Recent Developments in Low Temperature Solders

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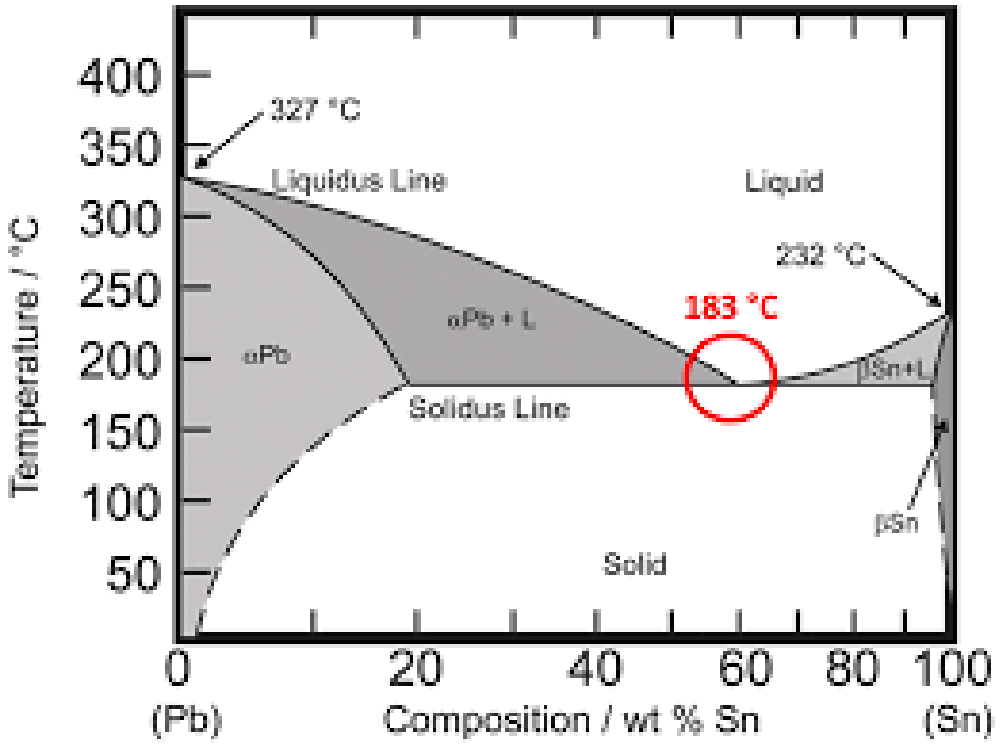
Outline/Agenda

- Introduction
- Advent of SAC305
- Low Temp Desire => Relook at SnBi
- New Alloy Concept
- Supercooled Liquid Solder™
- Q & A

It’s the 1990s and RoHS is Announced

- Yikes, we need a substitute for SnPb solder!
  - 100 years of reliability data
  - Low cost
  - Low melting temperature
  - Assembly process is very well established
  - Good reliability

SnPb Phase Diagram



Alloy Decision Process

- The melting point should be as close to Sn/Pb eutectic as possible
- The alloy must be eutectic or very close to eutectic
- It must contain no more than three elements
- Use of existing patents should be avoided to ease implementation
- Reliability should be equal or better than Sn/Pb

Edwin Bradley – NEMI chairperson, Motorola

So what new alloy to choose?

Classification	Sn	Ag	Au	Bi	Cu	Ga	In	Sb	Si	Zn	Other	Melting Range	Type
High Temperature Solders			96.8						3.2			363	Eutectic
			88.0								Ge(12)	356	Eutectic
	22.0		78.0									280-300	Non-eutectic
	20.0		80.0									280	Eutectic
				100.0								271	Elemental
	95.0							5.0				237-240	Non-eutectic
Mainstream Lead free Solders	95.0	5.0										221-240	Non-eutectic
	65.0	25.0						10.0				233	Eutectic
	99.3				0.7						Ni	227	Eutectic
	89.3	3.8			0.9		0.5	5.5				221-228	Non-eutectic
	98.5	1.0			0.5						Mn	217-226	Non-eutectic
	90.0	3.8		1.5	1.2			3.5				216-226	Non-eutectic
	95.5	4.0			0.5							217-225	Non-eutectic
	89.7	3.4		3.2	0.7			3.0			Ni	210-221	Non-eutectic
	96.5	3.0			0.5							217-221	Near-eutetic
	91.3	3.5		3.0	0.7			1.5			Ni	208-218	Non-eutectic
Medium Temperature Solders	89.2	3.5		0.5	0.8							202-206	Non-eutectic
	91.8	3.4		4.8								211-213	Non-eutectic
	86.9	3.1					10.0					204-205	Near-eutectic
	91.0									9.0		199	Eutectic
	77.2	2.8					20.0					175-187	Non-eutectic
	86.5			3.5			4.5			5.5		174-186	Non-eutectic
Low Temperature Solders	60.0			40.0								138-170	Non-eutectic
							100.0					156.7	Elemental
						0.7	99.5					150	Eutectic
		3.0					97.0					143.3	Eutectic
	42.0	1.0		57.0								139-140	Near-eutectic
	42.0			58.0								138.3	Eutectic
	52.0						48.0					118-131	Eutectic
	50.0						50.0					118-125	Non-eutectic
	48.0						52.0					118	Eutectic
Ultra-Low Temperature Solders				67.0			33.0					109	Eutectic
	46.0						52.2			1.8		108	Eutectic
	16.3			54.0			29.7					81	Eutectic
	17.0			57.0			26.0					79	Eutectic
				33.7			66.3					72	Eutectic
	16.5			32.5			51.0					60	Eutectic
						100.0						29.8	Elemental

Courtesy Raiyo Aspandiar

Scientific Realities: 58Sn/42Bi

- Melting point = 138 °C
- Years of experience
- Poor shock resistance, not a big issue in late 1990s
- 1% Ag addition strengthens this alloy
- Low MP eliminates temperature issues with components and board
- Forms weak alloy in presence of Pb

Scientific Realities: Sn/Ag/Cu

- Melting Point = 217°C
- Cu improves wettability, creep, thermal fatigue
- High solderability & reliability

Lead-Free Early History

- As early as the 1990s NCMS looks at Lead-free
- Tin-bismuth solders rejected
  - Low temp ternary alloy formation with lead contamination
  - Fillet lifting in wave soldering
  - Brittle
  - Poor performance above 100^{o}C
- The industry settles on SAC305 circa 2005
- But with some pain…

What Issues Does High T Cause?

- Component burning or reliability issues
- MSD issues
- Warping: head-in-pillow (HIP)

SAC 305 Tm = 219C

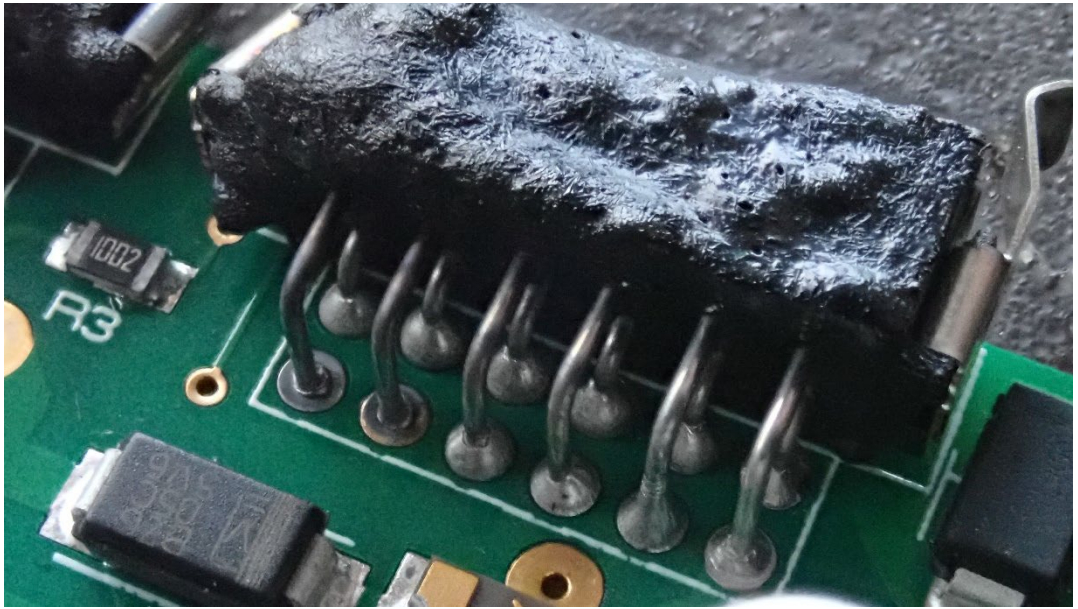


Image Courtesy
Of Bob Willis

MSD Issues

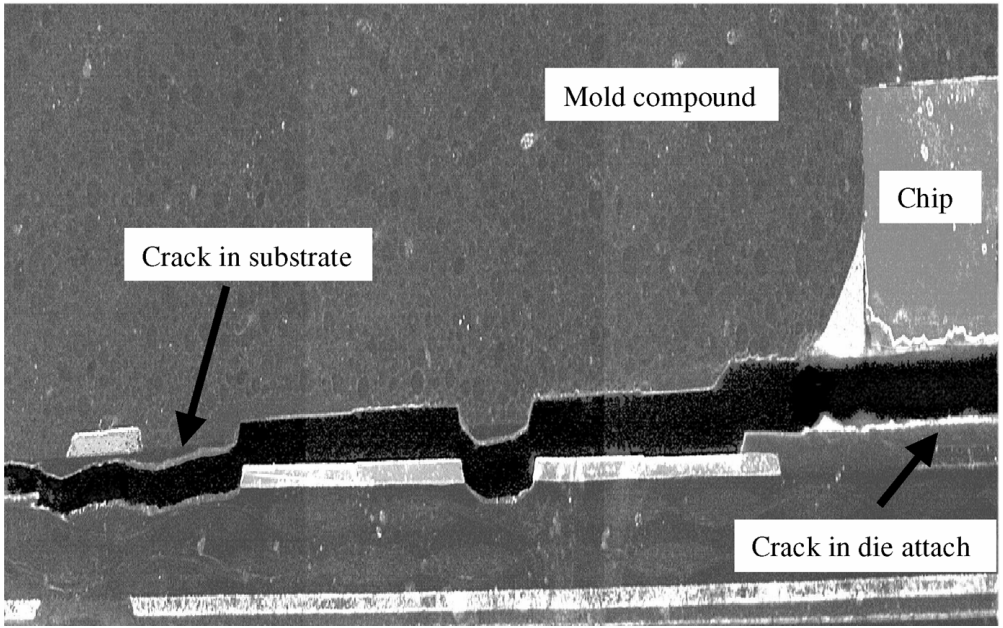
- MSD
  - Shift a level for small boards, two levels for complex boards due to higher temperatures
  - Water vapor pressure increases dramatically with temperature
- Higher Reflow Temps also affects the plastic in the body
  - >250 much, much more severe than > 235^{o}C

MSD Levels

M/S Level	Floor Life Time	At These Conditions
1	**Unlimited**	**≤30 C @85% RH**
2	**One year**	**≤30 C @ 60% RH**
2a	**Four weeks**	**≤30 C @ 60% RH**
3	**168 hours**	**≤30 C @ 60% RH**
4	**72 hours**	**≤30 C @ 60% RH**
5	**48 hours**	**≤30 C @ 60% RH**
5a	**24 hours**	**≤30 C @ 60% RH**
6	**Time on label**	**≤30 C @ 60% RH**

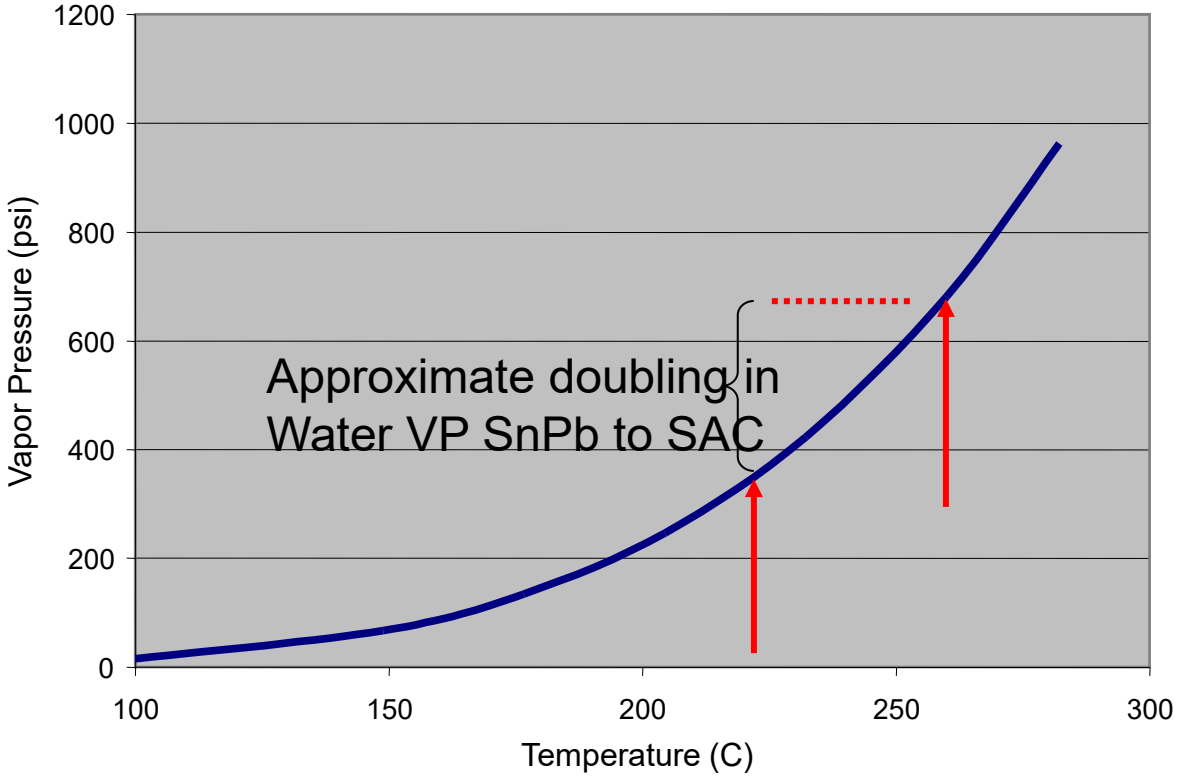
Table I. IPC moisture sensitivity levels give recommended unsealed floor life (i.e., time from parts being unsealed to reflow) for parts on the assembly floor when conventional reflow temperatures are used for lead-based solder. Lead-free solder will shorten these times significantly and, at least initially, result in more factory conditioning and sealing of parts. Source: IPC.

Cross-Section of the 2-Layer PBGA Package after Level 2a/260°C Stressing Indicating De-lamination within the Die Attach Layer and Internal Substrate Layers

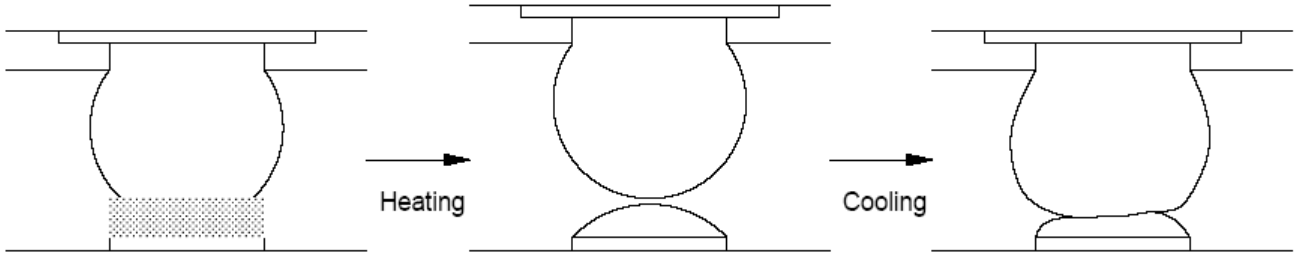


Ref: B.T. Vaccaro, R.L. Shook, D.L. Gerlach, “THE IMPACT OF LEAD-FREE REFLOW TEMPERATURES ON THE MOISTURE SENSITIVITY PERFORMANCE OF PLASTIC SURFACE MOUNT PACKAGES”, SMTA International, Chicago, IL, September 24-28, 2000.

Water Vapor Pressure vs. Temperature



How HIP Happens

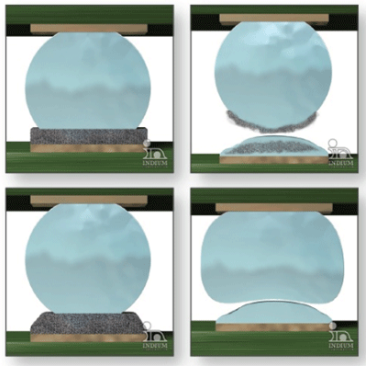


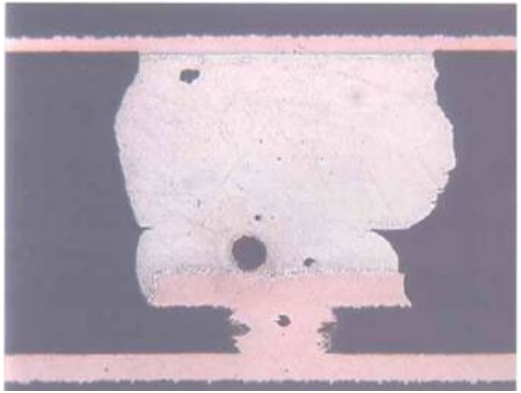
BGA placed on solder paste

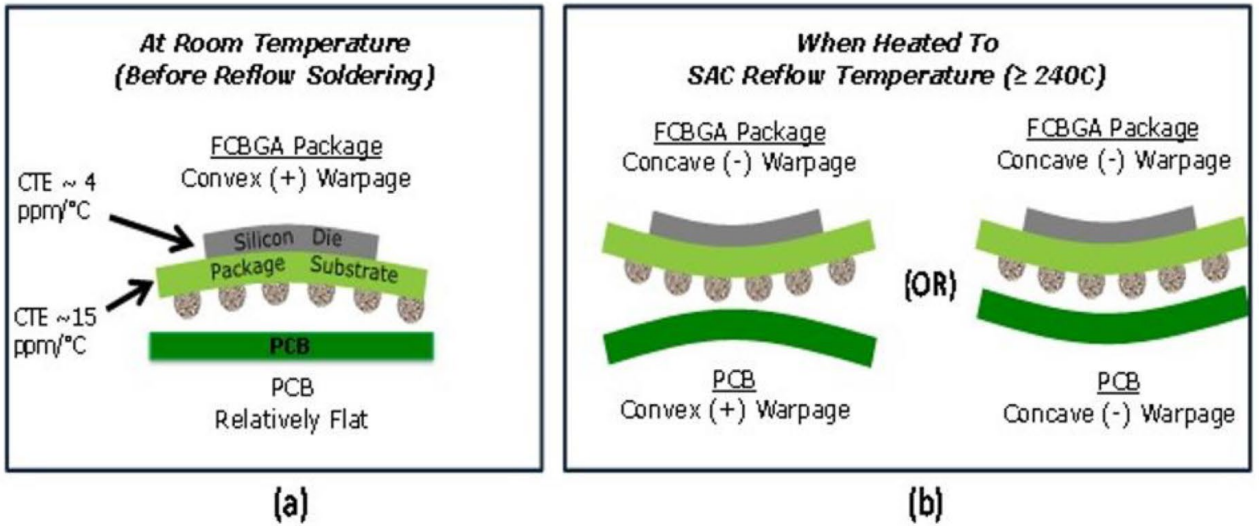
Increased spacing due to warping.
Both sides in liquid state.

Spacing closed down at cooling,
contacting each other after solidification

Problem:

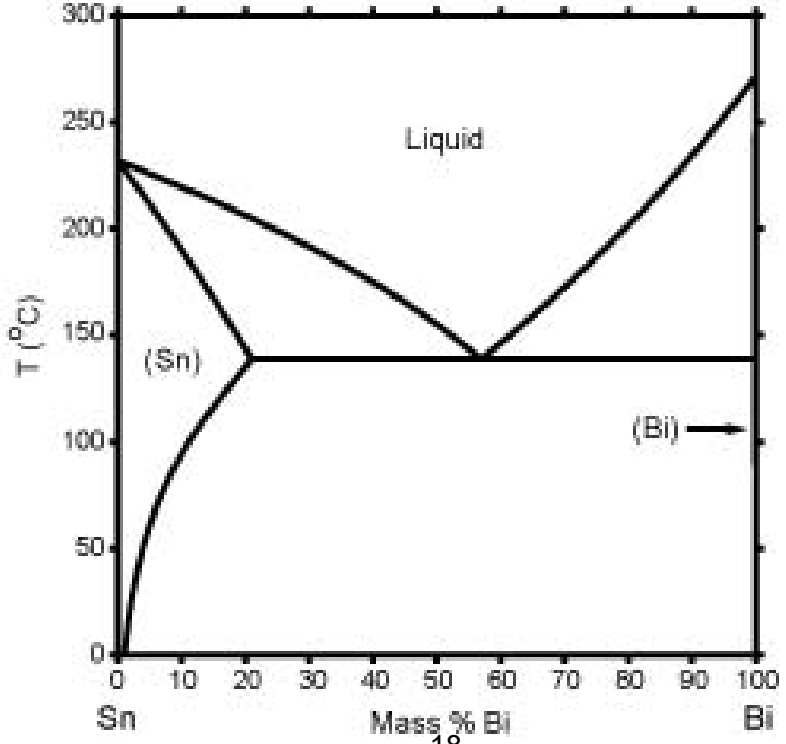






Courtesy Raiyo Aspandiar

So Let's Look at Low T Solders Again



SnBi Phase Diagram

Scientific Realities: 58Sn/42Bi

- Melting point = 138 °C
- Years of experience
- Poor shock resistance
- 1% Ag addition strengthens this alloy
  - But doesn't help drop shock
- Low MP eliminates temperature issues with components and board
- Forms weak alloy in presence of Pb (No issue today)
- Dopants arrive on the scene in the mid 2000s

The Effect of Dopants: Ni

A Nickel Addition was found to be most effective

The Effect of Dopants: Ge

The Ge acts as an antioxidant and surface active agent

Sn-0.7Cu-0.05Ni

15 minute
Ramp to 340°C
30 minute cool

Sn-0.7Cu-0.05Ni+Ge

Dopants and Sn-58Bi

Table 2. Potential dopants to Sn-58Bi and their impact on solder joint microstructure and material properties

Alloy Property	Dopants that improve this property	Dopants that impair this property
Refined microstructure	Sb, Co, Ce, La, Ti, Cr (0.2% ideal), Ag, Cu, W, In, Zn, Ni, P	
IMC regulator (esp. Cu_3Sn suppression)	Ni, Co, Zn, Fe (all effective at suppressing Cu_3Sn growth), Ag, Zn, Cr, Ce, Ga (form IMCs that hinder Cu/Sn diffusion), Mo	In
Pinning of grains	Sb, In, Zn, Ti, Ag, Cr	
Improved ductility	Sb, Cu (<1%), Ce, Ag, In, Cr, Zn (<1.5%), Fe, Ni, P (0.01%)	Cu (1%), Ti, P (≥0.05%)
Improved strength	Ag, Cr, Cu, Ti, Mo, Mn, W, Zn, N	In, Ce, Sb
Improved wettability	Ni, P, RE (Ce, La), Sb (<2%), Mo, Cu	Zn, Ti, Ag, In

Allen, Aileen, Holder, Helen, Benedetto, Elizabeth,
A Review of Dopants in Sn-Bi Solders, SMTAI 2022, Minneapolis.

Early Work on SnBi Solders

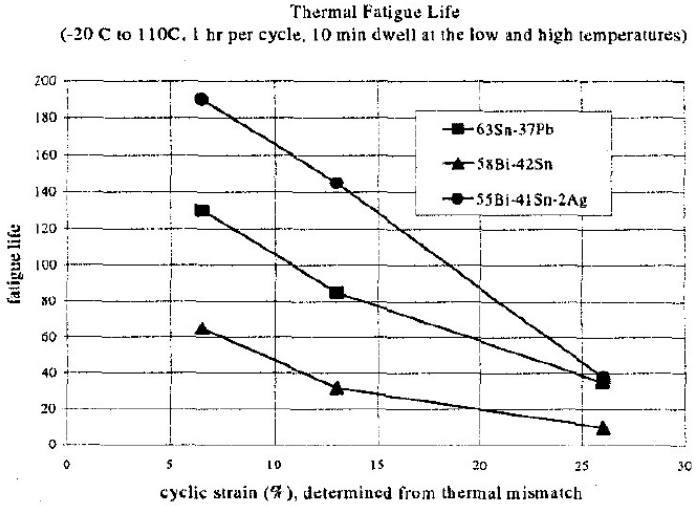


Figure 7. Thermal fatigue life of 58Bi-42Sn vs. 63Sn-37Pb vs. 55Bi-41Sn-2Ag

Hua, Fay, Mei, Zequn, and Glazer, Judy, *Eutectic Sn-Bi as an Alternative to Pb-Free Solders*, Proceedings of the IEEE Electronic Components and Terchnology Conference, 1998, p 277-283.

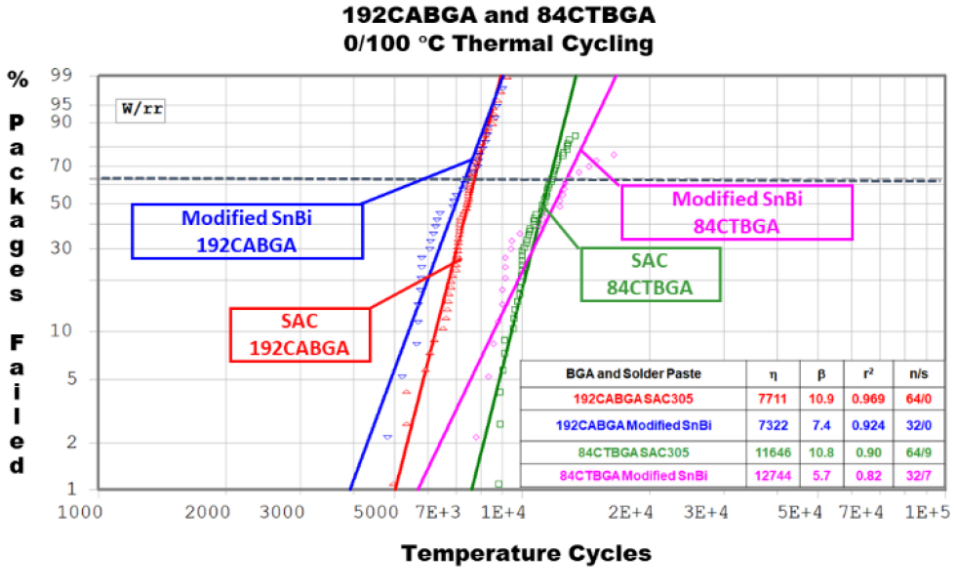


Figure 1. Weibull plots comparing thermal cycling performance for two ball grid array components fabricated and assembled with SAC305 solder or a modified SnBi-based solder [15, 16].

Coyle, Richard etal, *Thermal Fatigue of QFN and Chip Resistors Assembled With SnPb, SAC305, and SnBi Solders,* SMTAI 2022, Minneapolis.

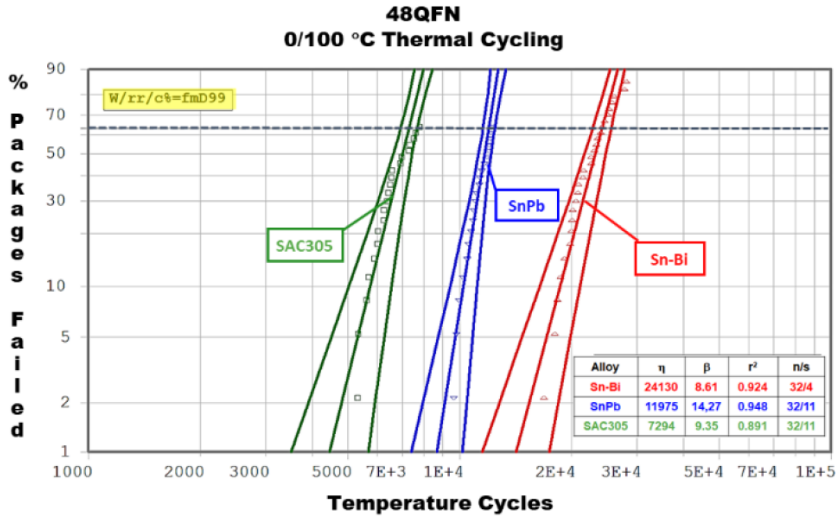
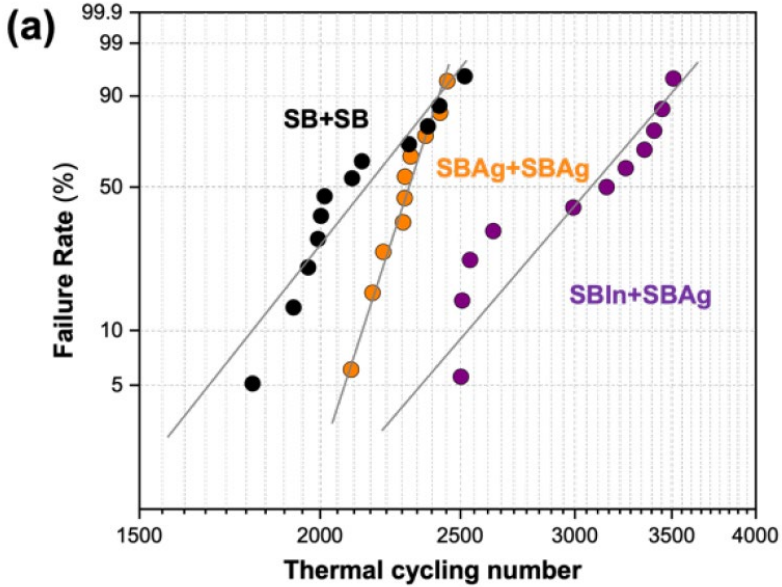


Figure 13. Weibull plots comparing the thermal cycling performance of the 48QFN. when assembled with SnBi, SnPb, and SAC305 solder alloys. The second plot has 99% confidence intervals overlaid.

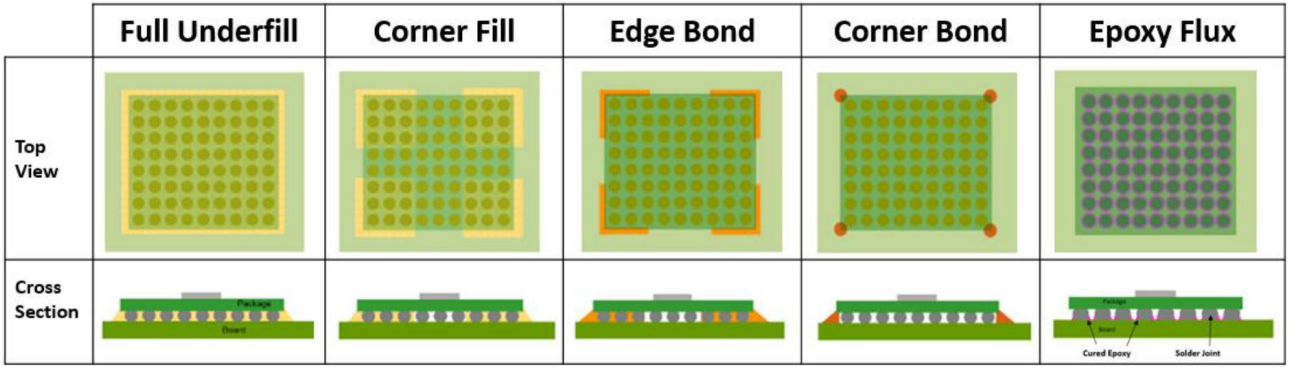
Coyle, Richard etal, *Thermal Fatigue of QFN and Chip Resistors Assembled With SnPb, SAC305, and SnBi Solders,* SMTAI 2022, Minneapolis.



Low Melting Temperature Solder Interconnect Thermal Cycling Performance Enhancement Using Elemental Tuning

[1]Kendra Young, [2,3]Nilesh Badwe, [2]Raiyo Aspandiar, [2]Satyajit Walwadkar, [4]Young-Woo Lee, [4]Hui-Joong Kim, [4]Jung-Tak Moon and [1,5]Tae-Kyu Lee

Underfills



Courtesy Raiyo Aspandiar

Underfill => Good Drop Shock

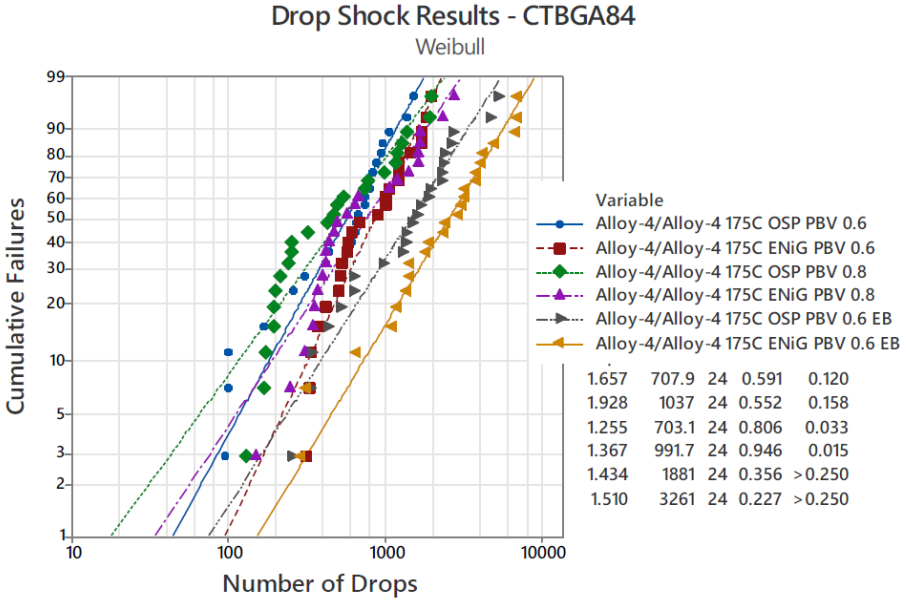


Figure 10. Effect of solder paste volume and polymeric edge bond on the drop shock of homogeneous Alloy-4

Reliability Performance of a Fourth Generation Low Temperature Solder Alloy in Homogeneous and Hybrid Solder Joints

Rebis, Morgana, etal, Reliability performance of a Fourth Generation Low T Solder Alloy SMTAI 2022 Minneapolis

SnBi Summary

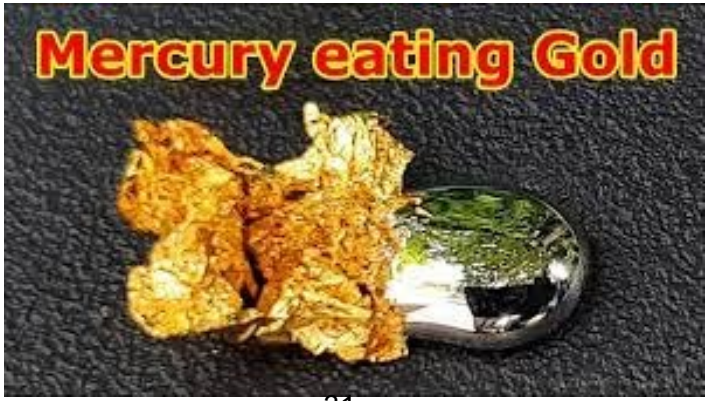
- 30 or so of 85 papers at SMTAI 2022 were on LTS mostly SnBi
  - $100Ms in R&D
- SnBi with dopants has excellent TC performance
  - But only 0 to 100C, not higher temps
  - Unsuitable for harsh environments?
- SnBi has poor drop shock performance, needs underfill to be used in portable devices

One Small Problem……

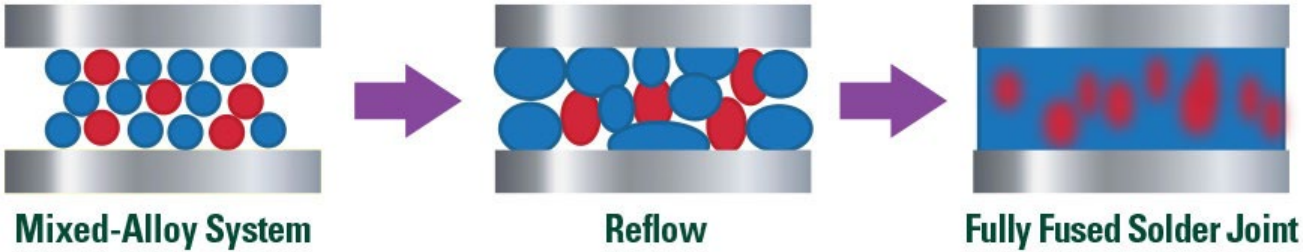
- **NO ONE IS USING SnBi!!!!**
- **Except:**
  - TVs, headphones
    - For cost savings mostly
  - Tried in some laptops with reliability issues
  - “I feel there will be a niche market for low temp alloys since beyond the current package warpage driver, silicon heterogenous technology smaller than 2 nm nodes will be affected in performance when exposed to temperature 200C after circuit formation in the wafer. But this will be in- the 2026 time frame. Then there is the photonic component fiber alignment issue that Intel and others are dealing with currently.” Raiyo Aspandiar

Mercury Dissolves Gold Suggests Another Approach

- Gold Melts at 1064°C
- Yet mercury dissolves it a room temperature
- Used in artisanal gold mining

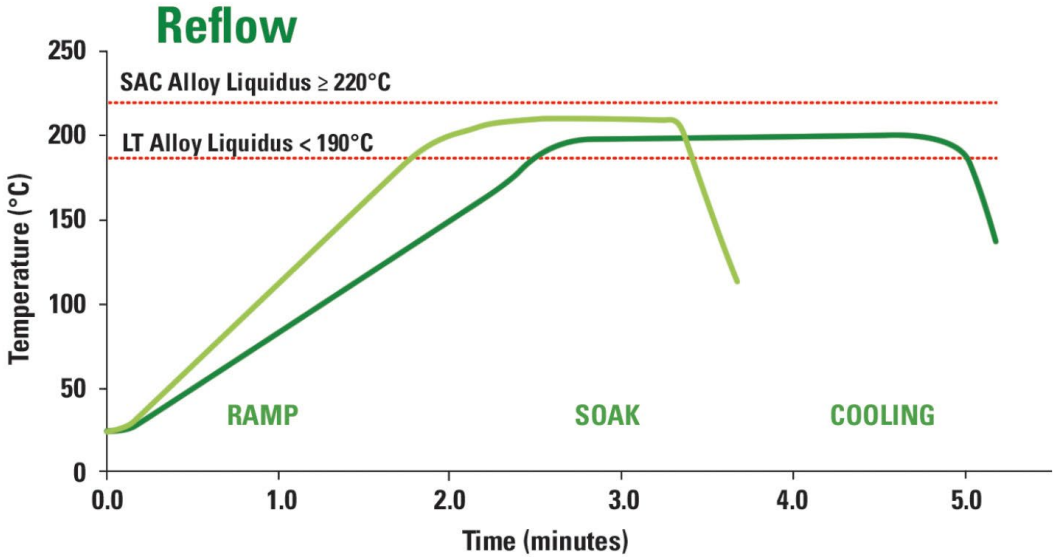


Soldering Application



Hongwen Zhang: A solder containing a low-melting indium-based alloy which initiates joint fusion, while the high-melting SAC alloy provides enhanced strength and durability

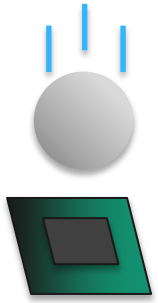
Reflow at 210°C for Typical Time

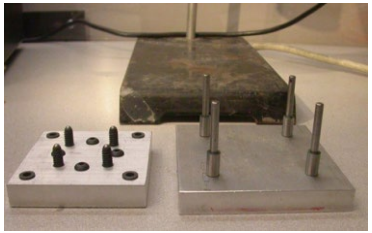


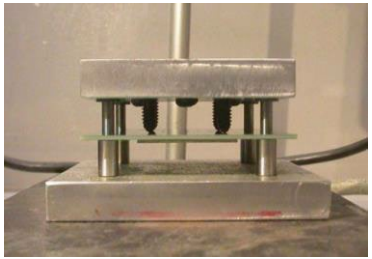
Remelt temperature about 200°C

Drop Shock Methodology

Indium Corporation uses a ball drop - type test to determine drop shock reliability

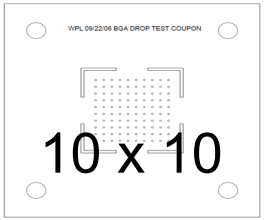


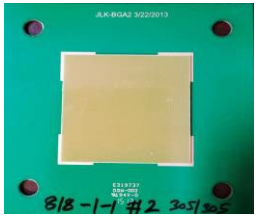




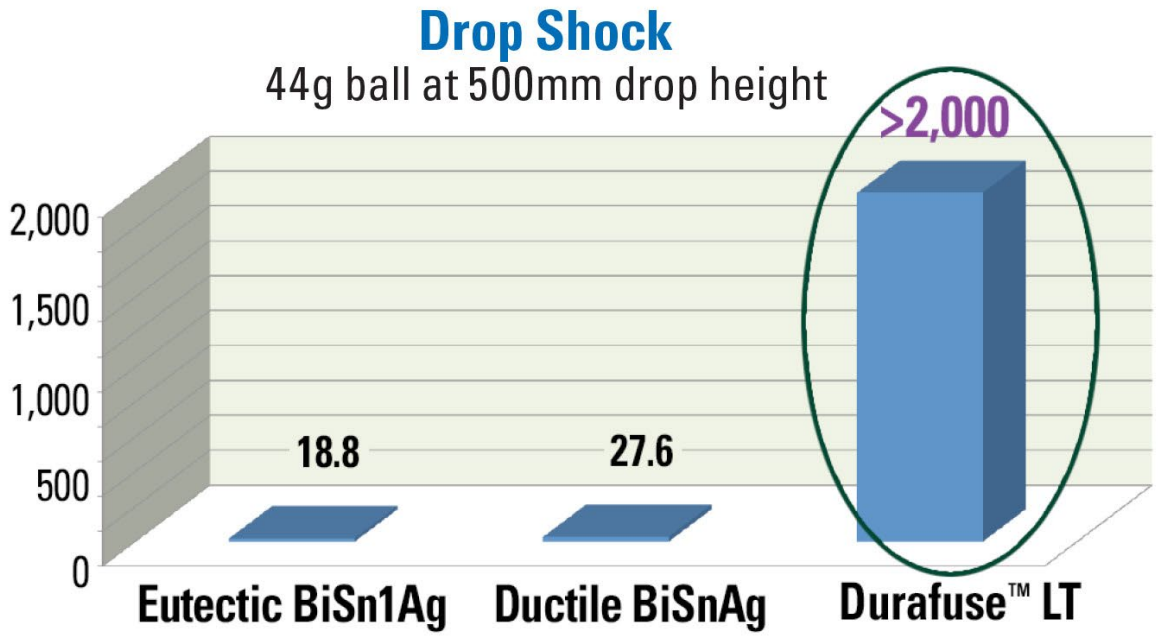
Drop Test BGA

10x10 grid
Diameter 0.6MM
Pitch 4.5MM





Superior Drop Shock

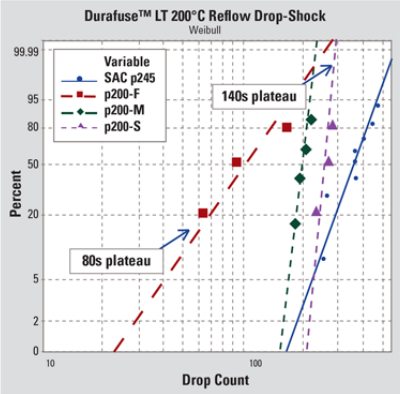


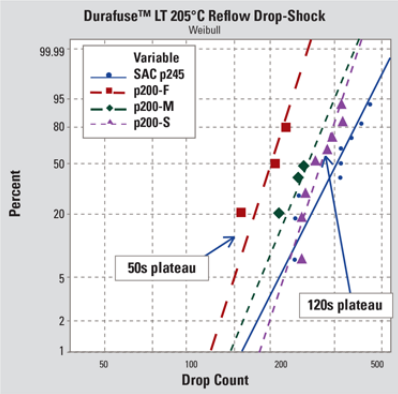
Reflow Optimization

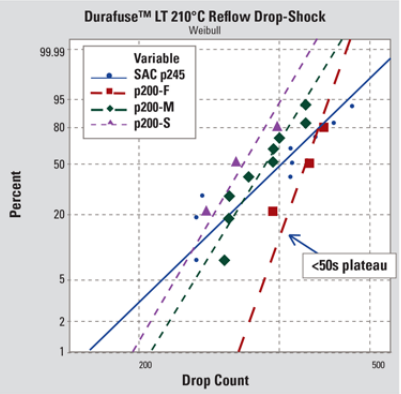
Fusion Time vs. Drop Shock Performance

Peak temperature and time at peak can be used to optimize for drop shock resilience

Reflow oven belt rate
Fast Medium Slow
SAC305

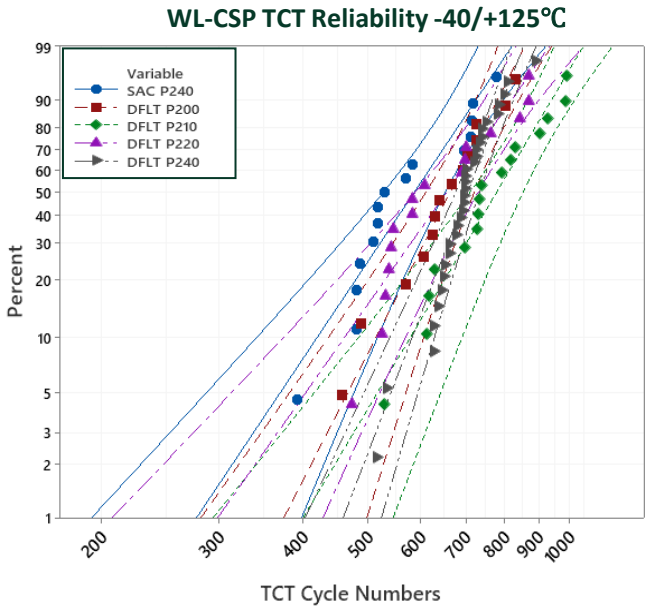






Thermal Cycling

-40/+125℃ TCT for CSP Components



Alloy	63% Lifetime	Improvement vs SAC
SAC305	625.8	N/A
Durafuse™ LT 200°C	697.2	11.41%
Durafuse™ LT 210℃	824.5	31.75%
Durafuse™ LT 220℃	701.9	12.16%
Durafuse™ LT 240℃	730.9	16.79%

Performance equal or superior to SAC305 on fine pitch (0.4mm) components

Wafer-level Package

- 6.4x6.4mm^2 chip
- 0.25mm SAC BGA ball
- 0.4mm pitch
- NSMD OSP Cu Pad
- 0.3mm pad size

Good News!

- It's being used by:
  - Major mobile phone manufacturers
  - A major electronic vehicle manufacturer
  - On tens of millions of PCBs in 2023

Supercooled Soldering™ Technology

Ian Tevis, PhD
Indium Corporation – SAFI-Tech Group
itevis@indium.com
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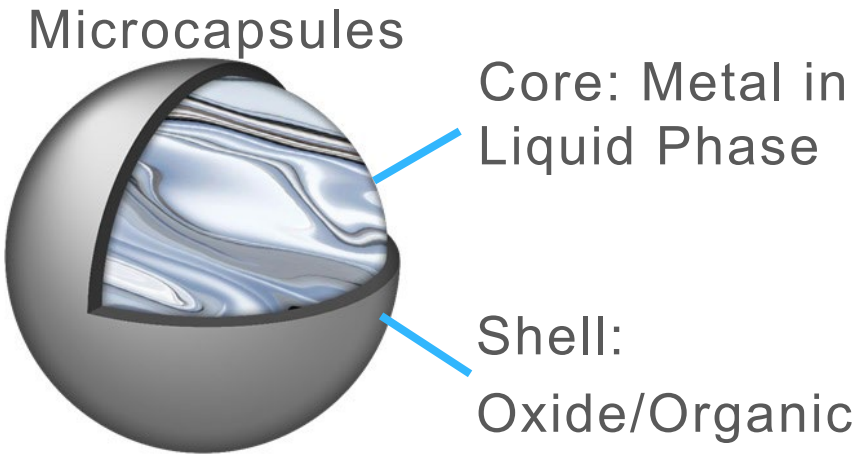
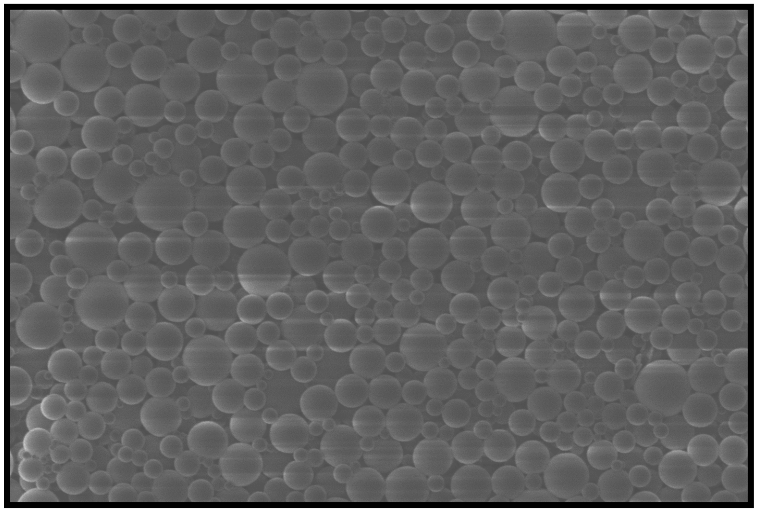
Supercooled Liquid Metal Microcapsules

Tiny Supercooled Liquid Metal Particles (microcapsules), when punctured or broken, turn into a solid metal.



SEM Video



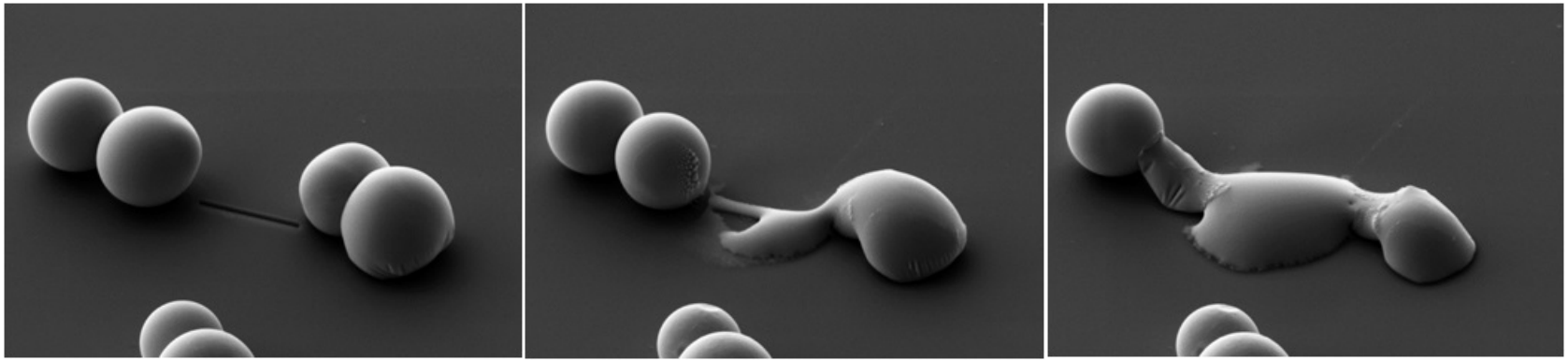
*Using Focused Ion Beam

Advantages:

Solder metals, On demand, With lower heat

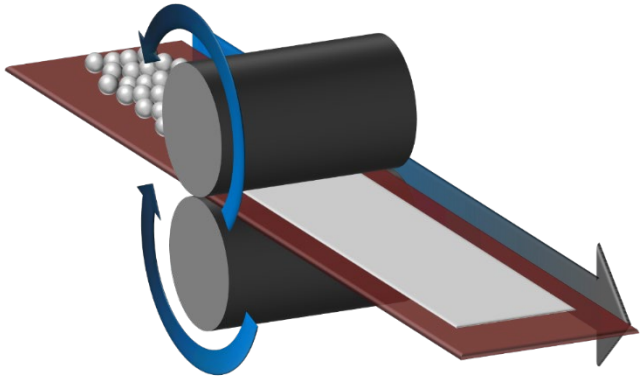
Background: Microcapsules in Action

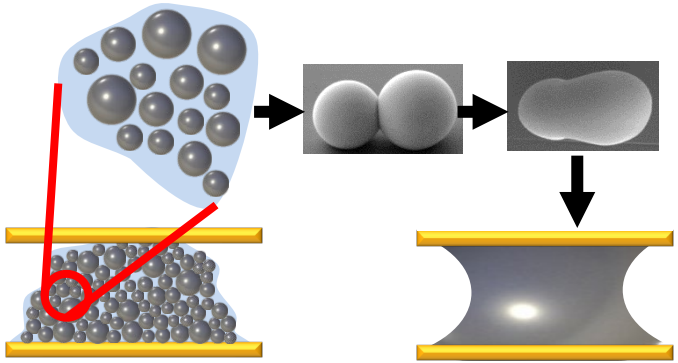
Removal of the outer shell allows the liquid metal inside to flow out, wet the contact surface, join, and solidify in seconds



Application

Activated both mechanically and chemically, allowing for dozens of potential activation processes

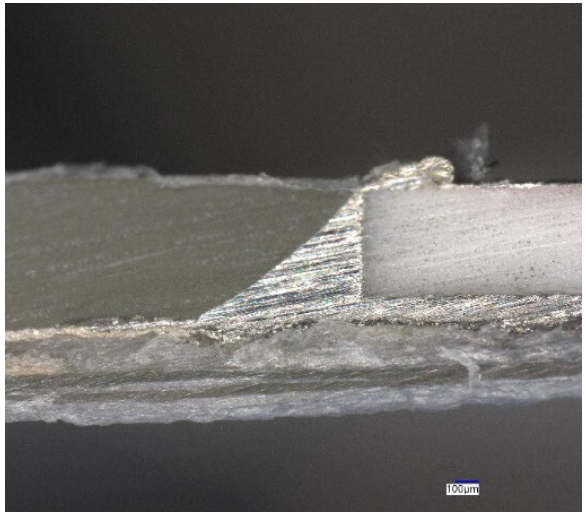


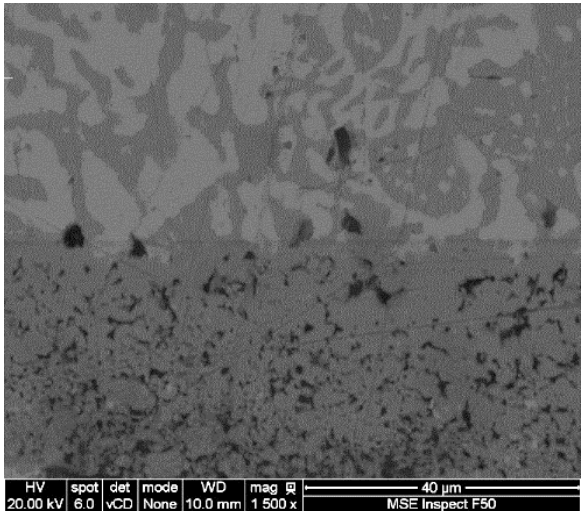


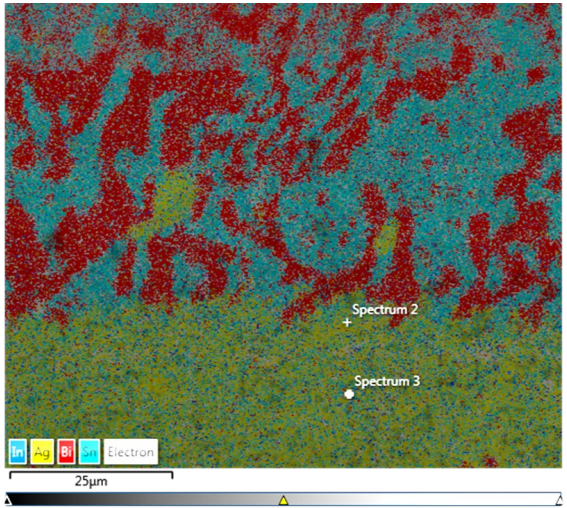
Mechanical Activation
Mechanical pressure breaks shell to release liquid metal

Chemical Activation
Acidic solder flux dissolves shell to release liquid

Supercooled BiSn Reflow

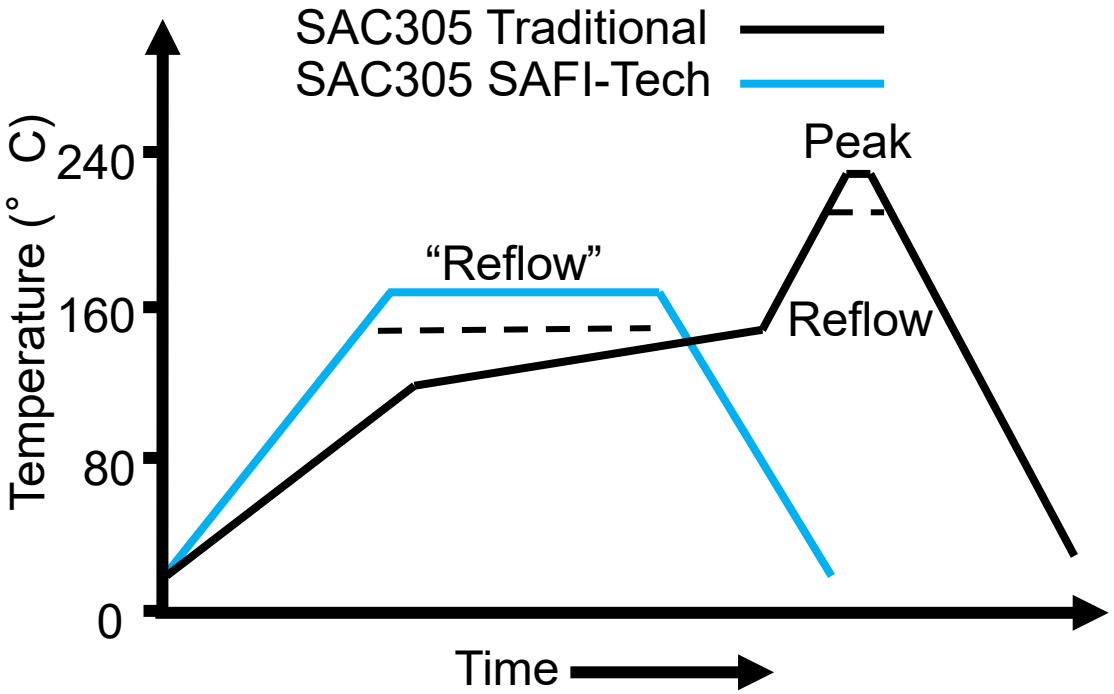






BiSn reflowed at 135 ° C on PET (normal reflow 150-160 ° C)

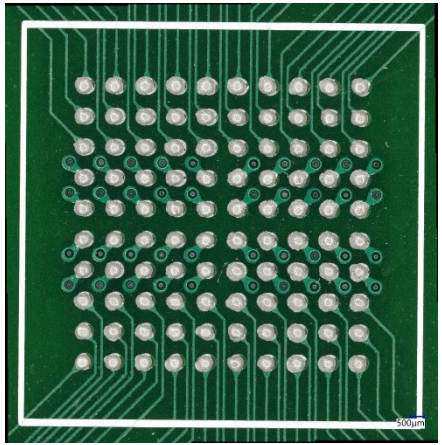
Target Interconnect Formation Process



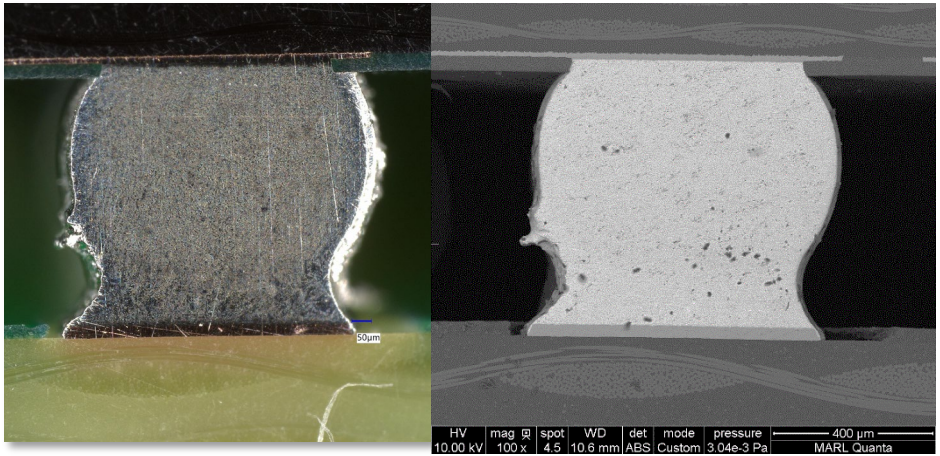
Supercooled Microcapsules in Action

Demonstrated SAC305 solder joint creation from Supercooled Microcapsules

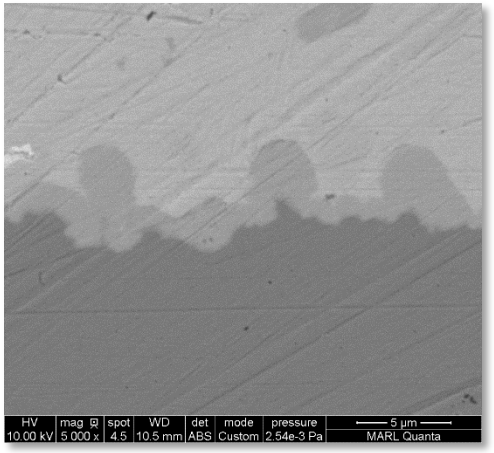
SAFI-Tech Reflow at 180 °C (Normal reflow at 240-260 °C)



SAFI-Tech printed BGA grid pattern



Cross-section of SAC305 BGA with SAFI-Tech SAC305 solder joint



Cross-section of SAFI-Tech SAC305 solder joint interface with intermetallics

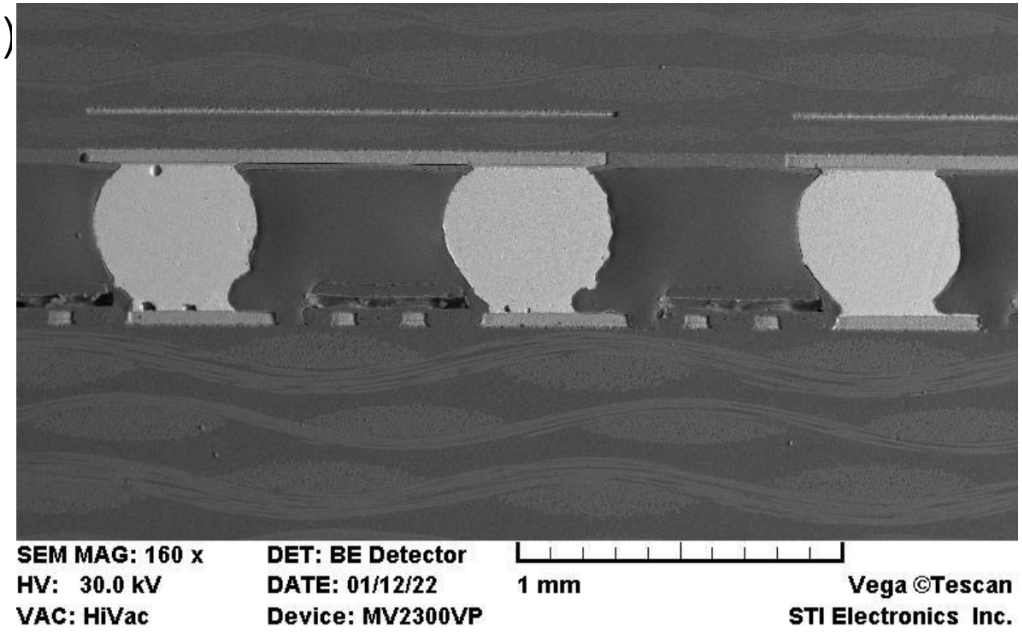
All BGA joints conductive with no failures for 1000 cycles of thermal shock (-40 to 110 ° C) - STI Electronics

Prototype Results: Thermal Cycle Reliability

Test Vehicle: BGA100 (Daisy Chained)
- 100 SAC305 Balls
- Ball Diameter: 465 µm
- Pitch: 1 mm

Thermal Cycle Conditions
- Cycle -40° C to 110 ° C
- 10 min at each extreme
- 3 cycles/hour
- 1000 cycles total

Cross-section after thermal shock



Results
- Passed electrical testing, no full fractures observed
- Voiding observed with some starting to fracture
- More paste volume needed

Question and Answers

Thank You!

Partially Funded by: DOE SBIR Award : DE-SC0020704
Partially Funded by: SEMI-FlexTech Award : FT19-19-190

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