Comparative study of microalloyed lead-free soldering pastes - Part 2

Microalloyed lead-free solid solders find broad use in automatic soldering processes (wave and dip soldering, hand soldering with solder wires). The advantages of microalloyed solders compared to non-microalloyed solders consist primarily in reducing copper dissolution in the solder and influencing the setting behaviour of the solder, which results in a finer-phased structure and smoother, shiny soldered connections without shrinkage cracks, as well as improving the mechanical strength of the soldered connections. Microalloy additives are found to have a positive influence on the service life of soldered connections, particularly for small soldered connections subject to thermal cycles [1]. Only little experience is available regarding the influence of microalloy additives in soldering pastes. The aim of these tests is to ascertain the influence of various microalloy additives, particularly with regard to the reliability of the resulting soldered connections.

1. Introduction and samples

Soldering pastes with alloyed lead-free solder alloys in powder form were made for the tests using the same soldering flux, and tested accordingly. Used flux AP-20 is a commercial flux containing absolutely no halogen, developed for lead-free applications; it is part of the ELSOLD delivery range. Standard alloys from ELSOLD production are used, and also special alloys. Together with the non-microalloyed solders SnCu0.7 and Sn96.5Ag3Cu0.5, for the purposes of comparison the soldering powders listed in Table 1 were also made and tested [2]. Nickel Ni/Ge [3], Co/Ni/Ce [4] and Co/Ni/Ce/In are used as doping elements. The concentrations of the doping elements are within the normal range for microalloyed solders (Ni, Co in the range of 0.02 - 0.05 %, In 0.6 – 0.7 %, Ce, Ge 0.002 - 0.007 %). The reason for using different powder types (T3, T4, T5) consists in the availability of the respective soldering powder. Given the small quantities required, non-standard soldering powders of various makes were produced, using partly different procedures with differing grain sizes (referred to as „special“). The soldering pastes were made using the standard procedure with the same flux and same metal contents to rule out as far as possible any influence of the flux on the soldering results. 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) [2].

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. Reliability tests

The test components were made using copper and NiP/Au coated printed circuit boards (PCBs). The soldering pastes were then applied with a 120 µm stencil and fitted with CR1206 chip resistors. Finally, the configured PCBs were soldered in the same way for all test components in the steam phase at 230°C. The method and results for the wetting tests are described in Part 1 of this article [5].
Destructive testing (shear tests) was carried out to ascertain the reliability of the soldered connection on 10 elements of each version, immediately after soldering and after accelerated ageing in alternating climate. The temperature cycle is defined as -25/+150°C with a cycle time of 90 mins in order to make statements for use at higher temperatures, e.g. for applications in the automotive sector. The test was carried out after 0, 250, 500 and 1000 cycles.

2.1 Results of the shear tests

As expected, the shear resistance of the soldered connection decreases for all solder alloys with an increasing number of temperature cycles. The initial values for the strength of the alloys are similar on both Cu and on NiP/Au, with slightly lower strength levels for silver-free solders (about 10% lower). After 1000 cycles, all alloys show a clear reduction in shear forces (Fig. 1, Fig. 2). While the decrease in shear force on Cu is already apparent after 250 temperature cycles, with continuing nearly linear decrease as the temperature cycles progress further, any clear decrease on NiP/Au occurs only later after 500 cycles (Fig. 3). Clear differences in the shear strengths of the individual alloys become apparent after 1000 temperature cycles. There are only slight differences between I Sn99.3Cu0.7, II Sn96.5Ag3Cu0.5(Ni,Ge), III Sn96.5Ag3Cu0.5(Co,Ni,Ce,In) and VI Sn96.5Ag3Cu0.5(Co,Ni,Ce) in the shear strength on Cu and NiP/Au surfaces (Fig. 4). By contrast, alloys IV Sn96.5Ag3Cu0.5(Ni), V Sn99.5Ag3Cu0.5(Co,Ni,Ce,In) and VII Sn96.5Ag3Cu0.5 (non-microalloyed) show a far greater decrease on Cu than on NiP/Au surfaces. This behaviour is particularly pronounced in the non-microalloyed solder VII Sn96.5Ag3Cu0.5, while the effect is not so apparent in the non-microalloyed solder I Sn99.3Cu0.7. There would appear to be a correlation between shear strength and wetting surfaces only on NiP/Au, but not on Cu surfaces. Cu surfaces with altogether reduced solder spread show no relation between spread and shear strength after 1000 cycles. However, it is apparent that the microalloyed solders containing silver have the highest shear strength values after the temperature cycles.

By contrast, on NiP/Au, solders with the largest wetting surfaces also show the highest strengths values.

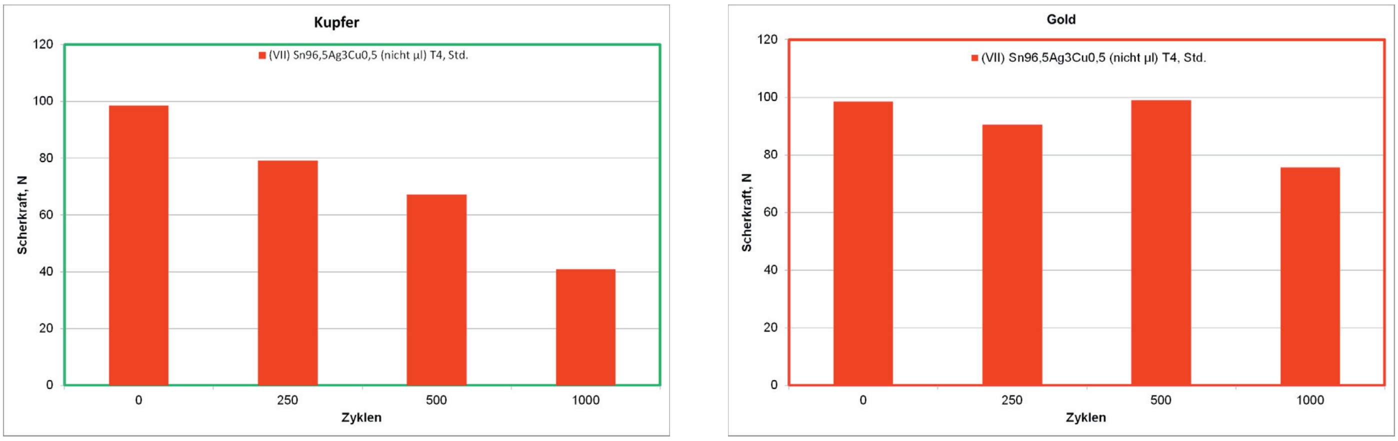


Fig. 1: Shear strength of 1206 chip resistors on Cu or NiP/Au PCB after 0, 250, 500, 1000 temperature cycles -25/+150 °C, soldered with VII AP-20 Sn96.5Ag3.0Cu0.5 T4, non-microalloyed

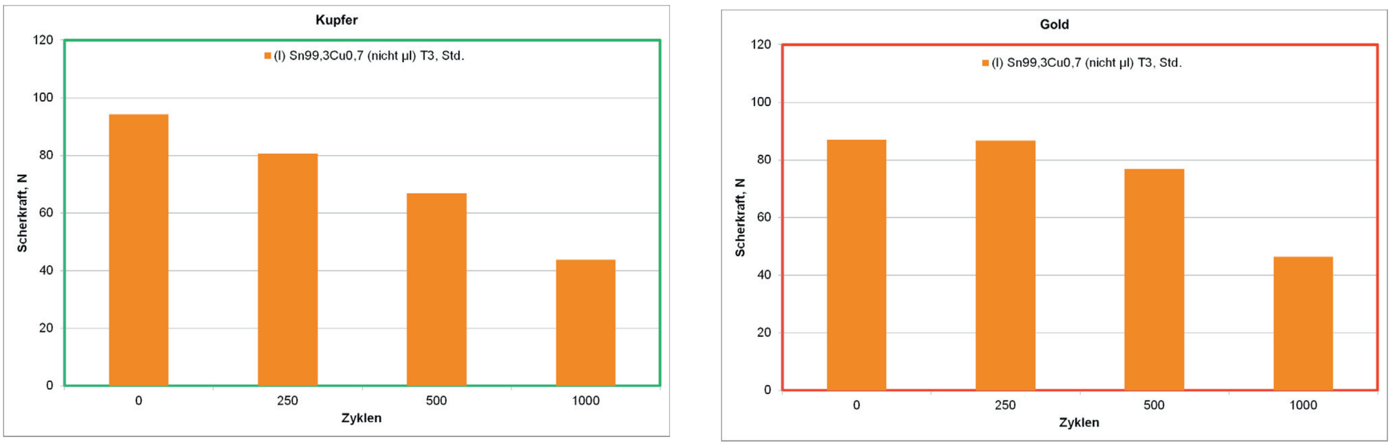


Fig. 2: Shear strength of 1206 chip resistors on Cu or NiP/Au PCB after 0, 250, 500, 1000 temperature cycles -25/+150 °C, soldered with I AP-20 Sn99.3Cu0.7 T3, non-microalloyed

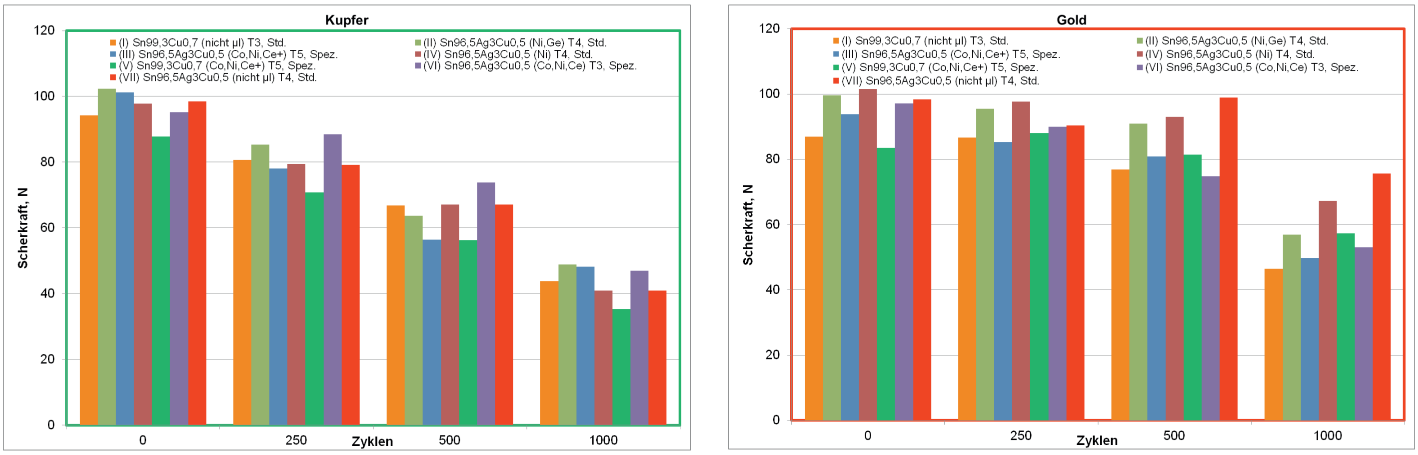


Fig. 3: Overview of the shear strengths of the tested solder alloys on Cu and NiP/Au

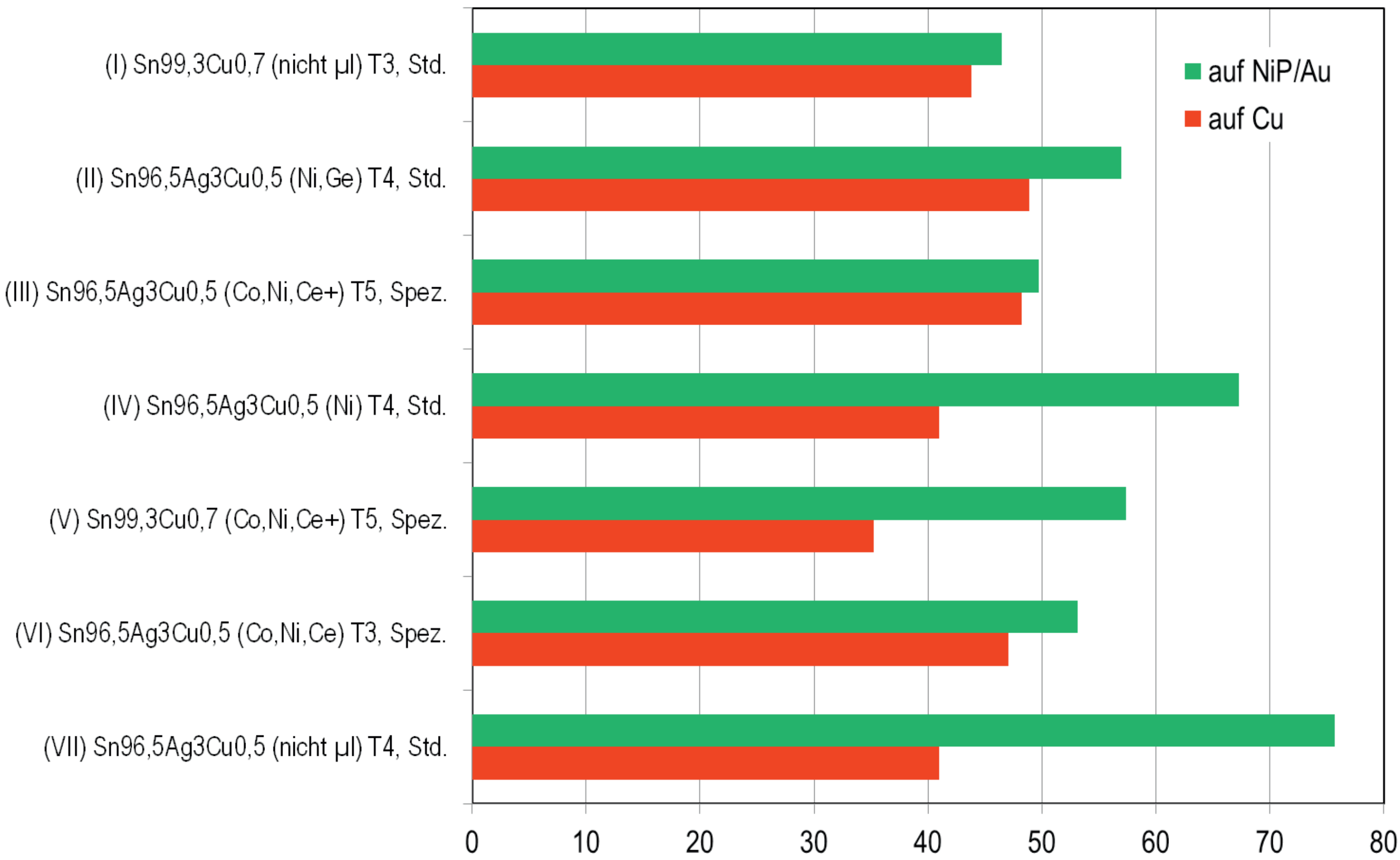


Fig. 4: Shear strengths after 1000 temperature cycles

2.2 Microsections

Microsections were produced of all alloys in initial state and after 250, 500 and 1000 temperature cycles (Figs. 5 and 6). For all alloys, the intermetallic phases are between 6 and 9 µm thick. Etching the microsections made the microstructure much clearer. Fig. 7 shows a selection of these soldering connections after 250 cycles in each case on copper and NiP/Au PCBs. This reveals that in particular the intermetallic copper/tin phases without microalloys reveal an irregular, dome-shaped structure, while the phases of the microalloyed soldered connections appear closed and more uniform. The structure also appears altogether finer through the microalloys.

From about 500 cycles, crack formation is observed on both Cu and NiP/Au PCBs. Alloy II Sn96.5Ag3Cu0.5(Ni,Ge) even cracks right through on NiP/Au after 1000 cycles; no other samples were observed to crack right through. Together with cracks in the soldering gap, critical gaps are also apparent in the solder meniscus. The clearest cracks occurred in alloys II Sn96.5Ag3Cu0.5(Ni,Ge), III Sn96.5Ag3Cu0.5(Co,Ni,Ce,In) and IV Sn96.5Ag3Cu0.5(Ni). This is not confirmed in the ascertained shear forces, with alloys II, III and IV showing even higher shear strengths than alloy I. According to the microsections, the smallest microstructural changes are seen in the non-microalloyed alloys I SnCu0.7 and VII Sn96.5Ag3Cu0.5.

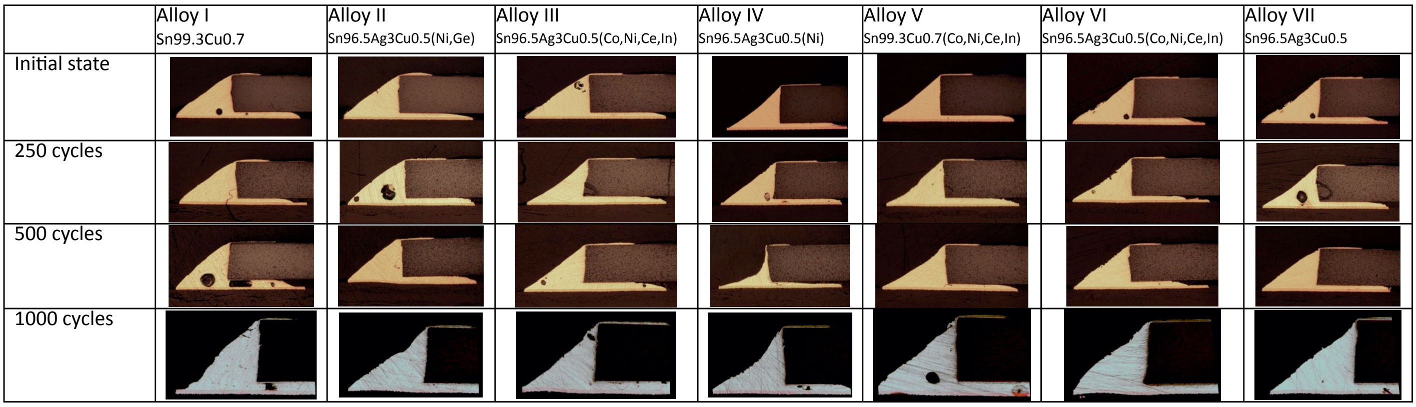


Fig. 5: Microsections on Cu PCB

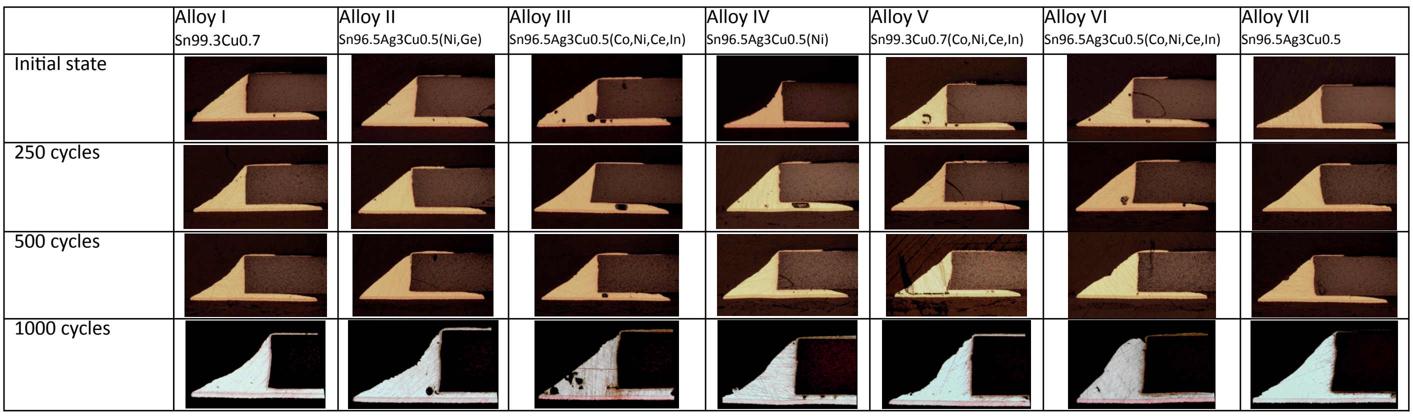
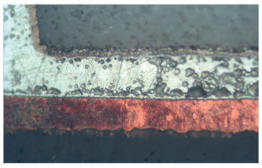
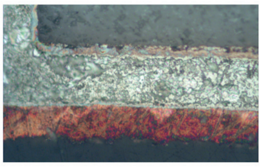
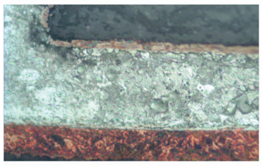
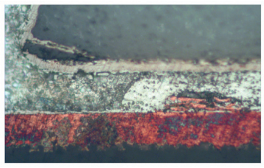
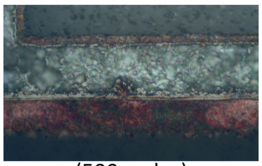
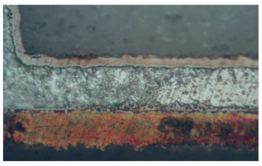
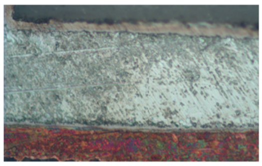
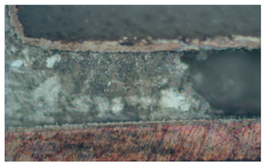


Fig. 6: Microsections on NiP/Au PCB

	Alloy I Sn99.3Cu0.7	Alloy II Sn96.5Ag3Cu0.5(Ni,Ge)	Alloy III Sn96.5Ag3Cu0.5(Co,Ni,Ce,In)	Alloy IV Sn96.5Ag3Cu0.5(Ni)	A S
250 cycles on Cu PCB					
250 cycles on NiP/Au PCB	 (500 cycles)				

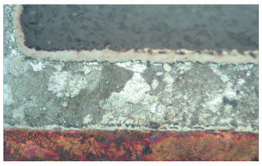
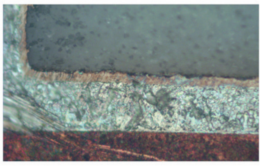
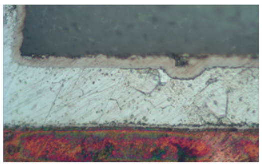
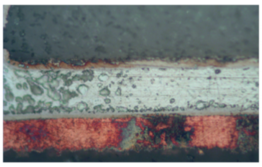
	Alloy V Sn99.3Cu0.7(Co,Ni,Ce,In)	Alloy VI Sn96.5Ag3Cu0.5(Co,Ni,Ce,In)	Alloy VII Sn96.5Ag3Cu0.5
250 cycles on Cu PCB			
250 cycles on NiP/Au PCB			

Fig. 7: Etched microsections

2.3 Discussion of the reliability tests

As expected, the shear forces decrease after temperature cycles. Samples on Cu show a far greater decrease in shear strengths than on NiP/Au PCBs. This is explained by the greater diffusion of copper at higher temperatures. The microalloyed solders II, III and VI containing silver show the highest strength values after 1000 cycles, and therefore would appear in fact to erect diffusion barriers. Solders IV and V are the exception to this rule, showing the lowest strength values on copper despite being microalloyed. This is explained by the fact that alloy IV only contains 0.02% Ni as additive. Practical experience indicates that copper dissolution is only effectively reduced by higher nickel levels of approx. 0.05%. Alloy V with the microalloy additives Co, Ni, Ce and In shows the lowest solder spread and the lowest strength on Cu, which indicates that the addition of In to Sn99.3Cu0.7 tends to have a detrimental effect.

On NiP/Au surfaces, solders containing silver have the highest strength values, both in initial state and after 1000 temperature cycles. Already after 500 cycles, the microalloyed solders all show lower strength values than the non-alloyed solder VII Sn96.5Ag3Cu0.5, although the highest strength values both in initial state and after 250 cycles are measured for the two types II Sn96.5Ag3Cu0.7(Ni,Ge) and in particular IV SnAg3Cu0.5(Ni). In terms of shear strength, microalloyed solders containing indium show no improvement compared to microalloyed solders without any indium. After 500 and 1000 cycles, the highest strength values are ascertained for VII Sn96.5Ag3Cu0.5 followed by IV Sn96.5Ag3Cu0.5(Ni).

In practice, half the shear strength in initial state is taken as failure criterion. A look at the standardised shear force values (Fig. 8) clearly shows that all soldered connections on Cu surfaces must be seen as failures after 1000 temperature cycles, with alloy IV Sn96.5Ag3Cu0.5(Co,Ni,Ce) only just falling below this value. On NiP/Au PCBs, all soldered connections are still intact. As a basic principle, the decrease in shear forces as a result of the temperature cycles is also apparent in the standardised visualisation.

The results of the reliability tests clearly show that the process of degradation in the soldered connections after undergoing the temperature cycles follows different mechanisms on Cu and on NiP/Au surfaces. While microalloyed solders on Cu surfaces certainly bring about a slight improvement in reliability by reducing copper migration, there would not appear to be any positive effects on NiP/Au PCBs. This coincides with the results of [1], where again there is scarcely any improvement in service life when using conventional microallo-

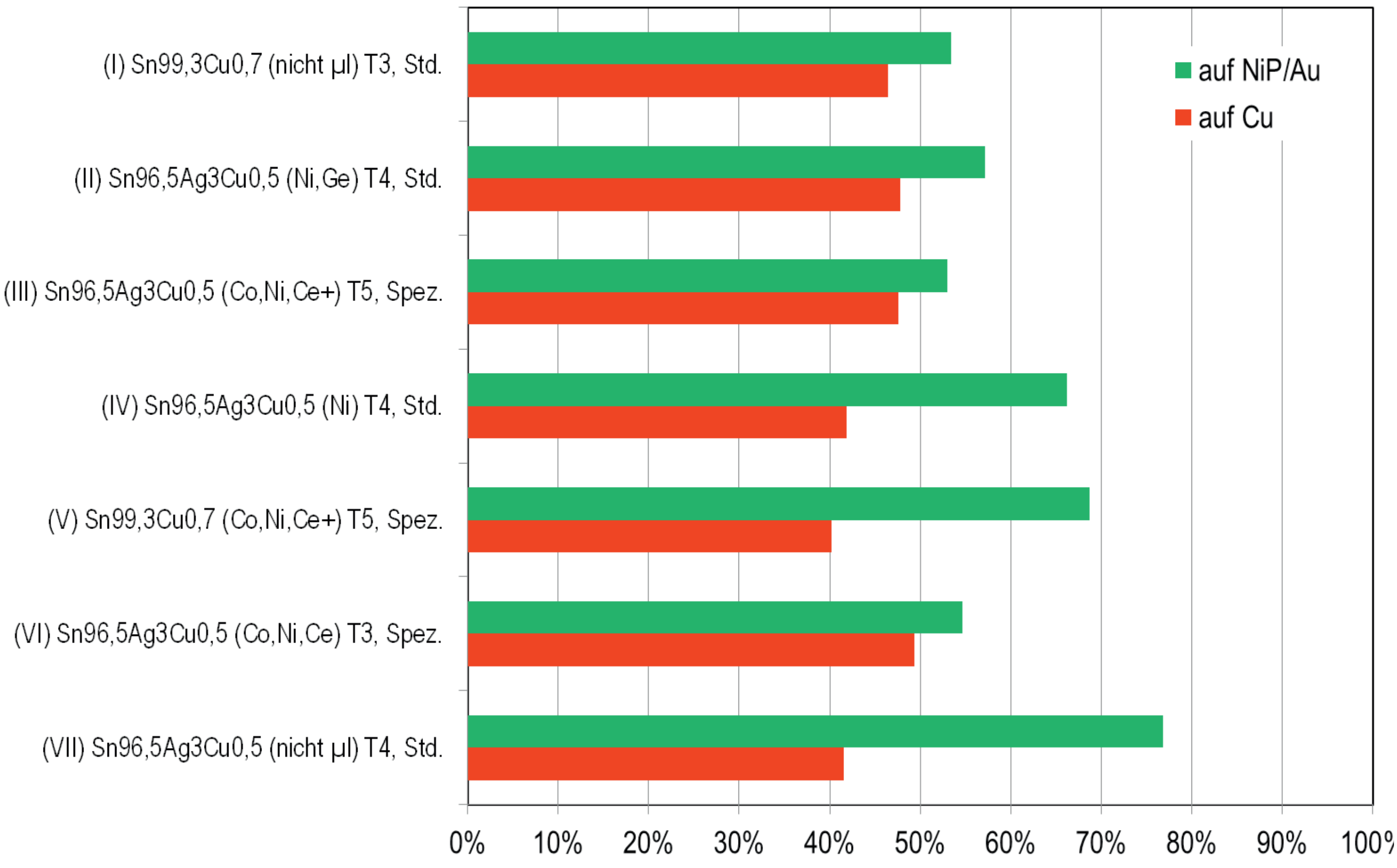


Fig. 8: Standardised shear forces after 1000 temperature cycles

yed soldering powders with Co or Fe.

The influence of the PCB metallisation on the stability of the soldered connections is far greater than the influence of the alloy variations. Without exception, higher shear strengths and lower decreases in shear strength are ascertained on NiP/Au surfaces compared to the Cu surface. However, microalloys do bring about at least a stabilisation on Cu surfaces.

3. Summary

Microalloyed soldering pastes were made up and tested in comparison with non-microalloyed soldering pastes. The shear strength of soldered connections made with the soldering pastes was ascertained after temperature cycles. Solders containing silver tend to show higher shear strengths than the SnCu solders, and Sn99.3Cu0.7(Co,Ni,Ce,In) on NiP/Au shows the second highest strength after 1000 cycles. The results of the reliability tests carried out by measuring shear strength values show that higher reliabilities can be expected on NiP/Au surfaces than on copper surfaces. Soldered connections with the non-microalloyed alloy VII Sn 96.5Ag3Cu0.5 show the greatest shear forces on NiP/Au surfaces after 1000 cycles. On Cu surfaces, the strength values for all tested alloys tend to assimilate as the number of cycles increases; after 1000 cycles, all tested soldered connections are deemed to have failed, while all soldered connections on NiP/Au are deemed to be intact after 1000 cycles. A summary of the test results [6] also ascertained the empiric correlation that this number of microalloy components tends to have a positive effect on the ageing behaviour of the soldered connections but a negative effect on the wetting behaviour of the solders. It is therefore necessary to find a suitable compromise between soldering ability and reliability for each specific application.

[1] A. Fix, P. Zerrer, A. Prihodovsky, B. Müller, D. Wormuth, W. Ludeck, H. Trageser, M. Hutter, und R. Diehm Nanoflux – Flussmittel mit nanochemisch aktiven Metallverbindungen zur Stabilisierung von Weichloten, DVS-Berichte Band 273, Weichlöten Forschung & Praxis für die Elektronikfertigung, S. 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, 23. November 2011

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

[4] FLOWTIN® registered trademark of Stannol GmbH

[5] K. Bartl, M. Nowottnick, Reduzierte Kupferauslösung Mikrolegierte, bleifreie Lotpasten im Vergleich – Teil 1, Productronic 11/2011, S. 60

[6] M. Nowottnick, A. Novikov, K. Bartl: Mikrolegierte Lotpasten und Lötverbindungen, PLUS – Fachzeitschrift für Aufbau- und Verbindungstechnik in der Elektronik 07/2012, S. 1638 - 1644