Development of a Lead-Free Alloy for High-Reliability, High-Temperature Applications

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ABSTRACT

Though the electronics industry is nearing the 3-year anniversary marking the ban of lead from electronics products, several challenges still remain with existing lead-free materials for certain applications. The commonly used and accepted SnAgCu (tin-silver-copper, also known as SAC) alloy has proven to be a suitable material for the production of many devices but, for those applications that require extremely high reliability, current SAC materials are less than ideal. In particular, devices that will find end use in automotive and military/aerospace products require a lead-free material that can withstand the higher temperatures operation life (e.g. automotive under-the-hood conditions), offer vibration resistance not commonly associated with traditional SAC alloys and deliver high temperature (> 125^{o}C) thermal cycling reliability levels beyond those available with current commercialized SAC materials.

Key words: Pb-free Alloy, High temperature reliability

INTRODUCTION

With increasing requirements for lead-free solders, the industry's research has veered towards studying the mechanical properties and behaviors of the Sn-Ag-Cu solder, particularly those with alloy composition near the eutectic point [1-4]. Such solders have proven their reliability in the area of thermal cycling and are in fact currently widely used as one of the lead-free solders in SMT assembly process for microelectronics. Thermal fatigue life of solder joints has been reported to increase with Ag content in Sn-xAg-Cu solders [3]. However, the exponential increase in the demand of portable products has caused growing concerns over drop reliability of these high Ag content solder joints. Recent studies show that Sn-xAg-Cu lead-free solders with low Ag content exhibited longer drop lifetimes than that with high Ag content [5]. Thermal fatigue life and drop performance are now competing factors for deciding the amount of Ag content in Sn-xAg-Cu solders. Some researches have also concluded favorably on the effect of metal dopants, such as Ni, on solder joint drop performance [4]. Such dopants are known to alter the microstructure and mechanical
behavior of Sn-Ag-Cu lead-free solder [6].

Recognizing these challenges, a group of specialists made up of industry users, members of the academic community, material, component, and equipment suppliers (Table 1) set out to develop an alloy that could meet or exceed the high-temperature, high-reliability requirements necessary for automotive and military applications, yet still be solderable at a reasonable temperature. The project members agreed on the following goals for the alloy:

- Material must be lead-free
- Work in an operating temperature of up to 150°C
- Solder joints should survive 1,000 cycles at -55°C to 150°C
- Reflow at 230°C or below
- Meet RoHS standards and be cost-competitive

Table 1. Team Members

Lead Member	Siemens Berlin (central lab)
Academic Partners	University of Bayreuth
	Fraunhofer inst. IZM
Users	Siemens
	Bosch
	Motorola
Suppliers	Henkel
	Stannol
	Cookson (Alpha Metals)
	Seho
	Infineon (Munich)
	TI (Munich)
	Epcos (Munich)
	Microtech (Maintz)
	Ruwel

EXPERIMENTAL_APPROACH

Analysis of existing alloys and the potential modifications to these alloys provided the foundation for the work. Knowledge of the limits of SnPb and the two most well-known SnAgCu alloys helped drive the direction of the new alloy development: While SnPb has good high-temperature resistance, it contains lead so is not a suitable material; and, both SAC alloys (SnAg3.5/SnCu0.7 and SnAg3.8Cu0.7) have limited reliability in high operating temperature applications. The team established that the required properties could not be achieved with a 3-component alloy but would require a multi-element approach. It was decided that SnAg3.8Cu0.7 (SAC387) would be the base alloy and its properties modified to meet the designated requirements by adding additional elements to the mix.

Using the Coffin-Mansion equation, $(N_f)^c \Delta\varepsilon_{pl} = C$, to predict the number of cycles to failure, the hypothesis is that a new alloy that has an activation energy ($\Delta\varepsilon_{pl}$) at 150°C equivalent to the activation energy of failure of SnPb at 85^{o}C and SnAgCu at 120^{o}C, provides the level of reliability required. Since the activation energy for failure is related to the thermal cycling temperature, having the same term for the new alloy at higher temperatures (150^{o}C) as the term for SnPb at 85^{o}C should provide the same level of reliability(e.g. number of cycles to failure).

There are several commonly known methods used to raise the creep resistance of solder alloys, including grain refinement, solid solution strengthening and precipitation (dispersion hardening/strengthening). Of these methods, grain refinement was ruled out as it is most applicable for lower temperature applications, and solid solution strengthening and precipitation hardening were the techniques chosen. Once the methods were determined, a variety of alloying elements were analyzed and the three that were ultimately selected for their properties, ability to raise creep resistance and maintain an acceptable melting temperature were bismuth (Bi), antimony (Sb) and nickel (Ni). The challenge, of course, was combining all of the elements in proper balance.

RESULTS

Analysis of creep strength characteristics indicated that the addition of Bi, or Sb to SAC387 delivered improved results, **Figure1**.

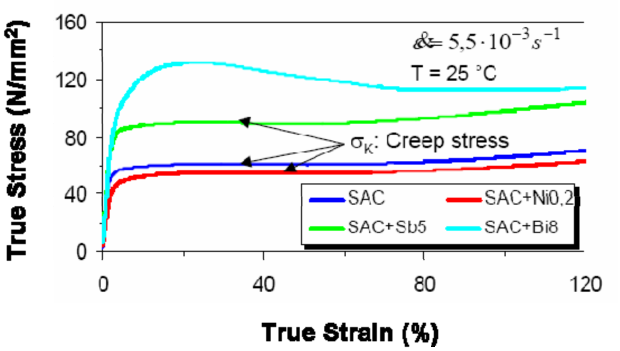

Figure 1. Creep characteristics of solder alloys. SAC = Sn, 3.8%Ag, 0.7%Cu.

The team then worked to optimize this property by fine-tuning the ratio of these elements and Ni in the 6-part alloy, and results revealed that the new alloy, called Innolot, provided the required increase in creep strength as compared to either SAC387 or SnPb37. **(Figures 2 and 3)**.

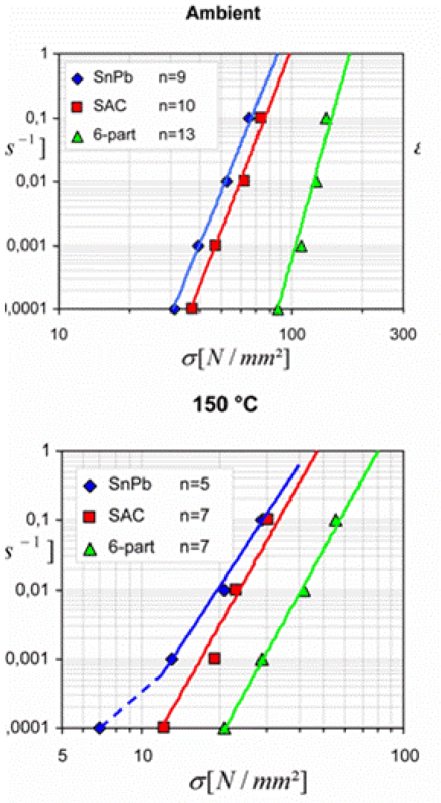

Figure 2. Creep Strength of SnPb, SAC and Innolot alloys were evaluated at ambient and at 150°C temperatures. The 6-part alloy showed the best creep strength performance.

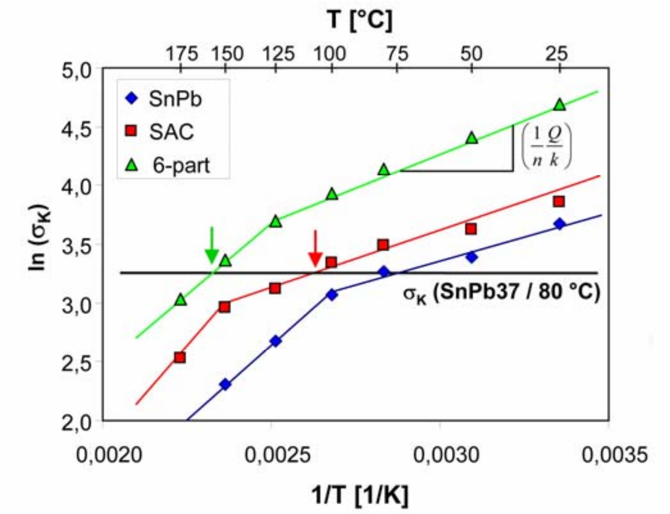

Figure 3. Maximum operating temperature of the new alloy was developed so that the new alloy would have the same creep resistance at 150°C as SnPb37 has at 80°C.

The final composition also had to meet the requirements for solder reflow in a similar range to that needed for conventional SAC alloys. he minimum soldering temperature (which must be exceeded in the soldering process) at which satisfactory wetting can be achieved shows the maximum operating temperature and soldering temperature for different elemental additions to SAC387, **Figure 4.**

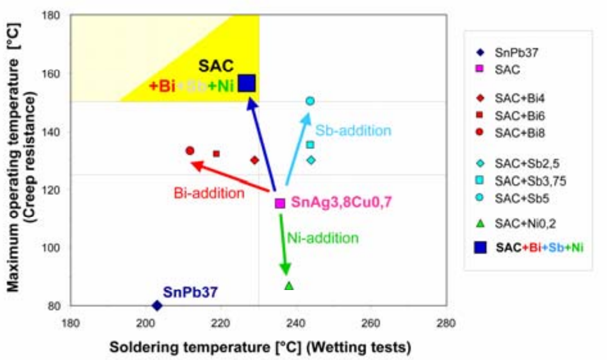

Figure 4. Graphical representation of alloy additions on soldering temperature.

Illustrating that this alloy could achieve liquidus in the range of SAC alloy reflow, wetting balance testing was performed to determine if sufficient wetting force and speed could be attained at these temperatures**.** In this test using 6-part alloy pellets (200mg size), the time to buoyancy and the force at 2 seconds were measured on a Cu wire and a 1206 resistor, using two "standard" fluxes, Actiec 2 and Actiec 5 (ref) with the solder temperature of 240°C, **Figure 5.**

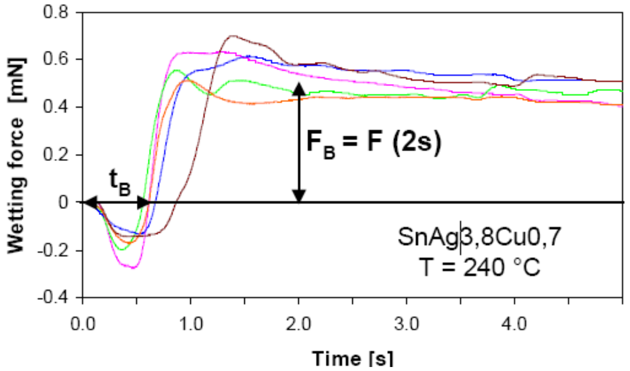

Figure 5. Wetting curves showing time to buoyancy (t_b) and force at 2 seconds (F_b).

The new, 6-part alloy was selected as the most robust formulation with high creep strength and excellent wetting ability. Although the solidus temperature was lowered to 209°C (as compare to that of SAC at 217°C), this did not, in practice, enable reflow at a lower temperature, and hence conferred no benefit of decreased thermal load on the board and the components.

Manufacturability and metallurgy of the multi-component alloy was then analyzed by the development team. Standard industry-accepted testing including spread, solder balling, thermal cycling reliability, shear strength, vibration, drop, and voiding analyses were all conducted. The alloy showed equivalent or superior performance to that of SAC387 for all tests conducted. Of course, the primary reason for the development of the new alloy was to create a material that could withstand higher operating temperatures, so the results of the thermal cycling testing were of particular interest. **Figure 6** clearly shows the superior thermal capabilities of the alloy as compared to that of SAC387 and SnPb37. Further data was presented at a recent seminar held in Berlin, Germany in October 2008 to disseminate the results of another cooperative project, LIVE; these confirmed the alloy to perform significantly better than SAC and even SnPb alloys in both thermal shock and temperature cycling.

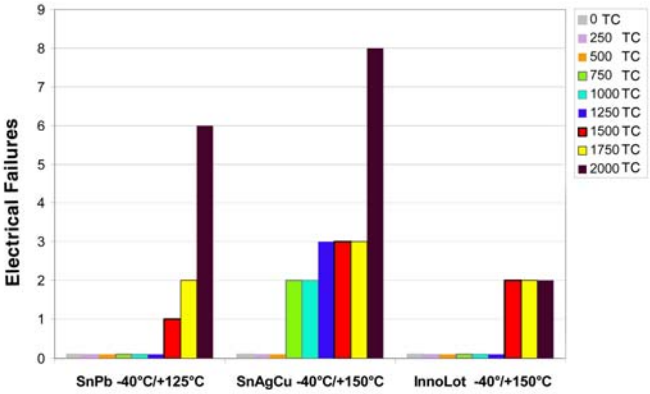

Figure 6. Solder joint thermal reliability testing.

CONCLUSIONS

The cooperative efforts of industry and academia have resulted in the successful development of a high operating temperature, lead-free alloy that reflows at the same temperatures as conventional SAC alloys and will enable increased reliability for certain applications, including automotive and defense. Results from testing of the new Innolot alloy show improved reliability in -40°C to +150°C thermal cycling versus that of SAC387. In addition, the new alloy offers comparable vibration resistance to that of SAC387, as proven in vibration testing after 500 thermal cycles, and the drop test performance of Innolot is comparable to that of SAC387.

It should be noted that, because the new alloy contains bismuth, manufacturers employing materials based on this new alloy must ensure that there is no lead on the components or boards. Lead-terminated components or HASL (hot air solder leveled) finished boards used in combination with the Innolot alloy will result in a low melting (98°C) eutectic, which means that joints will fail when exposed to temperatures above about 98°C. There must be no lead in the supply chain when using materials based on this alloy.

This new alloy is a very promising development for the electronics industry, as continued experience with lead-free materials enables improvements and alterations to meet the emerging requirements of various applications. With this new alloy, just as with other alloys, the base alloy is only part of the equation. Only patent holders will have access to the alloy, and optimizing solder paste materials with this alloy for maximum performance will also require flux chemistry expertise and formulation know-how. Partnering with the right supplier – one that can not only deliver a robust material but can also provide in-depth technical support -- will be essential to long-term success

Development of a Novel Lead- Free Solder for High Reliability Applications

Dr Hector Steen
Dr Brian Toleno

Participants

- Lead company
  - Siemens Berlin (central lab)
- Academic partners
  - Univ of Bayreuth
  - Fraunhofer inst. IZM
- Users
  - Siemens
  - Bosch
  - Motorola
- Suppliers
  - Henkel (Multicore)
  - Stannol
  - Cookson (Alpha Metals)
  - Seho
  - Infineon (Munich)
  - TI (Munich)
  - Epcos (Munich)
  - Microtech (Maintz)
  - Ruwel

Acknowledgements

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    - Dr H-J Albrecht (Siemens): Project leader
    - Dr K. Mueller (Bayreuth univ.): Alloy development, some slides used here
    - Dr M. Nowottnick (Fraunhofer inst.): Reliability assessments, some slides used here

Alloy Constraints

- Lead – Free
- 160 C operating temperature
- Joints must survive 2000 cycles –55C to +160C
  - – Later reduced to 1000 cycles, 150C peak
- Reflow at 230 C
  - – Later reduced to 220 C (temperature sensitive component)
- Acceptable from cost/toxicity considerations

Contents

- Starting point
- Project definition and approach
- Preselection of alloys and Optimisation process
- Metallurgy of Multi-component alloys
- Pasty range of Prealloyed- and Reaction solders
- Solder paste qualification
- Solutions for other soldering methods

Starting conditions

Background to the project

- **Increased requirements for temperature resistance and reliability of electronic assemblies**
- **Impending ban on Pb and other toxic substances (01 July 2006)**

Currently available Materials (In 2000)

SnPb37, SnPb36Ag2	**- Limited HighTemperature resistance** **- Pb content**
SnAg3,5 / SnCu0,7	**- Very high processing temperature** **- Limited Reliability in high op. Temp. applications**
SnAg3,8Cu0,7	**- Limited Reliability in high op. temp. applications**

Project Definition: Approach Taken

Project definition

Development of a solder fulfilling the following criteria:

- **Low melting** (Reflow temperature below that for SnAgCu)
- **High operating temperature** (At least up to 150 ° C)
- **Lead-free** (no highly toxic constituents)

Approach taken

- Development of a multi component solder alloy
- Base alloy: SnAg3,8Cu0,7 (SAC)
- Optimisation of properties by addition of further alloying elements

Theoretical approach

$$\left(N^{f}\right)^{c}\Delta\varepsilon^{pl} = const.$$ (Coffin/Manson)

Hypothesis:

SnPb(Ag) **SnAgCu** **InnoLot**

$\Delta\varepsilon^{pl}$ = $\Delta\varepsilon^{pl}$ = $\Delta\varepsilon^{pl}$ → **reliability**

85° C **120° C** **150° C**

→ **equal cycles to failure** N^{f}

Preselection of alloys

Methods to Raise Creep Resistance

- ☑ **Solid solution strengthening**
- ☑ **Precipitation- & other Dispersion Hardening/Strengthening**
- ☐ Grain refinement (not applicable for high temperature application)

Choice of suitable Alloying elements

Bi	Solid solution hardening, Lowers melting temperature
Sb	Solid solution hardening. Raises melting temperature
Ni	Dispersion hardening by intermetallic phase formation

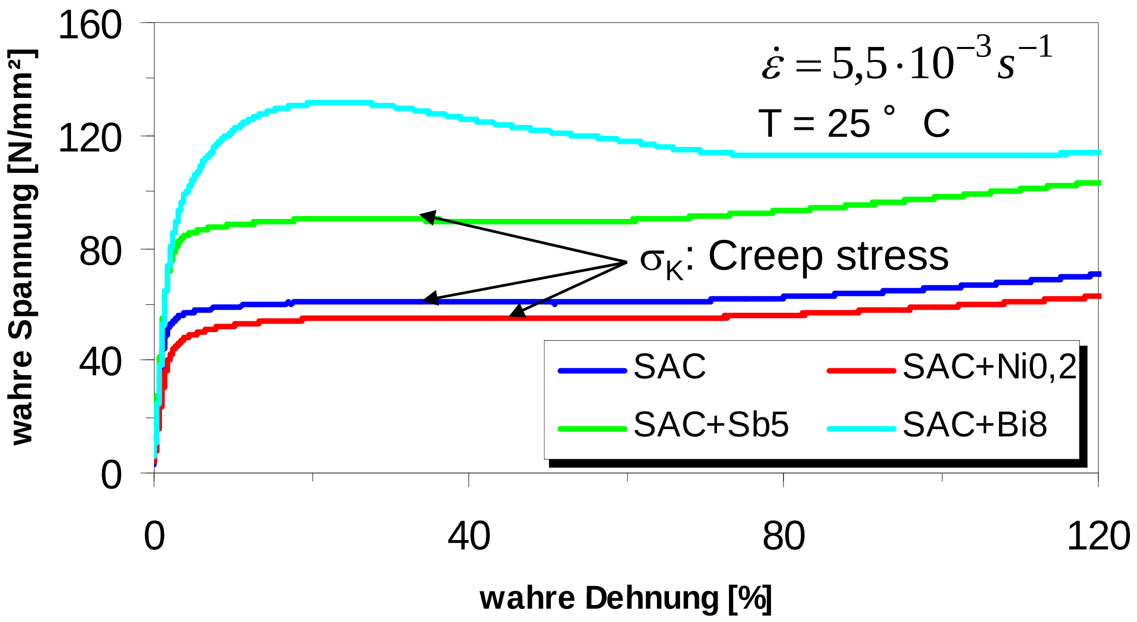
In	Cost, slight toxicity
Cs	toxic
Te	highly toxic, T_m ↑↑
Ce	toxic, Eutectic 220 ° C
Ba	Compounds toxic, T_m ↑
Fe	T_m ↑

Alloy Development

- SnAg3.8Cu0.7
  - Fails temperature cycling test
  - Reflow temperature too high
- Bi addition to reduce solidus & reflow T
- Bi, Sb, Ni additions to improve creep resistance – predicted to improve fatigue properties

Optimisation criteria

Creep Characteristics of Solder alloys



True Stress:

$$\sigma_w = \sigma \cdot (1 - \varepsilon)$$

True Strain:

$$\varepsilon_w = -\ln(1 - \varepsilon)$$

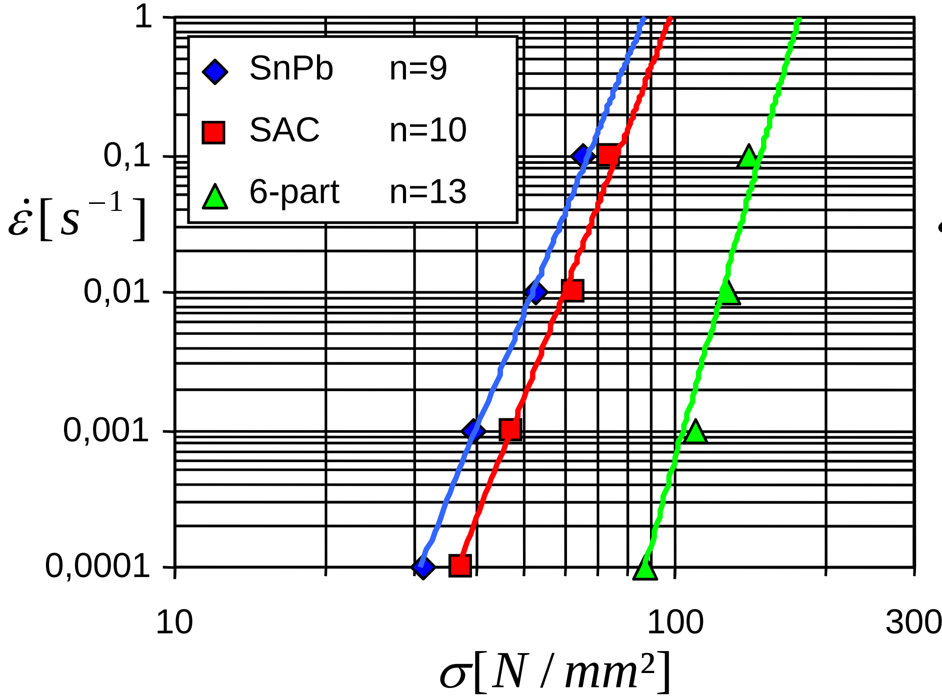
(SAC=SnAg3.8Cu0.7)

Optimisation criteria

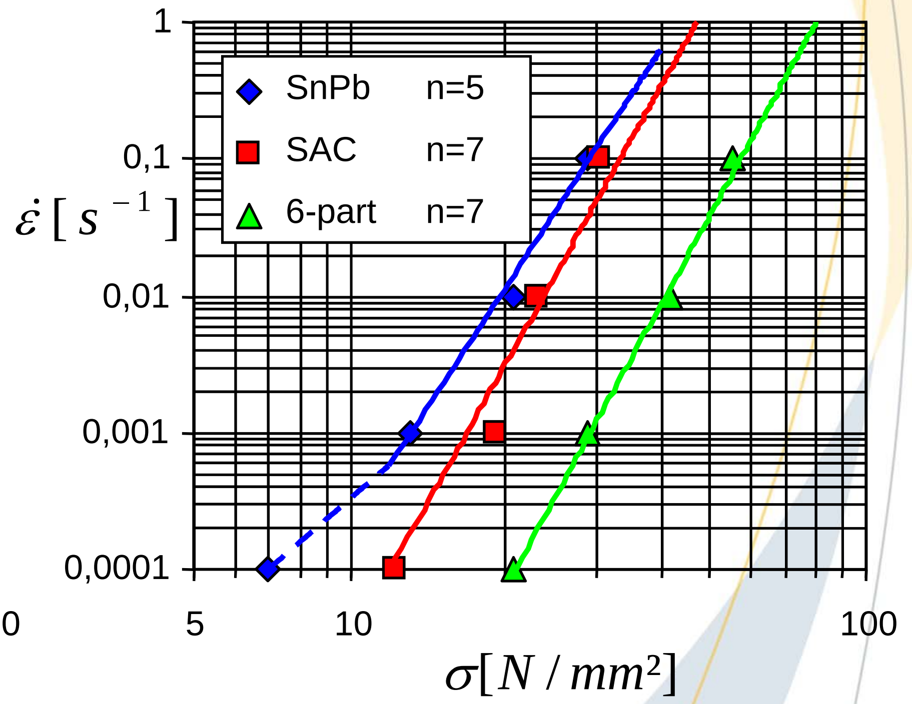
Creep Characteristics of Solder alloys

(SAC=SnAg3.8Cu0.7,
6 part = SAC+Bi3Sb1.5Ni0.2)

Ambient

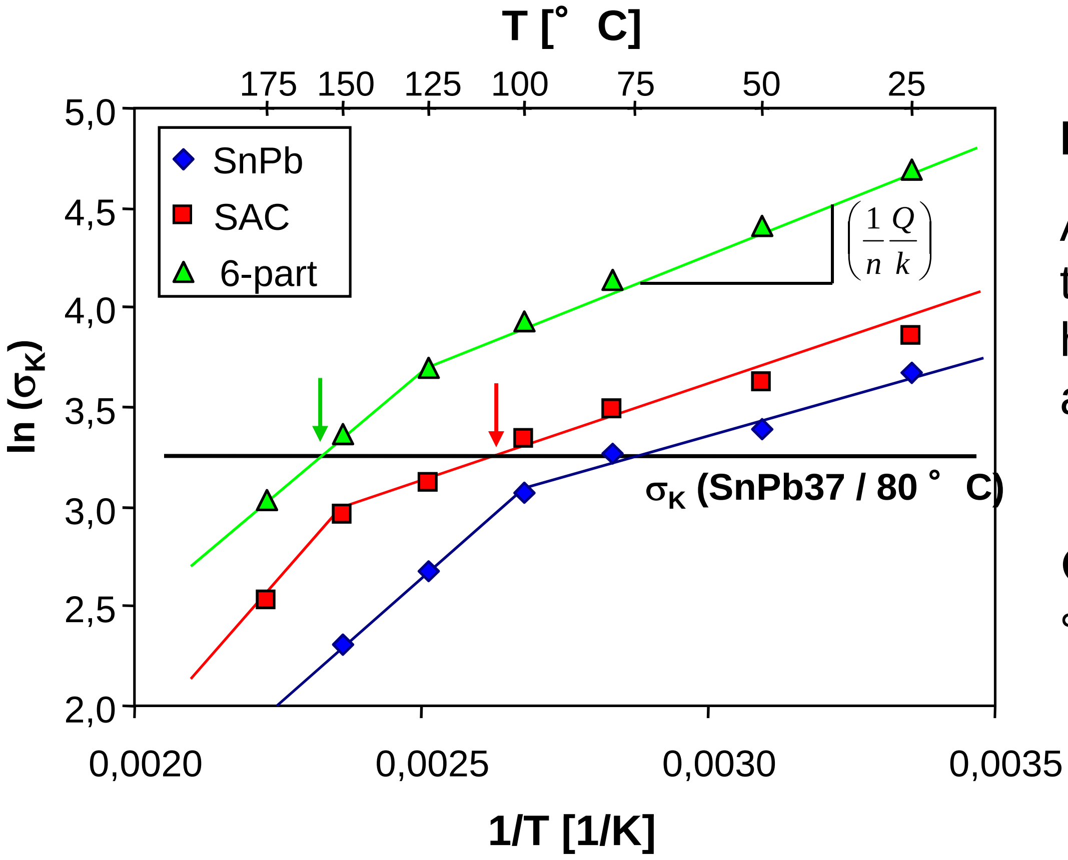


150 ° C



Optimisation criteria

Derivation of the maximum operating temperature



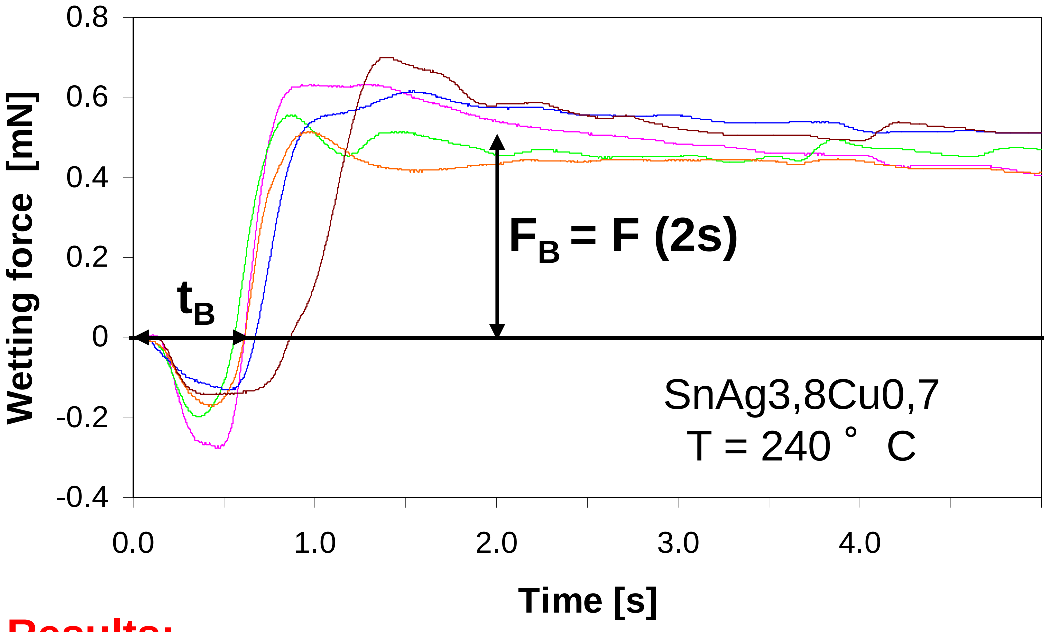
Definition:

At the maximum operating temperature the solder must have the same creep resistance as SnPb37 at 80 ° C.

$\sigma_K \geq \sigma_K$ (SnPb37, 80 ° C)

Optimisation criteria

Derivation of required reflow temperature



Results:

Minimum soldering temperature, which must be exceeded in the soldering process, for satisfactory wetting to be achieved

Wetting tests

- CR1206 tinned
- Solder pellets 200 mg

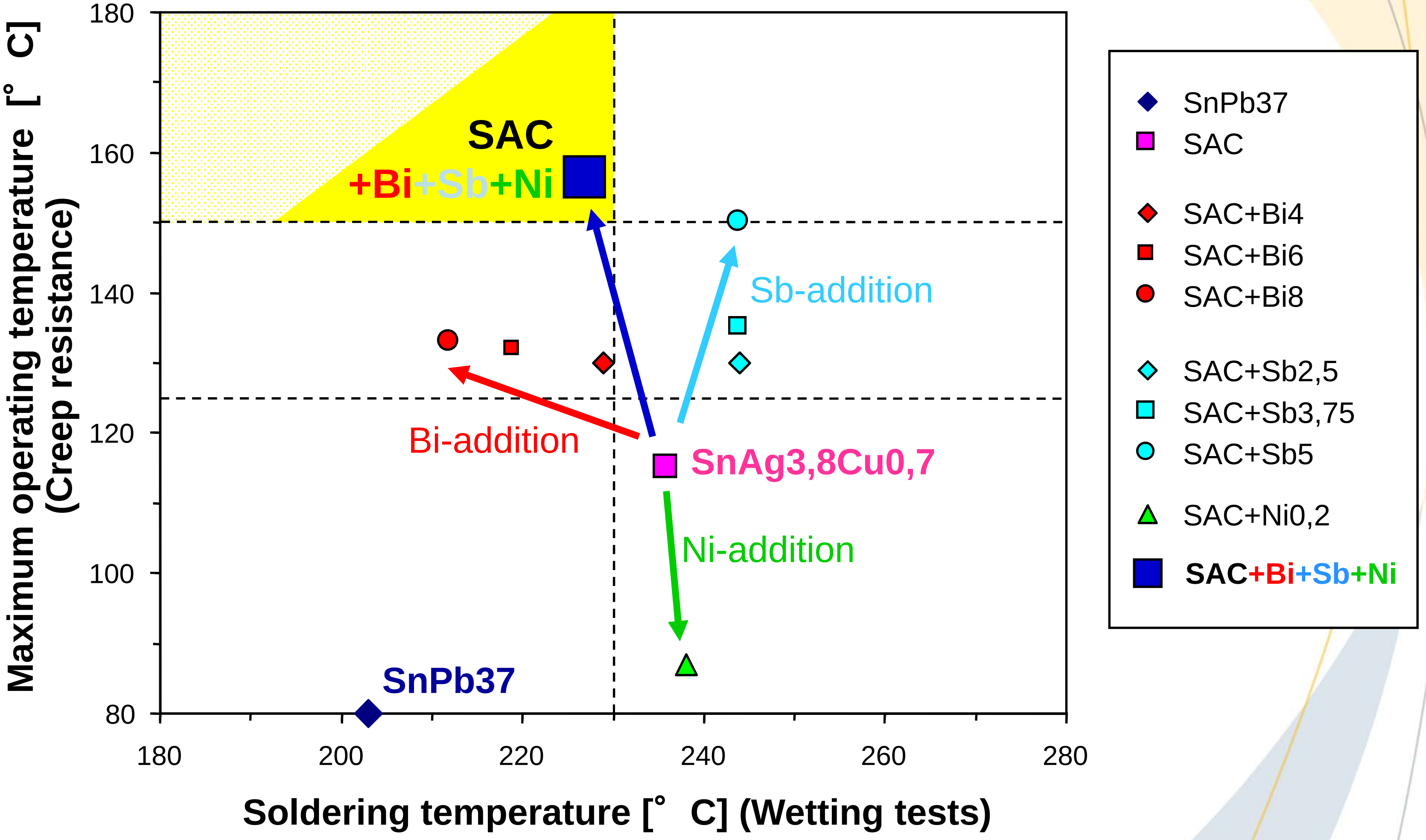
Flux

- ACTIEC 2
- ACTIEC 5

Acceptance criteria

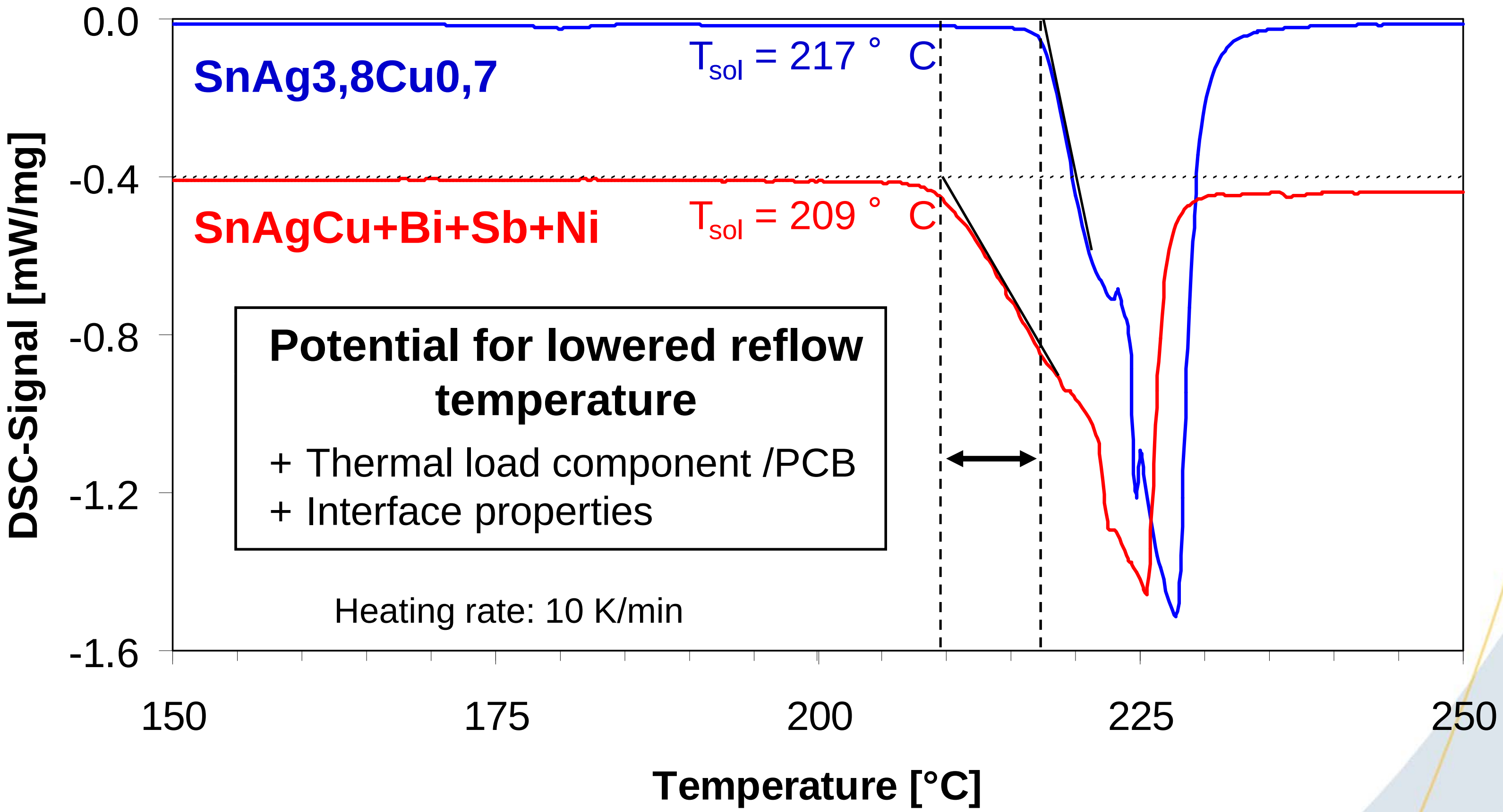
- CR1206: $t_B \leq 1{,}5$ s $F_B \geq 0{,}3$ mN
- Cu-wire: $t_B \leq 1{,}5$ s $F_B \geq 0{,}6$ mN

Optimisation criteria



Melting Ranges

Melting Range of Pre-alloyed solder



Potential for lowered reflow temperature

+ Thermal load component /PCB
+ Interface properties

Heating rate: 10 K/min

Final composition solution.

- SnAg3.8Cu0.7Bi3Sb1.4Ni0.15 Pre-alloyed solder
- Alloy patent applied for

Manufactuability of Multicomponent alloys

Alloy production

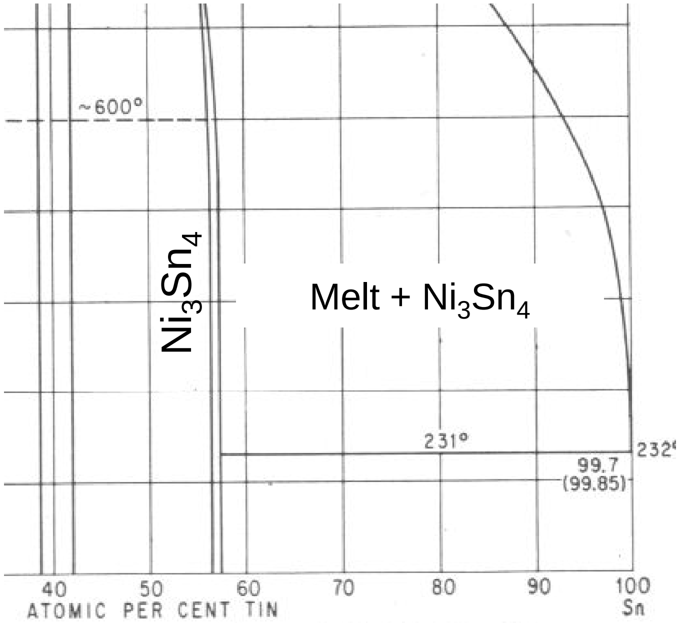
Ag Soluble and homogeneously distributed. Not critical

Cu Slow dissolution in Sn
Oxidation prone

Bi Low melting, fully soluble. Not critical

Sb Master Alloy, Homogeneous distribution easily ensured

Ni Eutectic at 0,15 %
Very steep liquidus slope
Very low solubility in Sn
intermetallic Ni-Sn-Phase



But:

Positive effect observed in combination with Bi

Formation of intermetallic Bi-Ni-Phase

Metallurgy of Multicomponent alloys

Solid solution strengthening

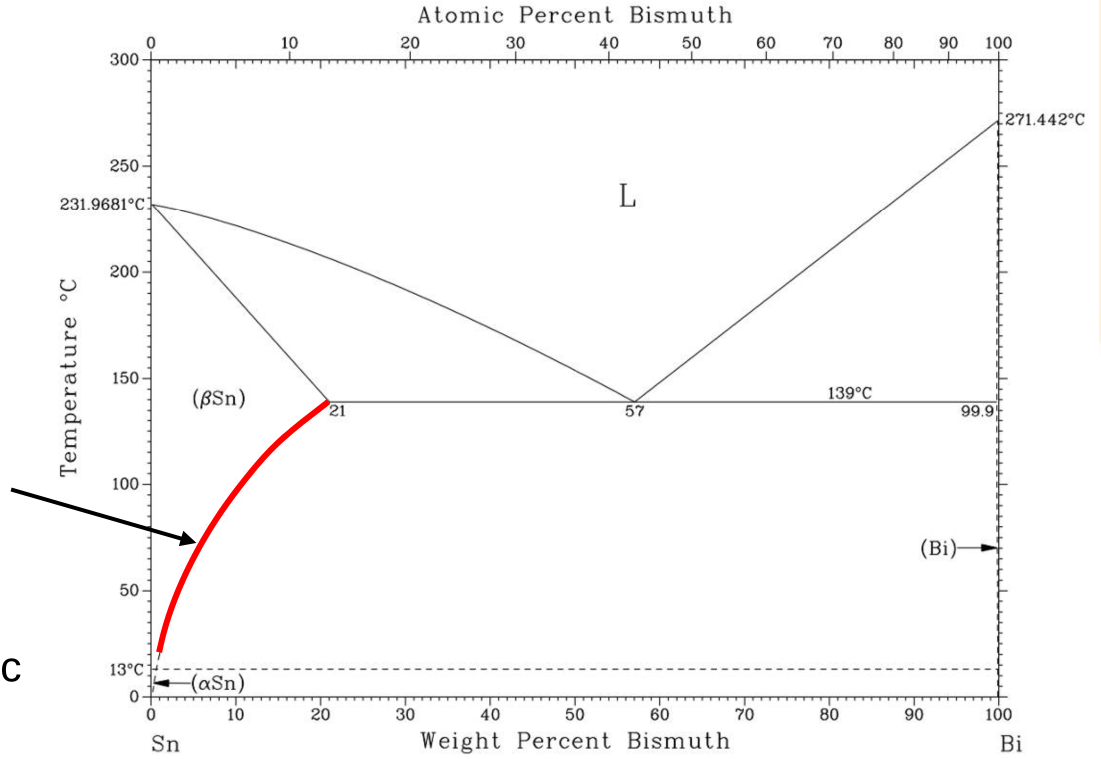
Effect of bismuth and antimony

	Bi	Sb
• Strength	↑	↑↑
• Melting temperature	↓	↑

- Temperature dependent solubility of Bi in Sn

⇒ Precipitation of disolved Bi in the microstructure (heat treatment)

⇒ Risk of formation of Sn-Bi-Eutectic



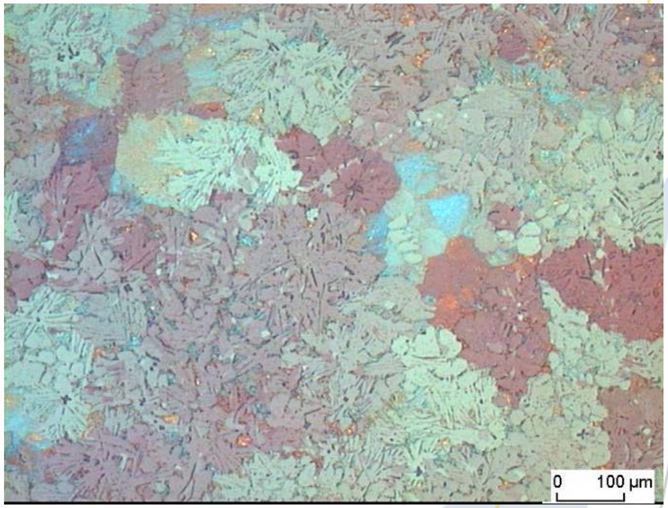
Metallurgy of Multicomponent alloys

Structure of Standard lead-free solder (SnAg3,8Cu0,7)

Sn-Matrix

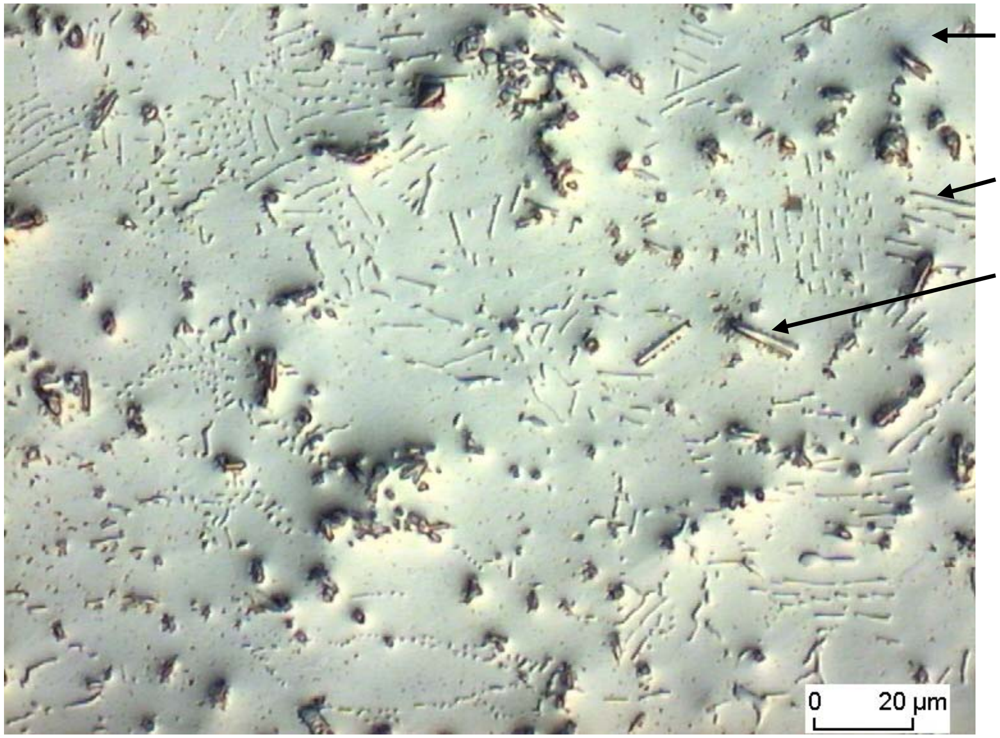
Ag_3Sn

Cu_6Sn_5



Metallurgy of Multicomponent alloys

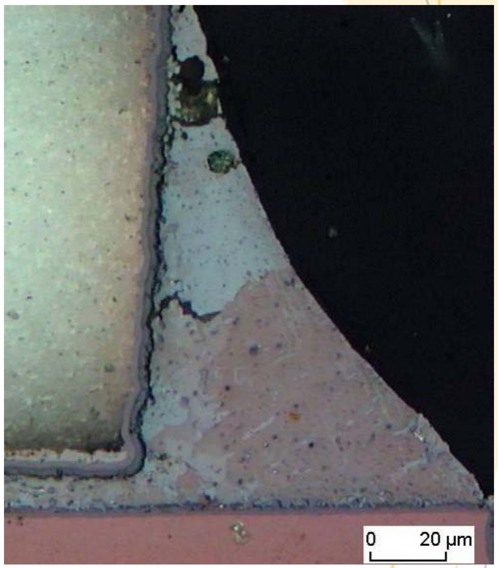
Structure of 6 component solder (SnAgCu+Bi+Sb+Ni)

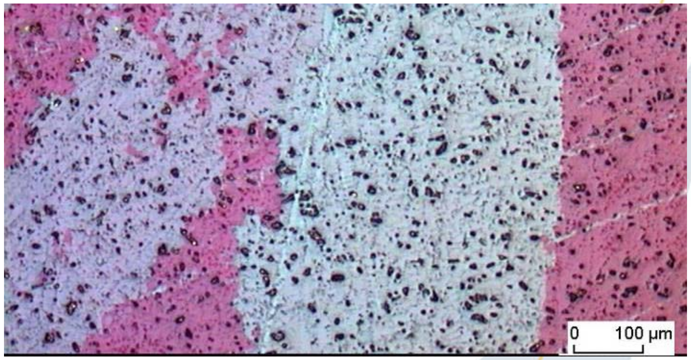


Sn-Matrix (Sb,Bi)

Ag_3Sn

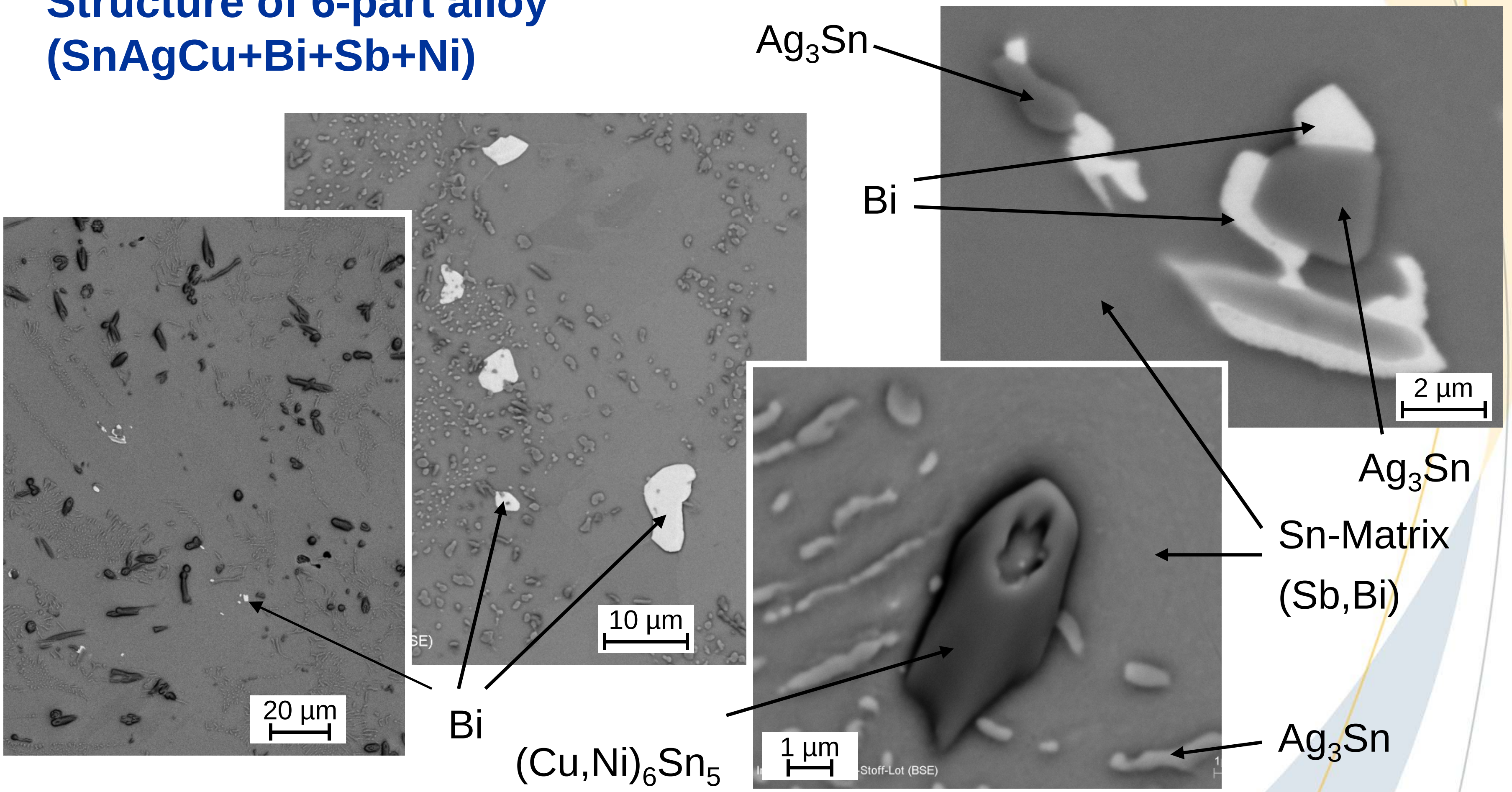
$(Cu,Ni)_6Sn_5$





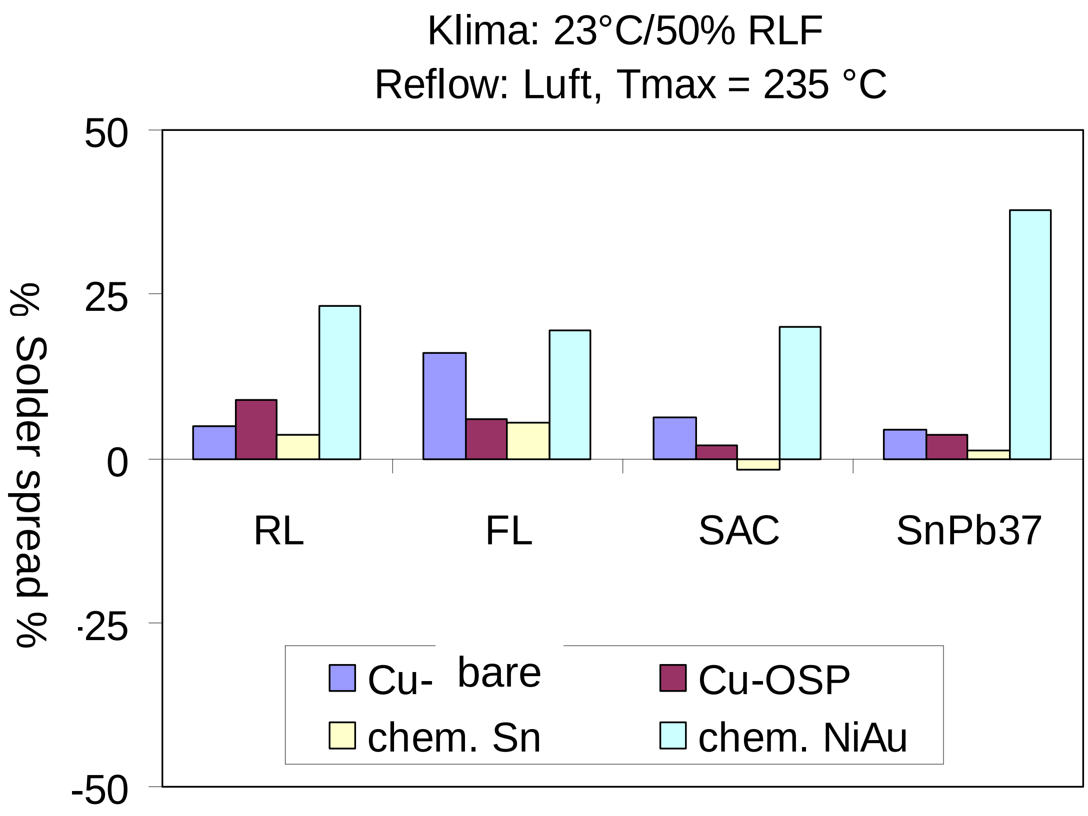
Metallurgy of Multicomponent alloys

Structure of 6-part alloy (SnAgCu+Bi+Sb+Ni)



Spread Test

Solder spread

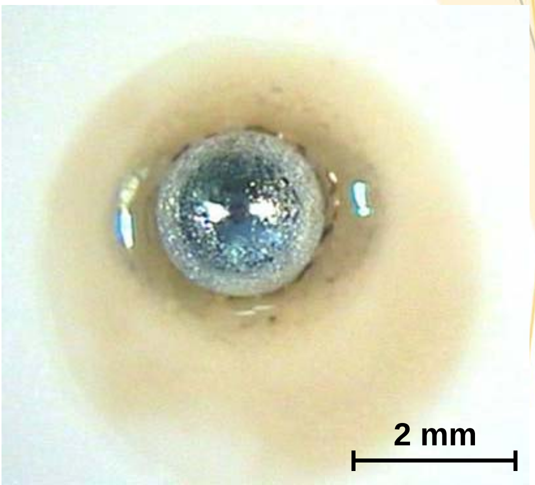


- Best spread: SnPb-Paste on Ni-substrate
- Generally less spread on Cu
- 6-Part-solder (Reaction and prealloyed solders) comparable with SnAgCu
- No significant difference between Reaction and prealloyed solders

Solder Balling

Solder Balling Test

6-part Reaction solder



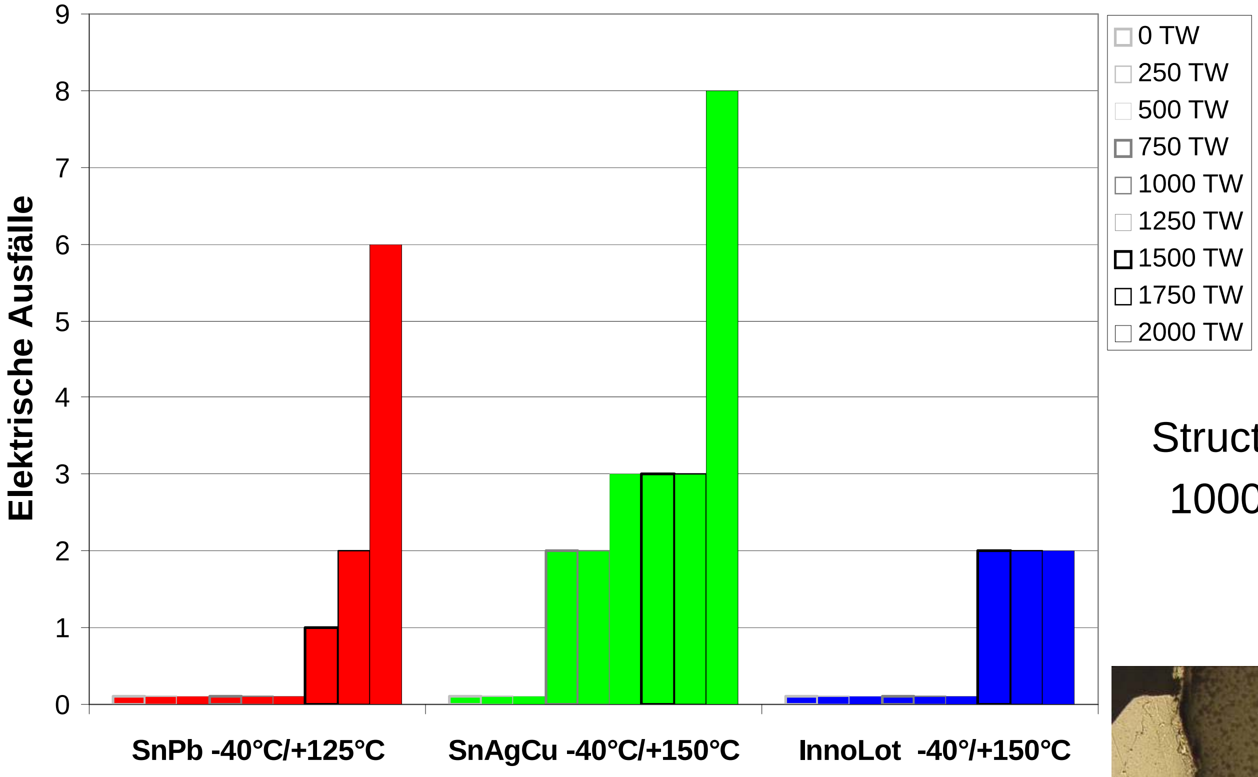
6-part prealloyed solder

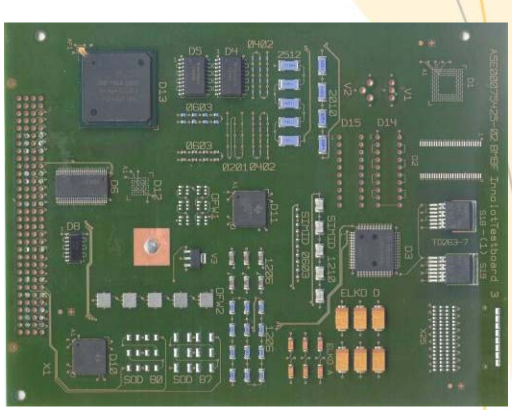
- All the paste reflows into a central ball (Class 1)
- Requirement fulfilled (max. 3 satellite balls = Class 2)

SnPb37

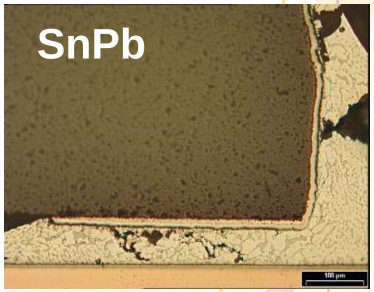
Innolot Alloy vs SAC387 & SN63

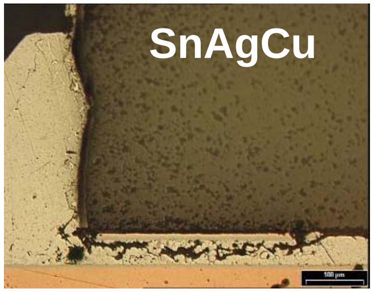
Assemblies – Electrical failures vs no of cycles

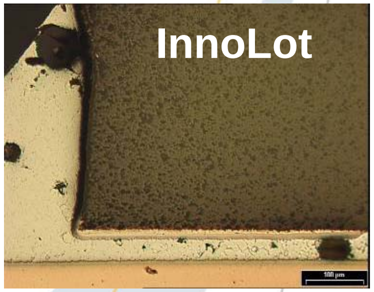




Structure after 1000 Cycles







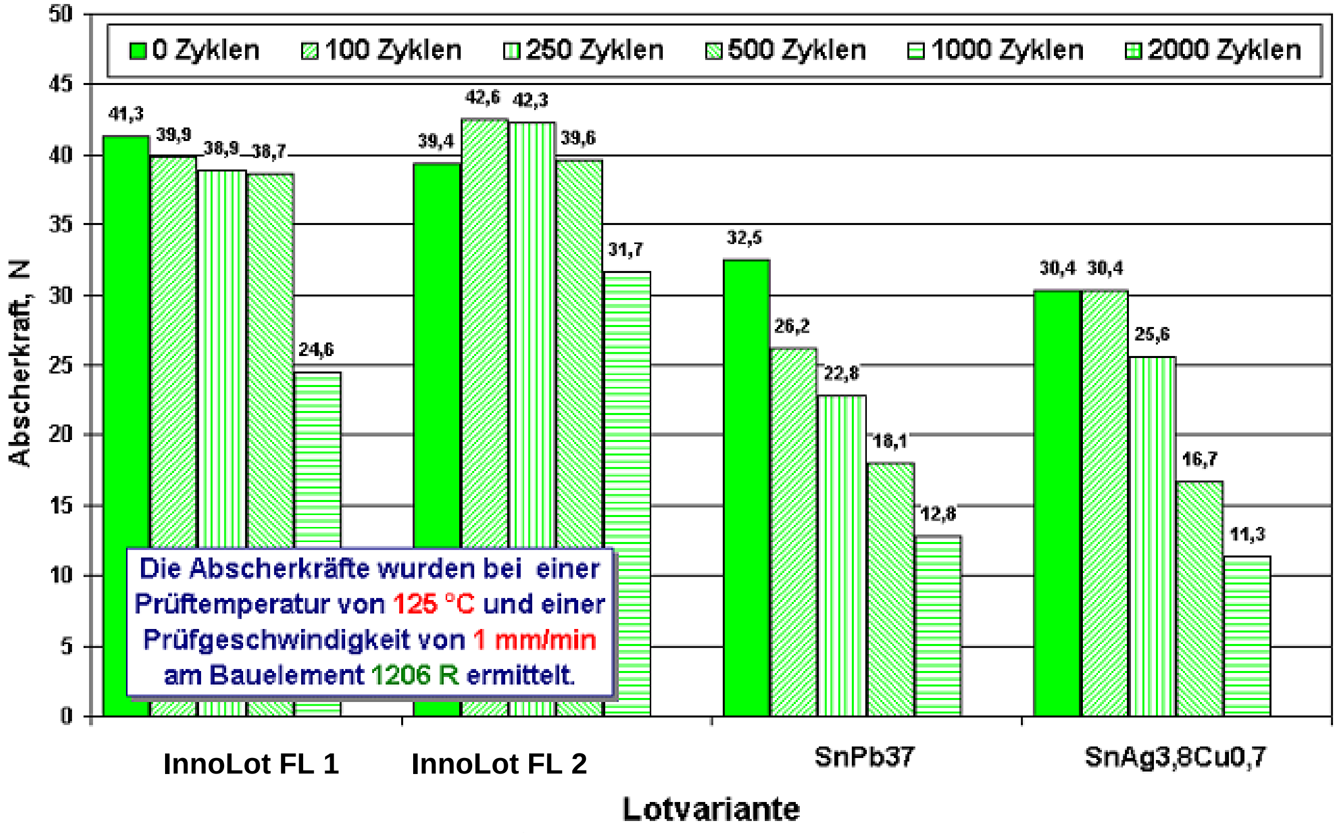
TBG4

40 Chip-components from CR0402 - CR2512 per Board, no failures on TO263, QFP and SO16

Innolot Alloy vs SAC387 & SN63

Assemblies – Shear Strength vs no of cycles

Shear strength at 125° C test temperature, 1206 Chip resistor



Die Abscherkräfte wurden bei einer Prüftemperatur von 125 °C und einer Prüfgeschwindigkeit von 1 mm/min am Bauelement 1206 R ermittelt.

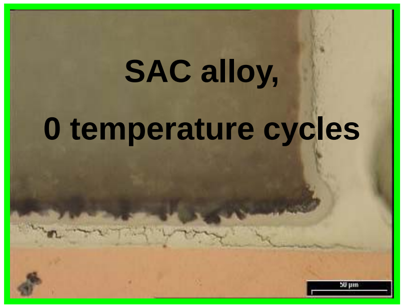
TBG1 / TCT –40/+125° C

Vibration Testing vs SAC387

0 TW	I 2g 3min	II 5g 3min	III 10g 3min	IIIa 15g 3min	IV 15g 15min	V 15g 15min	VI 15g 45min	VII 15g 60min	VIII 20g 15min	IX 20g 60min	X 30g 60min
SnAgCu											
CR1206											
P-TQFP (D3)								🟩			
SIMID 1210											
SIMID 0603											
TO263-7 (S19)											
SO (D8)											🟩
CR0603						🟩					
CR2512					🟩						
CR2010											
Innolot											
CR1206											
P-TQFP (D3)							🟦				
SIMID 1210										🟦	
SIMID 0603											
TO263-7 (S19)											
SO (D8)											
CR0603						🟦					
CR2512						🟦					
CR2010											🟦

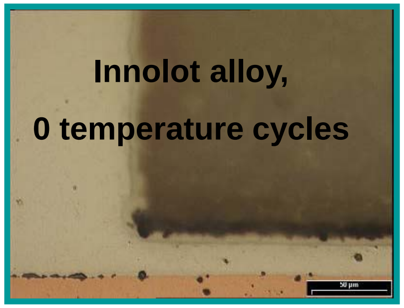
500 TW	I 2g 3min	II 5g 3min	III 10g 3min	IIIa 15g 3min	IV 15g 15min	V 15g 15min	VI 15g 45min	VII 15g 60min	VIII 20g 15min	IX 20g 60min	X 30g 60min
SnAgCu											
CR1206											
P-TQFP (D3)							🟩				
SIMID 1210											
SIMID 0603											
TO263-7 (S19)											
SO (D8)									🟩		
CR0603						🟩					
CR2512			🟩								
CR2010								🟩			
Innolot											
CR1206											
P-TQFP (D3)								🟦			
SIMID 1210											
SIMID 0603											
TO263-7 (S19)											
SO (D8)								🟦			
CR0603						🟦					
CR2512							🟦				
CR2010											

Failure characteristics in vibration testing with/without thermal cycling (TCT), 0603 resistor



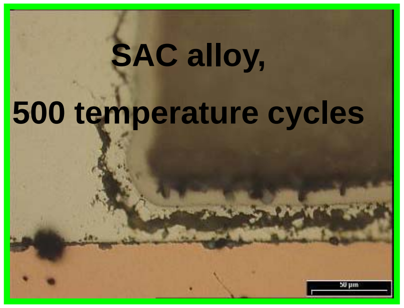
SAC alloy,

0 temperature cycles



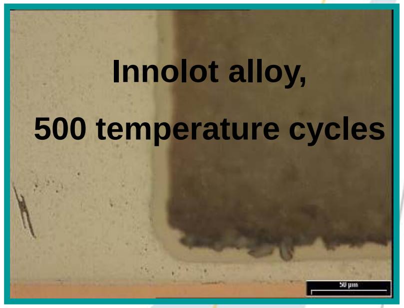
Innolot alloy,

0 temperature cycles



SAC alloy,

500 temperature cycles



Innolot alloy,

500 temperature cycles

Assemblies - mechanical testing - shear strength

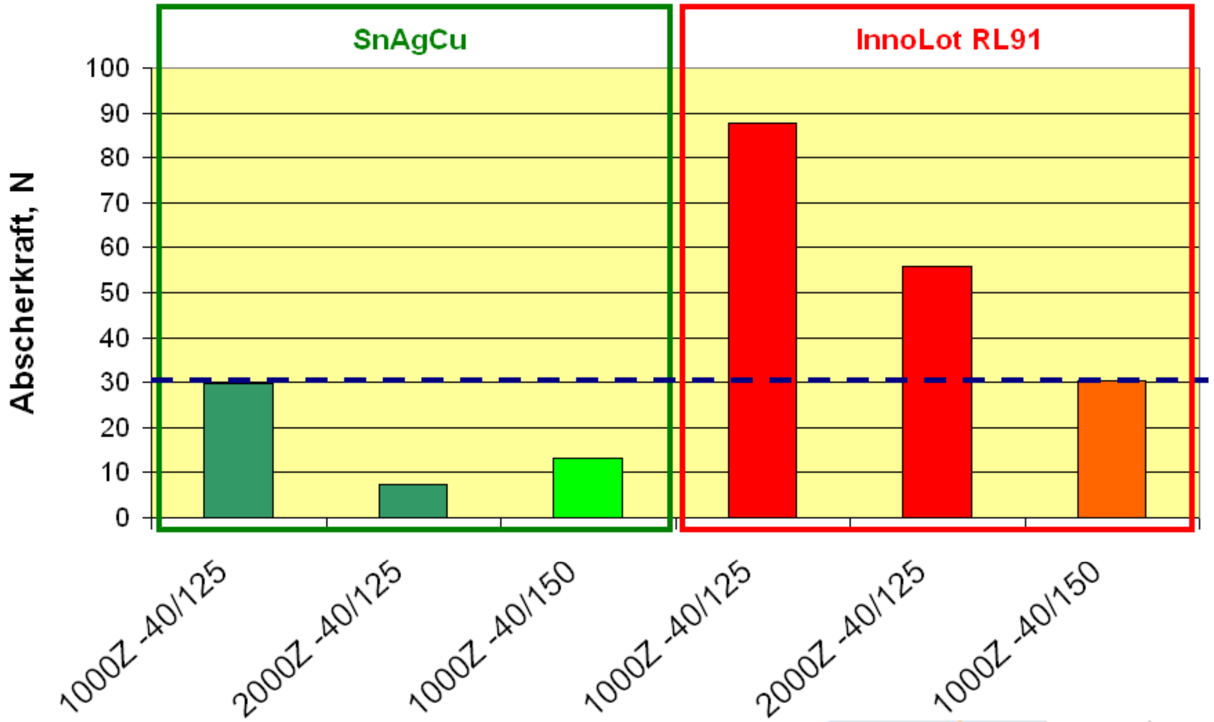
Projekthypothese:

SnPb(Ag)		SnAgCu		InnoLot		
$\Delta\varepsilon^{pl}$	=	$\Delta\varepsilon^{pl}$	=	$\Delta\varepsilon^{pl}$	→	zuverlässig
85°C		120°C		150°C		

Example: 0201 Chip resistor

Innolot solder
SAC+Bi3Sb1.5Ni0.2

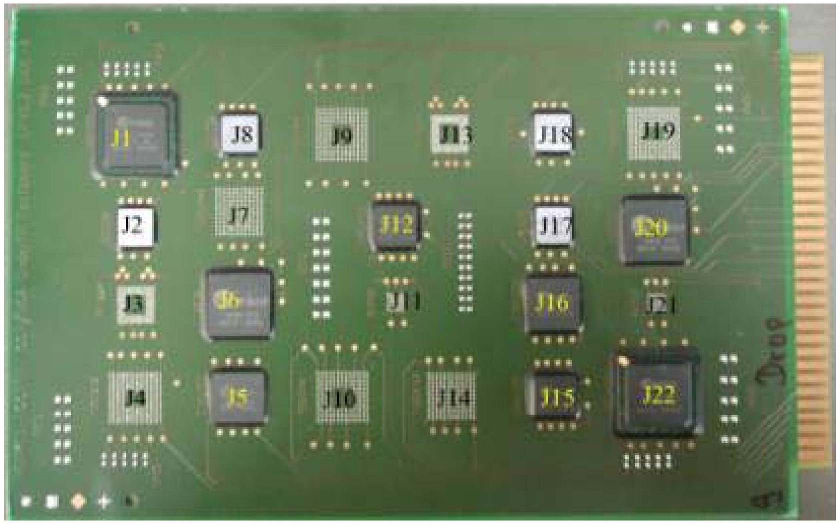
Shows that Innolot alloy at –40+150C is equivalent to SAC at –40 to+125C

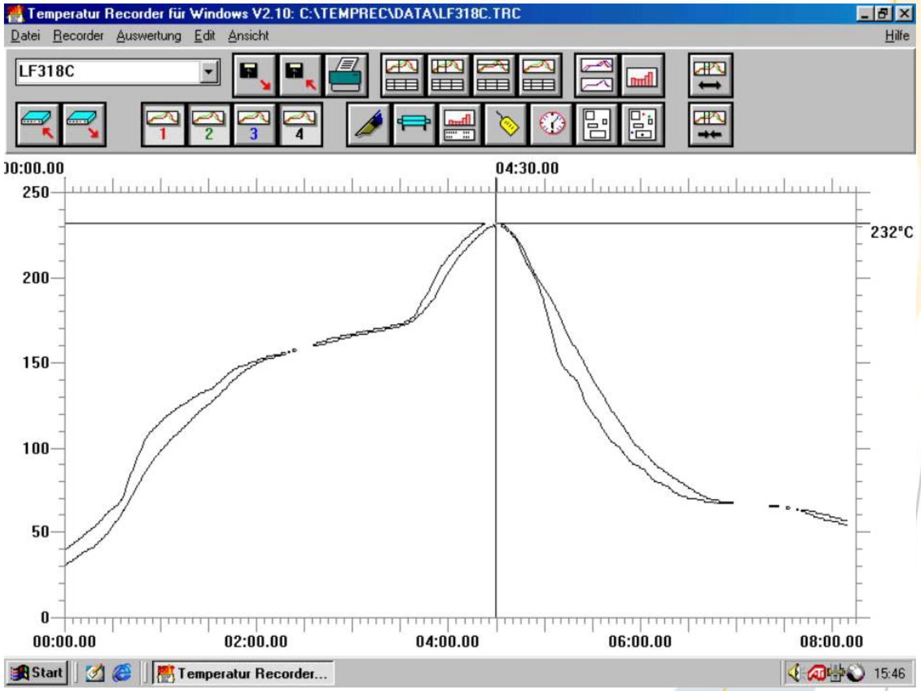


Drop Testing

- Since the alloy is considerably less ductile than both SnPb & SAC alloys there was a concern about drop-test performance

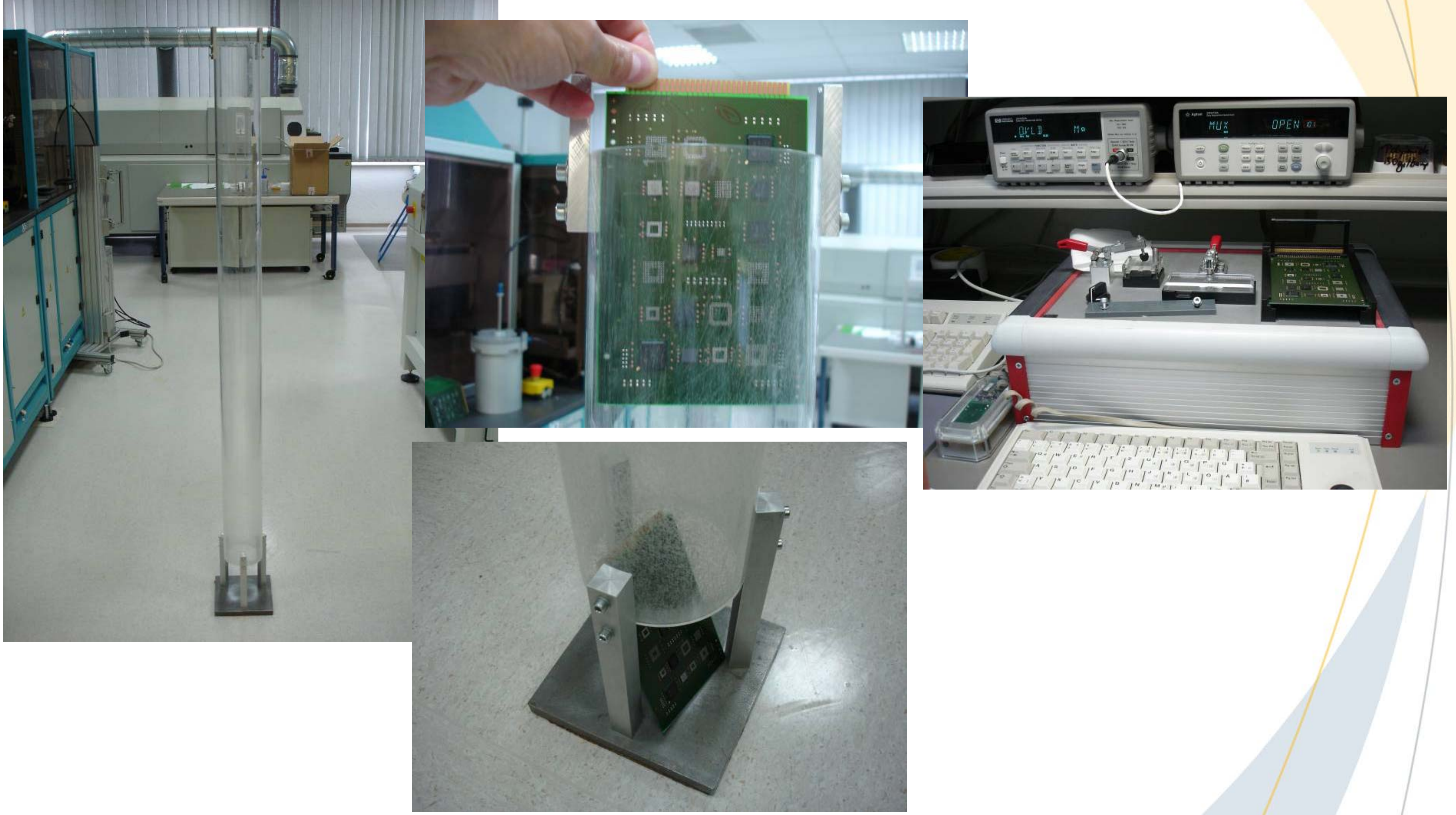
Test Board & Reflow Profile




Temperatur Recorder für Windows V2.10: C:\TEMPREC\DATA\LF318C.TRC

LF318C

Test Method



Results

	No of Drops to First Fail					
	OSP Finish		NiAu Finish			
Package	**SAC**	**Innolot**	**SAC**	**Innolot**	**SAC all**	**Innolot all**
TBGA144 (J14) Pitch 0,8mm	2	2	1	2	3	4
UCSP 192 (J8) Pitch 0,4mm	1	1	2	3	3	4
UCSP 192 (J18) Pitch 0,4mm	3	2	1	1	4	3
PBGA 196 (J1) Pitch 1,0mm	3	2	2	3	5	5
TABGA 144 (J7) Pitch 0,8mm	3	1	2	7	5	8
TBGA132 (J15) Pitch 0,5mm	2	2	3	1	5	3
TABGA 132 (J12) Pitch 0,5mm	2	1	4	8	6	9
UCSP 98 (J2) Pitch 0,5mm	4	8	7	8	11	16
UCSP 98 (J17) Pitch 0,5mm	6	8	20	10	26	18
PBGA 196 (J22) Pitch 1,0mm	30	20	20	10	50	30
Average	**5.6**	**4.7**	**6.2**	**5.3**	**5.9**	**5**

Results (2)

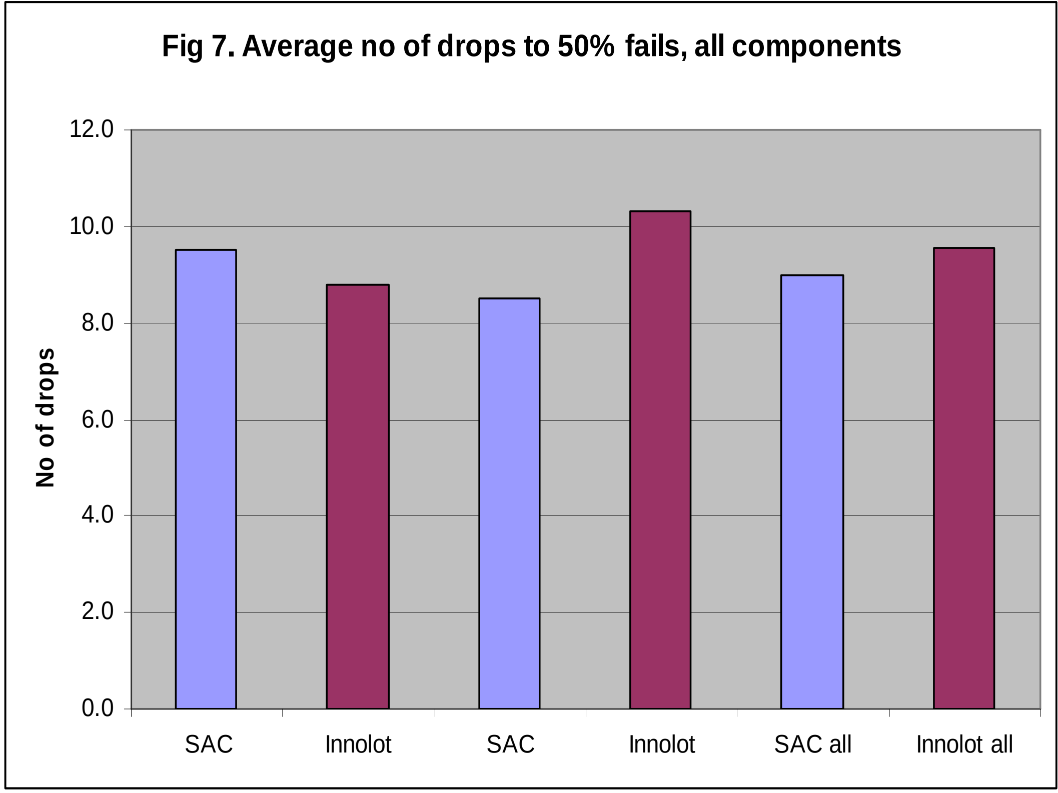
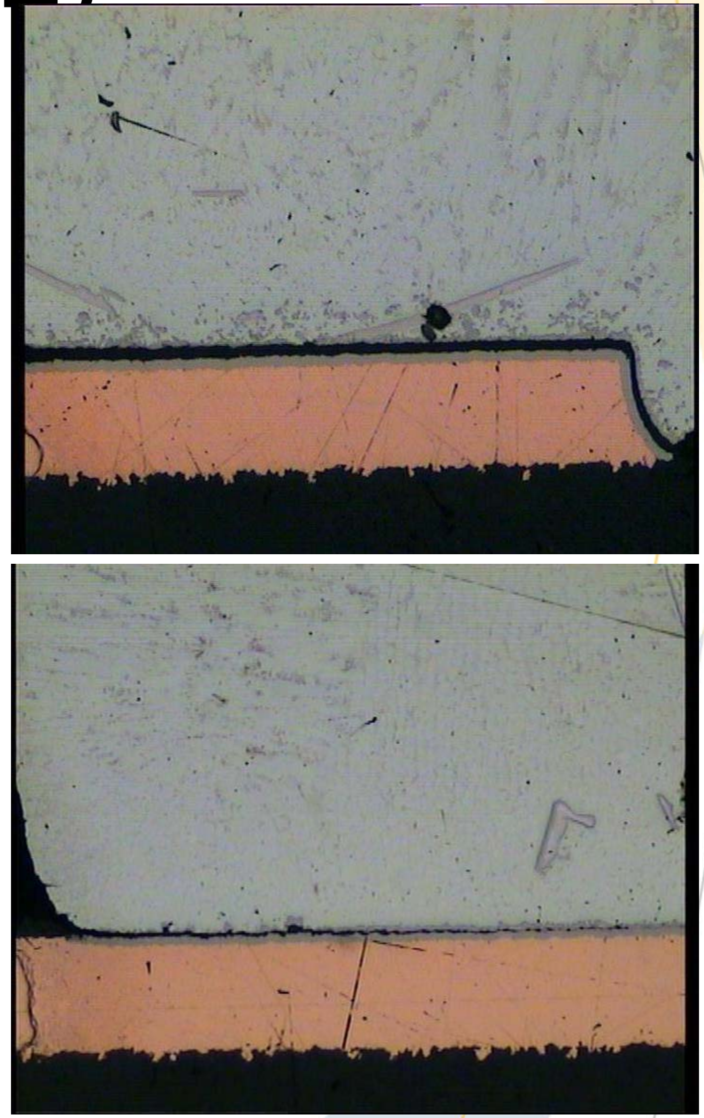


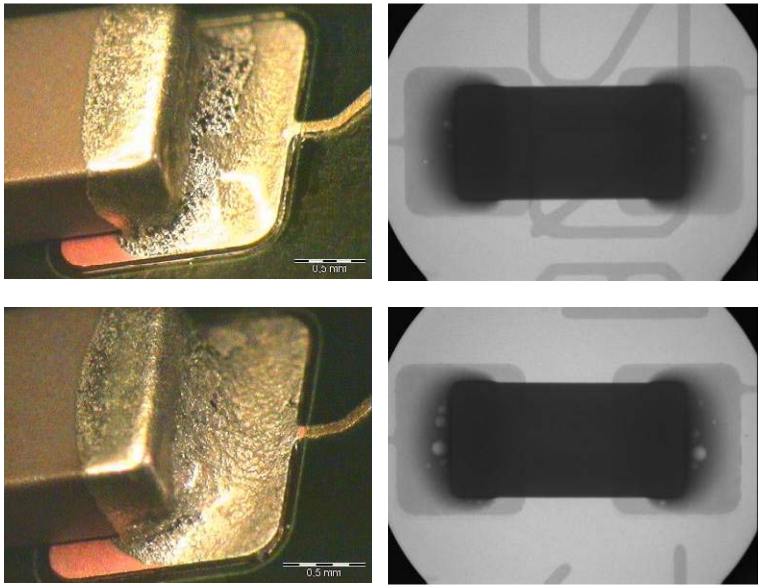
Fig 7. Average no of drops to 50% fails, all components
No of drops
12.0
10.0
8.0
6.0
4.0
2.0
0.0
SAC
Innolot
SAC
Innolot
SAC all
Innolot all



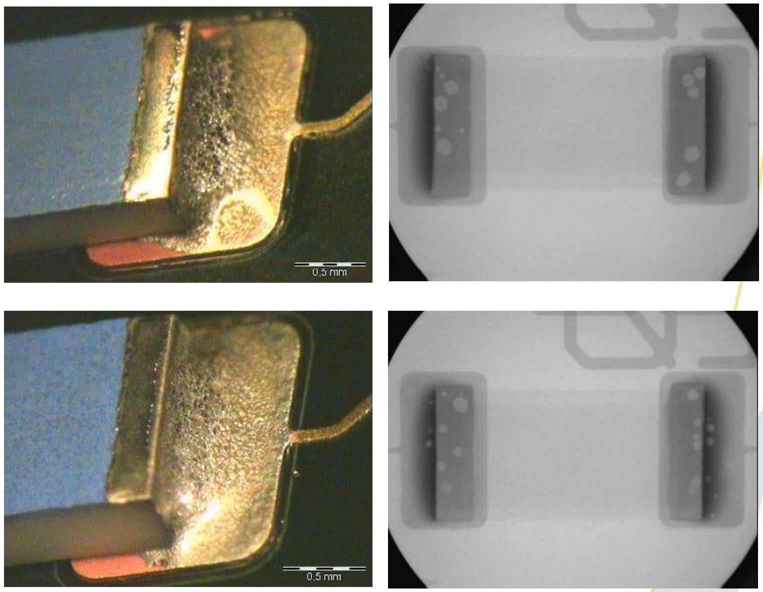
Example of Visual & X-ray Analysis

Cu OSP / Voiding

CC1206



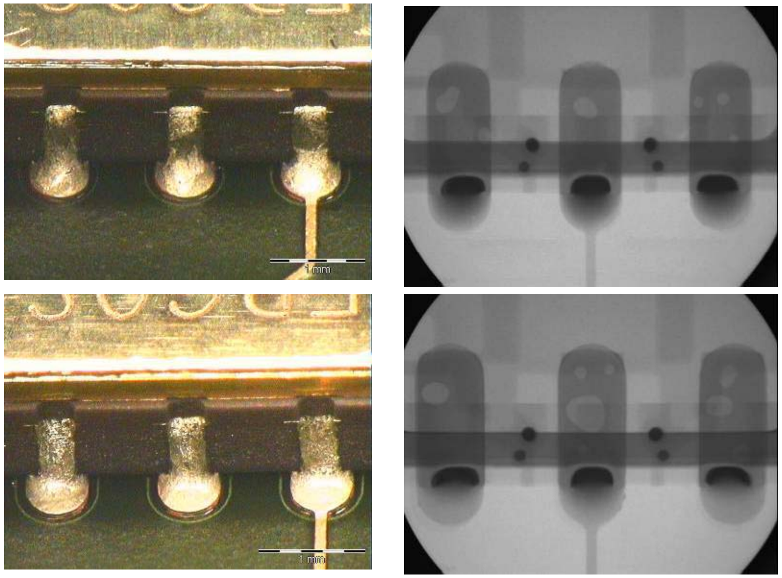
CR1206



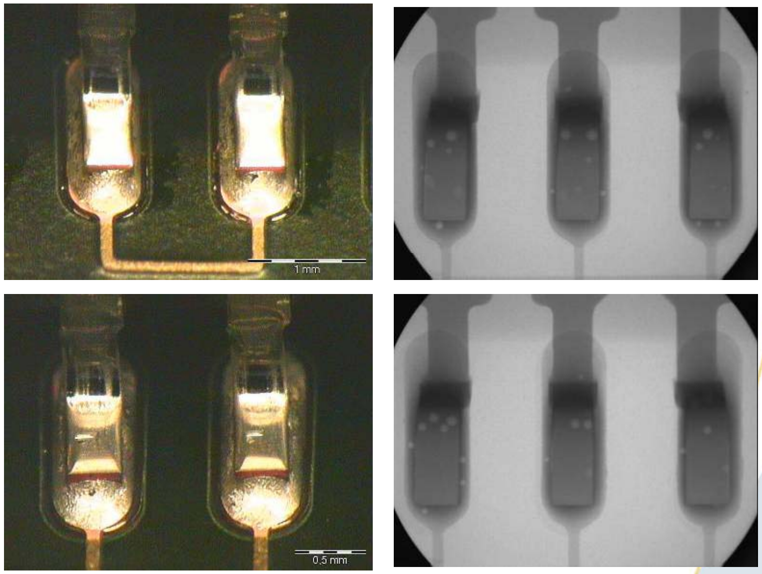
Example of Visual & X-ray Analysis

Cu OSP / Voiding

OFW



SO20



Summary

- Evidence of improved reliability in –40+150C cycling for Innolot alloy vs SAC387
- Innolot alloy clearly superior to SAC387 in Vibration testing after 500 thermal cycles
- Drop test performance is comparable to SAC alloy
- Innolot alloy is not compatible with any Pb contamination from SnPb finishes
  - Low melting SnPbBi eutectic forms, mpt 98C
  - Alloy not viable until 100% Pb-free components available

Thank You

Questions?