

Solder alloy contribution to robust selective soldering process.

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Abstract

The number of components and functionality on a printed circuit board increases continuously. SMD components become smaller, pitch dimensions shrink, but there are still some through-hole components left on most of the assemblies. All classes from high-reliability to consumer electronics have through-hole connections. For high-reliability products more expensive materials may be used compared to low-cost consumer electronics. This not only counts for board materials and component selection but also for the solder alloys in a selective solder process. Solder alloys are designed for SMD applications. Some of them have multiple elements to increase reliability. Sn3.0Ag0.5Cu has been the standard lead-free alloy for a decade or more. There are two drawbacks of this alloy:

1. Not reliable enough for high-reliability applications.
2. Too expensive for consumer products.

Under the hood and around the engine applications in automobiles require high-reliability electronics. These components have operation temperatures from -40°C to +150°C. A standard Sn3.0Ag0.5Cu is not good enough. Three specially designed high-reliability alloys were used in a point-to-point soldering machine to see how stable their composition is and how robust their solder process.

For consumer electronics there is a different trend with respect to solder alloys. Low temperature solders are of increasing interest for several reasons. Lower solder temperatures allow the use of cheaper materials and are less susceptible to warpage in reflow processes. These solders are SnBi based, and the absence of Ag makes them less expensive. The alloys have a larger melting range. How this affects the selective process is part of the study. Four different test-boards were used to investigate the robustness of the different alloys in a selective soldering process. The goal of these tests was to define the process windows of the alloys. Hole filling, bridging, solder balls, and open joints were quality characteristics for different Design of Experiments. The hole filling of over 18,000 through hole components were measured for high thermal mass boards as well as thin double layer boards. In two of the tested alloys, the composition of the alloy changed over time. Frozen solder and (Cu, Ni)₆Sn₅ needles were found during the experiments. Cross sections of the through-hole connections were made to measure the intermetallic thickness at different temperatures and solder conditions. The performance of six new lead-free alloys is compared to Sn3.0Ag0.5Cu.

Introduction

For decades the industry soldered the printed circuit boards in high and mixed volume processes with SnPb alloys in wave solder machines. Due to miniaturization more SMDs were introduced and changed the soldering process to reflow with some through-hole components soldered in selective pallets or on dedicated selective solder machines. For high volume applications a dip solder process is most efficient. This process has a high throughput but is less flexible. For mixed production and lower volumes, point-to-point soldering became popular and is now a common soldering process.

After introduction of lead-free soldering the process not only changed from wave to selective soldering, but the alloy also changed from SnPb to Sn3.0Ag0.5Cu or Sn0.7Cu0.05NiGe. This came with unexpected challenges. The Sn3.0Ag0.5Cu is very destructive to metals and this resulted in erosion of parts that were not treated. Solder pot materials changed to Titanium, cast iron or other methods to protect against erosion. Changing the alloys was not just a drop in. For this reason, this experiment was done to investigate how newly introduced alloys respond to point-to-point soldering.

The new alloys are mainly designed for reflow applications and therefore can have complex compositions of multiple elements. The main differences between standard alloys like SnPb and Sn3.0Ag0.5Cu with the alternative alloys are:

- New alloys have more elements to improve properties (some up to 6 elements)
- New alloys may have a melting range (SnPb is eutectic and Sn3.0Ag0.5Cu is near eutectic)
- New alloys have different liquidus and solidification temperatures

Solder pot and alloy impact

Most of the point-to-point selective solder machines use an electro magnetic pump to generate a liquid solder wave. An electromagnetic pump is a pump that moves electrically conductive solder using electromagnetism. Electromagnetic pumps work based on Faraday's principle, in which the electrical current interacts with the magnetic field generating the magnetic force. Therefore, this in turn controls the liquid metal flow.

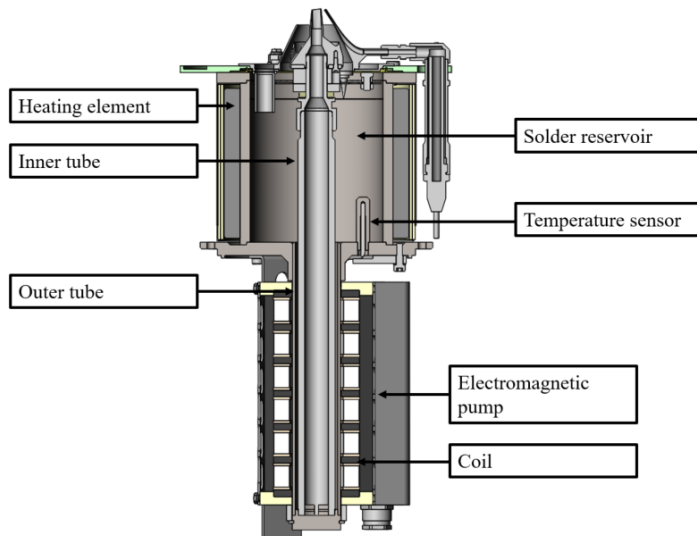


Figure 1. Schematic view of electromagnetic pump.

There are several alloy properties that influence the liquid solder flow and there are machine parameters to control the wave height. Due to the generated flow the solder will move from the solder reservoir to the bottom of the outer pipe (solder flowing between outer and inner pipe downwards). From the bottom it will flow through the inner pipe to the nozzle at the top generating a small wave. All parameters that have impact on the wave height are in the Fishbone diagram (figure 2). The properties listed under materials depend on the selected alloy and therefore need further investigation.

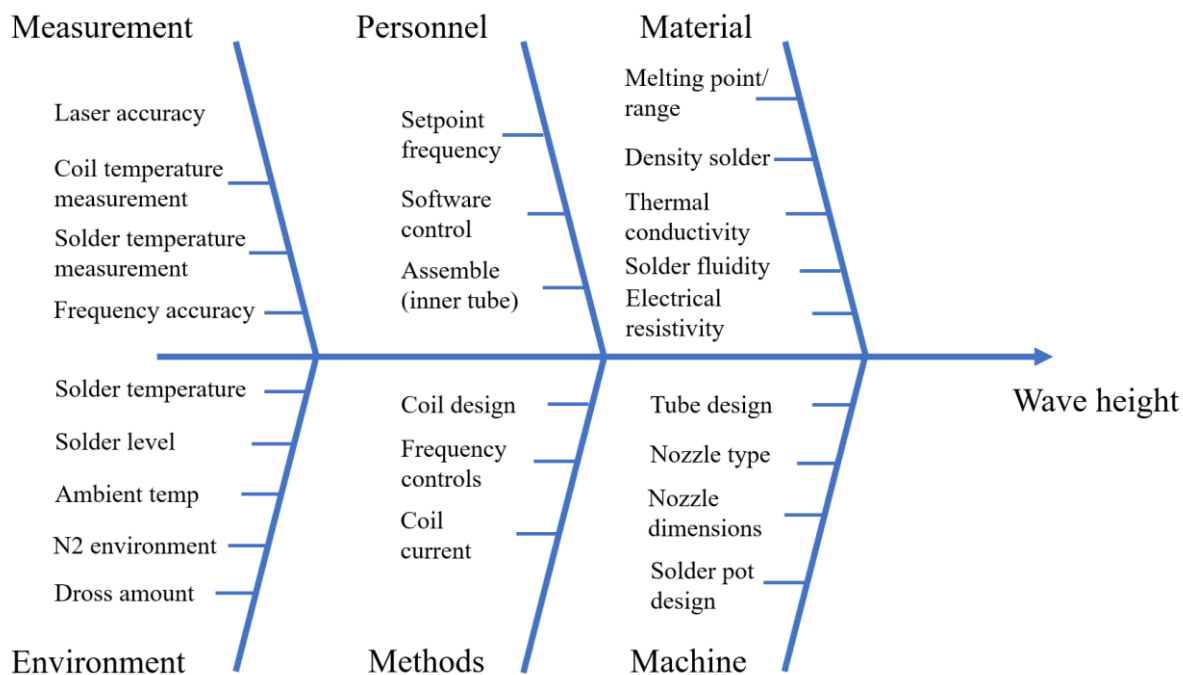


Figure 2. Fishbone diagram wave height

Like in the IPC-A-610 standard, in this experiment alloys for three classes are investigated. Alloys for general electric products, dedicated service, and high performance. For consumer (general electric) products low temperature alloys can be used. The low temperature alloys in this experiment are prototypes and not available for selective soldering today.

Table 1. Low temperature solders and properties.

		Alloy A	Alloy B
		Sn28BiX	Sn37BiY
Melting range	°C	139-190	139-174
Electrical resistivity	Ωm	0.242	0.290
Specific mass	kg/m^3	786	810
Thermal conductivity	W/mK	36	30

Typical for these alloys is the low solidus temperature of 139°C. The solidus temperature is the temperature where the melting begins. The alloys have a large melting range and Bi containing alloys have a higher electrical resistivity. Because of the lower melting range these alloys can't be used for applications that have higher operation temperatures.

The second group of alloys in this experiment are the alloys that are used in general and industrial applications. These alloys can be used for soldering all kinds of products with the exception of high-reliability applications.

Table 2. Commonly used SAC305 alloy and alternative.

		Alloy C	Alloy D
		Sn2.0Bi0.7Ag0.7Cu	Sn3.0Ag0.5Cu
Melting range	°C	208-215	217-220
Electrical resistivity	Ωm	0.156	0.132
Specific mass	kg/m^3	738	738
Thermal conductivity	W/mK	82	58

The last group of tested alloys are the high-reliability alternatives. These alloys must meet the higher reliability demands of electronics assemblies used in automotive or aerospace applications. The applications are used in extreme thermal operating environments such as under-hood automotive and other harsh conditions.

Table 3. High reliability lead-free solders and properties.

		Alloy E	Alloy F	Alloy G
		Sn3.8Ag3.0Bi0.7Cu 1.4Sb0.15Ni	Sn3.0Ag2.5Bi0.7Cu0.6Sb 0.05Ni	Sn1.5Bi0.7Cu0.05NiGe
Melting range	°C	206-218	210-219	221-225
Electrical resistivity	Ωm		0.152	0.140
Specific mass	kg/m^3	745	744	740
Thermal conductivity	W/mK	55	66	54

This group contains alloys that have additional elements to get better properties. The alloys contain 6 elements which make it hard to control the composition in a production environment. Typical elements used are Bi, Ni, Sb, and Ge. Germanium is there to reduce dross formation.

The electrical resistivity of an alloy is the property that defines how strongly it resists electric current. A low resistivity indicates an alloy that allows electric current, which influence the efficiency of the electromagnetic pump. The thermal conductivity of an alloy defines the ability of the alloy to conduct heat. This property influences the coil temperature of the magnetic pump and therefore also the wave height.

Heating up solder pot

All experiments are done in the same solder pot on the same machine to have the smallest number of variables. Like in the Fishbone diagram defined there are over 25 parameters. Solder pot, tube design, coil, all were kept the same. The solder pot contains approximately 10 kg solder.

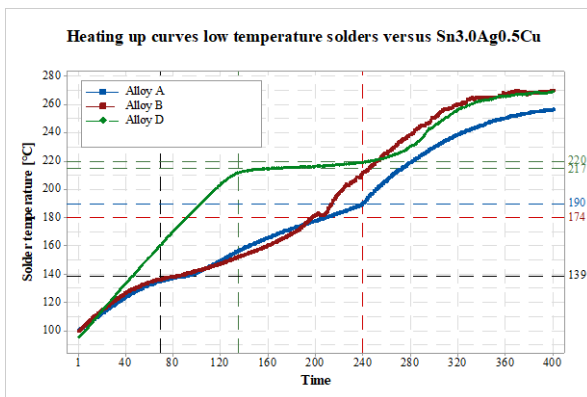


Figure 3. Low temperature solders with long melting range versus Sn3.0Ag0.5Cu

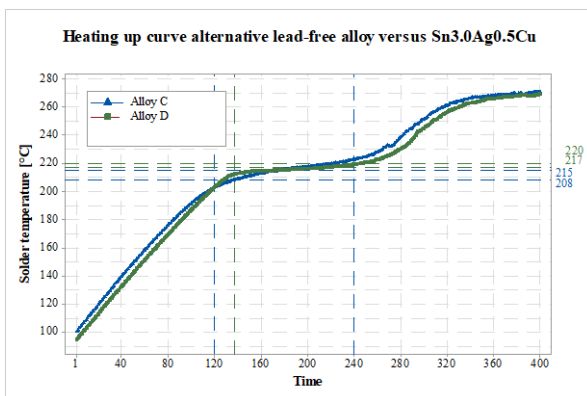


Figure 4. Heating up curve of the alternative lead-free alloy C versus the common Sn3.0Ag0.5Cu.

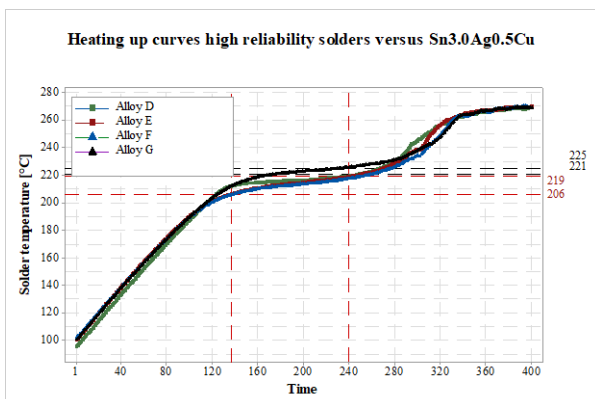


Figure 5. High-reliability solders versus the common Sn3.0Ag0.5Cu

Although the alloys have different properties and melting ranges the time from ambient temperature to set point is equal for all the alloys. In all the graphs the set-points are 270°C except for alloy B (250°C). The total time is about 30 minutes before the machine is ready to solder. The heat-up can be divided into three areas:

1. From ambient to melting range
2. Melting range
3. From melting range to set point

There is one significant difference between alloy A and B (low temperatures solders) and the other alloy settings and that is the pump release temperature. This is the minimum temperature of the solder before the magnetic pump can pump the solder. The solder on the top should be completely melted before the magnetic pump can run to avoid tin explosions.

Wave height of different alloys

The solders have different melting ranges. The operation temperature for point-to-point soldering starts about 50°C above the liquidus temperature of the solder. For the low temperatures alloys that is about $190 + 50 = 240^{\circ}\text{C}$ and for the other lead-free solders $220 + 50 = 270^{\circ}\text{C}$. In general, the higher the solder temperature the better wetting.

At different temperatures the solder responds differently. The fishbone diagram shows that temperature has an influence on wave height. Different parameters will change due to a different temperature. For a 6mm square titanium nozzle the wave height was measured using a laser sensor at different frequencies of the electromagnetic pump. The low temperature solders were compared to the standard Sn3.0Ag0.5Cu alloy D.

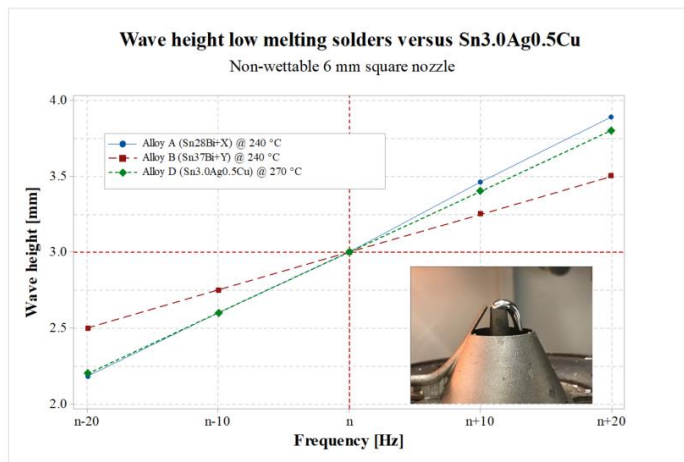


Figure 6. Wave height low temperature solders.

Alloy A responds like Sn3.0Ag0.5Cu at 50°C superheat. Alloy B requires higher frequencies to achieve the same wave height. Alloy C and D perform the same at 270°C.

A small design of experiment was run for the Sn3.0Ag0.5Cu alloy to identify the impact of the solder temperature on the wave height. At a higher temperature the solder will become more fluid, but the coil temperature will increase resulting in a lower wave height. The analysis of the DoE is plotted in the next graph.

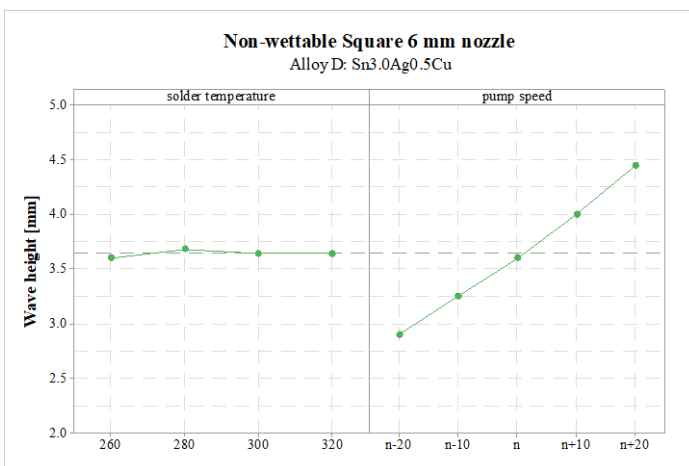


Figure 7. Solder temperature and wave height for Sn3.0Ag0.5Cu.

The analysis show that the solder temperature has no impact on the wave height for this alloy.

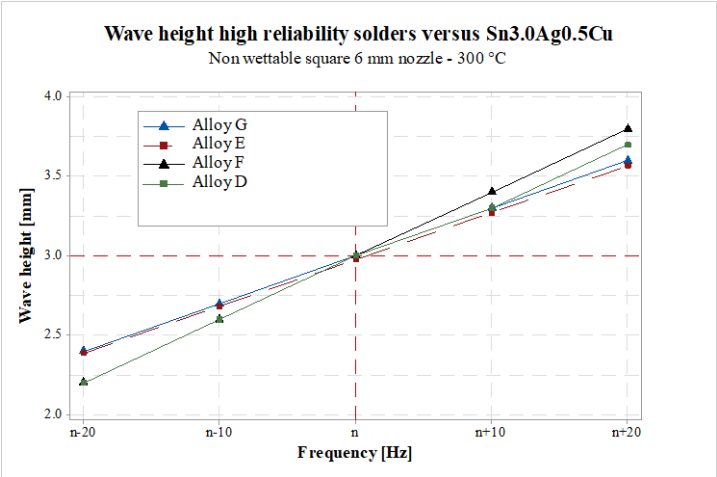


Figure 8. Wave height of high-reliability solders versus the standard Sn3.0Ag0.5Cu.

The solder coming out of a non-wettable nozzle flows to one side like in wave solder process. This flow is collected in a small bin and the flow time is measured. The solidified piece of solder is measured on a balance and the flow can be calculated. The next experiment is done to identify the impact of temperature and nozzle dimensions on the solder volume for the different alloys.

Table 4. Design of experiment solder flow.

Solder	Non-wettable nozzle square [mm]	Solder temperature [°C]	Wave height [mm]
Alloy C	4	260	2.5
Alloy D	6	300	3.0
Alloy E			3.5
Alloy F			
Alloy G			

If solder temperature increases, there are more parameters and properties (see Fishbone diagram) that change. Due to a higher coil temperature, the frequency needs to be changed to achieve the same wave height. Therefore, the wave height is selected as a parameter and not the frequency. The results are shown in the next graph.

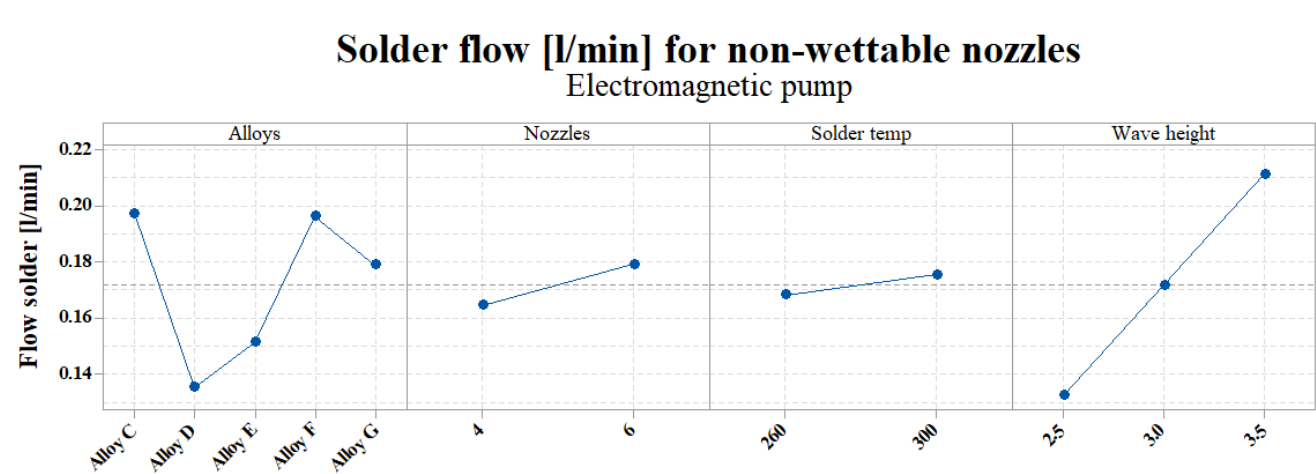


Figure 9. Solder flow different parameters and alloys.

The graph shows that the alloys have different flow rates due to different properties like fluidity and density.

Soldering different alloys

There were four different test-boards used in the evaluation of the different alloys. For all boards one flux was used. The flux is an important player in the soldering process. Since the project included alloys with different melting points and operation temperatures, a flux type that covers the complete temperature range was selected. A halogen-free, activated No-clean ROL0 flux was applied before soldering. This flux is also used in SnPb applications and can handle lower process temperatures required for the low melting alloys. The solid content is 5% and the flux has safe residues. The halide-free resin residues have a high surface insulation value. A subsequent cleaning operation can therefore be eliminated.

The flux also defines the topside board temperature after preheating. For good hole filling this temperature should meet the specification of the flux and preferably not too cold. The preheating should bring enough energy into the board. If the board is too cold the solder will solidify during the hole filling. For this flux the topside board should be between 110 and 130°C at the end of the heating.

Alloy A

The solder was received in bars and were melted in the solder pot. The solder release temperature and the coil temperature needed to be reduced for a low melting alloy. During the solder experiments the dross formation was relatively low, due to:

1. Lower temperatures (less oxidation)
2. Germanium in the alloy

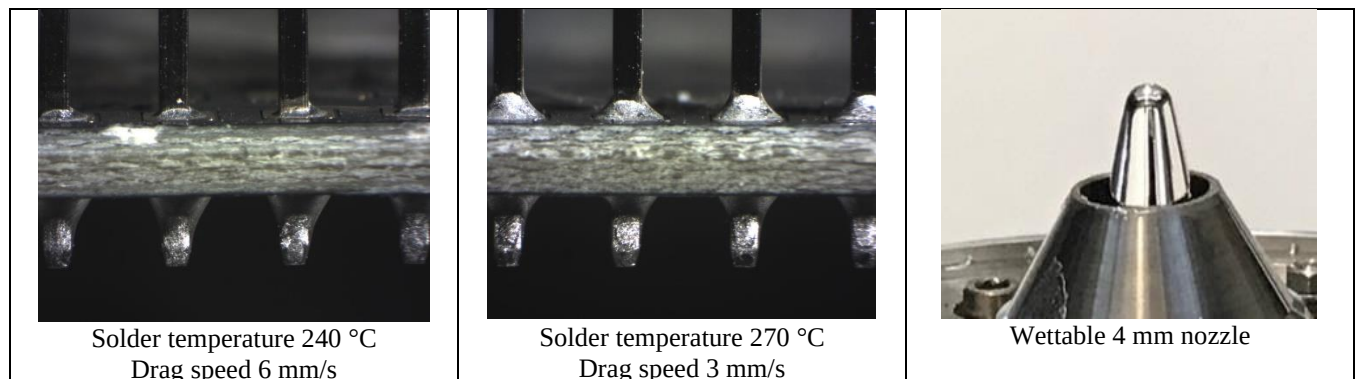


Figure 10. Good soldering at 270°C for test board 1 (Test board 1 – FR4 material – ENIG finish – 1.6 mm thick).

Test board 1 has single row 2.54mm pitch pin headers. The shape of the solder joints is like Sn3.0Ag0.5Cu. At lower temperatures the hole filling is minor. Good soldering is achieved at temperatures of >240°C.

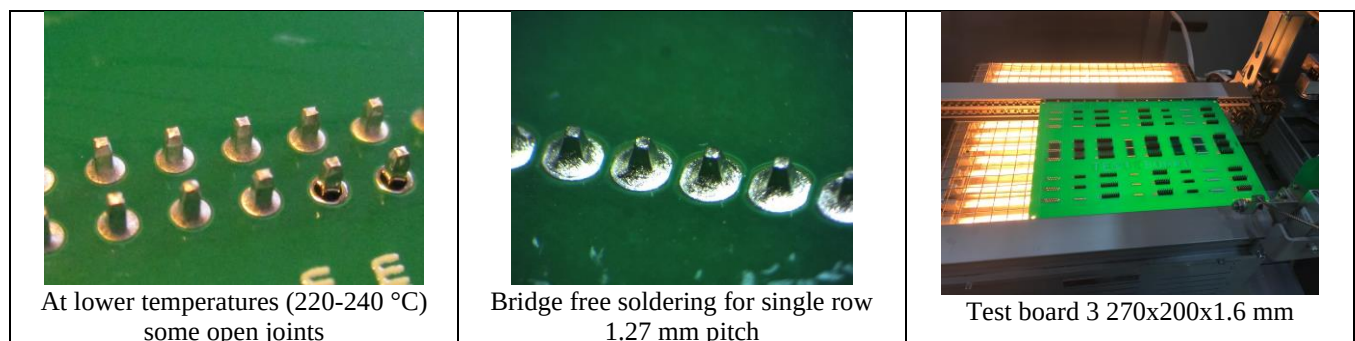


Figure 11. Soldering on fine pitch test board 3 (1.27, 1.50, 2.00-, and 2.54-mm pitch)

Summary of Alloy A:

The soldering is good at temperatures > 240°C. At solder temperatures of 270°C solder results are equal or better than Sn3.0Ag0.5Cu at 300°C. The lower temperature is beneficial for the materials that are used (board materials and components plastics can have lower Tg values).

Alloy B

This solder is designed for reflow soldering applications. Same as for alloy A some modifications on the machine are required to meet the lower soldering temperatures.

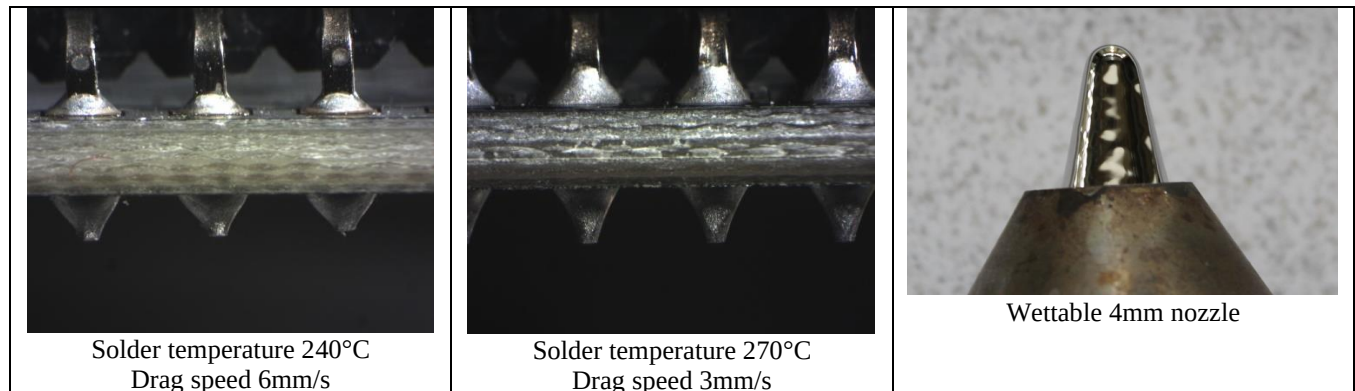


Figure 12. Soldering is good at temperatures equal or higher than 240°C for test board 1.

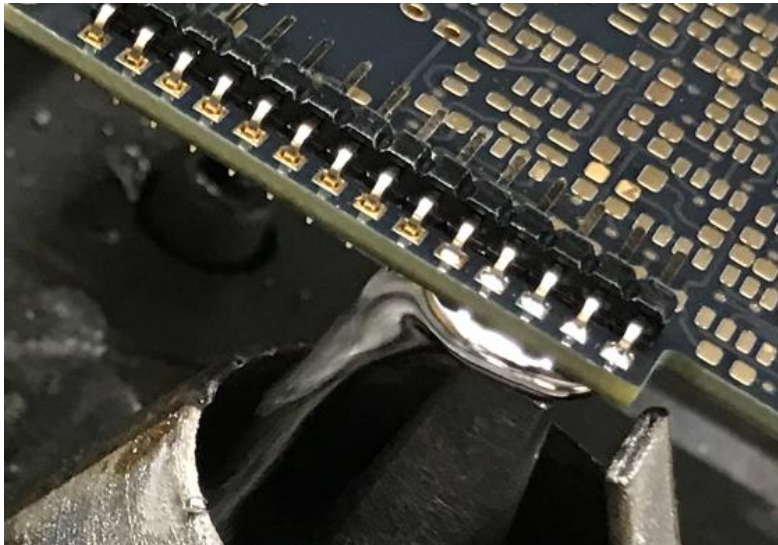


Figure 13. Showing test board 1 soldered with 4mm non-wettable nozzle.

During the experiments it was noticed that at the start when all parts are not at temperature the solder starts to clog. The solder solidifies and does not jet. This will disappear when temperatures are higher, and the frequency is increased. The melting range may also contribute to this phenomenon. Typical for wettable nozzles.



Figure 13. The solidification of the solder at lower temperatures and pump speed.

Alloy C

This alloy is a low silver SAC alloy. It is used for similar applications as the Sn3.0Ag0.7Cu but has less silver and therefore a melting range.

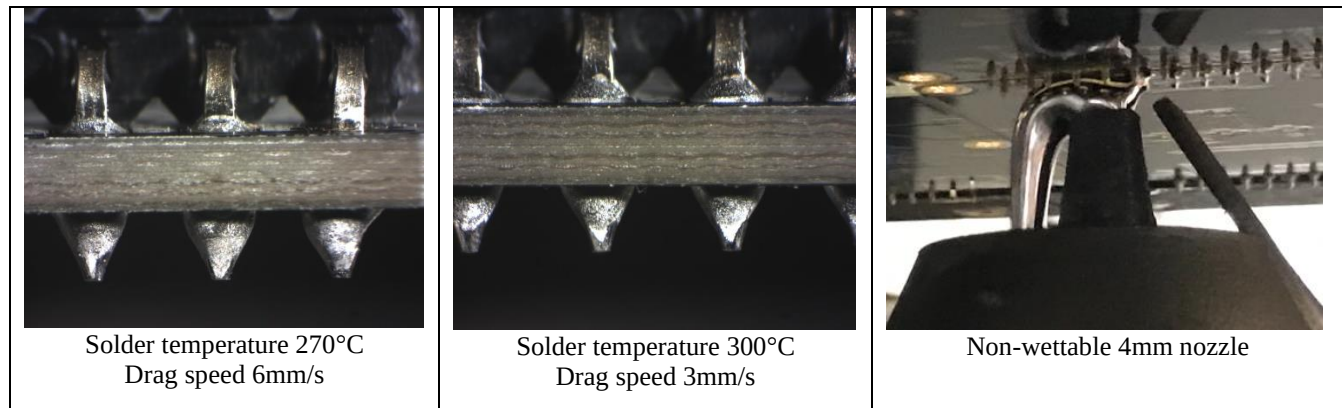


Figure 14. Soldering with this alloy is good at 270 but better at 300 °C for test board 1.

The alloy can be compared to Sn3.0Ag0.5Cu. The solder performance is equal. No issues were noted during the experiments. This alloy contains 2% of Bi which reduced the solidus temperature.

Alloy D

This is the Sn3.0Ag0.5Cu and is the baseline for the other alloys. The solder was used for all four test boards. The alloy has good soldering properties which is confirmed in the test with board 1.

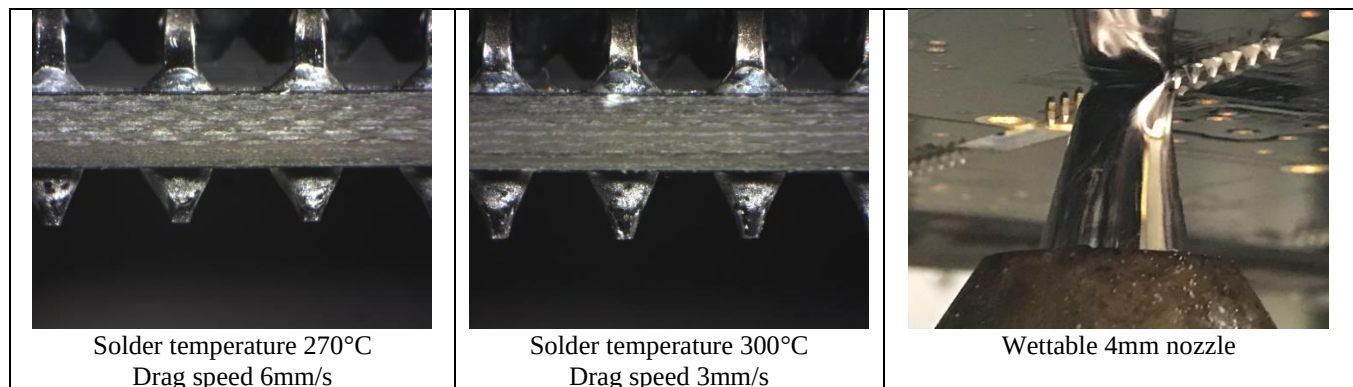


Figure 15. Different from the previous alloys the Sn3.0Ag0.5Cu shows excellent hole filling at 270°C.

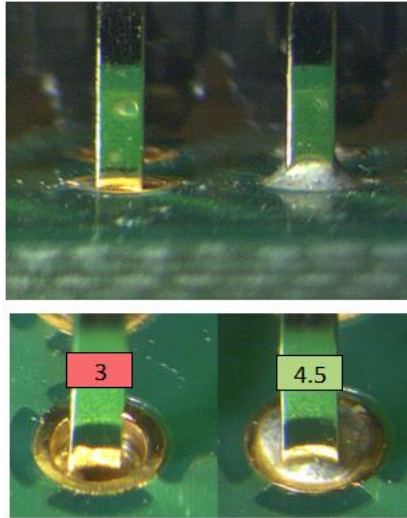
The tests showed the excellent wetting of this alloy. All soldering experiments and other tests like wave height and flow trials took two weeks for each alloy. During this period no maintenance was done. Only at the end, the dross was removed to compare the volumes. This alloy had more dross than others. Some of the new alloys have antioxidants, Sn3.0Ag0.5Cu has none.



Figure 16. Relatively high amount of dross after two weeks (no maintenance).

Design of Experiment test board 2.

The goal of this test was to investigate the hole filling properties of the solder for a two row connector. For this board two 6mm nozzles were used. A cylindric wettable nozzle versus a non-wettable square 3-D printed made from stainless steel. Boards were mounted in a pallet. Two pin connectors were soldered in one drag. The connector had 30 pins per row and there were two connectors on one board. The board dimension was 198x36x1.6mm and the board finish was ENIG (Electroless Nickel Immersion Gold).



Score table		
5	Target	100% +
4.5	Acceptable (some exposed metal topside pad)	100% +
4	Acceptable (solder fillet to top)	100%
3.5	Acceptable (solder fillet visible)	>75%
3	Defect	<75%
2	Defect	<50%
1	Defect	<25%

Figure 17. Score criteria for hole filling. Each single pin in hole is counted.

Table 5. The layout of the experiment. This is repeated for all alloys except the low melting (Alloy A and B).

	Parameter	Unit	Level 1	Level 2
1	Drag speed	[mm/s]	3	9
2	Solder temperature	[°C]	270	300
3	Nozzle type		Cylindric 6 mm	Square 6 mm

The boards were visually inspected, and scores entered in MiniTab software for statistical analysis:

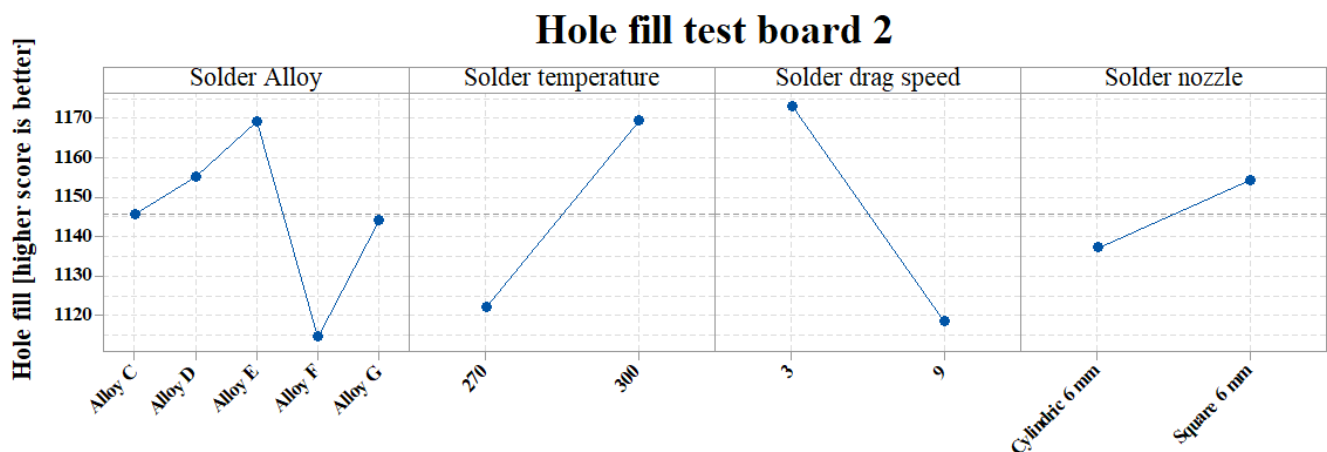


Figure 18. The higher the score the better hole filling.

Alloy E outperformed the baseline Sn3.0Ag0.5Cu alloy. The higher temperature and lower drag speed give longer contact time and better wetting. The drag speed is less significant when the solder is 300°C. At the higher temperature the barrels have better filling even at higher drag speeds.

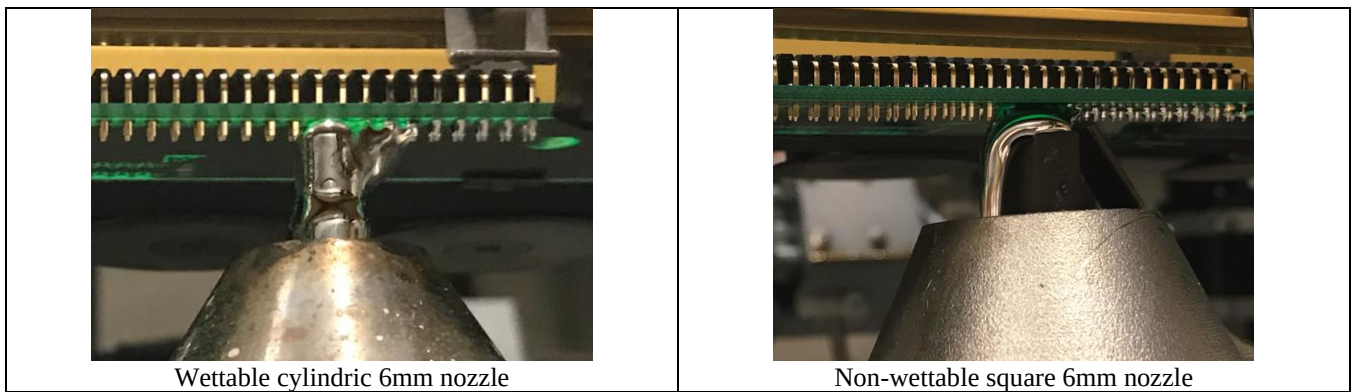


Figure 19. The two different solder methods.

Both nozzles showed good hole fill when correct parameters are selected. The impact of the nozzle type is less significant.

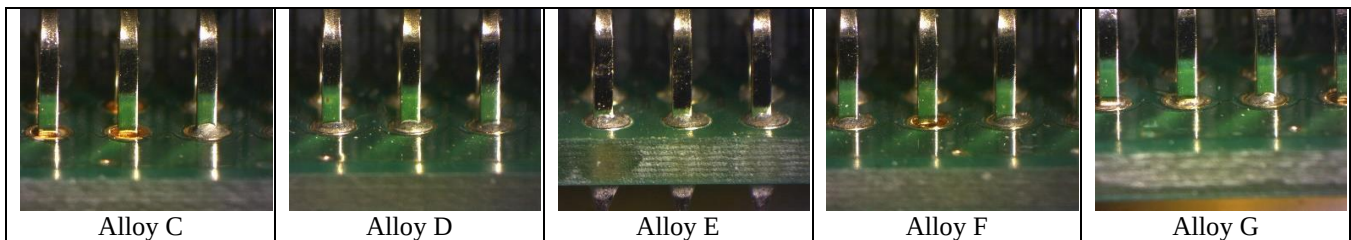


Figure 20. The hole filling at 270°C and drag speed of 9mm/s. Some alloys showed low scores for these tough conditions.

Alloy E

This high-reliability lead-free solder is used for selective soldering multi-dip applications. The alloy has six elements and composition is hard to control in a large solder pot of a multi-dip unit. This application has a small pot of only 10kg and is easy to refill in case the composition drifts. The soldering (wetting) performance of this alloy is good.

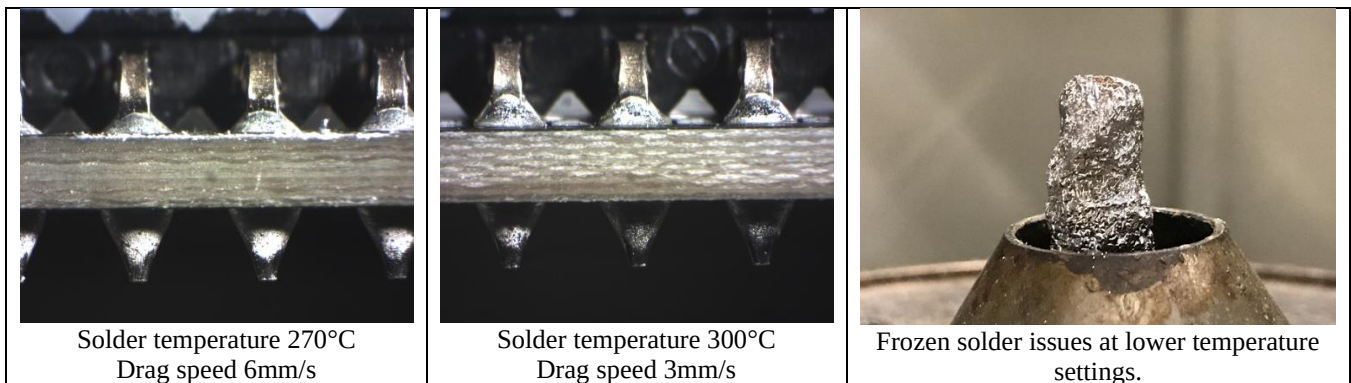


Figure 21. The soldering of Alloy E is excellent for board 1 great wetting give nice meniscus of solder.

When the solder pot is cleaned, and the solder is at temperature there are no issues. However, after some production time the alloy starts to decompose and clog. This will be discussed later in this paper.

Alloy F

This alloy contains the same elements as alloy E but in a different composition. This results in a slightly different melting range and in a different solder behavior. Some test boards had minor hole fill. Not for test board 1 where the soldering is excellent even at 270°C.

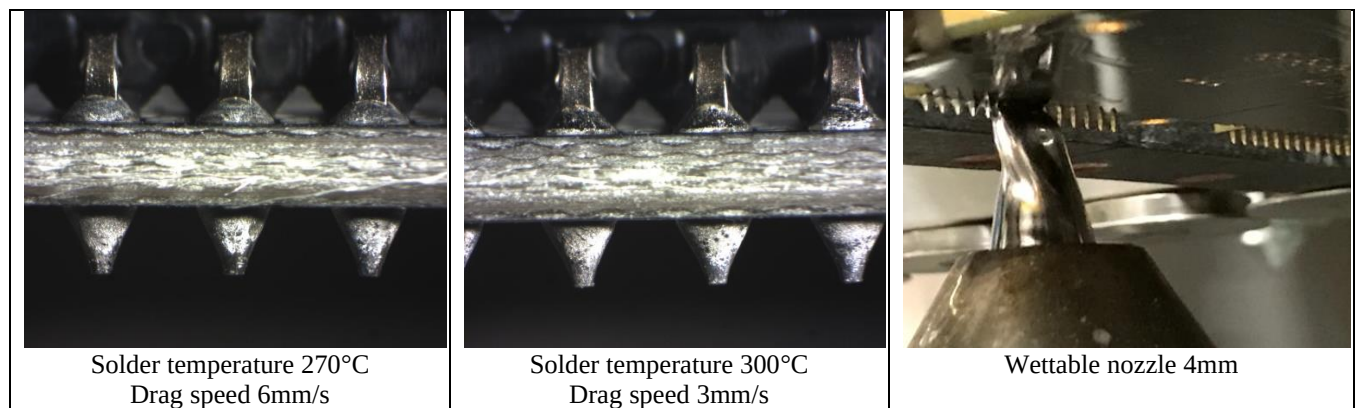


Figure 22. Excellent solder fillets. Nice meniscus on topside even at lower temperature.

Alloy G

Different from the other high-reliability alloys this one does not have Ag in the composition. So, there are no Ag_3Sn intermetallic compound particles in the bulk of the solder. This alloy has a slightly higher melting point. Therefore, the solder temperature of 300°C is only 40°C superheat. For this alloy 280 and 310°C would be a fairer comparison with the others. Nevertheless, solder wetting is still good.

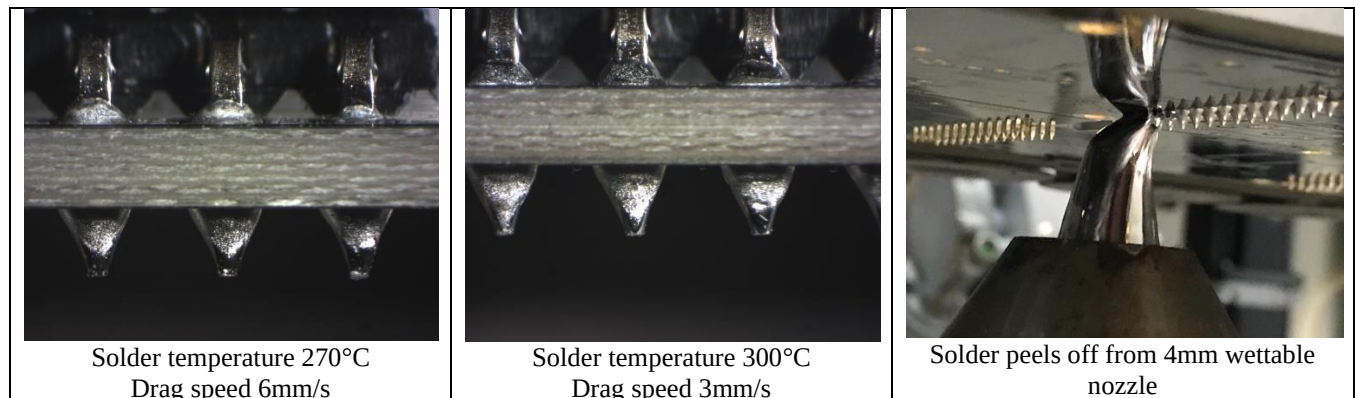


Figure 23. Nice soldering at 300°C. Wetting is less at lower temperatures.

Fine pitch

So far, the focus of the experiments has been on hole filling. Miniaturization is another trend in the printed circuit board assembly that also affects selective soldering. There are pin headers in the market that have a pitch of only 1.00mm. To investigate the contribution of the alloy on soldering fine pitch components a special test board (3) was designed with different hole and pad dimensions. All the alloys were capable to solder 1.27, 1.50, and 2.00mm pitch alloys without bridging when using a hot nitrogen flow tube (solder drainage conditioner) behind the nozzle to de-bridge. The flow of the nitrogen is higher for smaller pitch components.

The bridges could be eliminated but apart from that there were two different failures observed:

- Open joints – for the low melting alloys A and B at lower temperature settings and high drag speed (wetting).
- Fat solder joints – on the 1.27mm pitch pins. Alloy E had by far the most but also alloy F and G showed some excessive solder at the very small pins.

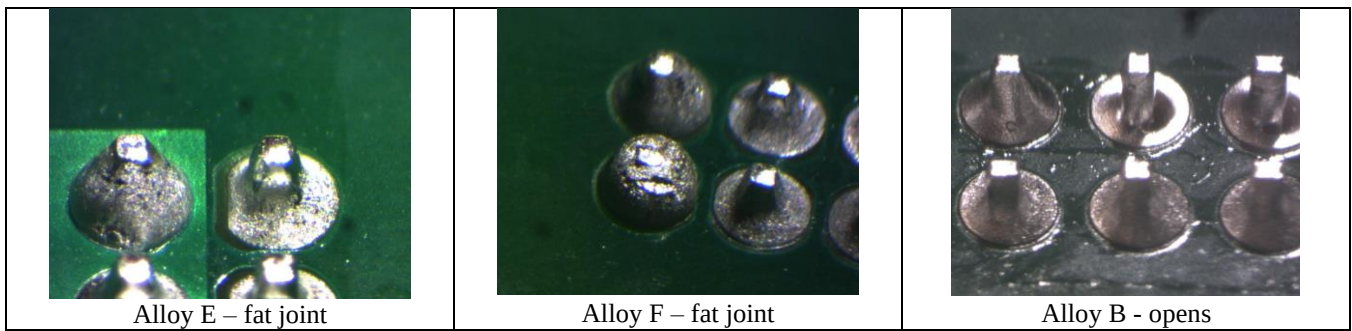


Figure 24. The issues with the 1.27mm for alloy E and F was excessive solder and for alloy B open joints.

The fat joints were always at the last pins of the drag. The capillary force and fluidity of the solder may benefit to this phenomenon. According to the IPC-A-610 standard the pin should be visible in the solder.

High thermal mass test board

All alloys (except alloy A) were used to solder a high thermal mass board. The board had 8 Cu layers and ENIG board finish. All boards were soldered at 270 and 300°C. For the low temperature solder alloy B, the solder temperatures were 240 and 270°C. The drag speed (contact time) is 3 and 6mm/s.

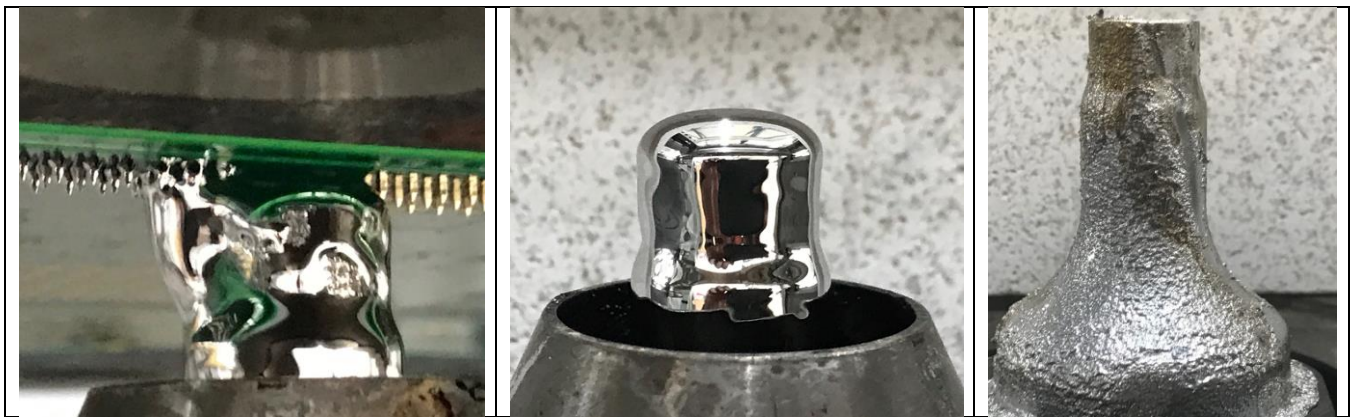


Figure 25. Alloy B soldering very good at 270°C but some issues at lower temperature with hole filling.

The clogging of the low temperature solders has been discussed but the hole filling is excellent when soldering high thermal mass boards. During preheating the test board is heated to 110°C so the temperature drop during hole filling is much smaller than from the other lead-free alloys that have higher melting points.

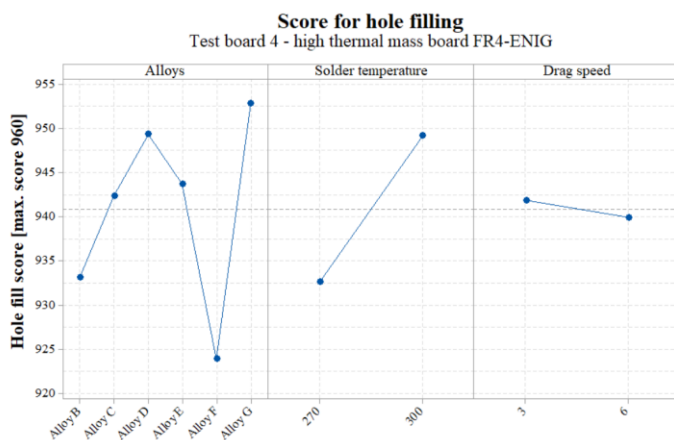


Figure 26. Alloy G is doing better than Sn3.0Ag0.5Cu. All others are minor but there are some interactions.

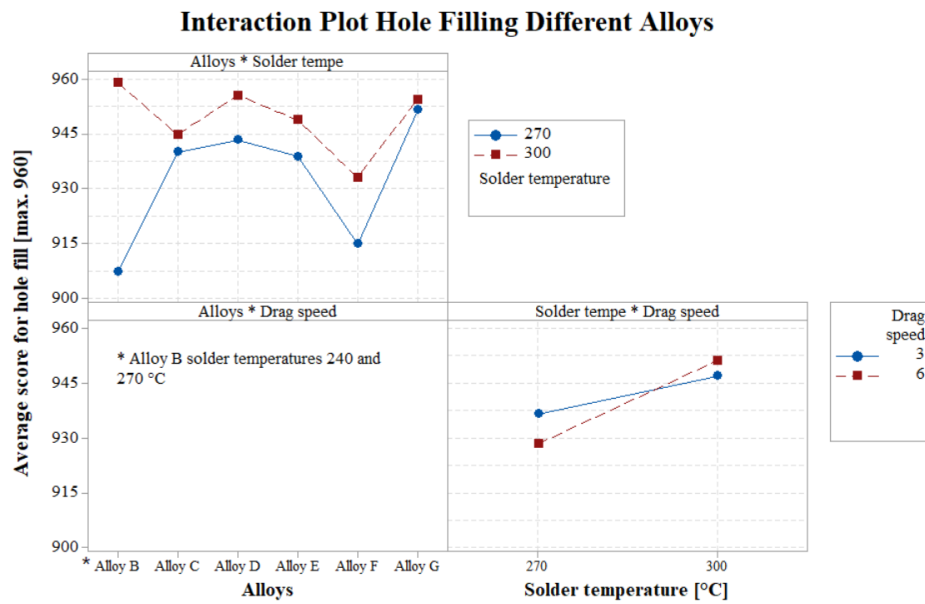


Figure 27. Interaction plot of the experiment.

The interaction plot shows two interesting points:

- Alloy A (and alloy F but less) is performing excellent at the higher solder temperature and poor at the lower.
- At 300°C the drag speed of 6mm/s is equal to the hole filling performance as 3mm/s because of the better wetting at higher temperature.

Cross sections high thermal mass test board.

The hole filling is checked by visual inspection. To see if the solder made a proper intermetallic with the barrel and the pin connector from all the alloys a cross section was made on the same spot of the assembly.

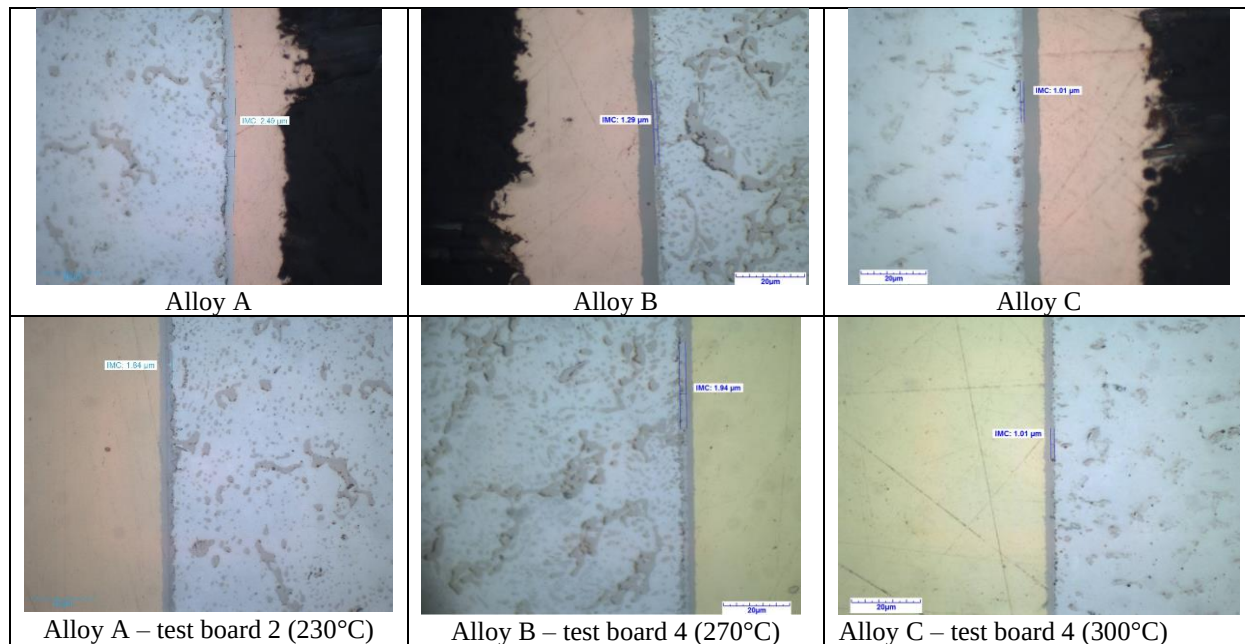


Figure 28. Cross sections barrel-solder (top) and pin-solder (bottom).

The difference between alloy A and B and the other alloys can be seen in the bulk of the solder. The Bi are the dark areas in the solder.

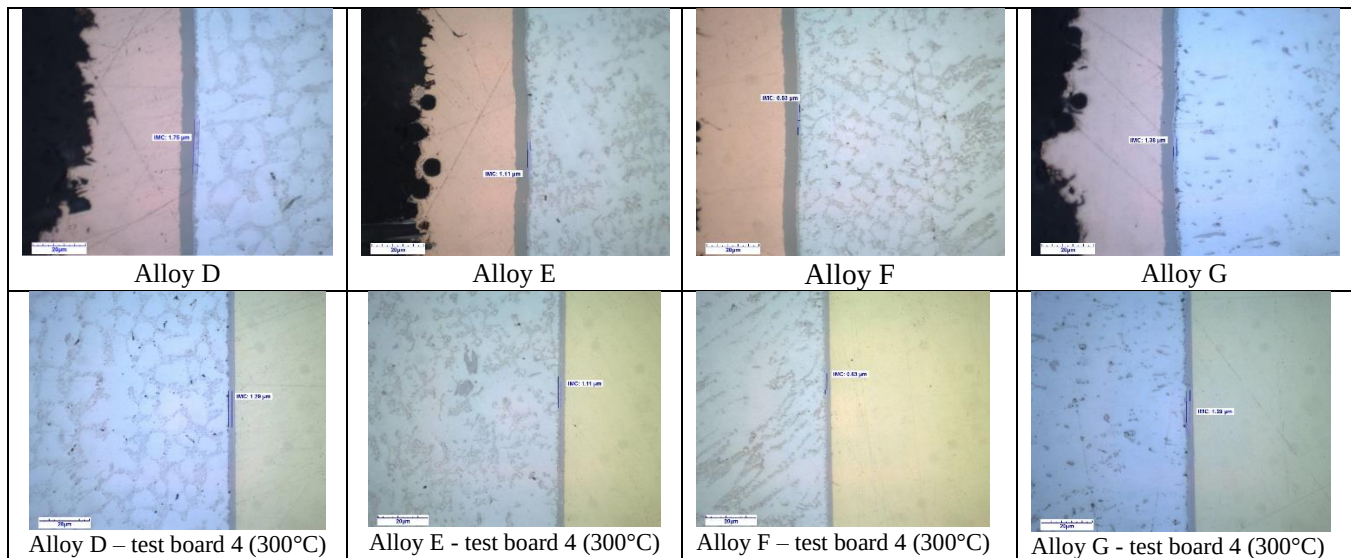


Figure 29. Left the Sn3.0Ag0.5Cu and the others are the high reliability alloys including strengthening elements.

All the alloys have an intermetallic layer of Cu_6Sn_5 and Cu_3Sn . The Ag containing alloys may have additional Ag_3Sn compounds. The thickness of the Cu_6Sn_5 layer is measured with a microscope.

Table 6. Intermetallic thickness Cu_6Sn_5

	Pin	Barrel
	[μm]	[μm]
Alloy A	1.84	2.49
Alloy B	1.94	1.29
Alloy C	1.01	1.01
Alloy D	1.29	1.75
Alloy E	1.11	1.11
Alloy F	0.83	0.83
Alloy G	1.29	1.38

Alloy composition stability

All the alloys were tested for approximately two weeks in the same machine using the same electromagnetic pump. Before the experiments started, and afterwards, the composition of the alloys was measured with optical emission spectroscopy. Of all the alloys in the experiment there were two that had a dramatic change in composition.

Table 7. Difference in concentration before and after experiment.

	Cu	Ni
Alloy A	-	No data
Alloy B	-27%	-84%
Alloy C	0%	-
Alloy D	No data	-
Alloy E	-27%	-47%
Alloy F	0%	-1%
Alloy G	0%	0%

There are two alloys, B and E, that are not compatible with selective soldering. For both alloys needles were found in the solder that prevented the solder flow. After removing these needles and removing the dross the boards could be soldered successfully.

$(\text{Cu,Ni})_6\text{Sn}_5$ and or Cu_6Sn_5 particles separate from the bulk solder and form needles. These particles accumulate in the nozzle and in the solder pot. Together with the dross they clog and prevent solder from flowing. In the solder pot some solid pieces of this were found for alloy E.

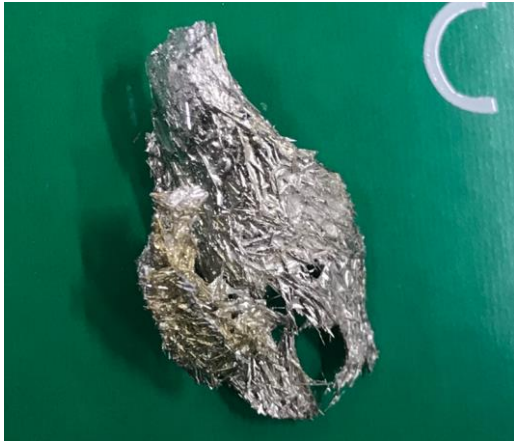


Figure 30. $(\text{Cu,Ni})_6\text{Sn}_5$ needles that separate from alloy E.



Figure 31. A mixture of dross and needles of alloy E found between inner and outer tube.

This kind of contamination is not typical for electromagnetic pumps. It is also found in production lines of selective solder machines that have impellor pumps.

Conclusions

Not all alloys that are successful in a reflow process can be implemented into selective soldering. There is a risk for alloys that have Cu and Ni in the composition. $(\text{Cu,Ni})_6\text{Sn}_5$ or Cu_6Sn_5 particles may form needles and separate out of the solder. They don't dissolve in the solder and may mix with dross and cause clogging. This phenomena has been observed for alloys which have higher amounts of elements and relatively high percentage of Cu and or Ni in the composition.

For low temperature solders it is recommended to sufficiently heat the solder pot and nozzle before starting production. If parts are too cold the solder may clog; solder solidifies and does not jet. Poor solder flows might be unstable. This will change when it heats up after time.

For fine pitch applications some alloys are more sensitive for open joints. The solder temperature should be well above the melting point to achieve good wetting. A superheat of $>50^\circ\text{C}$ is recommended. Excess solder has been observed for 1.27mm pitch components with short leads. Bulbous solder joints are found at the last pins of the connector that are soldered. To avoid

bridging of fine pitch components, a solder drainage conditioner (blow hot nitrogen in between the pins) was needed for all applications.

For good hole filling the contact time and solder temperature are the major parameters. In between the different solders there is not so much variation. The alloys that were used in the experiment were able to solder all test boards with excellent hole fill if the solder temperature was approximately 80°C above the melting range and the drag speed was relatively slow. Lower speed for longer contact time and therefore better wetting.

It is recommended to monitor the composition of the alloy. Depending on throughput, the solder should be sent for a composition check every month. Cu will dissolve from the pads of the board material and when ENIG finish is on the board there is a potential risk that the Ni content will increase.

References:

1. “Development of a Lead-Free Alloy for High-Reliability, High-Temperature Applications”, Hector Steen and Brian Toledo, Henkel Corporation, APEX.
2. “New Developments in High-Temperature, High-Performance Lead-Free Solder Alloys”, Anton Zoran Miric, Heraeus GmbH, SMTA International, 2010.
3. “How to Manage Wave Solder Alloy Contamination”, Gerjan Diepstraten and Harry Trip, Cobar Europe BV, Balver Zinn, IPC Midwest, 2010.
4. “Selective soldering Low Temperature Solder”, Gerjan Diepstraten, ITWEAE, SMTAI Rosemont, 2020.
5. “Selective Soldering with High-Performance Lead-Free Solders”, Gerjan Diepstraten, ITWEAE, SMTAI Minneapolis, 2021.