



## Comparison analysis of micro-alloyed, lead-free solder pastes – Part 1

Micro-alloyed, lead-free solder in massive form is widely used in automatic soldering processes (flow, dip and hand soldering with cored solder). The benefits of micro-alloyed solder compared with non-micro-alloyed solder are essentially the reduction of the copper dissolution in the solder, the influence of the solder's setting properties, which leads to a fine-phased structure and to a smoother, polished soldering point without shrinkage cracks and should increase the soldering point's mechanical

strength. A positive influence of micro-alloyed additives on the lifecycle of the soldering points is especially set for small soldering points for thermal cycling [1]. There has been little experience gathered on the influence of micro-alloyed solder powders in soldering pastes. The objective of the analyses is to establish the influence of different micro-alloyed additives, especially with regard to reliability of soldering connections produced using them.

### 1. Introduction and sample production

Lead-free solder alloys in a solid state (fully alloyed) are produced for the analyses and converted into powder. With these solder powders, solder pastes are produced and analysed with the same solder flux. The AP-20 solder flux used is a completely halogen-free flux from the ongoing production of ELSOLD soldering pastes, which are used commercially for lead-free applications. The solder powders listed in Tab 1 are produced and analysed as a comparison in addition to the non-micro-alloyed solders SnCu0.7 and Sn96.5Ag3Cu0.5. Nickel, Ni/Ge [3], Co/Ni/Ce [4] and Co/Ni/Ce/In are chosen as doping elements. The concentration of the doping elements was in the usual range for micro-alloyed solders (Ni, Co in the range of 0.02 – 0.05%, Ce, Ge 0.002 – 0.007%, In 0.6 – 0.7%). Both standard alloys from the ELSOLD solder paste production as well as

special alloys are used. The use of different powder types (T3, T4, T5) is dependant on the availability of solder powder. Due to the small amounts required, non-standard solder powder is produced by different solder powder producers using different procedures (marked as special in Tab 1). The solder pastes are produced using a standard procedure with the same solder flux and the same metal content to exclude the influence of solder flux on the solder results as far as possible.

The solder pastes are sent for analysis to the Steinbeis-Transfer Centre AVT in Rostock after successful testing and approval by quality assurance (metal content, viscosity, solder ball test).

No.	Alloy	Micro-alloyed	Powder	Metal content	Flux	Quality
I	Sn99,3Cu0,7	Not	Type 3	88 %	AP-20	Standard
II	Sn96,5Ag3Cu0,5	Ni, Ge	Type 4	88 %	AP-20	Standard
III	Sn96,5Ag3Cu0,5	Co, Ni, Ce, In	Type 5	88 %	AP-20	Special
IV	Sn96,5Ag3Cu0,5	Ni	Type 4	88 %	AP-20	Standard
V	Sn99,3Cu0,7	Co, Ni, Ce, In	Type 5	88 %	AP-20	Special
VI	Sn96,5Ag3Cu0,5	Co, Ni, Ce	Type 3	88 %	AP-20	Special
VII	Sn96,5Ag3Cu0,5	Not	Type 4	88 %	AP-20	Standard

Tab. 1: Analysed solder pastes

## 2. Analyses

Wetting tests are conducted on copper and NiP/Au-coated PCBs. The solder pastes are applied with a 120 µm template and soldered uniformly at 230 °C for all

test modules in the vapour phase. The methodology and results of the reliability analyses are described in Part 2 of this article.

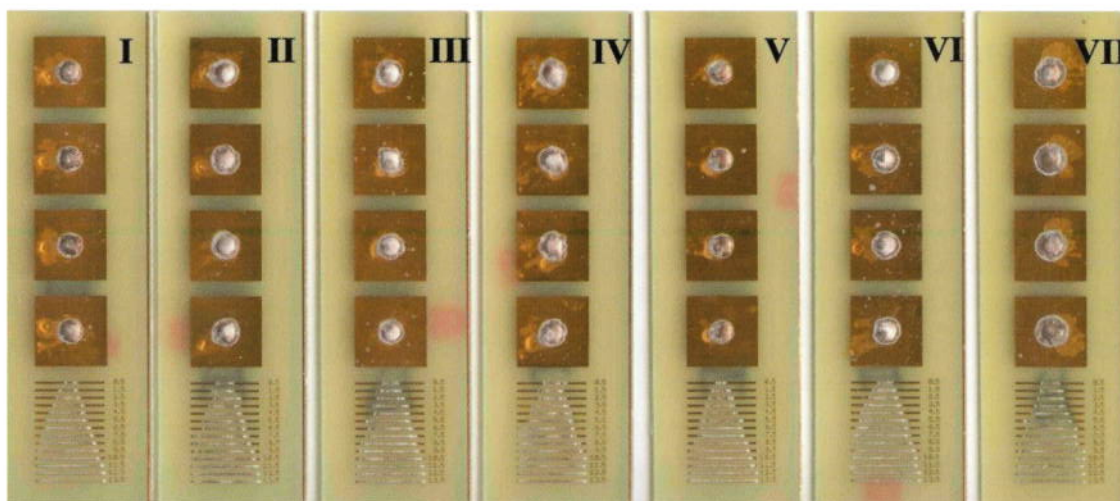


Figure 1: Spreading on NiP/Au-coated PCBs.

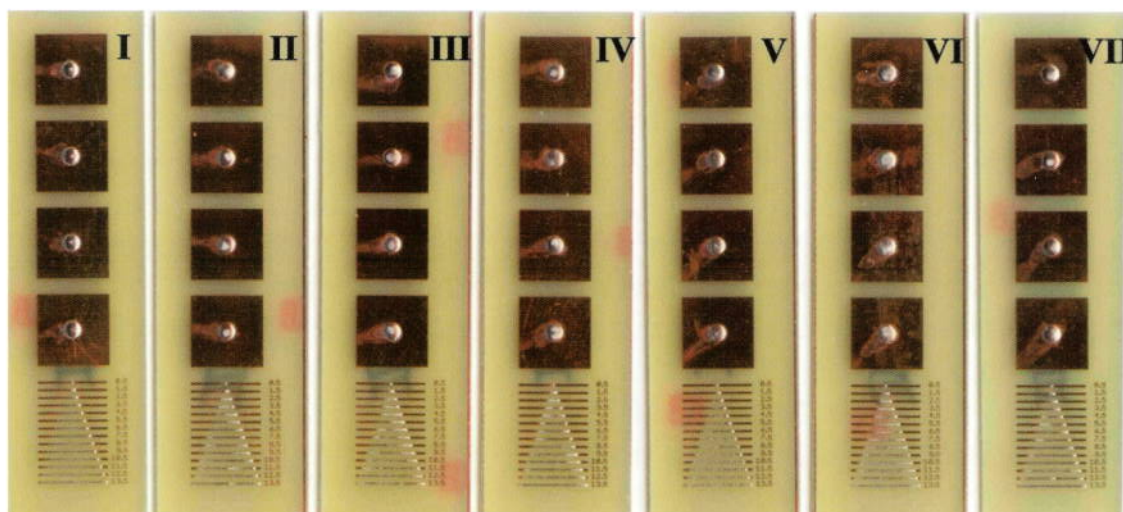


Figure 2: Spreading on copper PCBs

## 2.1 Wetting tests

The solder spreading on copper and NiP/Au-coated surfaces is determined. Figure 1 shows the wetting on NiP/Au-coated test PCBs; the wetting of solder pastes on copper is shown in Figure 2. As expected, the spreading on copper for all analysed solder pastes was significantly lower (Figure 3) than on NiP/Au (wetting surfaces on NiP/Au around twice as large (Figure 4)). The best result was achieved with the non-micro-alloyed solder paste VII Sn96.5Ag3Cu0.5 T4, which had the largest spreading on copper and on NiP/Au. The smallest wetting surfaces were

measured for solder paste V SnCu0.7(Co, Ni, Ce, In). The non-micro-alloyed solder paste I SnCu0.7 gave the second-best result on copper, while the solder pastes II, III, IV and VI had virtually identical spreading. The second-best result on NiP/Au was achieved with IV Sn96.5Ag3Cu0.5(Ni), followed by the solder paste VI Sn96.5Ag3Cu0.5(Co,Ni,Ce) and II Sn96.5Ag3Cu0.5(Ni,Ge) with virtually identical spreading. Both silver-free solder pastes, I SnCu0.7 and V SnCu0.7(Co,Ni,Ce,In), demonstrated the smallest wetting on NiP/Au.

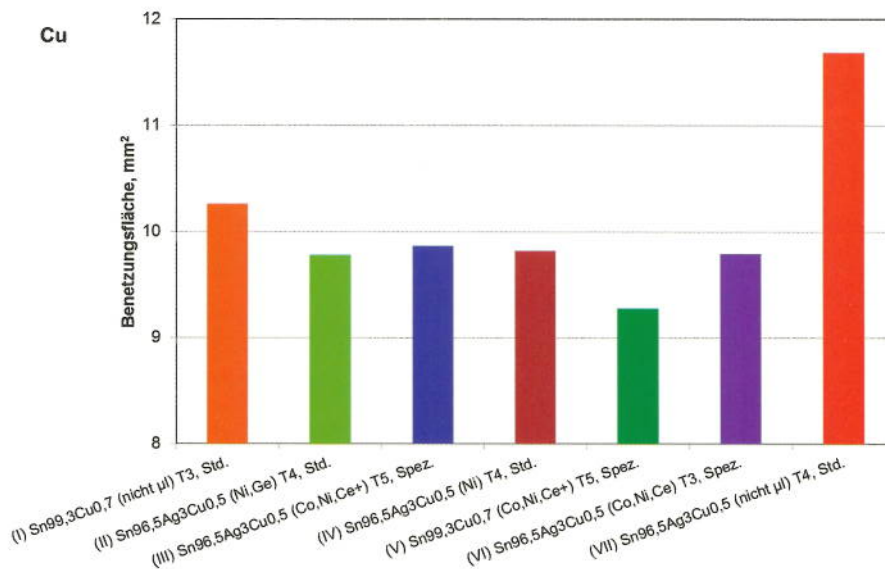


Figure 3: Wetting of copper

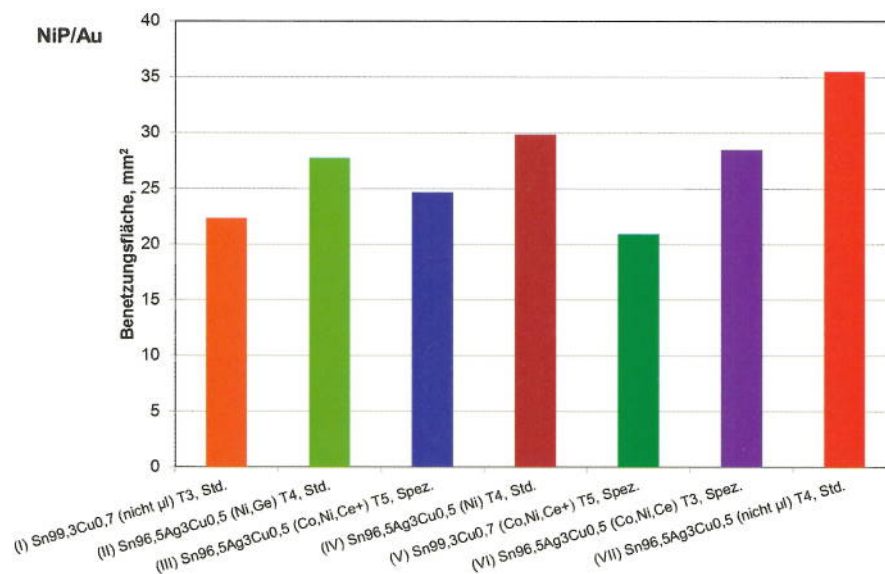


Figure 4: Wetting on NiP/Au

## 2.2 Evaluating the wetting tests

While the wetting results on the gold surface were evaluated as being very good for all solder pastes, smaller spreading surfaces were established on the copper surfaces as expected. The particle size of solder powder has only a small influence on the wetting properties. This is identifiable taking solder paste III Sn96.5Ag3Cu0.5(Co, Ni, Ce, In) T5 as an example, which presented average spreading on both substrates in the comparison (in third place for spreading on copper). An increased oxide share in the T5 fine powder can therefore be virtually excluded.

The non-micro-alloyed solder pastes give the best wetting results on copper, while the silver-based solder was fundamentally better on gold than SnCu0.7, regardless of whether it is micro-alloyed or not. However, it should be noted that the soldering temperature of 230 °C for SnCu0.7 is very low. Better wetting results can be achieved

by using higher temperatures.

The results indicate that doping additives do not contribute to improved wetting; on the contrary, it can even impair it. If the solder pastes are listed in a sequence with a decreasing percentage of micro-alloyed constituents, it corresponds with the sequence of wetting surface sizes. For the silver-free solders:

**ISnCu0.7(non-micro-alloyed)>VSnCu0.7(Co,Ni,Ce,In)**

This sequence is not as clear for silver-based solders on copper, with the wetting surface of the solder pastes II, III, IV and VI being virtually identical. Due to the larger differences in solder spreading on gold, the sequence can also be established for the silver-based solders:

**VII SnAg3Cu0.5 (non-micro-alloyed) > IV SnAg3Cu0.5(Ni) > VI SnAg3Cu0.5(Co,Ni,Ce) > II SnAg3Cu0.5(Ni,Ge) > V SnAg3Cu0.5(Co,Ni,Ce,In)**

## 3. Summary

Micro-alloyed solder pastes were produced and compared and analysed with non-micro-alloyed solder pastes. The spreading on copper is significantly lower for all analysed solder pastes than on NiP/Au surfaces. Non-micro-alloyed solder pastes achieved better wetting properties on both analysed surfaces than the micro-alloyed pastes. The results indicate that the wetting

is impaired by micro-alloying additives. This is explicable as the micro-alloys are put into the solder with the aim of reducing the dissolution of the basis material, which accompanies the wetting. As the proportion of micro-alloying elements increase, the wetting and therefore also the soldering spreading decreases.

[1] A. Fix, P. Zerrer, A. Prihodovsky, B. Müller, D. Wormuth, W. Ludeck, H. Trageser, M. Hutter and R. Diehm Nanoflux – Flussmittel mit nanochemisch aktiven Metallverbindungen zur Stabilisierung von Weichloten, DVS Reports Issue 273, Soft soldering research & practice for electronics manufacturing, p.22

[2] The analyses were undertaken at the Steinbeis-Transfer Centre Assembly and

Joining Techniques, Rostock, under the supervision of Prof. Dr.-Ing: M. Nowottnick, Analysis report Comparison Analysis of Micro-alloyed Solders, Project 10027, 3 May 2011.

[3] Patent DE 19816671, Fuji Electric Co., Ltd., Kawasaki, Kanagawa, Japan

[4] FLOWTIN® is a registered trademark of Stannol GmbH