

Recent Pb-free Electronic Packaging Issues

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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)

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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*

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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

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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)

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Appliance Recycling Bill

Specific Home Electronics Recycling Law

From April 1st in 2001
Collection, reuse and recycling

Basic requirement for recycling	
Air conditioner	: 60 %
TV	: 55 %
Refrigerator	: 50 %
Washing machine	: 50 %

Waste Treatment Law

After collection of waste electronics,
We need suitable treatment not to release Pb into the environment.

PWB of TV must be treated separately?

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

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Lead

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:

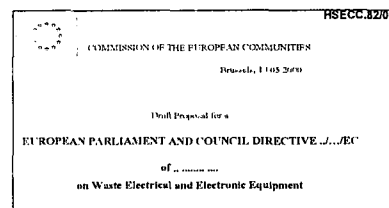
OJ L 196, 16/08/1967, p. 1.

- 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

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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 retardants and inherent difficulty to distinguish flame retardant 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.

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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

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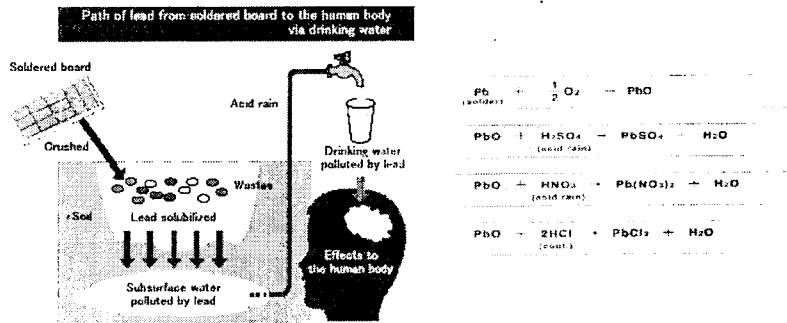
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When soldered Sn-Pb circuit boards are scrapped and buried

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

2) The subsurface water becomes polluted with Pb compounds

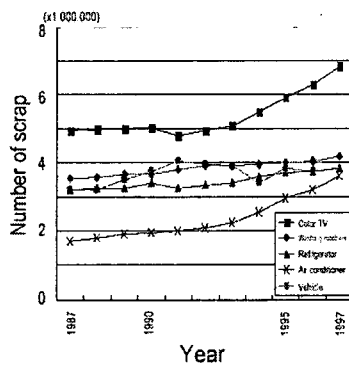
3) The polluted subsurface water is taken into the human body as drinking water



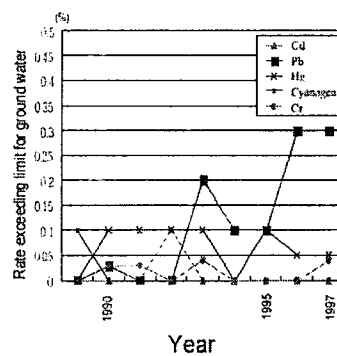
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Electronics Waste and water pollution in Japan



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 Sugauma, ISIR, Osaka University

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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 in 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/ip/jhistory/english/information/pbfree/roadmap.html>

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Worldwide Pb-free Activities

- SONY 2000/3 Apply Pb-free solder to 1 item min. of 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

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Japanese Electronics Manufacturing Roadmaps for Pb-free

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

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Japanese Electronics Manufacturing Roadmaps for Pb-free

(Updated)

Roadmap for implementation of a lead-free assembly process

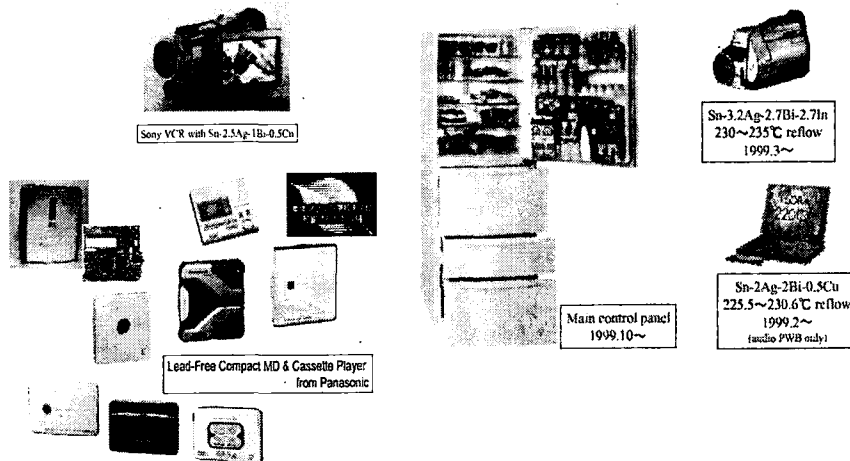
Company	Action	Target	Products
Panasonic	Complete abolition	March 2003	Mini-disk player, stereo headphone
Sony	Full implementation in Japan	March 2001	Camera, built-in VTR, TV, mini-disk player
	Start lead-free process overseas	March 2002	
Hitachi	Full implementation for in-house evaluation	March 2002	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.electronicetimes.com> 2001/03/26

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Worldwide Pb-free Activities



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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.*"

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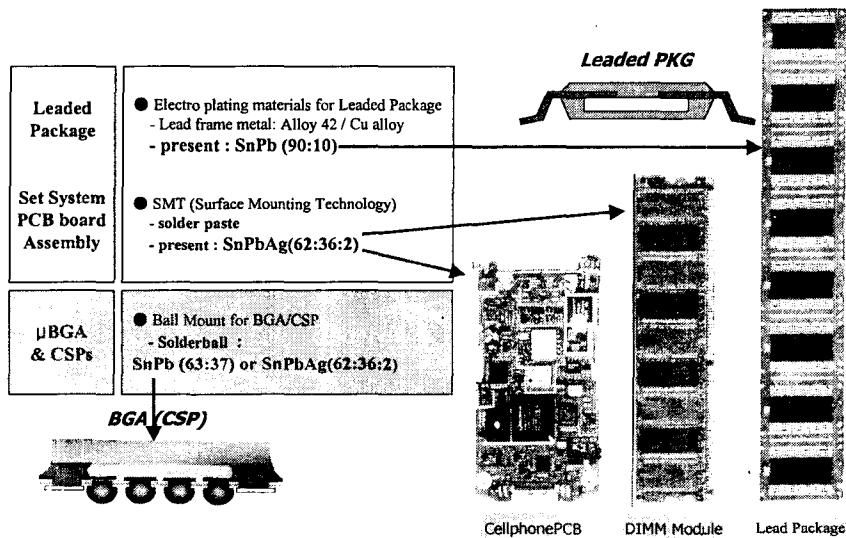
Worldwide Pb-free Activities

- **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 total 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 Institute)
- **INNOLOT** (Europe-Germany)

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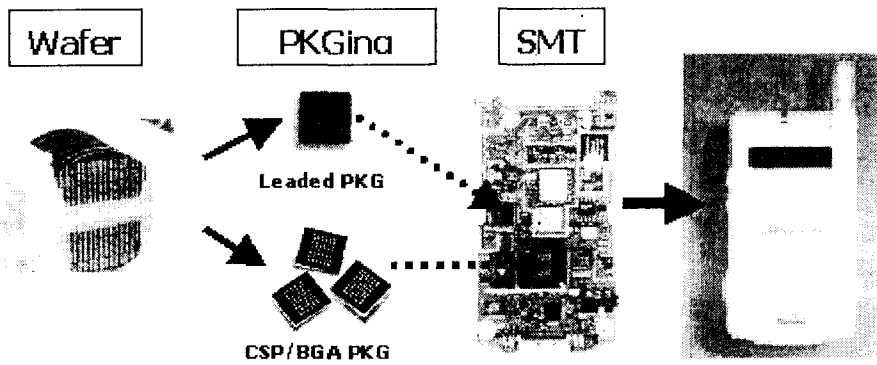
Pb usage in Electronic Packaging



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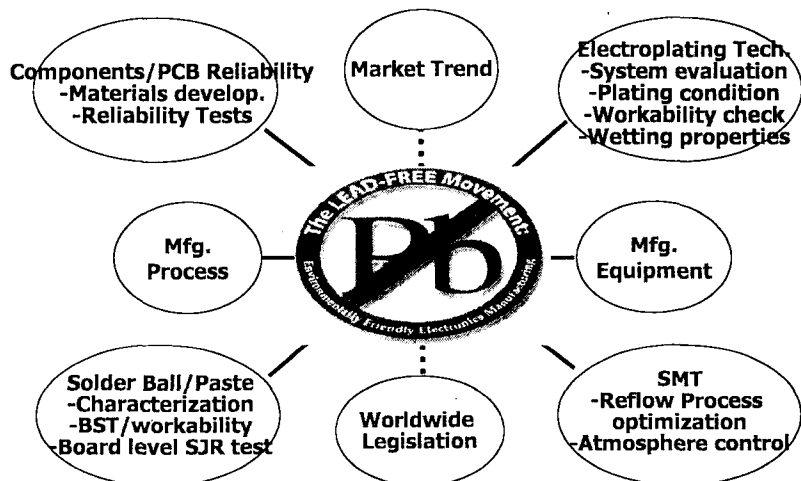
Electronic Assembly = Electronic Packaging + SMT



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Key Issues in Pb-free Solder Technology



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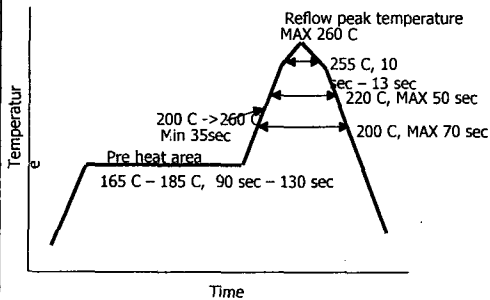
Challenging Items in Pb-free Technology

- Alloy
 - Alloy selection
 - 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.

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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.
Duration within 5C of peak Temp.	10 - 20 sec.	
Peak Reflow Temp.	220C(+5-0)	255C(+5/-0)
Cool Down Rate	6C/sec.	

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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*

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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**

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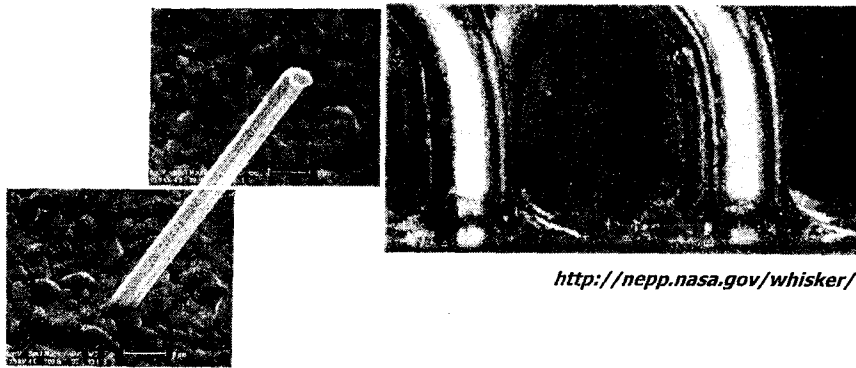
Consideration Factor for Pb-free Electroplating

- 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)

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Sn Whisker - Spontaneous single crystal growth



<http://nepp.nasa.gov/whisker/>

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

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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**

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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

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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	

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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

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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

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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

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● Creep

➤ $dy/dt = A\tau^n \exp(-Q/kT)$

dy/dt : strain rate, τ : 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% 227C	Good mechanical strength Low cost
Sn-Bi	Bi:3.0% 220C	Good stability of plating chemical liquid Low melting temperature Poor mechanical strength with Sn-Pb paste
Sn-Ag	Ag:3.5% 221C	Good mechanical strength High cost
Sn	Sn:100% 232C	Popular for plating Whisker
Pd-Au (pre-plating)	Pd:100% / Au:100% (2 layer) 1552C / 1063C	Difficult to apply 42alloy 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

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● 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 : wettability ↑
- 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*

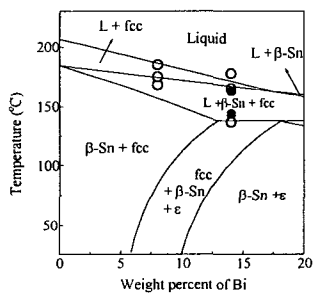
[Sn-Zn-X systems]

- 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

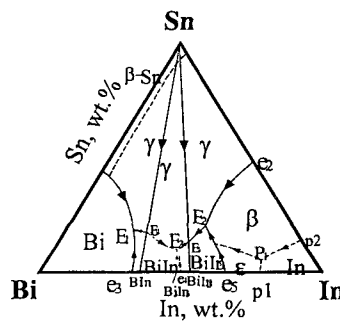
Design of Pb-free Solder Alloy

● Low Melting Temperature Solder

- ➔ ternary Sn-Bi-Pb system
- ➔ ternary Sn-Bi-In system



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



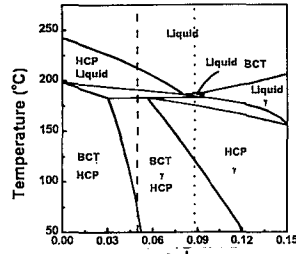
Liquidus Projection of ternary Sn-Bi-In system

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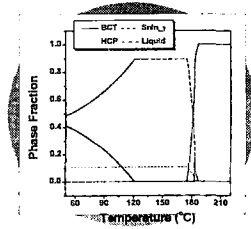
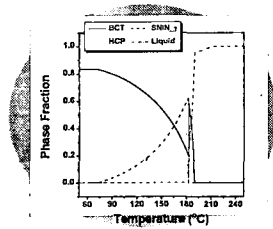
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● Mid Range Temperature Solder

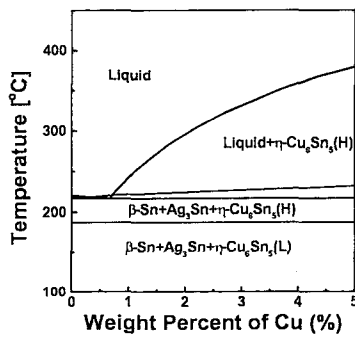
→ Sn-Zn-X (X=In, Bi) system



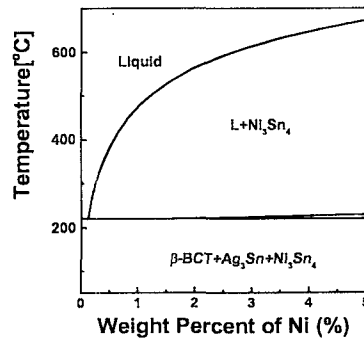
--- Sn-9Zn-5In, S.Jin European patent, 1994
 Sn-8.8In-7.6Zn, J.A.Slattery et al. US patent, 1995



→ Sn-Ag-X (X=In, Cu, Ni) system

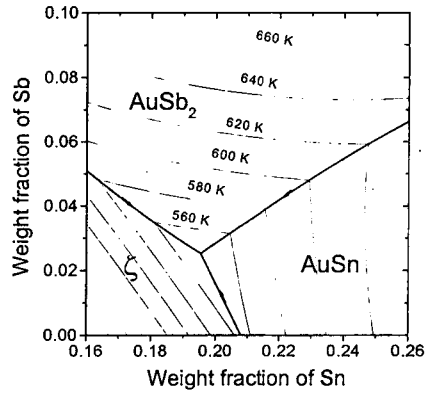


Phase Diagram of Sn-3.5Ag-xCu



Phase Diagram of Sn-3.5Ag-xNi

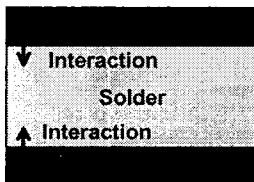
- High Temperature Solder
 - Au-Sn-Sb system



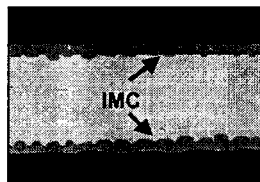
The ternary eutectic part of calculated Au-Sb-Sn ternary system

Base Metal/Solder Interactions

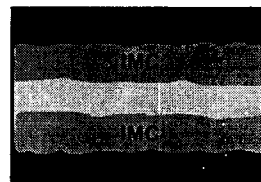
- During reflow processes, base metal and solder interact to form intermetallic compound (IMC).
- In service, IMC grows.
- IMC may result in the deterioration of the solder reliability.



< 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)

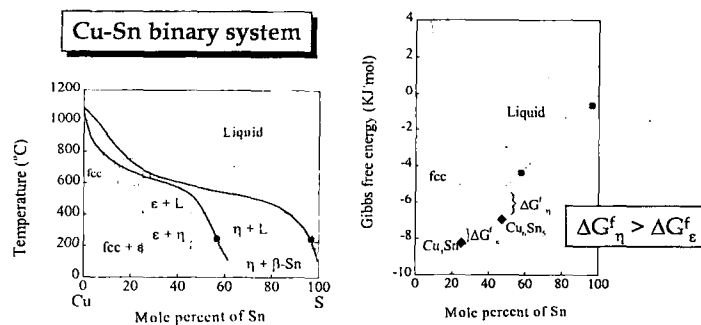
Property	Cu ₃ Sn ₈	Cu ₆ Sn ₅	Ni ₃ Sn ₄
Vickers Hardness (kg/mm ²)	378 ± 55	343 ± 47	365 ± 7
Toughness (MPa m ^{1/2})	1.4 ± 0.3	1.7 ± 0.3	1.2 ± 0.1
Young's Modulus (GPa)	85.56 ± 1/65	108.3 ± 4.4	133.3 ± 5.6
Shear Modulus (GPa)	50.21	42.41	45.0
Thermal Expansion (x10 ⁻⁶ /°C)	16.3 ± 0.3	19.0 ± 0.3	13.7 ± 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

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Prediction of Interface Reaction Products

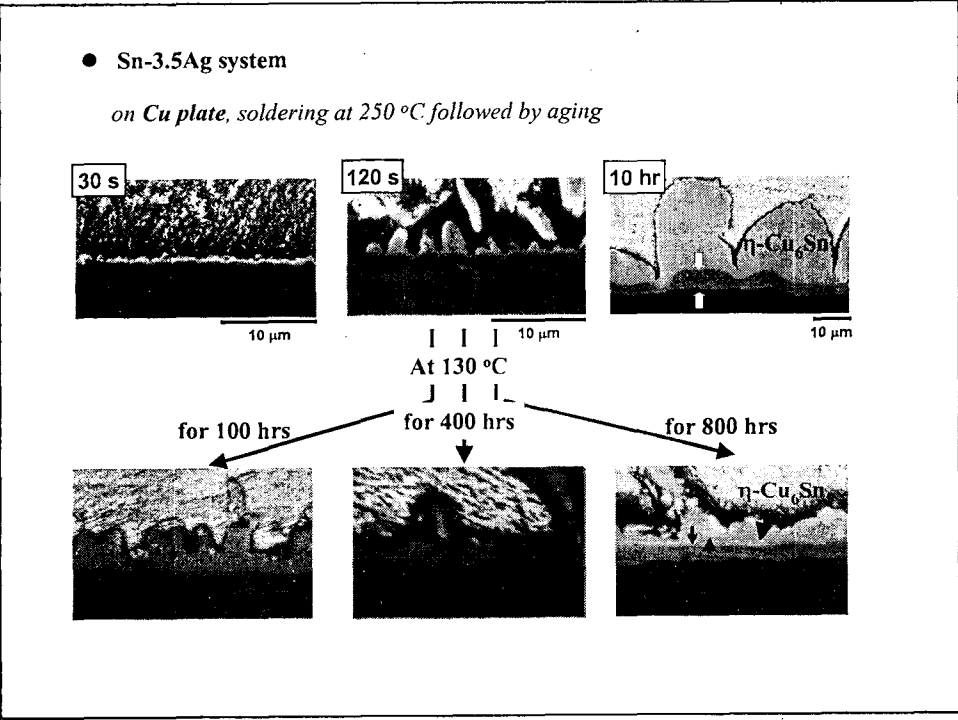
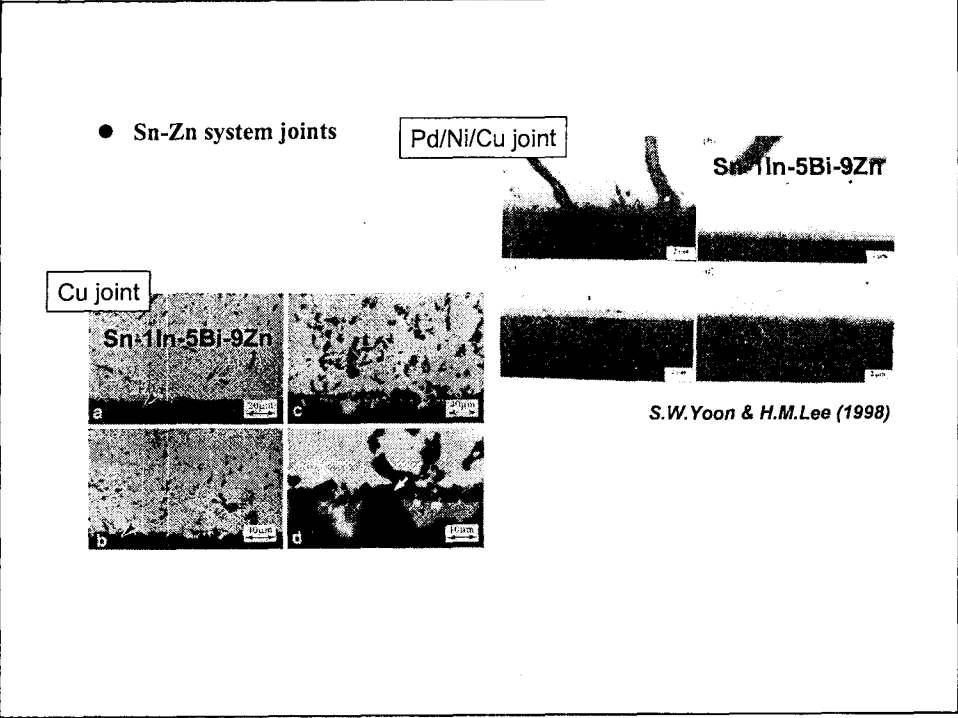
- Thermodynamic state at the interface between the liquid solder and the substrate
 - ➔ by calculating metastable equilibria between the initial phases
- The first forming Intermetallic phase
 - ➔ highest driving force under the metastable equilibrium



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

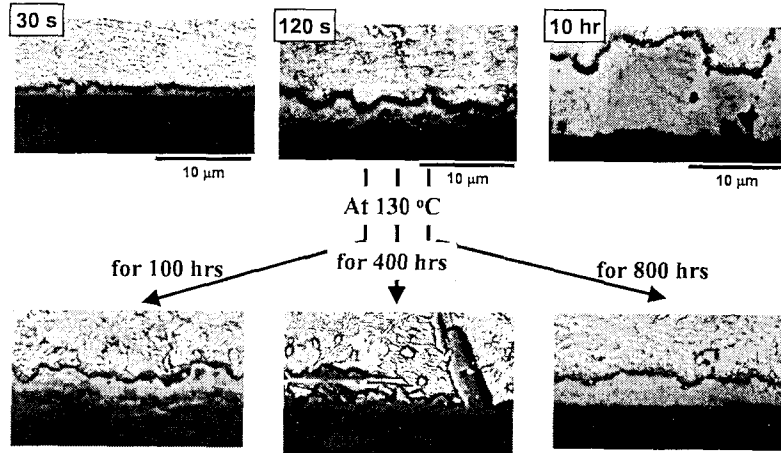
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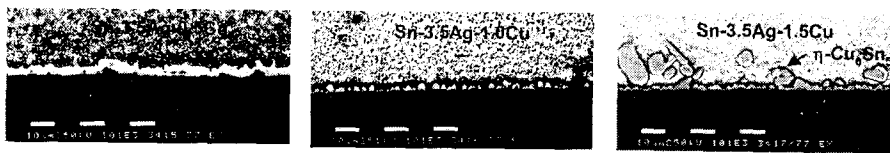
● Sn-3.5Ag system

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

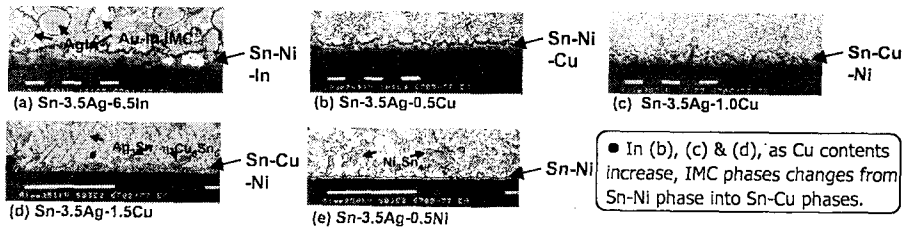


● Sn-3.5Ag-X solders

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



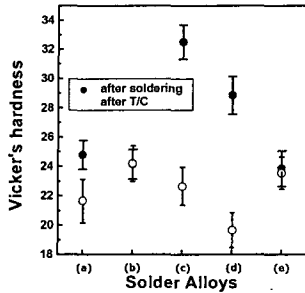
Sn-3.5Ag-X (X=(a)6.5In, (b)0.5Cu, (c)1.0Cu, (d)1.5Cu & (e)0.5Ni) on PCB (Cu/Ni(4)/Au(0.6))



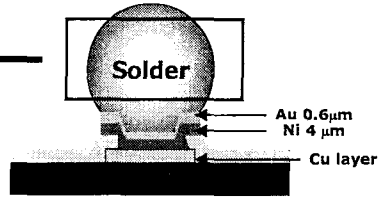
● In (b), (c) & (d), as Cu contents increase, IMC phases changes from Sn-Ni phase into Sn-Cu phases.

Solder Joint Reliability

- Micro Hardness Test after Soldering and T/C test



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

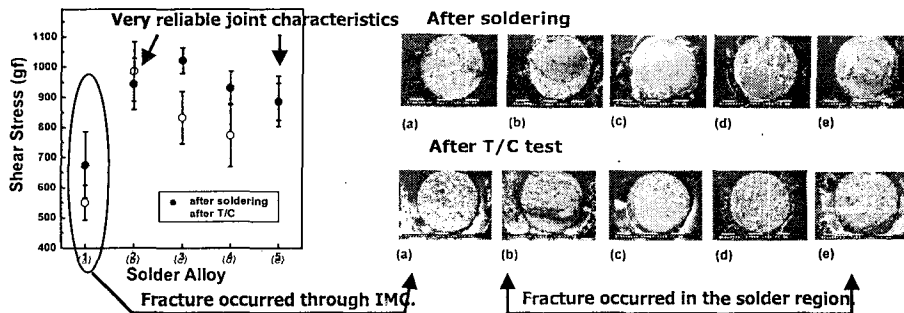


(a) Sn-3.5Ag-6.5In, (b) Sn-3.5Ag-0.5Cu, (c) Sn-3.5Ag-1.0Cu, (d) Sn-3.5Ag-1.5Cu and (e) Sn-3.5Ag-0.5Ni

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- Ball Shear Test after Soldering and T/C test



Fracture occurred through IMC.

Fracture occurred in the solder region.

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

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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

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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-free 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)

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