(ISMP 2003, Sept 24-25, Seoul, Korea)

Lead-Free Solders and Processing Issues Relevant to Microelectronics

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Recent Development

European Union passed two directives on 10/11/2002;

- **WEEE (Waste Electrical & Electronic Equip) for recycling, recovery, reuse by product producers**
- **RoHS (Restriction of Hazardous Substances), ban on 4 heavy elements (Pb, Cd, Hg, hex Cr) and brominated flame retardants (PBB and PBDE) from July 1st, 2006.**
- **The WEEE and RoHS Directives became European law on 2/13/03, and member states now have to implement them by 8/13/2004.**

(5/03, SKK)

Candidate Pb-free Solder Alloy Systems for Electronics Applications

- Sn-Ag System
  - Sn-3.5Ag, eutectic alloy (mp ~ 221°C),
  - Sn-3.5Ag-3.0Bi, non-eutectic (210 ~ 215°C),
  - Sn-Ag-Cu, near-ternary eutectic alloys (mp ~ 217°C)

- Sn-Cu System
  - Sn-0.7Cu, eutectic alloy (mp ~ 227°C)

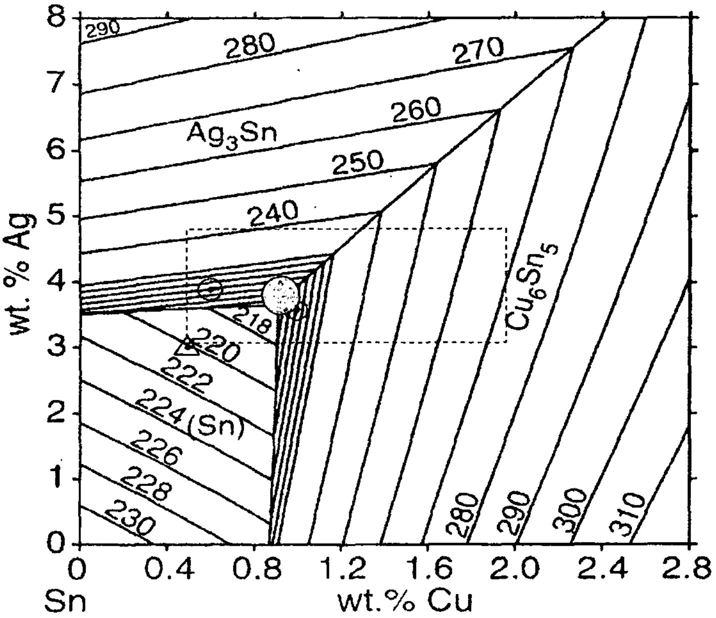
- Sn-Zn System
  - Sn-9.0Zn, eutectic alloy (mp ~198°C),
  - Sn-8.0Zn-3.0Bi, non-eutectic (190 ~ 197°C)

Sn-Ag-Cu System

- The Near-Ternary-Eutectic Sn-Ag-Cu System Becoming Clear Choice for Second Level Assembly
- The Ternary Eutectic Composition (wt.%) : m.p. ~ 217°C
  - Sn-3.5Ag-0.9Cu
    - Moon, et. al., J. Elec, Mat, 29, 1122 (2000)
    - Loomans and Fine, Metall. Mater. Trans. 31A, 1155, (2000)
  - Sn-3.24Ag -0.57Cu
    - Ohnuma, et. al., J. of Elec. Mater. 29, 1137 (2000)

- Commercial SAC Alloys:
  - Sn-4.7Ag-1.7Cu, Broad Patent on Sn-Ag-Cu Alloy System
  - Sn-3.8Ag-0.7Cu, US Comm Alloy / Europ IDEALS Consortium
  - Sn-4.0Ag-0.5Cu, US Commercial Alloy
  - Sn-3.9Ag-0.6Cu, NEMI Consortium Alloy
  - Sn-3.0Ag-0.5Cu, Japanese Comm / Consortia Alloy Choice

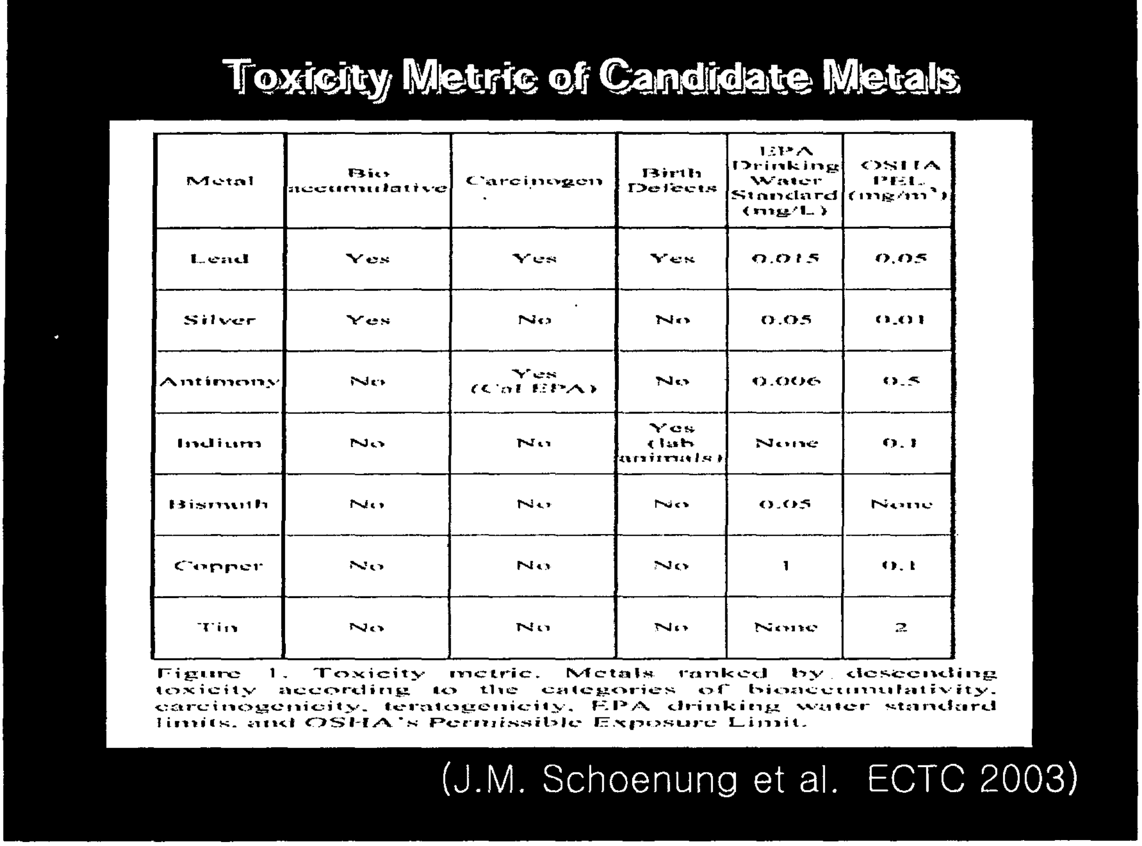
Sn-Ag-Cu Ternary Phase Diagram



(I.Anderson, et al, TMS 2002)

Selected Issues Related to Sn-Ag-Cu Alloys

- Toxicity, Availability and Impacts of Extraction
- Alloy Composition and Optimization
- Microstructure and Properties
- Solidification and Undercooling
- Control of Ag3Sn Plate Formation
- Thermomechanical Fatigue
- Creep Deformation
- Tin Pest (transformation to gray tin)
- Tin Whisker Growth on Surface Finish
- Interfacial Reactions and UBM
- Electromigration in Flip Chip Joints

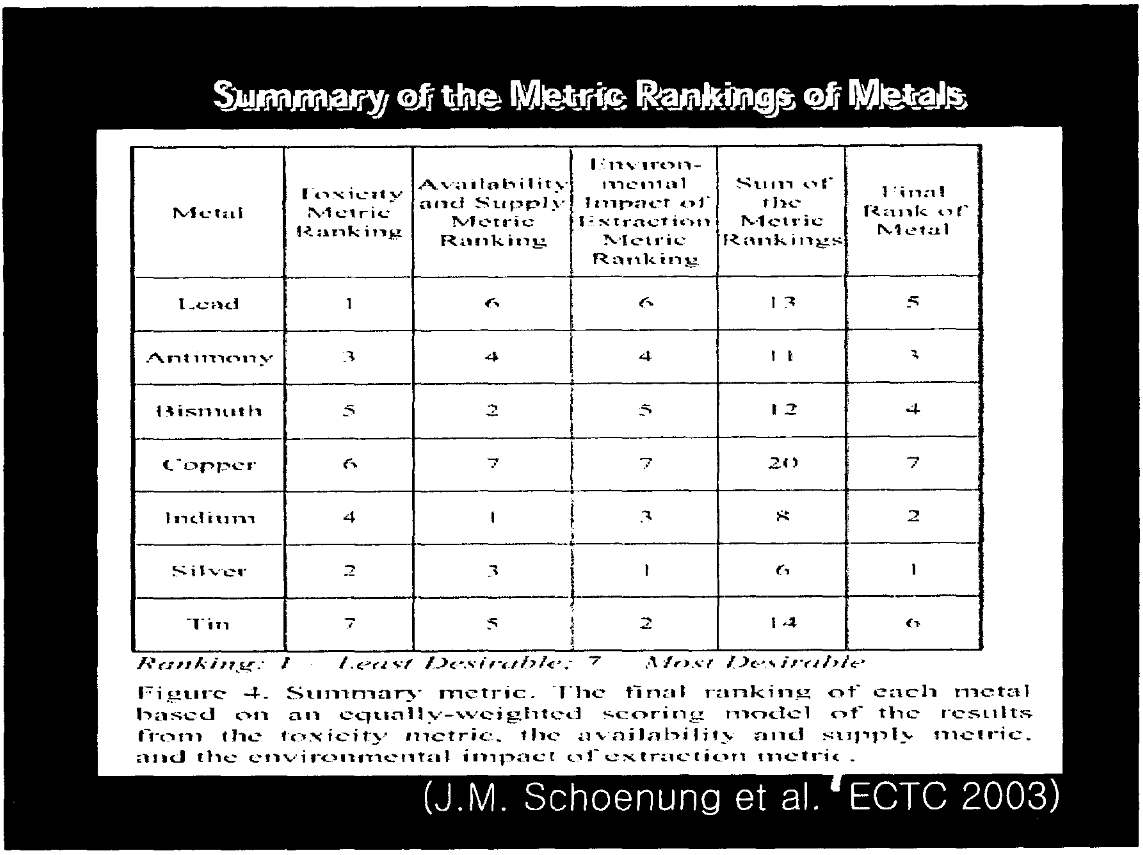


Toxicity Metric of Candidate Metals

Metal	Bio accumulative	Carcinogen	Birth Defects	EPA Drinking Water Standard (mg/L)	OSHA PEL (mg/m³)
Lead	Yes	Yes	Yes	0.015	0.05
Silver	Yes	No	No	0.05	0.01
Antimony	No	Yes (Cal EPA)	No	0.006	0.5
Indium	No	No	Yes (lab animals)	None	0.1
Bismuth	No	No	No	0.05	None
Copper	No	No	No	1	0.1
Tin	No	No	No	None	2

Figure 1. Toxicity metric. Metals ranked by descending toxicity according to the categories of bioaccumulativity, carcinogenicity, teratogenicity, EPA drinking water standard limits, and OSHA's Permissible Exposure Limit.

(J.M. Schoenung et al. ECTC 2003)



Summary of the Metric Rankings of Metals

Metal	Toxicity Metric Ranking	Availability and Supply Metric Ranking	Environmental Impact of Extraction Metric Ranking	Sum of the Metric Rankings	Final Rank of Metal
Lead	1	6	6	13	5
Antimony	3	4	4	11	3
Bismuth	5	2	5	12	4
Copper	6	7	7	20	7
Indium	4	1	3	8	2
Silver	2	3	1	6	1
Tin	7	5	2	14	6

Ranking: 1 Least Desirable; 7 Most Desirable

Figure 4. Summary metric. The final ranking of each metal based on an equally-weighted scoring model of the results from the toxicity metric, the availability and supply metric, and the environmental impact of extraction metric.

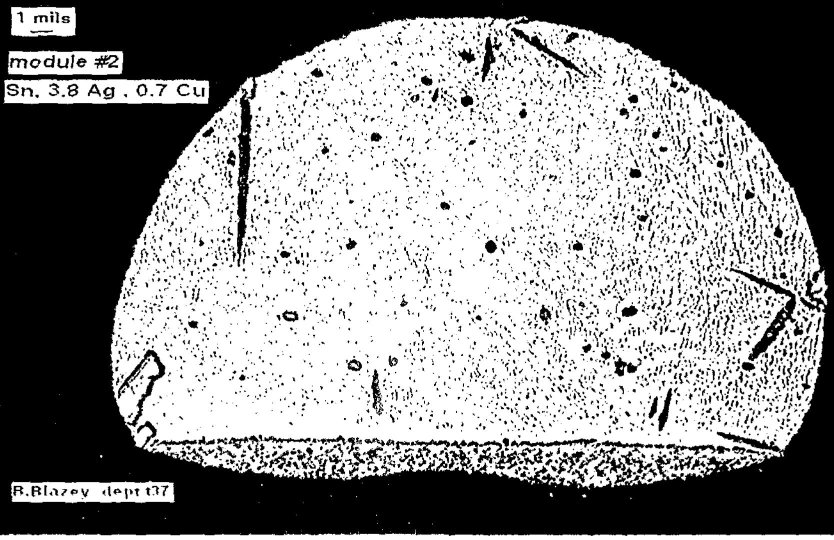
(J.M. Schoenung et al. ECTC 2003)

Microstructure of Sn-Ag-Cu Alloys

- Ternary Eutectic Phases; β-Sn, Ag_3Sn, Cu_6Sn_5
  (232°C, 480°C, 415°C)
- Large, Pro-eutectic Ag_3Sn Plate Formation
- Undercooling during Solidification
- Cooling Rate Effects on Microstructure
- Crack Propagation along Ag_3Sn Plate Interface
- Mechanical Properties vs Cooling Rate

Near Eutectic Sn-Ag-Cu Solidified Microstructure

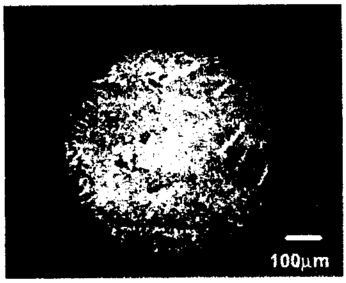
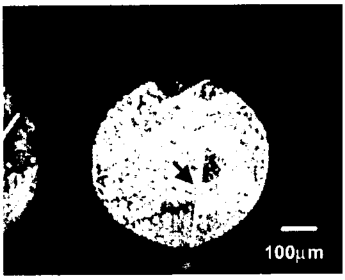
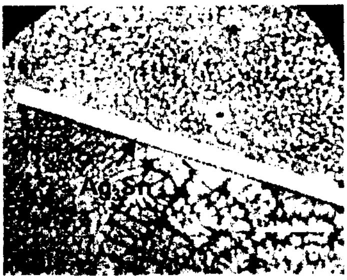
As Solidified BGA Solder Ball



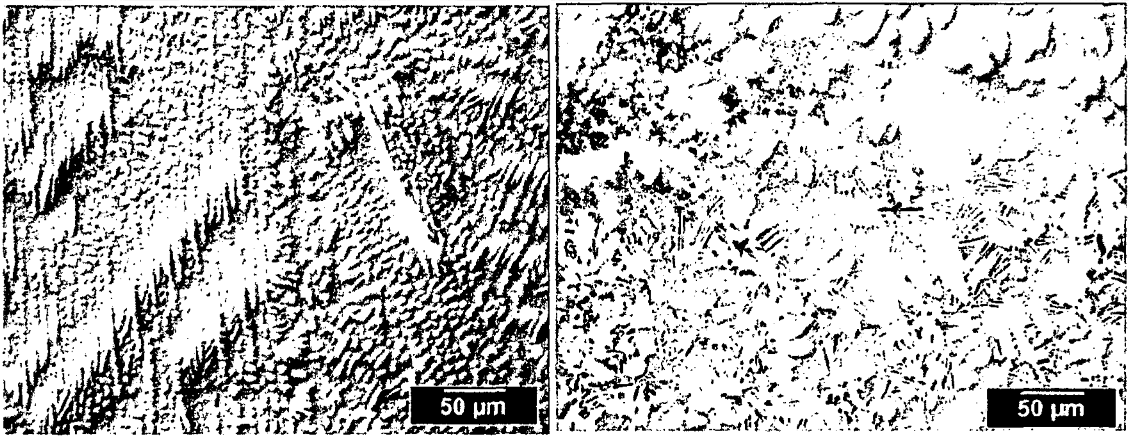
Near Eutectic Sn-Ag-Cu Solidified Microstructure

Cooling Rate Effects

- Sn-3.8Ag-0.7Cu

As-Received		
0.02 °C/sec cooled		

As-cast Microstructure of Sn-3.8Ag-0.7Cu

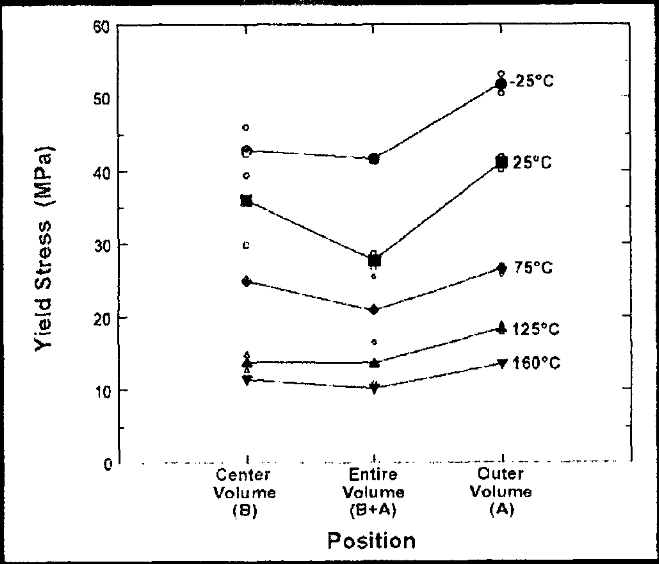


Outer radial surface

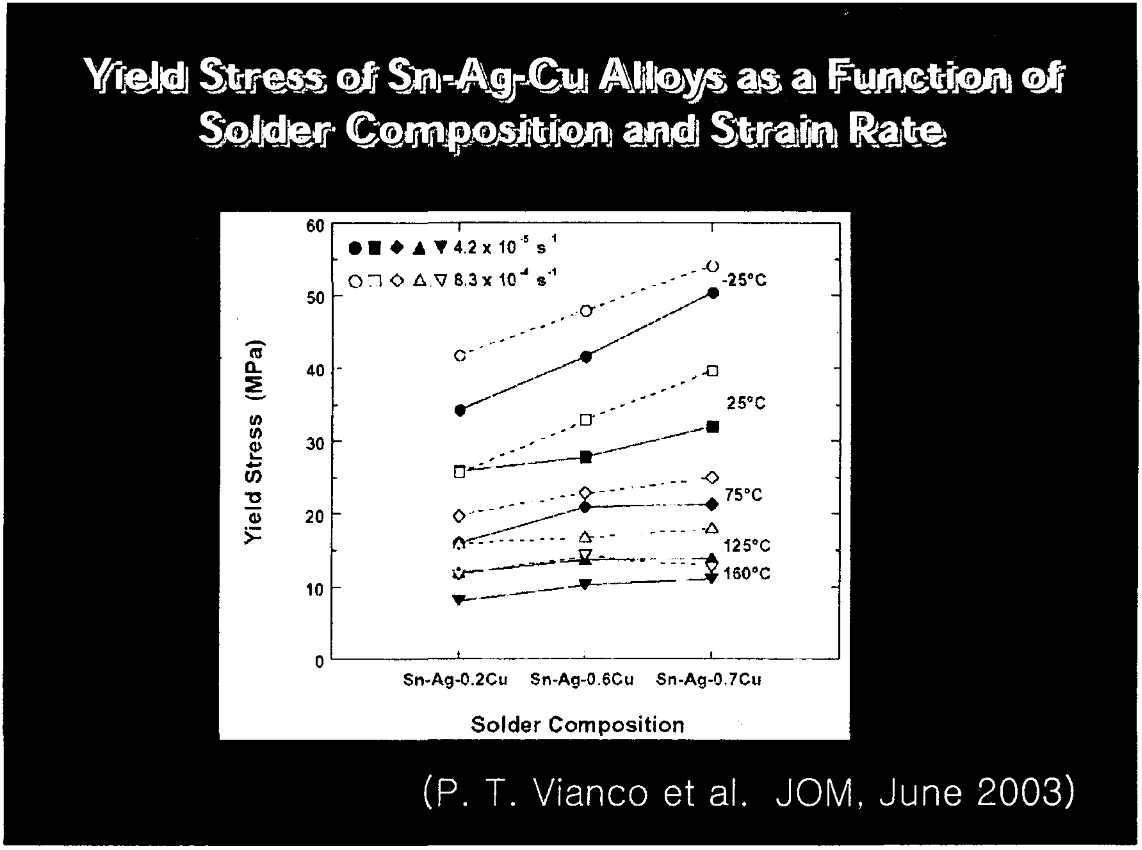
Center location

(P. T. Vianco et al. JOM, June 2003)

Yield Stress of Sn-3.9Ag-0.6Cu as a Function of Sample Position (strain rate = 4.2x10-5/s)

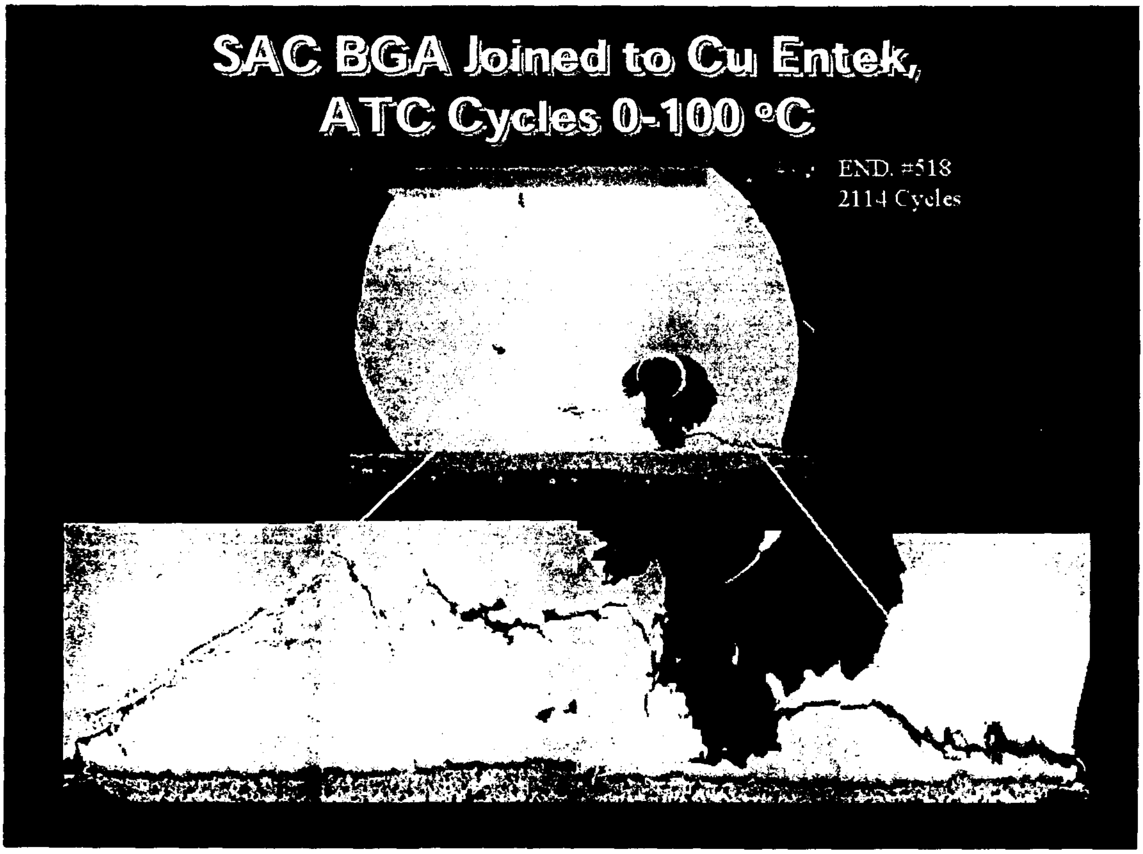


(P. T. Vianco et al. JOM, June 2003)



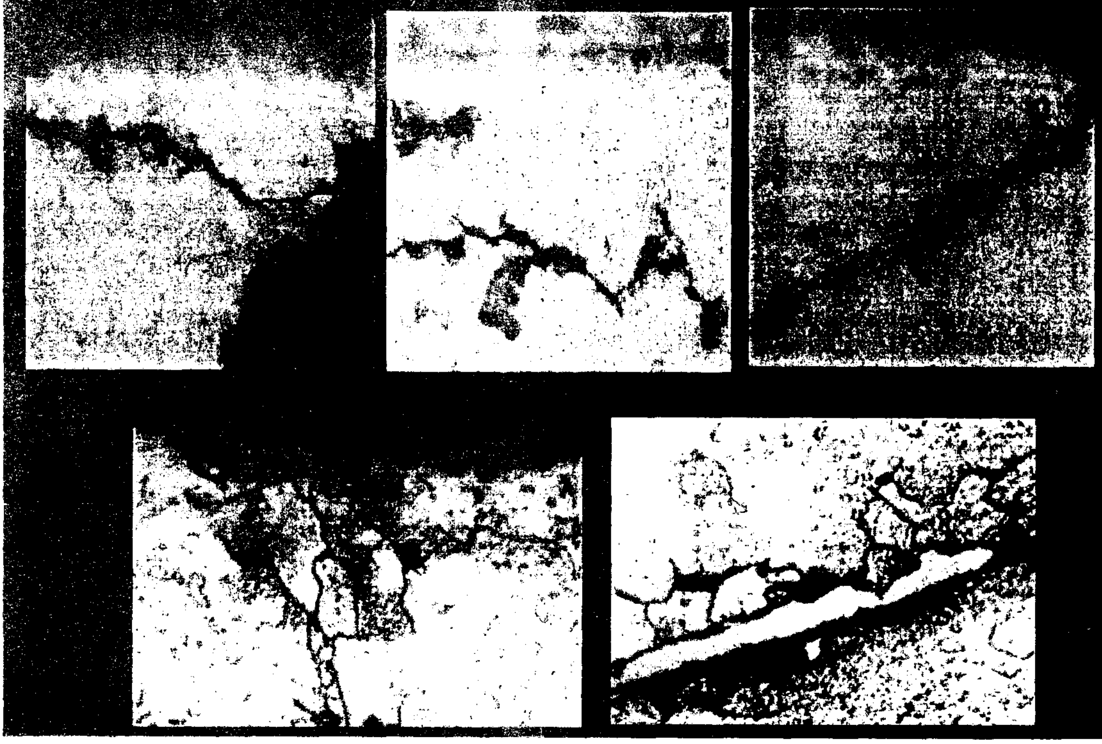
Yield Stress of Sn-Ag-Cu Alloys as a Function of Solder Composition and Strain Rate

(P. T. Vianco et al. JOM, June 2003)



SAC BGA Joined to Cu Entek, ATC Cycles 0-100 °C

SAC BGA Joined to Cu Entek, ATC Cylcles 0-100°C

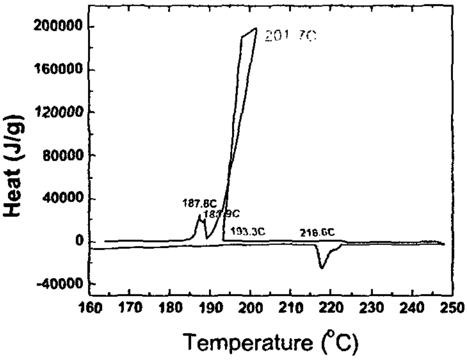


Undercooling of Solders

- Heating at a rate of 1°C/min
- Cooling at a rate of 6°C/min after holding at 250°C for 10 min.

	Melting Temp. during Heating (T_1)	Peak1 during Cooling	Peak2 during Cooling (T_2)	$\Delta T(T_1\text{-}T_2)$
Sn3.8Ag0.7Cu	216.9	209.9	188.3	28.6
Sn3.4Ag0.9Cu	217.0	200.9	199.0	18
Sn3.0Ag0.9Cu	216.8	205.7	194.9	21.9
Sn2.5Ag0.9Cu	216.8	204.1	182.5	34.3
Sn2.0Ag0.9Cu	216.9	208.3	187.6	29.3
Sn2.3Ag 0.43Cu0.19Bi	216.6		193.3	23.3
Sn8Zn3Bi	193.7		191.8	1.9

DSC of SACB

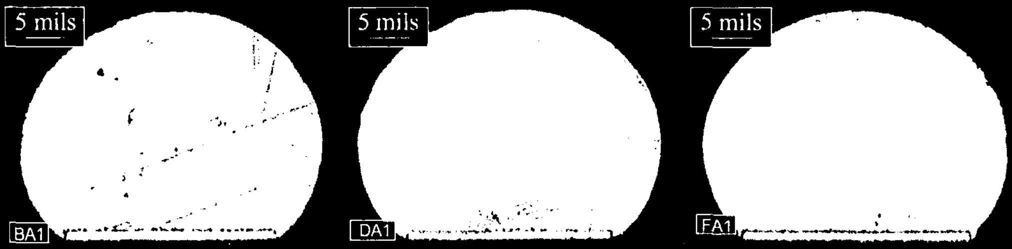


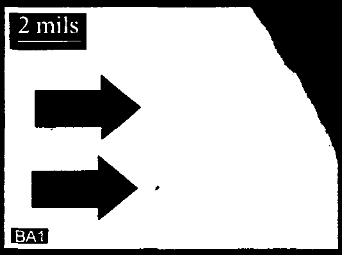
Control of Ag3Sn Plate Formation

❖ **Three Methods to Suppress Ag_3Sn Plates;**

1) Cooling rate control (>2C/s)
2) Modifying alloy composition (reduce Ag & Cu)
3) Reducing undercooling by adding minor alloying elements

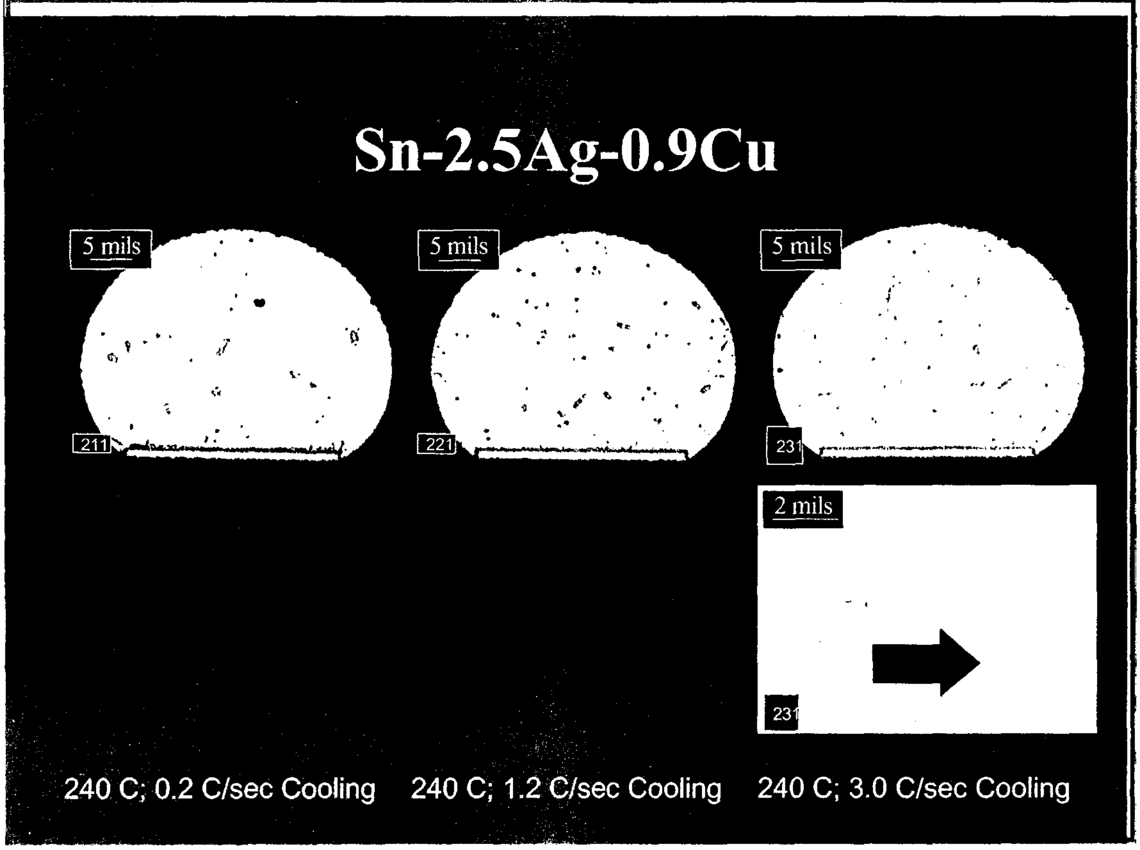
Ag_3Sn Plate Formation and Cooling Rate





(Sn-3.8Ag-0.7Cu)

240 C; 0.2 C/sec Cooling   240 C; 1.2 C/sec Cooling   240 C; 3.0 C/sec Cooling



Sn-2.5Ag-0.9Cu

240 C; 0.2 C/sec Cooling 240 C; 1.2 C/sec Cooling 240 C; 3.0 C/sec Cooling

Controlling Ag_3Sn Plates

Variable	Solder Composition	Solder Type	# of Big Ag_3Sn Plates Observed (cooling at 0.02C/s)
Reducing **Cu** content	Sn3.8Ag0.7Cu	As Cast	Yes
	Sn3.8Ag0.35Cu	As Cast	Yes
	Sn3.5Ag0Cu	As Cast	Few
Reducing **Ag** content	Sn3.8Ag0.7Cu	BGA ball	76/100
	Sn3.4Ag0.9Cu	BGA ball	5/100, 10/100
	Sn3.0Ag0.9Cu	BGA ball	6/100, 3/100
	Sn2.5Ag0.9Cu	BGA ball	1/100, 0/100
	Sn2.0Ag0.9Cu	BGA ball	0/100, 0/100
	Sn2.3Ag0.4CuBi	BGA ball	0/100
Replacing Cu with **Bi**	Sn3.8Ag0.7Cu	BGA ball	Yes
	Sn3.5Ag3.0Bi	BGA ball	Yes
	Sn3.5Ag	BGA ball	Few

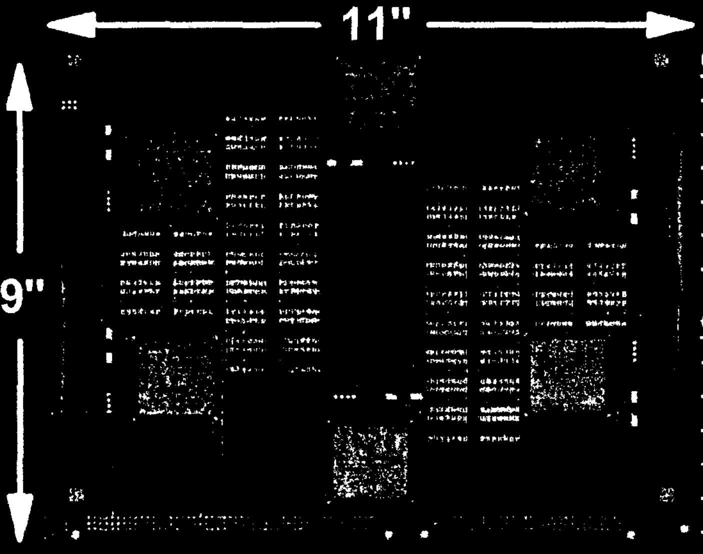
Plan for Reliability Test

- Solder Alloys to be tested
  - Sn-3.8Ag-0.7Cu (control)
  - Sn-2.3Ag-0.4Cu-0.2Bi (optimized alloy)
  - Sn-2.7Ag-0.7Cu (intermediate Ag)
  - Sn-2.3Ag-0.9Cu (low Ag, w/o Bi)

- Assembly cooling rates; 0.5 vs. 1.5°C/s
- Test vehicles; ceramic modules on organic card
- ATC test matrix
  - 0 to 100°C, -40 to 125°C, -40 to 60°C, 25 to 125°C
  - Cycle times; 30, 60, 240 min

(3/03, SKK)

Test Vehicle Construction

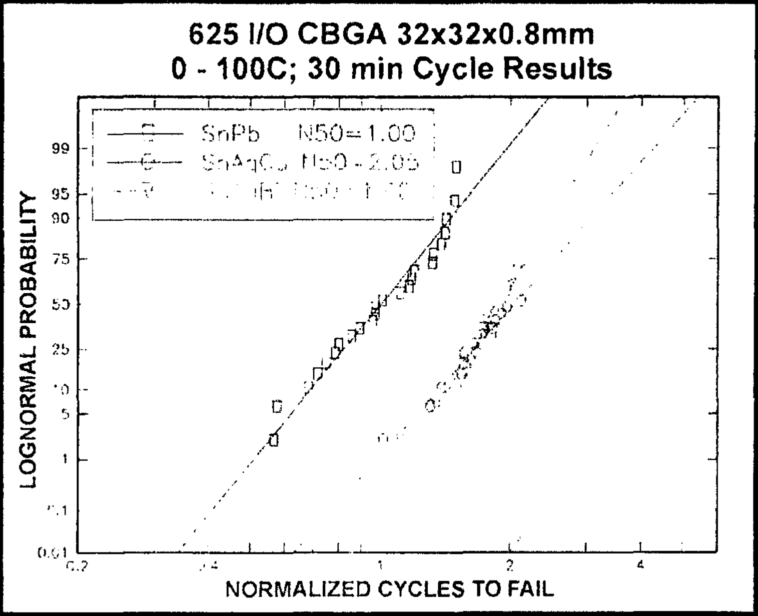


Card:
- 62 mil thick, 4s4p
- 6 CBGA sites
- 29 mil diameter pads
- OSP Cu surface finish
- Mid Tg FR-4
- CTE 19 ppm/°C

Ceramic Module:
- 32x32x0.8mm body
- 1.27mm BGA pitch
- 35 mil BGA balls
- 34 mil diameter pads
- Ni/Au surface finish
- CTE 6 ppm/°C

IBM (J. Bartelo et al, APEX 2001)

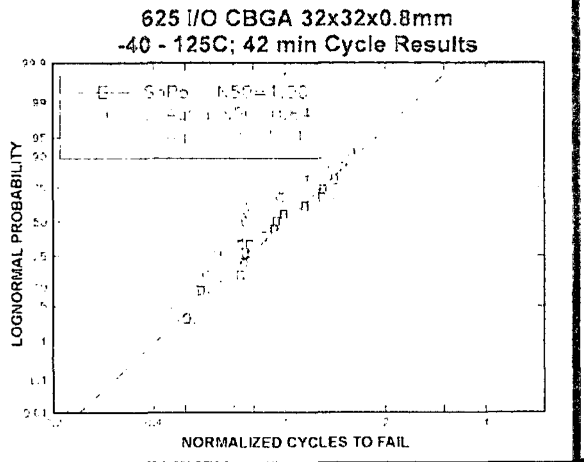
0 to 100°C, 30 min Cycle

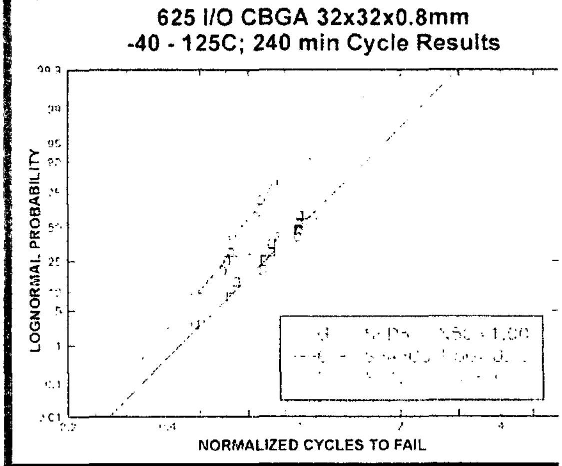

625 I/O CBGA 32x32x0.8mm
0 - 100C; 30 min Cycle Results

IBM

(J. Bartelo et al, APEX 2001)

-40 to 125°C, 42 & 240 min Cycles

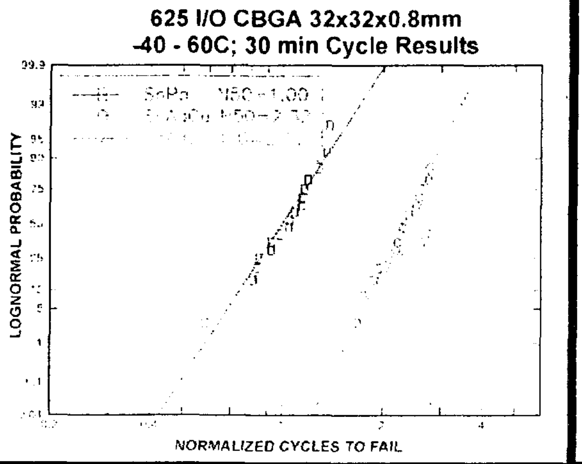

625 I/O CBGA 32x32x0.8mm
-40 - 125C; 42 min Cycle Results

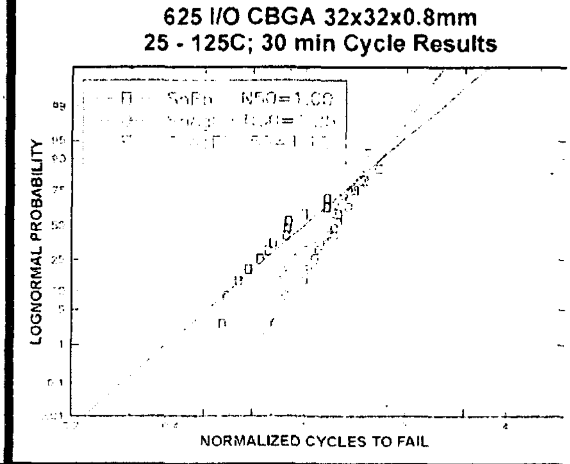

625 I/O CBGA 32x32x0.8mm
-40 - 125C; 240 min Cycle Results

IBM

(J. Bartelo et al, APEX 2001)

-40 to 60°C & 25 to 125°C, 30 min Cycle

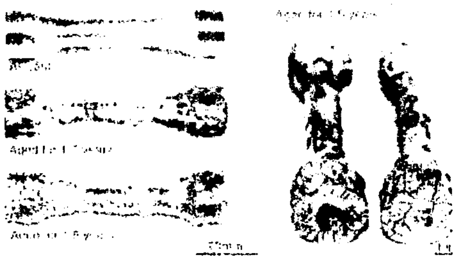

625 I/O CBGA 32x32x0.8mm
-40 - 60C; 30 min Cycle Results

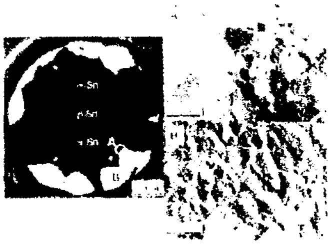

625 I/O CBGA 32x32x0.8mm
25 - 125C; 30 min Cycle Results

IBM

(J. Bartelo et al, APEX 2001)

Tin Pest



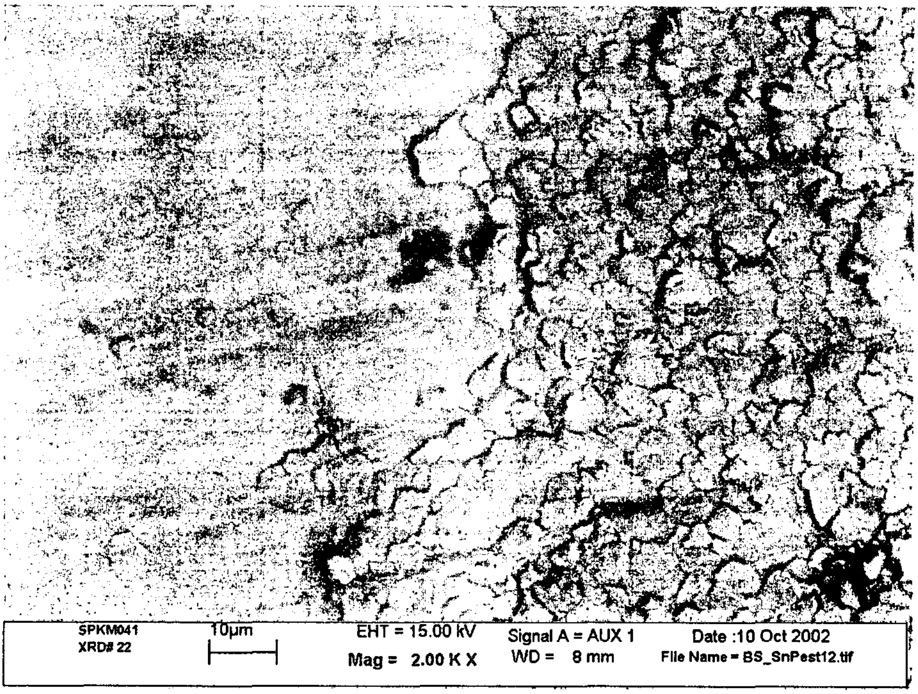


255K, 1.5 yr

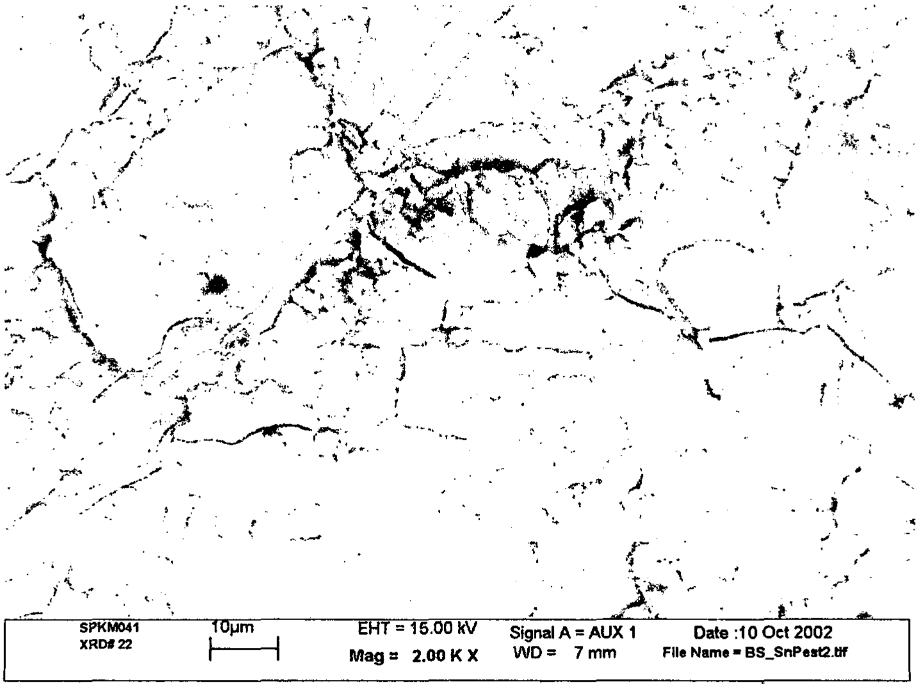
Sn-0.5 wt% Cu,
aged at 255K for 1.5 and 1.8 yr

(Y. Kariya, et al. JOM, June 2001)

Bulk Sn-0.7Cu Stored at -40°C(5 mon), -15°C(5 mon)



Bulk Sn-0.7Cu Stored at -40°C(5 mon), -15°C(5 mon)



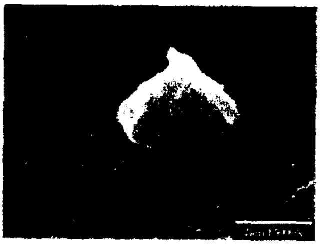
Allotropic Transformation of Tin (Sn Pest)

- Sn pest was reported by Y. Kariya, et al, in Sn-0.5%Cu alloy after aging at 255K for 1.5 yr, (JOM, June 2001, p.39).
- Allotropic transformation of white Sn (β-Sn, tetragonal) to gray tin (α-Sn, cubic) at temp below 13C to form Sn pest.
- Confirmed in this experiment with Sn-0.7%Cu bulk alloy stored at –40C for 5 months.
- X-ray diffraction analysis on Sn pest confirmed the cubic phase of gray tin.
- SEM analysis revealed the boundary between the virgin and transformed area, and the broken surface and microcracks due to the volume expansion associated with the transformation.

(3/03, SKK)

Whisker Types


Column


Hillock


Flower or OSE

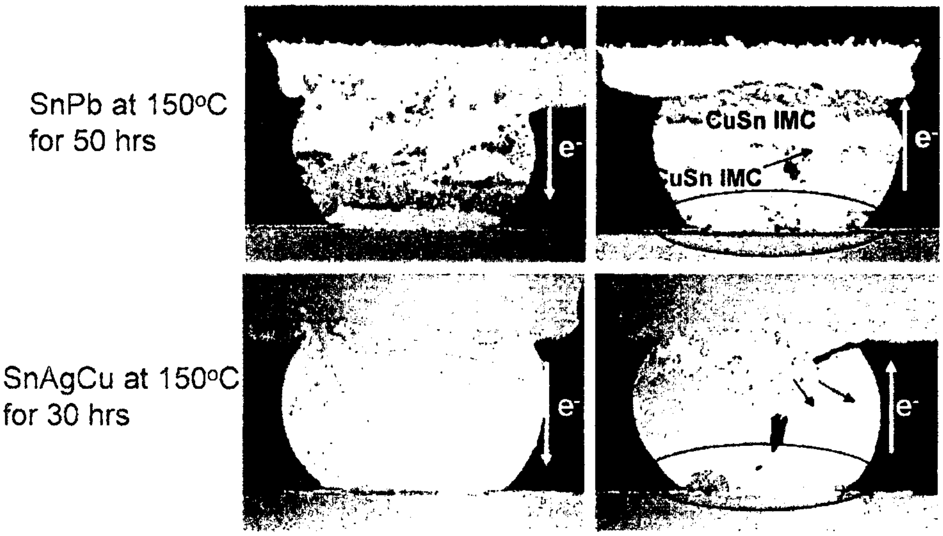

Needle


Needle growing out of hillock


Needle growing out of OSE

SEM photos – courtesy of P. Bush, SUNY at Buffalo

Electromigration at high current (3A = 5.1 × 10^4 A/cm^2)



- UBM is missing when die side is a cathode

J. K. Lin et al
ECTC 2003

Digital DNA
from Motorol

Summary

- ➢ European Union bans the usage of Pb in electronics from July 1st, 2006.
- ➢ The Near-eutectic Sn-Ag-Cu alloys are the leading candidate Pb-free solders (for SMT card assembly).
- ➢ The microstructure of Sn-Ag-Cu alloys is discussed in terms of solidification, composition and cooling rate.
- ➢ Methods of controlling Ag3Sn plates are discussed.
- ➢ Thermo-mechanical fatigue behaviors of Sn-Ag-Cu solder joints are reviewed.
- ➢ Tin pest, whisker growth, electromigration of Pb-free solders are discussed.

(9/03, SKK)