

DEVELOPMENT AND TESTING OF A LEAD-FREE LOW MELTING POINT ALLOY

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ABSTRACT

This paper describes the development and testing procedure of a new lead-free low melting point alloy.

Current lead-free soldering alloys involve soldering process temperatures that can be harsh on temperature sensitive electronic components and PCB materials. These temperature sensitive parts can be found on virtually every electronic unit. As a result electronic units can come out of the soldering process in an already aged condition, sometimes even damaged or pre-damaged. An obvious solution would be to lower the temperatures in those soldering processes. This however can only be realized when using soldering alloys with lower melting points. Current low melting point alloys are mainly the eutectic Sn42Bi58 and Sn42Bi57Ag1. Unfortunately they have limited shock and vibration resistance and are not really suitable for selective and wave soldering. This substantially limits their field of use.

The focus of the development of a lead-free low melting point alloy should be in improving these weak points in such a way that the alloy is suitable for most of the electronic applications nowadays being soldered with lead-free soldering alloys. Therefore the low melting point alloy will need to have acceptable mechanical properties and will have to pass intense mechanical reliability testing. Furthermore the low melting point alloy should be suitable for the soldering processes that currently are being used in electronics assembly production environments.

In a pre-study, a first selection of metals is made based upon their ability to reduce the melting point, availability, cost, hazard classification and impact on solderability. The first selection procedure of different development alloys is done by the analysis of the microstructure before and after an annealing test. An elongation test is performed to determine the ultimate tensile strength and the elongation at break. Thermal cycling properties were tested on different QFN components soldered on a NiAu surface. Shear testing has been performed on chip components on the Cu OSP surface and NiAu. Vibration and shock testing has been performed on real functional electronic boards. The suitability of the alloy for the wave and selective soldering processes has been tested in

cooperation with a leading manufacturer of soldering machines.

Test results indicate that the new low melting point alloy can be a viable alternative for current lead-free alloys.

Key words: low melting point soldering alloy, lead-free soldering, reduction of soldering temperature, temperature sensitive electronic components

INTRODUCTION

The preferred connection to attach an electronic component to a PCB board is the solder joint. This solder joint is made by a soldering alloy in a soldering process. The composition of this soldering alloy determines its melting point and inherently the soldering temperature in the soldering processes.

Current lead-free soldering temperatures can have various negative effects on the materials used in electronics. Capacitors can have a shift in their (di)electrical properties. Most sensitive are electrolytic and film capacitors but other types like tantalums can be affected too¹. Mechanical components like e.g. relays and contactors can be deformed, creating poor contact. Plastic body components like connectors can be deformed, inhibiting the counter contact to fit. LEDs can have a shift in their light emitting spectrum. The insulation coating of transformers and coils can partially melt. Displays can crack. Crystal oscillators can have a shift in their frequency. BGAs can warp causing the hidden pillow defect². Fuses can have a shift in their limiting current. PCB materials can delaminate, experience pad lifting or barrel cracking.

Some of these phenomena will have an immediate impact on the functionality of the electronic unit. These units will not pass functional testing and will be disposed of or repaired before they go into the field. The effect of other phenomena like e.g. shift in (di)electrical properties, will depend on the design of the electronic circuit itself. The signal can be affected by the shift or not. The effect of most of the phenomena however will show itself once the electronic unit is performing in the field. In the field the electronic unit can experience different temperature and humidity conditions including a sudden change of these, vibration, mechanical shock,... Due to these conditions the

phenomena that were created by a too high soldering temperature in the soldering process can suddenly become apparent and create functional problems. This can lead to dangerous situations and also high costs because the unit will have to be repaired or exchanged in the field.

Most electronic manufacturers that are aware of temperature sensitive components on their electronic unit will try to adjust their temperature profile in this way that the components will not go over their time-temperature limits specified in the datasheets. When this is not possible, these components are usually left out of the soldering process and soldered afterwards, usually by hand. However, due to the multitude of different phenomena and potentially affected components combined with the fact that the effects are not always immediately visible, not all manufacturers are aware that they have a problem. They usually find out the hard way when the units come back from the field.

An easy solution to avoid the risk of negative effects on PCB boards caused by too high soldering temperatures is the use of a low melting point alloy in the soldering processes. Current eutectic and near eutectic SnBi and SnBiAg low melting point alloys, however have limitations³. They have limited shock and vibration resistance and are not really suitable for selective and wave soldering. When these limitations are countered, it can substantially increase the field of use for such a low melting point alloy. Even to this extent that this low melting point alloy can replace most of the current lead-free soldering alloys used today for electronic applications.

This paper describes the development and testing procedure of such an enhanced lead-free low melting point alloy.

SELECTION OF THE BASIC ALLOYING ELEMENTS

Sn is the base element of virtually every existing soldering alloy used in electronics today. It already has a rather low melting by itself of 232°C (449.6°F). Furthermore it is able to make intermetallics with pretty much all surfaces to be soldered in electronics manufacturing. Price and long term availability are not an issue. No other element comes close to these beneficial properties. Sn is the logical choice as the base element for a new low melting point alloy.

The choice of the next alloying element should be in its ability to reduce the melting temperature of the alloy when added to pure Sn. Three candidate elements came into the picture: Zn, In, and Bi.

Beside its ability to lower the melting point, Zn is also very interesting element in terms of price and availability. The main disadvantage is that Zn oxidizes quite heavily⁴. As a result SnZn alloys will need pretty a strong de-oxidizing flux chemistry in the soldering processes. Wetting tests have proven that it is very hard to get good soldering results without halogenated flux chemistry. As most of electronics manufacturing industry is moving

away from halogenated flux chemistry, this could be seen as problematic by electronic manufacturers. Zn was not chosen as secondary alloying element.

The melting point reducing properties of In are well known^{4,6}. However there are some considerations that need to be taken into account. In is mainly produced as a byproduct of other ores and the availability and price of this metal could be problematic if it was to be used as secondary alloying element for a low melting point alloy⁵. In was not chosen as secondary alloying element.

Bi is an element with good availability and an interesting price. With a long history of use in cosmetics and some pharmaceuticals, Bi is considered to have low toxicity⁶. Furthermore, there is quite a lot of experience with Bi as an alloying element and its effect on solderability because the eutectic low melting point alloys Sn42Bi58 and Sn42Bi57Ag1 are already on the market for a long time. Bi was chosen as a secondary alloying element. Other elements were added to obtain the prototype alloys.

ANNEALING TEST

Many different prototype alloys were considered in the procedure of developing the new low melting point alloy. As a primary selection tool, an annealing test was used. In this test, test specimens are stored for 1000 hours at 85°C (185°F) to simulate ageing. Analysis of the microstructure and the intermetallic layer give an idea how the solder joint will maintain its properties in time. For many applications, this is very important as it will to some degree determine the life time of the electronic unit. Solder pastes were produced with all prototype alloys. A SnAg3Cu0,5 solder paste is also included in the test as a reference. These solder pastes were printed with a 150µm stencil on a PCB board with 35µm of Cu. Two types of PCB finishes were used, Cu OSP and NiAu. The PCB boards were assembled with Sn finished 1206 chip components. The boards were reflowed under air atmosphere with a peak temperature of 200°C (392°F), and 240°C (464°F) for SnAg3Cu0,5. Micro-sections were made after 0, 500 and 1000 hours. The microstructure of the solder joints and the intermetallic layers were analyzed with a Scanning Electron Microscope (SEM) with a magnification of 2000 on grain coarsening, and 5000 times on intermetallic growth and cracks.

Grain coarsening

Grain coarsening is a typical ageing phenomenon for many alloys. Too strong grain coarsening is undesirable as solder joints are more likely to crack along big grains when experiencing thermo-mechanical stress. Grain distribution and coarsening was analyzed with special image analysis software and quantified (Figure 1).

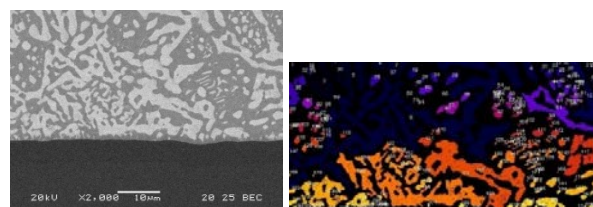


Figure 1. Grain distribution analysis (2000X magn.)

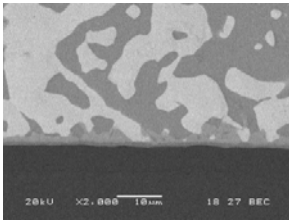


Figure 2. Too strong grain coarsening after 1000 hours of a rejected prototype alloy (2000X magn.)

Alloys with too strong grain coarsening compared to the others were rejected (Figure 2).

Intermetallic layer growth

The connection between the soldering alloy and the base metal, in this case Cu or Ni, is the intermetallic layer. Together they make the solder joint. The intermetallic layer by itself is rather hard and brittle and is best to be kept as thin as possible⁷. Intermetallic layers are known to grow in time and with temperature. Intermetallic thicknesses were measured on several locations of the micro-sections (Figure 3). The distribution of the measured intermetallic layer thicknesses of the left and right solder joint of the 1206 component are shown in Figure 4.

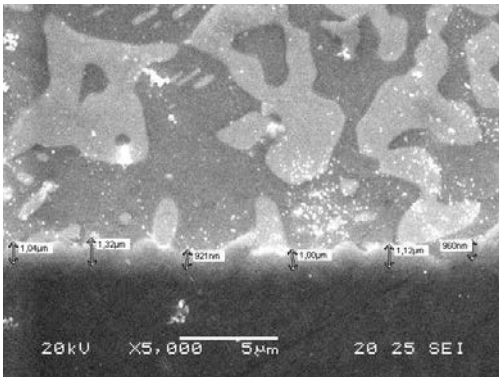


Figure 3. Intermetallic thickness measurement on different locations (5000X magn.)

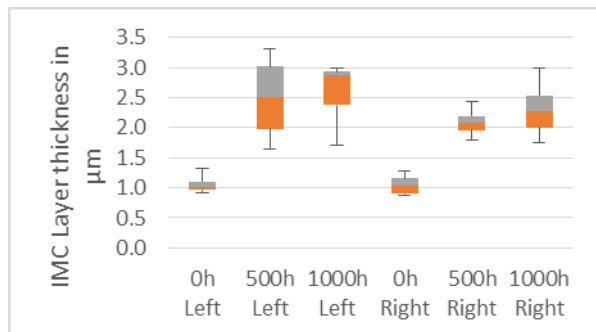


Figure 4. Intermetallic thickness distribution box plot graph for the chip components

After 1000hrs, none of the prototype alloys on neither Cu OSP nor NiAu showed higher median values for intermetallic thickness than the median value of the 0h intermetallic thickness of the SnAg3Cu0,5 alloy.

Microcrack formation

Microcrack formation in the intermetallic layers is a phenomenon that randomly can be witnessed with e.g.

SnAgCu alloys⁸ (Figure 5). It is not always clear if these microcracks have an influence on the long term reliability of the solder joint. For this project however, prototype alloys that showed microcrack formation after annealing were rejected.

Results

After analysis of the results of the annealing test, several prototype alloys were withheld for further testing and investigation. However, not all of the selected alloys passed further testing. In retrospect, prototype alloy 'Q', performed best. The test results that are discussed further in this paper are for alloy 'Q'.

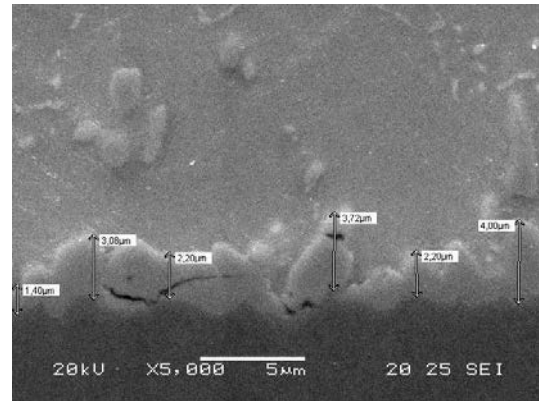


Figure 5. Microcracks in the intermetallic layer

ELONGATION TEST

An elongation test was chosen as a next step in the selection process of a new low melting point alloy. An elongation test is not performed on board level but on the alloy itself. Test samples of 2mm diameter and 100mm length were prepared with the prototype alloy, and as a reference also with SnAg3Cu0,5 and Sn63Pb37. They were submitted for testing on an Instron 5542 material tester. The samples are clamped and stretched at 5mm/min at room temperature. The force needed to do this and the elongation are monitored (Figure 6).

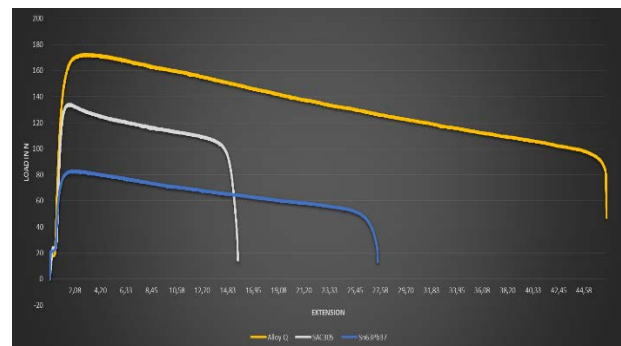


Figure 6. Elongation test

In the beginning a lot of force is needed to stretch the samples just a little bit. This is called the elastic range as the samples will regain their original form when the force would be released. At a certain moment, the samples will give in and deform permanently. This can be seen in Figure 6 as the top of the graphs. The corresponding value on the Y-axis says something about the resistance against deformation and determines the ultimate tensile strength of the alloy which can be calculated from the measured

force and the diameter (cross section surface) of the sample. The prototype alloy 'Q' has highest tensile strength followed by SnAg3Cu0,5 and then Sn63Pb 37. Deformation of a solder joint is not necessarily a problem as the solder joint will still be functional. Therefore it is interesting to know when the alloy will actually break once it starts deforming. This can be seen in Figure 6 as the point where the graphs drop down steeply. The corresponding value on the X-axis determines the elongation at break. Alloy 'Q' has highest elongation at break followed by Sn63Pb 37 and then SnAg3Cu0,5.

THERMAL CYCLING TEST

Introduction

A thermal cycling test is often used as an ageing test for electronic units. Assembled units are submitted to temperature cycles of a certain duration between a min. and a max. temperature in a test chamber. Due to differences in the coefficient of thermal expansion of the different materials used, the electronic unit will experience thermo-mechanical stress. This stress can lead to e.g. cracking of the solder joint. Particularly sensitive in this matter are QFN components in combination with current lead-free alloys⁹ (Figure 7). QFN components do not have leads for their I/O but solderable surfaces on the bottom side along their outline and a mass plane in the middle.

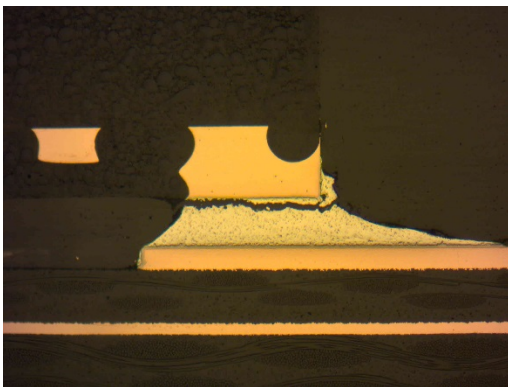


Figure 7. Crack on a QFN solder joint after thermal cycling

Test setup

QFNs were reflow soldered with a prototype alloy solder paste to a test PCB. As a reference, the same test vehicles were also produced with SnAg3Cu0,5 and SnAg0,8Cu0,7 solder pastes. Each test vehicle is reflow soldered with a dedicated profile for its alloy. The PCB base material is Isola 370HR. The PCB consists of 6 layers and is about 1,6mm thick. Cu-thickness of the inner layers is 25µm and the outer layers have 35µm Cu. The PCB finish is NiAu. Thermal via's are 0,45mm plated holes filled with conductive fill. There are 4 sections on the PCB board. Each section is populated with 4 identical pieces of a different type of Sn finished QFN 9X9mm (Figure 8). A version with a low CTE mold (7 ppm) and a high CTE mold (15 ppm) in combination with a large and a small mass plane (die paddle) were chosen. In the results, this will level out failures that are only related to a specific design of QFN.

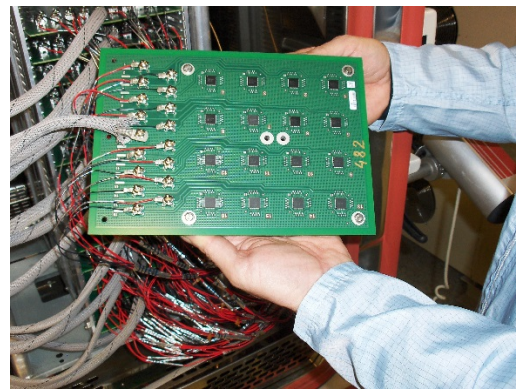


Figure 8. Test vehicle and test chamber

The industry standard JEDEC JESD-A104 condition G was chosen for the thermal cycling test. Test vehicles were submitted to a -40°C / + 125°C temperature cycle of one hour. Dwell time at the extremes is 10min and ramp rate in between is 10°C/min. The test chamber is a Weiss VTS 7027-10 (Figure 8). QFNs are daisy chained to enable continuous measuring. For that purpose an Analysis Tech Model 128/256 STD event detector was used. When an open circuit is detected 10x sequentially, it is considered a failure.

Results

The SnAg0,8Cu0,7 alloy was the first alloy to show failures in between 100 and 200 cycles, quickly accumulating to about 25% of all QFNs and to 90% of all QFNs after 3000 cycles.

The SnAg3Cu0,5 looks a bit better. It started failing after 500 cycles, quickly accumulating to about 25% of all QFNs and 65% of all QFNs after 3000 cycles.

Prototype alloy Q alloy lasted longest before showing any failures. First failures were registered after 800 cycles, accumulating to about 10% and 25% after 3000 cycles.

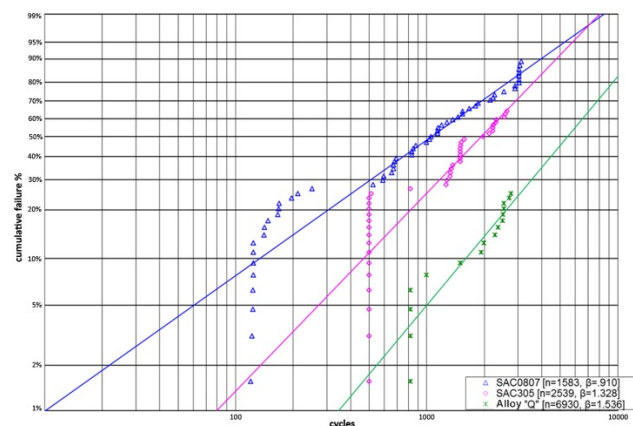


Figure 9. Cumulative failures on QFNs for each alloy

SHEAR FORCE TEST

Introduction

In a shear force test electronic components are pushed off the board from the side and the force needed to do this is registered. The solder joint in this case experiences a shear force. Shear force properties of current lead-free alloys are in general not an issue. However it makes sense to test this property for a new low melting point alloy.

Test setup

Sn finished 1206 SMD capacitors were reflow soldered with the prototype alloy on a PCB board with a NiAu and a Cu OSP finish. As a reference, test vehicles were also produced with SnAg3Cu0,5, Sn62Pb36Ag2 and SnBiAg1 solder pastes. All test vehicles were reflow soldered with a dedicated profile for the used alloy. A Dage Series 4000 shear tester was used to push the components off the board. Test load was set at 10kg, shear height at 200µm and test speed at 250µm/s.

Test Results

The measured shear force values for all alloys on both NiAu (Figure 10) and Cu OSP surfaces are within the same range.

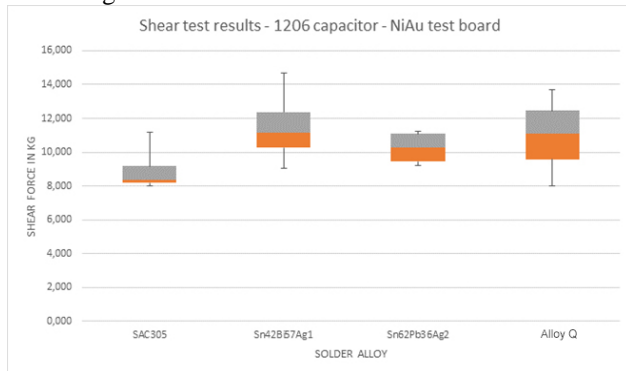


Figure 10. Shear force test results on the NiAu surface

The reason for this can be seen in Figure 11. The failure mode is the component body that breaks before the solder joint. Hence measured forces are not relating to the alloys. For this test, shear force resistance for all alloys is sufficient.

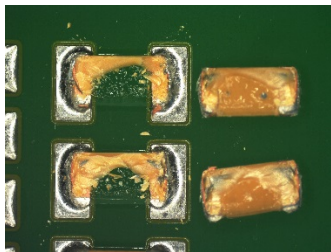


Figure 11. Shear force failure mode

VIBRATION AND SHOCK TESTING

Introduction

Current eutectic low melting point alloys Sn42Bi58 and Sn42Bi57Ag1 are known to have lower vibration and shock resistance than traditional lead-free alloys. A new low melting point alloy should have an improved shock and vibration resistance. The opportunity was presented to test these properties on a real application. A manufacturer of high accuracy measuring devices was looking for a low melting point alloy. The soldering temperature of their lead-free alloy was affecting the (di)electrical properties of some components to such an extent that the accuracy of the measuring devices was compromised. The Sn42Bi57Ag1 alloy was previously tested, however it failed the required shock and vibration testing. The prototype alloy Q was chosen for testing.

Test setup

The product for testing is a handheld measuring device. The PCB is a double sided I-Ag finished board with SMD and through hole components. SMD components were reflow soldered with a peak temperature of 205°C (401°F) under air with an alloy Q solder paste. Through hole components were hand soldered with an alloy Q solder wire.

The electronic devices were submitted for vibration and shock testing according BS EN 60945 and BS EN 60068 standards to an external lab (Figure 12).

The vibration test will start with a resonance frequency search on the electronic device in each of 3 axes. A 2H vibration endurance test with a peak acceleration of 3G will be performed on the found resonance frequency for that axis. If no resonance frequency is found, a standardized endurance frequency of 30Hz will be used with a peak acceleration of 3G.

The shock test will perform shocks in both directions of each of 3 axes. Shocks will last 11ms with a peak acceleration of 30G or defined by practical limitations of the test setup.

Afterwards the electronic units are sent back for ICT and functional testing.

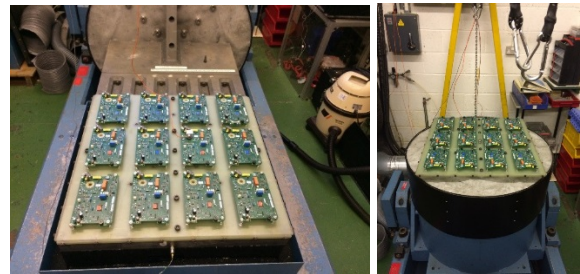


Figure 12. Vibration and shock testing

Test results

The electronic units were inspected after shock and vibration testing and none of the units showed signs of cracks, misalignments or other failures. Furthermore, all electronic units passed ICT and functional testing.

WAVE AND SELECTIVE SOLDERING

Introduction

Although reflow soldering can be considered as the main soldering technology for electronic assemblies, a big part of electronics manufacturing still uses wave and/or selective soldering processes. If a new low melting point alloy wants to be a viable alternative for current lead-free alloys, it should be compatible with these processes.

Beside good soldering results, the alloy should also be compatible with the materials it comes into contact with in the process. The alloy cannot damage or attack machine parts. A leading manufacturer of soldering machines was prepared to fill a selective soldering machine and a wave soldering machine with prototype alloy Q for evaluation.

Test setup

The solder pot of an electromagnetic pump driven selective soldering machine was filled with the prototype alloy Q. As a reference a solder pot with a SnCu based alloy was operating in parallel. For both alloys a 12/8 soldering nozzle was used to solder a DDR3 through hole connector on a double sided Cu OSP test board with 35µm of Cu. The maximum soldering speed that gave no bridging and +100% through hole wetting (with top side fillet, Figure 13) was established for three different soldering temperatures: 230°C (464°F), 260°C (500°F) and 285°C (545°F).

A wave soldering machine was also filled with the prototype alloy Q. The soldering temperature was set at 220°C (428°F) and a 5 row 'Wörthmann' soldering nozzle was mounted. The nitrogen supply was turned off. The same test board was used to find maximum speed settings that gave no bridging and +100% through hole wetting. All soldering results are analyzed under a microscope and with X-Ray (Figure 13). The behavior of the prototype alloy Q on machine parts was observed over a longer period of time for both machines.

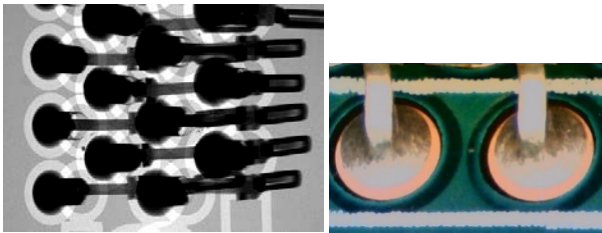


Figure 13. +100% through hole wetting on DDR3 connector soldered on a Cu OSP test PCB

Test results

Speed limits for the alloy Q were established at 20mm/s for 230°C (464°F) and 260°C(500°F) and at 30mm/s for 285°C (545°F).

For the SnCu based alloy the soldering speed limits were established at 5mm/s for 260°C(500°F) and 10mm/s for 285°C (545°F). At 230°C the SnCu based alloy was not liquid enough for soldering.

For wave soldering at 220°C (428°F) the soldering speed limit was established 2m/min. Higher speeds were not tested.

No attack or damage of machine parts has been reported by using the alloy Q over a longer period of time.

Speed / Alloy	Alloy Q	SnCu based
285°C (545°F)		
5mm/s	+100%	+100%
10mm/s	+100%	100%
20mm/s	+100%	-100%
30mm/s	+100%	-70%
40mm/s	100%	-70%
260°C (500°F)		
5mm/s	+100%	100%
10mm/s	+100%	-70%
20mm/s	+100%	-70%
30mm/s	100%	-70%
40mm/s	-100%	-70%
230°C (464°F)		
5mm/s	+100%	Not tested, too close to melting point
10mm/s	+100%	
20mm/s	+100%	
30mm/s	-100%	
40mm/s	-100%	

Figure 14. Through hole wetting results

CONCLUSIONS

Bi was chosen to be the most interesting alloying partner to reduce the melting point of Sn in order to create a new low melting point alloy that could be a viable alternative for soldering most electronic applications that are currently soldered with traditional lead-free alloys. Prototype alloys were developed and a first selection was made by performing an annealing test. Prototype alloys that gave too strong grain coarsening and showed cracks in the intermetallic layers were rejected. In an elongation test, prototype alloy Q showed very good values for tensile strength and elongation at break. Also in thermal cycling test on QFNs prototype alloy Q performed very well. In a shear force test on chip components, the component body broke before the solder joint did. Vibration and shock resistance was positively tested on a high accuracy electronic measuring device soldered with prototype alloy Q. Wave and selective soldering performance and the compatibility with machine parts was tested by a manufacturer of soldering machines with positive results.

Based upon the results, prototype alloy Q can be a viable alternative for current lead-free alloys.

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