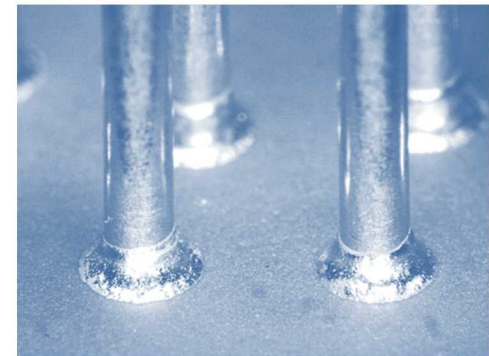


Low Temperature Solders – *Déjà vu*

Paul T. Vianco, Ph.D.

Sandia National Laboratories*
Albuquerque, NM 87185

Contact: ptvianc@sandia.gov

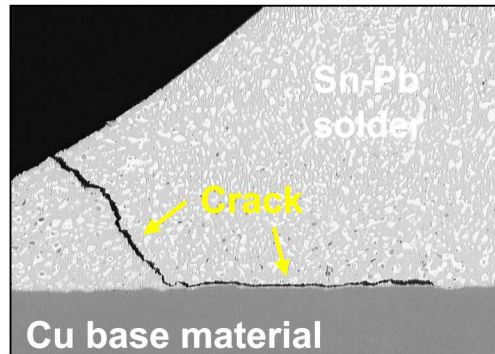


*Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

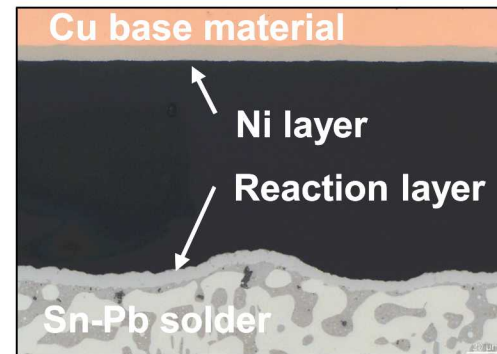


Mechanical Metallurgy

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



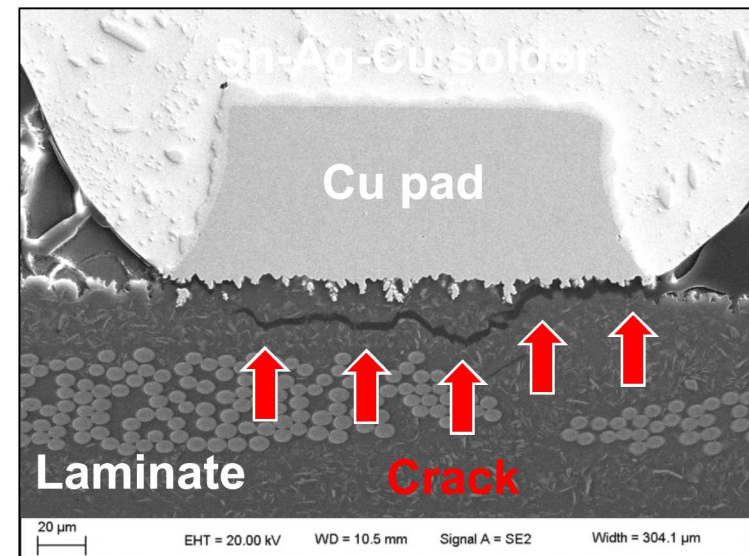
Solder (bulk) failure



Interface failure

- ◆ However, **high strength solders** can “push” the failure into printed circuit board (PCB) or component structures.

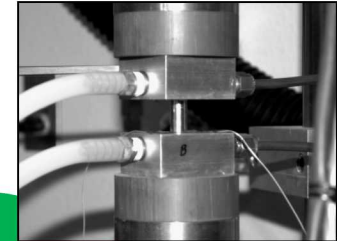
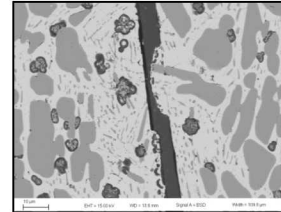
- As the strength of the solder increases, so does the risk of this “collateral damage.”



Current Low Temperature Solders – Sn-Ag-Bi

◆ Materials

- Alloy microstructure
- Mechanical performance



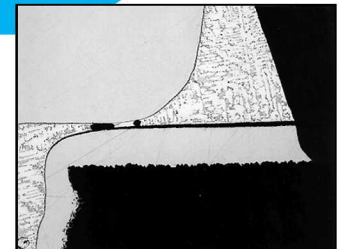
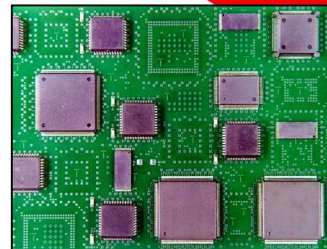
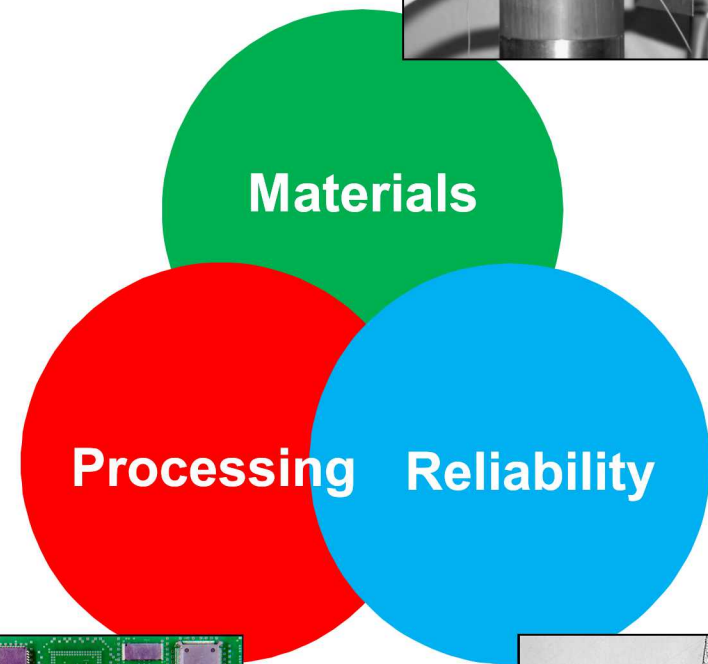
◆ Processing

- Solderability performance

◆ Reliability

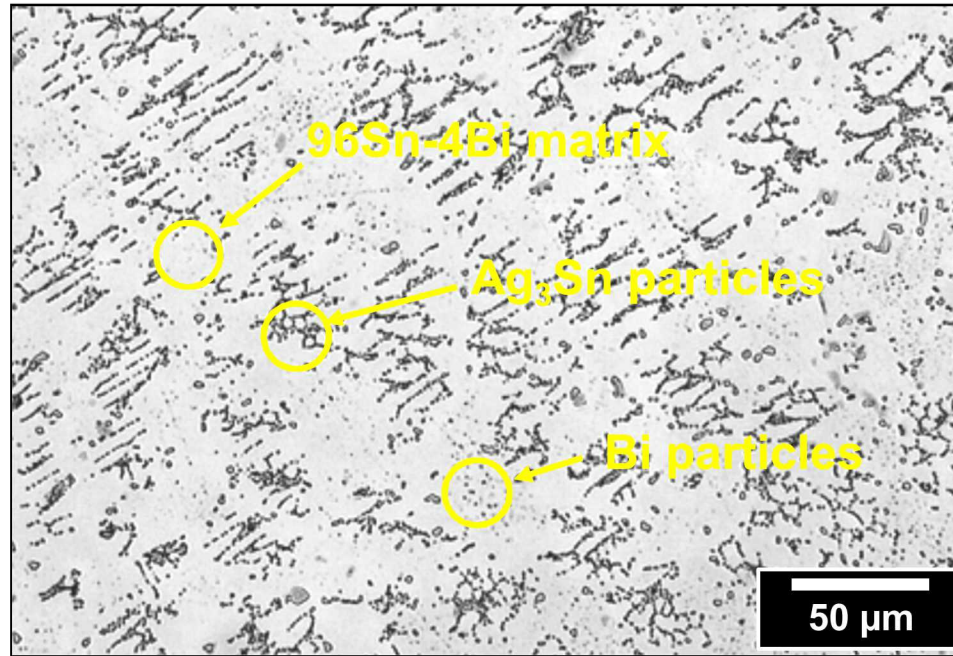
- Interface reactions
- Solder joint fatigue
- *Pb-contamination effects*

◆ Summary



Current Low Temperature Solders – Sn-Ag-Bi

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

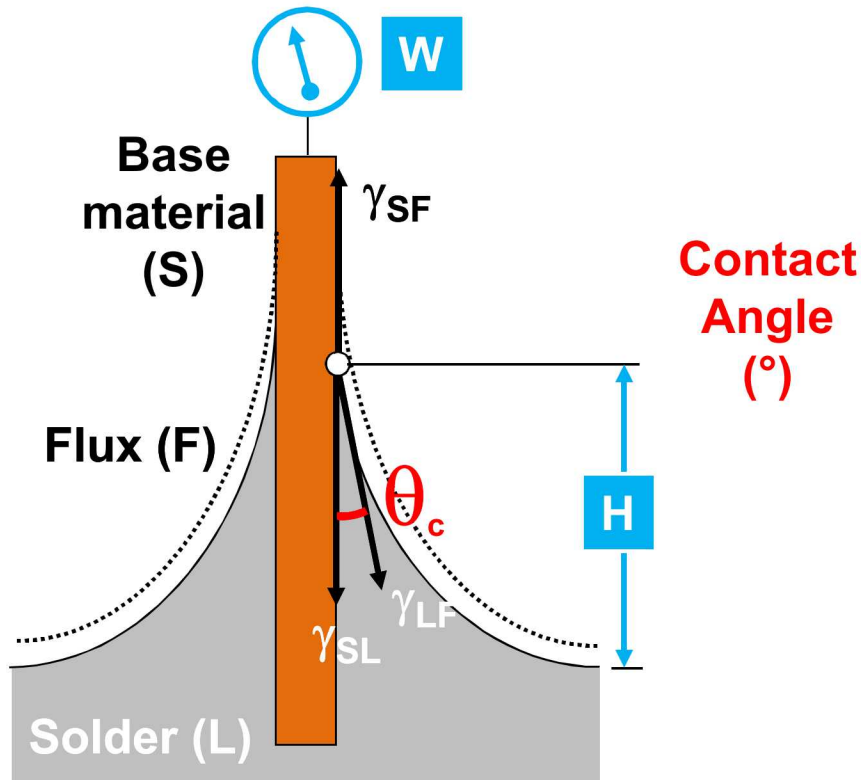


*P. Vianco, et al.,
JEM 28 (1999).*

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

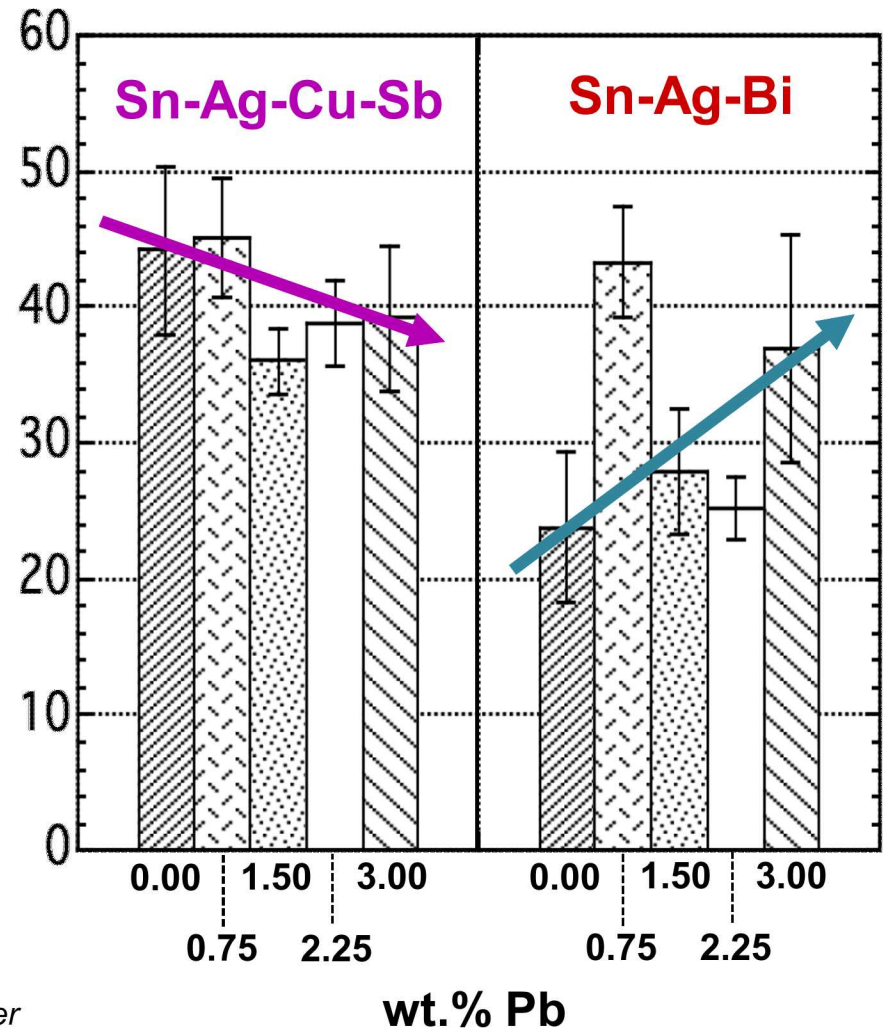
Current Low Temperature Solders – Sn-Ag-Bi

- ◆ Careful ... alloy additions also affect solderability.



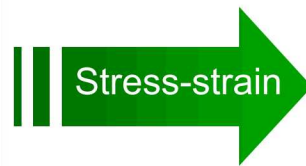
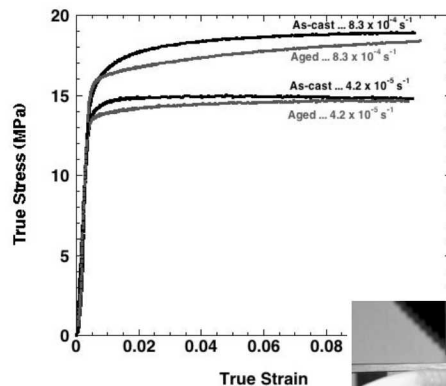
$$\theta_c = \arcsin \left[\frac{4 W^2 - (\rho g P H^2)^2}{4 W^2 + (\rho g P H^2)^2} \right]$$

ρ = solder density; g = accn. due to gravity; P = sample perimeter

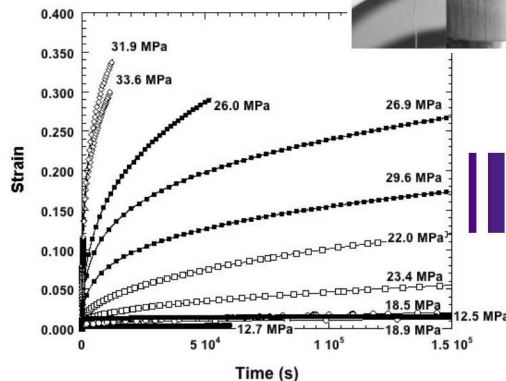


Traditional Low Temperature Solders

- ◆ 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; $d\gamma/dt = f(\sigma, T, E)$.



Time-Independent Deformation
 $\varepsilon = (\sigma, \varepsilon, T)$



Time-Dependent Deformation
 $\varepsilon = (\sigma, T)$

UCP
 constitutive
 equation

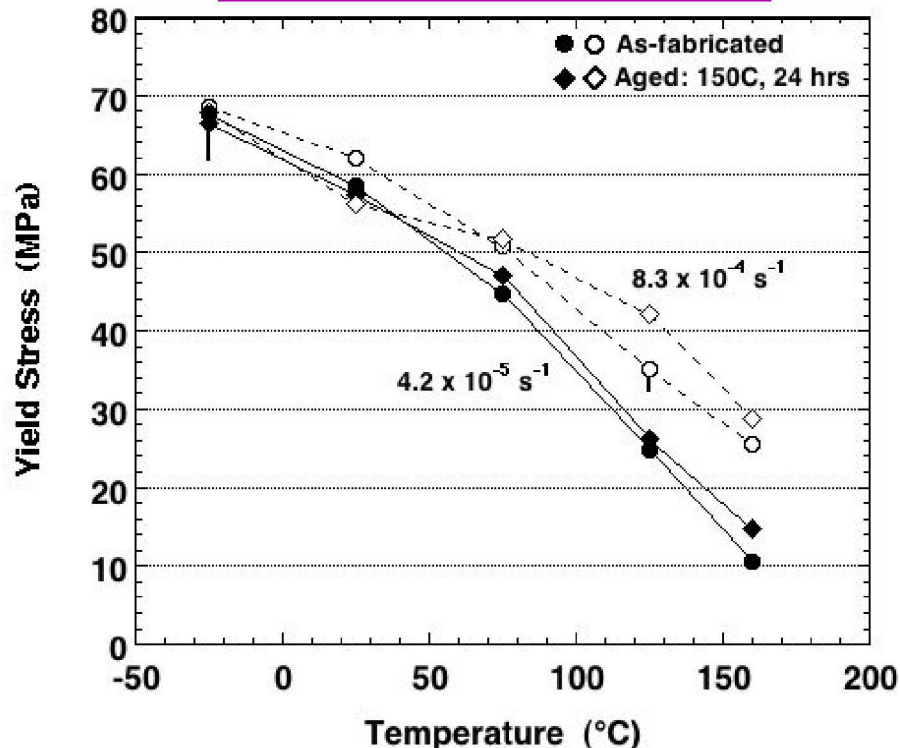
$$d\gamma/dt = f(\sigma, T, E)$$

- σ , stress matrix
- T , temperature
- Elastic and physical properties

Current Low Temperature Solders – Sn-Ag-Bi

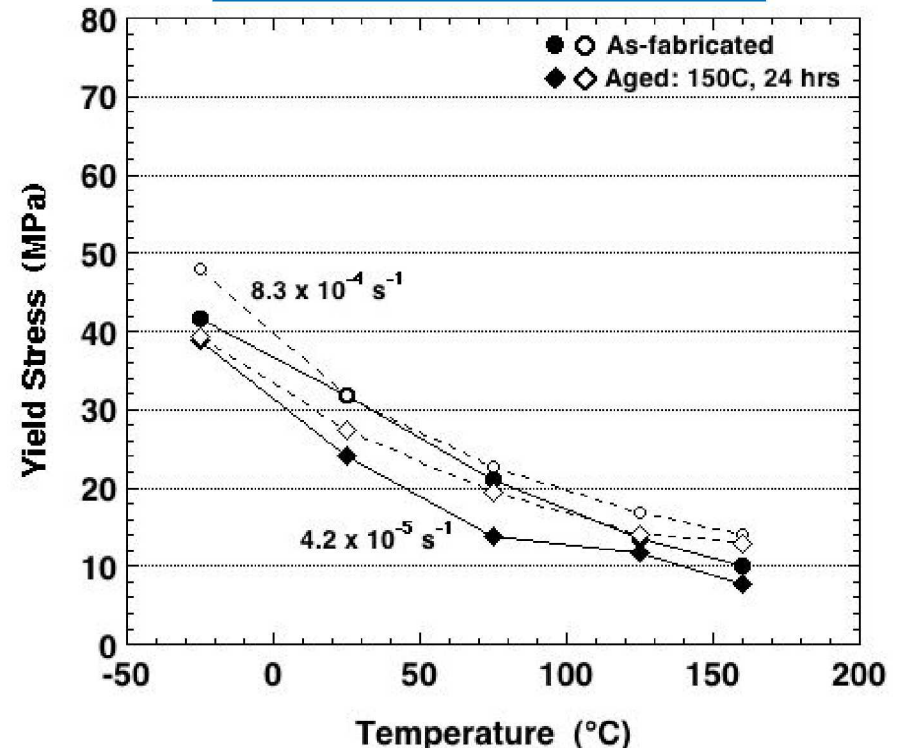
- ◆ The improved strength of Sn-Ag-Bi is evidenced by its yield stress properties when compared to those of the SAC396 alloy.
 - The Sn-Ag-Bi maintains a higher strength over temperature and shows little sensitivity to aging (125°C or 150°C, 24 hours).

91.84Sn – 3.33Ag – 4.83Bi



P. Vianco, et al., JEM 28 (1999).

95.5Sn – 3.9Ag – 0.6Cu

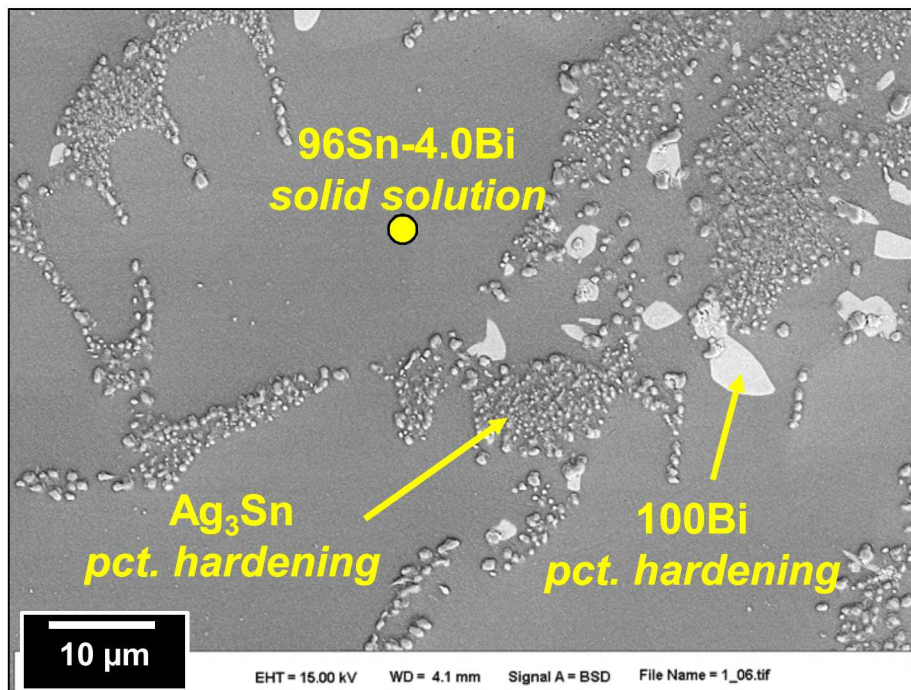


P. Vianco, et al., JEM 32 (2003).

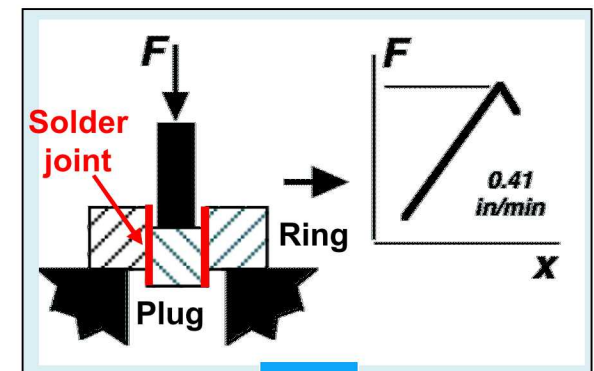
Current Low Temperature Solders – Sn-Ag-Bi

- ◆ 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

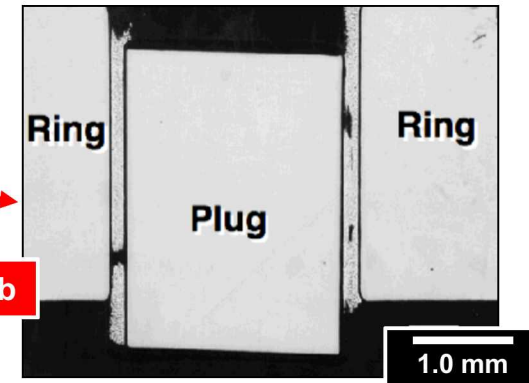
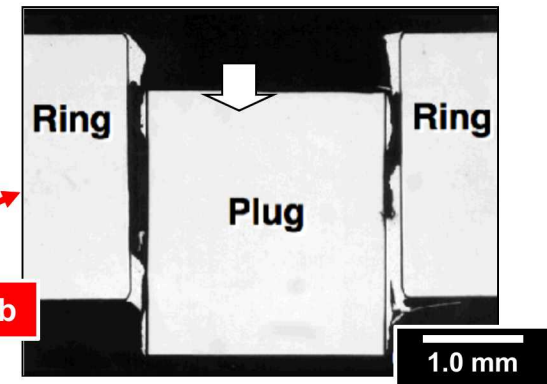
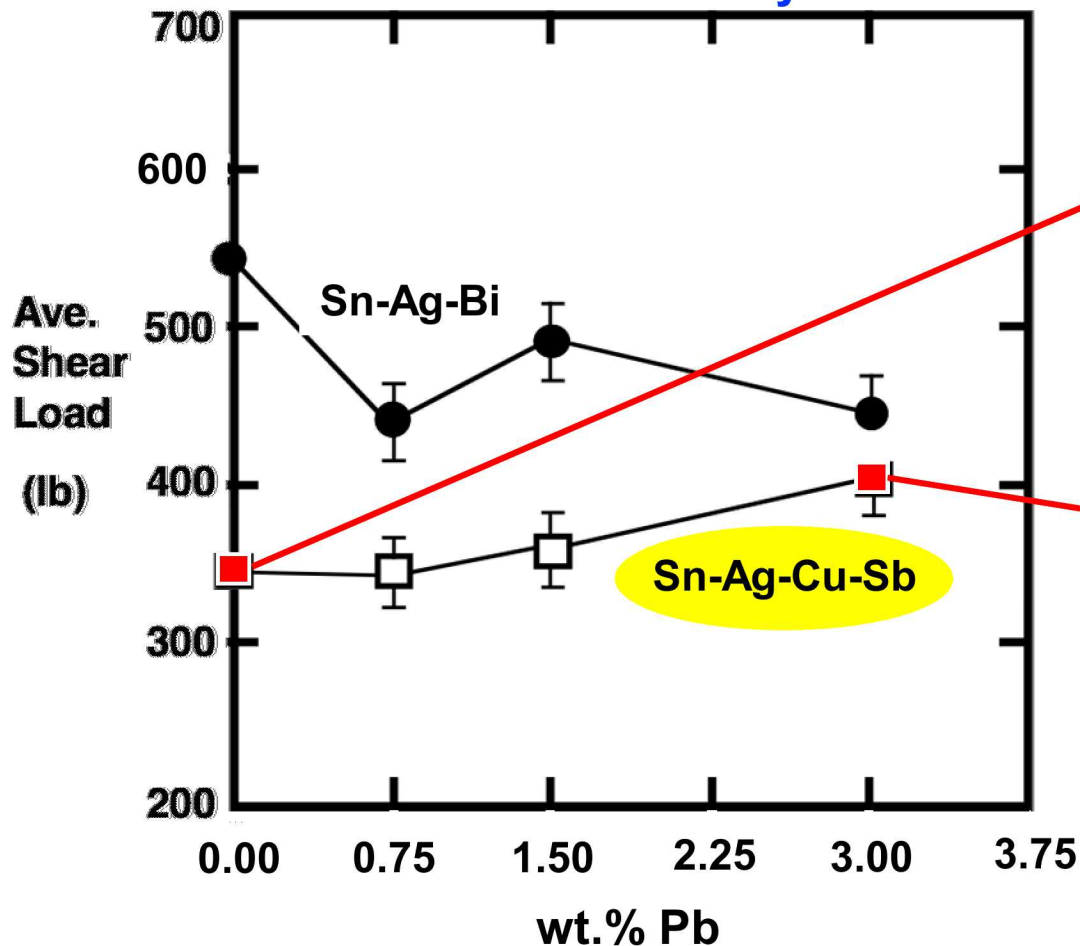


<u>Solder</u>	<u>Stress (psi)</u>
Sn-Pb	5840
Sn-Ag	7970
Sn-Ag-Bi	11800

Current Low Temperature Solders – Sn-Ag-Bi

◆ Alloy additions affect the mechanical properties of the solder.

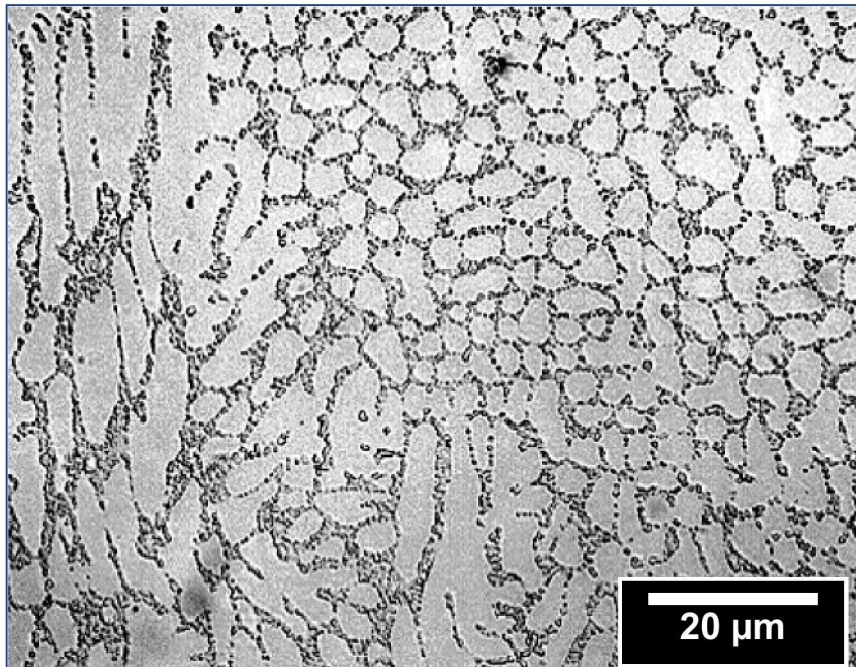
- Additions of 0 – 3.75 wt.% Pb were made to two alloys.



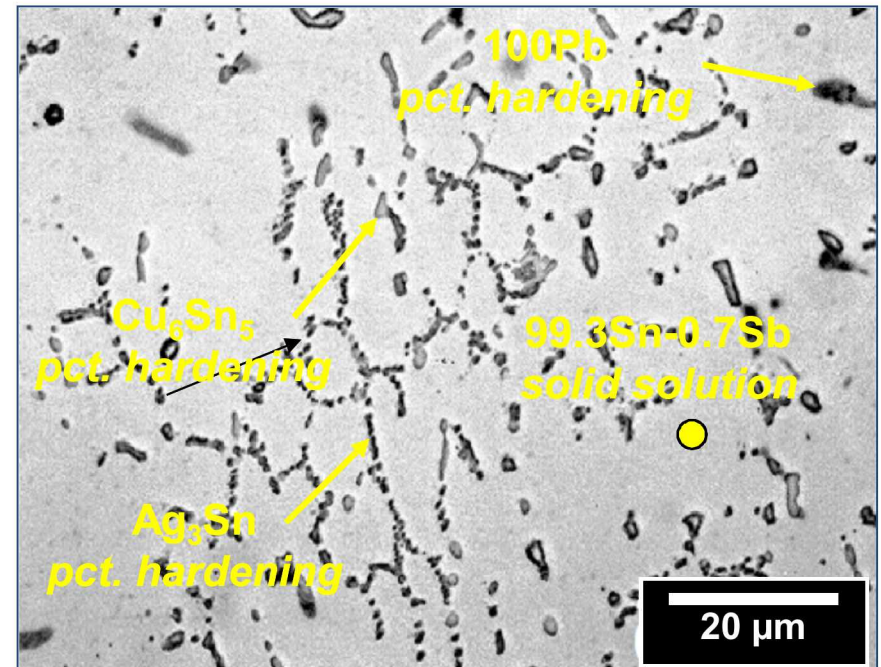
The strength increase was accompanied by a change of failure mode, from the bulk solder to the interface.

Current Low Temperature Solders – Sn-Ag-Bi

- ◆ **Sn-Ag-Cu-Sb:** The addition of Pb broke up the Ag_3Sn particle network, *thereby enhancing the precipitation hardening effect.*



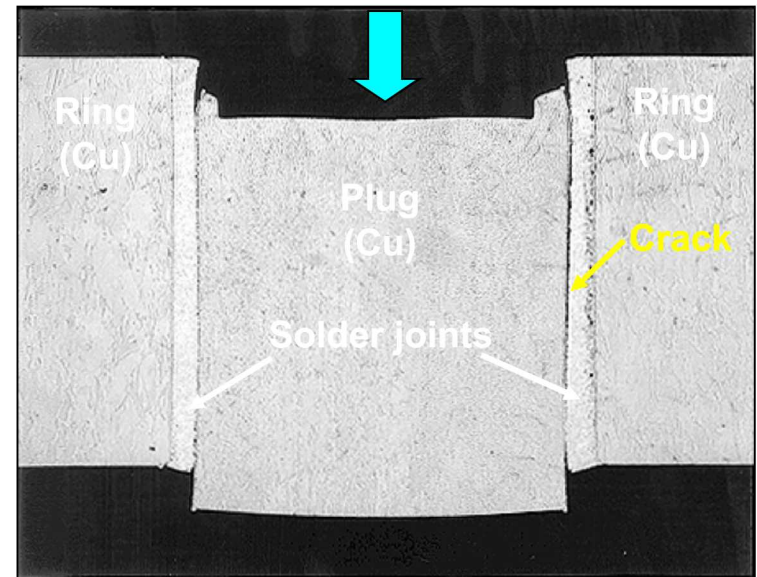
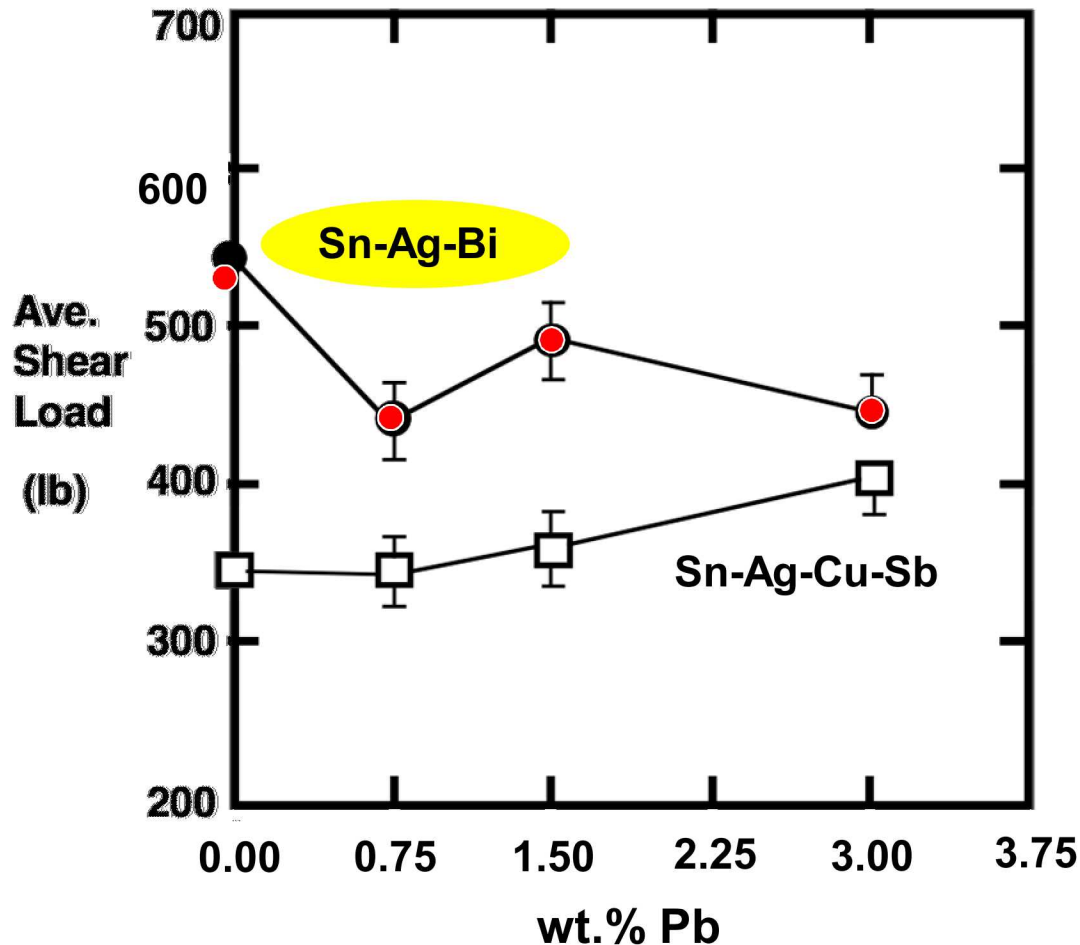
0.00 % Pb



3.00 % Pb

Current Low Temperature Solders – Sn-Ag-Bi

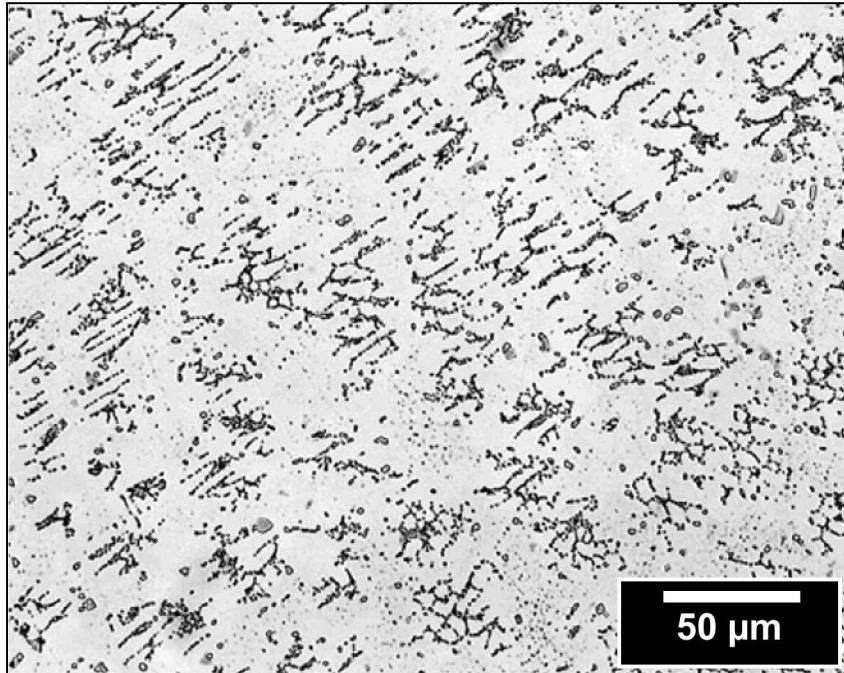
- ◆ **Sn-Ag-Bi:** The fracture path remained along the solder/base material interface for all Pb additions.



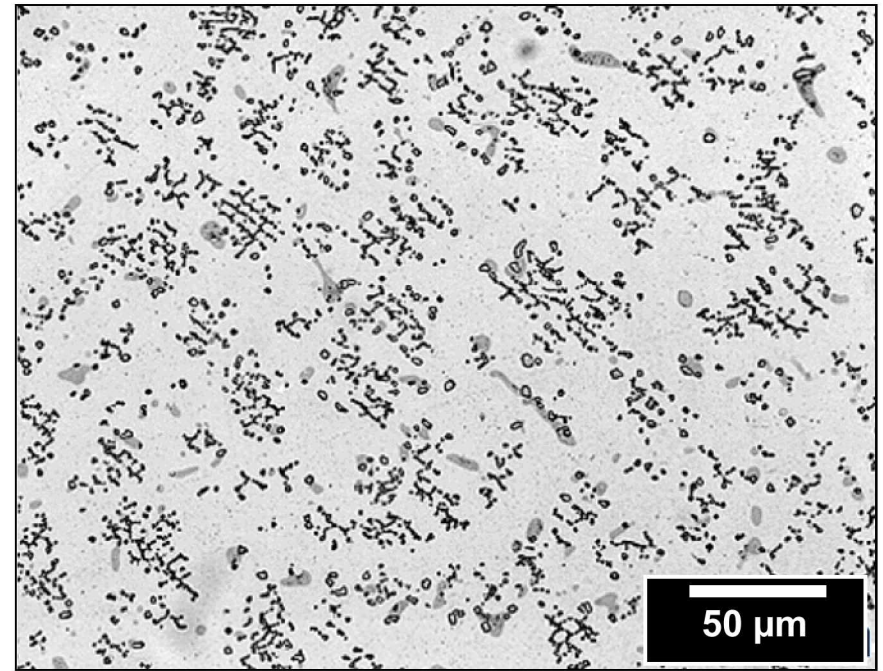
The nominal strength remained greater than the ≈ 400 lb. level above which failure occurs typically at the interface.

Current Low Temperature Solders – Sn-Ag-Bi

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



0.00 % Pb

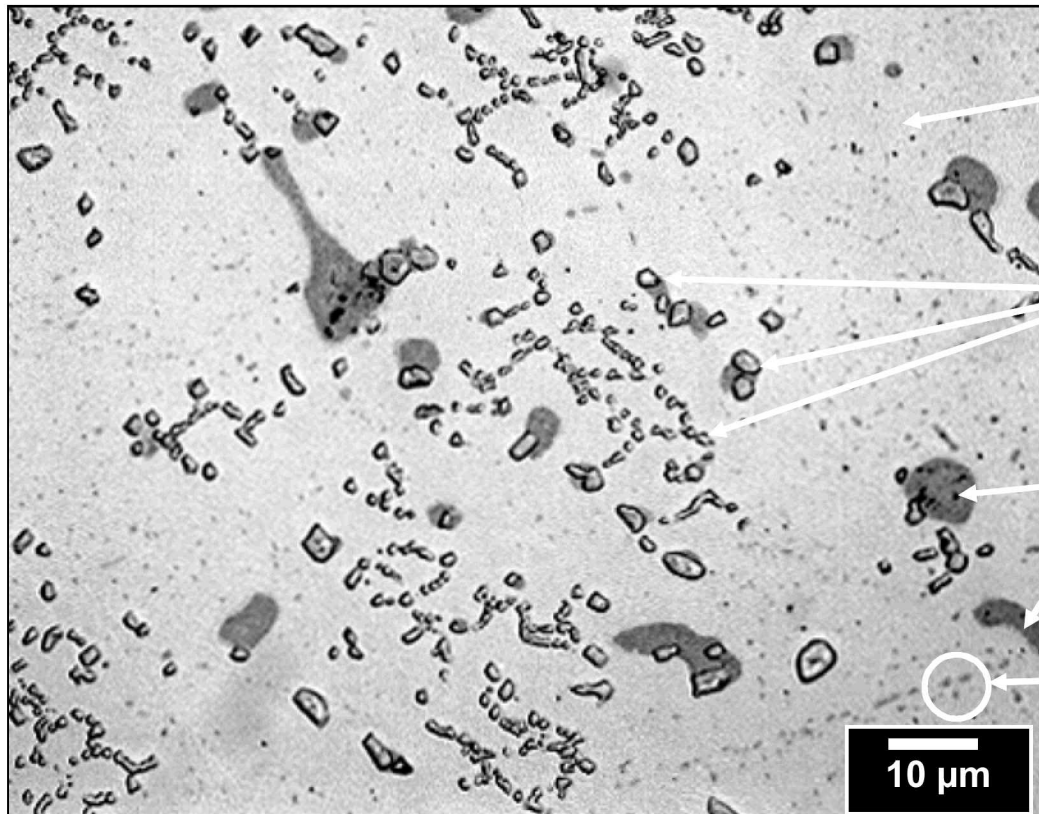


3.00 % Pb

- ◆ **On the other hand ...**

Current Low Temperature Solders – Sn-Ag-Bi

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



96.5Sn-3.5Bi
Solid solution

Ag₃Sn

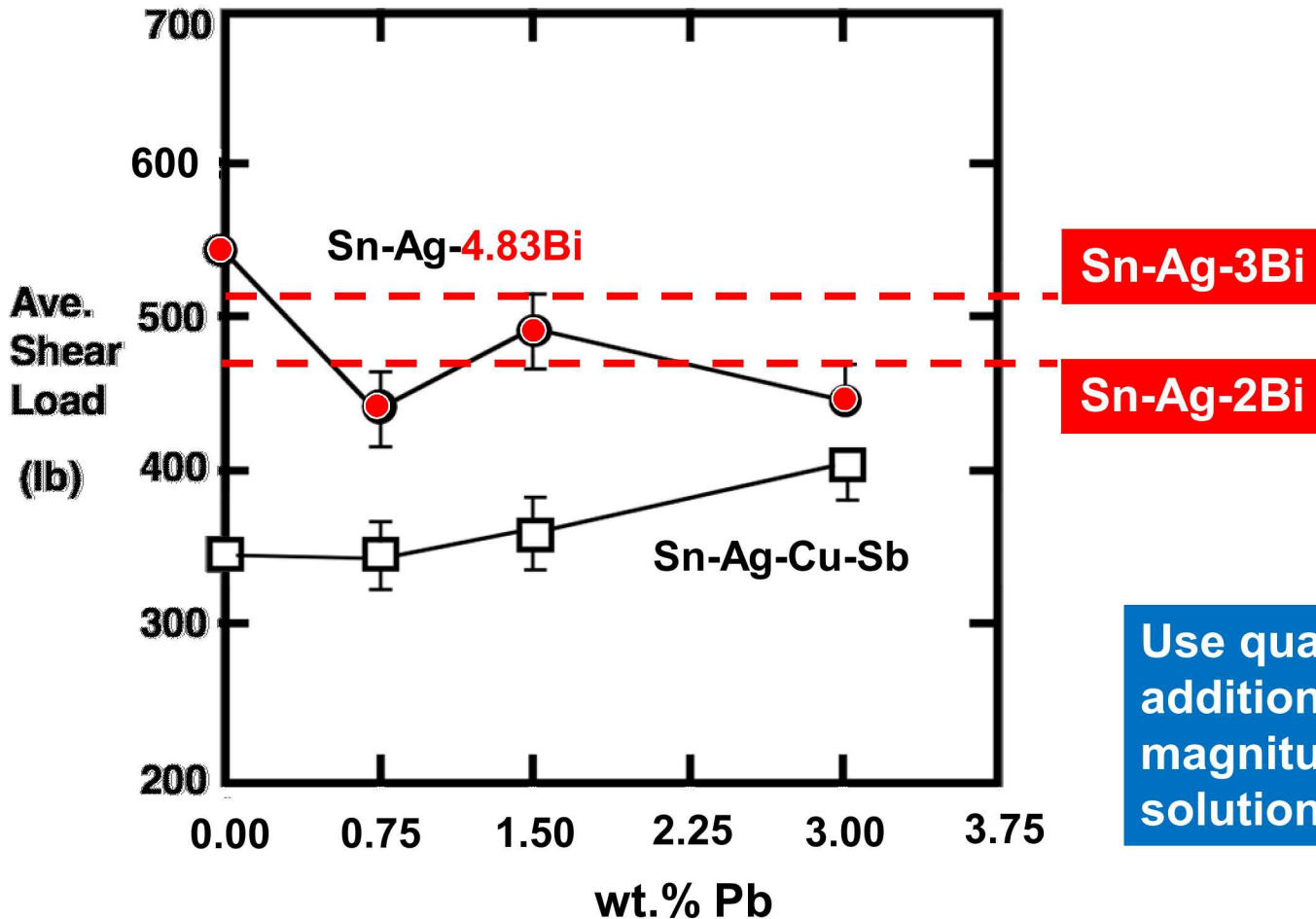
64Pb-**33Bi**-3Sn

63Sn-24Pb-**13Bi**

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

Current Low Temperature Solders – Sn-Ag-Bi

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

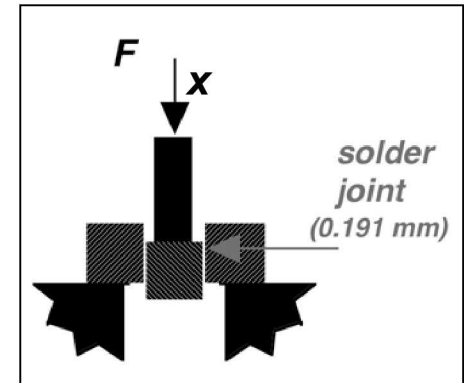


Use quaternary element additions to adjust the magnitude of the solid-solution strengthening.

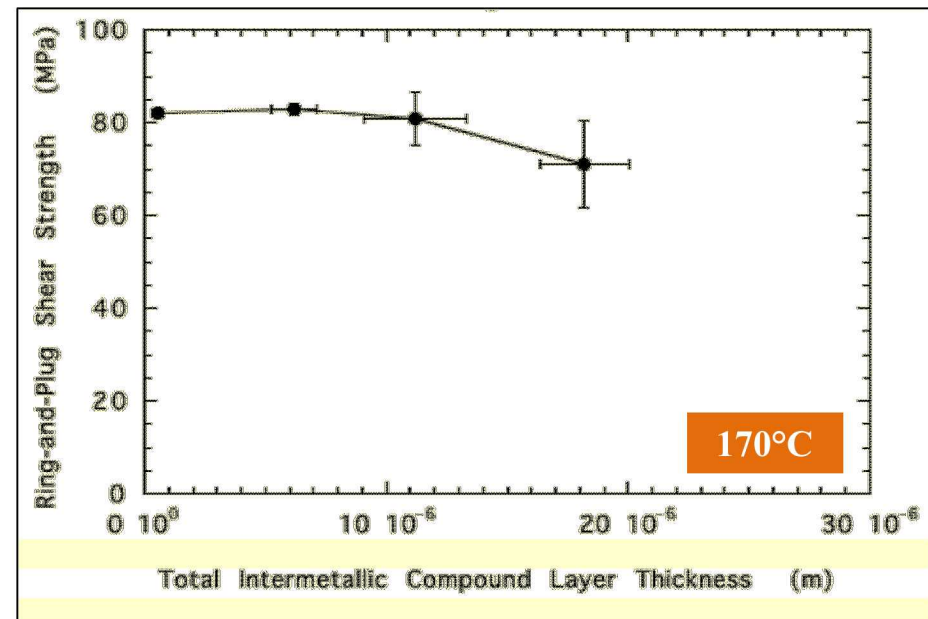
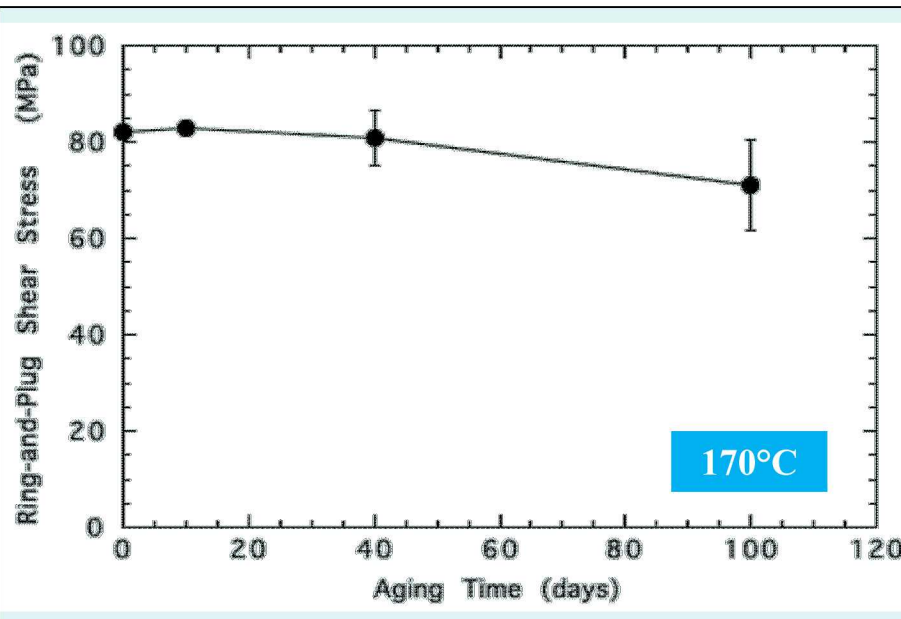
Current Low Temperature Solders – Sn-Ag-Bi

- ◆ 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 $\approx 10 \mu\text{m}$.

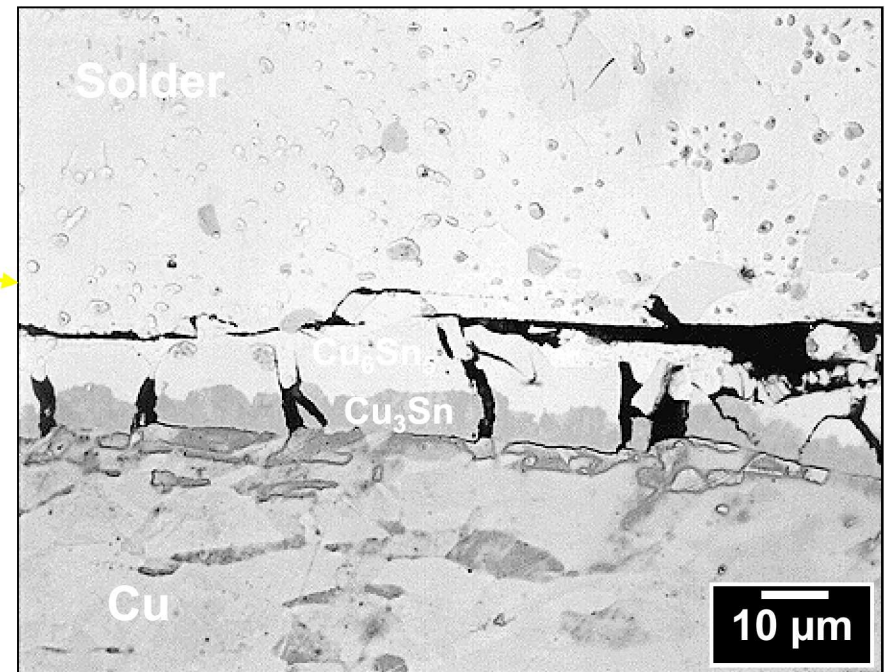
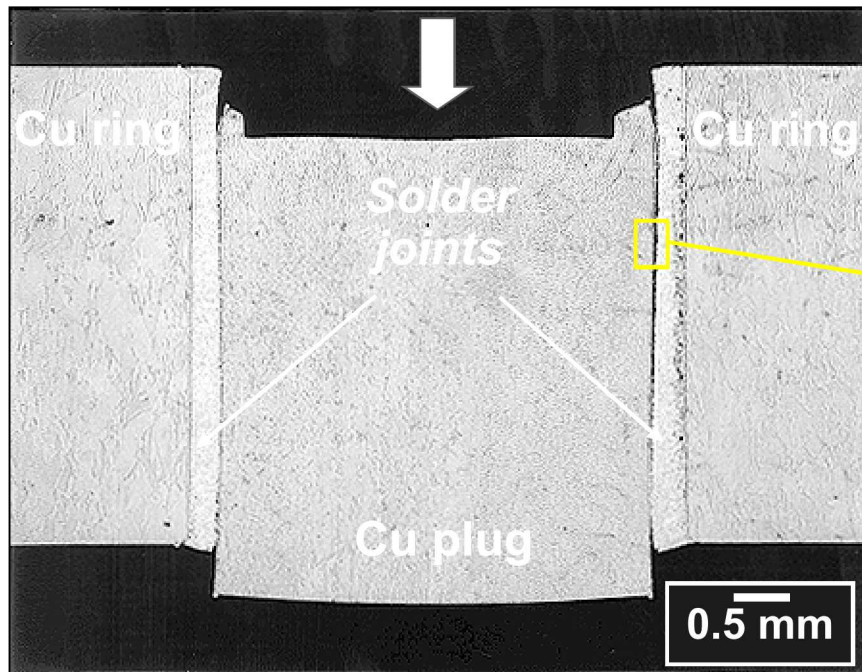


Ring-and-plug shear test



Current Low Temperature Solders – Sn-Ag-Bi

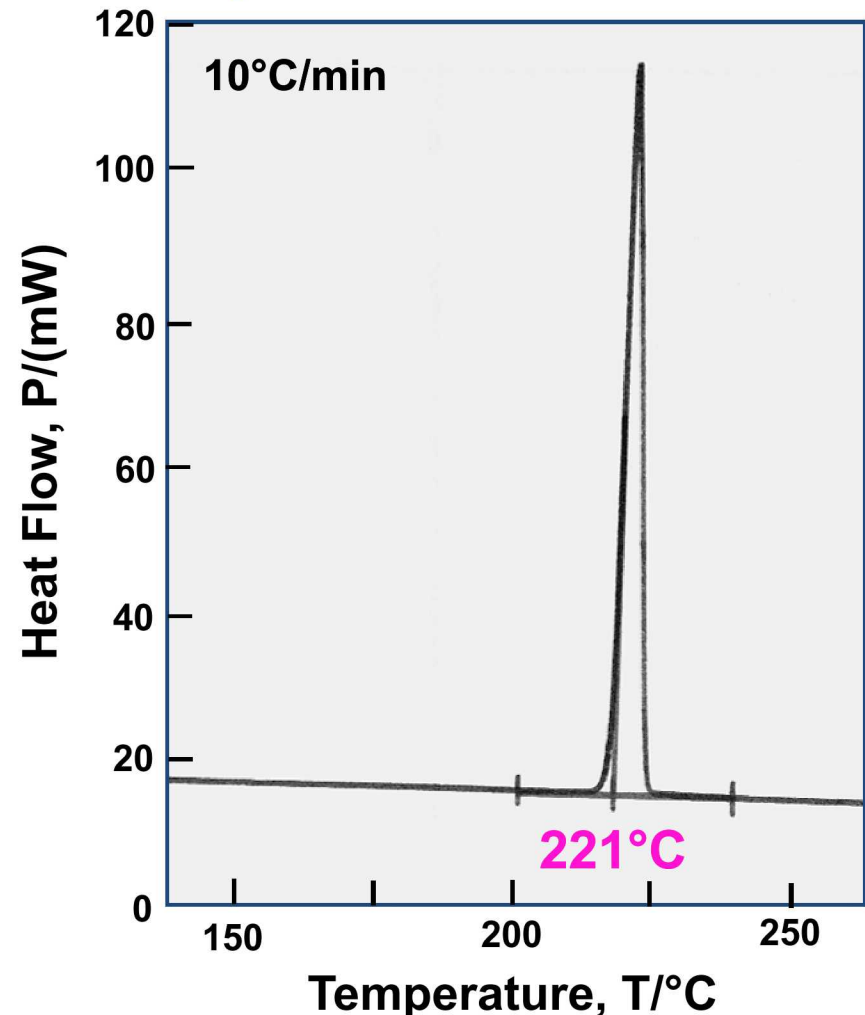
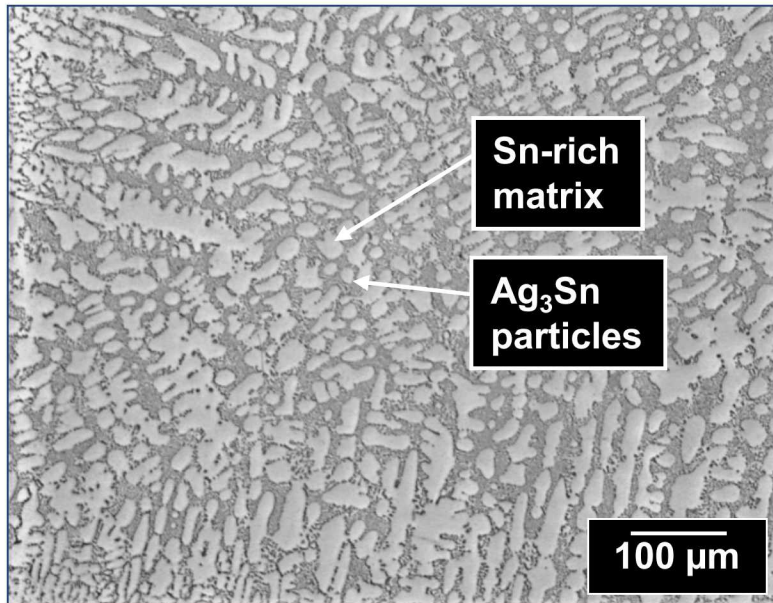
- ◆ The strength study included a **failure mode analysis**.
 - The crack path followed the IMC/solder interface, which is often the case at this displacement rate.
 - However, the concurrent presence of cracks in the IMC layer implies that Bi at the IMC/solder interface did not, itself, reduce solder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



170°C, 100 days

Novel Low Temperature Solders

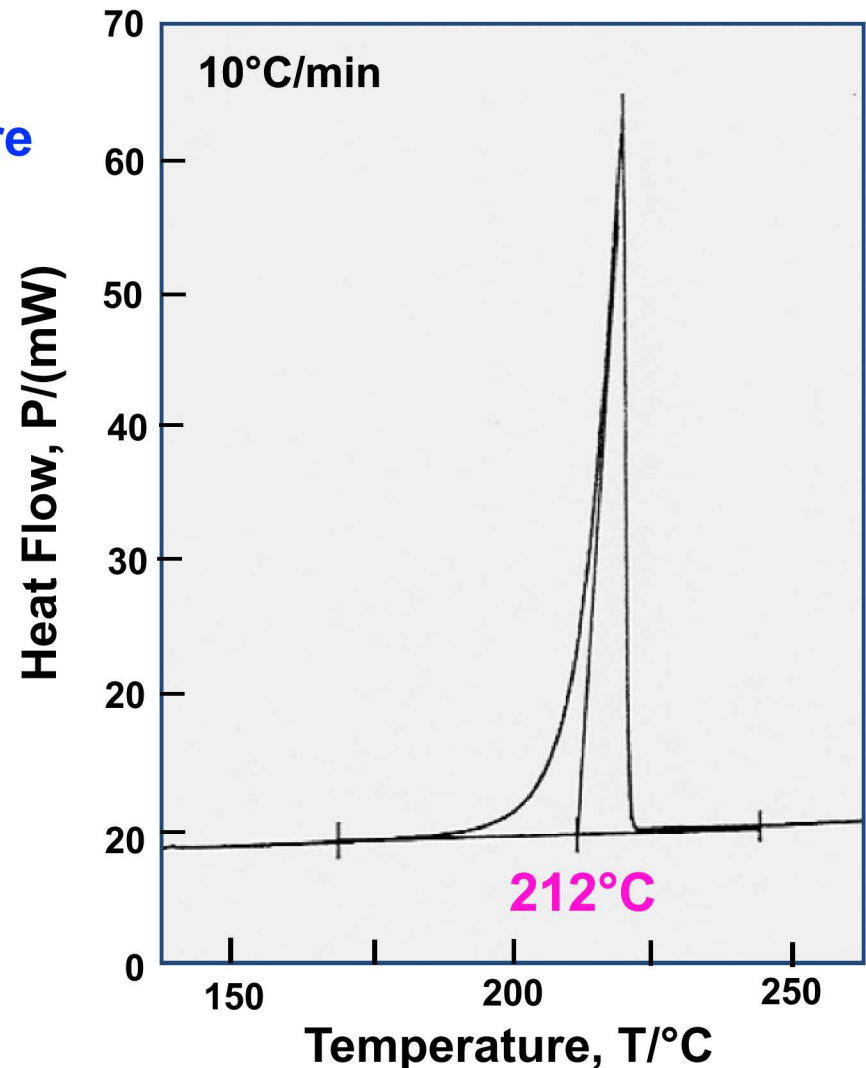
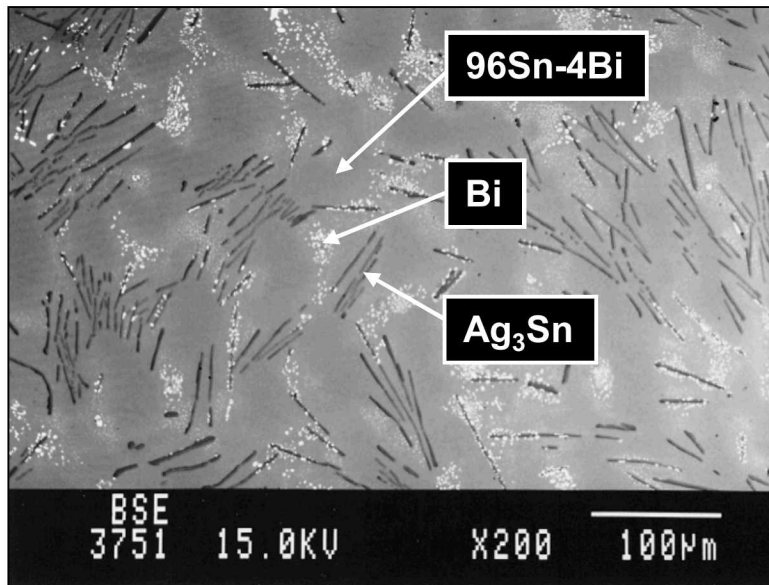
- ◆ **Objective:** “Develop a Pb-free solder having solidus and liquidus temperatures close to the 183°C eutectic temperature of 63Sn-37Pb.”
- ◆ The starting point was the eutectic 96.5Sn-3.5Ag alloy ($T_e = 221^\circ\text{C}$).



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

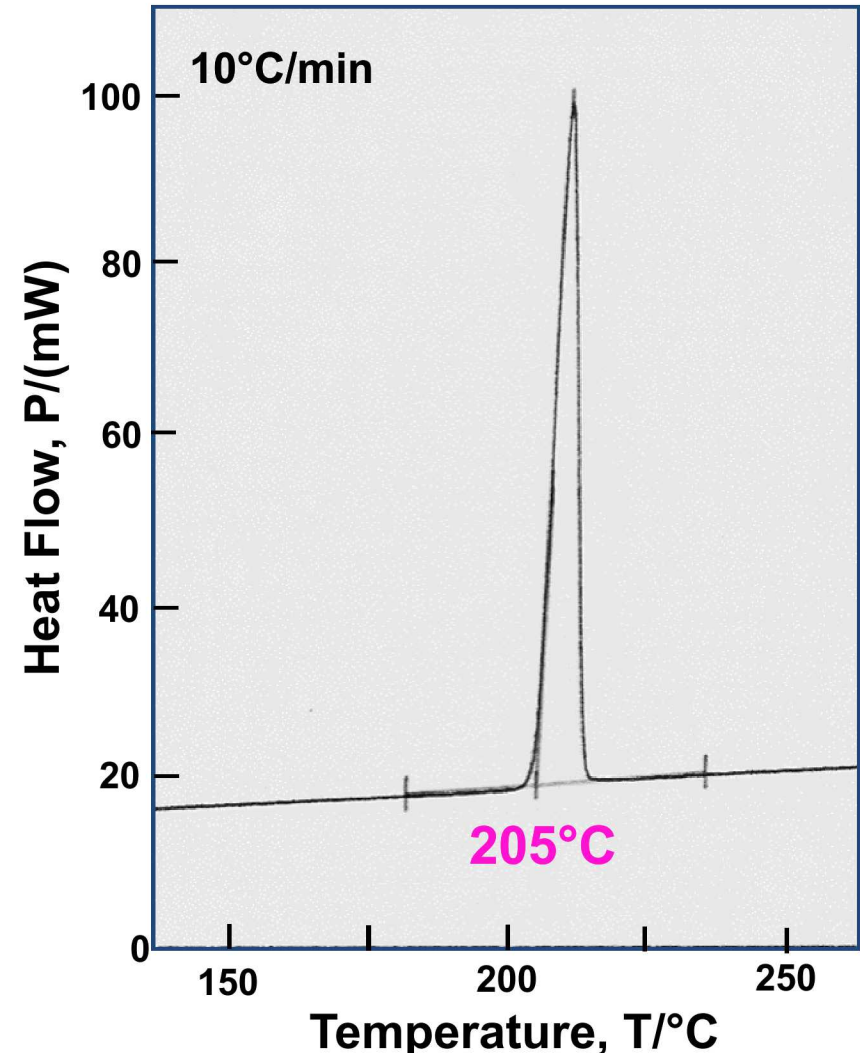
Novel Low Temperature Solders

- ◆ An extensive development effort led to the **91.84Sn-3.33Ag-4.83Bi** alloy having a **solidus temperature of 212°C** ($\Delta H = 55 \text{ J/g}$).



Novel Low Temperature Solders

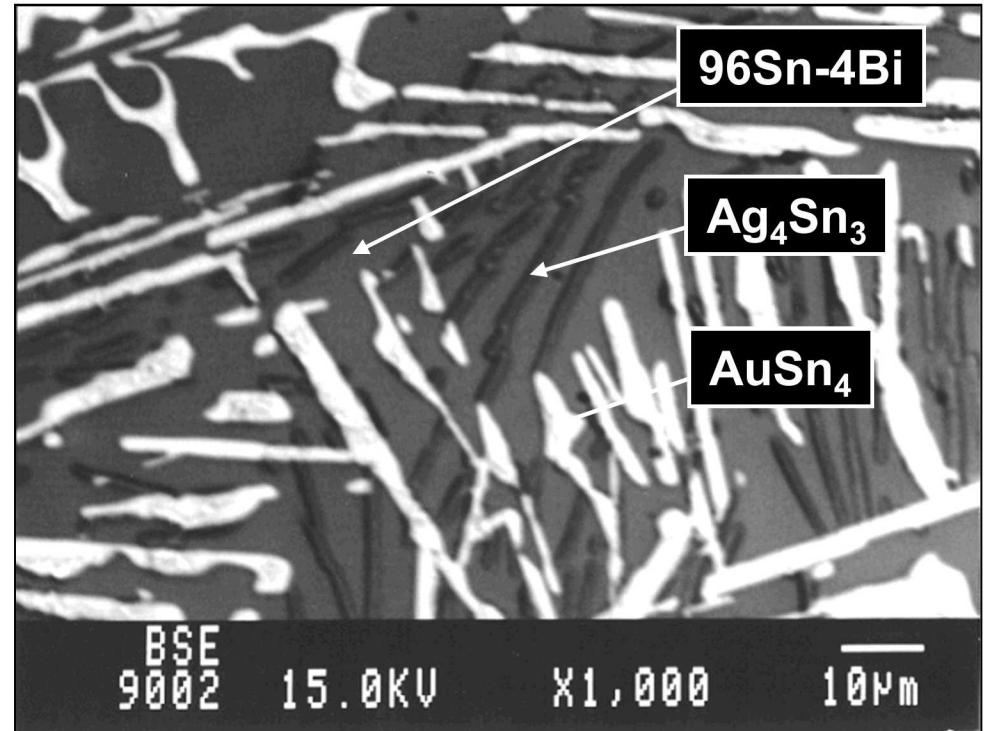
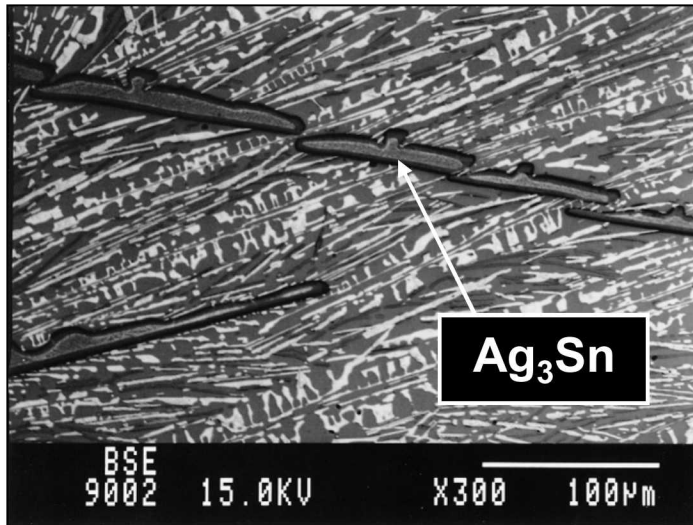
- ◆ Two ternary alloys were developed that confirmed the effectiveness of **gold (Au)** as a melting point depressant.
- ◆ The **86.4Sn-5.1Ag-8.5Au** was developed from this precept:
 - 95% confidence intervals (mass%) were: Sn, 1.5; Ag, 0.33; and Au, 0.06
 - $T_s = 205^\circ\text{C}$; $\Delta H = 55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



Novel Low Temperature Solders

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

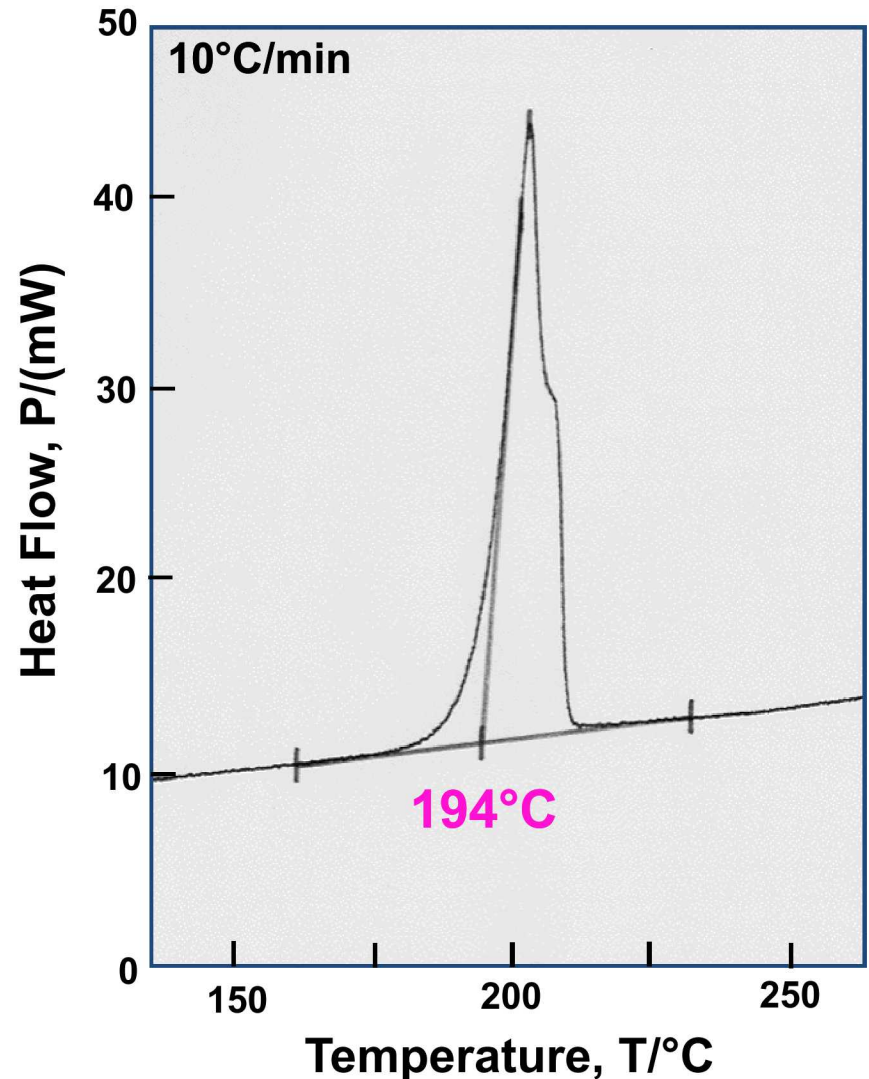
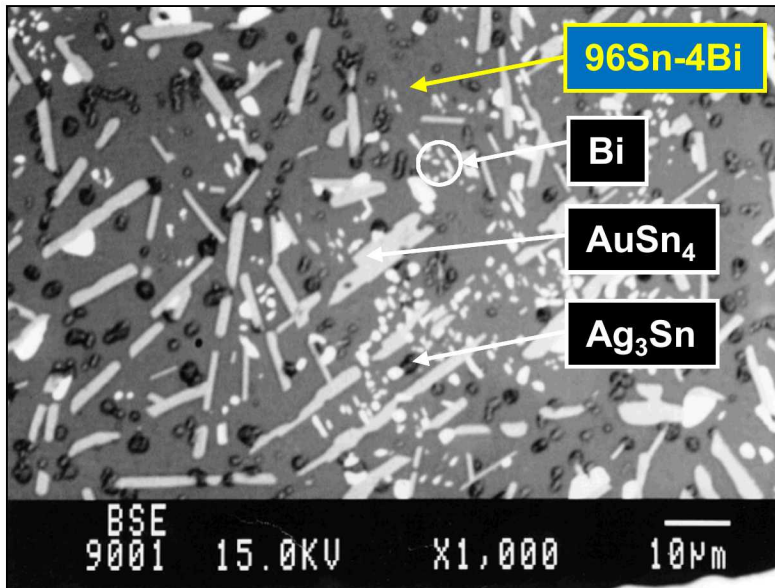
- Ag_3Sn
- Ag_4Sn_3
- AuSn_4



Novel Low Temperature Solders

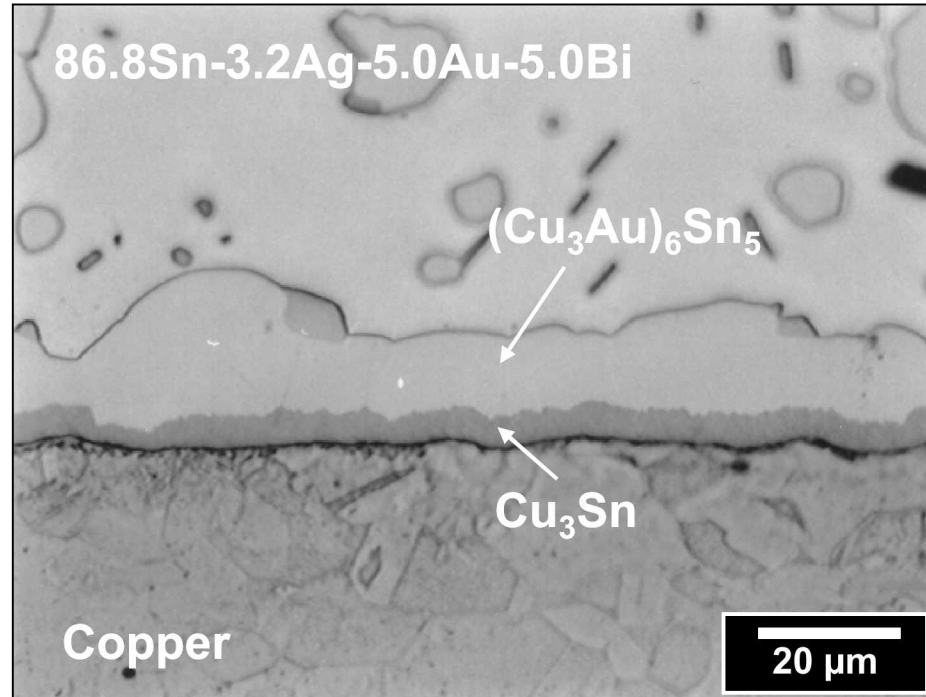
- ◆ The $86.8\text{Sn}-3.2\text{Ag}-5.0\text{Au}-5.0\text{Bi}$ exhibited a shoulder that is indicative of a liquidus point of $\approx 204^\circ\text{C}$.

- $T_s = 194^\circ\text{C}$; $\Delta H = 53 \text{ J/g}$
- Besides the particle phase, the matrix phase was a solid solution: $96\text{Sn}-4\text{Bi}$.



Novel Low Temperature Solders

- ◆ An extensive amount of analysis was performed on the **86.8Sn-3.2Ag-5.0Au-5.0Bi** alloy ($T_s = 194^\circ\text{C}$).



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.

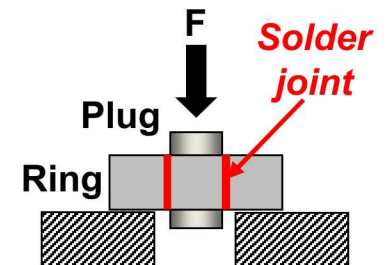
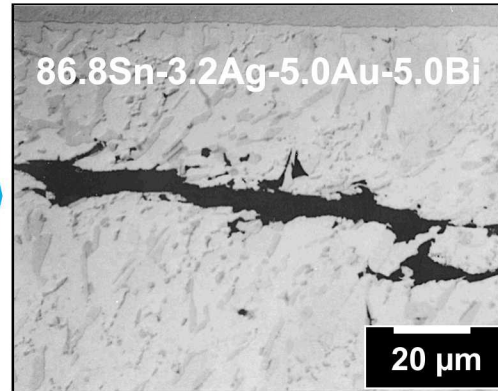
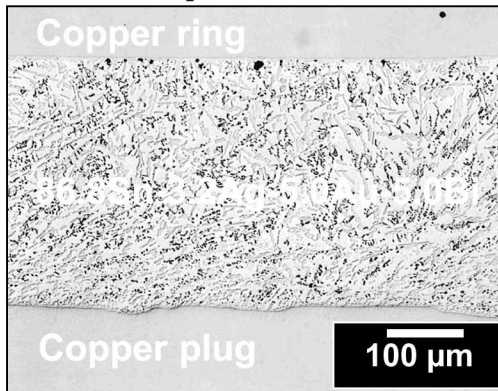
Novel Low Temperature Solders

- ◆ Ring-and-plug mechanical testing was performed using the **86.8Sn-3.2Ag-5.0Au-5.0Bi alloy ($T_s = 194^\circ\text{C}$)**.

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

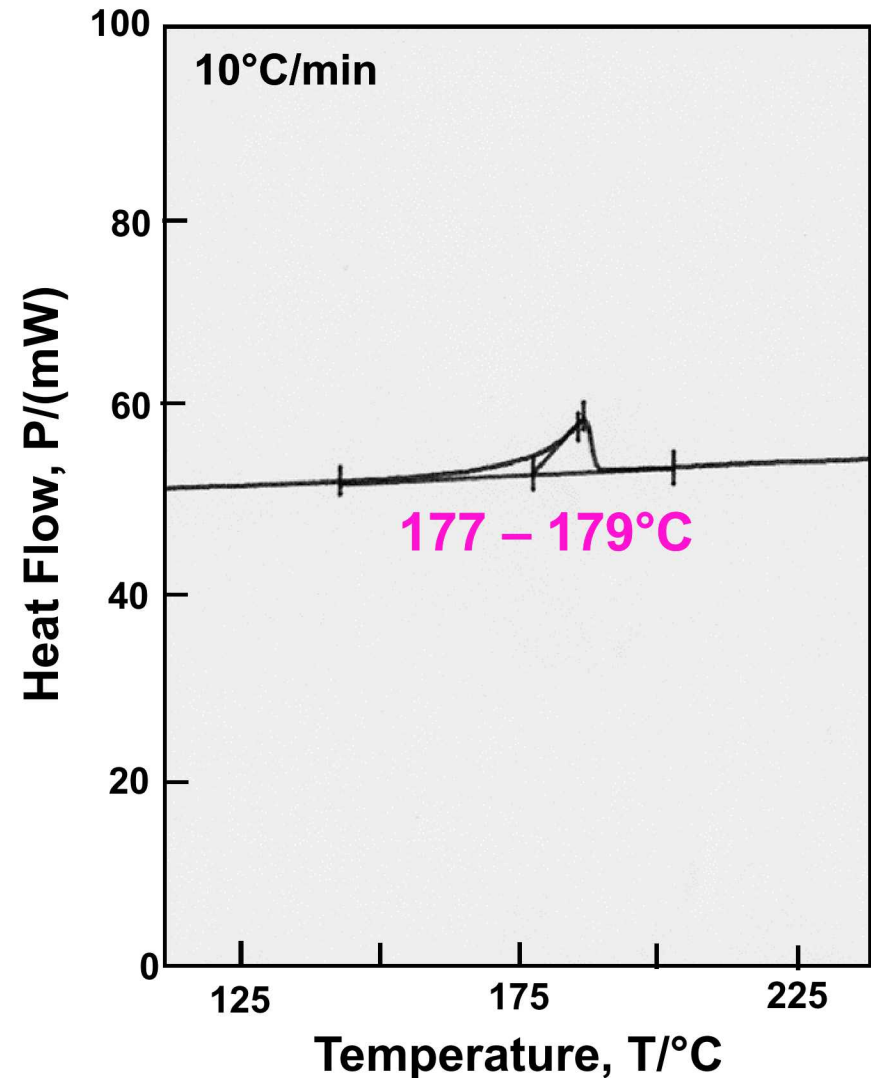
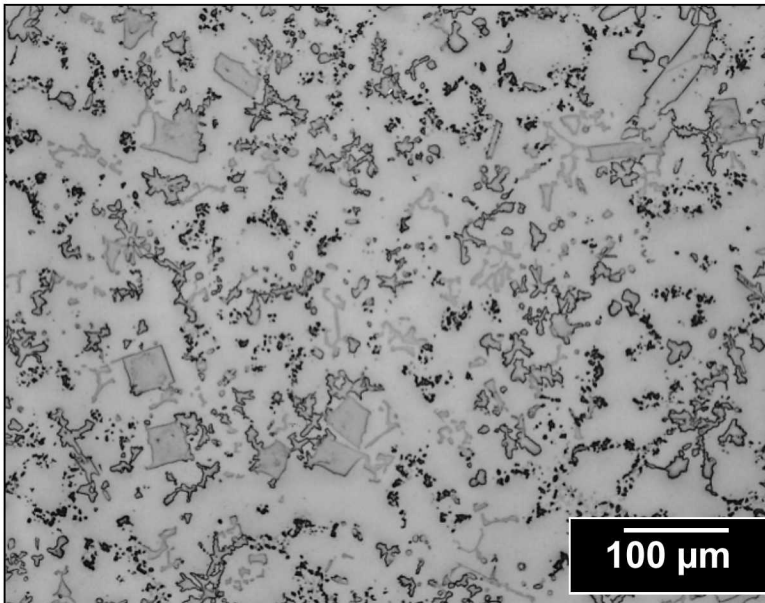
**The ring-and-plug shear strength of the Sn-Ag-Bi-Au alloy remains as the highest value recorded of any solder alloy.*

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



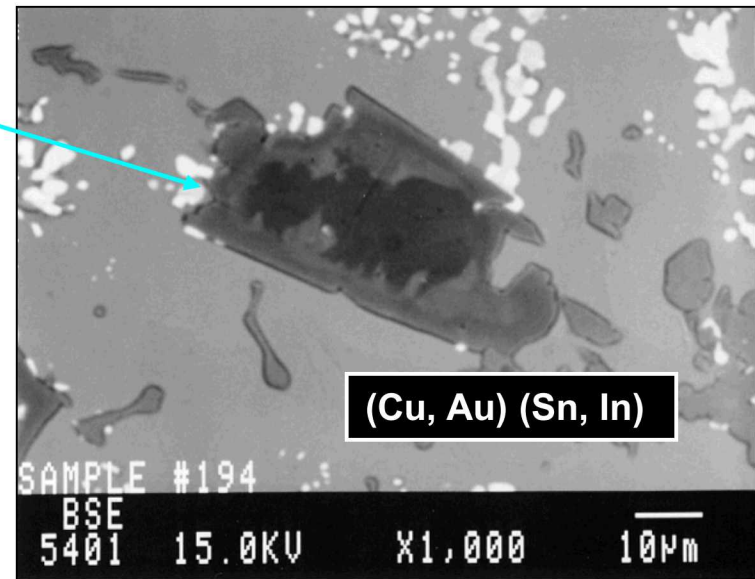
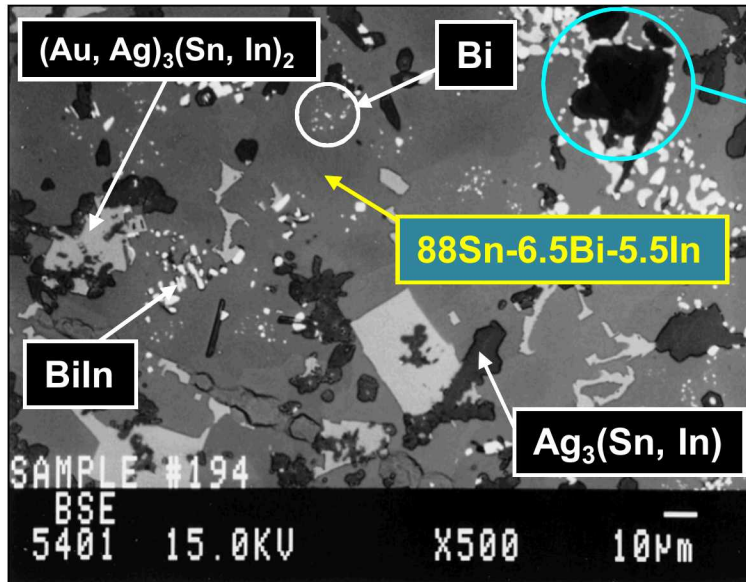
Novel Low Temperature Solders

- ◆ **66Sn-5.0Ag-10Bi-5Au-10In-4.0Cu** had a solidus temperature that was in the range of **177-179°C** and $\Delta H = 31 \text{ J/g}$.
- ◆ Although complicated, the particle phases were uniformly distributed within the microstructure.



Novel Low Temperature Solders

- ◆ The **66Sn-5.0Ag-10Bi-5Au-10In-4.0Cu** microstructure was comprised of several particles and a **88Sn-6.5Bi-5.5In** 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±0.7	418±9
96.5Sn-3.5Ag	36±3	460±30
95.5Sn-3.9Ag-0.6Cu	40±5	500±40
91.84Sn-3.33Ag-4.83Bi	31±5	420±30

250°C,
RMA flux

Summary

- ◆ The current low temperature 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 in-line with that of the eutectic Sn-Pb alloy.
 - Although highly unlikely to achieve “mainstream status,” they showcased *metallurgical methods to optimize alloy performance.*