DEVELOPMENT AND CHARACTERIZATION OF SOLDER PASTES BASED ON TWO ALTERNATIVE ALLOYS: BISMUTH-TIN-SILVER (BISN42AG0.4-1%) FOR LOW TEMPERATURE AND TIN-ANTIMONY (SNSB5-8.5) FOR HIGH TEMPERATURE

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ABSTRACT
The Tin-silver copper alloy SAC305 is the most commonly used in lead-free electronic assembly, especially in SMT process. Due to the evolution and the diversification of assembly technologies, needs for suitable lead-free alternative alloys have appeared.
While remaining a relatively small market, the demand for alloys with low melting temperature, to allow soldering of temperature sensitive components or substrates, has grown significantly in the last few years.
On the other hand, alloys with a significantly higher melting temperature than SAC305 are required in the first soldering process of the daughter boards, to avoid the reflow during the assembly of the main board.
After outlining the state of the art, the paper will describe the characteristics of the alloys with the expected properties, the development of suitable flux media according to their specificities, the solder pastes performance and the reliability of their solder joints.

Key words: low temperature, high temperature, bismuth-tin-silver, tin-antimony, wettability

INTRODUCTION
The tin-bismuth alloy Sn42Bi58 is eutectic with a melting point of 138°C. It has a high strength but is brittle and sensitive to shear-rate. Furthermore, when it is used with leaded substrates and/or leaded components, the risk to form crystals of Sn16Pb32Bi52 must be taken into account: with its melting point of 96°C, this compound may cause solder joint failures at low temperature. For the above-mentioned reasons, SnBi solder wires and solder pastes have been used in some low-cost assemblies for many years. Thanks to the implementation of the RoHS directive, the ban of the lead in assembly is effective in many countries and industries the risk to create very the low melting point intermetallic Sn16Pb32Bi52 is greatly reduced. Moreover, it has been showed that the addition of small amounts of silver (up to 1%) in the Sn42Bi58 alloy improved its mechanical properties: the high strain-rate ductility in tensile strength at a strain-rate of 10^{-2} sec^{-1} exceeds by at least 20% that of a Sn42Bi58 solidified at the same cooling rate [1]. The small amount of silver allows maintaining a low melting point. As far as thermal cycling is concerned, studies have shown the reliability of SAC305 BGAs soldered with SnBiAg solder paste (-20°C/+85°C, 4000 cycles) [2]. From the environmental point of view, bismuth is not considered toxic. Its availability is enough to cover some of the needs in electronic assembly. The main benefit to expect from the use of this alloy is the cost reduction brought by the following: typically 0.4 to 1% silver in the alloy compared with 3% silver in SnAg3Cu0.5, less energy consumption for the reflow equipment (lower temperature and shorter cycle time) and improved soldering yield for temperature sensitive components. Several studies were already realized to highlight the performance of the low-temperature solder paste: good printing and reflow performance with equivalent or better shear and pull strength than SnAg3Cu0.5 (SAC305) were reported [3].
On the other hand, lead-free alloys with higher melting point than SAC305 are still needed. First, to replace the high-lead content alloys used in power components manufacturing [4] and second, in microelectronics or stacking assemblies where a higher melting point may be required in first soldering process (i.e. daughter board). To answer the demand in such type of assembly, tin-antimony SnSb5 have been used. However the melting point difference compared to SAC305 is more significant with SnSb8.5 (Table 1). Thus, SnSb8.5 was chosen for the study.

Table 1. Melting point of different alloys

Alloy	Melting point (°C)	Melting point difference to SAC305
Sn42Bi58	138	-79
Sn42Bi57.6Ag0.4	138-140	-78
Sn42Bi57Ag1	139-140	-78
SnAg3Cu0.5	217	0
SnSb5	235	+18
SnSb8.5	241-248	+28

STUDY
A SAC305 type 3 (T3) solder paste was used as reference: 305-A. A tin-antimony SnSb8.5 type 3 paste, based on a similar chemistry as 305-A, but able to stand higher temperature was developped: 245-B.

An optimization of the no-clean SnBiAg0.4 type 3 paste which development was previously described in [5] was studied: SBA04-C. The same chemistry was used to prepare SBA1-C with SnAg57Ag1 type 3 powder and SB-C with Sn42Bi58 type 3 powder. A new chemistry was especially developed for the study and mixed with SnAg57Ag1 type 3 (SBA1-D) and Sn42Bi58 type 3 (SB-D). Minor adjustments in alloy content were made. The pastes characteristics are presented in Table 2.

Table 2. Pastes characteristics

Paste	Alloy	Alloy %	Viscosity
305-A	SAC305 T3	88	900
245-B	SnSb8.5 T3	88	920
SBA04-C	SnBiAg0.4 T3	90	900
SBA1-C	SnBiAg1 T3	90	890
SB-C	Sn42Bi58 T3	90	770
SBA1-D	SnBiAg1 T3	89.5	810
SB-D	Sn42Bi58 T3	89.5	720

Printing tests were performed at 25°C in a Dek Horizon 05 printer using the Efsot Verification board (EVB). This board was designed by Philips, Thomson and AB Mikroelektronik during the EFSOT project [6]. As shown in Figure 1 it consists in a 150x100mm double-sided 1.6mm high Tg FR4 board including a large range of components: from 0201 to 1206 passive components, several fine pitch BGAs, large heat sink packages, pin in paste connectors as well as several test patterns (printing pattern, surface insulation resistance, solderballing and wetting pattern).


Figure 1. EFSOT Verification Board (EVB)

A 120 microns laser cut stainless steel stencil and 250mm length squeegees were used. The minimum pressure according to printing speed was determined for each paste. Pastes 305-A, SBA1-D and SB-D need a lower pressure than 245-B and C pastes (Table 3). The printing quality was checked using the printing pattern criteria according to Philips Notation, which is fully described in the EFSOT project. Though the detailed table is not reported in this paper, the following observations were done: excellent printing quality and no tendency to smearing/slumping for 305-A, 245-B, SBA1-D and SB-D; tendency to slump after 4 to 5 boards without understencil cleaning for SBA04-C, SBA1-C and SB-C.

Table 3. Minimal pressure according to printing speed

Speed (mm/s) / Minimum pressure (kg)	50	100	150
305-A	3.2	5.4	6.8
245-B	4.0	6.0	8.0
SBA04-C	4.4	6.5	8.4
SBA1-C	4.0	6.0	8.0
SB-C	4.0	6.0	8.0
SBA1-D	3.0	4.6	6.4
SB-D	3.0	4.6	6.2

Solderballing performances were checked on a hotplate. The pastes were printed on alumina substrates through a 0.250mm thick stencil with two round openings of 5mm diameter, with a distance between centers of 25mm. The temperature of the hotplate was set at 250°C for SAC305, 280°C for SnSn8.5 and 180°C for SnBi and SnBiAg. Tests were realized with and without preheat. The solderballing classification ranks from class 1 to class 5, the balls being counted with 30x magnification according to the NF-C-90550 standard (Table 4). In addition, solderballing was performed, applying a “medium” thermal profile for each paste.

Table 4. Solderballing classification (NF-C-90550)

Class 1	5 solderballs maximum
Class 2	6 - 10 solderballs
Class 3	11 - 20 solderballs
Class 4	21 - 50 with possibility of a slight lisere
Class 5	> 50 solderballs with clusters and lisere

Solderballing result was class 1 (C1) for 305-A and 245-B pastes on the hotplate as well as in the oven (Table 5).

Table 5. Solderballing results 305-A and 245-B

Solderballing	Direct	Preheat 2min 160°C	Preheat 2min 160°C	Preheat 2min 160°C	Oven
305-A	C1	C1	C1	C1	C1
245-B	C1	C1	C1	C1	C1

As expected, due to the lower surface tension of the alloy during melting, and due to the presence of more solvents which evaporate at a slower rate than for SAC pastes, the tin-bismuth and tin-bismuth-silver pastes exhibited significantly less good results (Table 6). The results were acceptable for SBA04-C but many small balls (lisere) were sometimes observed for the other pastes: some typical pictures are reported in Figure 2.

Table 6. **S**olderballing results on tin-bismuth based pastes

Solderballing	Direct	Preheat 1min 100°C / 30s 120°C	Oven
SBA04-C	C1	C4	C3
SBA1-C	C5	C4	C5
SB-C	C4	C3	C5
SBA1-D	C4	C4	C5
SB-D	C5	C5	C5

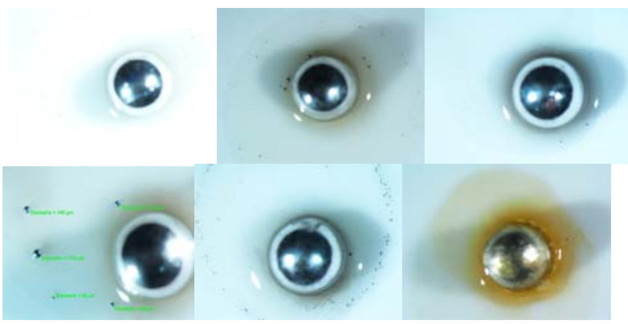


Figure 2. Examples of pictures after Solderballing Test

Wettability was assessed on EVB using its wetting pattern. The wetting pattern is described in Figure 3 and is made of five pads of 5mm with corresponding stencil openings of respectively 5mm, 3mm, 1mm, 0.65mm and 0.285mm diameter.

Figure 3. Wetting pattern description

Three finishes were used to evaluate the wetting performance:

- Organic Solderability Preservative (OSP),
- Chemical tin (Sn),
- Electroless Nickel Immersion Gold (ENIG).

The test boards were manufactured two months before the test and remained in their original sealed bags until testing.

In order to simulate a double-reflow assembly, some boards were submitted to one prior reflow under air to pre-oxidize the finishes. A severe discoloration occurred on all copper OSP boards after this step whereas no noticeable change was observed for the other finishes (Figure 4). Chemical tin boards were always submitted to a prior reflow.

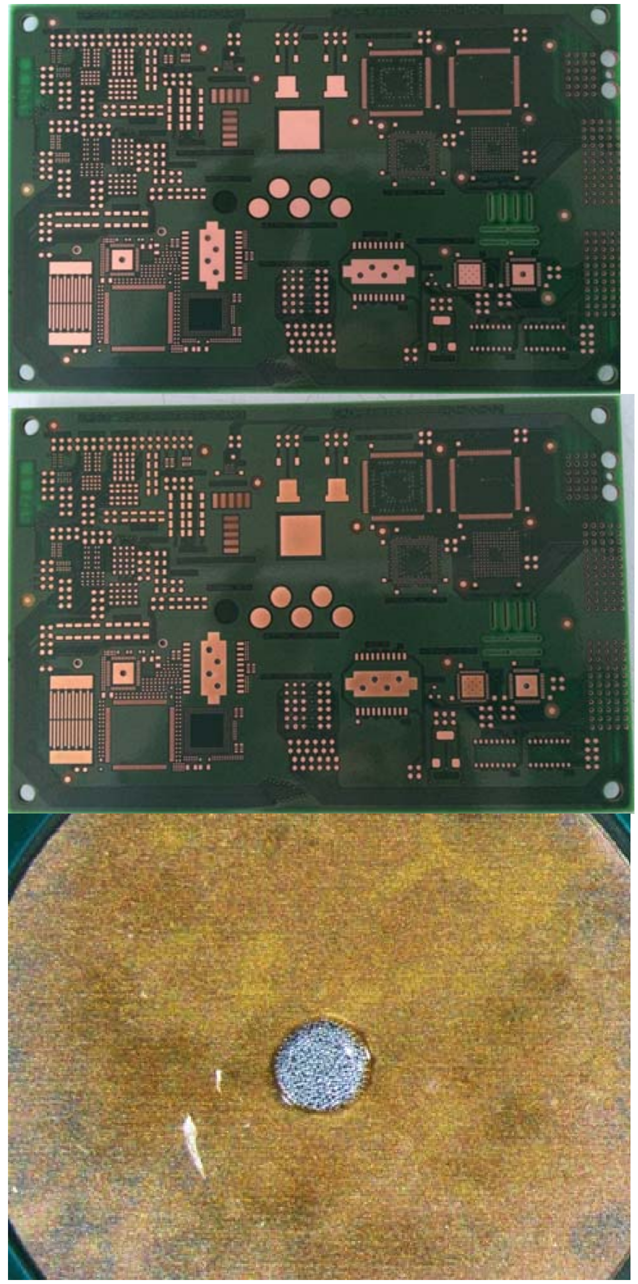


Figure 4. EVB OSP finish a) prior to reflow, b) after pre-reflow, c) 0.65mm wetting area detail after pre-reflow

The pastes were printed through a 125µm (5mil) thick stencil. The printing quality on small wetting areas was checked by visual control. The initial diameter (Di) was measured under magnification on a few boards to check the good correlation between openings and printed areas: some measurements are shown in Figure 5. Though a slight cold slump tendency was observed for SBA04-C, SBA1-C and

SB-C compared to the other pastes (7% maximum) it was decided not to take into account the real diameter in order to save time and to simplify the calculation.

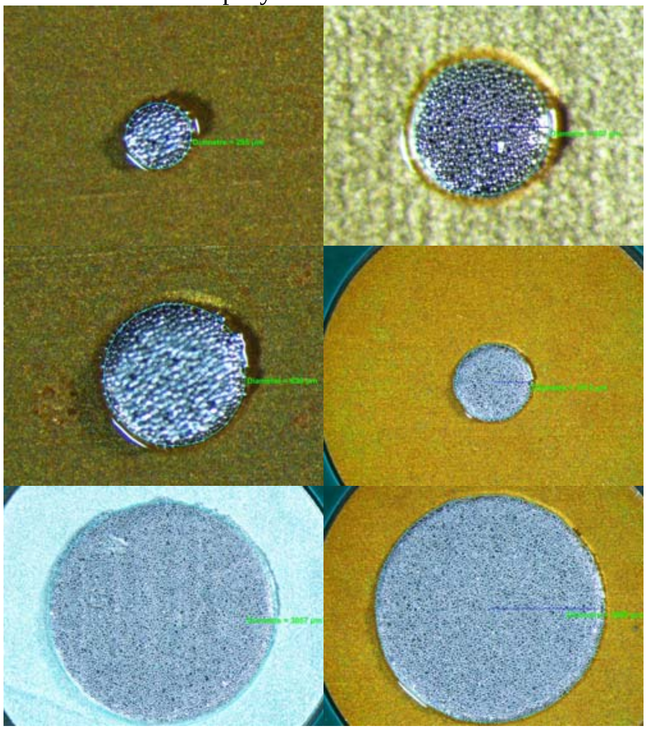


Figure 5. Diameter after printing

A few 0603 and 1206 passive components were placed to observe the solder joint shape and appearance according to the paste type, reflow conditions and finishes (Figure 6).

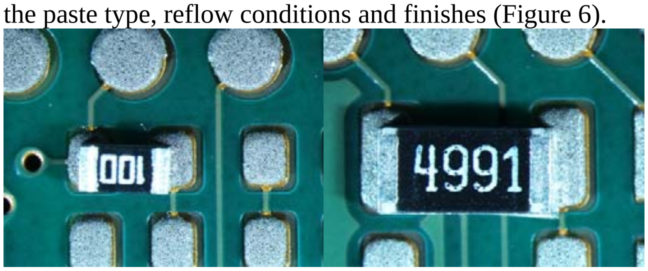


Figure 6. Passive 0603 and 1206 after placement

For each type of paste a "medium" thermal profile was defined, the boards were then soldered in air atmosphere using a 5 zones oven. The characteristics of each type of profile are summarized in Table 7 and Table 8. The graph for SnBi and SnBiAg solder pastes is reported in Figure 7.

Table 7. Thermal Profile Characteristics for SAC305 and SnSb8.5 solder pastes

	Reflow profile SAC305 - SnSb8.5
Total time to peak	270s 270s
Time above liquidus or TAL	85s 75s
Peak temperature	248°C 271°C
Oven temperature set-up (°C)	120/160/190/225/260 170/190/200/240/285
Oven speed set-up	40cm/min 40cm/min

Table 8. Thermal Profile Characteristics for SnBi and SnBiAg solder pastes

	Reflow profile SnBi-SnBiAg
Total time to peak	215s
Time above 138°C (TAL)	59s
Peak temperature	177°C
Oven temperature set-up (°C)	80/100/110/130/180
Oven speed set-up	45cm/min

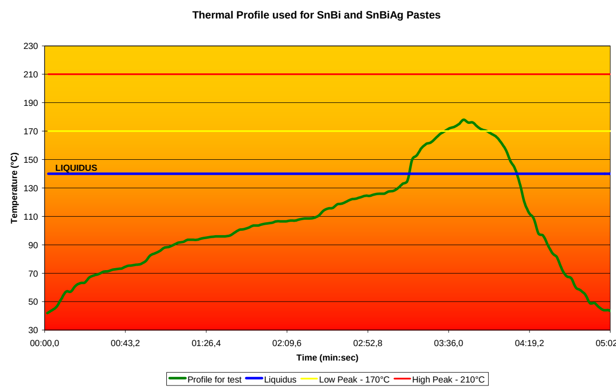


Figure 7. Thermal Profile Graph for SnBi and SnBiAg solder pastes

The diameter after reflow or final diameter (Df) was measured for every wetting pad and any comment regarding poor wetting, solderballing or graping was recorded. The wetting percentages Df/Di are presented in Figure 8 for the SAC305 Reference Paste (305-A) and for the tin-antimony SnSb8.5 (245-B). Chemical Tin exhibits the best wetting performance compared to OSP, the difference is higher on small deposits (250 and 650 microns). 245-B has generally a lower wetting than 305-A.

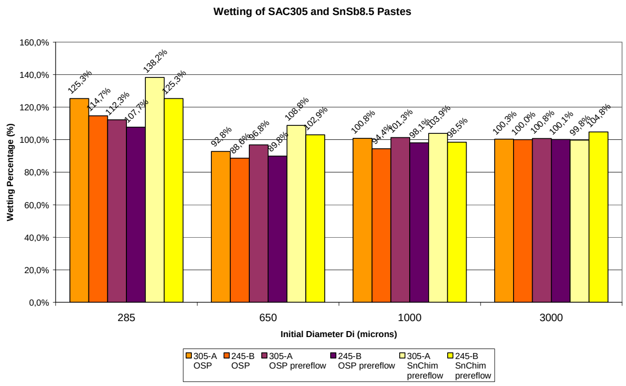


Figure 8. Wetting Comparison between 305-A and 245-B

For low temperature solder pastes, the first test consisted in the comparison on OSP finish. The details are reported in Table 9 and Figure 9. The results were above 100% for the smaller opening of 0.285mm and below or slightly below 100% for the larger ones. No clear influence of flux chemistry and silver content (SBA04-C / SBA1-D) was observed. One board was left at room temperature (23°C/55% relative humidity) during 18 hours before reflow, which did not change the wetting behavior. One board was submitted to a pre-reflow using the SAC305 parameters and described above: many microballs were observed for the 285 and 650 microns openings. Another board was submitted to a harsher profile (longer profile with soak zone at 180°C): the paste did not wet the surface at all but coalesced into a single ball (Figure 10, Figure 11); the result was noted “5%” in order to be visible in the graph.

Table 9. Wetting results on OSP

Diameter (microns)	305-A OSP	305-A OSP prereflow	SBA04-C OSP	SBA04-C OSP 18h AP	SBA1-D OSP	SBA04-C OSP prereflow	SBA04-C OSP prereflow hot
285	357	320	353	372	380	310 many balls	single ball - no wetting
650	603	629	635	568	632	541 many balls	single ball - no wetting
1000	1008	1013	945	950	974	873	single ball - no wetting
3000	3010	3023	2982	2967	2958	2906	single ball - no wetting
Df/Di (%)	**305-A OSP**	**305-A OSP prereflow**	**SBA04-C OSP**	**SBA04-C OSP 18h AP**	**SBA1-D OSP**	**SBA04-C OSP prereflow**	**SBA04-C OSP prereflow hot**
285	125,3%	112,3%	123,9%	130,5%	133,3%	**108,0%**	**5,0%**
650	92,8%	96,8%	97,7%	87,4%	97,2%	**83,2%**	**5,0%**
1000	100,8%	101,3%	94,5%	95,0%	97,4%	87,3%	**5,0%**
3000	100,3%	100,8%	99,4%	98,9%	98,6%	96,9%	**5,0%**

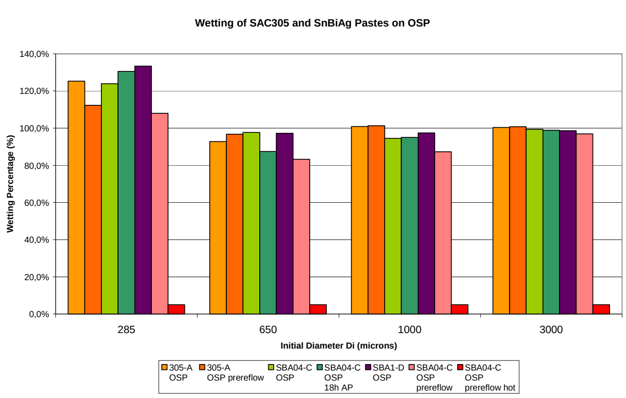


Figure 9. Wetting results on OSP

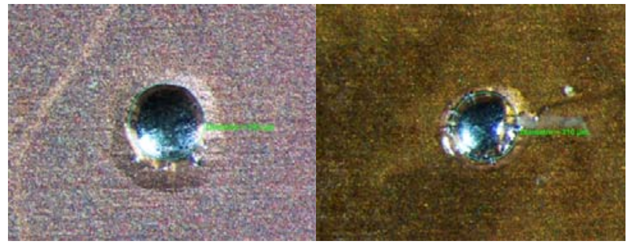


Figure 10. Appearance of SBA04-C on 0.285mm opening. a) No prior reflow, b) standard SAC305 prior reflow

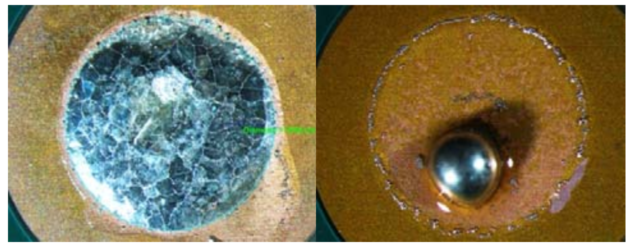


Figure 11. Appearance of SBA04-C on 3.0 mm opening. a) Standard SAC305 prior reflow, b) harsh SAC305 prior reflow

The behaviour of low temperature pastes SBA04-C and SBA1-D were compared on chemical tin finish with a prior reflow: the wetting was significantly larger for the tin-bismuth-silver pastes than for the SAC305 reference (Figure 12). However, a strong dewetting was observed for SBA04-C on the smallest deposits when the harsh pre-reflow was used.. This phenomenon did not occur for SBA1-D although a few microballs were seen on the top of the alloy (Figure 13).

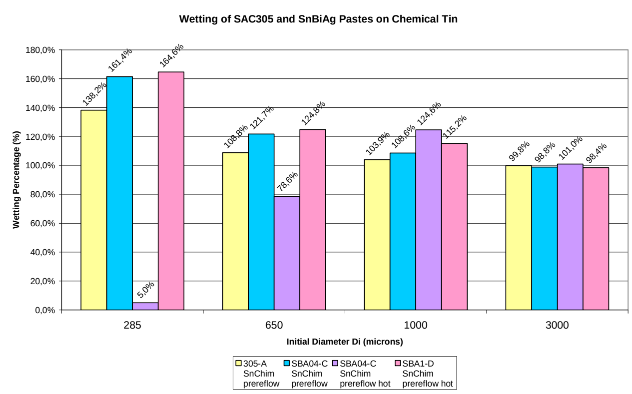


Figure 12. Wetting results on chemical tin

Figure 13. Appearance of SnBiAg pastes on 0.285mm opening with prior reflow under harsh profile. a) SBA04-C, b) SBA1-D

The wettability was assessed on ENIG finish for all the low temperature pastes: the results were excellent and significantly higher than 100% for all the boards; more than 150% for 0.285mm openings and 120 to 140% for 0.650mm and 1.00mm. The performance of the paste SBA04-C was similar with and without an idle time of 18 hours at room temperature. The results were lower for SBA1-C on 0.285mm opening (154.4%) than for the other SB and SBA pastes (180 to 208%). The best wetting was achieved with SBA1-D (Figure 14).

The 0603 and 1206 passive components were inspected after reflow. The solder fillet shape was within IPC-A-610 criteria for 305-A and 245-B: pictures are reported in Figure 15.

For the low temperature solder pastes, the solderability of components was in accordance with the wetting performances: good fillet shape on OSP without pre-reflow but highly insufficient solderability when the OSP substrates were pre-reflowed using the harsh profile (Figure 16 and 17).

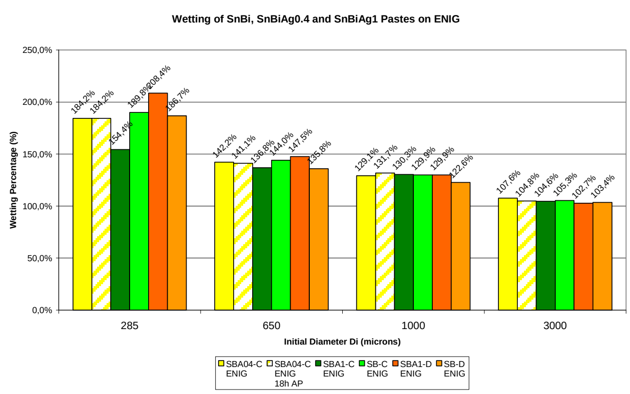
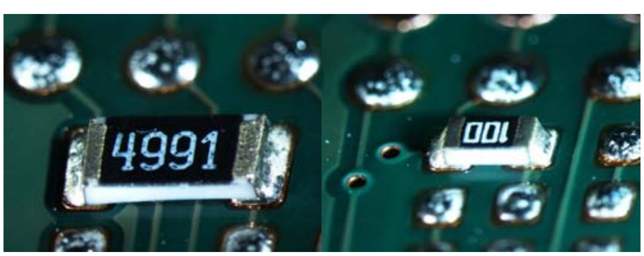
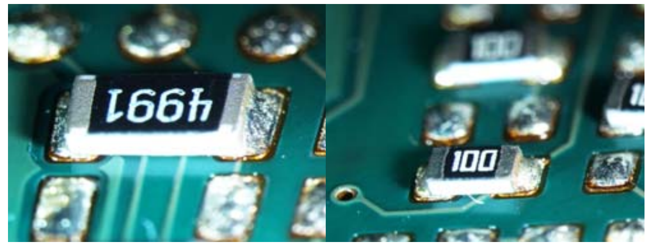


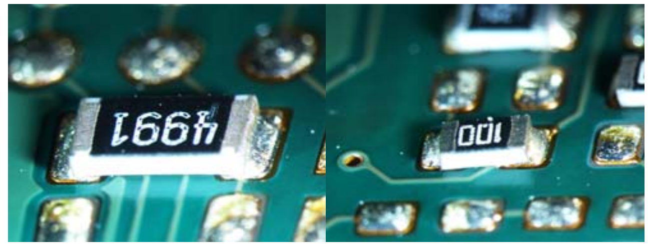
Figure 14. Wetting results on ENIG



305-A / 1206/OSP 305-A / 0603/OSP

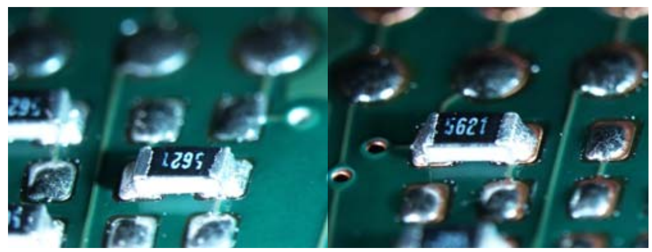


245-B / 1206/OSP 245-B / 0603/OSP



245-B / 1206 /OSP prereflow 245-B / 0603 /OSP prereflow

Figure 15. 305-A and 245-B Solderability on OSP



a) Sn b) OSP

Figure 16. SBA04-C Solderability of 0603 on substrates submitted to harsh pre-reflow

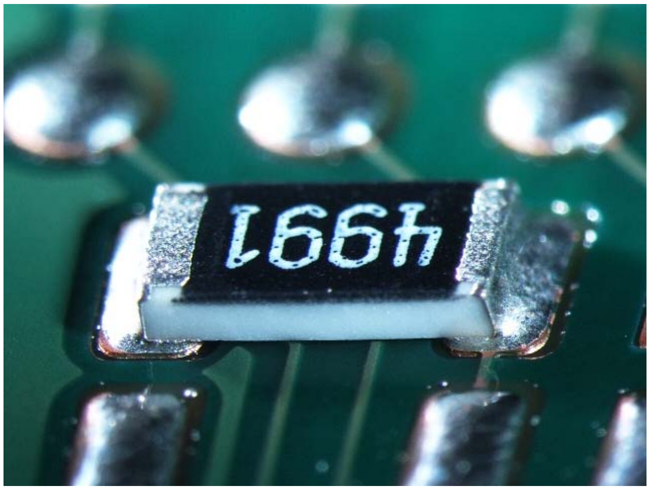
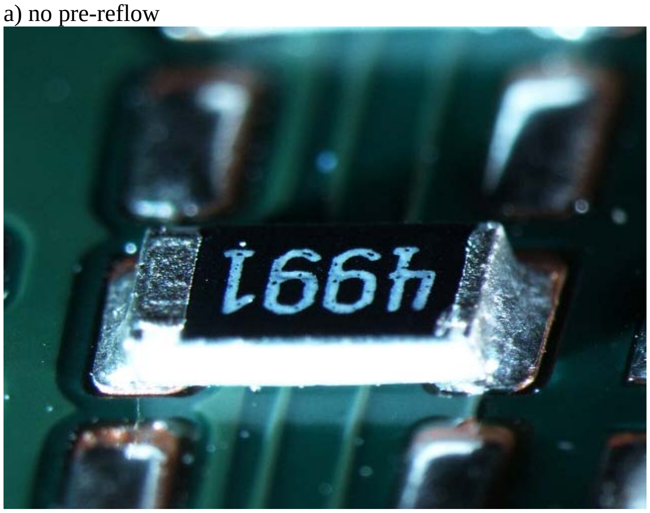
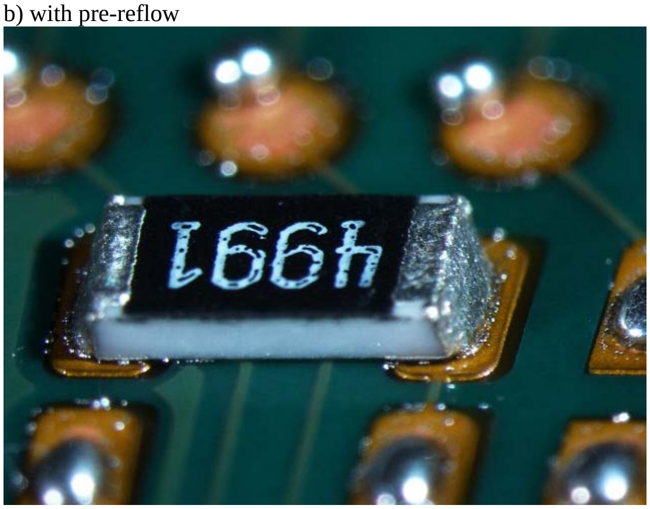

a) no pre-reflow

b) with pre-reflow

c) with harsh pre-reflow

Figure 17. SBA04-C Solderability of 1206 on OSP

CONCLUSION

A high temperature solder paste based on SnSb8.5 was developed for the study. This paste showed good results in terms of printing, solderballing and wetting. In fact, its performance was very similar to SAC305 solder paste with a slightly lower wettability.

The low temperature pastes based on “C” chemistry were sensitive to cold and shear slump. The same alloys combined with “D” chemistry were not sensitive to slump and allowed higher printing speed thanks to the lower minimum pressure needed.

The solderballing results were relatively poor for all the low temperature pastes compared to SAC305, this trend is known and is due to the type of alloy itself (higher oxide content, sensitivity to oxidation, lower surface tension). However, only a few solderballs were detected on the boards when using standard reflow conditions.
The wettability of low temperature pastes was excellent on ENIG finish, good on tin finish and relatively good on fresh copper OSP.

Neither “C” nor “D” chemistries were sensitive to humidity when stored 18 hours at room temperature, leading to the same wetting performance with and without idle time.
Some dewetting was clearly observed on OSP and on chemical tin when the boards were submitted to a prior reflow. The use of a harsh profile prior to the test totally prevented the alloy to wet the copper OSP.
It was not possible to rank the pastes neither according to the alloy type (SnBi58, SnBiAg57.60.4, SnBi57Ag1) nor according to the flux chemistry (C or D) in terms of solderability as there was no clear trend.
Some investigations to understand the wetting issues encountered on low temperature solder pastes in specific conditions have already started.

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