Presented at IPC Printed Circuits Expo®
SMEMA Council APEX®
Designers Summit 04

Liquid Solders for High Temperature Solder Joints

Mathias Nowottnick,
Wolfgang Scheel, Klaus Wittke, Uwe Pape
Fraunhofer IZM
Berlin, Deutschland

Abstract
This paper presents a new joining technology for high-temperature application of solder joints, based on the results of the joint research project "TLSD". By the use of temporary liquid solder joints, it is possible to ensure operating temperatures up to 200°C or 250°C reliable. After the selection of a suitable base alloy it was possible to develop a stable interface between liquid solder and solid base metal by special material developments and modifications. In the first step it was necessary to prove the feasibility, the assembly and testing of functional demonstrators was the main task of the second step. A special focus of testing was the development of suitable testing methods and strategies to show the reliability of assemblies. First available results and an outlook for the further development of this new technology will be shown in this paper.

Introduction
A growing need for electronic assemblies for higher operating temperatures is recognizable in the last years. Beside of space and aviation, military use and well logging devices, the automotive industry has an important part above all. Electronic assemblies, sensors and control units must be placed in the car e.g. directly at the engine or in the gear (oil).[1] For this extreme conditions following temperatures must be realized[2-5] (see Figure 1).

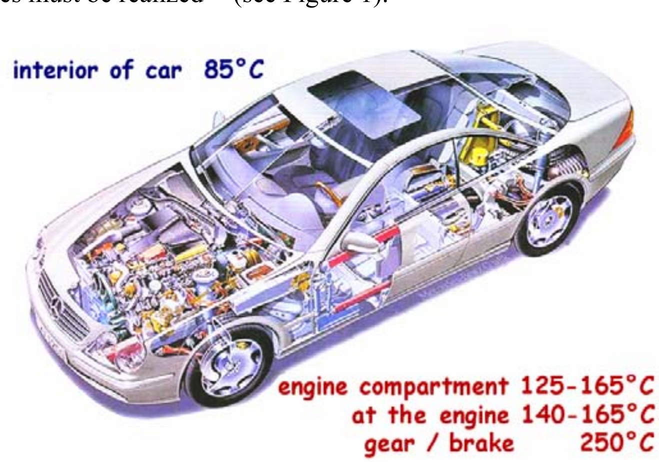


Figure 1 – Typical Operating Temperatures in a Car[5]

Apart of rising ambient temperatures other developments will cause a need for high temperature electronics too. Because of miniaturization the density of functions and power is also increasing. Also the higher clock frequencies, e.g. for microprocessor chips, results in higher power dissipation and operating temperatures. The ambient heat and the internal warming as well can cause the demanded higher operating temperatures. Whereas semiconductors are normally resistant up to 200°C anyway and new developments like "silicon on insulator" will allow even much higher temperatures, the limitation of operating conditions results frequently from packages or joining materials.

Common electronic assemblies, usually soldered with eutectic SnPb-solders, can be used reliable for operating temperatures up to 85°C…100°C. With SnAg-solders it will be possible to achieve operating temperatures of 125°C with certain constraints. Above these limitations the region of high temperature electronics is located. Some special stabilized solder joints were developed e.g. for 150°C operating temperatures, by the application of reacting solders. For higher temperatures are usually only high melting solders like PbSn or AuSn possible. However the melting temperatures of such high melting alloys are demanding also soldering temperatures higher than 300°C. Low-priced electronic components and organic substrate materials can't be used for these high soldering temperatures.

An alternative possibility for this problem could be the use of "liquid solder joints", even though such solder joints don't have a mechanical stability of course. The application of liquid metal contacts is known in the electrical engineering, e.g. for mercury relays or contact thermometers, which are also solder joints on principle. This interesting principle could be used also for thermal and mechanical high stressed electronic assemblies instead of common solder joints. Such liquid solder joints can make the electrical and the thermal contact as well, but the mechanical function has to be realized by suitable additional design measures. The advantages of so-called "combined joints[3]" can be used for this. A possible solution for the mechanical fixing and stabilization is the application of heat resistant adhesives, because there is a lot of experience in the field of COB- and flip-chip technology (glob-top and underfiller). Figure 2 shows the scheme of the fundamental principle of such a combined joint.

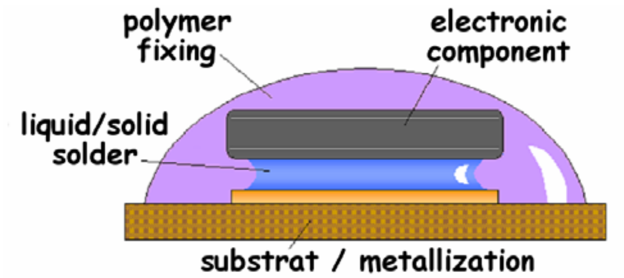


Figure 2 – Principle Scheme of a Combined Joint with Solid/Liquid Solder

Liquid metal contacts are also the state of the art for electronics, even if it is mainly unknown. A realized application of liquid solder joints was published already 1974,[4] Figure 4. The comparison of this liquid solder joint for a semiconductor chip with a common solder joints shows a significant improvement of reliability. Because of degradation, the junction temperature rises after 500 power cycles steeply for conventional solder joints, whereas no change was observed even after 100,000 cycles for liquid solder joints.

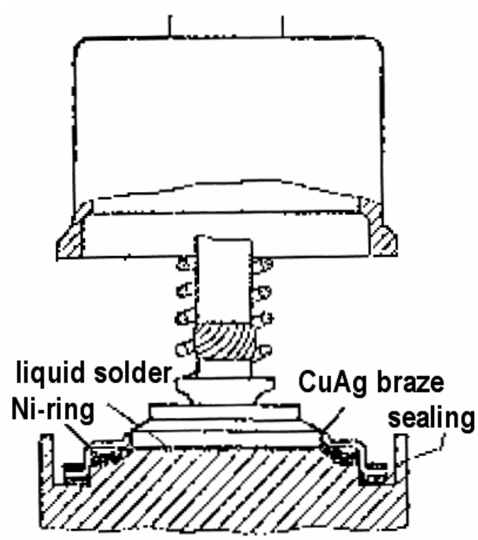


Figure 3 – Semiconductor Chip with Liquid Solder Joint[4]

A disadvantage of this solution is that metals and alloys, which are liquid at room temperature, contain either toxic elements like Hg or Cd, or very expensive components like GaInSn-alloy. Besides it is impossible to process liquid solders with standard equipment and technologies of PWB-manufacturing. The handling, deposition and dosing of liquid solders is expensive and demands additional equipment. Because of this reasons the described solutions are not very popular.

The new solution was investigated and realized in the joint research project "Temporary Liquid Solder Design – TLSD", supported by the German Department of Education and Research, BMBF. It was the idea to use solder alloys, which are solids at room temperature and processable like common solders with solder pastes or preforms. For reaching of operating temperature, the solder alloy turns into the liquid state. These solders should meet the requirements of environmental friendly processes and products. For the alloy selection a minimum melting temperature of 30°C is needed, for handling the solid at room temperature. On the other hand a maximum melting temperature of 180°C is demanded, if the operating temperature should be in the range of 200°C.

Technical Solution

The usual listings of solders show a lot of alloys, which meet the described requirements of melting temperature. Because of the environmental incompatibility and toxicity, all Cd- or Pb- containing variants are dropped, which reduces the number of possible alloys considerably. Furthermore In-containing alloys are not preferred, because of the expenses and availability. The selection is limited essentially to the Sn-Bi alloys, however it is not restricted to the eutectic alloy but also compositions with a melting range are possible. Figure 4 shows the possible range of SnBi-alloys, which enable a liquid application for the aimed operating temperature. A bismuth amount between 25…80% is possible for the operating temperature of 200°C, without solidification of the solder alloys.

Because of the intended change between the liquid and the solid state of the solder joint, the volume transition of the alloy is very important for the reliability. Tin has, like most metals and alloys, a positive volume transition for melting (reverse for solidification). This is visible for solidified solder bathes, which are forming typical cavities. In contrast to this, bismuth is one of the few metals, which shows the opposite characteristics and is expanding for solidification. This causes the danger to burst the solder crucible by solidification of bismuth, especially if it is made of ceramics. The combination of metals Sn and Bi shows the possibility to produce an alloy, which has a volume transition close zero, which is very advantageous for temporary liquid solder joints.

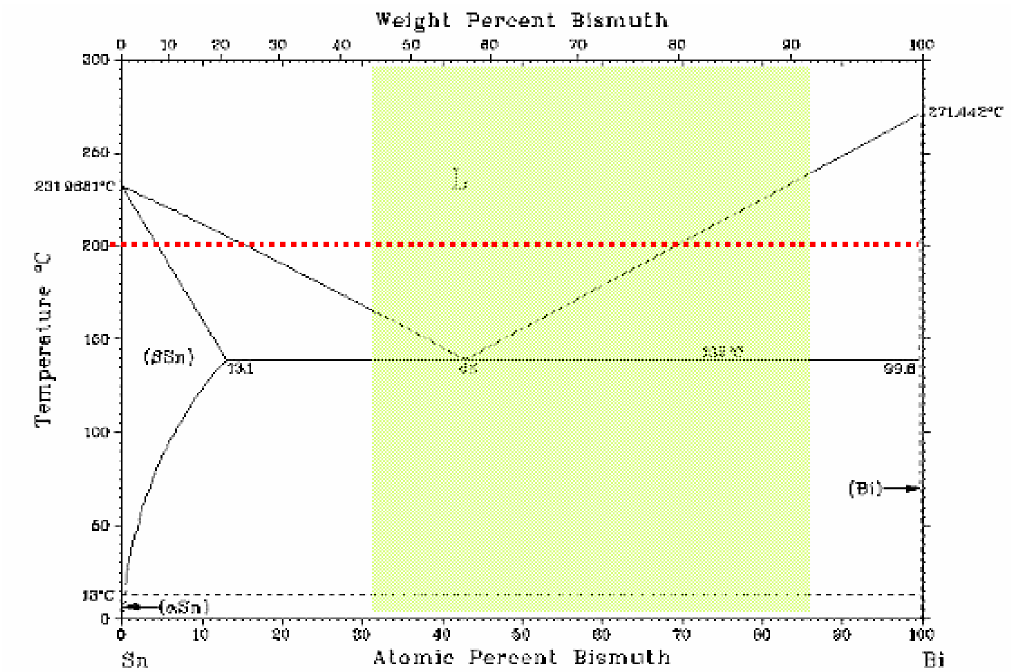


Figure 4 – Phase Diagram of the Sn-Bi-System with the Suitable Range for the TLSD-Solution

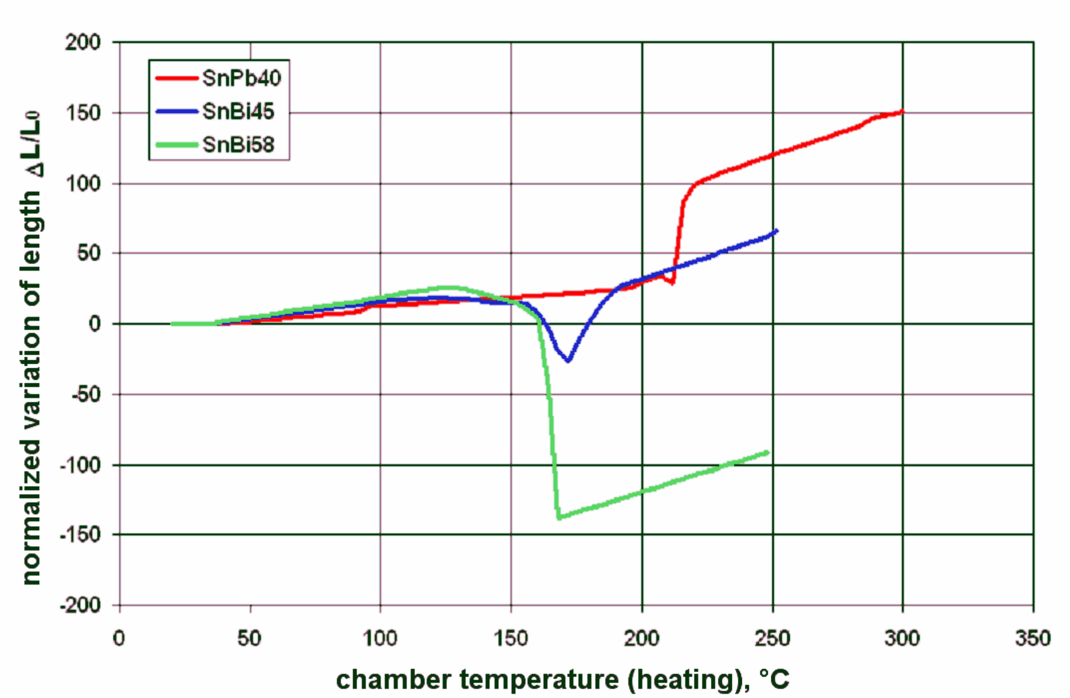


Figure 5 – Measuring of Volume Expansion/Contraction for Phase Transition of Solders by TMA Analysis

Figure 5 shows the measured volume transition for the alloys SnPb40 (as a reference), SnBi58 (eutectic) and SnBi45 (adopted). The positive volume transition for melting of SnPb40 and the negative transition for SnBi58 are clear visible, as well the minimized transition for the optimized alloy SnBi45. It was possible to verify the prognosticated minimum by these measurements. For this alloy, with a liquidus temperature of 175°C, a sufficient distance to the operating temperature is ensured.

Surface Metallization

Already during the first trials was an intensive chemical interaction of the liquid SnBi solder with the solid base metal detected for operating temperature. A visible growing of intermetallic compounds and dissolution of the copper base was recognized. Figure 6 shows an interface between SnBi58 solder and a copper foil on polyimide after storage with 160°C for 100 h. Besides the growing of intermetallic phases, the base metal dissolution is especially critical for the reliability of the liquid/solid solder joint, because a 35 µm pwb copper layer can be dissolved completely in a very short time. The copper solved in the solder is increasing the liquidus temperature of the alloy additionally, the solder joint is solidifying gradually and the liquid character of the joint disappears. Therefore this interfacial interaction must be prevented or significant slowed down for a reliable application.

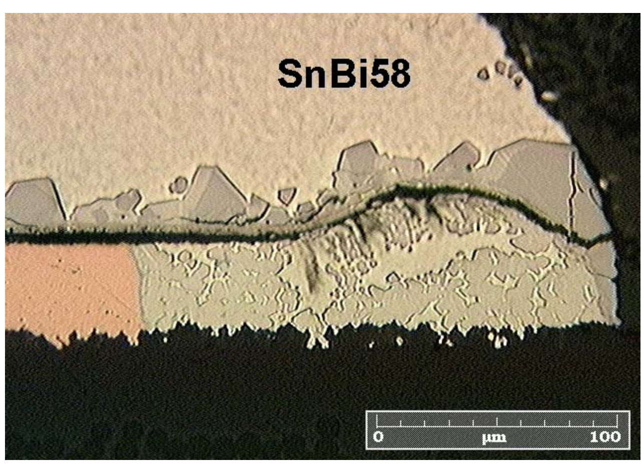


Figure 6 – Interface between Sn58Bi Solder and Copper after 100 h with 160°C Storage

In the possible region of alloy ratio between Bi and Sn, the problem of interfacial reactions was always the same. Because of this, an investigation of special adapted diffusion barriers was started, to prevent the chemical interaction. The common used Ni metallizations of printed circuit boards with a thickness of some micrometers proves to be insufficient for these high temperatures. It was shown, that porous Ni layers can even accelerate the copper corrosion by liquid solders, because the impact of melt concentrates on these spots. The tin diffusion and CuSn intermetallic phases can undermine and lift the Ni layer.

Best results were realized by a solution with an electroplated Cr layer on the Cu surface. This Cr layer remains unaffected by the molten solder for 360 h and 250°C, shown in figure 7. Because of the stability of the chromium oxides, such surfaces are not solderable with common fluxes. An additional metal finish realized a solderable surface. This very thin and wettable finish will be also solved in the liquid solder, but the chromium surface is still staying wetted by the liquid solder.

A drawback of this solution is the complicated plating process, which is difficult for printed circuit boards and almost impracticable for electronic components. Furthermore an absolute pore-free layer is demanded too, what is a problem at the edges and for component leads, especially if they must be bended. Therefore it was necessary to look for other alternative solutions for this problem.

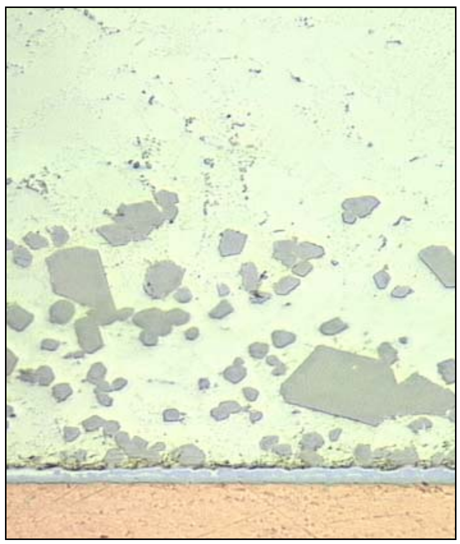


Figure 7 – SnAgCu Solder is Wetting a Cr Surface on a Cu Substrate, after 360 h / 250°C Storage (solution by ZMU)

Stabilization of the Interface

An alternative to the surface preparation could be the use of so-called "inhibitors" directly in the solder melt. Such inhibitors are additives to the solder alloy, which can prevent ore decrease the dissolution of base metal in the melt. This can be caused by minimizing the receptivity of the solder, or by materials, which have a special affinity to the base metal and are forming a stable interface layer as a diffusion barrier. The choice of suitable inhibitor materials is difficult and theoretically impossible. Therefore a large-scale test series was started with different additives in SnBi solder. The evaluation criterion was the dissolution rate of dipped copper- and nickel-wires. After the storage of wires in the different bathes, the remaining diameters were measured in cross sections. Wires dipped in pure SnBi-alloy were acting as a reverence. While some of the tested additives, like Ag or In, are effecting a measurable decrease of dissolution, other materials, like Sb or Zn, can even expedite this process. For a single tested variant it was also possible to reduce the dissolution of copper, as much, that no change of wire diameter was measurable after 5000 h. The difference between the melt with and without inhibitor is visible already after 500 h, Figure 8, whereas now wire is remaining after 5000 h in the standard SnBi.

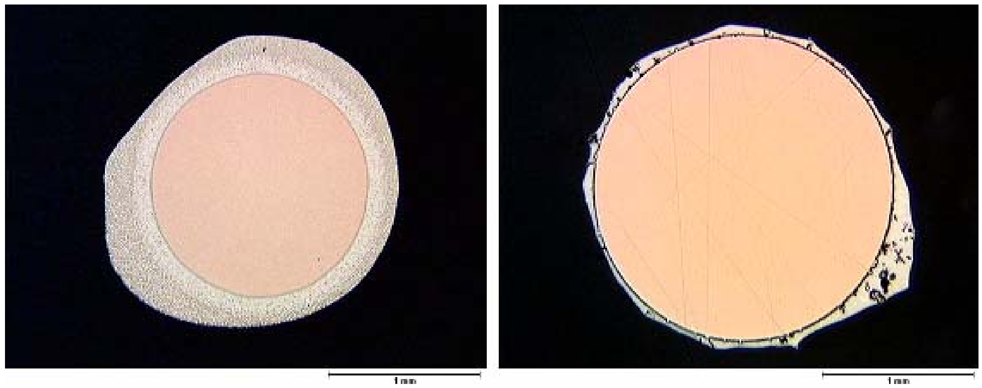


Figure 8 - Cross Section of Copper Wires after 500h Storage in Molten Solder with a Temperature of 200°C, left in Bi58Sn42 and right in BiSn with 1% Inhibitor Addition

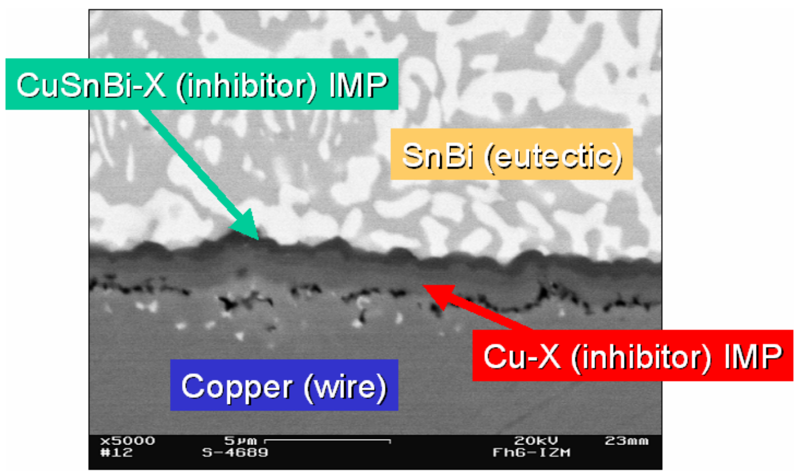


Figure 9 – Interface between Copper and SnBi-Solder, Stabilized by an Inhibitor X

This favorable effect of the inhibitor can be explained after a SEM investigation of the cross section. Figure 9 shows a part of the interface with an intermetallic phase between copper and inhibitor material, designated as X. This thin intermetallic phase is obviously stable and is able to stop the further growing of CuSn-phases. Then it was necessary to find the minimum needed inhibitor amount to ensure the described effect. The base solder was mixed with 0.5, 1, 2 and 5 % of inhibitor addition, following the solderability and dissolution inhibition was measured. Already a small amount of 1 % addition is enough, to prove a significant effect of inhibition. Furthermore the inhibitor effect was also detectable for other solder alloys and higher temperatures, SnAgCu and SnCu.

The Polymer Fixing

It was already explained, that the liquid solder can realize only the thermal an electrical function, but it can't ensure the mechanical stability, suitable measures are needed. The partners of the "TLSD" project decide on an organic material, which can be applied as an encapsulation and act as a fixing for the components and solder joints. This polymer fixing has a special importance for the reliability of the whole joint. In principle this polymer is an organic adhesive, certainly it must resist all high temperature stresses like the assembly. It should be stable also for permanent temperatures of 200°C or 250°C. For the adoption to the assembly it is also important, that the polymer fixing is electrical insulating, has a matched temperature coefficient of expansion and a good adhesion on the substrate material. For the further processing the flowing properties are also important, especially for the application on small spacing.

The development and trials were leading to a special casting resin for the application up to 200°C, a one-pack epoxy-amine system with good storage stability at 5°C. This formulation is designed for a long-term stability for 200°C and shows favorable thermo-mechanical properties, especially for the temperature shock test. It can be hardened for less than an hour with 150°C. Further tests were showing a low loss of mass of 2% after 1000 h and 200°C. Another test with 2000 cycles -40/+200°C was passed and the adhesion on organic substrate materials is excellent. The combination of liquid/solid solder joints with high temperature resistant adhesives was tested for polyimide pwb with power transistors and also for bonding of bare power diode chips even with 250°C operating temperature.

Outlook and Acknowledgement

After a first feasibility study,[6] the joint research project "TLSD" was started. After the presentation of first steps and results,[7] the testing of demonstrator assemblies is now in processing. Another important task for the near future is the manufacturing and provision of the inhibitor solder as perform and solder paste. The presented developments in this paper are the result of the cooperation in the "TLSD" project. Special thanks are due to the collaboration with Dr. Klaus-Peter Galuschki, Barbara Lehner, Dr. Caroline Cassignol and Dr. Ernst Wipfelder from Siemens, Walter Baetz and Stefan Dietz from OSRAM, Dr. Juergen Freytag from DaimlerChrysler, Martin Rittner, Dr. Heike Konrad and Ralf Miessner from Robert Bosch, Dr. Harry Berek and Antje Einenkel from ZMU, Bernd Speil and Dr. Christina Benedek from WEVO Chemie.

References

1. E. Hastreiter: „Hoehere Einsatztemperaturen in der Automobilelektronik“ (Higher application temperatures for automotive Electronics); ZVE-Technology Forum. Assemblies for Higher Operating Temperatures. 13.04.1999
2. AEA Technology: “The world market for high temperature electronics”. A HITEN Report. Harwell 1997
3. K. Wittke, U. Fuessel: „Kombinierte Fuegeverbindungen“ (Combined joints). Springer-Verlag, Berlin 1996
4. A. A. Abramov, E. K. Belebaschev, L. P. Kotschetkova: „Sosdanije silowych poluprowodnikowych priborov s kombinirowannymi kontaktami“ (Manufacturing of power semiconductor devices with combined interconnects). Journal of Electrotechnical Industry, series "Converter Technique", Edition 14, 1971, S. 8-10
5. W. Wondrak; W. Senske; R. Thompson; R. Viancino: „Demands on high temperature electronics for automotive engineering“; MicroCar 2003, Leipzig 26.06.2003
6. K. Wittke, M. Nowottnick; W. Scheel, U. Pape, J. Gamalski, K. P. Galuschki: „Fluessige Loetverbindungen - eine alternative Verbindungstechnik fuer die Elektronik“ (Liquid solder joints – an alternative joining technology for electronics); VTE; issue 3; Jun 2001; S. 129-134
7. M. Nowottnick, W. Scheel, K. Wittke: TLSD – eine neue Generation von Hochtemperatur – Loetverbindungen (TLSD – A new generation of high temperature solder joints), SMT-Congress, Nuremberg, 6.-8. Mai 2003

Liquid Solders for High Temperature Solder Joints

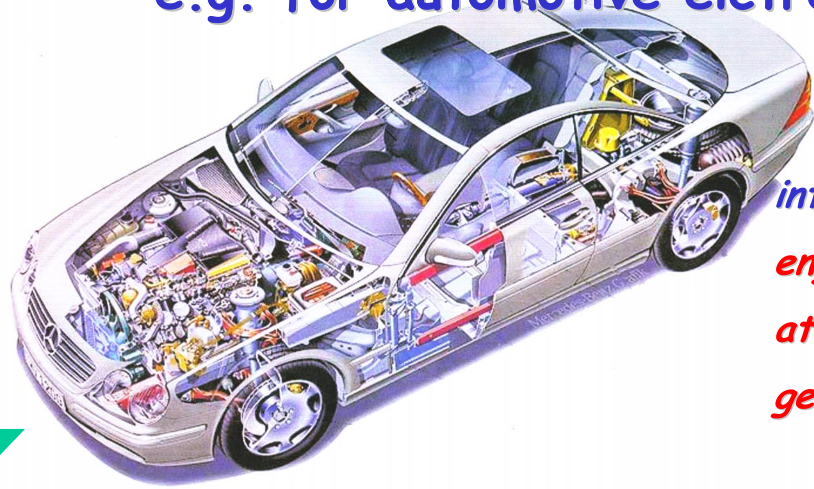
Mathias Nowottnick,
Wolfgang Scheel,
Klaus Wittke,
Uwe Pape,

Fraunhofer IZM,
Gustav-Meyer-Allee 25
D-13355 Berlin, GERMANY

contact: nowottnick@izm.fraunhofer.de

Liquid Solders

reason: increasing operating temperatures
e.g. for automotive elctronics

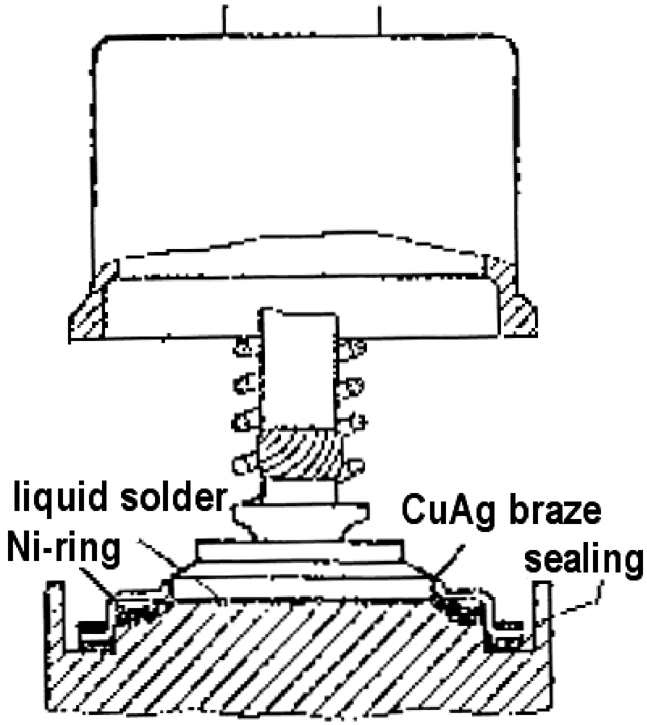


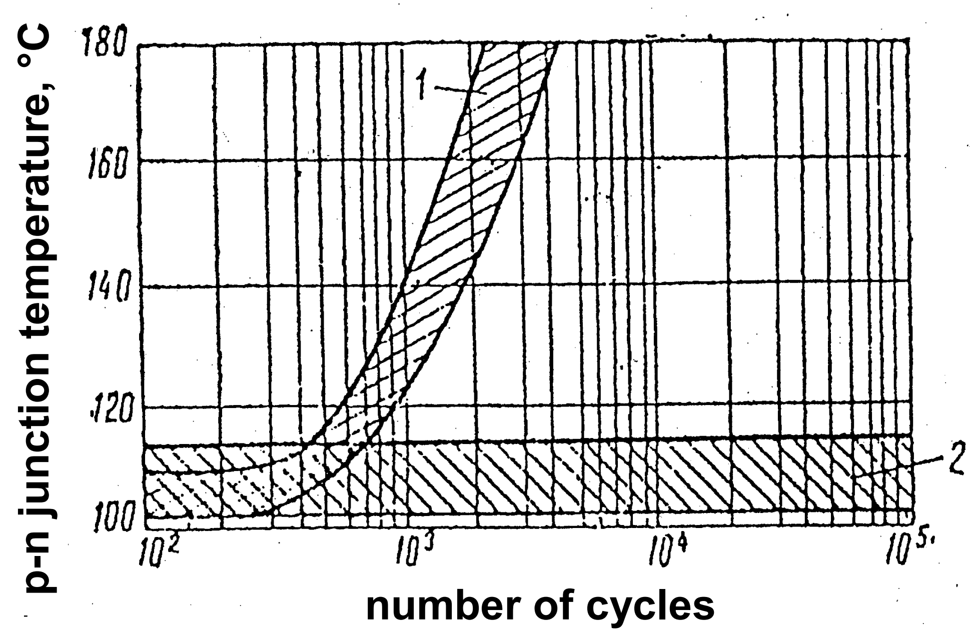
interior of car:	*85°C*
engine compartment:	*125..165°C*
at the engine:	*140...165°C*
gear / brake:	*250°C*

project team - TLSD:

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders





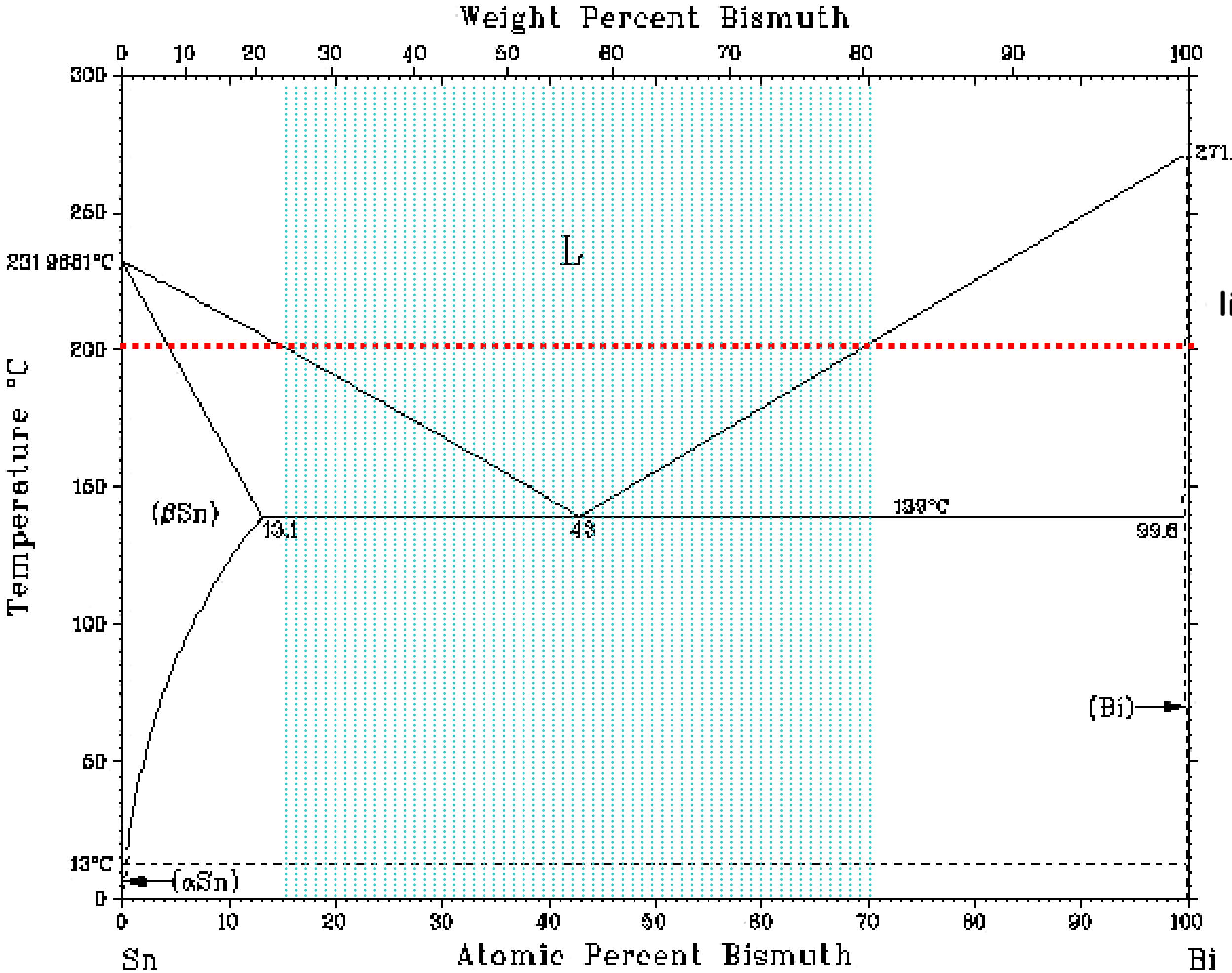
semiconductor chip with a liquid solder joint (left) and the influence of power cycles on stability (right)

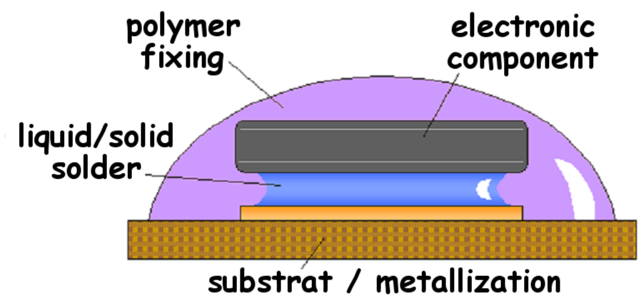
[A. A. Abramov, E. K. Belebaschev, L. P. Kotschetkova: „Sosdanije silowych poluprowodnikowych priborov s kombinirowannymi kontaktami“ (Manufacturing of Power Semiconductor Devices with Combined Contacts). J. Electrical Engineering, 14, 1971, p. 8-10]

state of the art

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders





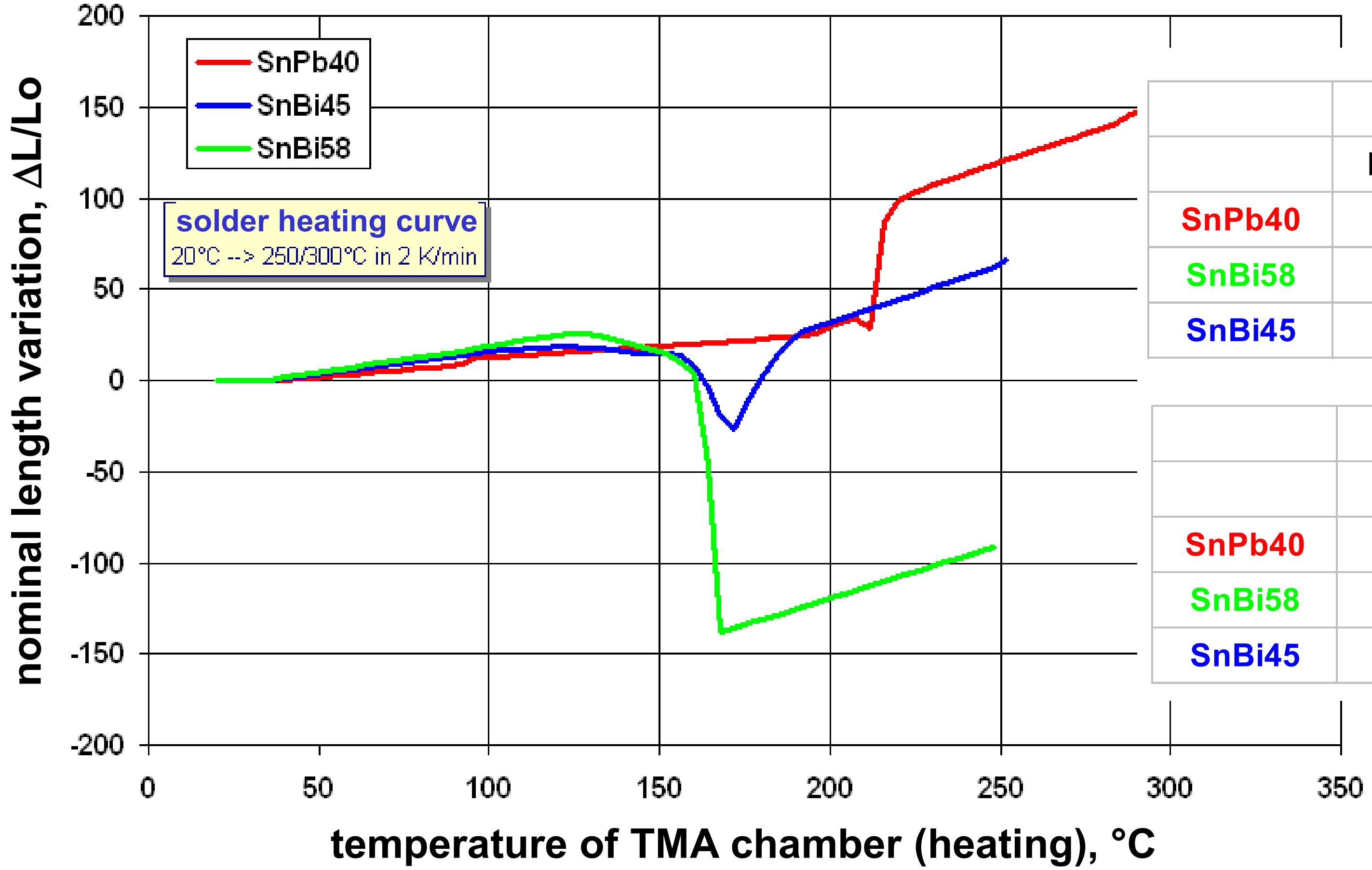
1. processable as solder paste or preforms at room temperature

2. liquid at operating temperature (200°C or 250°C)

suitable solder materials for solid/liquid solder joints

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders



	< melting point	
	heating	cooling
SnPb40	17,6	17,1
SnBi58	29,3	-0,8
SnBi45	16,5	-11,3

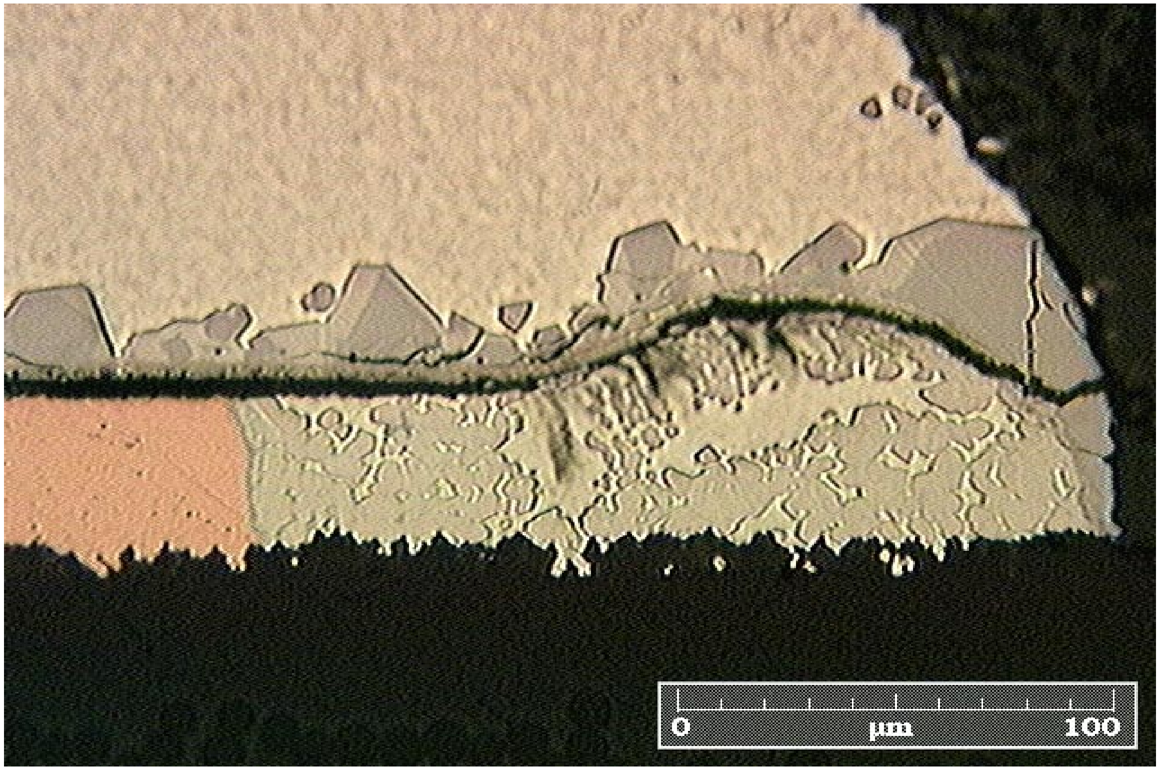
	> melting point	
	heating	cooling
SnPb40	67,2	67,0
SnBi58	64,0	65,3
SnBi45	69,7	65,5

measuring of expansion with TMA

(Hans Walter, IZM)

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

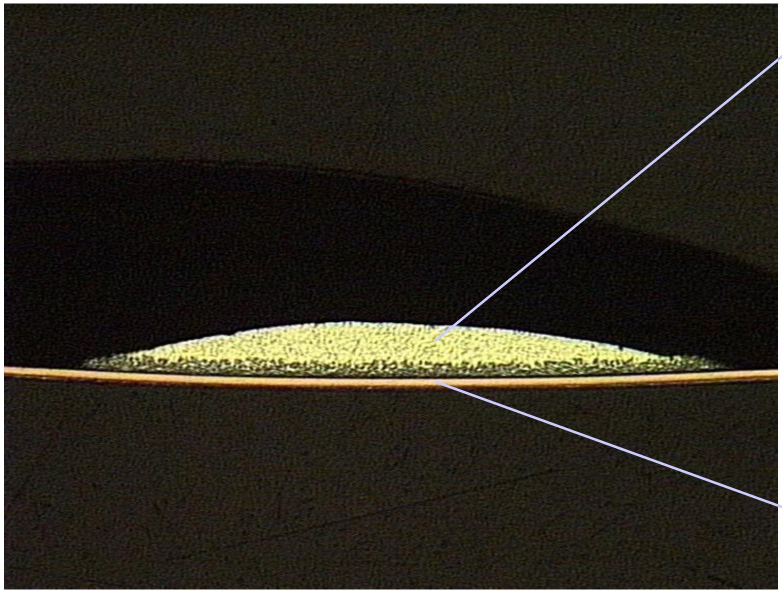
L i q u i d   S o l d e r s

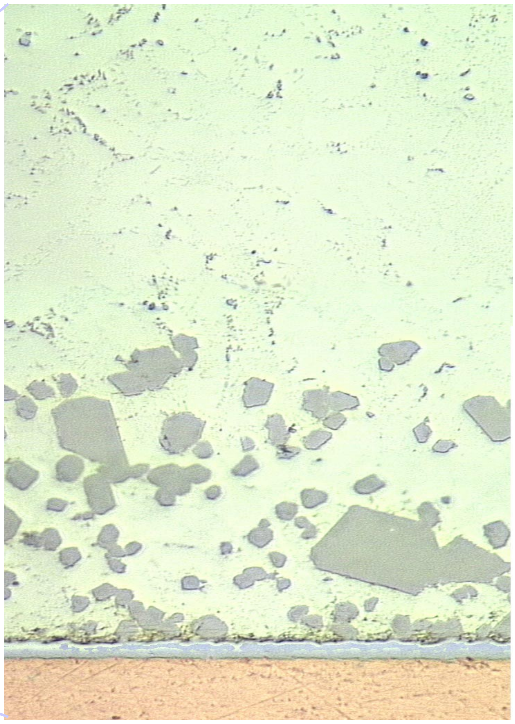


copper foil of pwb with NiP-layer
after 500h/200°C with liquid BiSn-solder

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders





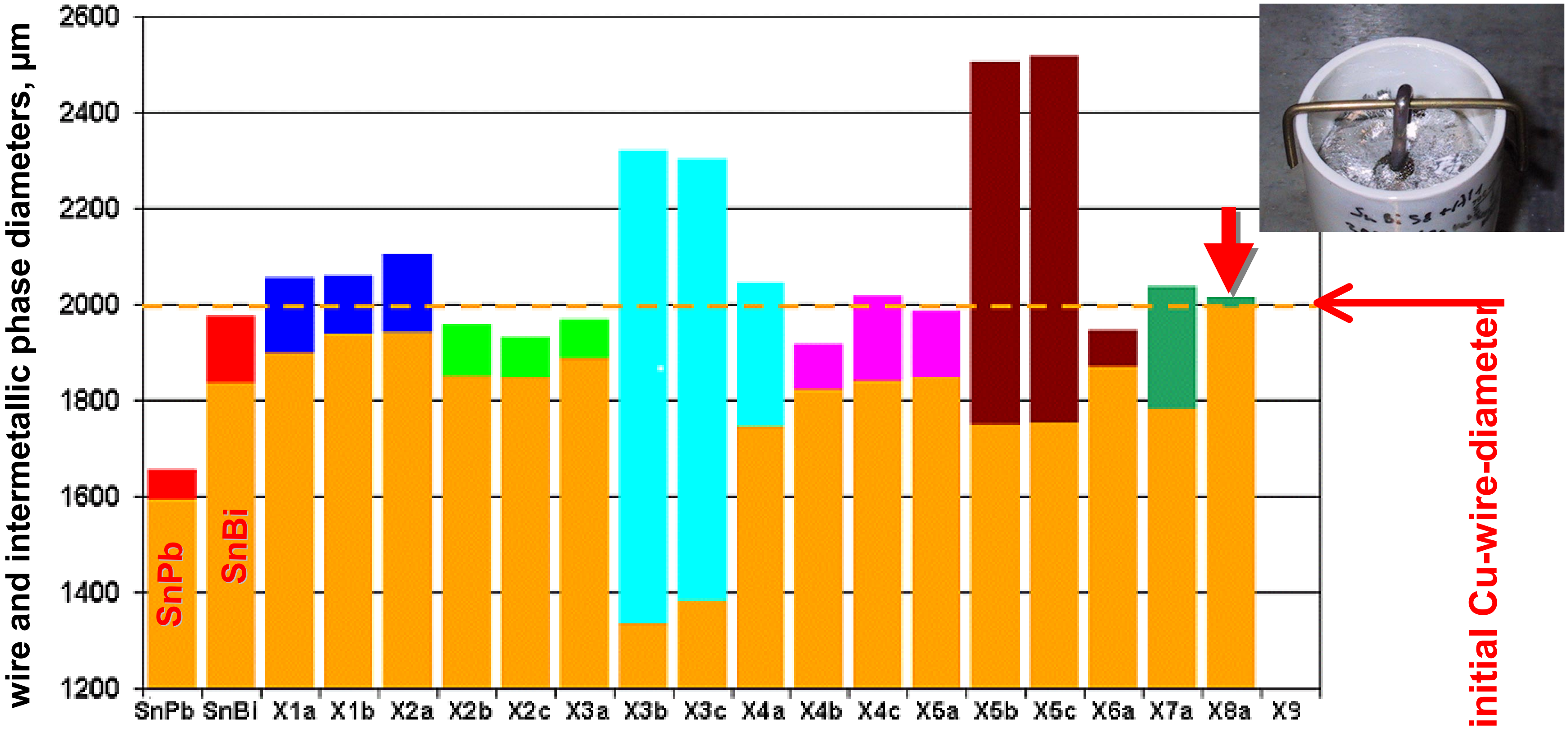
360 h aging with 250 °C

SnAgCu-solder an Cu-foil – Ni/Cr plated

(developed by ZMU-Freiberg)

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders



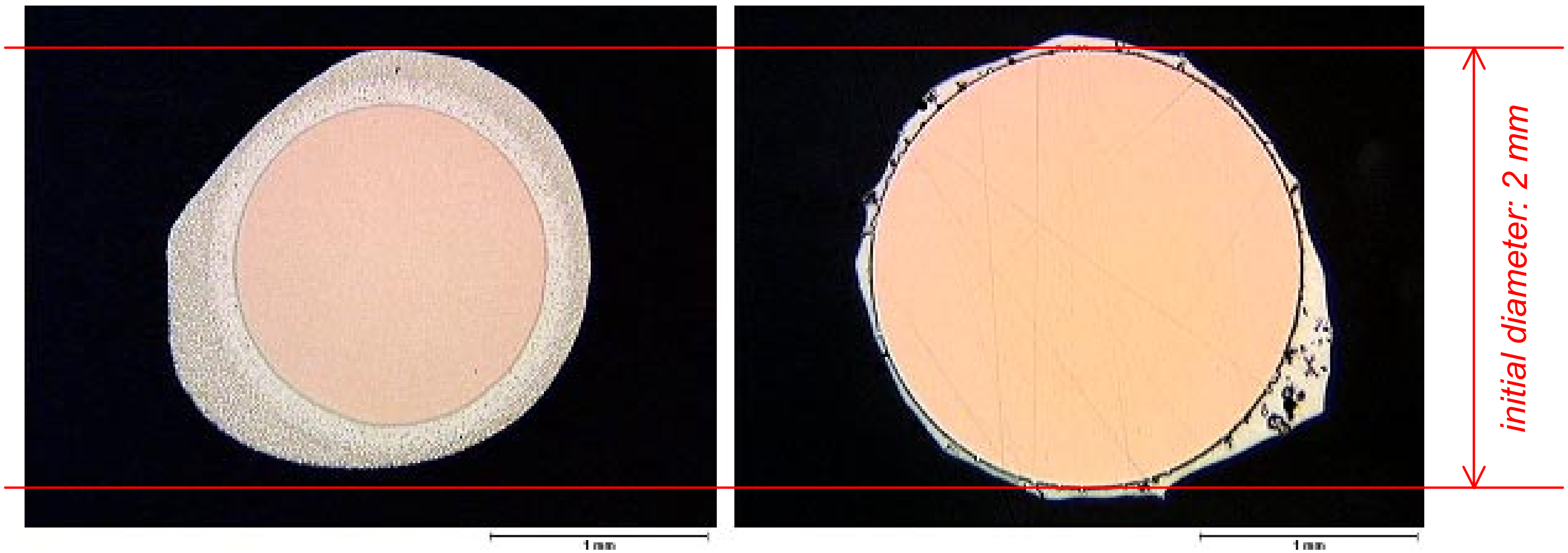
wire and intermetallic phase diameters after 500 h and 200 °C in BiSn+X1....X9

stabilization of the interface (solid-liquid) by inhibitors

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

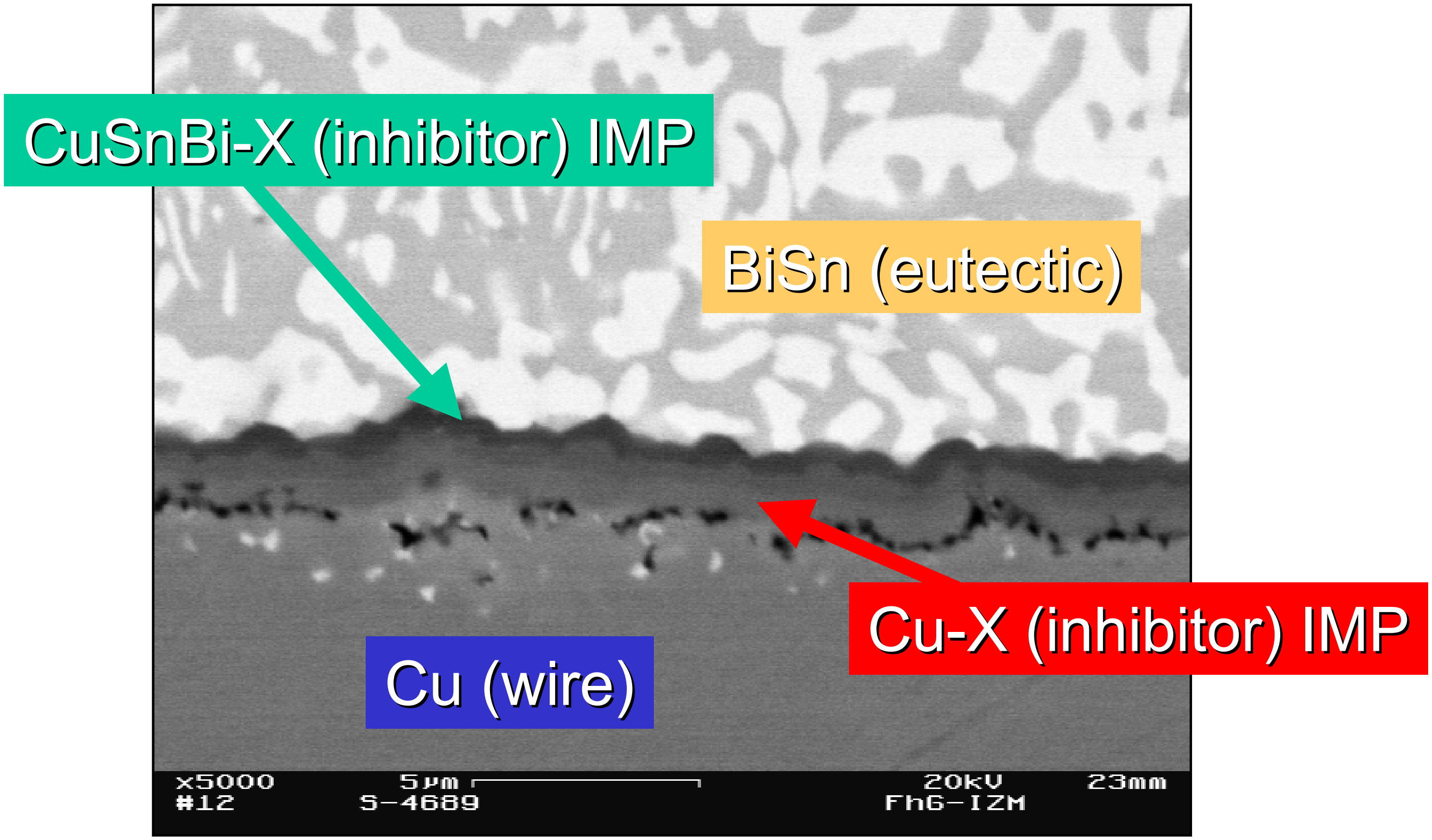
Liquid Solders

Cu-wire in Bi58Sn42 | Cu-wire in BiSn +1% inhibitor



diameter of copper wires – cross section after 500h storage in liquid solder at 200°C

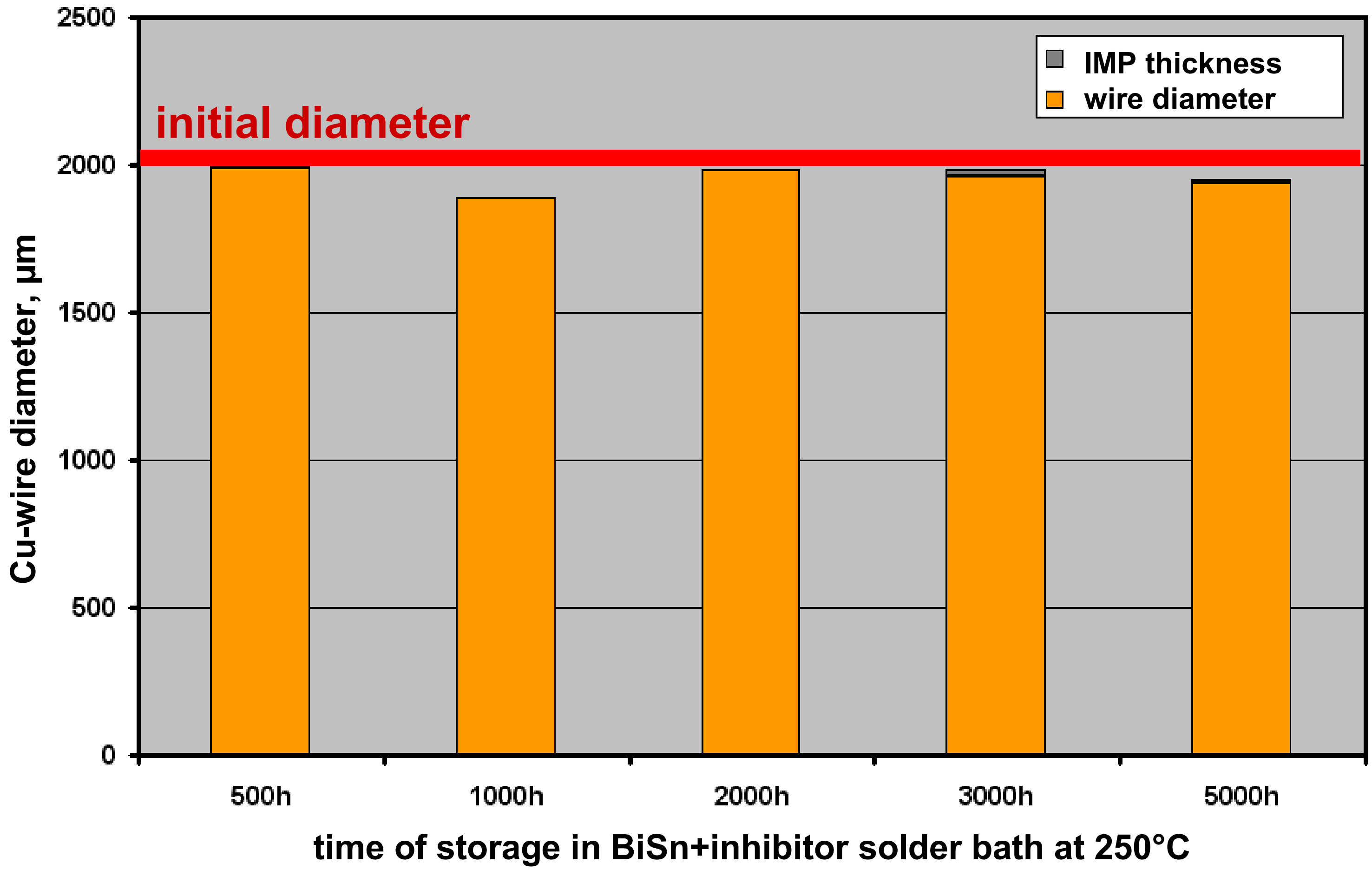
Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape



SEM/EDX-analysis of the Cu-wire surface after 500h / 200°C in a BiSn+X (inhibitor) solder bath

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

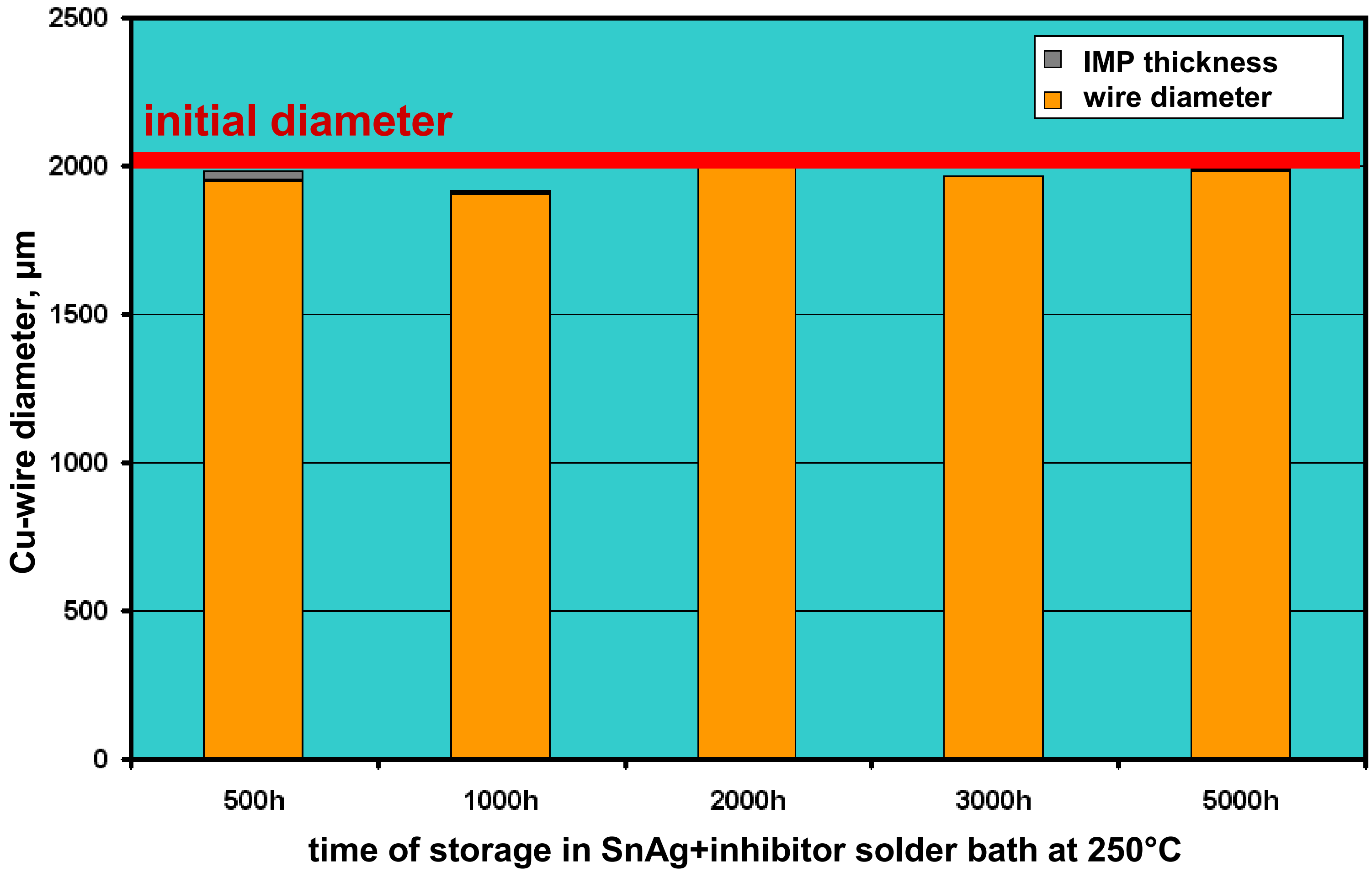
Liquid Solders



endurance test in BiSn+X solder bath, 7 month / 250°C

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

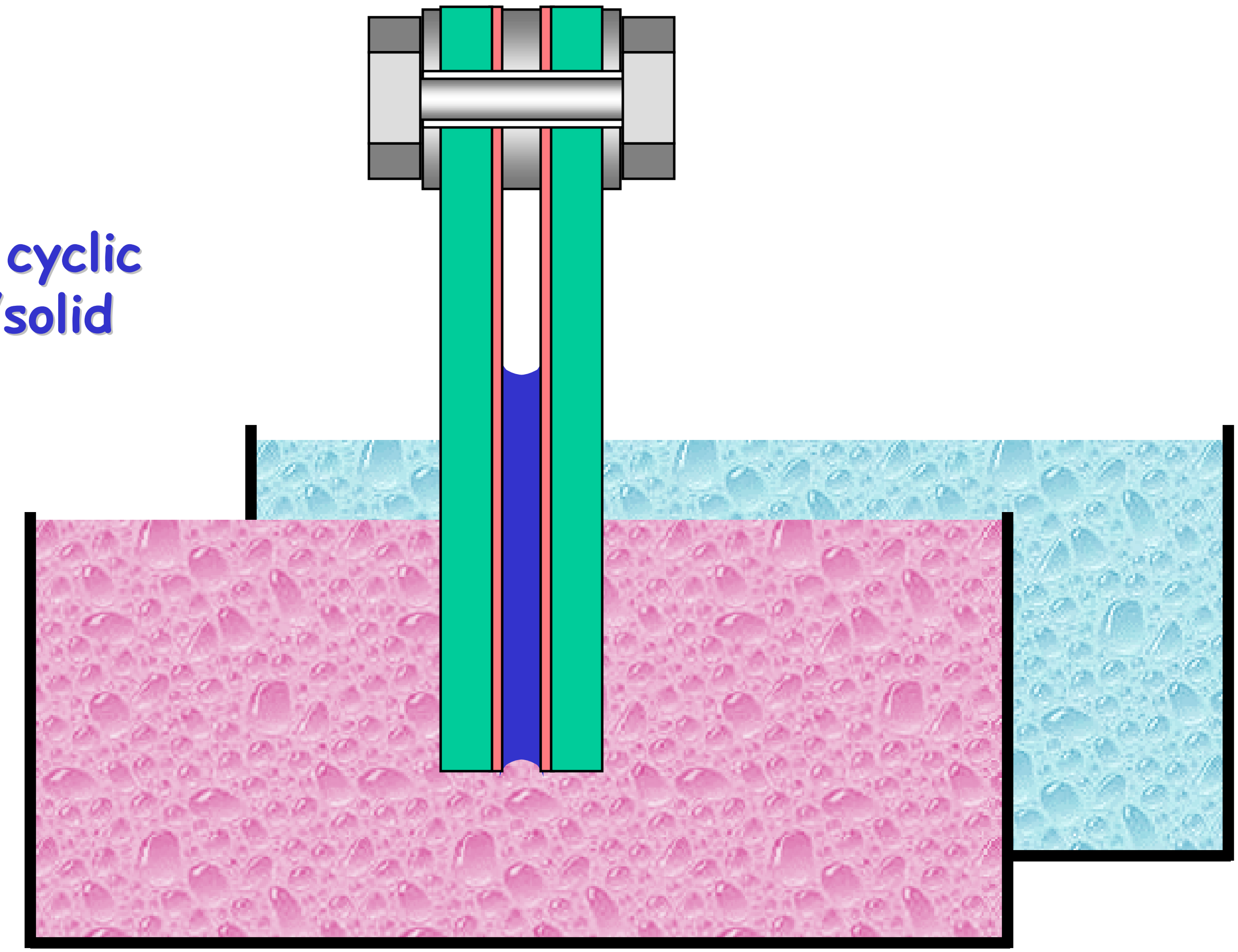
Liquid Solders



endurance test in SnAg+X solder bath, 7 month / 250°C

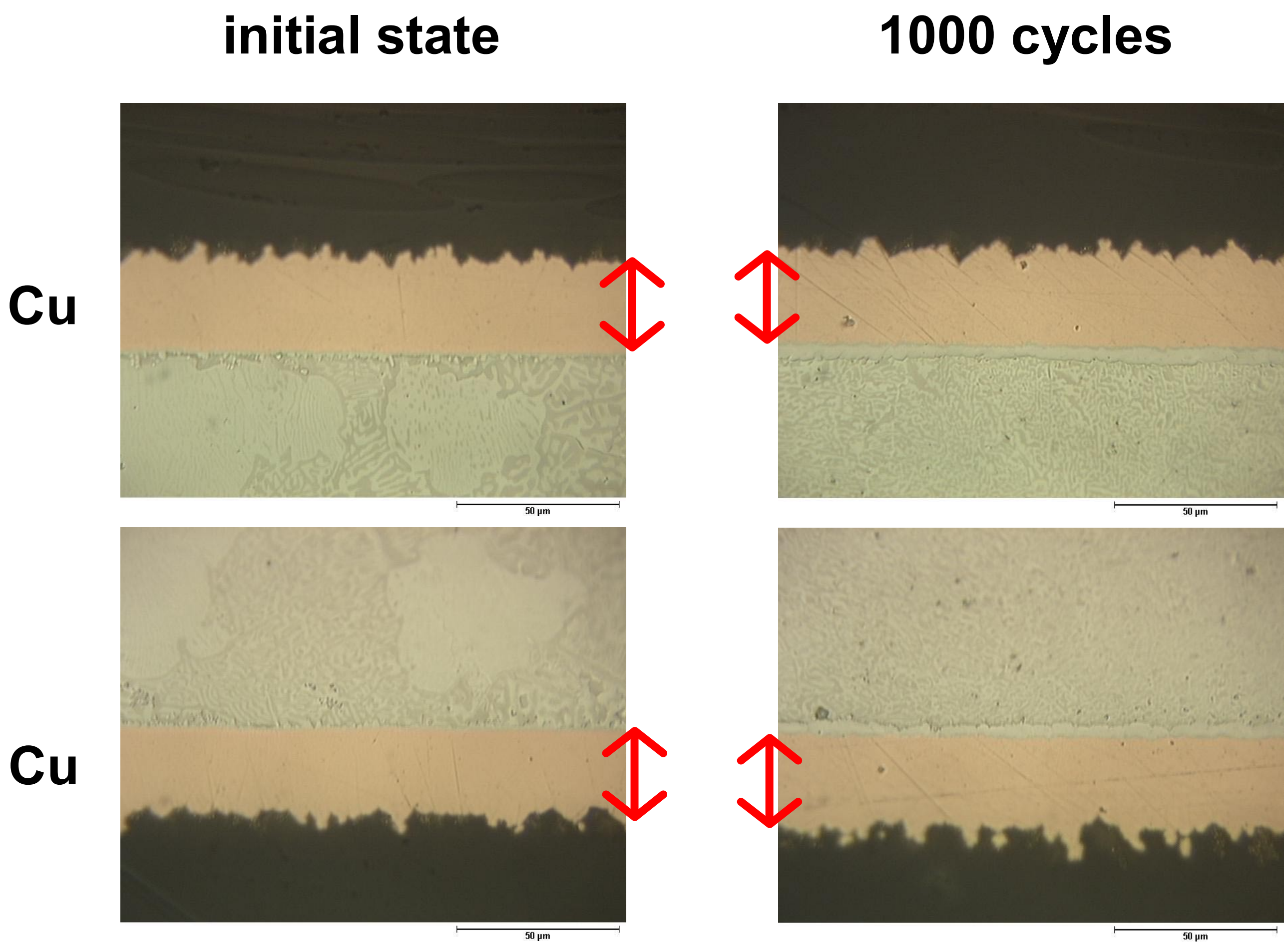
Liquid Solders

immersion test for cyclic zone melting liquid/solid at 200°C / 80°C, 1000 cycles



Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders



metallographic analysis of interfaces after immersion testing

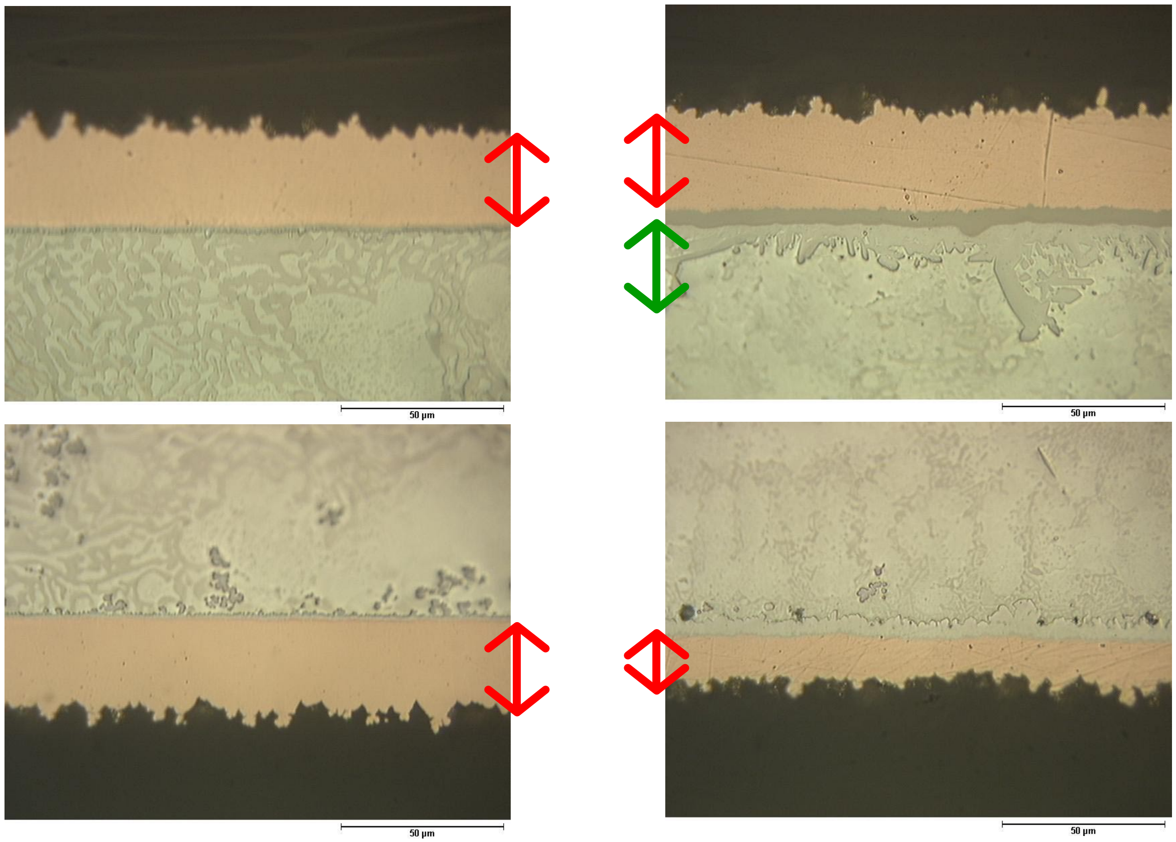
Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders

initial state | 1000 cycles

Cu + NiP

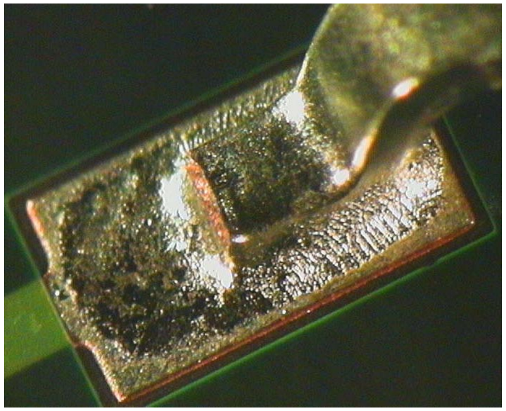
Cu



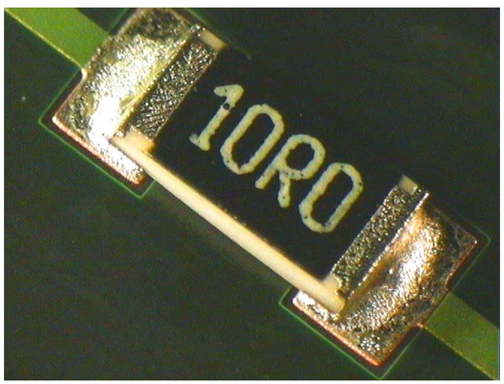
metallographic analysis of interfaces after immersion testing

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

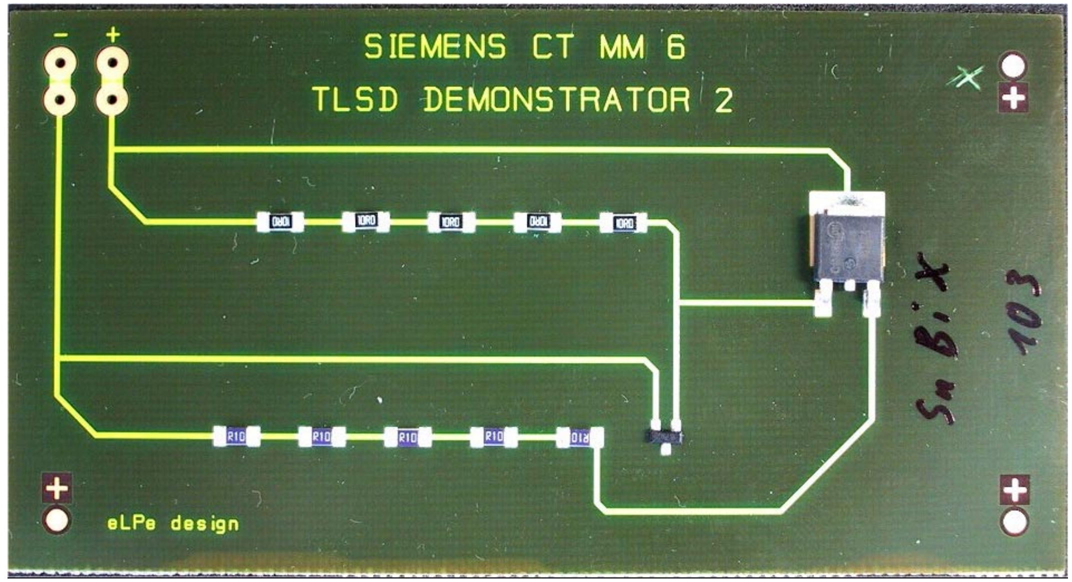
Liquid Solders



transistor terminal



chip resistor

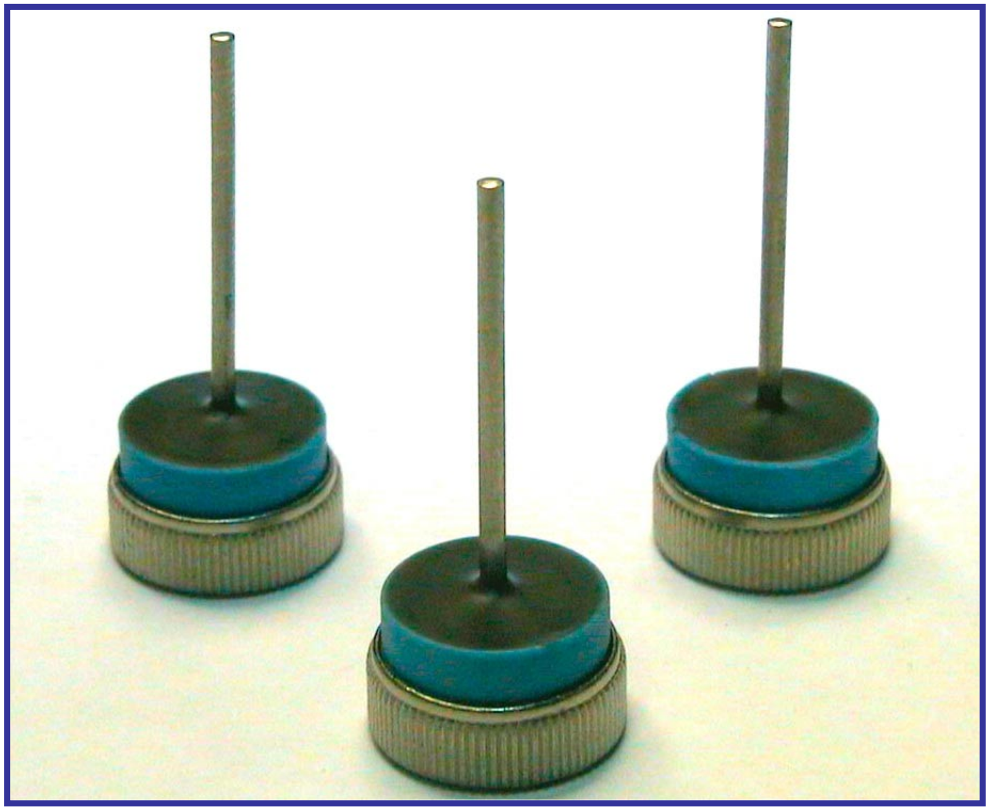


application of inhibitor-solder as solder paste

demonstration pwb (Siemens)

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

Liquid Solders



application of inhibitor-solder as solder paste or preforms

demonstration power diode (Bosch)

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape

SUMMARY:

- selection of BiSn solder system for operating temperature >150°C
- adaptation of volume expansion jump by Bi : Sn relation
- stabilization of interface by inhibitor
- inhibitor effecting also for higher melting solders (SnAg)
- long term test for 7 month successful
- cycling test/zone melting shows interaction of interfaces
- processing and application will be investigated at present

Mathias Nowottnick
Wolfgang Scheel
Klaus Wittke
Uwe Pape