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How to Manage Wave Solder Alloy Contaminations

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Abstract

European electronics industry is soldering with lead-free alloys for one decade now. In this period not only the knowledge of the alloys in the assembly process has been improved, but also a high amount of data is collected. Technology has changed over these ten years including the prices of the metal. The dramatic increase of operation costs due to high metal prices forces engineers to look more critical to their wave soldering process. Balver Zinn has been studying the consistency of alloys in wave soldering process since the implementation of lead-free. The lab measures the contamination of lead-free solder alloy samples of their costumers and thus enables them to do statistical process control on the alloy composition. In these ten years of lead-free soldering over 25.000 samples were investigated looking at contaminations of lead, the drift of the Copper content, and or increase of iron in the alloy due to solder pot erosion. Analyzing this data returns a lot of information on copper leaching for the different alloys. How to manage the copper level in the lead-free solder alloy to avoid an increase of soldering defects will be discussed. The data of these alloy analysis contains samples of all kind of production environments: low and high volumes, different solder machines and solder pot contents, solder temperatures, alloys, board finishes and inert systems versus soldering in air. With this presentation we try to give guidelines for the costumers how to control their alloy in order to minimize solder defects in combination with keeping the metal consumption/operational cost as low as possible.

Key words: Solder alloys, contamination.

Introduction

All solder alloys contain small amounts of other elements. These contaminations are called additives if the supplier has added them to improve solder properties. Showing up during the soldering process they are seen as impurities or contaminations.

Impurities can come from different areas:

- Component finishes
- Board material finishes
- Solder pot erosion
- Impurity in fresh solder bars
- Mixing solder of different alloys

The impurity levels will change during the soldering process. Alloy composition will change. Not only due to leaching of metals, but also due to maintenance of dross.

The dross may have a different composition then the rest of the solder.

Figure 1. Solder samples are OES analyzed

Contamination by other elements is acceptable, but should be maintained below the acceptable maximum. These maximum levels are defined in the IPC J-STD-006 standard for SnPb and SAC305 alloys. Other lead-free alloy contamination limits may be used upon agreement between user and vendor.

Contaminant	Max.limit
Copper	0,3
Gold	0,2
Cadmium	0,005
Zinc	0,005
Aluminium	0,006
Antimony	0,5
Iron	0,02
Arsenic	0,03
Bismuth	0,25
Silver	0,1
Nickel	0,01
Total of Cu,Au Cd, Zn and Al	0,4

Table 1 Maximum contamination levels for SnPb alloys.

IMPURITIES IN TIN LEAD SOLDERING

Sample frequency

The requirements for soldered electrical and electronic assemblies are defined in the IPC J-STD-001E standard. Chapter 3.2.2 describes the solder purity maintenance. The frequency of analysis should be determined on basis of historical data, or monthly analyses. If contamination levels exceeds the limits (see Table 1), intervals between the analyses should be shortened. [1]

Process engineers should keep track on number of soldered PCB's with their surface (area through-put), amounts of replaced solder, and removed dross, process settings and more for each solder line to build up knowledge required to keep control over the solder composition.

A typical wave solder bath is inspected every quarter of the year. For selective solder baths the time interval is much shorter. Due to the higher solder temperature leaching of copper and other metals is much faster. Therefore the average time interval for a SnPb selective solder bath analysis is one month.

Result of SnPb analyses

The rate of dissolution of a metal in SnPb depends on a number of factors including:

- Base metal
- Solder composition
- Solder temperature
- Flow velocity of the solder
- Kind of wave former

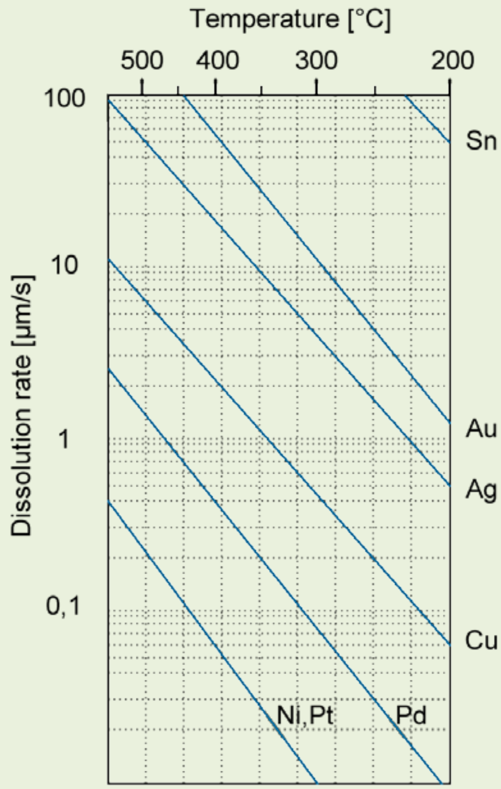

Figure 2. Soldering in Electronics R.J. Klein Wassink (Fig. 4.29) [2]

Figure 2 shows the impact the solder temperature on the dissolution rate of different elements. From this figure we learn that Ni dissolves slowly in SnPb where Au will immediately disappear in the solder. This is what we see with ENIG plated printed circuit boards where the gold layer is there to protect the surface from oxidation, but once in contact with the liquidus solder it will dissolve.

Despite the slow dissolving rate of the Ni the analyses show that this element is gives the most out of specification scores. Nickel impurities are coming from board and component finishes. The nickel will settle itself in the intermetallic layer of the solder joint. Copper dissolution in the solder is more an issue because too much copper (for SnPb >0,2%) will give more defects like bridging.

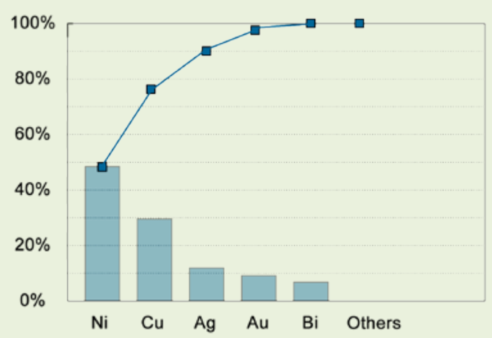

Figure 3. Pareto chart for SnPb inspections. Specification limits are defined in table1.

The excessive copper will form fine needles of Cu_6Sn_5. As a result the viscosity of the SnPb solder will increase. In SnPb solder copper can be removed by pouring the solder at a temperature around 190 °C with a stainless steel strainer.

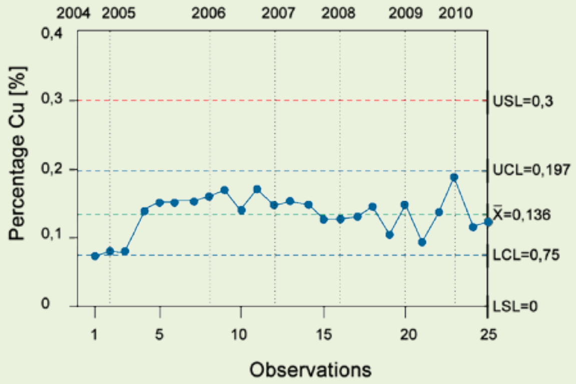

Figure 4 Control chart of copper contamination in a SnPb wave solder line.

Figure 4 shows the copper content of a wave solder line during the last 7 years. All scores are within the specification limits. On the line different industrial products are run in a full nitrogen wave solder machine having a solder bath with approximately 550 kg of SnPb solder. The solder temperature is 250 °C.

In selective soldering the solder temperature is much higher. In the next table records from two solder baths are compared. Both have the similar products (mainly ENIG finished boards). One is a wave soldering line, the other a selective soldering. Solder temperatures are 250 °C for wave soldering versus 290 °C for the selective soldering process. The data is collected from 30 analyses in a time frame of more than one year.

Tin lead solder - wave versus selective				
	Wave solder line		Selective solder line	
Element	Average [%]	Standard deviation [%]	Average [%]	Standard deviation [%]
Sn	62,489	0,362	62,565	0,347
Pb	37,454	0,365	37,258	0,348
Ni	0,0045	0,0006	0,0201	0,0034
Cu	0,0172	0,0025	0,0082	0,0018
Ag	0,0040	0,0008	0,0358	0,0032
Au	0,0070	0,0006	0,0221	0,0030

Table 2 Impurity levels for SnPb alloys wave versus selective soldering.

The data shows that the leaching of Ag, Au and Ni is much higher (factor 5-10) for selective soldering. Main reason for this is the temperature since contact time and flow properties are longer/ higher for the wave process. However none of the measured values is outside of the specification.

Solderbath Change

Lead-free implementation starts with replacing the SnPb solder with a lead-free alloy. Wave formers, pumps and heat elements should be removed out of the solder pot and cleaned. For some solder pot constructions it is almost impossible to get all the solder out. Some SnPb may remain in the pot and be mixed with the lead-free alloy. In order to avoid that the lead-free solder is contaminated with too much Pb it is recommended to wash the solder pot with pure Sn before refilling it with the lead-free alloy.

Lead-free alloy exchange solderpot				
Remaining SnPb [kg]	Selective pot [50 kg]	Small wave pot [400 kg]	Typical wave pot [800 kg]	Large wave pot [1000 kg]
10	8,179	1,046	0,524	0,419
5	4,144	0,524	0,262	0,210
2	1,671	0,210	0,105	0,084
1	0,838	0,105	0,052	0,042
0,5	0,419	0,052	0,026	0,021
0,1	0,084	0,010	0,005	0,004

Table 3. The impact of the remaining SnPb [%] in the solder pot on the Pb impurity level of lead-free solder after alloy change. (Red is out of specification according to RoHS)

If not all SnPb solder is removed, this will contaminate the lead-free alloy. Table 3 shows the impact of remaining SnPb for different solder pot dimensions. A 50 kg solder pot is a small selective unit; 400 kg is typical used in a small wave solder machine. 800 and 1000 kg is the size of the large wave solder pots. For example if in a small solder pot of 400 kg during the solder swap 2 kg SnPb remain this will result in a Pb impurity of 0,210 % after refill. (Maximum level of Pb according RoHS is 0,1%). After an additional wash cycle this would be 0,001%.

If the solder pot is washed with pure Sn will result in a minimum Pb contamination. The effect is shown in table 4 in case the solder pot was washed with 100% Sn.

Lead-free alloy exchange solderpot with Sn wash				
Remaining SnPb [kg]	Selective pot [50 kg]	Small wave pot [400 kg]	Typical wave pot [800 kg]	Large wave pot [1000 kg]
10	1,834	0,030	0,008	0,005
5	0,470	0,008	0,002	0,001
2	0,076	0,001	0,000	0,000
1	0,019	0,000	0,000	0,000
0,5	0,005	0,000	0,000	0,000
0,1	0,000	0,000	0,000	0,000

Table 4. Same as table 3; but now with extra Sn wash before SAC305 implementation. (Red is out of specification according to RoHS). Numbers are % Pb in the alloy.

Changing SAC305 solder to SN100C is much less critical. Since the main ingredients are similar only the Ag, Ni and Ge content have to be verified. To achieve the proper Ni and Ge content special solder bars or pallets can be used if necessary.

Maximum Contamination Levels Lead-Free

Maximum contamination levels are defined by the supplier for SN100C. For SAC305 the IPC-J-STD-006 is the reference. For SAC alloys the majority of the impurities being out of specification were caused by Pb.

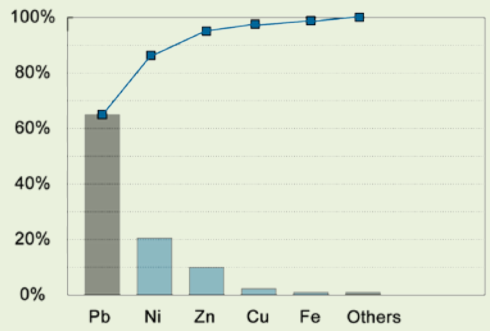

Figure 5. Pareto chart of the impurities in the SAC305 alloy.

The number of samples containing too much Pb is decreasing fast for some reasons:

- Legislation – RoHS
- Many samples were from bath changes. Today's samples are mainly from periodic solder control.
- The leaded components and board materials are faced out.
- Refreshing the solder with lead-free alloys reduces the Pb content.

Where does the Pb contamination come from?
The solder bath changes have already been discussed. Not everybody uses wash tin so a number of lines start already with contaminated lead-free solder.
Component finishes and HAL boards are replaced so there is no Pb leaching anymore.
The data also show that accidents like mixing new lead-free solder with "old" SnPb bars happen more than once.

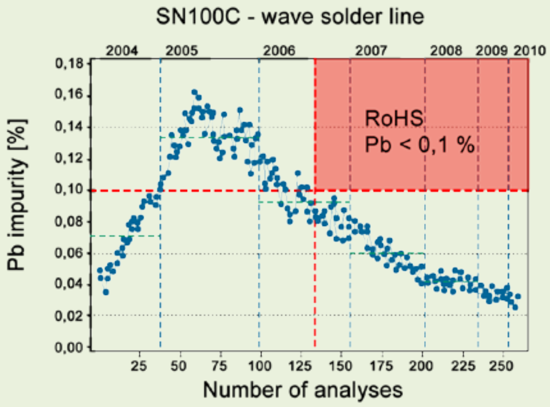

Figure 6 shows a historical graph of Pb impurity level in SN100C since the introduction of lead-free solder in this line.

One can read the lead-free history in figure 6. The SN100C solder was introduced in this wave solder line in 2004. At that time the majority of available components were still with a SnPb finish. Also the HAL boards had a SnPb finish. Therefore we see the Pb impurity increase. In the year 2005 more and more lead-free materials were introduced. The lead impurity curve levels off. After 2006 all used materials were lead-free and due to solder consumption and refreshment the Pb impurity decreases.

Copper Leaching In Lead-Free Alloys
Copper will dissolve in solder alloys. This happened also with SnPb, but in lead-free it has become more critical.
For some reasons copper dissolve faster:
Higher solder temperatures
Higher Sn contents
Presence of Ag

Increasing copper levels result in higher liquidus temperatures. In wave soldering this means that solder joints will solidify faster; increasing the risk for solder defects like bridging, spikes or webbing.

The next production data is from a manufacturer having two identical full tunnel wave soldering lines. This company produces for medical and makes industrial products. The medical line is exempted for the RoHS so is still running with SnPb solder, where the second line has SN100C in the solder pot. The solder temperatures are identical; SN100C is only 10°C higher.

Solder samples were inspected over the last seven years and the results are shown in the next two graphs. The maximum copper content should be less than 0,85% (recommended by supplier). The SnPb the IPC-J-STD-006 defines the maximum of 0, 30%.

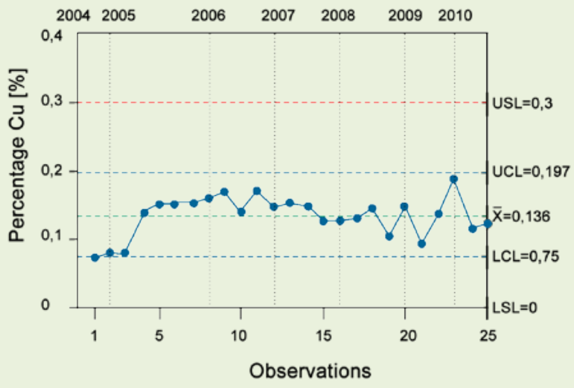

Figure 7. The leaded wave soldering line producing printed circuit boards for medical products.

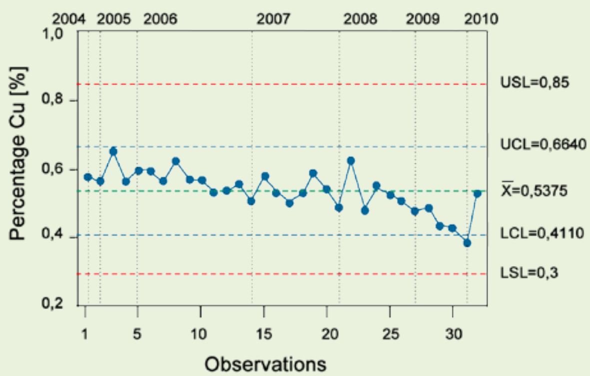

Figure 8. The SN100C wave solder-line produces industrial applications.

Both SPC charts show that the copper level is well in control over the years. For the SN100C the increase of copper can be reduced by adding SnNiGe bars containing no copper.

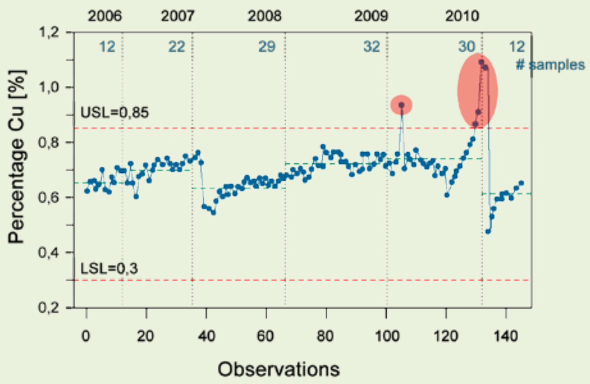

Figure 9 The SPC-chart of a wave solder-line running OSP boards.

An OCAP (out of control action plan) is needed when the copper levels exceeding maximum percentages. This can be adding fresh bars without copper or even take some part of the solder out and replace it with copper-less fresh solder.

Copper Contents In A Sac Alloy

In a SAC alloy the silver and copper level are changing continuously. Ag/Cu contents will define the melting range of the alloy.

Selective soldering is critical because temperatures are higher and copper leaching in SAC alloys will be higher to the presence of silver and a high tin content.

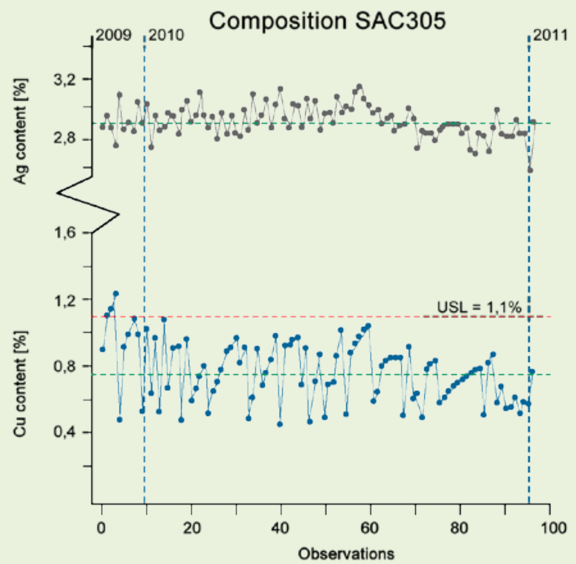

Figure 10 Cu content in the alloy fluctuates in the selective solder machine.

Due to the ratio between the silver and copper content the melting range of the SAC305 alloy is not 217-219 °C, but can vary from 217 up to even 240 °C (See phase diagram in figure 11).

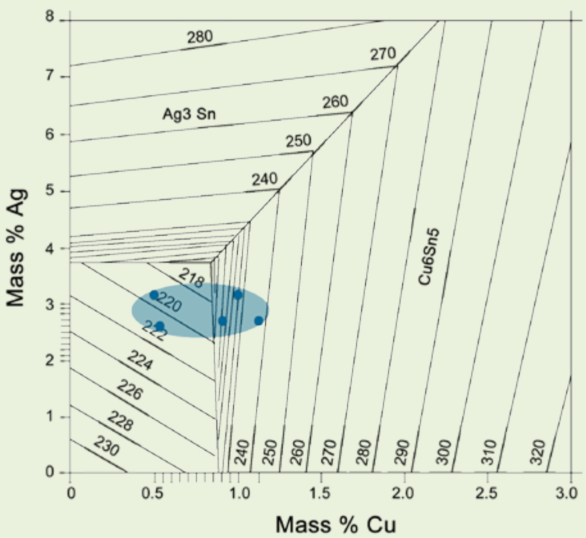

Figure 11 In the phase diagram is shown what the effect is of the fluctuation of the copper and silver content.

Copper levels can be controlled by adding fresh solder solid wire or bars of Sn3,5Ag instead of SAC305.
Copper leaching is less critical in SnPb and SN100C. The leaching rate depends on:

- Solder temperature
- Flow speed of the solder
- Contact time/length
- Solder alloy – additives
- Amount of solder in the solder pot

Copper leaching at a temperature of 310 °C was 2,5x more for SAC305 in comparison to SN100C. [3]

Iron Contents Lead-Free Solder

With the introduction of lead-free solders the erosion of solder pot and inner part materials is increased. The addition of nickel will slow the erosion rate, but proper material selection is required. Iron from parts may dissolve into the solder and $FeSn_2$ needles will be formed. Since the melting point of these $FeSn_2$ needles is approximately 510 °C they remain solid in the liquidus solder.

Needles in the solder are critical because if they are caught in the flow of liquidus solder they may end up between two tracks or pins causing a short.
Typically these needles can be found in areas of the solder pot where there is no flow (corners).

Figure 12. FeSn2 needles found in a selective solder pot with SAC305 alloy.

To avoid the formation of FeSn2 needles proper materials should be used. Cast iron or solder pots made out of titanium will eliminate this risk.
It is hard to detect the erosion of iron by solder analyses because of the needle formation. The parts should be visual inspected during maintenance to avoid excessive iron in the solder.

Nickel in sn100c

SN100C (Sn-0.7Cu-0.05Ni+Ge) forms a stable slow growing Ni-stabilized intermetallic compound layer (CuNiSn) at the interface with both Cu-OSP and ENIG substrates. The nickel percentage is critical for the properties of the alloy. The benefits of the nickel include:

- Better fluidity
- Finer grain structure
- Reduced growth of intermetallic layer
- Limits cracking in the intermetallic layer

In order to maintain these good properties the nickel content should stay between 400 and 600 PPM. Lower nickel content will reduce fluidity. Nickel is present in some component finishes and in ENIG board finishes.
The nickel may dissolve slowly in the solder increasing the content. [4]
The nickel in the solder joint will only be present in the intermetallic phase. In the bulk of the solder the nickel will not be found.

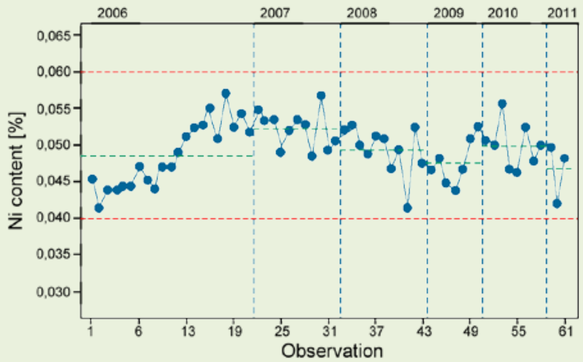

Figure 13 Ni concentration in SN100C alloy used in a wave soldering line producing communication products.

Studies have shown that phosphor impurities are able to destroy the fine grain structure that the nickel gives to the alloy. Phosphor levels >70 PPM will degrades the structure.

Dross and Solder Composition

On top of the liquidus solder a small oxide skin will be formed. The oxides that are formed are called dross. Dross consists of cells of solder metal enveloped by an oxide skin.
To minimize the formation of dross germanium is added in the SN100C. Germanium is present on the surface of the solder. The germanium in combination with the nickel also improves the fluidity and result in less icicles and bridging. Germanium content of approximately 50 PPM is enough to maintain low dross formation.
Since the germanium stays on the surface of the solder its content will reduce during production. To keep an enough amount of germanium in the alloy special tablets can be added. More than 0,1% germanium may result in poor wetting and is therefore not recommended.
Small levels of other elements like Al, Zn or Cd as low as 50 PPM may already cause excessive dross forming.

Summary:

Lead-free soldering requires more alloy analyses:
Higher temperatures
Higher tin content
More elements in the alloy to control

Copper contents in lead-free solder alloys should be monitored on a frequently basis. More then 0, 85 % copper will increase the solder defects like bridging and spikes.
In lead-free alloys (including SAC305) more than 1% copper may result in a wide melting range.

Lead impurities are decreasing in lead-free alloys, because there is no lead present in materials (components and boards). For a typical lead-free wave solder shows a 0, 01 - 0, 03% lead reduction per year.

Metal erosion (solder pot parts) is hard to identify by solder analysis. Because iron will format $FeSn_2$ needles that typically do not flow through the solder pot.

Acknowledgements:
Thanks to the Balver Zinn lab for doing over 65.000 solder alloy analysis over the last eight years.

References:

[1] IPC J-STD-001E standard.

[2] “Soldering in Electronics”, R.J. Klein Wassink.

[3] “Reliability of SN100C in Reflow and Wave Soldering”, Hans-Jürgen Albrecht, Klaus Wilke and Team of the Reliability Group Siemens AG, CT MM 6.

[4] “The Fluidity of the Ni-Modified Sn-Cu Eutectic Lead Free Solder”, Keith Sweatman & Tetsuro Nishimura Nihon Superior Co., Ltd, Osaka, Japan.

BALVER ZINN®

How to Manage Wave Solder Alloy Contaminations

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Content

- SnPb solder and impurities
- Lead-free solder change
- Pb contaminations in lead-free
- Measure solder composition
- Sample interval
- Recommendations
- Wave soldering versus selective

Dissolution of Base Metals in SnPb

Rate of dissolution:

- Base metal
- Solder composition
- Solder temperature
- Flow velocity

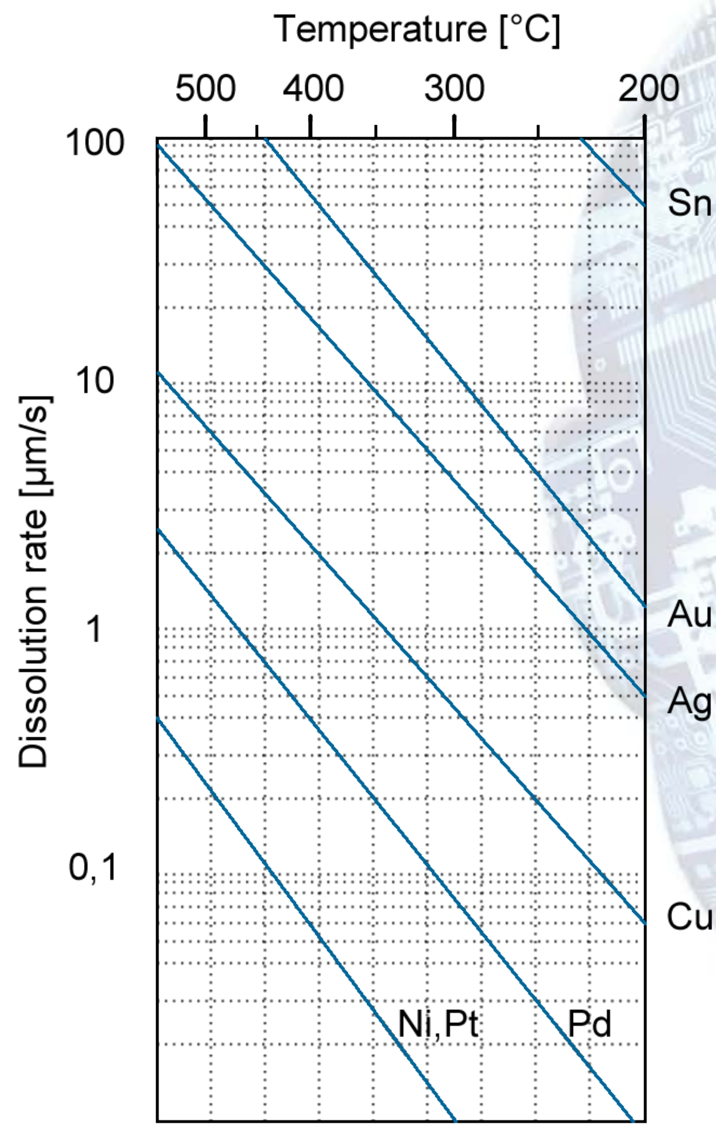
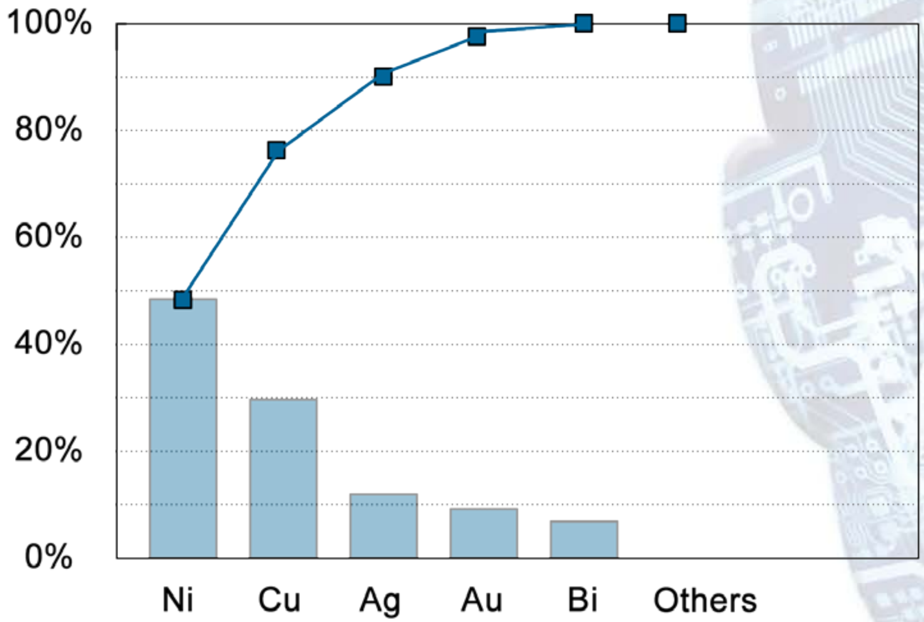


Fig. 4.29 Soldering in Electronics
R.J. Klein Wassink

SnPb impurities

Contaminant	Max.limit
Copper	0,3
Gold	0,2
Cadmium	0,005
Zinc	0,005
Aluminium	0,006
Antimony	0,5
Iron	0,02
Arsenic	0,03
Bismuth	0,25
Silver	0,1
Nickel	0,01
Total of Cu,Au Cd, Zn and Al	0,4

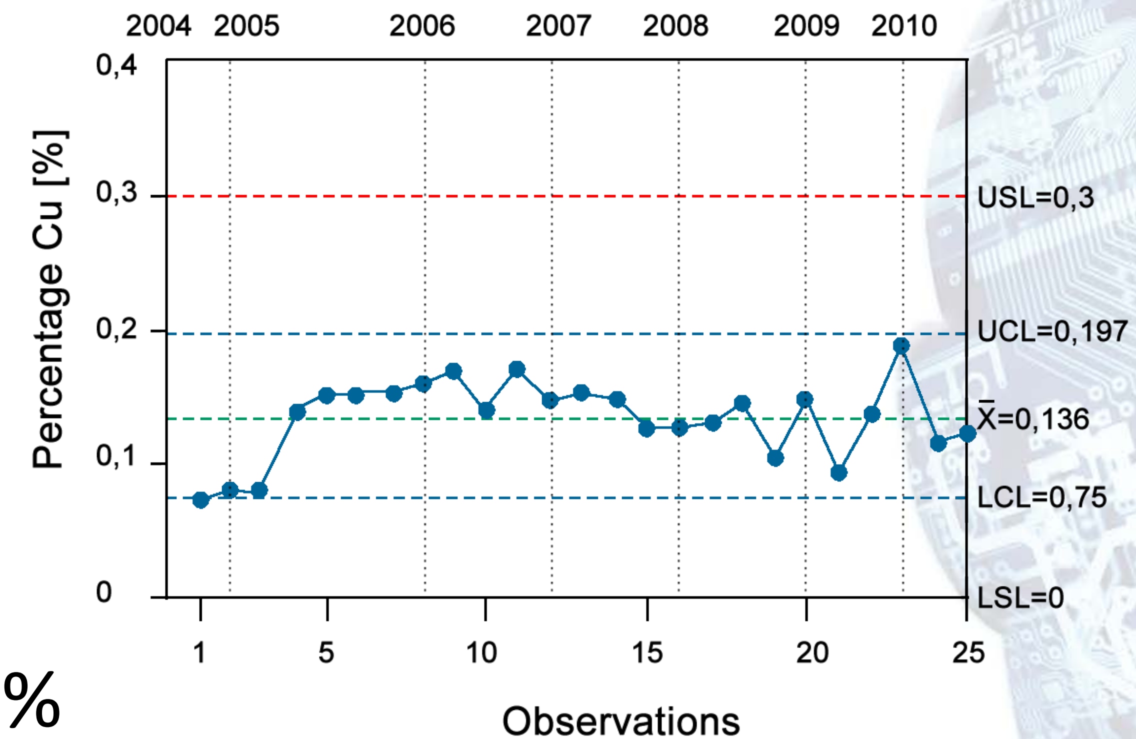
Out of specification:



Limits according to IPC-J-STD001E

Scores from >1500 solder pot analysis

Copper contamination in SnPb



Maximum 0,3%

Remove at 190 °C with stainless steel strainer

Exchange solder

Procedure:

1. Empty solder pot
2. Clean all parts
3. Refill pot with pure Sn (wash Sn)
4. Run solder pumps for > 0,5 hour
4. Empty solder pot
5. Refill solder pot with lead-free solder

Solder exchange – Sn wash

Lead-free alloy exchange solderpot				
Remaining SnPb [kg]	Selective pot [50 kg]	Small wave pot [400 kg]	Typical wave pot [800 kg]	Large wave pot [1000 kg]
10	8,179	1,046	0,524	0,419
5	4,144	0,524	0,262	0,210
2	1,671	0,210	0,105	0,084
1	0,838	0,105	0,052	0,042
0,5	0,419	0,052	0,026	0,021
0,1	0,084	0,010	0,005	0,004

Percentage of SnPb after lead-free refill

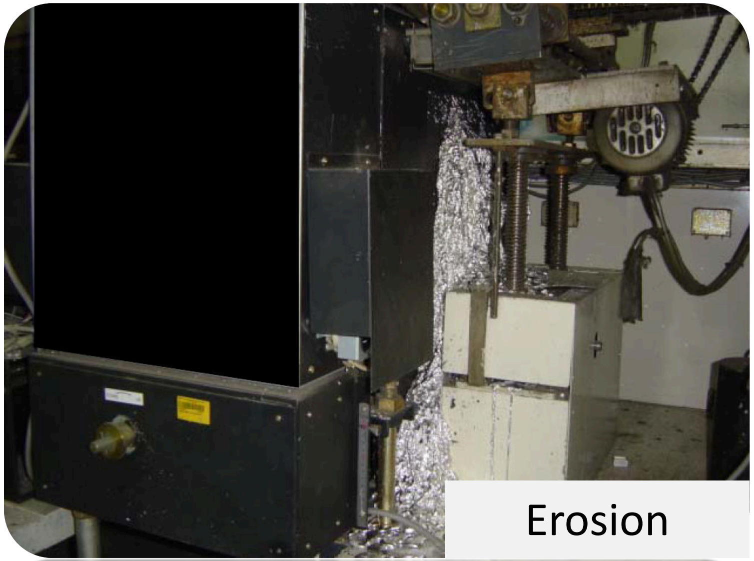
Use wash Sn to get low Pb impurities

Lead-free alloy exchange solderpot with Sn wash				
Remaining SnPb [kg]	Selective pot [50 kg]	Small wave pot [400 kg]	Typical wave pot [800 kg]	Large wave pot [1000 kg]
10	1,834	0,030	0,008	0,005
5	0,470	0,008	0,002	0,001
2	0,076	0,001	0,000	0,000
1	0,019	0,000	0,000	0,000
0,5	0,005	0,000	0,000	0,000
0,1	0,000	0,000	0,000	0,000

Spectro analysis

1. Sample: flowing solder middle of the wave
2. Preparation sample
3. OES Analysis

Erosion solder pot

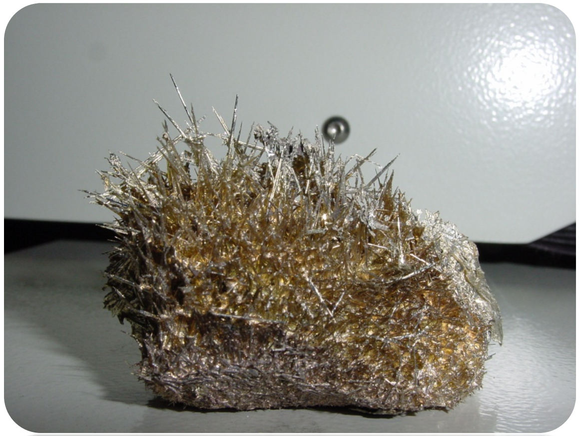


Lead-free:

- Higher solder temperatures
- Higher Sn content

Potential alternatives:
Titanium
Cast iron
Chrome carbid

Fe contamination

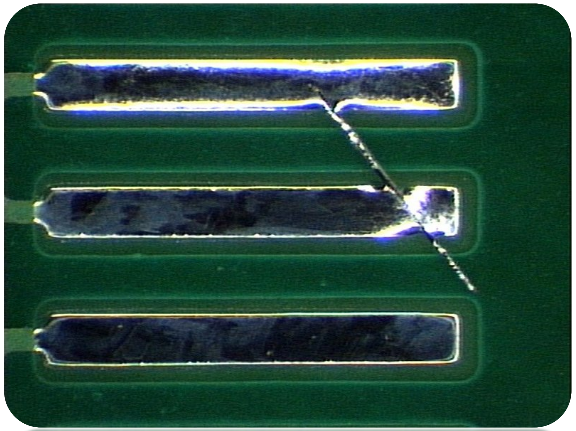


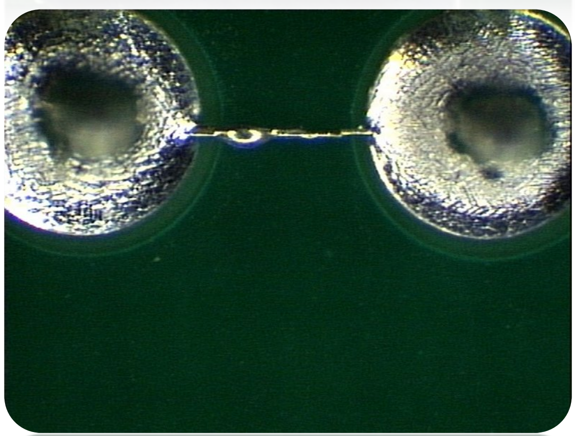
- $FeSn_2$ needles
- SAC alloys sensitive for erosion
- Co or Ni doping to minimize erosion

	SnPb	SAC	SN100C
Average	0,0027	0,0020	0,0021
Standard dev.	0,00055	0,00259	0,00237

Fe Max. Values 0,02 %

SPC Chart Fe contamination





$FeSn_2$ needles:

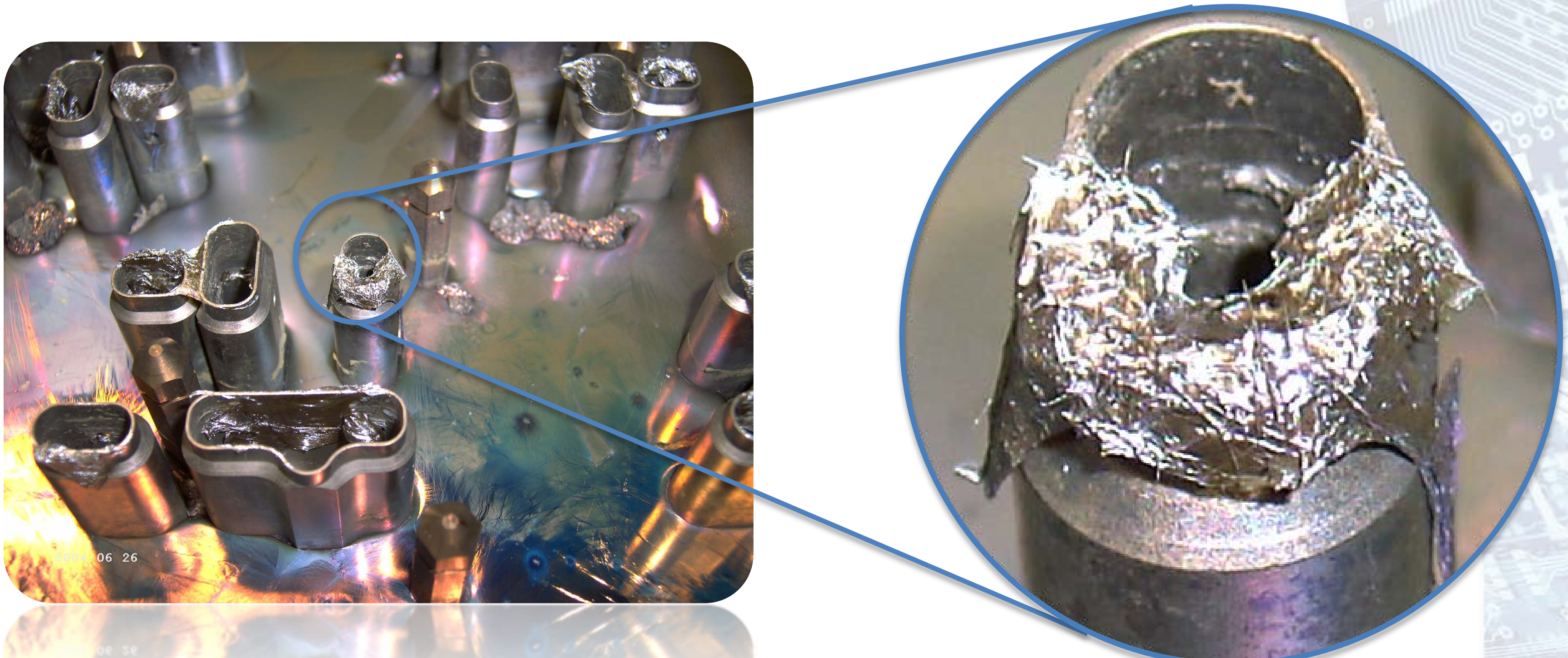
- Melting point >500 °C
- In areas where there is no flow
- Bridging potentials

Hard to define iron erosion by analyzing solder samples

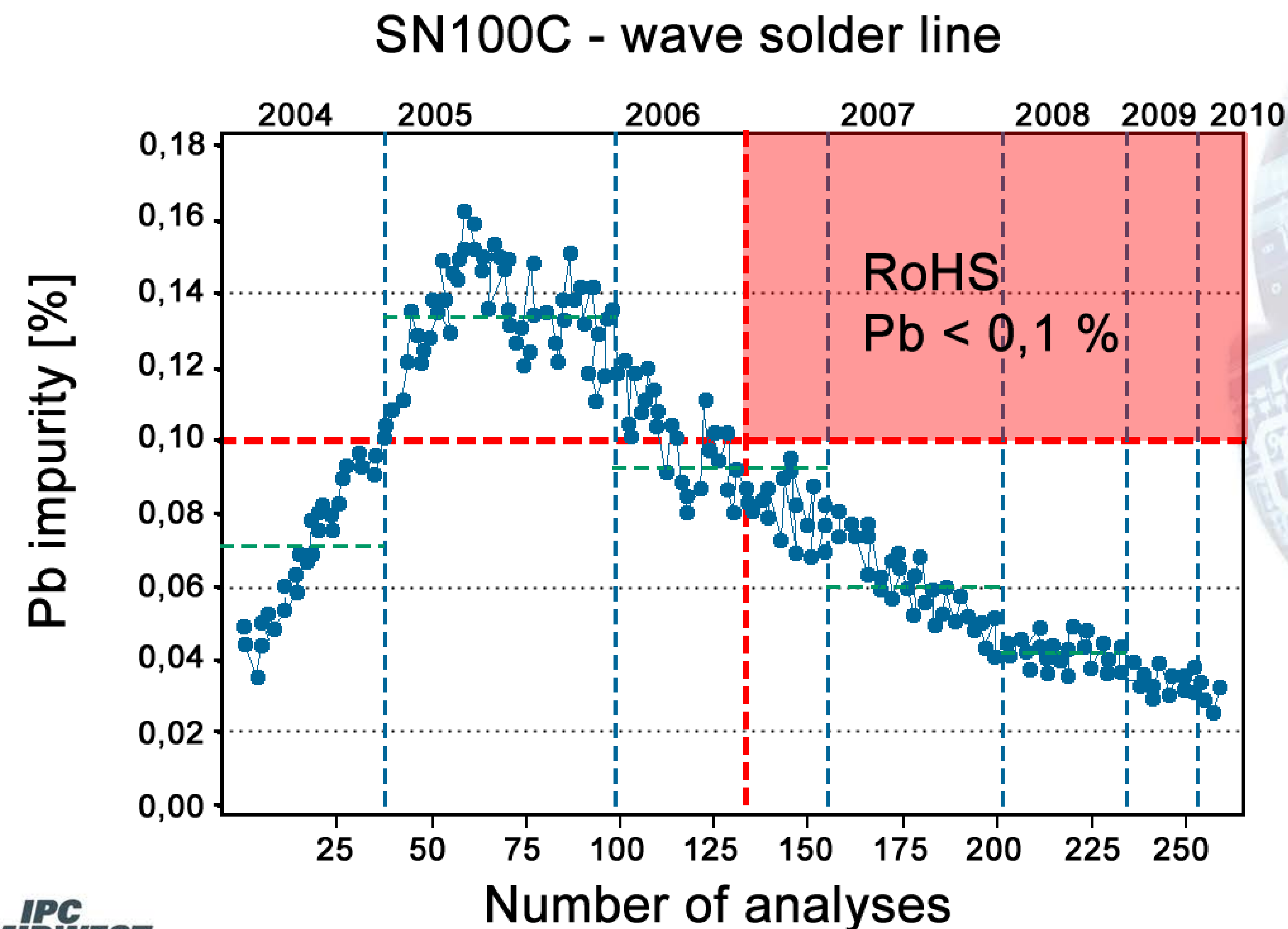
$FeSn_2$ Needles Selective SnPb

Also in SnPb alloys there is steel erosion.

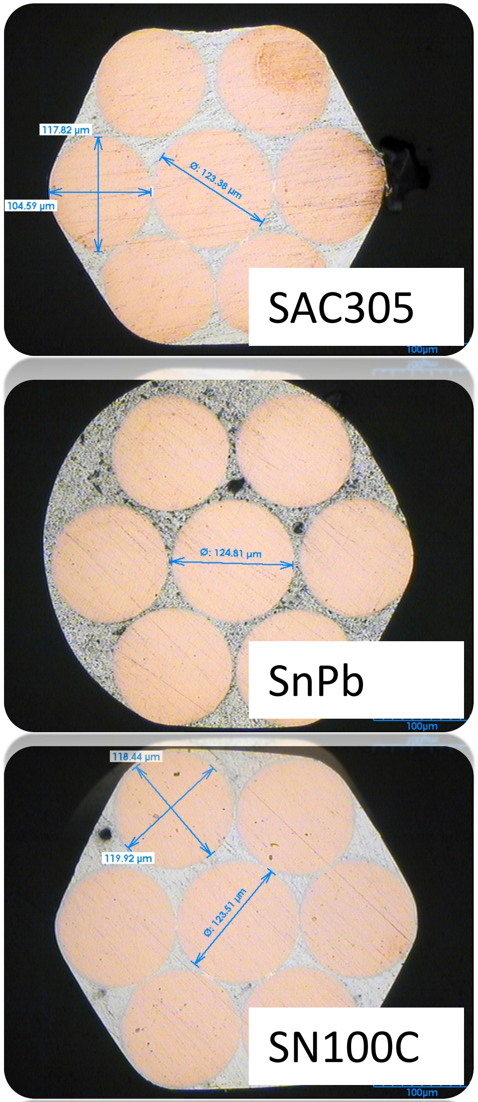
Reduces flow properties.

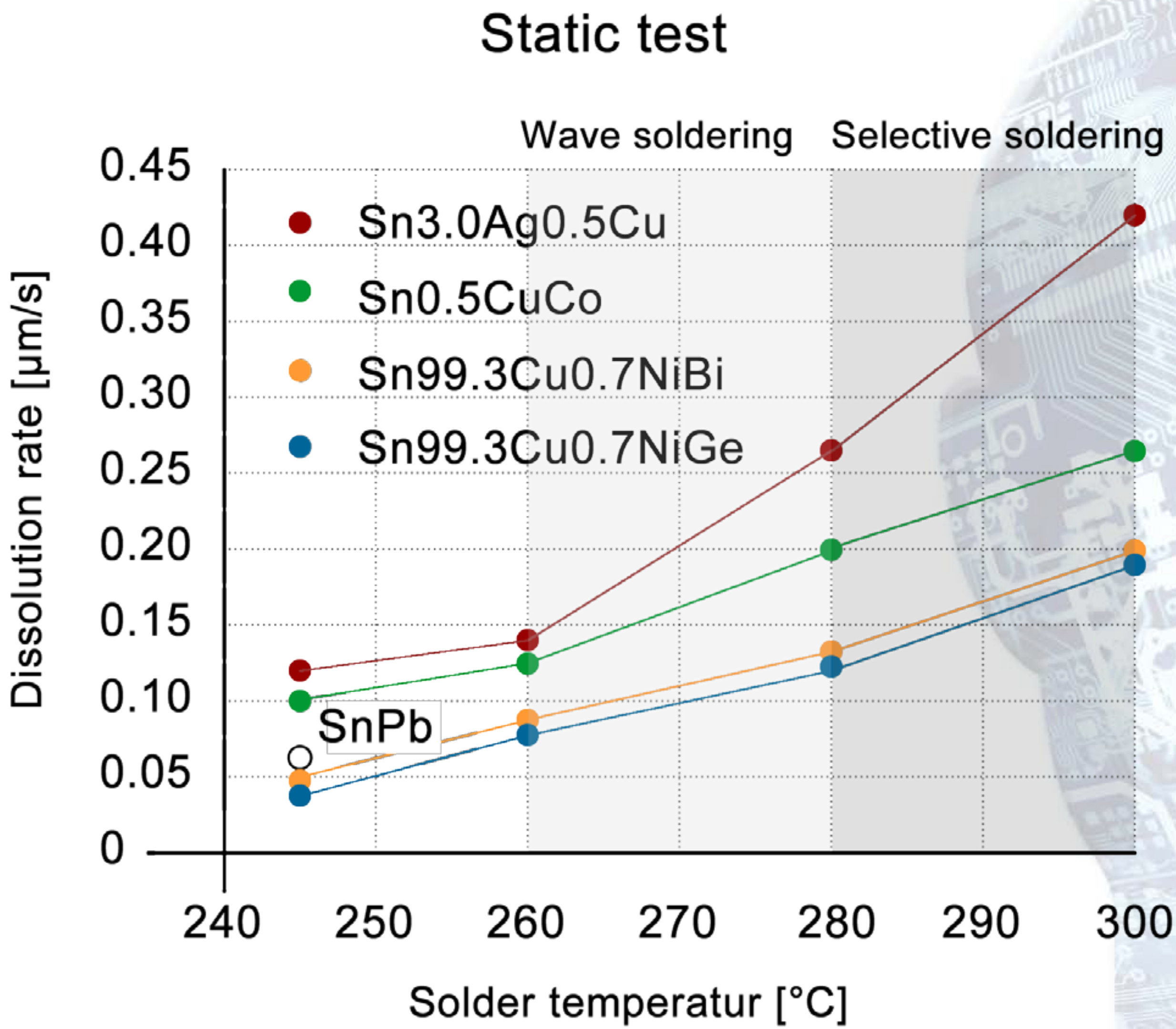


Pb impurity historical graph



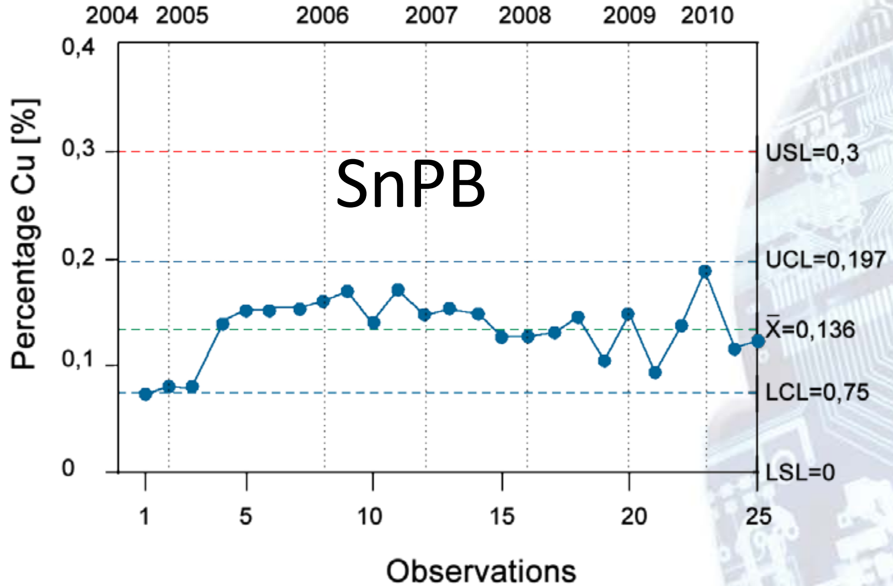
Copper leaching



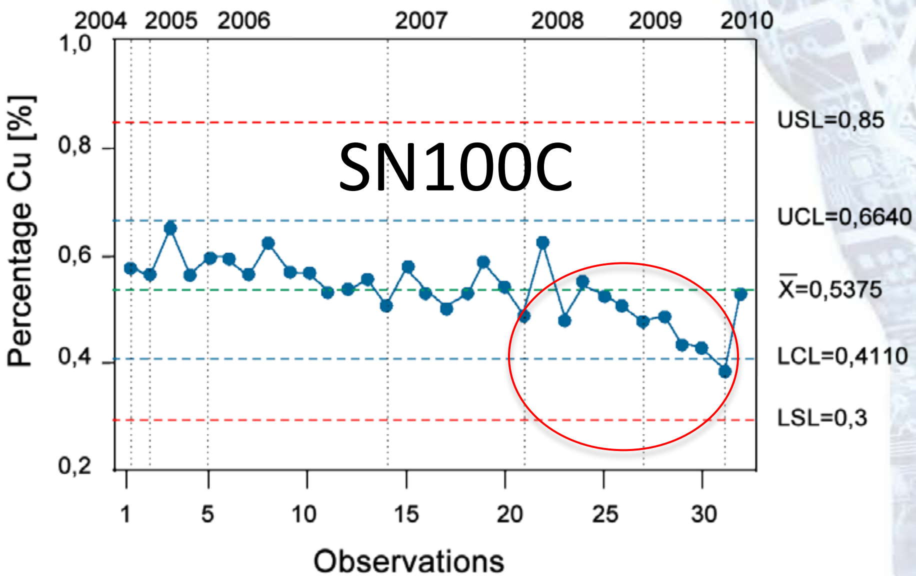


SPC: Cu content in solder

Nitrogen wave solder process (full tunnel) (identical machines, same customer): Automotive, Medical products (SnPb)

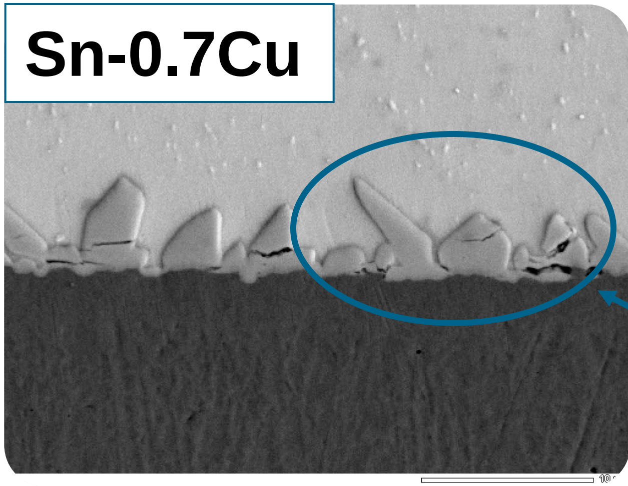


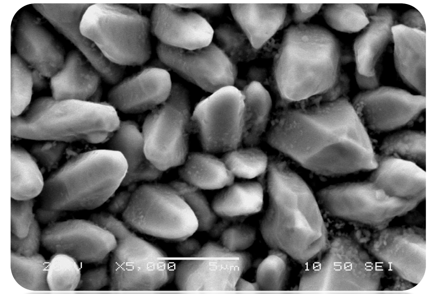
Industrial (lead-free)



Ni additive

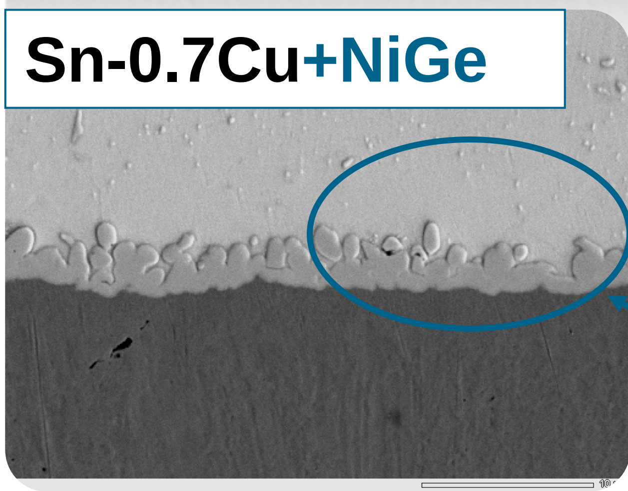
Sn-0.7Cu





Sn_6Cu_5 IMC

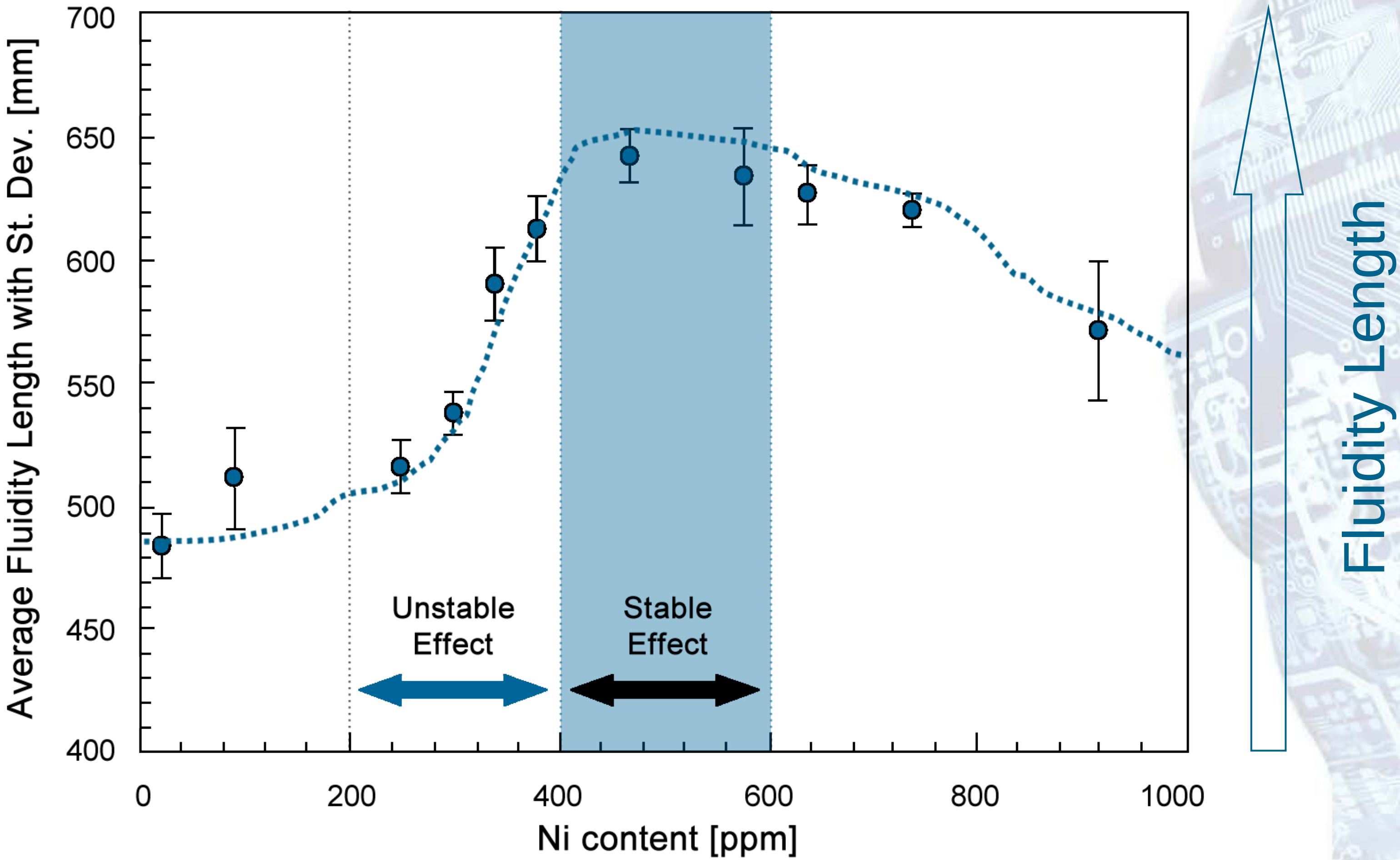
Sn-0.7Cu+NiGe



at ~ 3 % Ni in $(Cu,Ni)_6Sn_5$

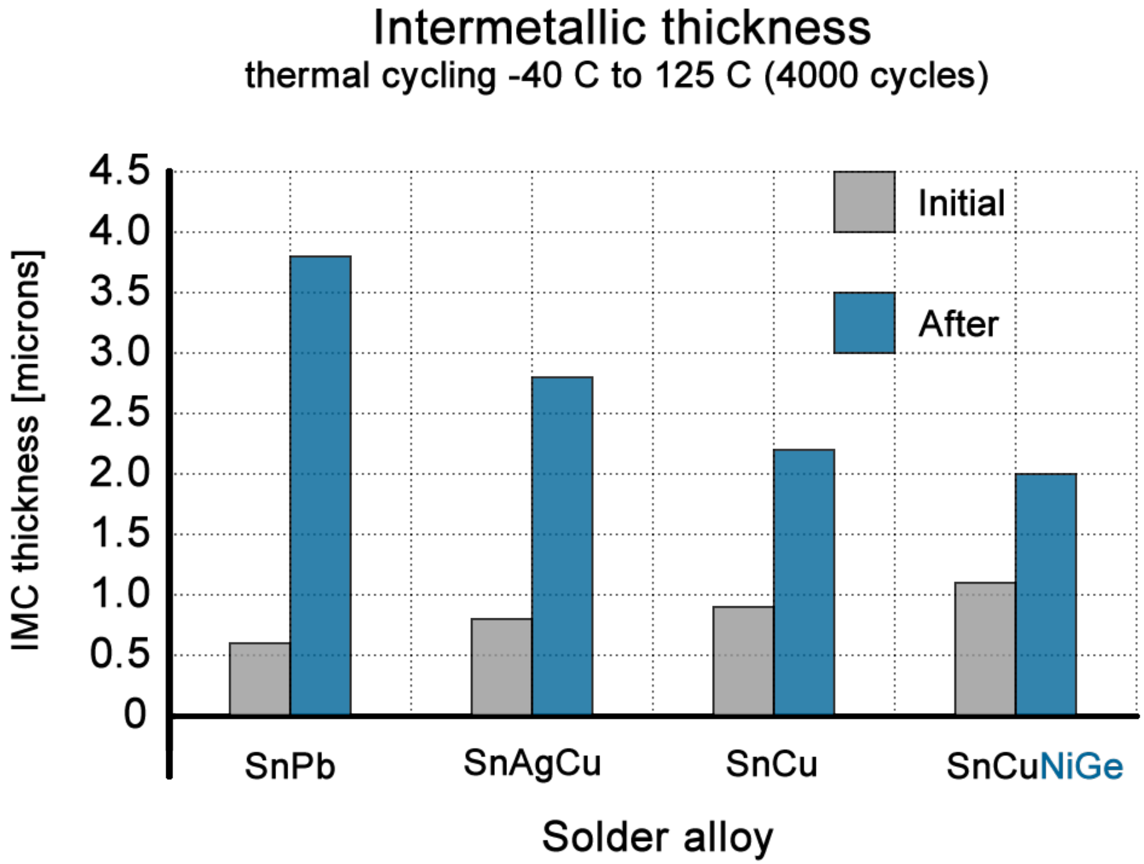
$(Cu,Ni)_6Sn_5$

Ni Content



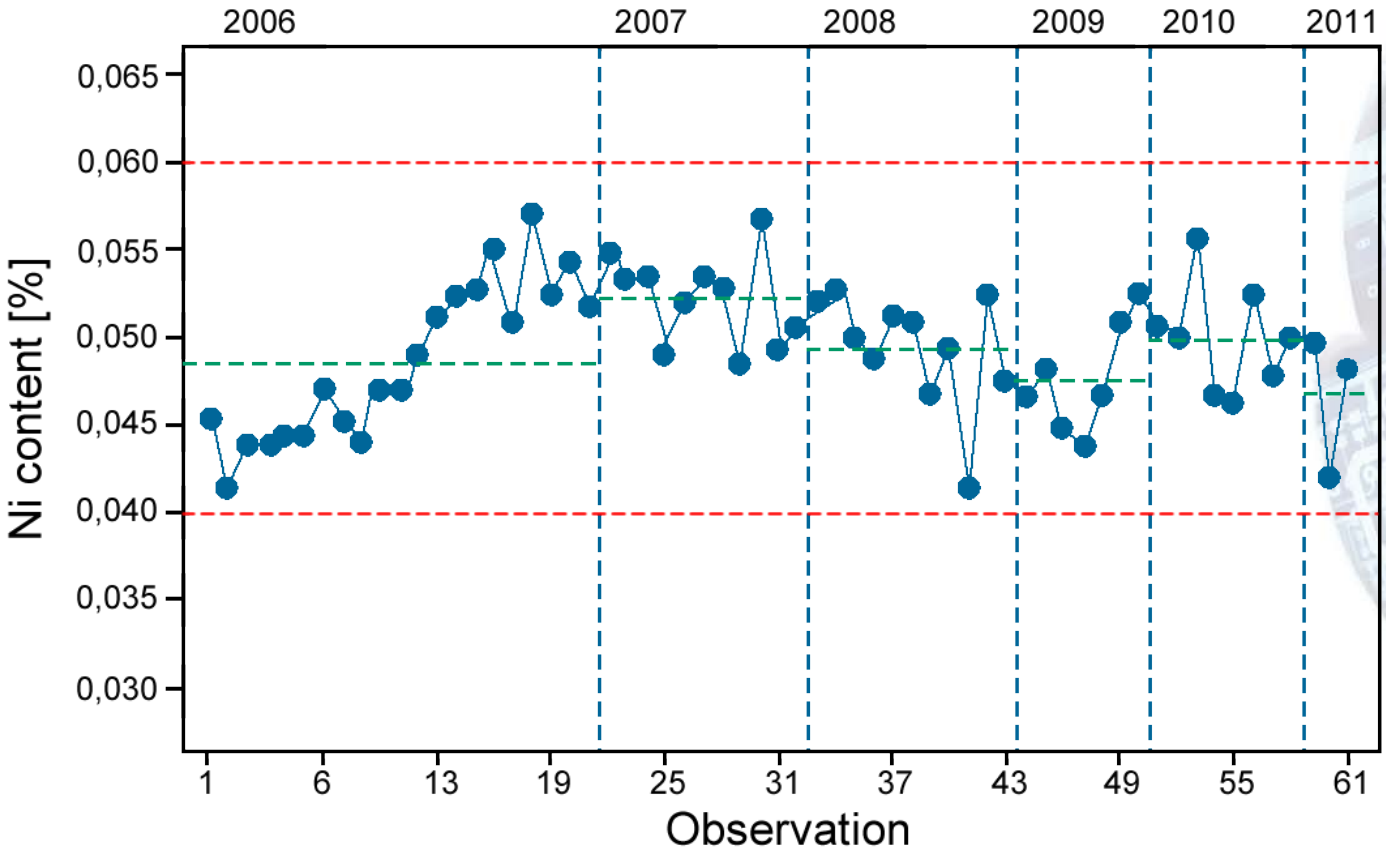
Average Fluidity Length with St. Dev. [mm]
700
650
600
550
500
450
400
0
200
400
600
800
1000
Ni content [ppm]
Unstable Effect
Stable Effect
Fluidity Length

IMC growth



The Ni in the IMC has the effect of suppressing columnar morphology stabilizing the hexagonal packed form of the Cu_6Sn_5 and slowing it's growth

Ni SPC-chart SN100C

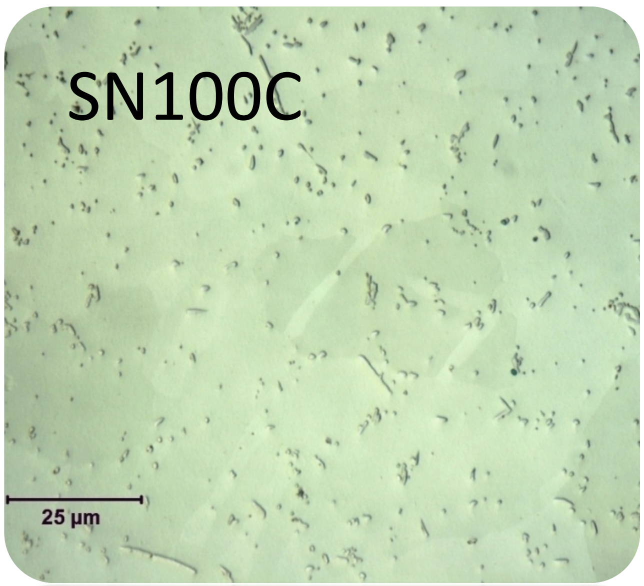


Ni content is consistent over the years.

Ni-rich solder bars available.

High Ni content

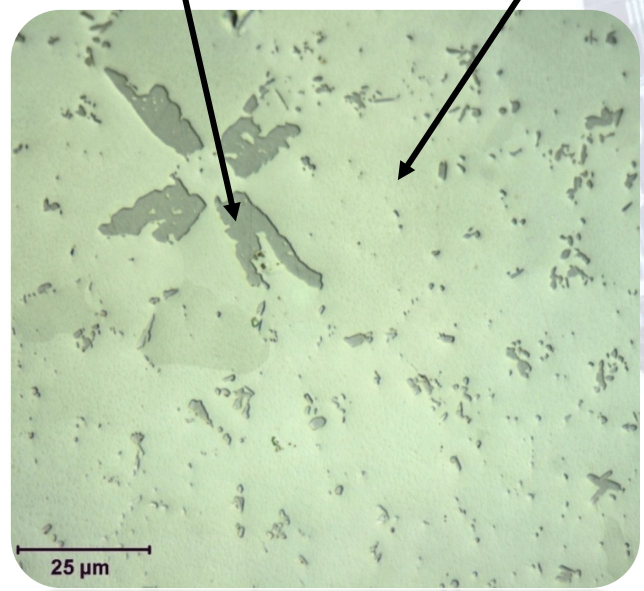
Uniform eutectic structure



600 PPM

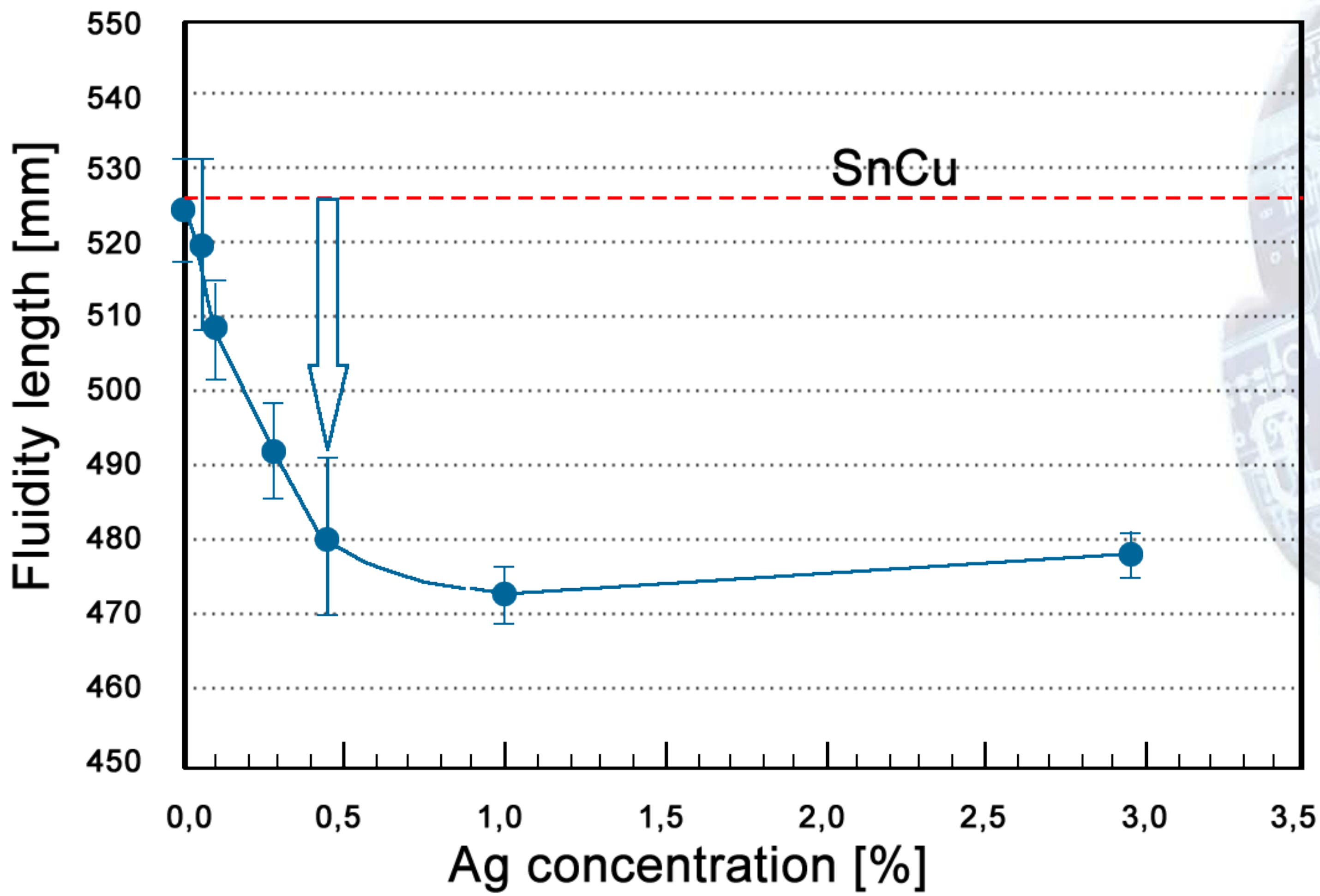
Primary $(Cu,Ni)_6Sn_5$ Crystals

Eutectic between crystals



>1000 PPM

Impact of Ag on fluidity

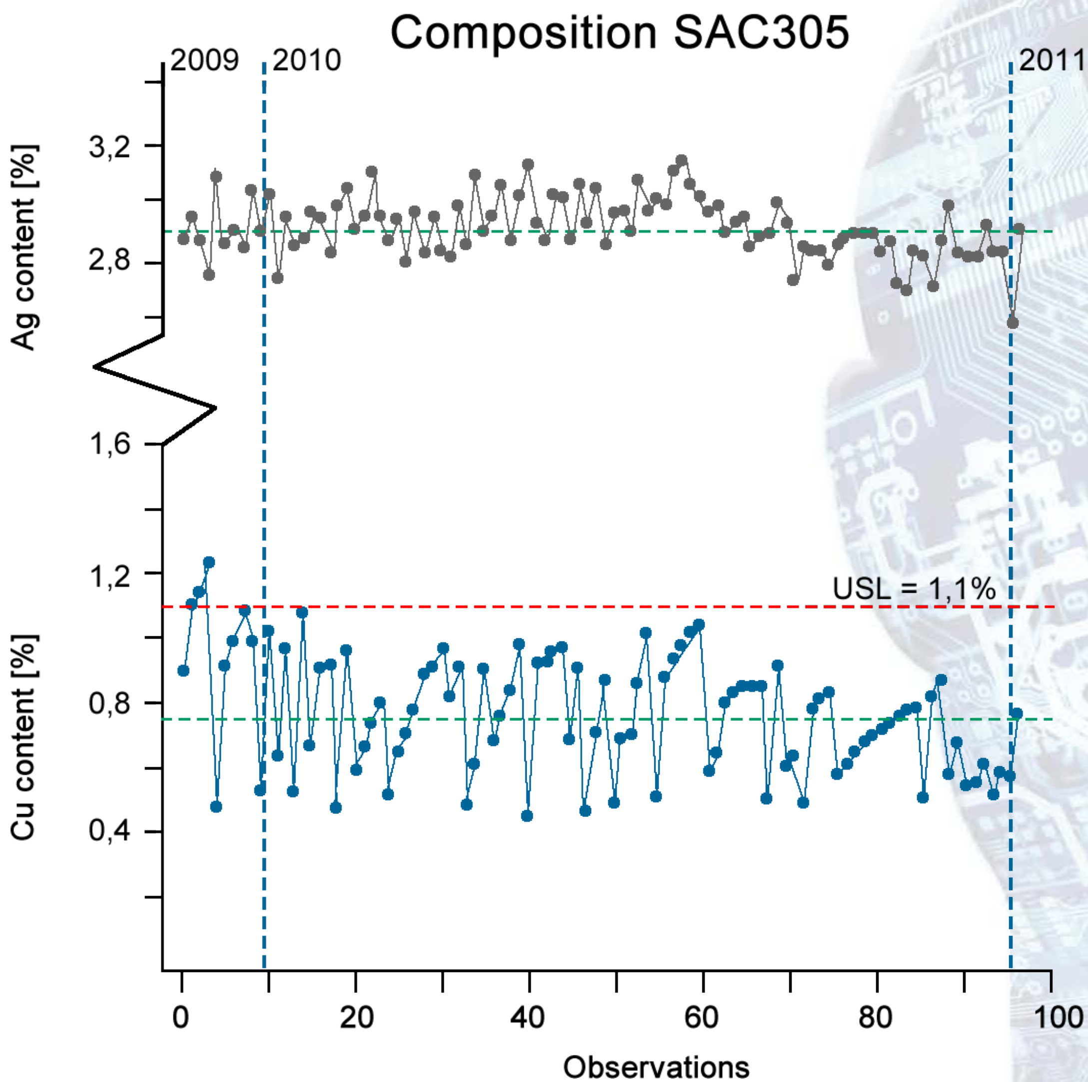


SAC 305 elements contents

Selective soldering process

Cu drifts more due:

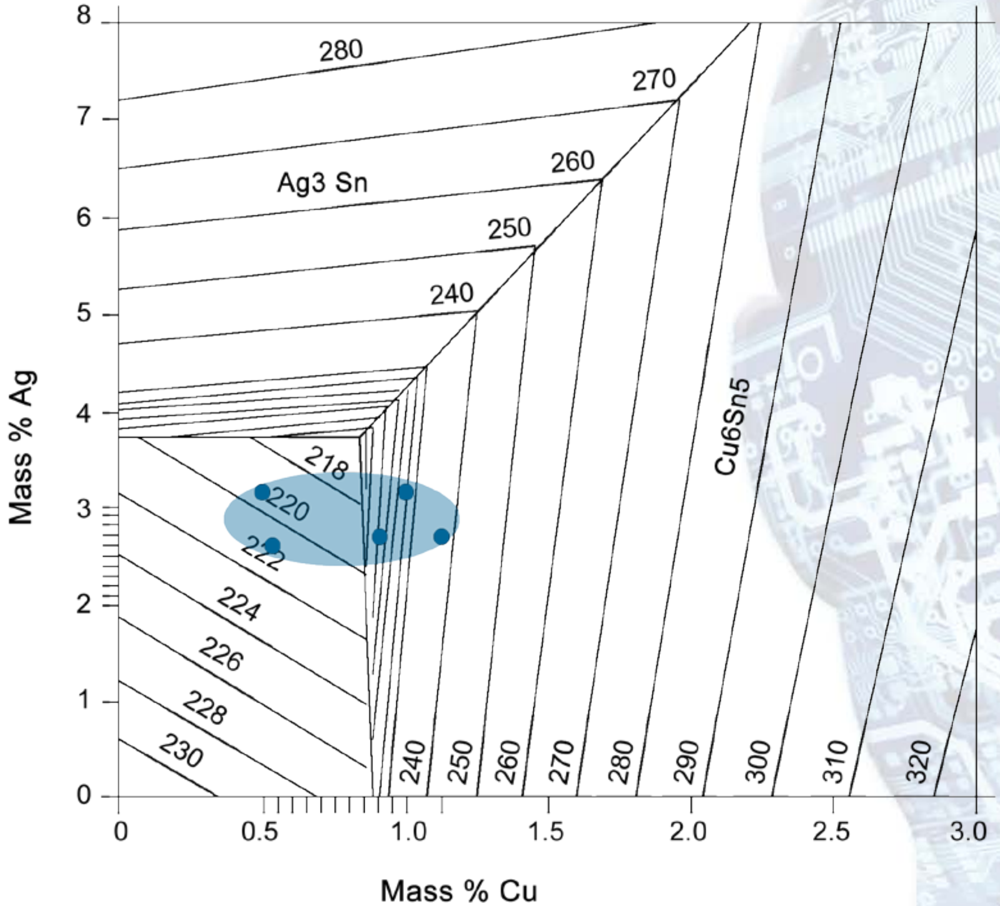
1. Leaching
2. SnAg or SAC bars



Silver/copper content in SAC305

Higher melting range:

- Fast solidification of solder
- Bridging
- Spikes



Germanium

Ge acts as an antioxidant and surface active agent.

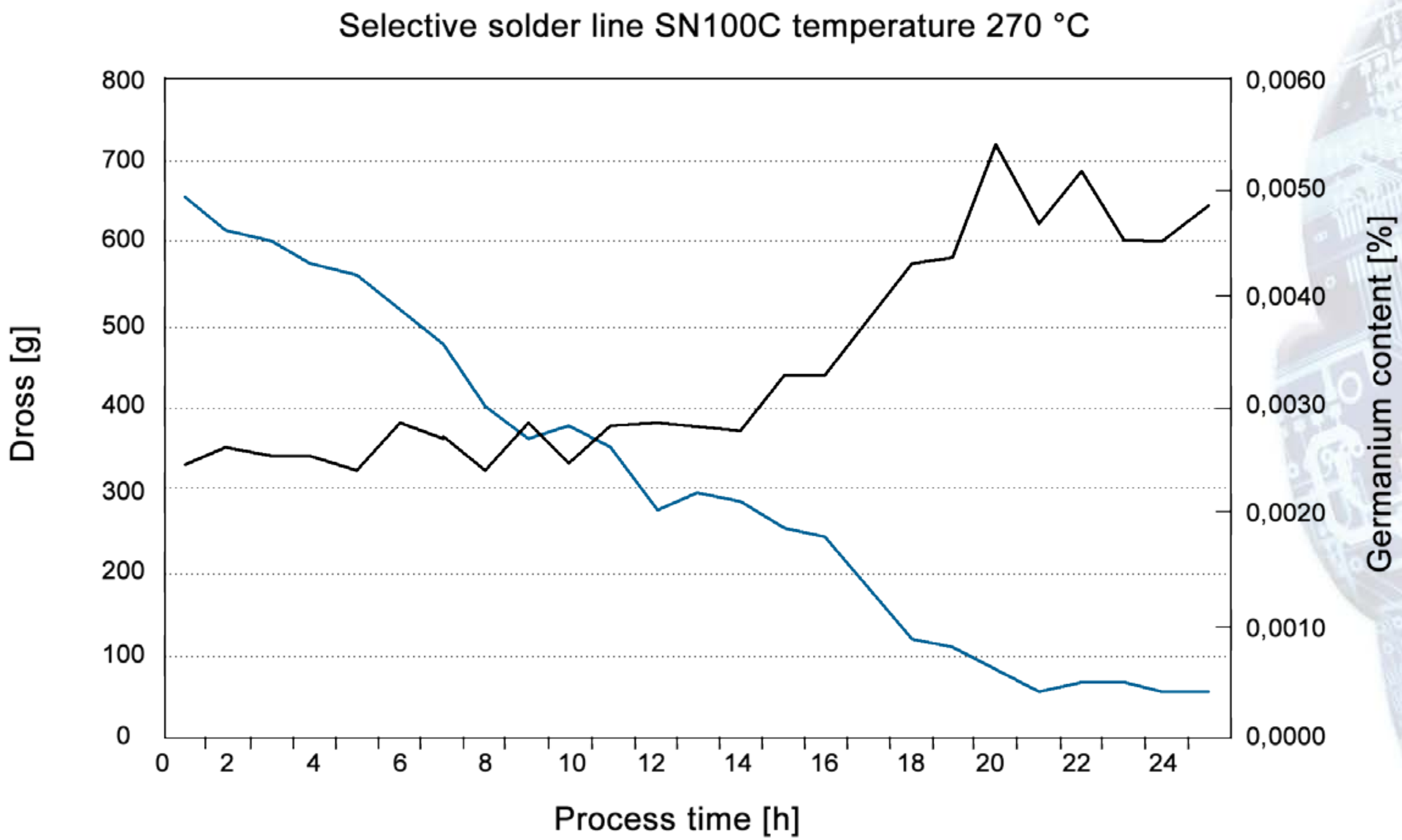
15 minutes ramp up to 340 °C - 30 minutes cooling

SnCuNi

SnCuNiGe

K Watling, A Chandler, K Nogita. A Dahle, University of Queensland

Dross and Germanium



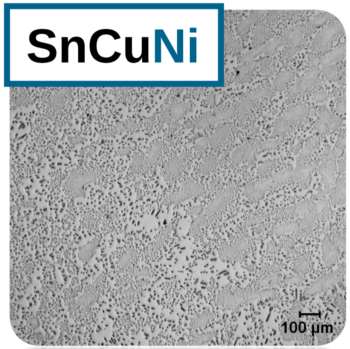
Less Ge results in more dross.

Impact of P

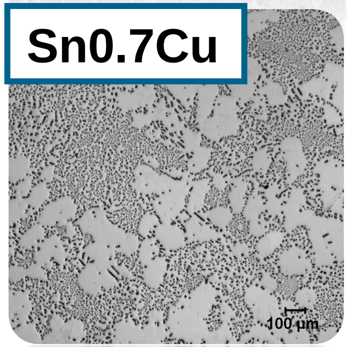
Phosphorus in lead-free solder (SAC) increases stainless steel erosion. P acts like a flux.

Adding P to SnCuNi destroys the beneficial effect of Ni.

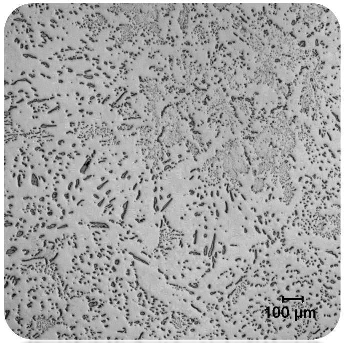
SnCuNi



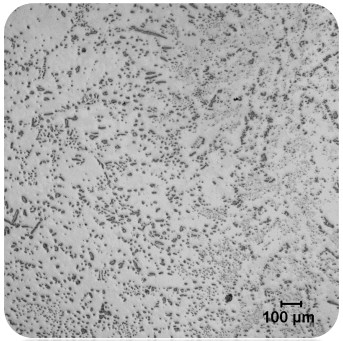
Sn0.7Cu



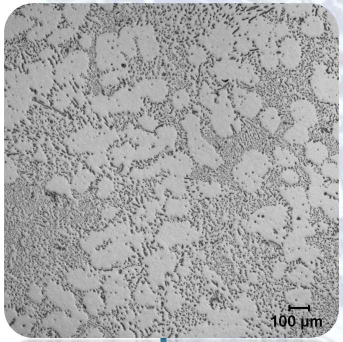
SnCuNi+0.007P



SnCuNi+0.02P

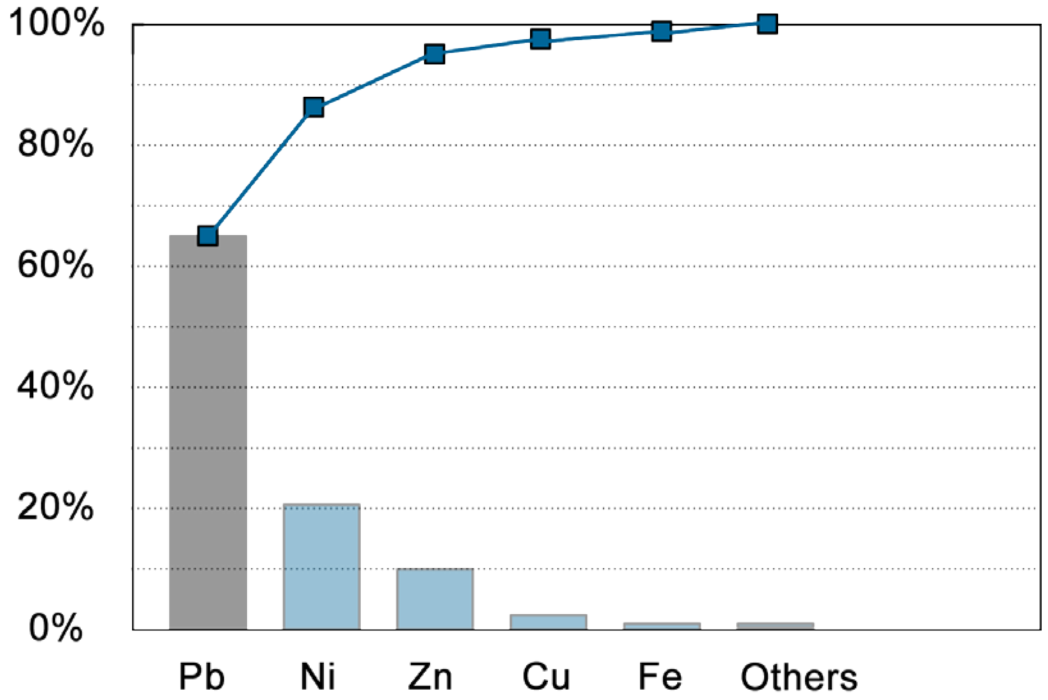


SnCuNi+0.06P



Similar – Ni benefit gone

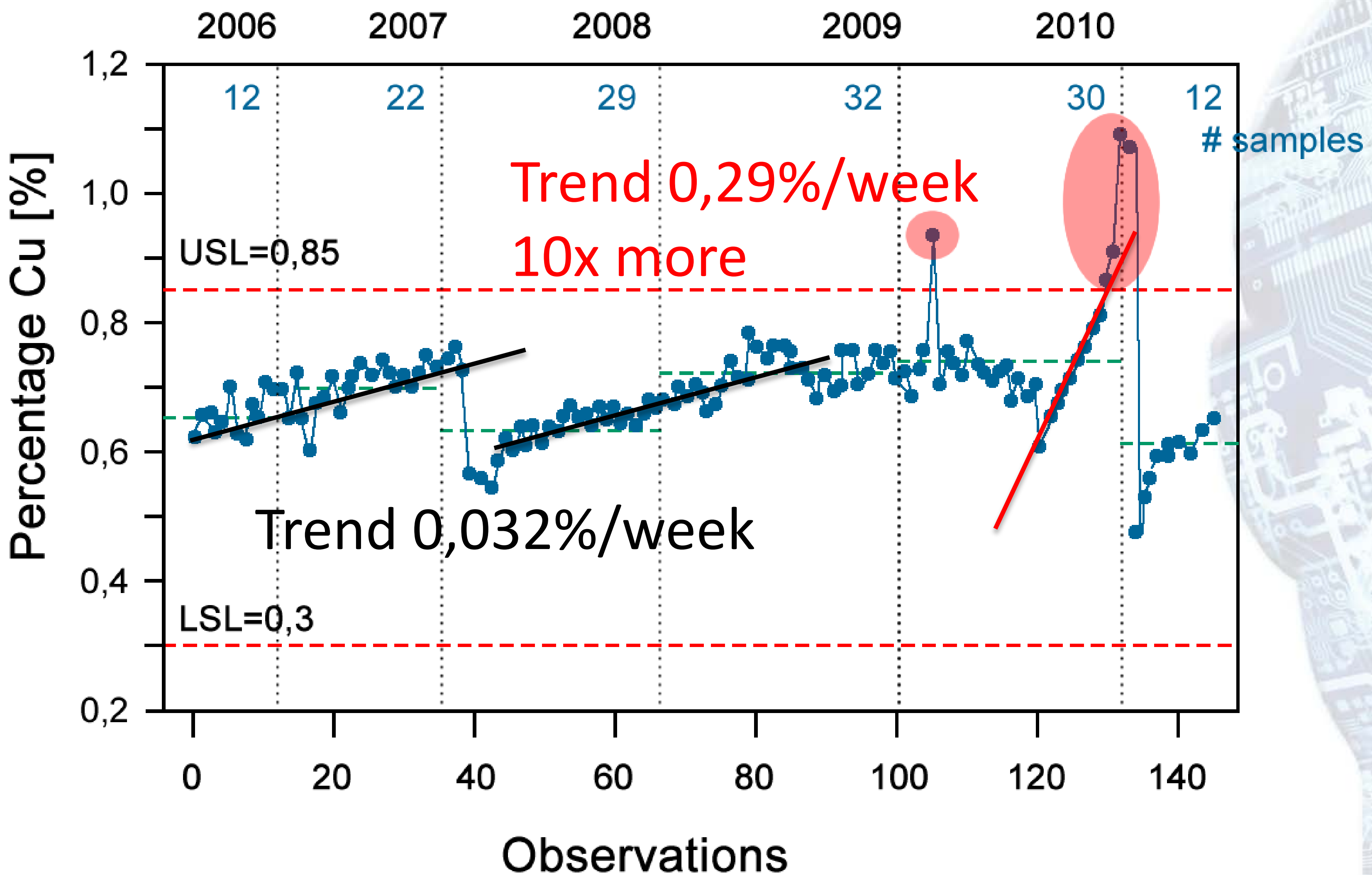
SAC alloys out of spec



Number of Pb defects is decreasing

Ni is less critical

Sampling interval



Recommendations

IPC J-STD-001^{E} chapter 3.2.2. Solder Purity Maintenance:

"If contamination exceed limits, intervals between the analyses, replacement or replenishment **shall [N1D2D3]** be shortened."

"The frequency of analysis should be dertermined on the basis of historical data or montly analysis."

Dross

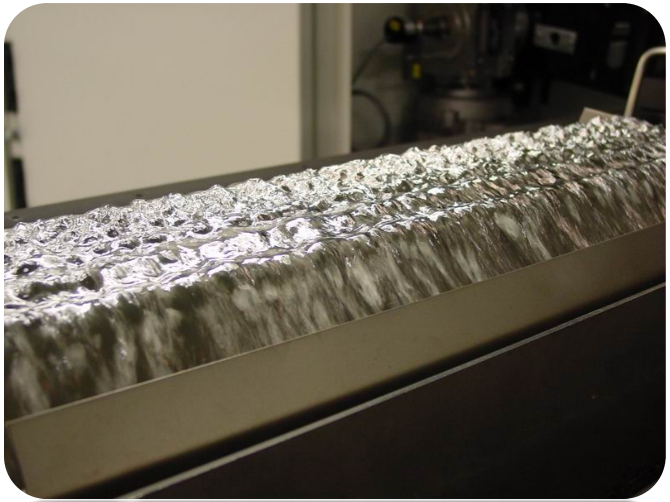
After running 20 hours (no maintenance)

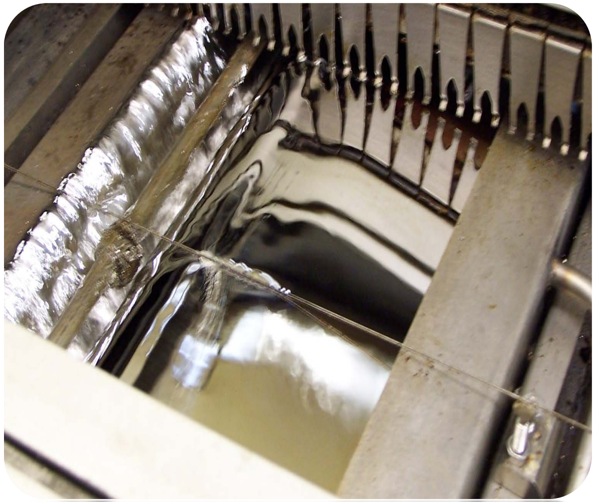
Alloy	Time [h]	Dross [kg]	Rate [kg/h]
Sn3.8Ag0.7Cu ref.	52	10.5	0.202
Sn3.8Ag0.7CuCoGe	70	2.73	0.039
Sn0.3Ag0.7CuNiGe	20	0.78	0.039

Solder (wave) continuous running. Solder temperature 260 C.

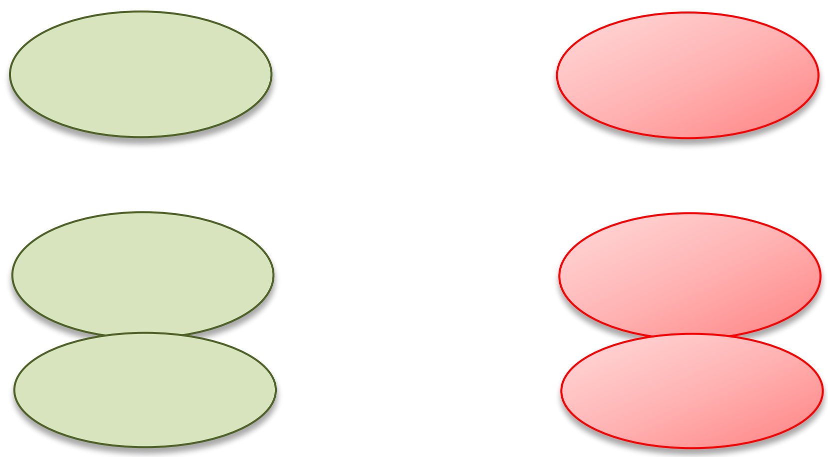
Minimize dross

- Use Nitrogen blanket
- Reduce solder fall height
- Ge tablets
- Wave former





SnPb wave versus selective



Automotive line (identical products)

One year average scores

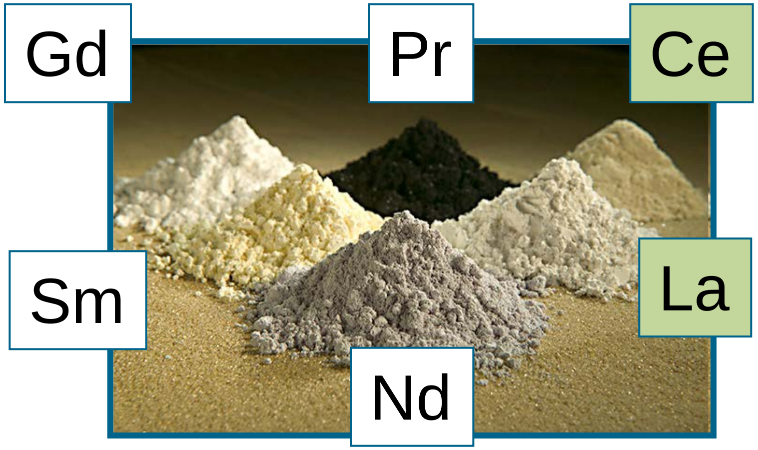
Periodic table

Halogens

Anti-oxidants

RoHS

Rare Earth elements
(Vitamins)



Conclusions:

- Lead-free soldering requires more alloy analyses.
- Copper contents in lead-free solder alloys should be monitored on a frequently basis. (Minimal 12 x /year for selective soldering)
- Lead impurities are decreasing in lead-free alloys.
- Metal erosion (solder pot parts) is hard to identify by solder analysis. Check during maintenance.

Acknowledgement

- Balver Lab
- Nihon Superior