A Study of Lead-Free Solders

AIM

20-Mar-03

Lead-Free Soldering- Why?

FEAR

- Legislation
- Trade barriers
- Competition

Resistance to Changing to Lead-Free Soldering

- Costs
  - Materials
  - Incidental
- Reliability concerns
  - Solder joint quality
  - Component and substrate temperature damage

Lead-Free Alloy Requirements

- A great deal of effort has been put into the development of lead-free solder alloys.
  - Certain criteria must be taken into account and met before a lead-free solder may be put into use:
    - Physical reliability
    - Temperature requirements
    - Compatibility with parts and processes
    - Repairs and rework

Searching for a Suitable Alloy

- Using the periodic table of elements, AIM began to search for a suitable lead-free alloy.
- Several metals were quickly removed as potential base materials:
  - Bismuth- embrittlement, thermal fatigue
  - Cadmium- toxicity
  - Gallium- availability, cost, embrittlement
  - Indium- cost, availability, thermal fatigue
  - Zinc- corrosivity, oxidation, ease of use

Melting Points

- As a general rule, most lead-free solders melt at higher temperatures than those of Sn/Pb.

- There are two main exceptions to this:
  - Indium alloys
  - Bismuth alloys

Indium Alloys

- The main disadvantage of Indium is its cost.
- Another problem is supply (80-100 tons/year).
- Indium alloys also suffer from poor resistance to corrosion and rapid oxide formation during melting.
- Indium based lead-free solders are best used with temperature sensitive components that do not require high joint strength and will not be exposed to harsh or high-stress environments.

Bismuth Alloys

- Bismuth alloys offer a lower melting point than Sn/Pb alloys.
- Bismuth has a similar cost to tin.
- Unfortunately, bismuth in soldering alloys tends to create embrittlement.
- If a bismuth alloy picks up any lead, the melting temperature will drop again (secondary eutectic formed at 96°C, resulting in poor fatigue resistance.
- Bismuth alloys also are prone to failure in peel strength tests due to poor fatigue resistance.

Most of the lead-free alloys currently available are rich in tin.

- Many of these are binary alloys that have been used for years in non-electronic applications.
  - Sn/Ag
  - Sn/Sb
- Many of these alloys offer advantages over Sn/Pb alloys.
  - Joint strength
  - Thermal fatigue resistance
- However, these benefits vary greatly among the various lead-free alloys.

Tin/Silver Alloys

- Sn_{96}/Ag_4 is a fairly common alloy with a long history in the hybrid circuit industry.

- The melting point of this alloy (221°C) is too high for many SMT applications.

- Another disadvantage of this alloy is the cost.

Ternary Tin/Silver/Copper Alloys

- This family of lead-free alloys has shown high promise.
  - Sufficient supply
  - Good wetting characteristics
  - Good fatigue resistance
  - Good overall joint strength

Searching for a Suitable Alloy

- After a review of the acceptable elements and a good deal of experimentation, the following elements were chosen to be the constituents of the lead-free alloy to be studied further:
  - Tin
  - Copper
  - Silver
  - Dopant of Antimony

- The nominal composition of the alloy studied is Sn96.2/Ag2.5/Cu0.8/Sb0.5
  - Melting point of 215°C - 217°C.

The Addition of Antimony to Tin/Copper/Silver Alloys

- When Sn/Cu/Ag alloys are doped with Sb, the alloy demonstrates several advantages.
  - Improved thermal fatigue resistance
  - Harder solder joints
  - Finer grain structure
  - Slightly lower melting point
  - Ames Lab and the IDEALS study note that the addition of a dopant, including antimony, to the SnAgCu alloy may be used to enhance the soldering performance of alloys

Concerns About the Toxicity of Antimony

- As with most metals, the salts, oxides, and organo-metallic compounds of antimony typically are the most toxic forms of the element.
- However, these do not form in standard soldering reflow processes.
- In Sn/Pb Solders, IPC-J-STD-006 allows for .5% Sb.
- OSHA's IDLH for antimony is 50 mg/m^3, compared to 10 mg/m^3 for silver.
- In pewter tableware, commonly used in the preparation of food, antimony often is found at levels of 7 to 9 percent.
- The antimony-doped alloy will not leach silver or copper into ground water.
- The EPA does not recognize antimony as an element that must be tested for in TCLP testing.
  - For additional information about antimony, refer to the U.S. Department of Health & Human Services toxicological profile # TP-91/02 and request "A Study of Antimony" from AIM.

Sn/Ag/Cu/Sb vs. Sn63/Pb37

- In order to learn how Sn/Ag/Cu/Sb would perform as a substitute for the traditional tin/lead solder, a comparison of the physical properties of Sn/Ag/Cu/Sb and Sn63/Pb37 was made.

Physical Properties

Tensile*	Sn63S	Sn/Ag/Cu/Sb
– UTS (ksi)	4.92	5.73
– Yield Strength (ksi)	4.38	4.86
– Young’s Modulus (msi)	4.87	7.42
– % Elongation**	52.87	50.00

– * tested per ASTM E-8

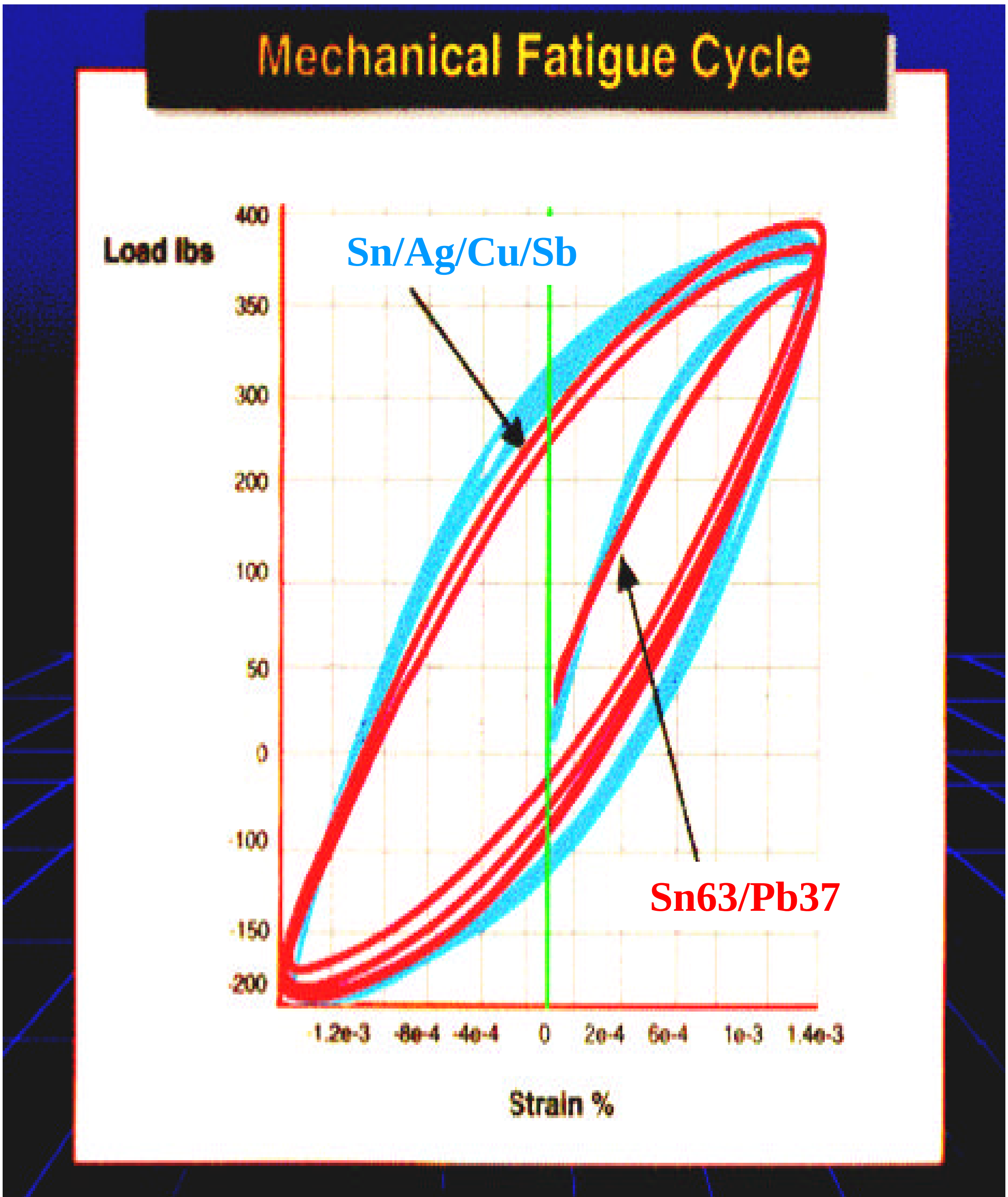
– **results between 30% - 70% generally are considered acceptable.

Physical Properties

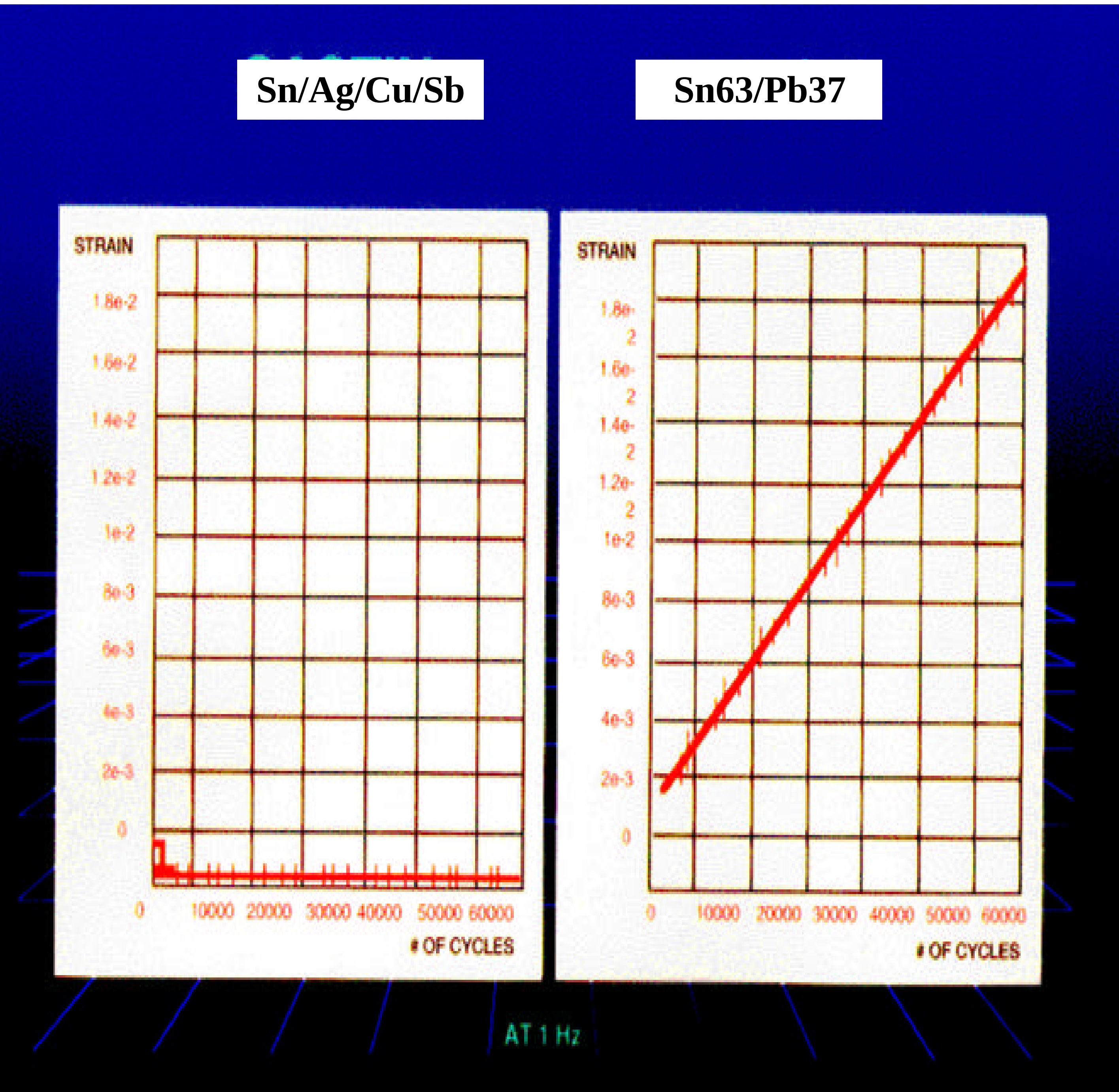
	Sn63	Sn/Ag/Cu/Sb
■ Compression*		
– Elastic Modulus (msi)	3.99	4.26
– YS (ksi)	4.52	4.33
– Stress 25 °/u (ksi)	7.17	8.54
■ Hardness**	10.08	13.5

– * tested per ASTM E-9
– ** tested per Rockwell Test, 15W Scale Hardness

When the curves of mild stresses affected on Sn/Ag/Cu/Sb and Sn63/Pb37 are overlaid, they are virtually identical.



Sn/Ag/Cu/Sb has demonstrated the ability to be more adaptable to a wide range of stresses than Sn63/Pb37.



Thermal and Electrical Properties*

similar to Sn/Pb, superior to conductive adhesives

	Sn/Ag/Cu/Sb	Sn63/Pb37
Thermal Diffusivity	35.82+/-.18mm^2/s	
Specific Heat	218.99 J/(kg.K)	150.0J /(kg.K)
Thermal Conductivity	57.26 W/m.K	50.0 W/m.K
Electrical Resistivity	1.21 E^{-7}ohm.m	1.45 E^{-7}ohm.m
Electrical Conductivity	8.25M(ohm^{-1}m)	

- *Testing performed by ITRI

Thermal Fatigue Properties of Sn/Ag/Cu/Sb

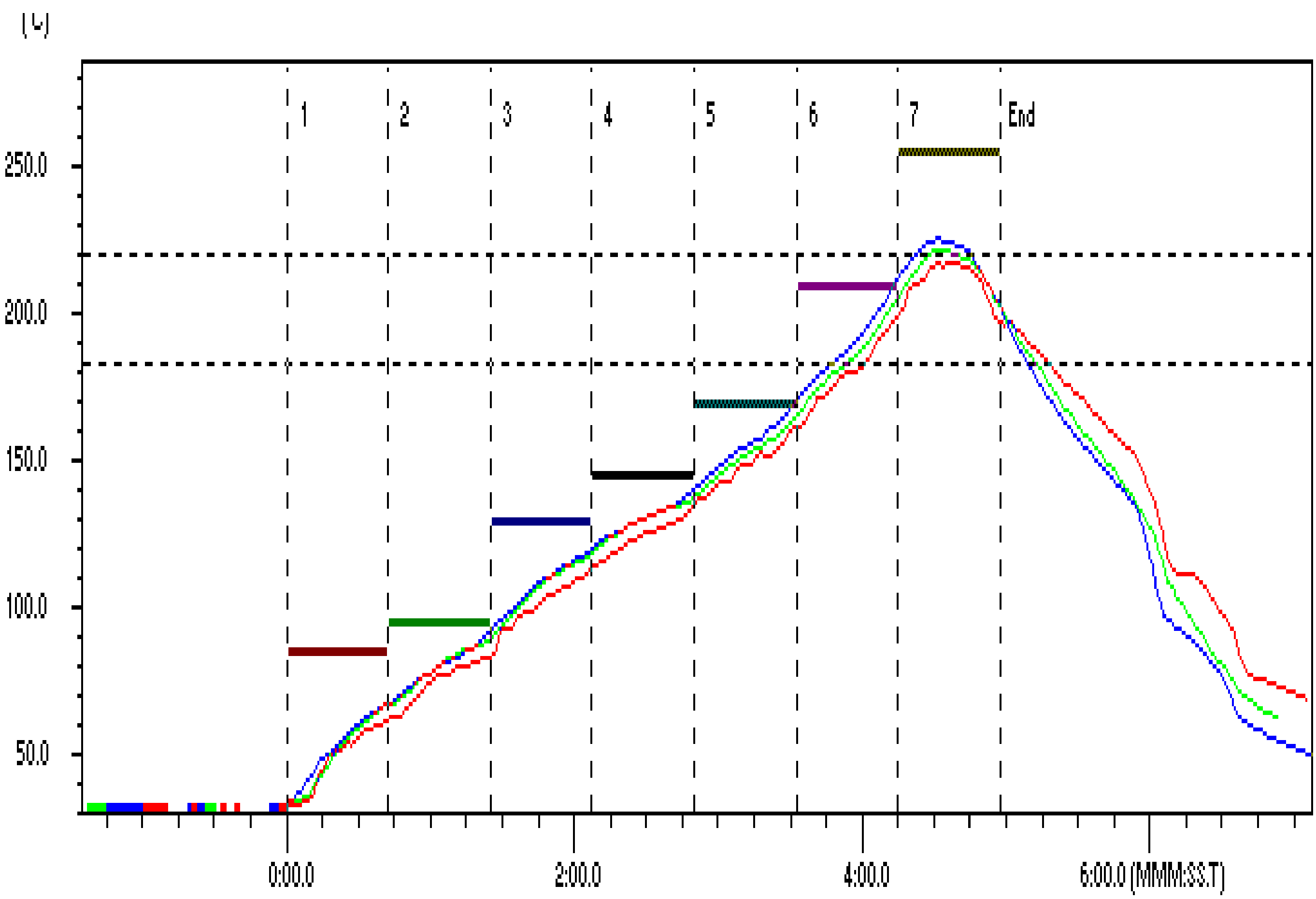
Cycles/Time	Temperature	Result
200 cycles/400 hrs	-40°C+125°C	Pass
840 cycles	-40°C+85°C	Pass
1000 – 1500 hrs	-40°C+125°C	Pass
Accelerated Fatigue Resistance	-50°C+150°C	Pass
	-40°C+125°C	Pass

Testing performed by independent laboratories.

Soldering with Sn/Ag/Cu/Sb

- Sn/Ag/Cu/Sb requires similar temperatures as Sn63/Pb37 for most soldering applications.
  - Wave Soldering- same pot temperature: 250°C - 260°C
  - Hand Soldering- same tip temperature: 600°F - 650°F
  - SMT- slightly higher peak temperature: 235°C vs. 220°C (see next slide)

The Sn/Ag/Cu/Sb Reflow Profile is similar to that of Sn63/Pb37, with a higher peak temperature.



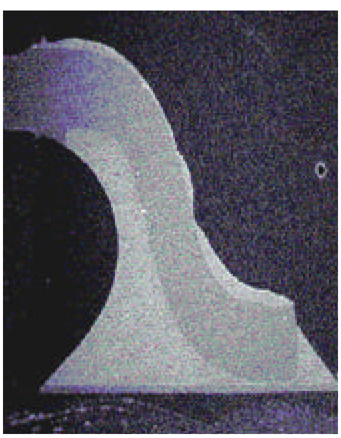
Solder Coating PCBs with Sn/Ag/Cu/Sb

- The process of solder coating circuit boards with Sn/Ag/Cu/Sb also has shown promise.
  - Flatter pads
  - Good storage properties

Sn/Ag/Cu/Sb Compatibility

- Compatibility with Tin/Lead alloys is an important criteria of a lead-free alloy.

- Sn/Ag/Cu/Sb has proven to solder well in conjunction with tin/lead coated components and boards, organic coated boards, silver, palladium, and gold-over-nickel boards.



Sn/Pb

Ni/Pd

Ni/Pd/Au

- Sn/Ag/Cu/Sb is compatible with the flux chemistries currently used in conjunction with tin/lead alloys

Tin/Silver/Copper Reliability When Exposed to Lead

- Tin/Silver/Copper alloys contaminated with lead due see a reduction in mechanical strength.

Fatigue Test	TSC	+ 0.5% Pb	+ 1% Pb
# Cycles to Failure	13,400	6,320*	3,252*

  - According to ASTM E606, 1Hz triangular waveform oscillated between 0.15% strain and -0.15% strain.
  - 10,000 cycles constituted a passing mark.
  - *Failure, Load Amplitude dropped >20%

- Bismuth bearing alloys see an even greater reduction in mechanical and thermal reliability.

Three families of lead-free alloys have emerged as candidates to become potential standards for the industry:

- **Sn/Cu**
- **Sn/Ag**
- **Sn/Ag/Cu**
  - **Sn/Ag2.5/Cu0.7(/Sb0.5) (CASTIN)**
  - **Sn/Ag4.7/Cu1.7 (Ames Lab)**
  - **Sn/Ag3.9/0.6 (NEMI)**
  - **Sn/Ag3.0/Cu0.5 (JEIDA)**

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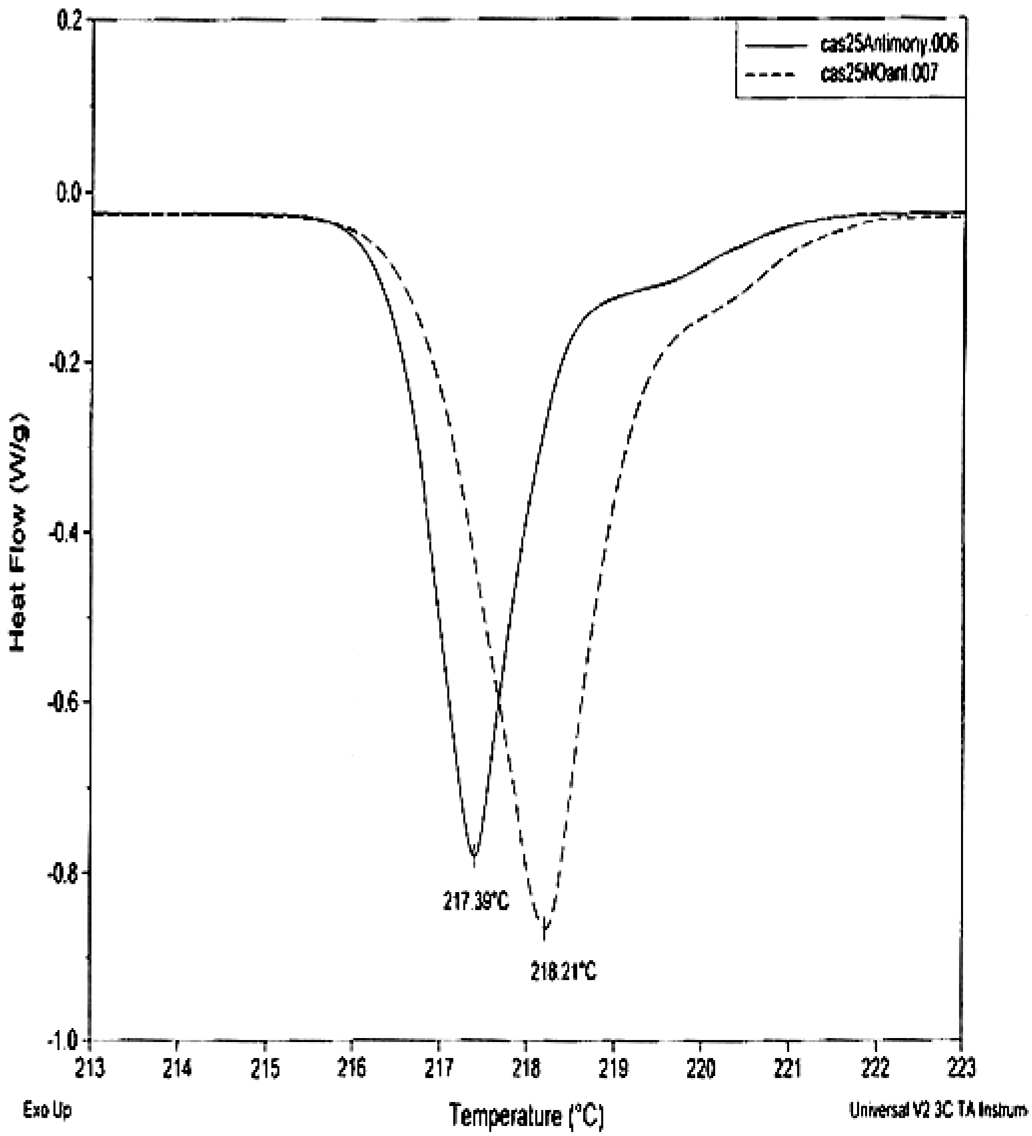
Melting Points

- **Sn/Ag/Cu/Sb 215-217°C**
- **Sn/Ag/Cu 217-218 °C**
  - **Exact eutectic formulation not known**
- **Sn96.5/Ag3.5 221°C**
- **Sn99.3/Cu0.7 227°C**

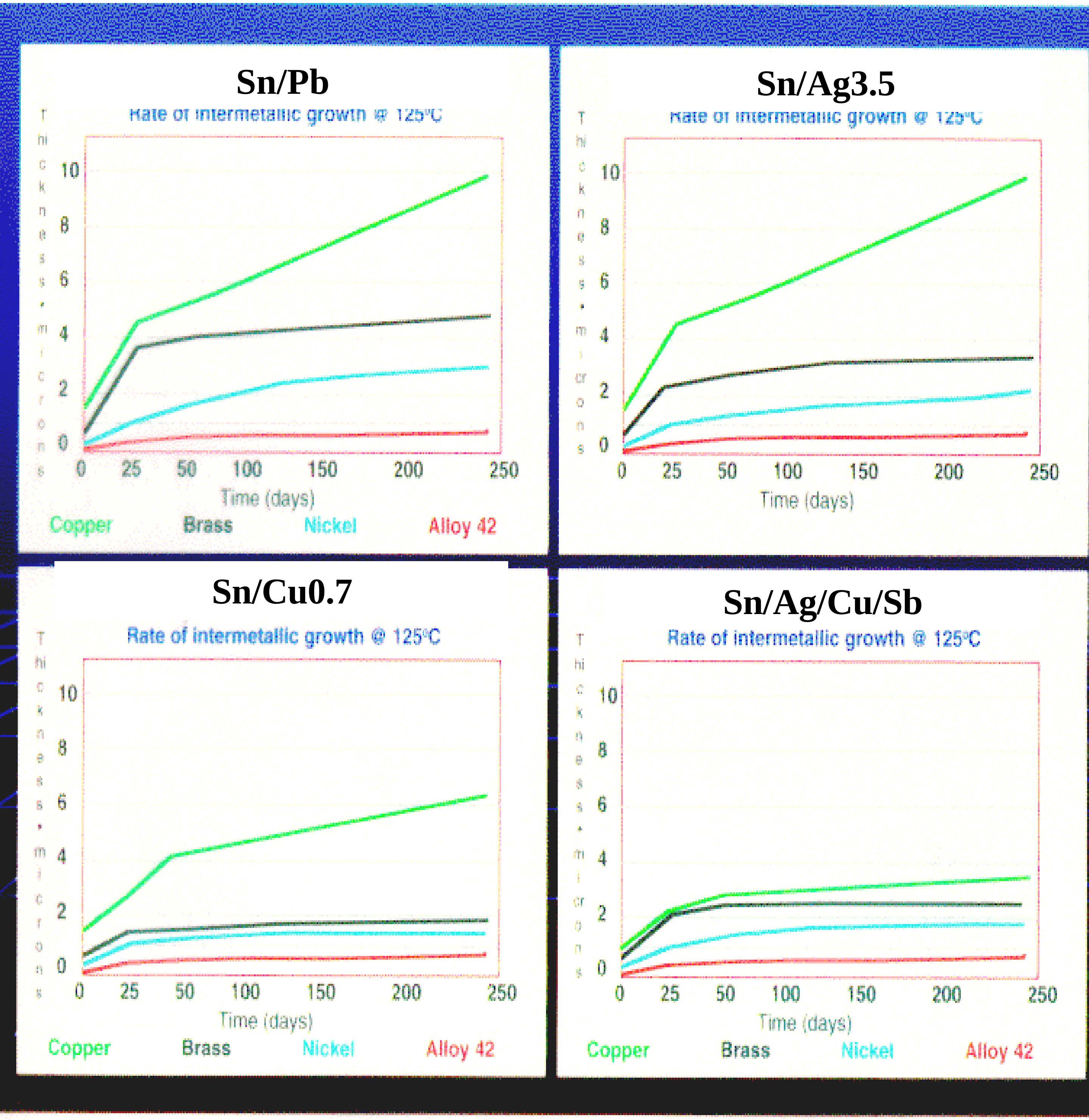
Melting Point Comparison of Tin-Silver-Copper Alloys

- Tin-silver-copper alloys with a dopant of antimony have a slightly lower liquidus temperature than those without



Intermetallic Growth Rates

- Sn/Ag/Cu/Sb has the lowest copper intermetallic growth rate of the alloys below.



Physical Comparison

- As seen on the chart below, Sn/Ag/Cu/Sb and Sn96.5/Ag3.5 appear very similar physically.

Tensile*	Sn/Ag/Cu/Sb	Sn96.5
– UTS (ksi)	5.56	5.91
– Yield Strength (ksi)	4.03	4.07
– Young's Modulus	4.30 msi	5.74 msi
– % Elongation	50.00	43.66

– *tested per ASTM E-8

Compression**	Sn/Ag/Cu/Sb	Sn96.5
– Stress @ 25% strain	10.07	9.88
– YS .2% strain (ksi)	4.53	4.84
– Young Modulus	10.89	16.60

– ** tested per ASTM E-9

Hardness***	13.5	12.2

– *** tested per Rockwell Test, 15W Scale Hardness

Fatigue Testing

- Note that during fatigue testing Sn96.5/Ag3.5 failed one of the set cycles, whereas Sn/Ag/Cu/Sb passed all tests. Further investigation leads to the conclusion that this failure was due to a phase change. This is thought to be due to cooling rates.

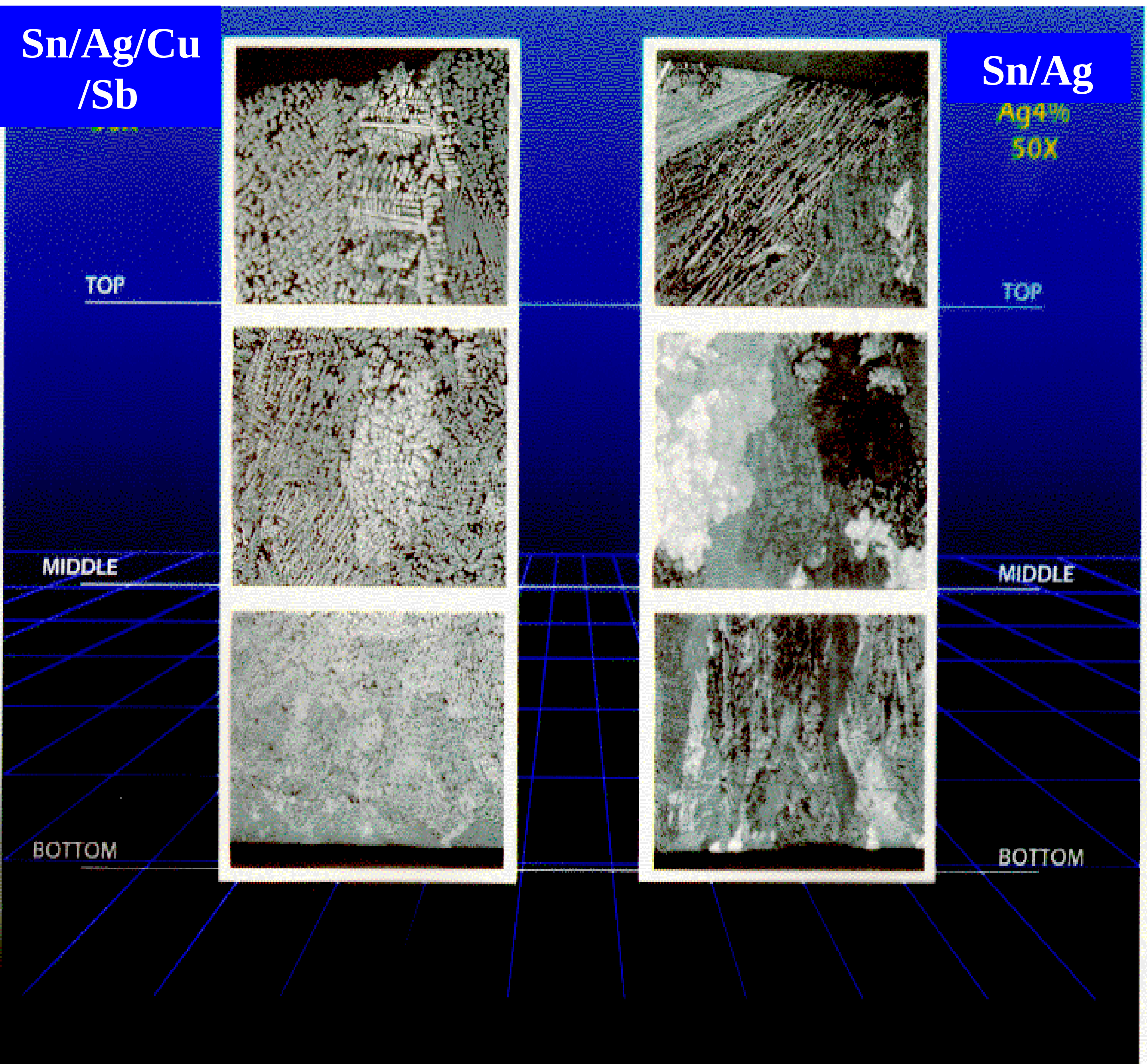
- Fatigue Test

Fatigue Test	Sn/Ag/Cu/Sb	Sn96.5
– # Cycles to Failure	11,194	10,003
–	26,921	6,267*
–	24,527	11,329

  - According to ASTME 606, 1Hz triangular waveform oscillated between .15% strain and -.15% strain.
  - 10,000 cycles constituted a passing mark.
  - *Failure

Microstructures Testing

- One bar each of Sn/Ag/Cu/Sb and Sn96.5/Ag3.5 were melted and subjected to different cooling rates.



Toxicity Characteristics Leaching Procedure Testing*

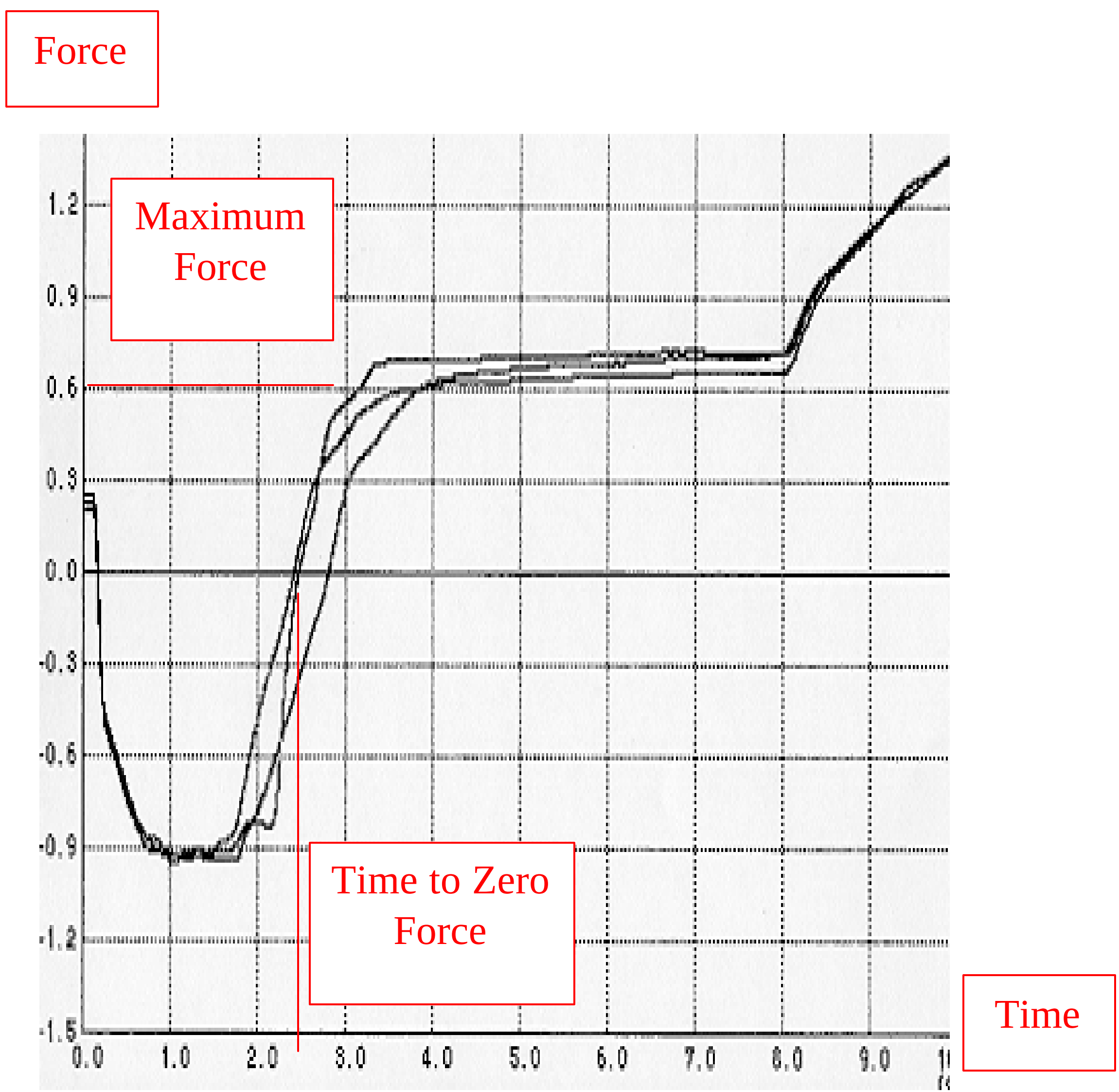
- Sn/Ag/Cu/Sb, as well as Sn96/Ag4 and Sn97/Cu3, will not leach into the soil at a rate to keep it out of a landfill per Federal TCLP regulations.

- In fact, the levels found in the TCLP testing were considered to be less than "ND" (not detected).

  - *Testing performed by ESS Laboratories, Rhode Island

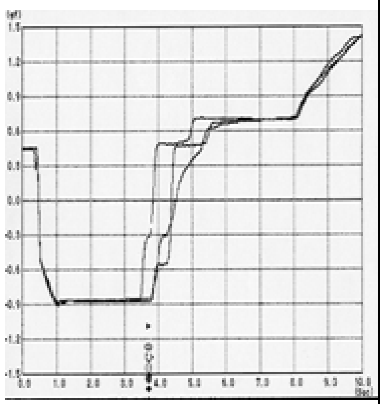
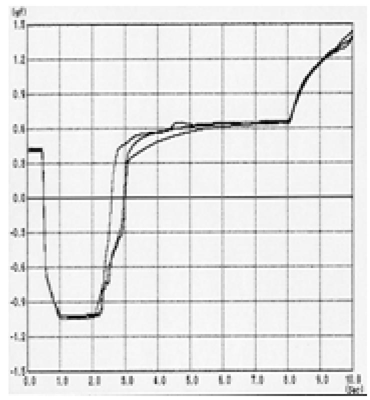
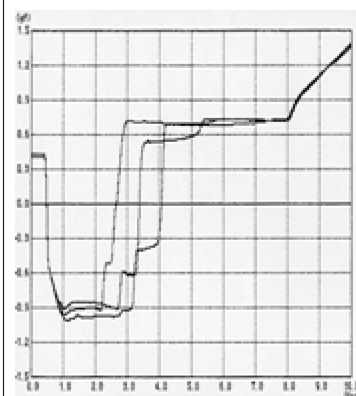
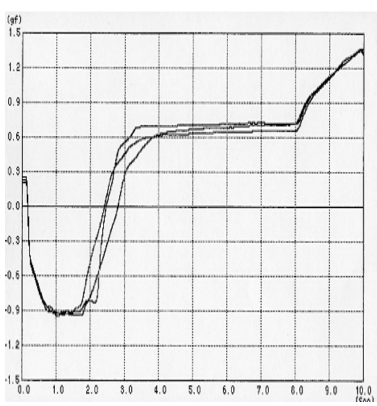
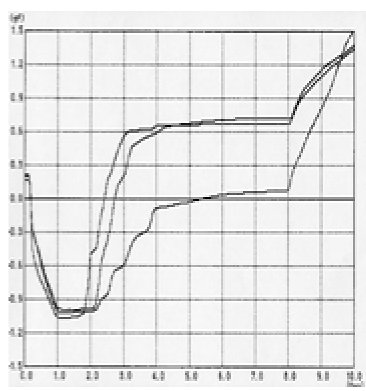
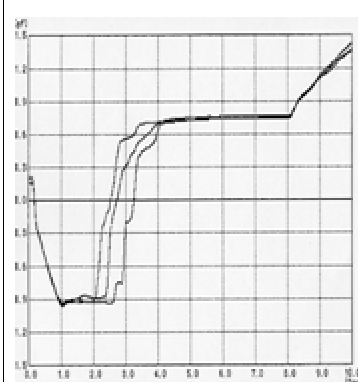
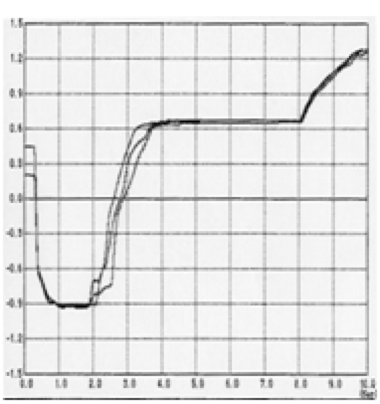
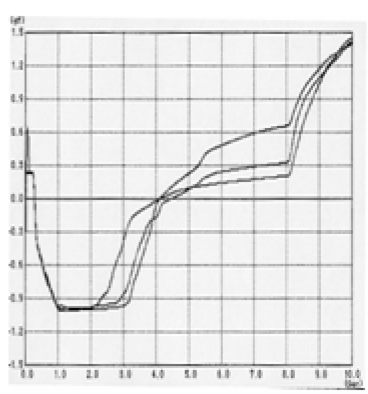
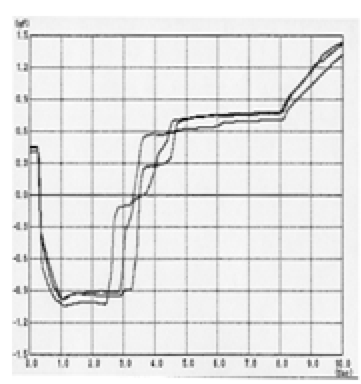
Wetting Testing

- As the wetting curves on the following slide demonstrate, alloys that contain 2.5% or less silver wet faster and have better wetting force than alloys with higher silver loads.



Wetting Curves

Testing for Maximum Wetting Time &Force

	RMA Flux	No Clean Flux	OA Flux
1% Ag	fair 	best 	good 
2.5% Ag	best 	good 	best 
3.5% Ag	good 	fair 	good 

Copper Dissolution Rates

Copper is dissolved into Sn/Ag/Cu/Sb at a slower rate than Sn/Pb, Sn/Ag, and Sn/Cu, which is a benefit for wave soldering operations.

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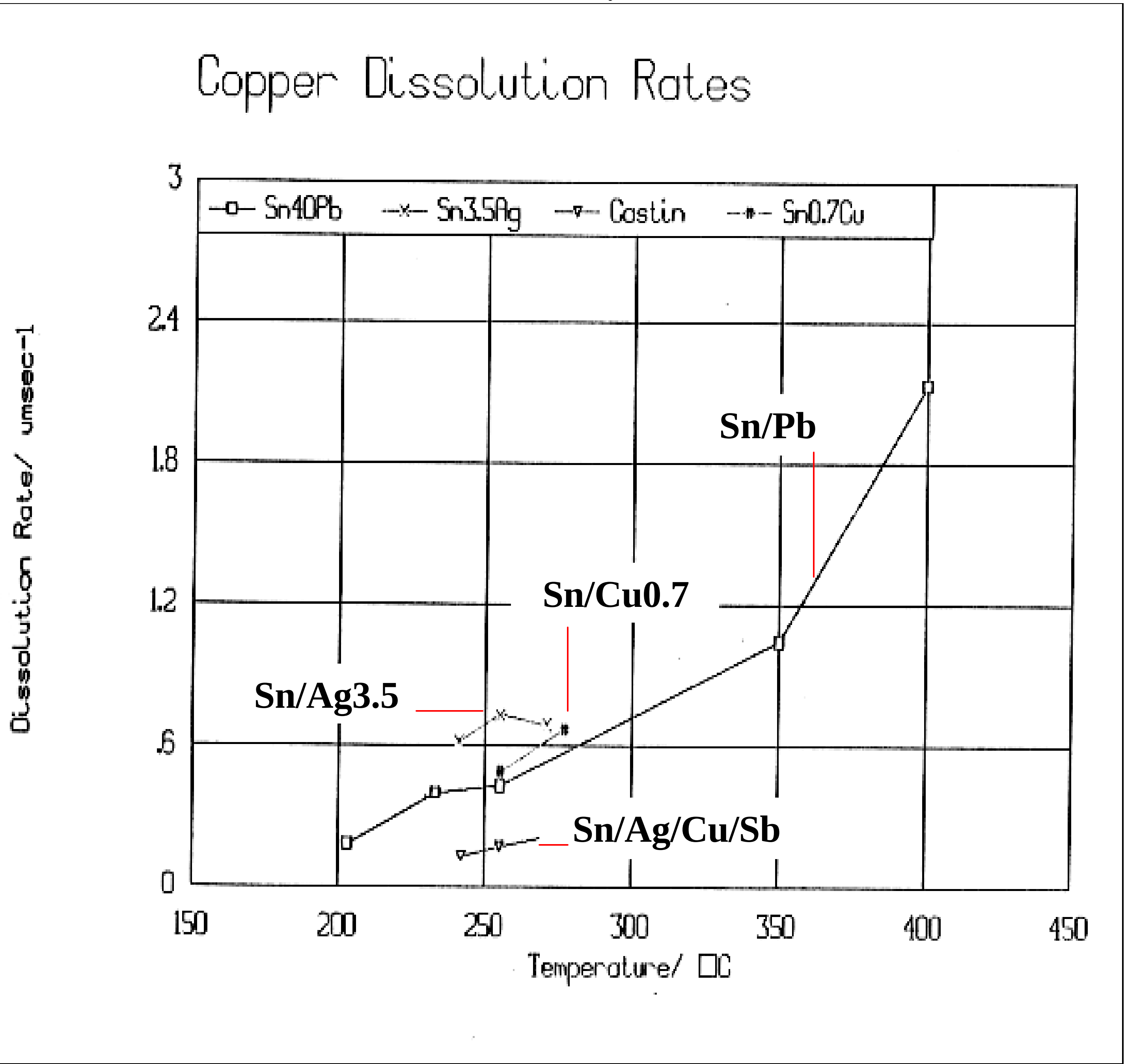
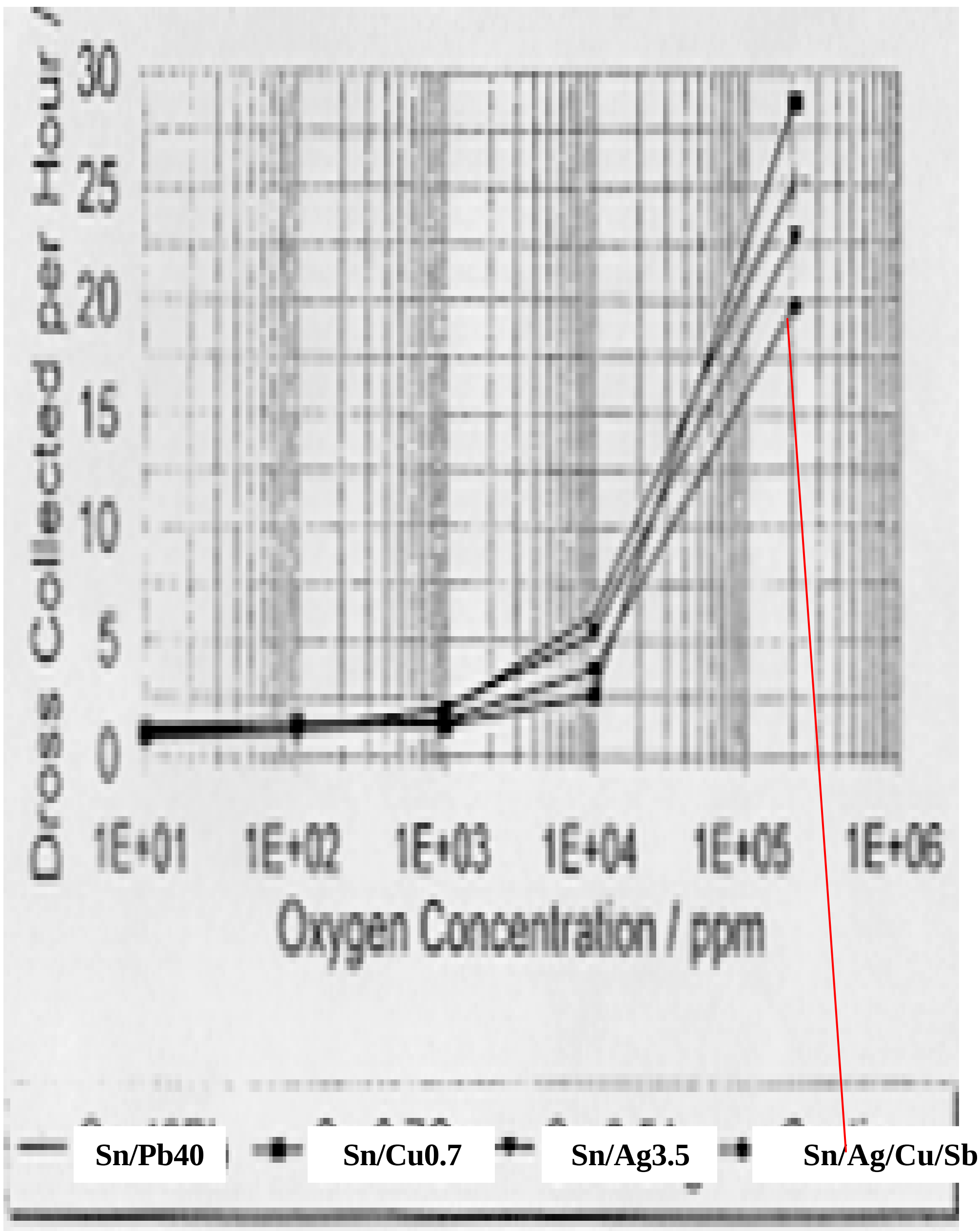


Drossing Rates

Sn/Ag/Cu/Sb drosses at a slower rate than Sn/Pb, Sn/Ag, and Sn/Cu.



Per ITRI Testing

Alloy Price

Sn/Ag/Cu/Sb	Sn96/Ag4 & Sn/Ag4/Cu
$4.58/lb	$5.67/lb
Sn62/Pb36/Ag2	Sn63/Pb37
$3.31/lb	$1.78/lb

- U.S. Dollars, Based on raw cost of metals

Opportunities for Cost Reductions

- Disposal expenses reduced
- Less dross- especially with Sn/Ag/Cu/Sb
- Higher dross reclaim value
- Volume- More joints per weight with Pb-Frees

Alloy	Density	% Difference
Sn63/Pb37	8.79 g/cm^3 (.3177 lb/in^3)	N/A
Sn/Ag/Cu/Sb	7.39 g/cm^3 (.2669 lb/in^3)	15.96%
Sn/Ag	7.41 g/cm^3 (.2678 lb/in^3)	15.71%
Sn/Cu	7.31 g/cm^3 (.2641 lb/in^3)	16.86%

- For additional information, please see “Can You Imagine? Paying More Brings Cost Savings”, by Vincent Corsaro of AT&T

Lead-Free Solder Forms

- Lead-Free Solders are available in:
  - Solder Paste
  - Bar Solder
  - Solid Wire Solder
  - Cored Wire Solder *
  - Solder Preforms*

    - * Many bismuth and indium bearing alloys are not available in cored wire and some preform shapes due to production limitations associated with brittleness and poor thermal fatigue properties.

Sn/Ag/Cu/Sb Availability

- Sn/Ag/Cu/Sb has been recognized within the solder industry as a viable lead-free alternative.

- Sn/Ag/Cu/Sb has been licensed to and is available from the following companies:
  - Bow Solders
  - Cookson Group
    - Alpha Metals
    - Fry Technologies
    - Witmetaal B.V.
  - Indium Corporation
  - Koki Company
  - Nihon Handa Company
  - Senju Metal Industry

Conclusion

- Eventually lead will be eliminated from soldering.
- When implementing the use of a lead-free solder, certain criteria have to be met.
- Many ongoing and completed studies and industry groups suggest that the Sn/Cu/Ag based alloys offer the most viable replacement to Sn/Pb alloys for the majority of applications.
- In addition, Sn/Cu/Ag alloys that are doped with Sb prove to have several advantages.
- These alloys offer several advantages in terms of melting temperature, physical properties, compatibility with current processes, availability, and price.
- Component tinning, bare board coating, surface mount assembly, wave and hand soldering all are achievable with the proper understanding of lead-free alloys and processes.

THANK YOU

- For additional information, please contact the AIM Technical Department, tel: 401-463-5605, fax: 401-463-0203, or find us on the web at www.aimsolder.com