# Review on the Lead-Free Solder Technology

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## *Outline*

- *World Wide Environmental Regulation Status*
- *World Wide Pb-free Activities*
- *Key items in Pb-free Technology*
- *Challenging of Pb-free materials*
  - *Solder ball/solder paste*
  - *Electroplating systems*
- *Examples of Pb-free solder developed*
- *Roadblocks for Pb-free Transition*
- *Summary*

## Design for Environment (DFE)

- Materials of concern
  - → Reduction
  - → Elimination / substitution

- Design for disassembly and reuse
  - → Assembly technology and materials
  - → Reduction in number of materials used
  - → Reduction in use of coatings and other inseparable materials configurations

- Volume reduction
  - → Manufacturing
  - → Products (EOL disposition)

## Pending Legislation in Europe

- European Parliament adopted the proposal of Restriction on Hazardous Substances (RoHS)/WEEE on May 15, 2001
- RoHS bans cover:
  *Lead, Mercury, Cadmium & Hex. Chromium*
  *PBB and PBDE fire retardants*
- Proposed implementation: January 2006
- Lead is the most frequently used metal on the list
  - → *At least 200,000 electronic products and at least 200,000 sub-assemblies will be affected –but mission critical*
- A limited number of exemptions
  - → *Lead contained in high melting temperature type solder*
  - → *Lead in glass in electronic components*
  - → *Lead in piezoelectric devices*
  - → *Lead in servers, storage and storage, array systems, voice and data transmission and networking equipment*

## WSC Recommended Statement

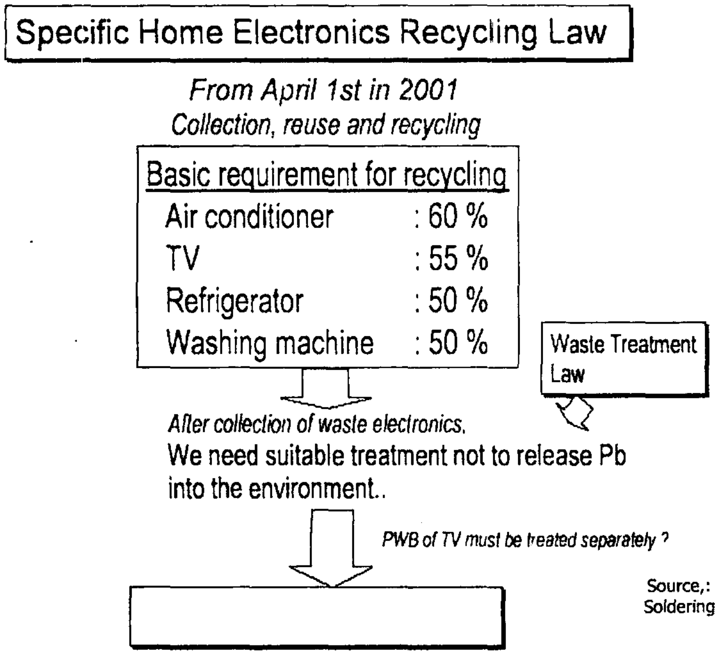
- Industry is working to develop lead free technology
- Development of "lead free" compatible components is a massive effort
- Industry must work together to establish standards
- Converting the industry to totally "lead free" products will take many years – and for some products may not be possible
- EU timescale is very aggressive for total product & industry conversion
- Exemptions will be required to assure product reliability for consumers
- We must also be clear with governments that "lead free" products have lead free solder paste, may or may not have lead free components

*From 5th World Semiconductor Council Meeting held in Okinawa, May 2001*

## World Wide Environmental Regulation

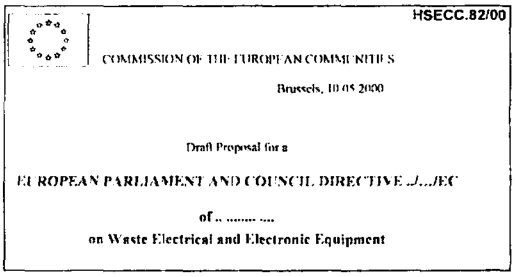
- OECD tightens regulation for Pb concentration in subterranean water (0.025mg/L from 2000)
- Denmark - Ban on usage of Pb in metal or substance
  Statutory order No.1012 of Nov. 13, 2000, On Prohibition of import and marketing of Products containing LEAD.
- US EPA - TRI (Toxics Release Inventory) activated in 2001.
  Any company that uses 100 pounds of Pb must file an annual report to EPA.
- JAPAN
  MITI take-back legislation
  Appliance recycling bill in full force by April 2001
  *MITI (Ministry of International Trade and Industry)

# Appliance Recycling Bill




Source,: SEMI 2000 Current Lead-Free Soldering in Japan, Katsuaki Suganuma, ISIR, Osaka University

# Lead



HSECC.82/00

COMMISSION OF THE EUROPEAN COMMUNITIES

Brussels, 10.05.2000

Draft Proposal for a

EUROPEAN PARLIAMENT AND COUNCIL DIRECTIVE ../.../EC

of .. ....... ....

on Waste Electrical and Electronic Equipment

Lead can cause damage to both **the central and peripheral nervous systems of humans.** Effects on the endocrine system have also been observed. In addition, lead can have negative effects on **the blood system and the kidneys.**
**Lead accumulates in the environment and has high acute and chronic toxic effects on plants, animals and micro-organisms.**

Compare Risk Reduction Monograph No 1 Lead Background and national experience with reducing risk, OECD Paris 1993.

Under Council Directive 67/548/EEC on the classification and labelling of dangerous substances as amended lead compounds are classified:

OJ L 196, 16/08/1967, p. 1.

- R20/22 Harmful by inhalation and if swallowed
- R33 Danger of cumulative effects.

The relative importance of any single source of exposure is difficult to predict and will vary with geographic location, climate and local geochemistry. In any case, consumer electronics constitute 40% of lead found in landfills. The main concern in regard to the presence of lead in landfills is the potential for the lead to leach and contaminate drinking water supplies

# Recycling of WEEE

One of the main objectives of the present initiative is to increase the recycling of WEEE. In general, increased recycling saves resources and capacities of disposal, in particular landfill. In spite of the positive effects, the recovery operation might add to environmental pollution if the waste is not properly pre-treated.

Due to plastics containing **halogenated substances**, **both dioxins and furans** are generated as a consequence of recycling the metal content of WEEE. Halogenated substances contained in WEEE, in particular brominated flame retardants, are also of concern during the extrusion of plastics, which is part of the plastic recycling. **Due to the risk of generating dioxins and furans**, recyclers usually abstain from recycling flame retarded plastics from WEEE. In view of the lack of proper identification of plastic containing flame retardents and inherent difficulty to distinguish flame retardetretardant plastic from ordinary plastic most of the recyclers do not process any plastic from WEEE.

As an example, the case of the metal reclamation plant Brixlegg/Austria (Comparison of PCDD/PCDF levels in soil, grass, cows milk, human blood and spruce needles in an area of PCDD/PCDF contamination through emissions from a metal reclamation plant Riss, Hagenmaier, Chemosphere, Vol 21, no.12, ppVol. 21, No 12, pp. 1451-1456, 1990.)1990). According to the report Brominated flame retardants Substance Flow Analysis and Assessment of Alternatives of the Danish EPA (1999), **no recycling activities are taking place for materials containing brominated flame retardants.**

Environmental problems during the recycling of WEEE are not only linked to halogenated substances. **Hazardous emissions to the air also result from the recycling of WEEE containing heavy metals, such as lead and cadmium.** These emissions could be significantly reduced through the substitution of the respective materials by less polluting substances in new electrical and electronic equipment and by means of proper pre-treatment of WEEE. Another problem with heavy metals and halogenated substances in untreated WEEE occurs during the shredding process. As in most cases WEEE is shredded without proper disassembly, hazardous substances, such as PCBs contained in capacitors, may be dispersed into the recovered metals and the shredder waste.

# Toxicology of Pb

- **Environmental, human healthy issue**
  - ➔ Pb poisoning 25 mg/dl (micrograms per deciliter)
  - ➔ The influence of Pb on the human body

    *It has been known for more than a hundred years that Pb affects the human nervous system and cause a range of serious problems. It is reported that the growth rate and intelligence of children that ingest Pb are adversely affected as a results*

- **Special industrial waste**
  - ➔ Waste products formed during the assembly of PCB (solder dross)
  - ➔ Disposal of electronic assemblies

# *When soldered Sn-Pb circuit boards are scrapped and buried*

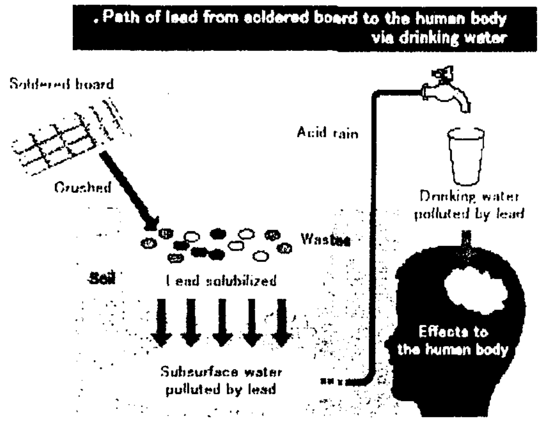
1) Acid rain gradually dissolves the Pb out of the solder

↓

2) The subsurface water the becomes polluted with Pb compounds

↓

3) The polluted subsurface water is taken into the human body as drinking water



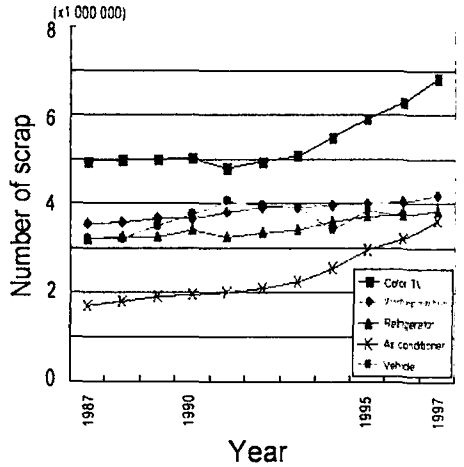

$$Pb + \frac{1}{2}O_2 \rightarrow PbO$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$ (acid rain)

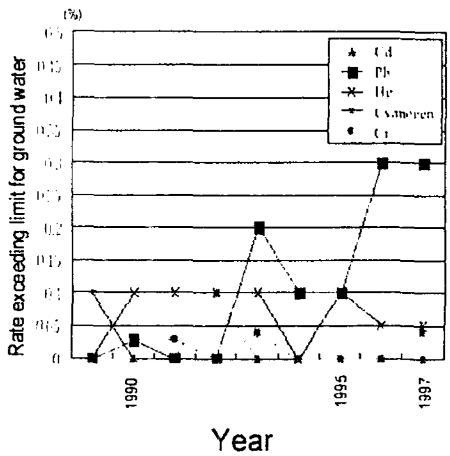
$$PbO + HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$ (acid rain)

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O$$

# *Electronics Waste and water pollution in Japan*




Number of home electronics scrap in the last 10 years in Japan.




Rate exceeding the limit for each toxic element in ground water in Japan.

*Source.: SEMI 2000 Current Lead-Free Soldering in Japan, Katsuaki Suganuma, ISIR, Osaka University*

# Worldwide Pb-free Activities

- *Japanese Pb-free Roadmap*

| | |
|---|---|
| 1999 | First adoption of Pb-free solders in mass-production goods |
| 2000 | Adoption of Pb-free components |
| | Adoption of Pb-free solders in wave soldering |
| 2001 | Expansion of use of Pb-free components |
| | Expansion of use of Pb-free solders in new products |
| 2002 | General use of Pb-free solders I new products |
| 2003 | Full use of Pb-free solders in all new products |
| 2005 | Pb-containing solder used only exceptionally. |

Source : *http://it.jeita.org/jp/jhistory/english/information/pbfree/roadmap.html*

# Worldwide Pb-free Activities

| | | |
|---|---|---|
| SONY | 2000/3 | Apply Pb-free solder to 1 item min. or each products field |
| | 2001/3 | Promote to apply Pb-free solder to all items produced in domestic factory |
| | 2002/3 | Apply Pb-free solder to all items produced in overseas factory |
| Fujitsu | 2000/10 | Make all LSI products Pb-free |
| | 2001/12 | Apply Pb-free solder to half of PCB used in set-products |
| | 2002/12 | Abolish Pb from all products |
| Mitsubishi | 2001 | Promote reduction of Pb in products |
| | 2005 | Promote to abolish Pb in products |
| NEC | 2001/3 | 50% Pb solder usage of the 1997 level |
| | 2002/12 | None of Pb solder |

## *Japanese Electronics Manufacturing Roadmaps for Pb-free*

| Manufacturor | Target | Issues | Notes |
|---|---|---|---|
| Panasonic | ALL | 2001 | Major 4 products |
| | Compact MD<br>Cassette tape<br>Video Player | Oct. 1, 1998<br>Feb., 2000<br>1999 | Sn-Ag-Bi-In<br><br>Sn-Cu |
| Hitachi | Half of 1997<br>All | 1999<br>2001 | - |
| | Regrigeratyor | Oct. 1999 | Sn-Ag-Bi |
| NEC | Half of 1997 | 2002 | |
| | Note PC | Oct. 1999 | Sn-Zn-Bi |
| SONY | All | 2001 | - |
| | VCR | Mar. 20, 2000 | Sn-Ag-Cu-Bi |
| Toshiba | Mobile Phones | 2000 | |
| Mitsubishi | Half<br>All | 2004<br>2005 | Major 4 products |
| Fujitsu | All LSIs<br>Half of PWBs<br>All | Oct. 2000.<br>Dec. 2001<br>Dec. 2002 | http://www.fujitsu.co.jp |
| Automobile | Half<br>1/3 | 2000<br>2005 | Except for battery |

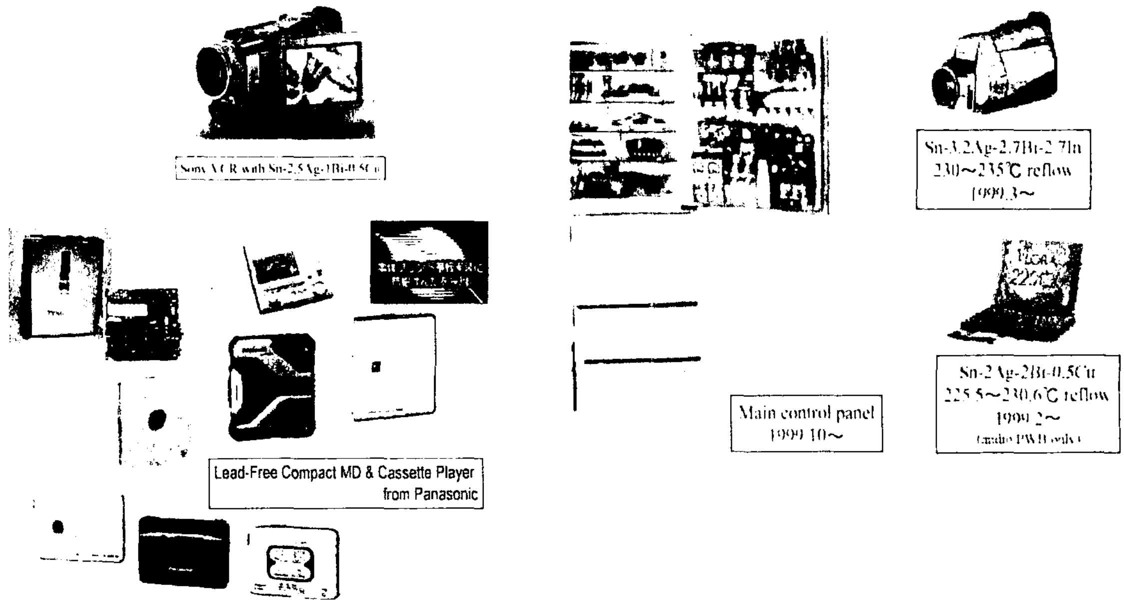
## *Japanese Electronics Manufacturing Roadmaps for Pb-free (Updated)*

| Company | Action | Target | Products |
|---|---|---|---|
| Panasonic | Complete abolition | March 2003 | Mini-disk player, stereo headphone |
| Sony | Full implementation in Japan | March 2001 | Camera, built-in VTR, TV, mini-disk player |
| | Start lead-free process overseas | March 2002 | |
| Hitachi | Full implementation for in-house evaluation | March 2002 | 8mm camera, notebook PC, washing machine |
| | Complete abolition, except overseas | March 2004 | |
| NEC | Complete abolition | End, 2002 | Pager, notebook |
| Mitsubishi | Establishment of lead-free technology | 2002 | Refrigerator |
| Electric | Reduction to half present use | 2004 | |
| | Complete abolition | 2005 | |
| Fujitsu | Reduction to half present use | End 2001 | PC, LCD, server |
| | Full-scale application | End 2002 | |
| Sanyo | Produce one lead-free product at each company | March 2001 | |
| | Implementation for main products produced in Japan | April 2002 | |
| Sharp | Implement for products produced in Japan | April 2001 | |
| | Implement for overseas production | April 2002 | |
| Seiko Epson | Complete abolition | End 2001 | |
| Car industry | Reduction to one-third present use, except battery | 2005 | |

Source: Electronic Times *http://www.electronictimes.com 2001/03/26*

**KAIST** **Phase Equilibria Lab.**

## Worldwide Pb-free Activities




## Worldwide Pb-free Activities

● *U S A*

IPC (*Institute of Interconnection, Packaging and Electronic Circuit*)'s Activity

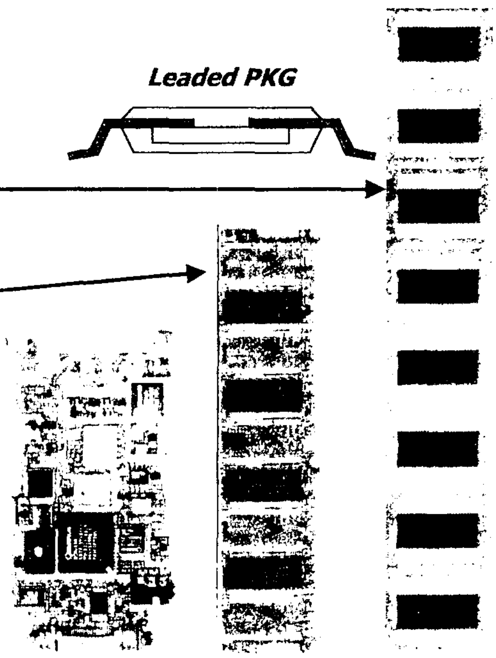
> **"The U.S. electronic interconnection industry, represented by the IPC, uses less than two percent of the world's annual lead consumption. Furthermore, all available scientific evidence and U.S. government reports indicate that the lead used in U.S. printed wiring board manufacturing and electronic assembly produces no significant environmental or health hazards.**
>
> **"Nonetheless, in the opinion of IPC, the pressure to eliminate lead in electronic interconnections will continue in the future from both the legislative and competitive sides. IPC encourages and supports research and development of lead-free materials and technologies. These new technologies should provide product integrity, performance and reliability equivalent to lead-containing products without introducing new environmental risks or health hazards.** ***IPC prefers global rather than regional solutions to this issue, and is encouraging a coordinated approach to the voluntary reduction or elimination of lead by the electronic interconnection industry."***

# Worldwide Pb-free Activities

- NCMS
  → *Pb-free solder project - 1997 , 4-year project, 70 Pb-free solders study*
- NEMI
  → *North America needs to prepare to deliver Pb-free products by 2001, with an "eye" for toal Pb elimination 2004.*
  → *Collaboration with groups such as EIA, IPC and JEDEC*
- HDPUG (*High Density Package User Group*)
- IDEAL (*Improved Design Life and Environmentally Aware manufacturing of Electronics Assemblies by Lead-free Soldering*)
- ITRI (*Tin Research Institutue*)
- INNOLOT (*Europe-Germany*)

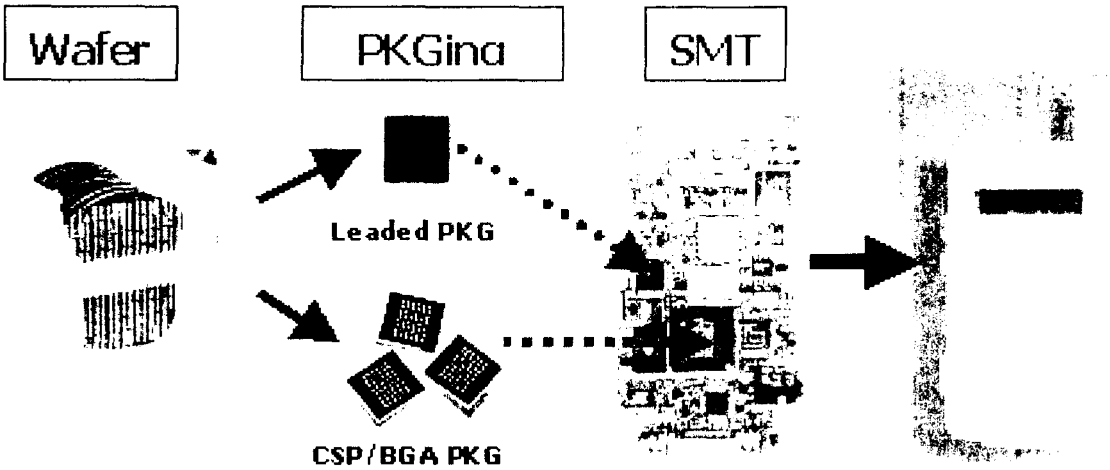
# Pb usage in Electronic Packaging

| | |
|---|---|
| Leaded Package | ● Electro plating materials for Leaded Package<br>- Lead frame metal: Alloy 42 / Cu alloy<br>- **present : SnPb (90:10)** |
| Set System PCB board Assembly | ● SMT (Surface Mounting Technology)<br>- solder paste<br>- present : **SnPbAg(62:36:2)** |
| μBGA & CSPs | ● Ball Mount for BGA/CSP<br>- **Solderball :**<br>**SnPb (63:37) or SnPbAg(62:36:2)** |

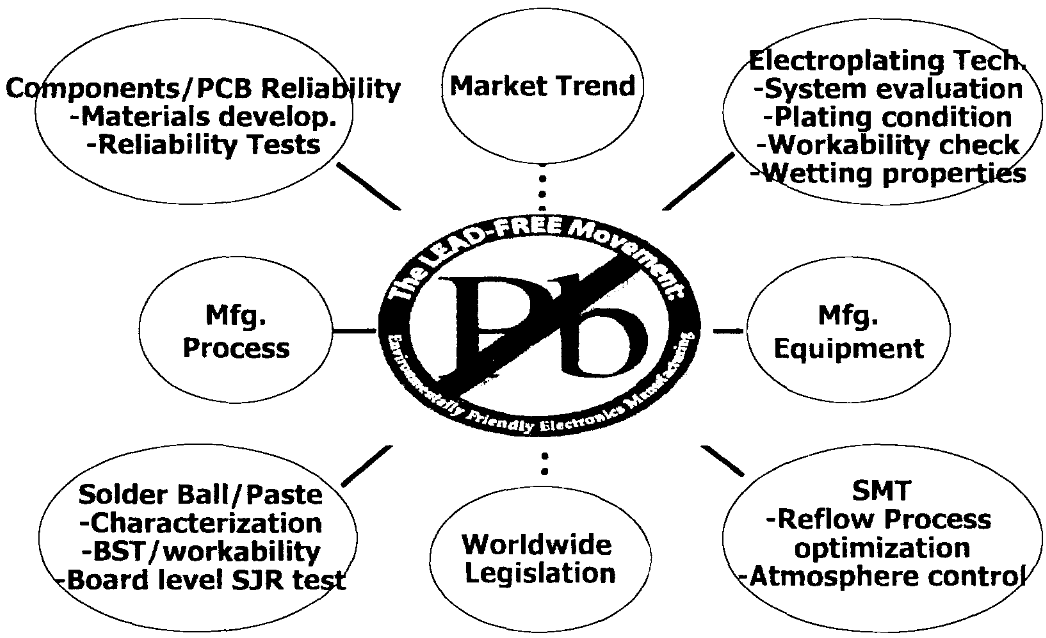




CellphonePCB DIMM Module Lead Package

## *Electronic Assembly*
## *= Electronic Packaging + SMT*



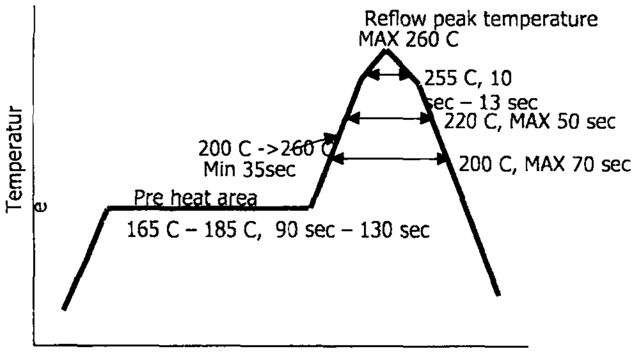

## *Key Issues in Pb-free Solder Technology*



## *Challenging Items in Pb-free Technology*

- **Alloy**
  - ➔ **Alloy section**
  - ➔ **Material Property Database generation.**
  - ➔ **Interface w/academia, gov't agencies.**
- **Components, PCBs**
  - ➔ **High temperature reflow**
  - ➔ **Pb-free terminations**
- **Solder Reliability**
  - ➔ **Transparent test procedure.**
  - ➔ **Common data to share with industry.**
- **Process Development**
  - ➔ **Generic process for Reliability test boards.**

## *Pb-free Reflow Profile for Anti-cracking of Package Evaluation*




| Reflow Profile Parameter | J-STE-020 Profile for Sn-Pb | NEMI Phase I test Profile for SnAgCu |
|---|---|---|
| Average Ramp Rate to MP | 2.5C/sec. Max. | 2.5-3.0C/sec. Max. |
| Preheat Temp | 125+/-25C | |
| Preheat Dwell | 60-120 sec. | |
| Time Above Liquidus | 60-150sec. | 80 sec. Min. |
| Duratio within 5C of peak Temp. | 10 - 20 sec. | |
| Peak Reflow Temp. | 220C(+5-0) | 255C(+5/-0) |
| Cool Down Rate | 6C/sec. | |

## *Challenging of Pb-free Materials*

- **Pb-free solder ball/ solder paste**
  - ➔ **SnAgCu** - *NEMI, NCMS etc.*
  - ➔ **SnAgCuBi** - *SONY (recently changed as SnAgCu)*
  - ➔ **SnZnX** - *under studying*

- **Electroplating Systems**
  - ➔ **PPF (Ni/Pd, Ni/Au)**
  - ➔ **Pure-Sn**
  - ➔ **SnBi** ; *most japanese companies are driving now*

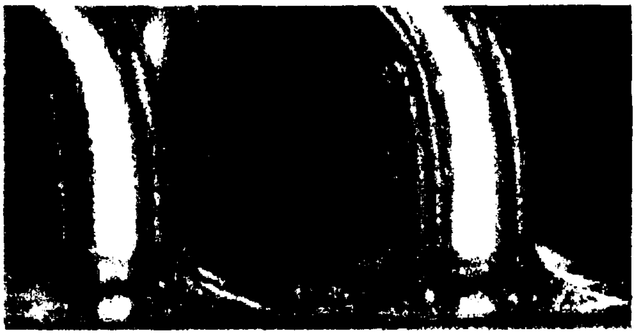
## *Consideration factor for Pb-free solders*

- **Melting behavior (Drop-In solution)**
- **Mechanical properties (Thermo Mechanical)**
- **Compatible with Pb-containing surface finishes**
- **Depletion of existing stock of alloys (resource)**
- **Must work with reflow, wave, hand and rework/repair soldering**

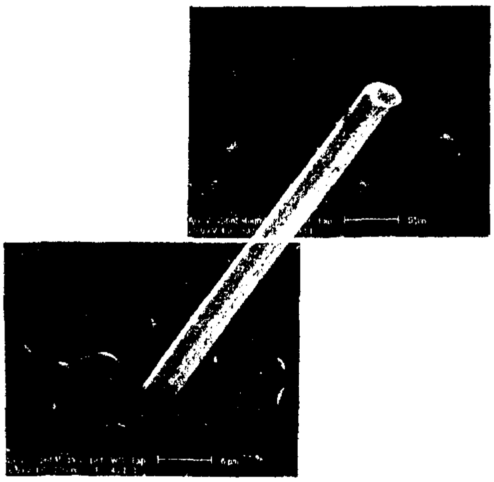
## Consideration Factor for Pb-free Electroplating

- Must be compatible with existing high speed plating equipment
- *No whisker problem*
- Minimum deposition rate of 7.5 microns per minute
- Familiar, preferably MSA electrolyte
- All products in the process must be fully analyzable
- Deposits must possess good solderability (same as/better than Sn-Pb)
- Deposits must possess good ductility (same as/better than Sn-Pb)

## Sn Whisker - Spontaneous single crystal growth



*http://nepp.nasa.gov/whisker/*



*"Spontaneous growth mchanism of Sn whiskers," B.Z. Lee and D. N. Lee, Acta. Mater. Vol.46, No.10, pp.3710-3714 (1998)*

## *Classification of the Solder Alloys*

- **Pb-Sn alloys**
  - ➔ ***Ideal properties for the soldering application, melting temperature, large electrical conductivity, good strength and good wettability***
- **Other solder alloys**
  - ➔ ***Suitability to base metals other than Cu***
  - ➔ ***Special mechanical or physical properties :*** *controlled contraction on freezing, better matched C.T.E, higher strength, better corrosion resistance, better electrical properties*
  - ➔ ***Special applications :*** *fusible links, tooling, step-soldering*
  - ➔ *CONCERN OVER ENVIRONMENTAL PROTECTION*

## *Pb-free Solders with Melting Temperature*

**< Low Melting Temperature : less than 180°C~200°C >**

- Usually in the 110°C ~ 140°C
- Sn-52In : 118°C
- Sn-58Bi : 138°C
- Sn-9Zn : 199°C

**<Mid-Range Melting Temperature : 200 ~ 230°C>**

- Sn-3.5Ag : 221°C
- Sn-4.0Ag-0.5Cu : 217 ~ 219°C
- Sn-0.7Cu : 227°C
- Sn-2.5Ag-0.8Cu-0.5Sb (Castin) : 217 ~ 220°C

**<High Temperature : 230 ~ 350°C>**

- Sn-5Sb : 232 ~ 240°C
- Sn-80Au : 280°C

## *Pb-free Solders with Composition and Melting Temperature*

| Alloy Composition (wt%) | | | | | | | | Temperature (°C) | |
|---|---|---|---|---|---|---|---|---|---|
| Sn | In | Ag | Bi | Sb | Zn | Cu | Mg | Ts | Tl |
| 48 | 52 | | | | | | | 118 | - |
| 50 | 50 | | | | | | | 118 | 125 |
| 52 | 48 | | | | | | | 118 | 131 |
| 58 | 42 | | | | | | | 118 | 145 |
| 42 | | | 58 | | | | | 138 | - |
| | 97 | 3 | | | | | | 143 | - |
| | 100 | | | | | | | 156.7 | 156.7 |
| 91 | | | | | 9 | | | 199 | - |
| 95.5 | | 5 | | | | 4 | | 216 | 222 |
| 96.5 | | 3.5 | | | | | | 221 | - |
| 95 | | 5 | | | | | | 221 | 240 |
| 95 | | | | 5 | | | | 233 | 240 |
| 100 | | | | | | | | 232 | 232 |
| | | | 100 | | | | | 271 | 271 |
| | | | 100 | | | | | 961 | 961 |
| 98 | | 2 | | | | | | 221 | 226 |
| 99.3 | | | | | | 7 | | 227 | |
| 90 | | 2 | 7.5 | | | 0.5 | | 207 | 212 |
| 98 | | | | | | | 2 | 200 | |
| 65 | | 25 | | 10 | | | | 233 | |
| | | 10 | 90 | | | | | 262 | 350 |
| 16 | 51 | | 3 | | | | | 61 | |
| | 66 | 34 | | | | | | 166 | 420 |
| 17 | 26 | | 57 | | | | | 79 | |
| | 32 | | 68 | | | | | 109 | 180 |
| 86 | 5 | | | | 9 | | | 188 | |
| 81 | 10 | | | | 9 | | | 178 | |
| 81 | 10 | | | 2 | 7 | | | 181 | |

## *Physical Properties of Pb-free Solders*

| Alloy | CTE (ppm/K) | Density (Kg/m$^3$) | Thermal Conductivity (W/mK) | Surface Tension (mN/m) Air / $N_2$ |
|---|---|---|---|---|
| Sn-3.5Ag | 22 | 7360 | 33 | 431 / 493 |
| Sn-58Bi | 15 | 8700 | | 319 / 349 |
| Sn-52In | 20 | 7300 | 34 | |
| In-3Ag | 20 | 7680 | 73 | |
| Sn-37Pb | 25 | 8400 | 50 | 417 / 464 |
| Cu | 17 | 8942 | 391 | |
| Plastics | 6 | | | |
| Alloy42 | 5 | 8150 | 14.7 | |
| FR-4 | 16 | 1800 | 35 | |
| Sn-9Zn | | | | 518 / 487 |
| Sn-0.7Cu | | | | 491 / 461 |
| Sn-5Sb | | | | 468 /495 |

# Physical Properties of Pb-free Solders

| Materials | Young's Modulus (Gpa) | Yield Strength (Mpa) | | Shear strength (Mpa) | Strain rate (1/sec) | Resistivity (? Ω-cm) |
|---|---|---|---|---|---|---|
| | | 0.2% | 0.01% | | | |
| Pb | 13.1 | | | | | 20.7 |
| Sn | 46.9 | | | | | 10.1 |
| Ag | 82.7 | | | | | 1. 59 |
| Bi | 34.0 | | | | | 2. 115 |
| In | 10.6 | | | | | 8.62 |
| Cu | 129.6 | | | | | 1.678 |
| Sn-58Bi | 43 | 41 | 26 | 26 | 6.2 e-4 | 34.4 |
| Sn-52In | 19.5 | | | 14 | 8.3 e-4 | 14.7 |
| Sn-37Pb | 30.5 | | | 36 | 6.2 e-4 | 14.4 |
| Sn-3.5Ag | | 48 | 36 | 22 | 6.2 e-4 | 10 |
| Sn-5Ag | | 34 | 27 | | | |
| Sn-30In | | 17 | 10 | | | |
| Sn-60In | | 4.5 | 3.5 | | | |
| Alloy42 | | | | | | 57 |

# Mechanical Properties

- **Strength and ductility**

| Strain rate ($s^{-1}$) | Processing (Bulk) | Solder Alloys | UTS (ksi) | Elong (%) | Ref. |
|---|---|---|---|---|---|
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-37Pb | 5.8 | 90 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-9Zn | 9.4 | 45 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-3.5Ag | 6.2 | 42.5 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-3.5Ag-5Bi | 10.4 | 15 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-3.5Ag-5In | 9.0 | 20 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-3.5Ag-1Zn | 8.0 | 27.5 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-3.5Ag-1Zn-0.5Cu | 7.0 | 46 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-8Zn-4In | 7.3 | 25 | 1 |
| $1.0*10^{-3}$ | 5°C/min.cooling | Sn-8Zn-5In-0.1Ag | 7.6 | 40 | 1 |
| Unspecified | 5°C/min.cooling | Sn-20In-2.8Ag | 6.8 | 47 | 2 |

*1 : M.McCormack et al. 1994*
*2 : Indium Corp. patent*

- **Creep**
  - $d\gamma/dt = A\tau^n \exp(-Q/kT)$

  $d\gamma/dt$ : strain rate, $\tau$ : stress, n: stress exponent, Q : activation energy

| Alloys | Temp. (°C) | A | n | Q (kcal/mole) | Ref. |
|---|---|---|---|---|---|
| Sn-40Pb | 20,70,120 | 0.15 | 4.52 | 14.32 | 3 |
| Sn-3.5Ag | 20,75,125 | $9.3*10^{-5}$ | 6.05 | 14.61 | 3 |
| Sn-58Bi | 20,75,125 | $4.04*10^{-5}$ | 3.42 | 21.85 | 3 |
| Sn-3.6Ag-1.52Cu | 20,75,125 | $2.6*10^{-5}$ | 3.69 | 8.6 | 3 |
| Sn-4.83Bi-3.33Ag | 20,75,125 | $3.0*10^{-1}$ | 3.56 | 11.56 | 3 |

- **Interfacial fracture**

| Solder Alloys | Failure (IMC thickness ↑) |
|---|---|
| Sn-40Pb | Inside the solder → through the IMC |
| Sn-58Bi | Inside the solder |
| Sn-3.5Ag | Solder/IMC interface → through the IMC |
| Sn-3.62Ag-1.52Cu, Sn-4.83Ag-3.33Cu | Solder/IMC interface |

*3 : D.R.Frear, 1995, 1996*

# *Characteristics of Pb free plating*

| Material | Composition and Melting temperature | Feature |
|---|---|---|
| Sn-Cu | Cu:1.5%<br>227C | Good mechanical strength<br>Low cost |
| Sn-Bi | Bi:3.0%<br>220C | Good stability of plating chemical liquid<br>Low melting temperature<br>Poor mechanical strength with Sn-Pb paste |
| Sn-Ag | Ag:3.5%<br>221C | Good mechanical strength<br>High cost |
| Sn | Sn:100%<br>232C | Popular for plating<br>Whisker |
| Pd-Au (pre-plating) | Pd:100% / Au:100%<br>( 2 layer ) 1552C / 1063C | Difficult to apply 42alloy<br>Fluctuating Pd cost |

# *Pb-Free Solders vs. Pb-Sn Solders*

[ **Sn-Ag systems** ]

- *automobile electronic soldering application*
- *better thermal fatigue resistance*
  - ➔*Sn-3.5Ag-1Zn (217°C) : tensile strength ↑, creep deformation ↓*
  - ➔*Sn-4.7Ag-1.7Cu (216.8°C), Sn-2Ag-0.8Cu (210-216°C)*
  - ➔*Sn-3.5Ag-(≤6%)Bi (211-221°C) : single phase transition*
  - ➔*Sn-(1-6%)Ag-(4-35%)In (167.9-179°C, 212-213.5°C)*

- **Sn-Ag-Cu systems**
  - Sn-4.7Ag-1.7Cu : 216-218°C, AMES labs
  - Sn-4.0Ag-1Cu : 217-219°C, AMES labs
  - Sn-3.0Ag-0.5Cu : Harris Brazing Co.
  - Sn-4.0Ag-0.5Cu : 217-219°C, unpatentable
  - Sn-3.8Ag-0.7Cu : 217-219°C, unpatentable
  - Sn-3.2Ag-0.5Cu : 217-218°C, unpatentable
  - Sn-3.5Ag-0.75Cu : Senju
  - Sn-0.7Cu : 227°C, Poorest in Mechanical properties

- **Sn-Ag-Cu-X**
  - Sn-2.5Ag-0.8Cu-0.5Sb : 9213-218°C, Castin Alloy
  - International Tin Research Inst., Lucent, Ford, and Sandia Labs.
  - Sn-2Cu-0.8Sb-0.2Ag, Sn-Ag-Cu-In : Promising
- **Sn-Ag-Bi-X**
  - Addition of <5wt%Bi : wettablility ↑
  - Indium Corp. Matsushita
  - Sn-3.5Ag-4.8Bi : 202-215°C, Sandia Labs., NCMS-> most promising
  - Sn-3.5Ag-3Bi ; 210-217°C, Tamura Handa
  - Sn-7.5Bi-2Ag : 191-210°C, Tamura Kaken
  - Sn-Ag-Bi : Matsushita
  - Sn-3Ag-3Bi : 213°C
  - Sn-3Ag-5Bi : 210°C
  - Sn-3.2Ag-3Bi-1.1Ci-Ge : Japan Solder
  - Sn-3.5Ag-0.5Bi-3In : Harima, Mitsui Metals
  - Sn-2Ag-7.5Bi-0.5Cu : Alloy H, Alpha Metals, developed at ITRI
  - Sn-(2.0-2.8)Ag-(13-17)Bi-(0-1)Cu : Hitachi
  - Sn-2.8Ag-10Bi-0.6Cu : Ono

- Sn-Ag-3Bi : 210°C, Matsushita
- Sn-Ag-6Bi : 220°C, Matsushita
- Sn-Ag-10Bi : 205°C, Matsushita
- Sn-Ag-15Bi : 209°C, Matsushita

**[ Sn-Sb & Sn-Sb-Pb systems ]**

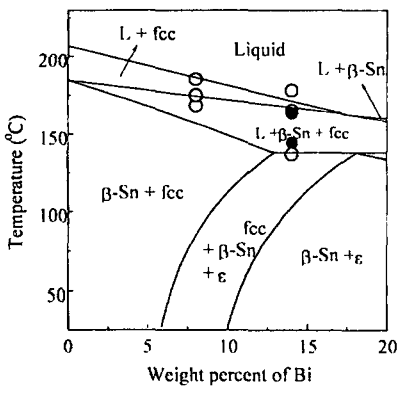
- *stronger*
- *improved creep strength*
- *narrow melting range*
- *toxicity of Sb*

**[ Sn-Zn-X systems ]**

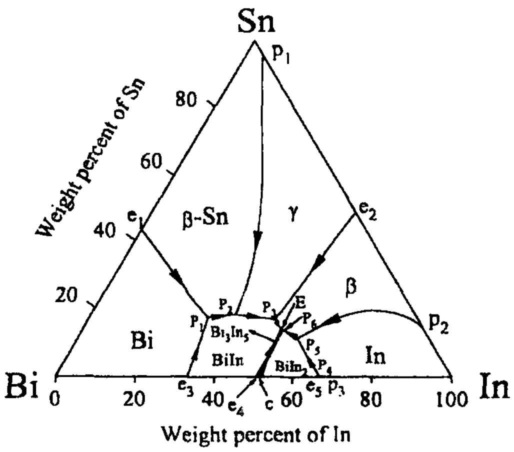
- Sn-9Zn : 199°C, reactive
- Sn-8Zn-3Bi : Japan
- Sn-9Zn-1In : AT&T
- Sn8Zn-3Bi : 191-195°C, Matsushita, Senju
- Sn-Zn-Bi-X : Hitachi Harima, Tamura

# *Design of Pb-free Solder Alloy*

- **Low Melting Temperature Solder**
  - → ternary Sn-Bi-Pb system
  - → ternary Sn-Bi-In system



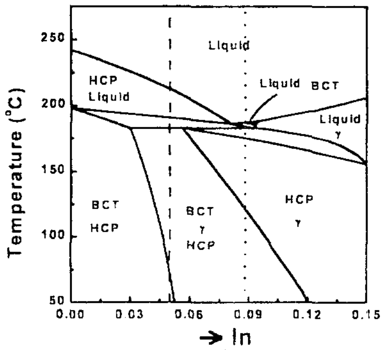

**Vertical phase diagram calculated along a constant amount of 43% Pb.**



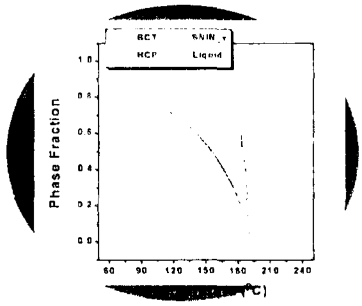

**Liquidus Projection of ternary Sn-Bi-In system**

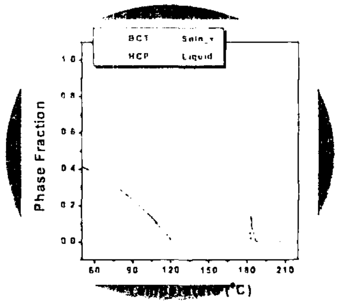
● **Mid Range Temperature Solder**

➔ Sn-Zn-X (X=In, Bi) system

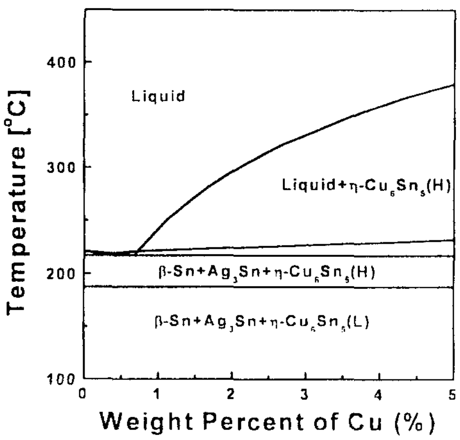



– – Sn-9Zn-5In , S.Jin European patent, 1994
..... Sn-8.8In-7.6Zn, J.A.Slattery et al. US patent, 1995

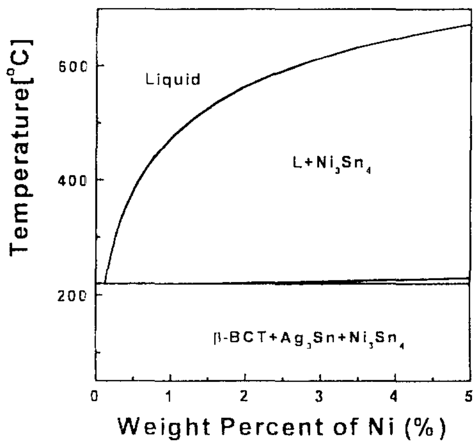



➔ Sn-Ag-X (X=In, Cu, Ni) system

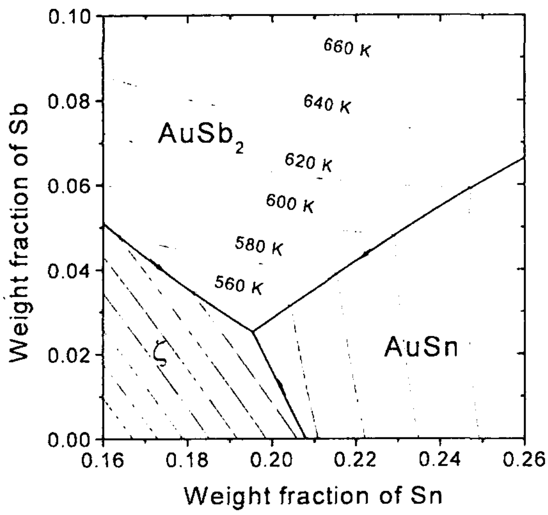



**Phase Diagram of Sn-3.5Ag-xCu**




**Phase Diagram of Sn-3.5Ag-xNi**

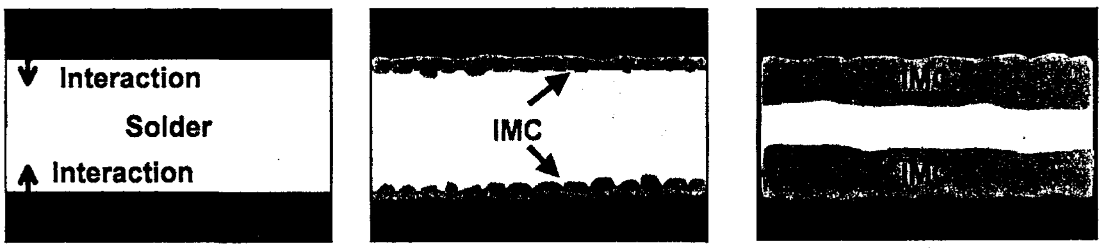
- **High Temperature Solder**
  ➔ Au-Sn-Sb system




**The ternary eutectic part of calculated Au-Sb-Sn ternary system**

## *Base Metal/Solder Interactions*

- During reflow processes, base metal and solder interact to form intermetallic compound (IMC).
- In service, IMC grows.
- IMC may result in the deterioration of the solder reliability.




< During Wetting > < In Service >

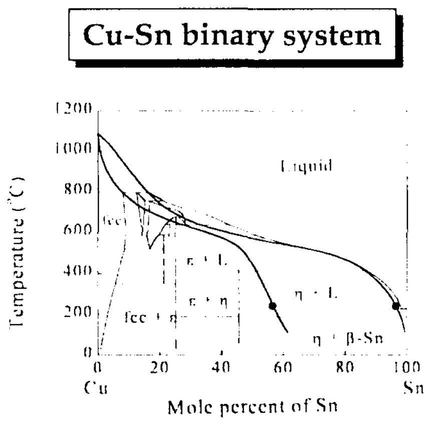
# Intermetallics

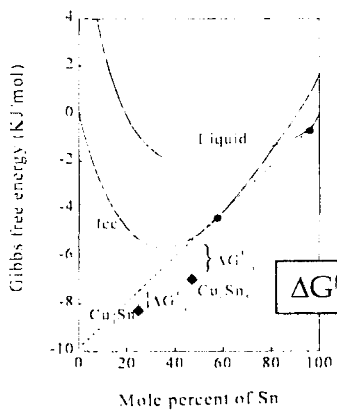
- **IMC formation during reflow**
  - Reaction between the molten solder and the substrate
    - → Dissolution of substrate into the molten solder
    - → Solubility of the active element in the solder in the substrate
  - Duration time above the solder's liquidus temperature
  - Lead to loss of strength under certain loading condition
- **Physical properties of IMC (at RT)**

| Property | $Cu_6Sn_5$ | $Cu_3Sn$ | $Ni_3Sn_4$ |
|---|---|---|---|
| Vickers Hardness ($kg/mm^2$) | 378±55 | 343±47 | 365±7 |
| Toughness ($MPa\ m^{1/2}$) | 1.4±0.3 | 1.7±0.3 | 1.2±0.1 |
| Young's Modulus (GPa) | 85.56± 1/65 | 108.3±4.4 | 133.3±5.6 |
| Shear Modulus (GPa) | 50.21 | 42.41 | 45.0 |
| Thermal Expansion ($x10^{-6}/°C$) | 16.3±0.3 | 19.0±0.3 | 13.7±0.3 |
| Thermal Diffusivity ($cm^2/sec$) | 0.145±0.015 | 0.24±0.024 | 0.083±0.008 |
| Resistivity (μΩcm) | 17.5±0.1 | 8.93±0.02 | 28.5±0.1 |

# Prediction of Interface Reaction Products

- **Thermodynamic state at the interface between the liquid solder and the substrate**
  - → by calculating metastable equilibria between the initial phases
- **The first forming Intermetallic phase**
  - → highest driving force under the metastable equilibrium

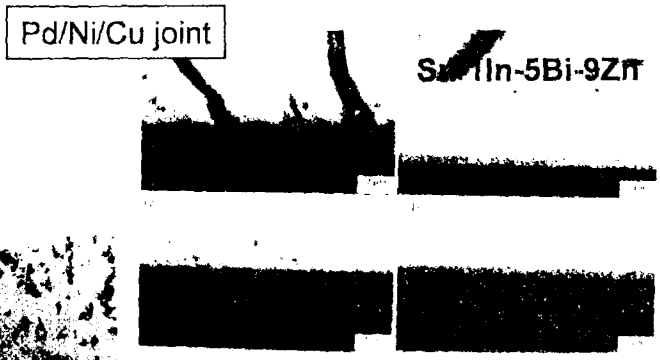


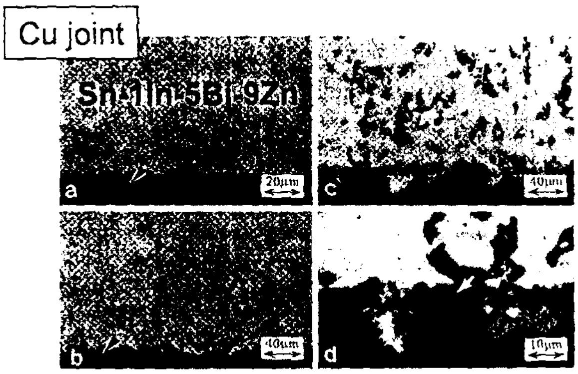

$\Delta G^f_\eta > \Delta G^f_\varepsilon$

- **This can be applied to the ternary system, solder/Cu.**

- **Sn-Zn system joints**

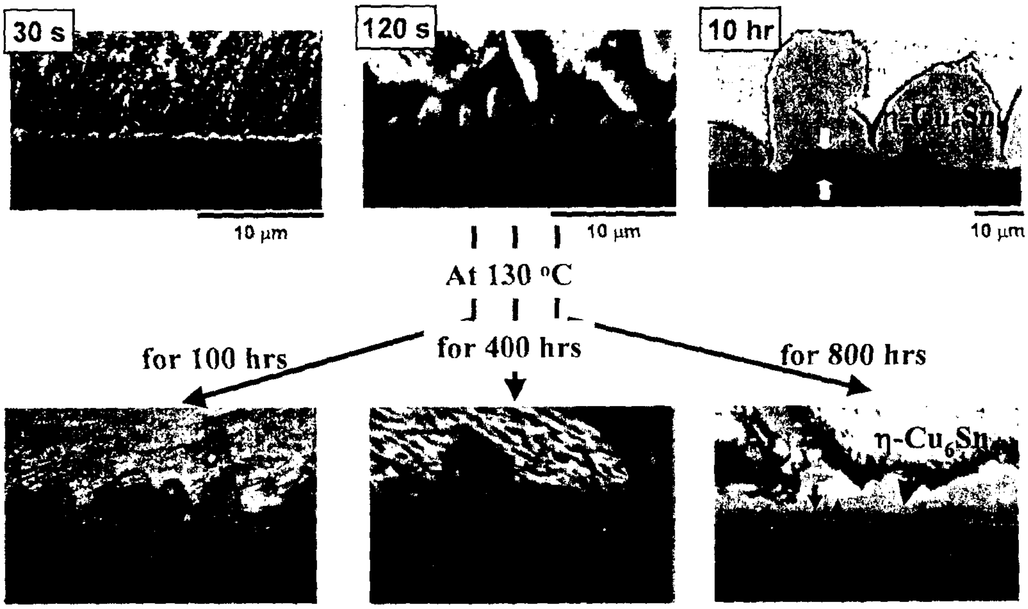



S.W.Yoon & H.M.Lee (1998)



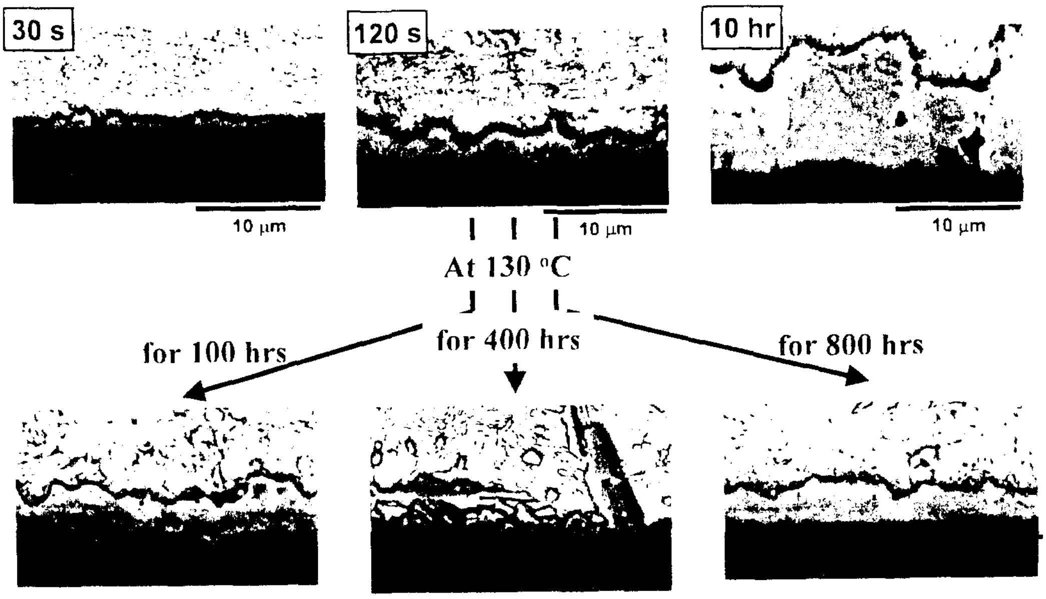

- **Sn-3.5Ag system**

*on **Cu plate**, soldering at 250 °C followed by aging*



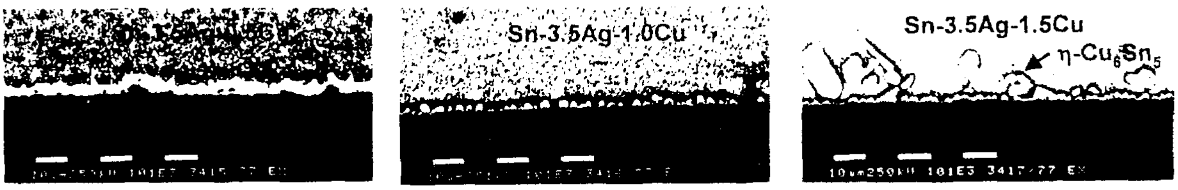
- **Sn-3.5Ag system**

*on Ni plate, soldering at 250 °C followed by aging*

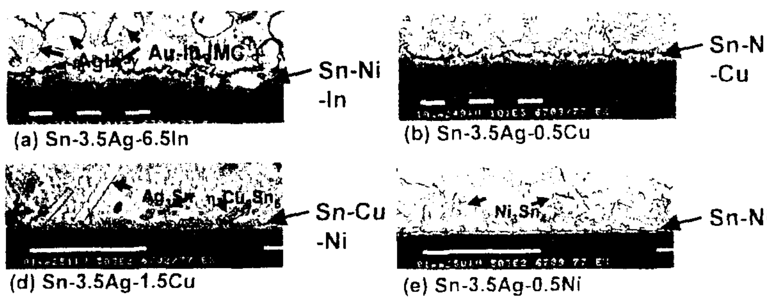



- **Sn-3.5Ag-X solders**

Sn-3.5Ag-(0.5, 1.0, 1.5)Cu systems on Cu plates




Sn-3.5Ag-X (X=(a)6.5In, (b)0.5Cu, (c)1.0Cu, (d)1.5Cu & (e)0.5Ni) on PCB (Cu/Ni(4)/Au(0.6))



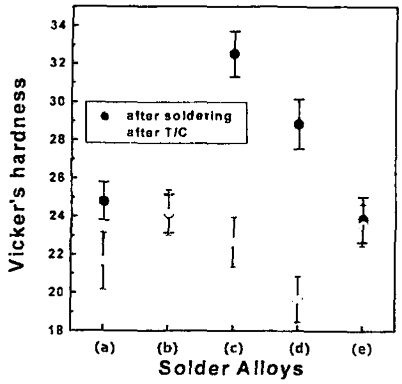

(a) Sn-3.5Ag-6.5In (b) Sn-3.5Ag-0.5Cu (c) Sn-3.5Ag-1.0Cu

(d) Sn-3.5Ag-1.5Cu (e) Sn-3.5Ag-0.5Ni

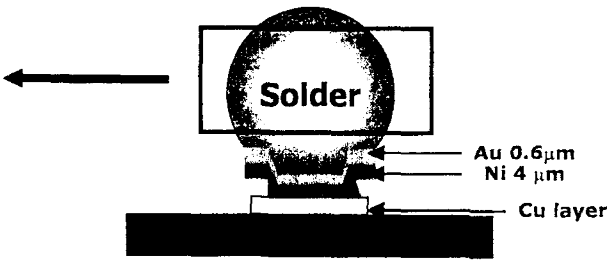
- In (b), (c) & (d), as Cu contents increase, IMC phases changes from Sn-Ni phase into Sn-Cu phases.

# *Solder Joint Reliability*

- Micro Hardness Test after Soldering and T/C test

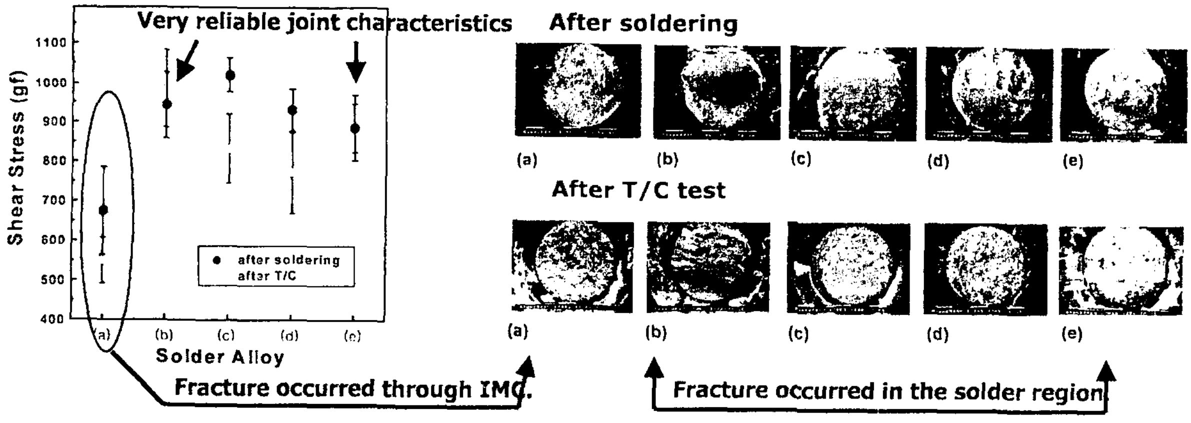



➢ **Tests were performed for the solder region in the jointed specimens.**




**(a) Sn-3.5Ag-6.5In, (b) Sn-3.5Ag-0.5Cu, (c) Sn-3.5Ag-1.0Cu,**
**(d) Sn-3.5Ag-1.5Cu and (e) Sn-3.5Ag-0.5Ni**

- Ball Shear Test after Soldering and T/C test




**Vickers Hardness vs. Shear Stress**

**When the fracture occurs in the solder region, the shear stress value is linearly related with the hardness value of the solder region of joints.**
**The IMC thickness effects on the stress concentration site by calculation using FEM.**
**Sn-3.5Ag-0.5Cu and Sn-3.5Ag-0.5Ni show reliable joint characteristics after soldering and T/C tests.**

## *Roadblock for Pb-free Transition*

- Lack of global-agreed system requirements
- Component temperature durability
- Lack of reliable data and knowledge from field use
- Insufficient data about the environmental impact of Pb-free alternatives
- No single drop in Pb-free solution exists. Severe compatibility
- Additional technical roadblocks maybe identified when materials systems are defined
- No agreement on test specification and methods

## *Future works need.....*

- Portable more sensitive to Pb-free issues
- Environmental is becoming essential electronics equipment
- Earth-friendly material need
- Mass production
- ➔ Eco-Ages ➔ *Safe Materials*
  ➔ Green Market Economy (green consumer)
- More works on
  - ➢ recycling or combustion disposal
  - ➢ Halogen/Antimony free
  - ➢ New environmental materials

## *Summary*

- EC's/Japanese environmental regulation drive the Pb-free/Halogen-free application
- Most Japanese electronics companies are preparing the green products.
- All items concerning to Pb-free/Halogen-ree technology should be coparallely designed and developed.
- More works need to clear the unknowns on Pb-free materials
- Need of consensus on materials and standards
- EBM (Environmental Benign Manufacturing)