(Workshop on Pb-Free Solders, UCLA, 9/5-6/2002)

# Recent Progress in Lead (Pb)-Free Solders and Soldering Technology

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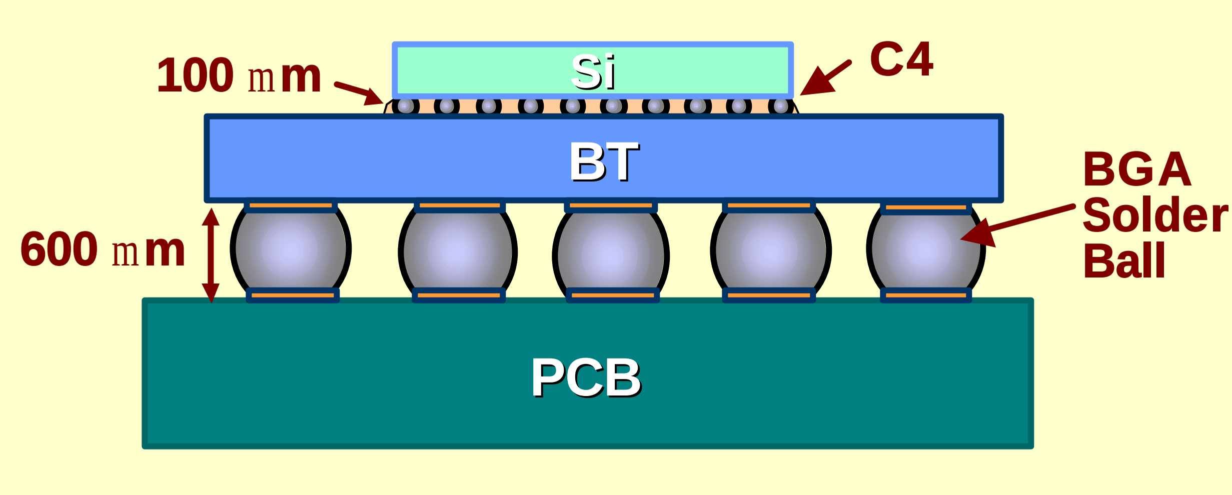
# Outline

- Introduction
- Pb-Free Candidate Solders
- Technical Issues in Pb-Free Solders
- Review on Bulk Properties
- Review on Solder Joint Properties
- Thermal Fatigue Properties
- Interfacial Reactions
- Other Reliability Issues
- Summary

(5/02, SKK)

# Introduction

- **Plastic Ball Grid Array (PBGA)**



- **Desirable Properties of Solder Joints**
  - ***Soft Solder*** **to relax the stress/strain caused by thermal fatigue**
  - ***Slow growth of intermetallic compound*** **(IMC) at the solder joints**

# Pb Consumption

**Worldwide Pb Consumption:** 5 M tons

- Primary uses;
  - Electric batteries (80 %)
  - Ammunition
  - Electronic applications (less than 1 %)

**Electronic Applications**

- Board assemblies (~40K tons)
  - PIH, SMT, HASL (surface finish)
  - Sn-37Pb

- Components (~10K tons)
  - SOP, QFP, DIP, BGA, FC
  - Sn-10Pb, Sn-37Pb, 97Pb-3Sn

# Recent Development

## Europe

- Legislation banning Pb in electronics proposed by WEEE* pushed to 2007
- Product take-back proposed

## Asia

- No legislation pending
- Japanese companies driving “Green” consumer products by 2003

## US

- No legislation on horizon
- Renewed interest by electronic industry
- EIA, IPC, NEMI demonstrated technical initiatives
- Push back of WEEE date + lack of other legislation has taken immediate pressure off drive to implement (NEMI, Jan. 2002)

(* WEEE = Waste in Electrical & Electronic Equipment)

(09/02)

# US Patents on Pb-Free Solders

| | US Pat # | Assignees | Sn (wt %) | Bi (wt %) | Ag | In | Sb | Cu | Zn | Others | Major Composit'n |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7/88 | 4758407 | Harris | 87-93 | | 0.1-0.5 | | 4-6 | 3-5 | | Ni(1) | Sn Sb Cu |
| | 4778733 | Engelhard | 92-99 | | 0.05-3 | | | 0.7-6 | | | Sn Cu Ag |
| | 4806309 | Willard | 90-95 | 1-4 | 0.1-0.5 | | 3-5 | | | | Sn Sb Bi |
| 7/93 | 5229070 | Motorola | 90 | 5 | | 5 | | | | | Sn Bi In |
| | 5328660 | IBM | 78 | 10 | 2 | 10 | | | | | Sn Bi In Ag |
| | 5344607 | IBM | 90 | 2 | | 8 | | | | | Sn In Bi |
| | 5393489 | IBM | 93 | 2 | 3 | | 1 | 1 | | | Sn Ag Bi Sb |
| | 5411703 | IBM | 94 | 2 | | | 3 | 1 | | | Sn Sb Bi Cu |
| | 5368814 | IBM | 42 | 56 | | 2 | | | | | Bi Sn In |
| 5/95 | 5414303 | IBM | 70-90 | 2-10 | | 8-20 | | | | | Sn In Bi |
| | 5455004 | Indium Co. | 82-90 | 1-5 | | 3-6 | | | 4-6 | | Sn In Ag Bi |
| | 5580520 | Indium Co. | 71-92 | | 2-4 | 4-26 | | | | | Sn In Ag |
| | 5410184 | Motorola | 92-97 | | | | | 3-8 | | | Sn Cu |
| | 5435968 | Touchston | 79-97 | 0-1 | 0-4 | | | 3-15 | | Se(1) | Sn Cu Ag |
| | 5429689 | Ford | 80 | 4-15 | 0.5 | 5-15 | | | | | Sn Bi In |
| | 5538686 | Lucent | 86 | | | 5 | | | 9 | | Sn Zn Ag |
| | 5569433 | Lucent | 40-60 | 40-60 | 0.2-0.5 | | | | | | Sn Bi Ag |
| | 5698160 | Lucent | 59-82 | | 2-11 | | | | 16-30 | | Sn Zn Ag |
| | 5352407 | Seelig | 93-98 | | 1.5-3.5 | | 0.2-2 | 0.2-2 | | | Sn Ag Sb Cu |
| | 5405577 | Seelig | 90-99 | | 0.5-3.5 | | 0.2-2 | 0.1-3 | | | Sn Ag Sb Cu |
| | 5520572 | US Army | 86-97 | 0-5 | 0.3-4.5 | 0-9.3 | | 0-5 | | interm | SnAg BiInCu |
| 6/96 | 5527628 | Iowa St. U. | 89 | | 3.5-7.7 | | | 1-4 | | | Sn Ag Cu |
| | 5658528 | Mitsui | 90 | 0.5-1.5 | 1-4 | 3-4 | | | | | Sn In Ag Bi |
| | 5718868 | Mitsui | 90 | 2-3 | | | | 0.5 | 7-9 | | Sn Zn Bi |
| | 5733501 | Toyota | 65-95 | 0.1-9.5 | 0.8-5 | 0.1-9.5 | 0.1-10 | | | | SnSbBiInAg |
| | 5730932 | IBM | 80 | 12 | 3 | 5 | | | | | Sn BI In Ag |
| | 5762866 | Lucent | 76-98 | 0.2-6 | 1-6 | 0.2-6 | | | 0.2-6 | | Sn Ag BiInZn |
| 10/98 | 5755896 | Ford | 37-57<br>48-58 | 37-57<br>40-50 | | 6-10<br>2-5 | | | | | Bi Sn In<br>Sn Bi In |
| | 5833921 | Ford | 43-58 | 38-52 | 1-2 | 2 | 5-15 | 1-4 | | | SnBiSbCuIn |
| | 5837191 | Johnson | 95 | | 0.6 | | 0.75-2 | 0.6 | | Ni(0.6) | Sn Sb Ag |
| | 5843371 | Samsung | 77-89 | 6-14 | 3-4 | 2-5 | | | | | Sn Bi Ag In |
| 2/99 | 5851482 | KIMM | 80 | 1-20 | | 0.1-3 | | | 0.01-3 | Al,Mg, | Sn Bi In Zn |
| | 5863493 | Ford | 91-97 | | 2-5 | | | 0-3 | | Ni(0-3) | Sn AgCuNi |
| | 5874043 | IBM | 70-74 | | 6.5-7.5 | 12-24 | | | | | Sn In Ag |
| | 5938862 | Delco | 84-90 | | 2.5-3.5 | 7-11 | | 0.5-1.5 | | | Sn In Ag Cu |
| | 5985212 | H-Tech | >75 | | | 0-6 | | 0.1-9.5 | | Ga(<5 | Sn Cu In Ga |
| | 5993736 | Mitsui | 91-95 | 2-3 | 2-4 | | | | 0.5-2 | | Sn Ag Bi Zn |
| 12/00 | 5942185 | Hitachi | 72-87 | 10-23 | | | | | 3-5 | | Sn Bi Zn |
| | 6077477 | Matsushita | 81-91 | 5-10 | 3-6 | 0.1-1.0 | | 0.1-2 | | | Sn Bi Ag Cu |
| | 6086687 | Alpha Fry | >90 | 0-9.25 | 0-9.25 | 0-0.25 | 0-9.25 | 0-9.25 | 0-0.2 | Ti(0.2) | Sn ++ |
| | 6139979 | Murata | 92-96 | | | | 3-5 | 0.7-2.0 | | Ni(0.5) | Sn Sb Cu Ni |
| | 6156132 | Fuji Elec | 40-70 | 30-58 | 0-5 | | 0-5 | 0-1 | Ge | Ni(0.2) | Sn Bi Ag Sb |

(01/01, SKK)

# US PATs on Pb-Free Solders (II)

| | US Pat # | Assignees | Sn (wt %) | Bi (wt %) | Ag | In | Sb | Cu | Zn | Others | Major Composit'n |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1/01 | 6176947 | H-Tech | bal | (0.5-5) | 2.5-4.5 | 6-12 | (0.5-2) | 0.5-2.5 | | | Sn In Ag Cu |
| | 6179935 | Fuji Elec | bal | | 0-4.0 | | (0-3.5) | 0-2.0 | | Ni, Ge | Sn Ag Cu Ni |
| | 6180055 | Nihon Supr | bal | | | | | 0.3-07 | | Ni(0.1 | Sn Cu Ni |
| | 6184475 | Fujitsu | 34-40 | 46-55 | (Ag) | 5-20 | | | (Zn) | Ge | Bi Sn In |
| | 6187114 | Matsushita | bal | | | | | (0.1-5) | (Ni) | Pd(3.0 | Sn Pd Cu Ni |
| | 6229248 | Murata Mfg | bal | | 1.0-2.0 | | 1.0-3.0 | 0.5-1.0 | | | Sn Sb Ag Cu |
| | 6224690 | IBM | bal | 1-20 | 1-5 | (0.5-10) | 1-10 | (0.5-5) | (0.5-5 | (Ni,Co | SnBiAgSb++ |
| | 6228322 | Sony | bal | 0.5-8.0 | 1.5-6.0 | | | 0.1-5.0 | Sm,Gd | La,Ce, | Sn Bi Ag Cu |
| | 6231691 | Iowa St. U. | bal | | 3.0-7.7 | | | 0.5-4 | Fe(0.5 | Co(0.5 | SnAgCuFeCo |
| | 6241942 | Matsushita | bal<br>bal | (0.2-6)<br>10-30 | 0.1-3.5<br>0.05-2 | (0.5-3) | | 0.1-3 | 7-10<br>2-10 | P(<1)<br>P(<1) | Sn Zn Ag Cu<br>Sn Bi Zn Ag |
| | 6253988 | Antaya Tec | 30 | (0.25) | 4.5 | 65 | (0.75) | 0.5 | | | In Sn Ag Cu |
| 12/01 | 6267823 | Matsushita | bal | 5-18 | 2-3.5 | (0.1-1.5 | | (<0.7) | (<10) | | Sn Bi Zn Ag |
| | 6296722 | Nihon Supr | bal | | | | | 0.1-2 | (Ga<1) | Ni(<1) | Sn Cu Ni (Ga) |
| | 6319461 | Nippon Gls | bal | (<10) | 0.1-6 | | (<10) | 0.1-6 | 0.1-3 | Al,Ti | SnAgCuZnAl |
| | 6325279 | Matsushita | bal | 5-10 | 3.0-6.0 | 0.1-1.0 | | 0.1-2.0 | | | SnBiAgCuIn |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |

(02/02, SKK)

# Pb-Free Candidate Solders

| Composition (wt %) | Melting Point (°C) | Applications | Concerns |
|---|---|---|---|
| 58Bi-42Sn | 139 | PTH<br>Low temp | Poor wetting<br>Low mp phase (BiPbSn) |
| Sn-3.5Ag | 221 | SMT,<br>Flip chip | Cu dissolution,<br>IMC, |
| Sn-3.5Ag-5Bi | 208-215 | SMT | Fillet lift in PTH<br>Low mp phase, |
| Sn-3.5Ag-0.7Cu | 217 | SMT, PTH, | OSP wetting,<br>Voiding,<br>IMC |
| Sn-0.7Cu | 227 | PTH,<br>Flip chip, | Poor wetting,<br>Cu dissolution,<br>IMC |
| 63Sn-37Pb | 183 | PTH, SMT,<br>BGA | Pb- environ |
| 95Pb-5Sn,<br>97Pb-3Sn, | 314,<br>317, | Flip Chip,<br>C4, | Pb- environ |

(5/02, SKK)

# Technical Issues in Pb-Free Solders

- What are the candidate Pb-free solders?
- What are the selection criteria?
- Can we make reliable Pb-free joints?
- What are the implications of higher reflow temp req. for the new solders?
- Are the new surface finishes needed?
- What is the Pb-free solder for flip chip?
- Are the new UBM(BLM) needed?
- Can we maintain the solder hierarchy?
- What are the reliability issues?
- What are the solidification mechanisms?
- Microstructure-property relations?
- Thermal fatigue mechanisms?
- Corrosion behavior of the new solders?
- Tin pest (transformation to gray tin)?
- Tin whisker growth?
- Electromigration of Pb-free solders?

(5/02, SKK)

# Bulk Properties of Pb-Free Solders

| Properties | Sn-37Pb | Sn-3.5Ag | Sn-5Sb | Sn-0.7Cu | Sn-9Zn |
|---|---|---|---|---|---|
| Melting point (°C) | 183 | 221 | 238 | 227 | 199 |
| UTS (MPa) | 31-46<br>[1] | 55<br>[2] | 23-42<br>[3] | 31<br>[4] | 60-65<br>[5] |
| Elongation (%) | 35-176<br>[1] | 35<br>[2] | 90-350<br>[3] | 12<br>[4] | 38<br>[5] |
| Hardness (HV) | 12.9<br>[6] | 17.9<br>[7] | 17.2<br>[7] | 14.4<br>[8] | 23<br>[9] |
| Elec resistivity (μΩ-cm) | 17.0<br>[7] | 7.7<br>[7] | 17.1<br>[7] | 10-15<br>[10] | 10-15<br>[10] |

References:

1. H. Rack and J. Maurin, J. Testing and Eval. Vol.2, p.351, (1974).
2. M. McCormack, et. al., Appl. Phys. Lett., Vol.63(1), pp.15-17, 1993.
3. R.K. Mahidhara, et al., J. Mat's Sci. Lett., Vol.13, pp.1387-1389, 1994.
4. S. Huh, et al., Mater. Trans.(Japan I. Metals), Vol.42(5), pp.739-744, 2001.
5. C.M. Chuang, et al., J. Elec. Mat's, Vol.30(9), p.1232, 2001.
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7. S.K. Kang, et al, Proc. 49th ECTC, pp.283-288, (1999).
8. P. Lauro, private communication, November, 2001.
9. Y. Miyazawa, T. Ariga, Mater. Trans. (Japan I. Metals), Vol.42(5), pp.776-782, (2001).
10. J. Glazer, J. Elec. Mat's, Vol.23(8), p.693 (1994).

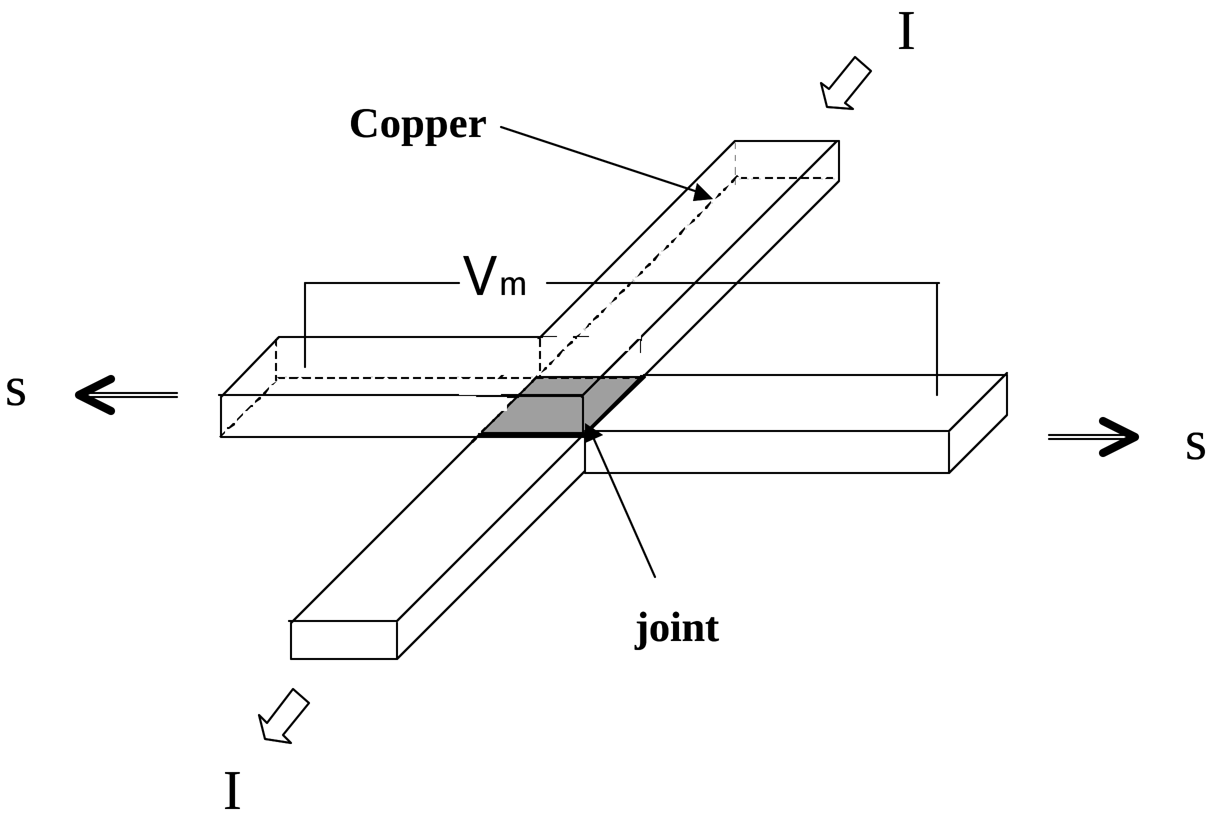
(2/02, SKK)

# Shear Strength of Pb-Free Solder Joints (to Cu substrate)

| Solder Alloy (wt %) | Shear Strength (MPa) | Shear Strength (MPa) | Shear Strength (MPa) | Presemt Study (MPa) |
|---|---|---|---|---|
| 63Sn-37Pb | 32.7 | 29 | 9.2 | 50 |
| Sn-3.65Ag | 37.2 | 28<br>(Sn-3.5Ag) | 11.4 | 38<br>(Sn-3.5Ag) |
| Sn-0.7Cu | 27.0 | | 9.2 | |
| Sn-3.8Ag-0.7Cu | 35.1 | 47<br>(3.6Ag-1Cu) | 12.5 | 39 |
| Sn-3.5Ag-3Bi | | | | 49.6 |
| Strain rate (mm/min) | 0.10 | 0.10 | 15 | 0.25 |
| Solder joint Gap (mm) | 175 | 76 | 100 ? | 20 |
| Test method | Ring & plug | 4 point bend | Flip chip in shear | Shear test |
| Reference | J..Foley, et al, p.1258JEM, 2000 | B.Cook, et al, p.1214,JEM, 2001 | D. Frear, et al p.28, June JOM, 2001 | S. Kang, et al, TMS2002 |

(2/02, SKK)

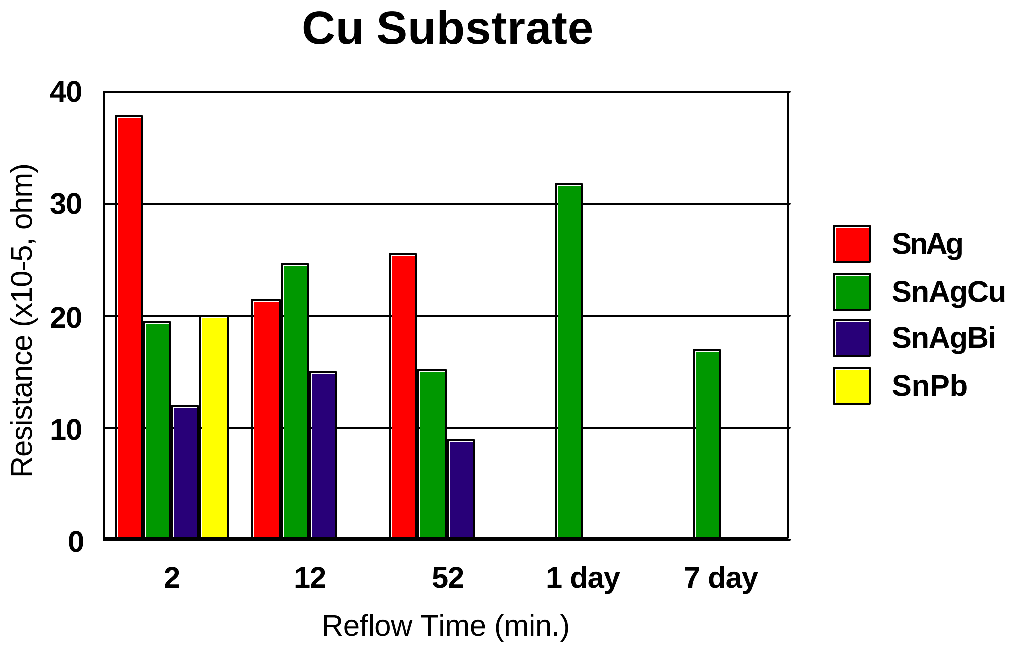
# Fabrication of Model Solder Joints

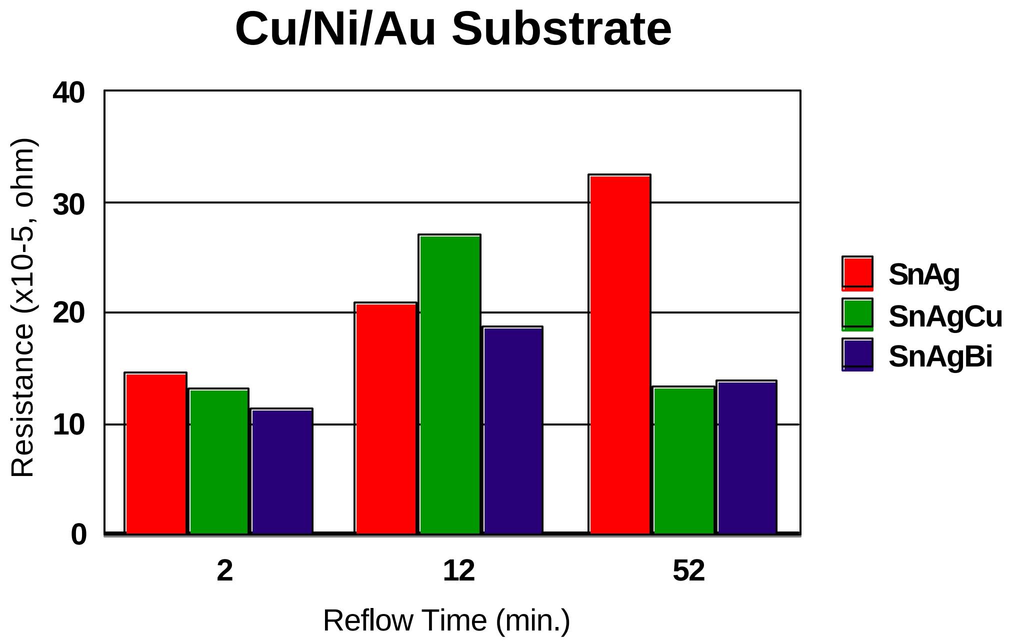


A model solder joint made of two copper coupons of "L-shape" for electrical and mechanical evaluation.

(SKK, 2/02)

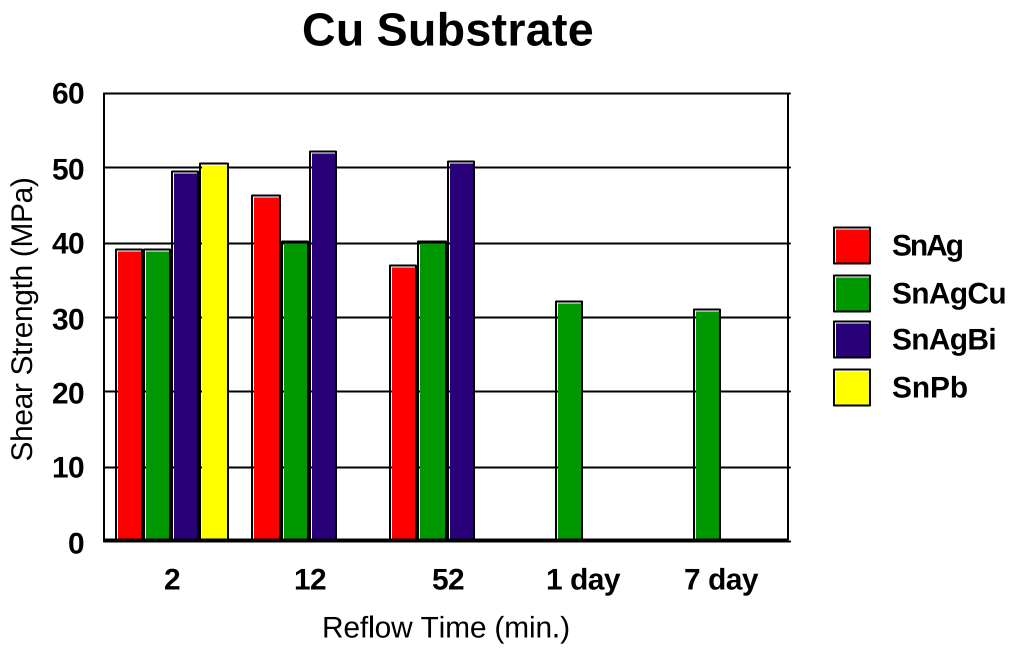
# Electrical Resistance of Pb-Free Solder Joints

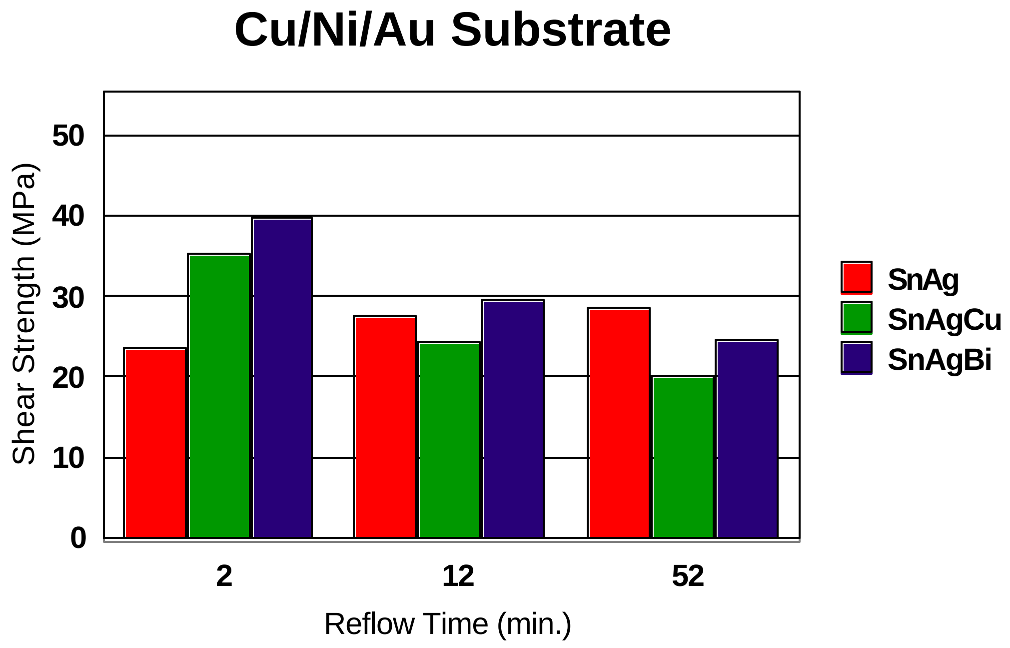




(SKK, 2/02)

# Shear Strength of Pb-Free Solder Joints





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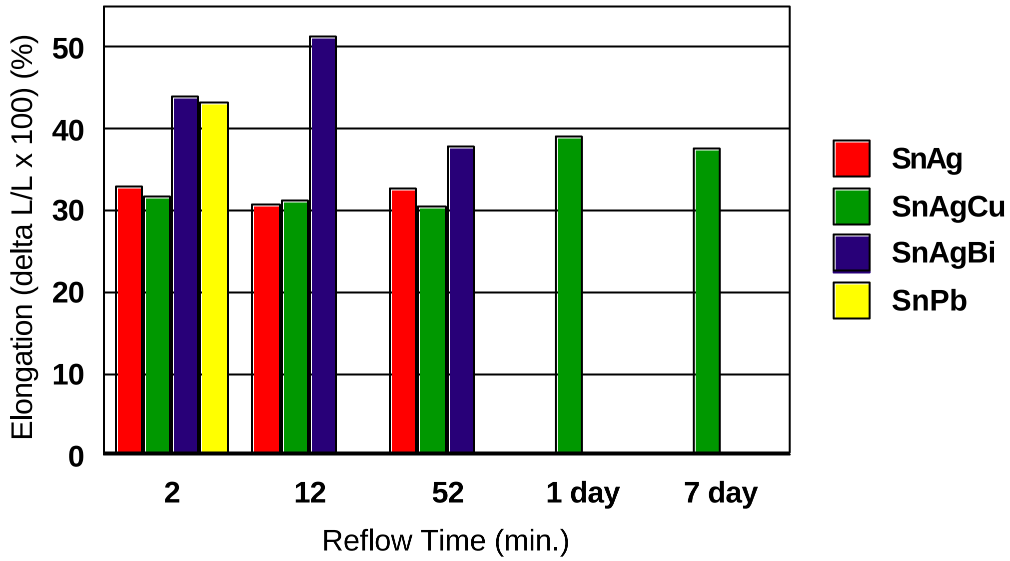
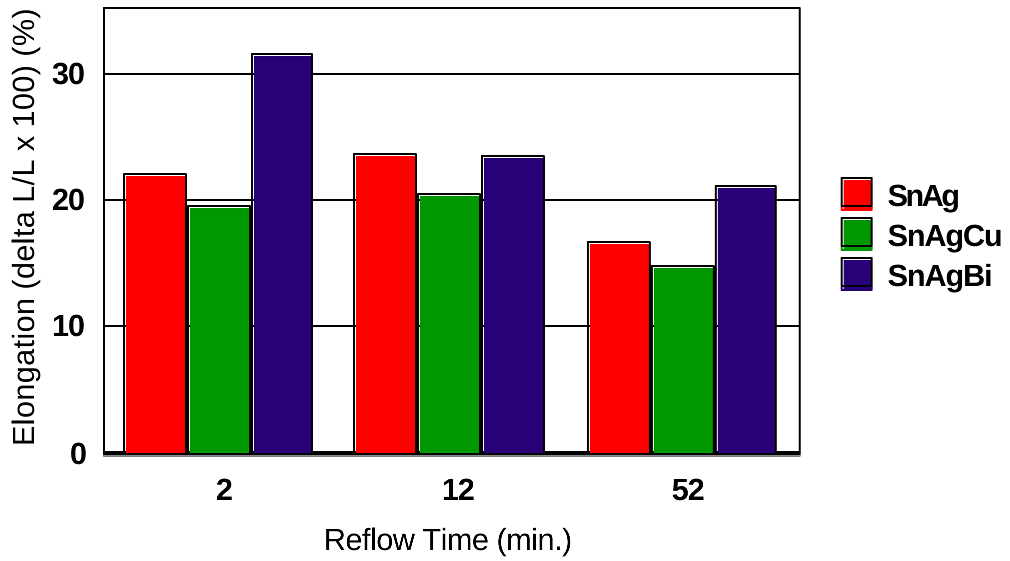
# Percent Elongation of Pb-Free Solder Joints


Cu Substrate


Cu/Ni/Au Substrate

(SKK, 2/02)

(52nd ECTC, San Diego, May 2002)

# Interfacial Reactions, Microstructure and Mechanical Properties of Pb-Free Solder Joints in PBGA Laminates

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# Scope of Study

**Objectives**

- Effect of Surface Finish
- Effect of Multiple Reflows

**Materials**

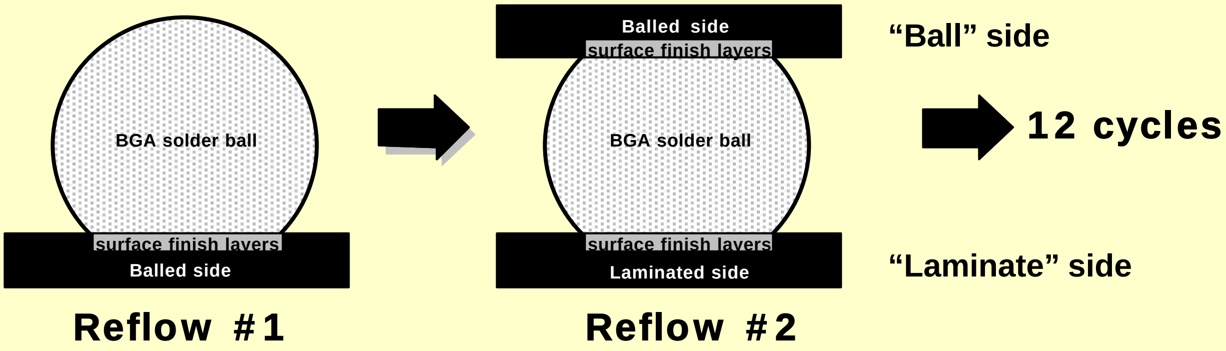
- BGA Solder Composition
  - Sn-3.8Ag-0.7Cu (SAC)

- Surface Finishes
  - Cu / OSP
  - Au / Ni(P)
  - Au / Pd / Ni(P)

**Joining Process**

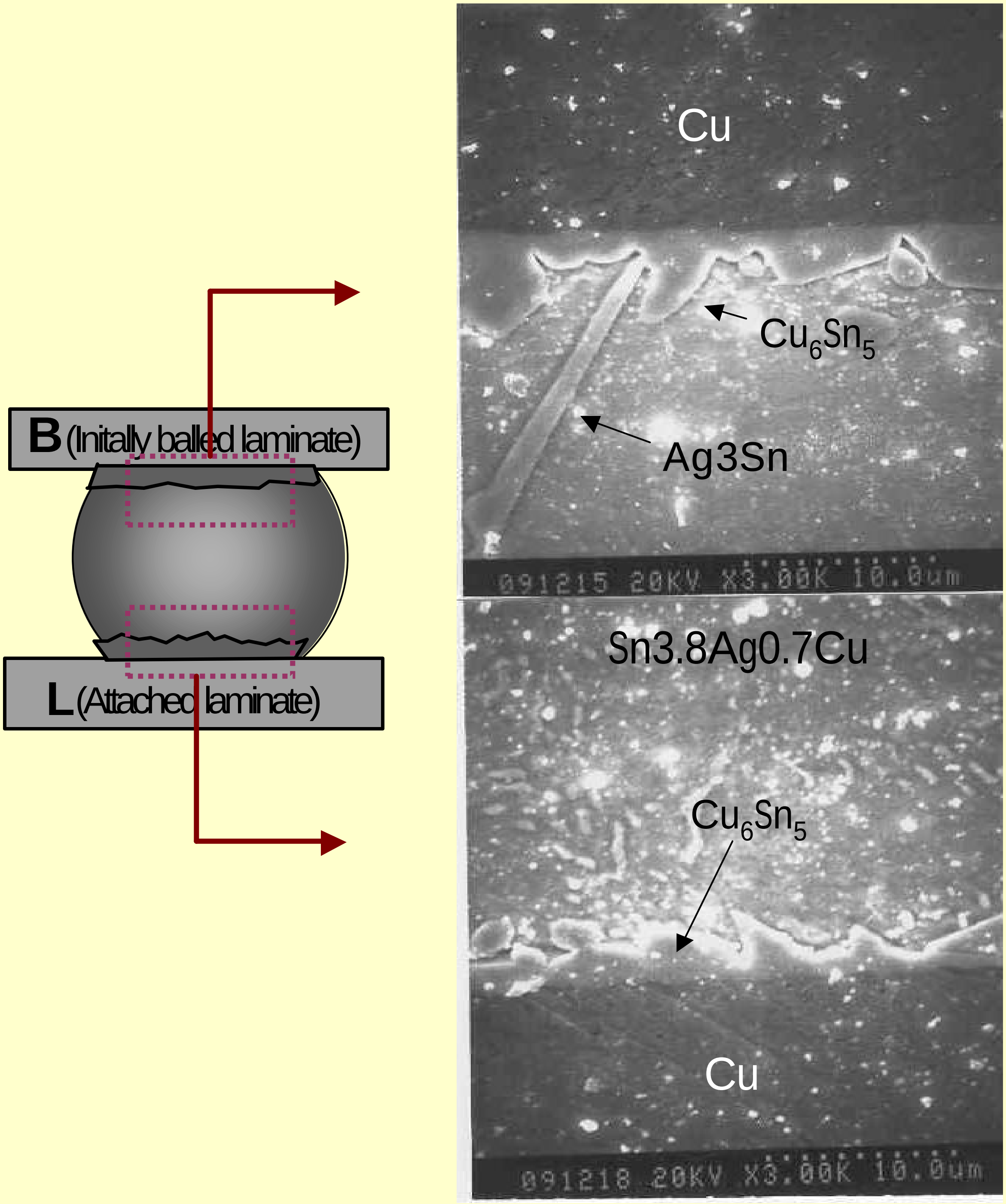
- Reflow up to 12 cycles at 260$^{o}$C

# Joining Process



| Module # | Surface Finish (side B) | Surface Finish (side L) | Reflow # at 260 $^{o}$C |
|---|---|---|---|
| 1 | Cu | Cu | 2,1 |
| 2 | Cu | Cu | 7,6 |
| 3 | Cu | Cu | 12,11 |
| 4 | Au/Ni(P) | Cu | 2,1 |
| 5 | Au/Ni(P) | Cu | 7,6 |
| 6 | Au/Ni(P) | Cu | 12,11 |
| 7 | Au/Ni(P) | Au/Ni(P) | 2,1 |
| 8 | Au/Ni(P) | Au/Ni(P) | 7,6 |
| 9 | Au/Ni(P) | Au/Ni(P) | 12,11 |
| 10 | Au/Pd/Ni(P) | Cu | 2,1 |
| 11 | Au/Pd/Ni(P) | Cu | 7,6 |
| 12 | Au/Pd/Ni(P) | Cu | 12,11 |
| 13 | Au/Pd/Ni(P) | Au/Pd/Ni(P) | 2,1 |
| 14 | Au/Pd/Ni(P) | Au/Pd/Ni(P) | 7,6 |
| 15 | Au/Pd/Ni(P) | Au/Pd/Ni(P) | 12,11 |

# Interfacial Microstructure of Sn3.8Ag0.7Cu with Cu-Cu after 2/1 Reflows at 260C



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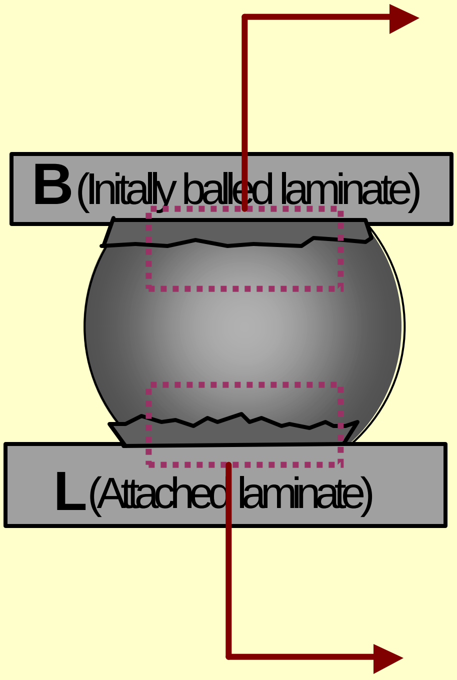
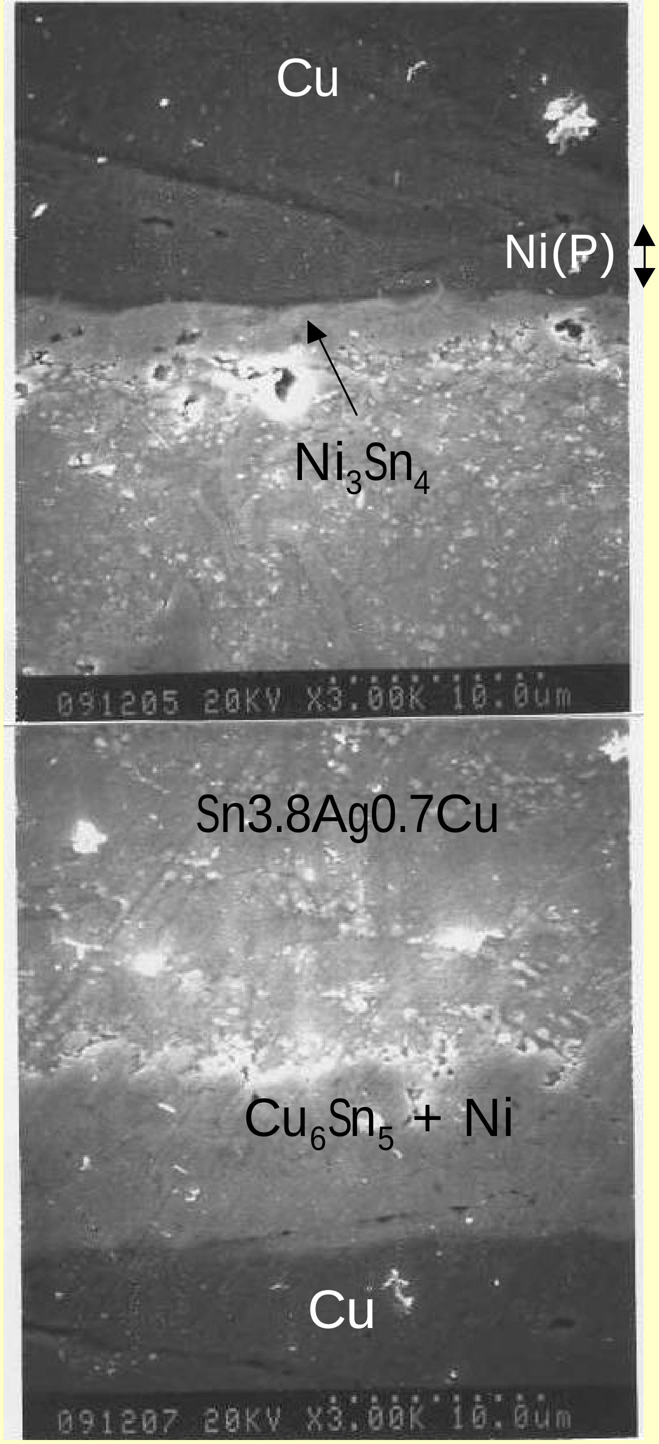
# Interfacial Microstructure of Sn3.8Ag0.7Cu with Au/Ni(P)-Cu after 2/1 Reflows at 260C





(5/02, SKK)

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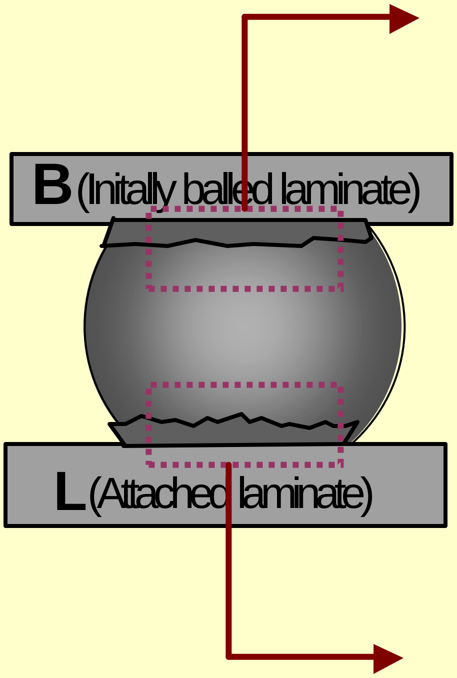
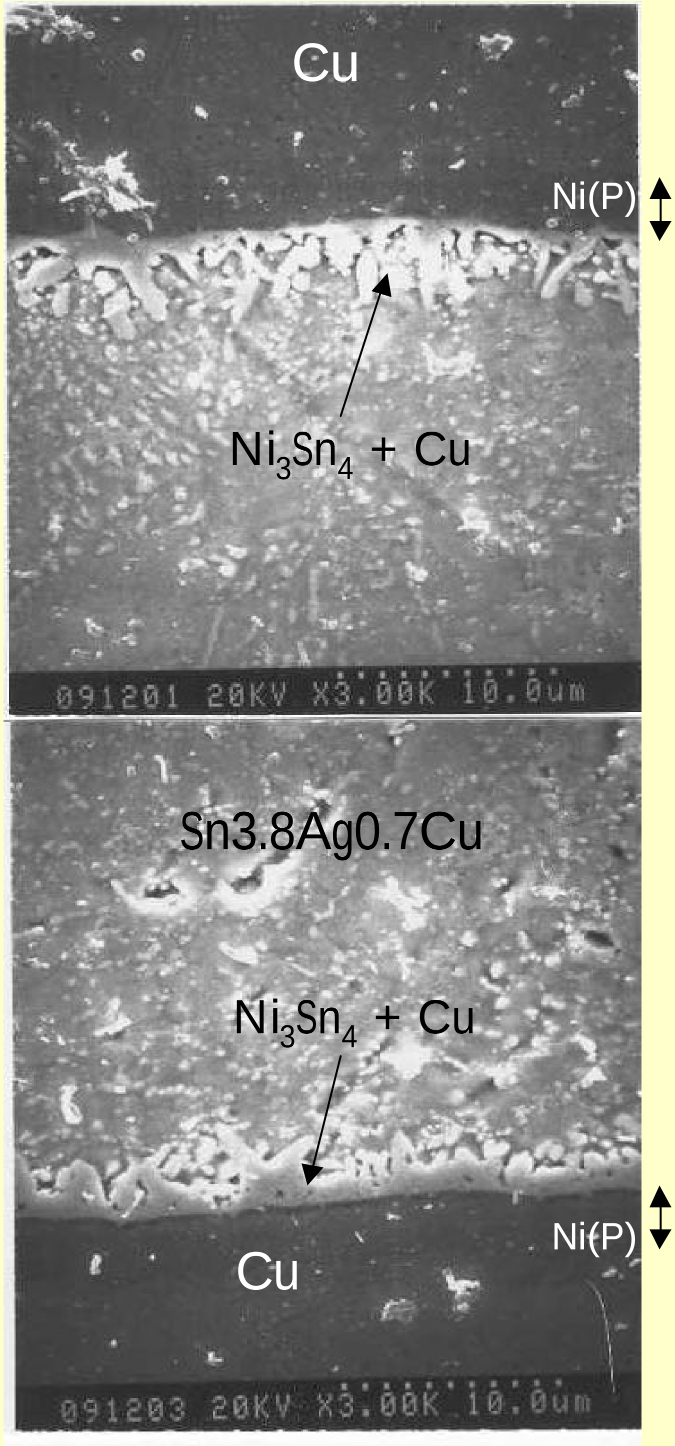
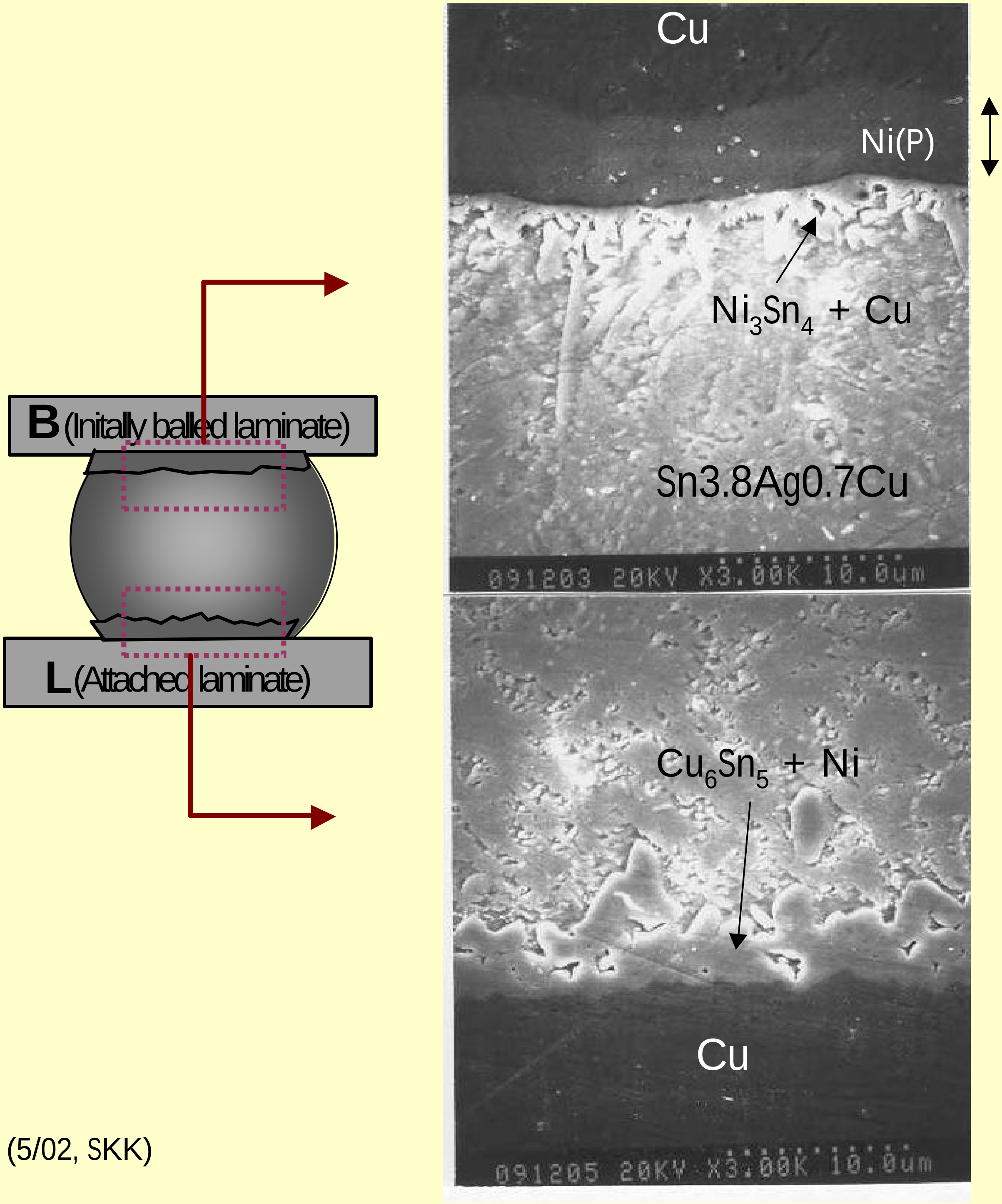
# Interfacial Microstructure of Sn3.8Ag0.7Cu with Au/Ni(P)-Au/Ni(P) after 2/1 Reflows at 260C





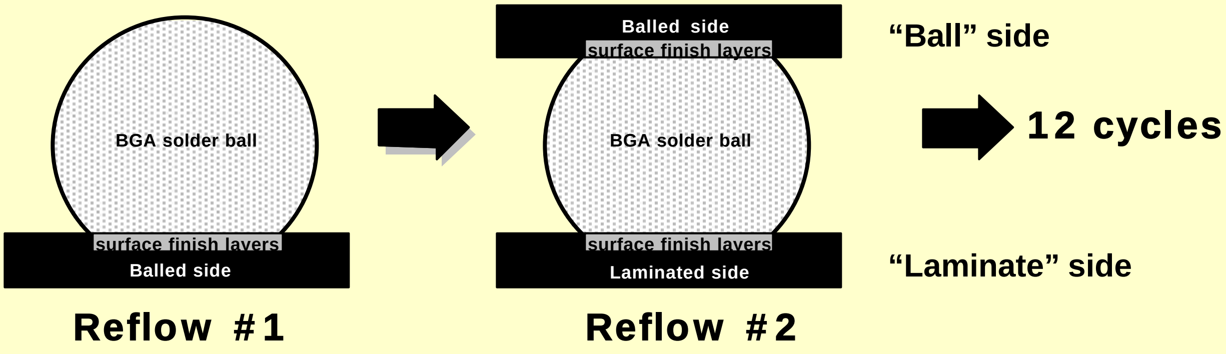
(5/02, SKK)

# Interfacial Microstructure of Sn3.8Ag0.7Cu with Au/Pd/Ni(P)-Cu after 2/1 Reflows at 260C



(5/02, SKK)

# IMC Growth as a Function of Reflow Cycle & Surface Finish



“Ball” side

12 cycles

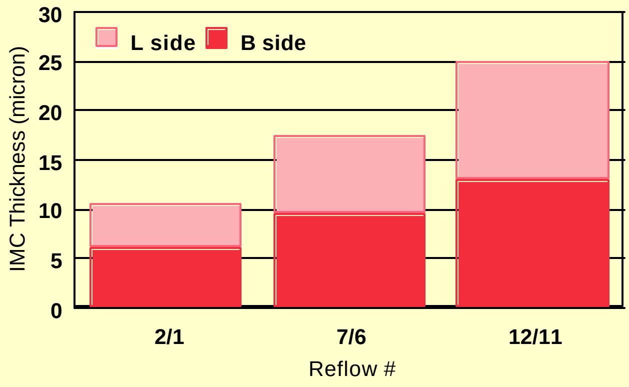
“Laminate” side

**Reflow #1**

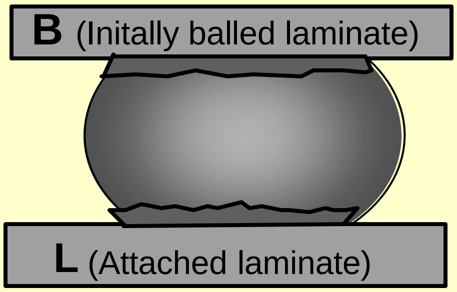
**Reflow #2**

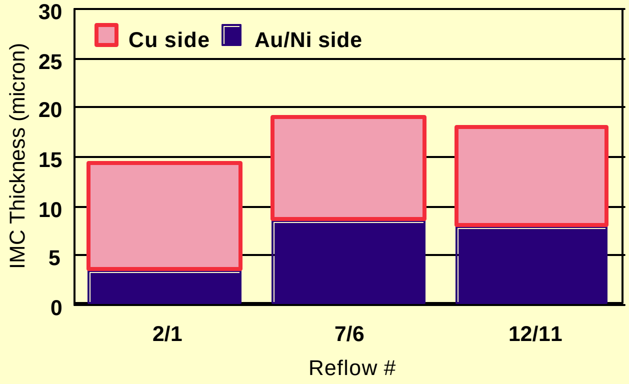
| Module # | Surface Finish (side B) | IMC Thick. (mm) | Surface Finish (side L) | IMC Thick. (mm) | Reflow # at 260 C |
|---|---|---|---|---|---|
| 1 | Cu | 5-7 | Cu | 4-5 | 2, 1 |
| 2 | Cu | 7-12 | Cu | 7-9 | 7, 6 |
| 3 | Cu | 9-17 | Cu | 9-15 | 12, 11 |
| 4 | Au/Ni(P) | 3-4 | Cu | 10-12 | 2, 1 |
| 5 | Au/Ni(P) | 7-10 | Cu | 10-11 | 7, 6 |
| 6 | Au/Ni(P) | 6-10 | Cu | 8-12 | 12, 11 |
| 7 | Au/Ni(P) | 3-4 | Au/Ni(P) | 3-4 | 2, 1 |
| 8 | Au/Ni(P) | 4-5 | Au/Ni(P) | 5-6 | 7, 6 |
| 9 | Au/Ni(P) | 4-6 | Au/Ni(P) | 4-6 | 12, 11 |
| 10 | Au/Pd/Ni(P) | 3-5 | Cu | 5-7 | 2, 1 |
| 11 | Au/Pd/Ni(P) | 5-8 | Cu | 5-8 | 7, 6 |
| 12 | Au/Pd/Ni(P) | 5-12 | Cu | 8-10 | 12, 11 |
| 13 | Au/Pd/Ni(P) | 3-5 | Au/Pd/Ni(P) | 2-5 | 2, 1 |
| 14 | Au/Pd/Ni(P) | 5-7 | Au/Pd/Ni(P) | 3-5 | 7, 6 |
| 15 | Au/Pd/Ni(P) | 4-6 | Au/Pd/Ni(P) | 3-5 | 12, 11 |

# IMC Growth as a Function of Reflow Cycle & Surface Finish

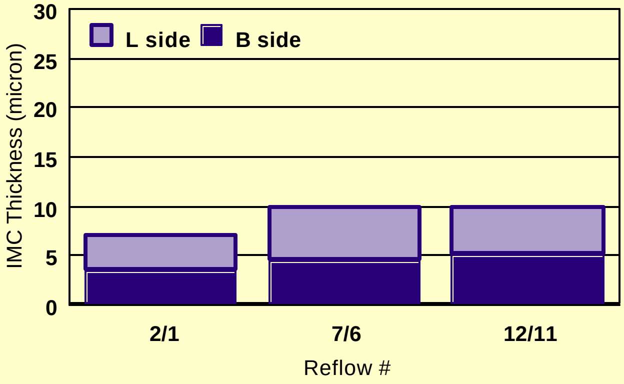


Cu (B) - Cu (L)

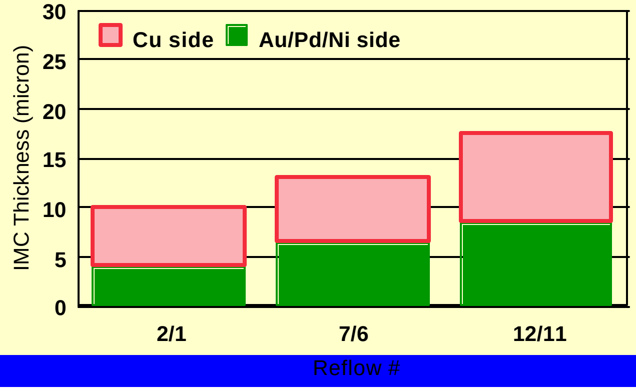




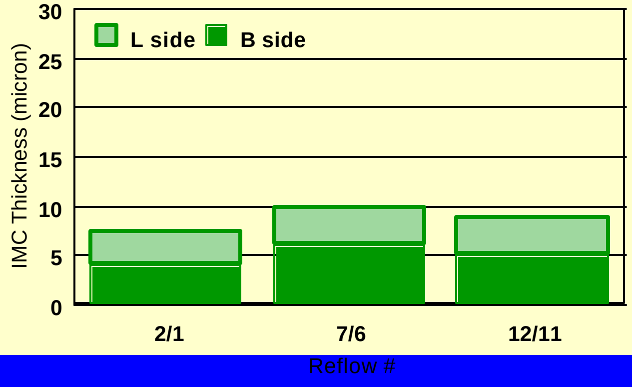
Au/Ni(P) (B) - Cu (L)



Au/Ni(P) (B) - Au/Ni(P) (L)



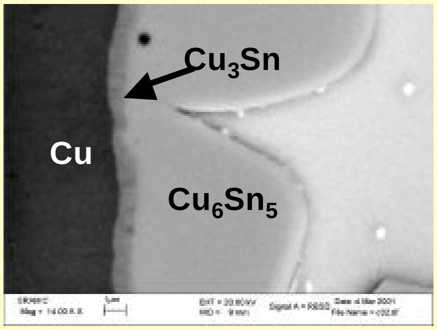
Au/Pd/Ni(P) (B) - Cu (L)



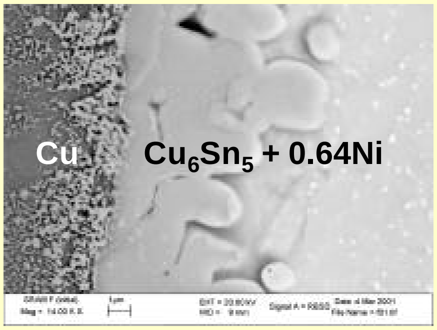
Au/Pd/Ni(P) (B) - Au/Pd/Ni(P) (L)

# Composition Analysis of the Interfacial IMC after 12/11 Reflows

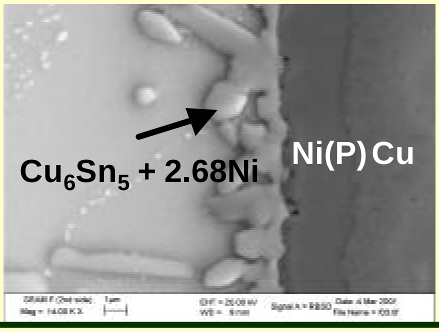
① **Cu side of Cu-Cu**



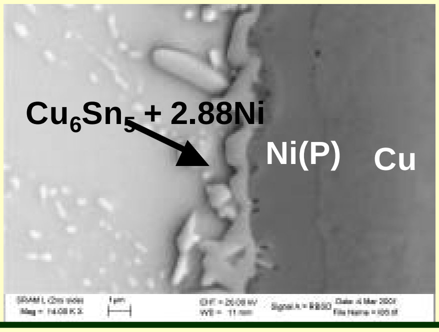
② **Cu side of Au/Ni(P)-Cu**



③ **Au/Ni(P) side of Au/Ni(P)-Cu**

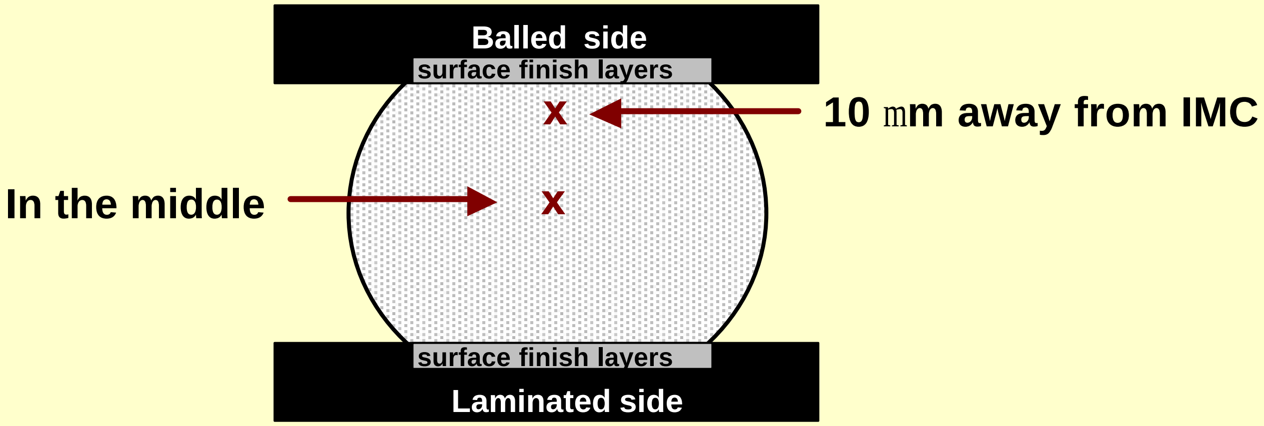


④ **Au/Ni(P) side of Au/Ni(P)-Au/Ni(P)**



| Surface Finish | | IMC (wt%) | | | |
|---|---|---|---|---|---|
| | | Sn (wt%) | Ag (wt%) | Cu (wt%) | Ni (wt%) |
| Cu-Cu ① | | 63.05 | - | 36.95 | - |
| Cu-Au/Ni(P) | Cu side ② | 63.93 | 0.33 | 35.1 | 0.64 |
| | Au/Ni(P) side ③ | 63.32 | 0.3 | 33.7 | 2.68 |
| Au/Ni(P)-Au/Ni(P) ④ | | 71.39 | 0.24 | 25.49 | 2.88 |

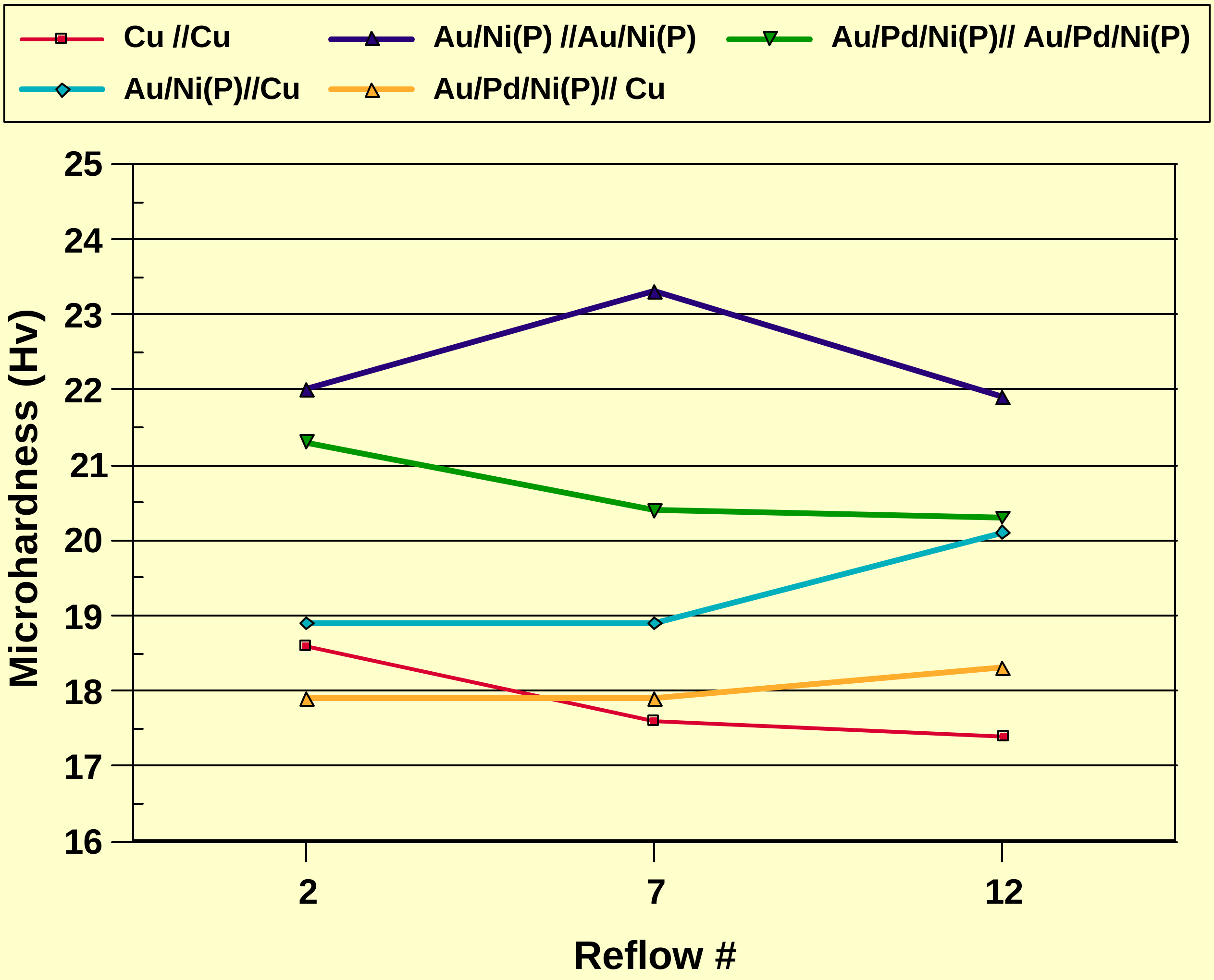
# Composition Analysis in the Solder Matrix after 12/11 Reflow



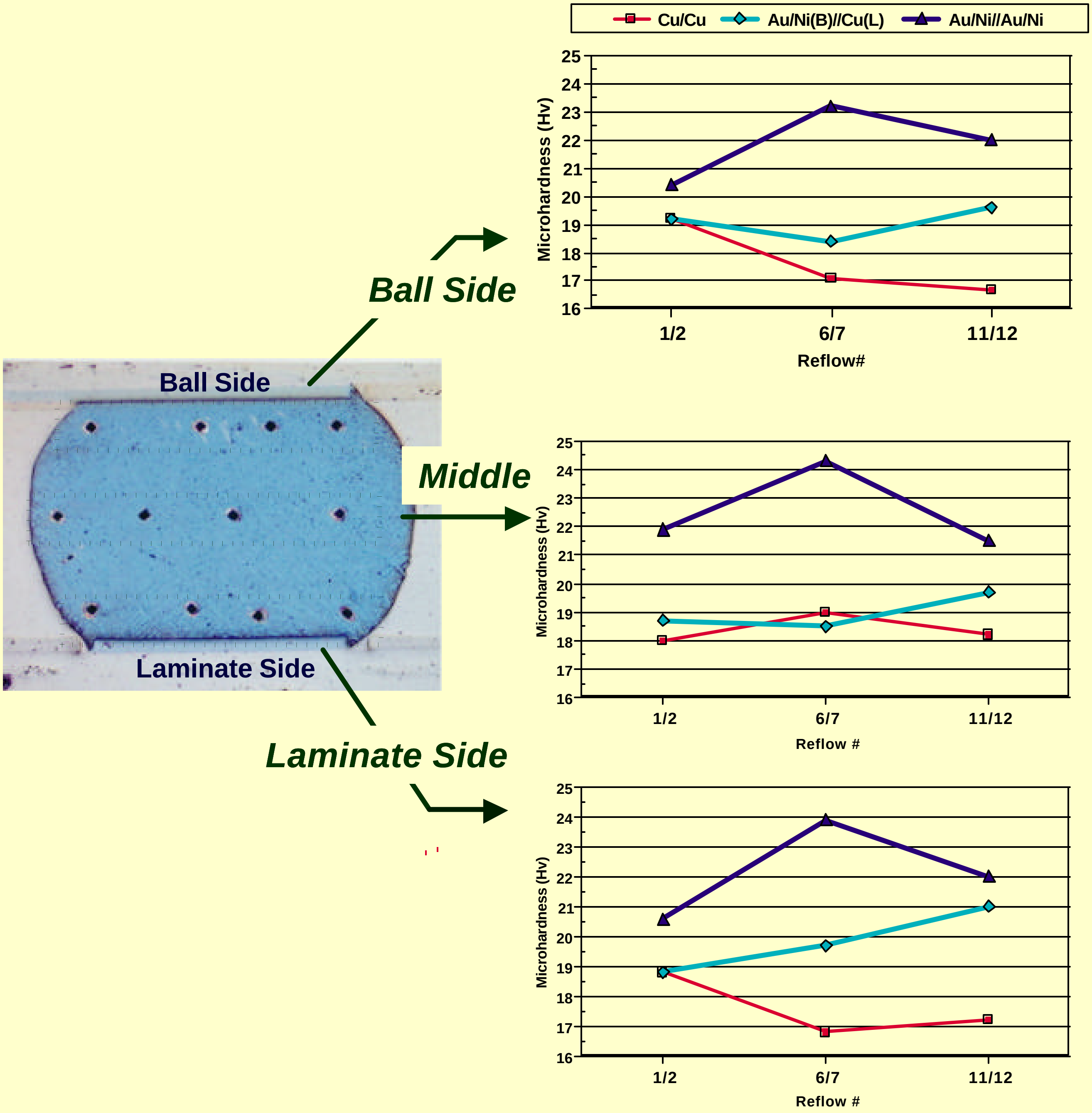
| Surface Finish | Site | Sn (wt%) | Ag (wt%) | Cu (wt%) | Ni (wt%) |
|---|---|---|---|---|---|
| Cu-Cu | Near Cu side | 97.71 | 1.34 | 0.95 | |
| | In the middle | 94.81 | 3.95 | 1.24 | |
| Cu-Au/Ni(P) | Near Cu side | 96.31 | 3.03 | 0.6 | 0.06 |
| | In the middle | 95.17 | 3.57 | 1.26 | |
| Au/Ni(P) - Au/Ni(P)) | Near Au/Ni side | 95.21 | 3.87 | 0.49 | 0.43 |
| | In the middle | 95.12 | 3.65 | 1.23 | |

# Microhardness Variations as a Function of Reflow Cycle

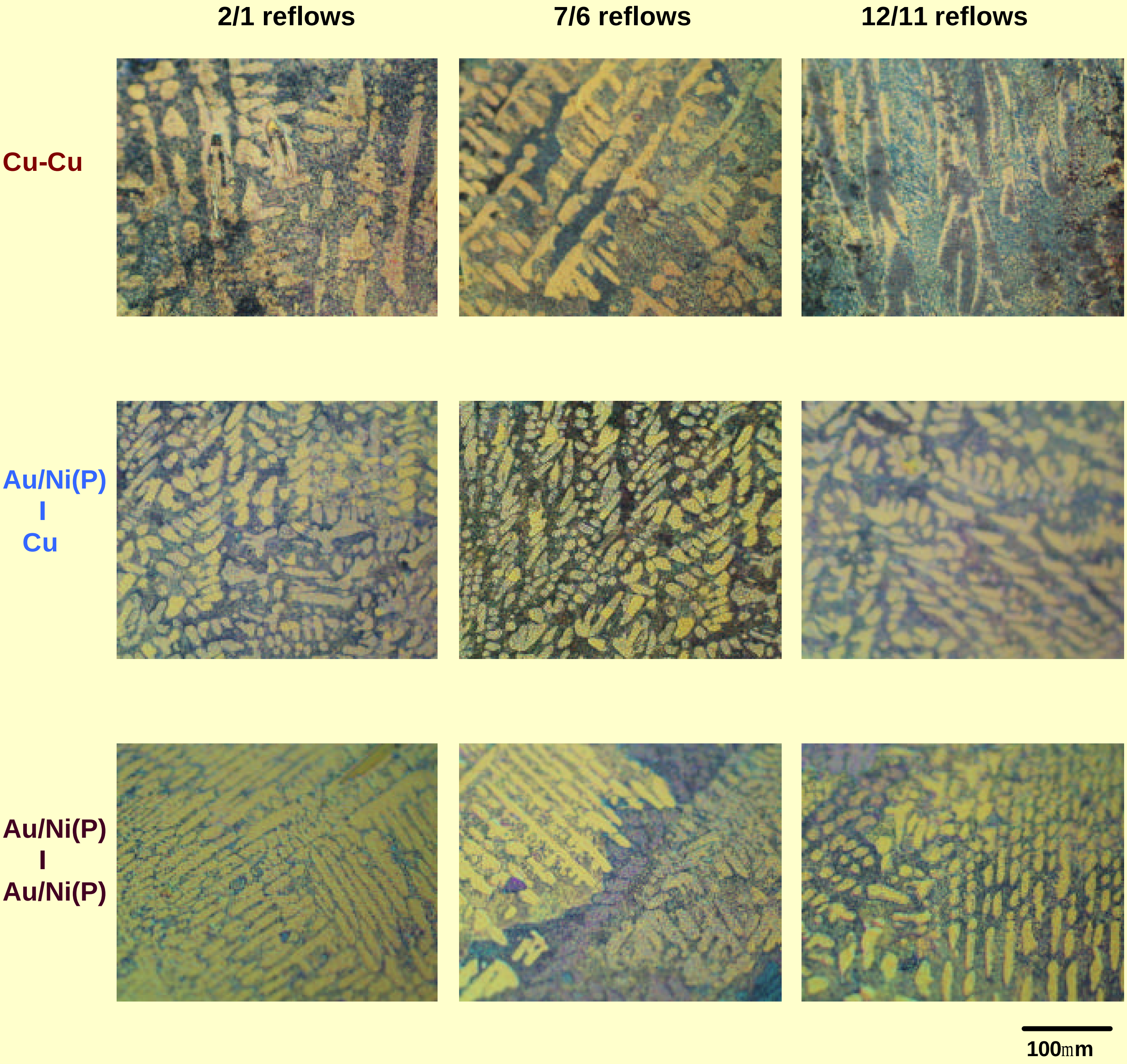
- **Average values in each BGA solder ball**



# Microhardness Variations as a Function of Ball Location



# Microstructure of BGA Solder Balls as a Function of Surface Finish and Reflow Cycle



# Conclusions

- Surface finish plays a dominant role in determining the microstructure, mechanical properties, and possibly the reliability of BGA solder joints.
- IMC growth is faster on Cu than on Au/Ni or Au/Pd/Ni surface finish.
- Microhardness of solder joints is more affected by surface finish, and less affected by reflow cycle.
- Ni-Ni joint is harder than Cu-Cu joint, possibly resulting in reduced fatigue life.
- The microstructure of BGA joints changes with reflow cycles, affected by the dissolution of surface finish layers.

(5/02, SKK)