</u> 9 |
| 96.5Sn-3.5Ag | 36 <u>+</u> 3 | 460 <u>+</u> 30 |
| 95.5Sn3.9Ag-0.6Cu | 40 <u>+</u> 5 | 500<u>+</u>40 250°C, |
| 91.84Sn-3.33Ag-4.83Bi | 31 <u>+</u> 5 | 420±30 RMA flux |

Summary

- Low and medium melting temperature solders were examined with respect to the current segments of the electronics marketplace:
 - High volume, consumer electronic product
 - Low-to-medium volume, medium reliability products
 - Low volume, high-reliability aerospace and defense products
- The traditional, low melting temperature alloys ...
 - 52In-42Sn,
 - 58Bi-42Sn, and
 - 97In-3Ag

... are not supported by the supply chain to implement into any of the three marketplaces.

Summary

- Current medium meltingtemperature solders are based upon the 91.84Sn-3.33Ag-4.83Bi ternary composition.
 - An extensive database exists of the physical and mechanical properties of the material.
 - Semi-quantitative, thermal cycling studies were performed on older technologies (e.g., peripheral leaded packages).
 - "High-fidelity", temperature cycling reliability data (e.g., IPC-9701) are just now being accumulated for the Sn-Ag-Bi alloy.
 - Data is limited with respect to long-term interactions between this solder and current PCB surface finish technologies.
- Several novel compositions were developed that had melting temperatures commensurate with the eutectic Sn-Pb alloy.
 - Although highly unlikely to achieve "mainstream status," they showcased metallurgical methods to optimize alloy performance.

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