Performance of China Alloy SnAgCuCe in Reflow Soldering

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ABSTRACT
Work on assisting China's Ministry of Information Industry (MII) to assess the performance of a solder paste using the China alloy Sn3.0Ag0.5Cu0.019Ce (SACCe) was completed. Two Indium fluxes were incorporated as controls. Ce showed no effect on paste printing, slump, or probe testability on flux residue for SAC system. The difference between SACCe and SAC mainly resides in soldering. SACCe exhibits a slightly lower solder beading rate, comparable voiding, a considerably higher tombstoning rate, and is more prone to oxidation hence wets poorer under harsh reflow conditions. No difference in IMC structure or growth rate can be discerned for joints formed on either Cu or NiAu. Overall, China alloy is acceptable in reflow applications. The paste made from the China alloy exhibits a poorer print and a considerably narrower reflow window than the two paste controls.

Key Words: China, solder, solder paste, reflow, lead-free, SnAgCu, SnAgCuCe

INTRODUCTION
The world is moving quickly toward green manufacturing. In Japan, the home electronics recycling law came into force in April 2001. In Europe, the "restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS) took effect on July 1st, 2006. Those legislation activities drove the electronic industry into lead-free soldering, with SnAgCu (SAC) system being the dominant recommended choice of solder alloys. Being the most rapidly growing manufacturing country, China also drafted RoHS-like law, with target effective date as March 1st, 2007. However, different from those earlier legislation activities, China may specify the lead-free alloys allowed, particularly the alloys doped with Cerium (Ce). Thus it is extremely critical to assure those specified alloys can perform properly. This work is an effort to assist China government in assessing the performance of China alloy in reflow applications. In this study, the China alloy, 96.5Sn3Ag0.5Cu0.019Ce, was benchmarked against Sn3Ag0.5Cu (SAC305) for its performance for reflow applications. The results are presented and discussed below.

EXPERIMENTAL
1. Materials
A 96.5Sn3Ag0.5Cu0.019Ce (SACCe) solder paste sample, labeled as Gold Arrow, was provided by China's Ministry of Information Industry (MII) for performance evaluation. This SACCe alloy was tested against SAC305 alloy. Since the new flux is not available for SAC305 solder paste, two commercial fluxes, A and B, were employed to make both SACCe and SAC305 solder pastes, as shown in **Table 1**. The difference in behavior of SACCe and SAC305 can be determined by comparing pastes with the same flux but different alloys. The effect of Ce on SAC305 performance is assessed when the same effect is observed for both flux systems. The difference between new flux and the commercial fluxes is also assessed by comparing the new flux with the commercial pastes using SACCe alloy. For convenience, SAC305 may also be denoted as SAC in this study.

2. Tests
The performance was evaluated on the following tests.

Table 1 - Lead-free solder pastes tested

Flux of Solder Paste	Alloy	Solder Paste Code	Powder Type	Metal Load (wt %)
Gold Arrow	96.5Sn3Ag0.5Cu0.019Ce	GA	3	89.5
Indium A (No-Clean)	96.5Sn3Ag0.5Cu0.019Ce	Paste A-Ce	3	89
Indium A (No Clean)	96.5Sn3Ag0.5Cu	Paste A	3	89
Indium B (No Clean)	96.5Sn3Ag0.5Cu0.019Ce	Paste B-Ce	3	89
Indium B (No Clean)	96.5Sn3Ag0.5Cu	Paste B	3	89

Printability

A stencil pattern with area ratio (area of open to area of aperture wall) of apertures ranging from 0.30 to 0.85 was used in this printability test, as shown in **Figure 1**. The thickness of the electroformed stencil is 5 mils (127 μ).

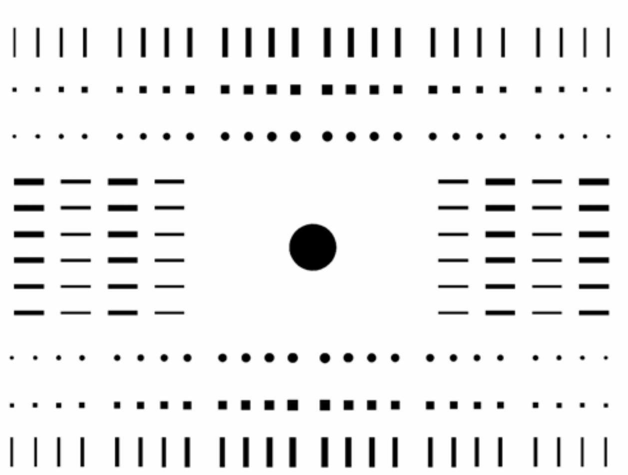


Figure 1 - Stencil pattern for printability test. The stencil thickness is 5 mils (127 μ). The area ratios (area of open to area of aperture wall) of all series of rectangular apertures, round apertures, and square apertures are 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, and 0.85.

The printing test was conducted with the following procedure.

1) Run 25 prints; evaluate 1st, 5th, 25th prints.
2) Pause 1 hr
3) Repeat step 1)
4) Pause 4 hrs
5) Repeat step 1)
6) Knead 200 prints
7) Repeat step 1)
8) Record the largest area ratio showing partial release or clogging under 20X optical microscope.

Note: No wiping on each of 25 prints. Only a single dry wiping (with vacuum) after each 25th print. After 200 kneading strokes, a thorough stencil cleaning (with IPA and tower paper, tooth brush) plus machine wiping was conducted.

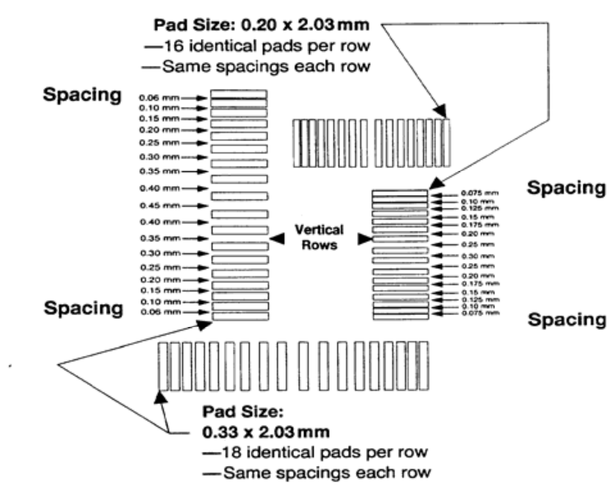


Figure 2 - IPC-A-20 stencil pattern for slump test. Stencil thickness is 0.10 mm.

Slump

1) Print solder paste using a 0.10 mm thickness stencil with the IPC slump test pattern (IPC-A-20, as shown in **Figure 2**) onto a ceramic coupon.
2) Place coupons at 150ºC/10 min.
3) Check minimum spacing without bridge.

Wetting (Dewetting)

The wetting behavior can be determined by examining the extent of dewetting of a large area print. The surface tension will drive the liquid solder to pull back, unless it wets quickly to the base metal upon reflow.

1). Stencil pattern shown in **Figure 3** is used for dewetting evaluation. The circle pattern exhibits a gradual decreasing diameter, with the diameter being 85 mils (2.16 mm), 56.5 mils (1.44 mm), 33 mils (0.88 mm), and 16.6 mils (0.42 mm), respectively. The stencil thickness is 5 mils (127 μ).

2). FR-4 test coupons with 4 different surface finishes are used, including organic solderability preservative (OSP), immersion silver (ImAg), immersion tin (ImSn), and electroless nickel immersion gold (ENIG).

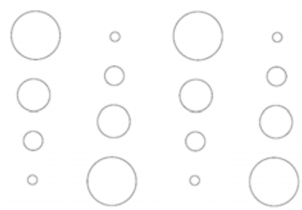


Figure 3 - Stencil pattern for wetting (dewetting) test. The circle diameter is 0.42 mm, 0.88 mm, 1.44 mm, and 2.16 mm, respectively. The stencil thickness is 127 μ.

3). Three reflow profiles are used - short, medium, and long, as shown in **Figure 4**. The reflow atmosphere used is air.

4). The paste was printed onto coupons, conditioned at RT/90%RH for 1 hour, followed with reflow. The reflowed coupon is then inspected for dewetting. The largest circle was used to exemplify the wetting performance of solder paste tested.

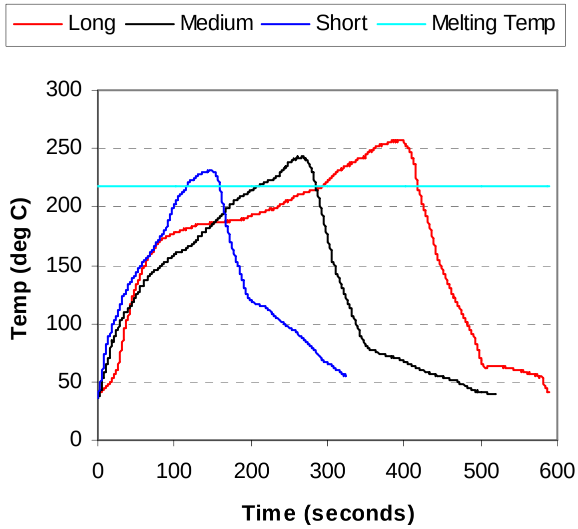


Figure 4 - Reflow profiles used in this study.

Wetting (Spreading)

1). Stencil pattern shown in **Figure 5** is used for spreading evaluation. The pitch of each set is 20 mils (0.5 mm), and the length of each rectangular aperture is 50 mils (1.27 mm). The spacing is 7 mils (178 µ), 8 mils (203 µ), 9 mils (229 µ), 10 mils (254 µ), 11 mils (279 µ), 12 mils (305 µ), and 13 mils (330 µ) for each set, respectively. The stencil thickness is 5 mils (127 µ).

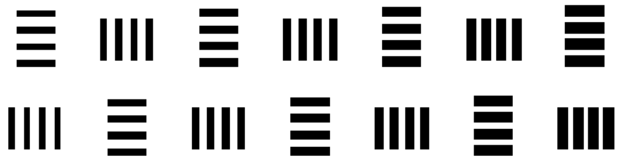


Figure 5 - Stencil pattern for spreading test. The pitch of each set is 20 mils (0.5 mm). The spacing is 7, 8, 9, 10, 11, 12, and 13 mils for each set, respectively. The stencil thickness is 127 µ.

2). FR-4 test coupons with 4 different surface finishes are used, including organic solderability preservative (OSP), immersion silver (ImAg), immersion tin (ImSn), and electroless nickel immersion gold (ENIG).
3). Three reflow profiles are used - short, medium, and long, as shown in **Figure 4**. The reflow atmosphere used is air.
4). The paste was printed onto coupons, conditioned at RT/90%RH for 1 hour, followed with reflow. The reflowed coupon is then inspected for spreading. The number of total bridges formed is counted for each coupon. The more the bridges formed, the better the wetting ability of solder paste.

<u>Solder Balling</u>

1). Stencil pattern shown in **Figure 3** is used for solder balling evaluation.
2). Three reflow profiles are used - short, medium, and long, as shown in **Figure 4**. The reflow atmosphere used is air.
3). The paste was printed onto ceramic coupons, conditioned at RT/90%RH for 1 hour, then followed with reflow. The reflowed coupon is then inspected for solder balling.

<u>Voiding</u>

1). BGA substrate with 24x24 pads, with 40 mils (1.02 mm) pitch, 25 mils (635 µ) Cu pad diameter, as shown in **Figure 6**. The microvia is 4 mils (102 µ) in diameter, and 4 mils (127 µ) in depth.
2). A dummy BGA is first prepared by printing solder paste under study onto BGA substrate using a stencil with 4 mils (102 µ) thickness, then followed by placing SAC387 ball with 25 mils (635 µ) diameter. This device is then reflowed with short profile to form a dummy BGA. (see **Figure 7**).
3). The solder paste in study is printed again onto a fresh BGA substrate using the 4 mils (102 µ) stencil, then conditioned at RT/90%RH for 1 hour.
4). Place the dummy BGA made earlier onto the BGA substrate printed with solder paste.
5). Reflow the sandwiched device using a short profile under air.
6). Voiding is examined with X-ray for all joints. The software used is PCB Inspector, version 4

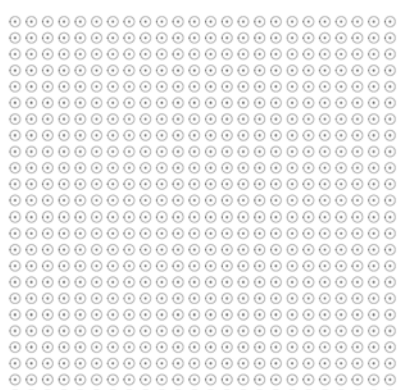


Figure 6 - BGA substrate with 24x24 pads, with 40 mils (1.02 mm) pitch, 25 mils (635 µ) Cu pad diameter, as shown in Figure 6. The microvia is 4 mils (102 µ) in diameter, and 5 mils (127 µ) in depth.

Flux entrapped in the dead corner in microvia is the primary voiding mechanism for BGA with via-in-pad design [1, 2]. In the voiding test, via-in-pad design and solder paste were used on both sides of solder sphere in simulated BGA device in order to augment the voiding potential.

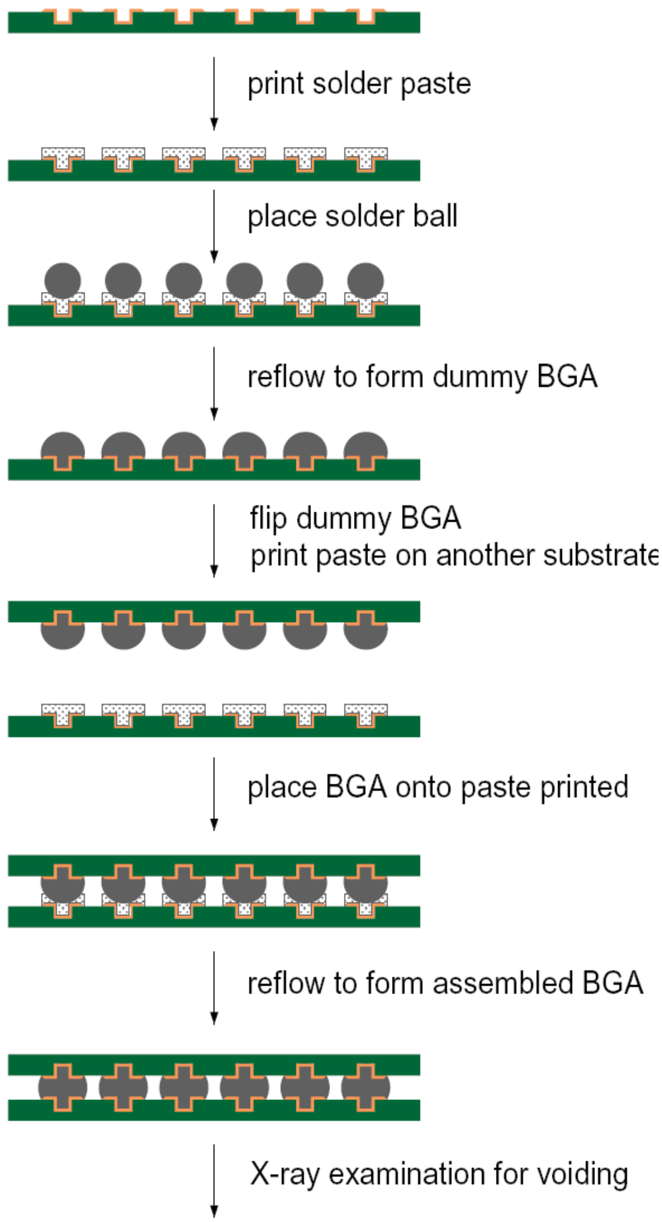


Figure 7 - Procedure for solder paste voiding test.

Solder Beading

1). The test board used is shown in **Figure 8**, with OSP surface finish.
2). The paste was printed with a 5 mils (127 μ) thick stencil. Chip capacitor 0603 (179 /PCB) and chip capacitor 0402 (240/PCB) were then placed onto the red bracket region.
3). The board was then conditioned at RT/90%RH for 1 hour, followed by reflow in air with short profile.
4). The solder beading rate is expressed as percentage of all chips tested.

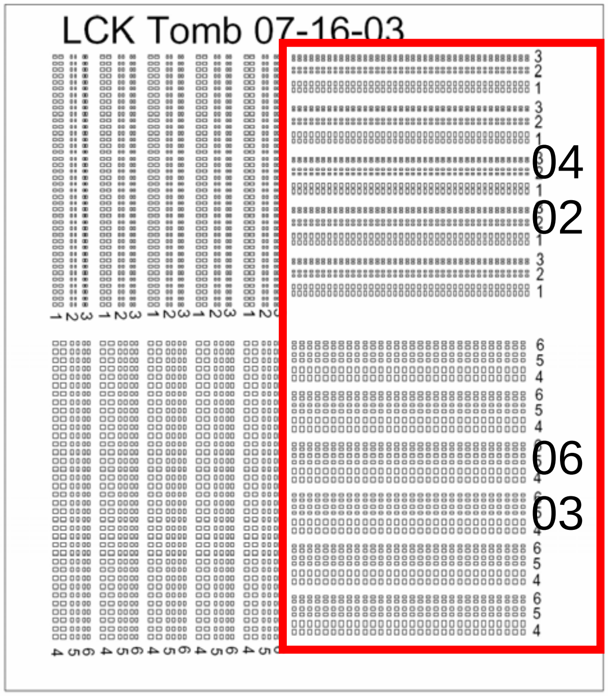


Figure 8 - Test board used for solder beading and tombstoning study. Test patterns designed for 0402 and 0603.

Tombstoning

1). The test board used is shown in **Figure 8**, with OSP surface finish.
2). The paste was printed with a 5 mils (127 μ) thick stencil. Chip capacitor 0603 (179 /PCB) and chip capacitor 0402 (240/PCB) were then placed onto the red bracket region.
3). The board was then conditioned at RT/90%RH for 1 hour, followed by reflow in vapor phase reflow oven in order to magnify the defect rate. The fluid boiling is 255-260ºC.
4). The tombstoning rate is expressed as percentage of all chips tested.

Probe Testing

1). Paste was printed onto top side of board using 10 mils thick stencil, and reflowed with medium profile.
2). The reflowed boards were put aside for 24 hrs, and probed at the through-hole pads (enclosed by red brackets) with spear probe for electrical continuity.
3). Both sides are probed, with 900 test spots for each side. Three boards were used for each paste. Overall 5400 through-hole spots were tested for each paste.
4). The average of first pass rate of front side and back side is reported as Probing 1st pass rate.

Figure 9 - Test board used for probe testing. Only through-hole regions were tested.

Intermetallic Formation

1). The OSP and NiAu FR-4 test coupons used in dewetting test were also used for intermetallics study.
2). For each surface finish, print solder paste onto 3 sets of coupon using procedure specified in dewetting test. Reflow with medium profile under air.
3). Set 1 was cross-sectioned as un-aged, fresh sample.
4). Set 2 was aged at 150ºC for 10 days, then cross-sectioned.
5). Set 3 was aged at 150ºC for 20 days, then cross-sectioned.
6). All cross-sectioned samples were examined with SEM and EDS.
7). The composition and thickness of intermetallic layers at interface of solder and base metal were determined. The thickness was determined by taking the average of 8 thickness readings evenly spaced on the SEM pictures.

RESULTS

1. Printability

The print performance is inversely proportional to the largest area ratio clogged, as shown in **Figure 10 to 12**. In general, the print performance degraded with increasing pause time; GA being most sensitive and Paste A and Paste IA-Ce being the least sensitive to pause time.

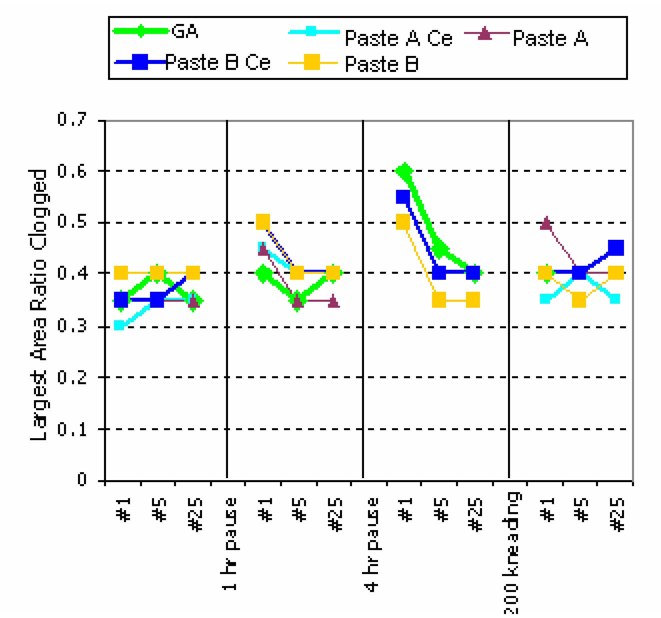


Figure 10 - Print performance for aperture parallel to print direction

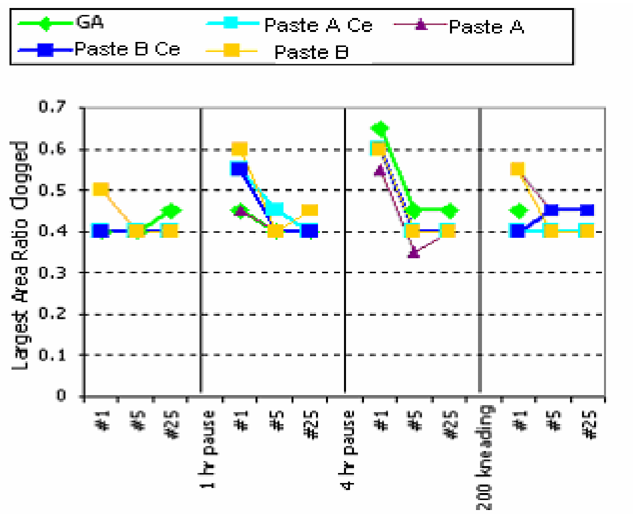


Figure 11 - Print performance for aperture vertical to print direction

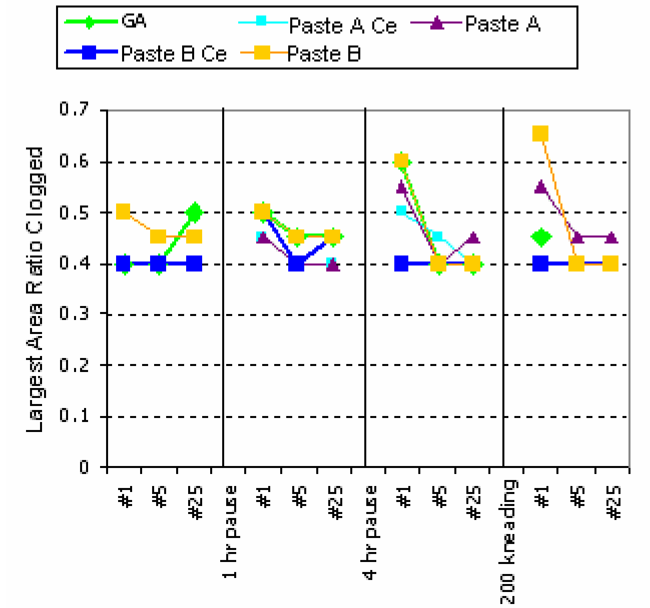


Figure 12 - Print performance for round aperture

Figure 13 shows comparison of first print of horizontal aperture after 4 hours pause. Continuous printing helped the paste to recover the print performance, as shown by the 200 kneading effect in most cases. Ce showed no effect on printability.

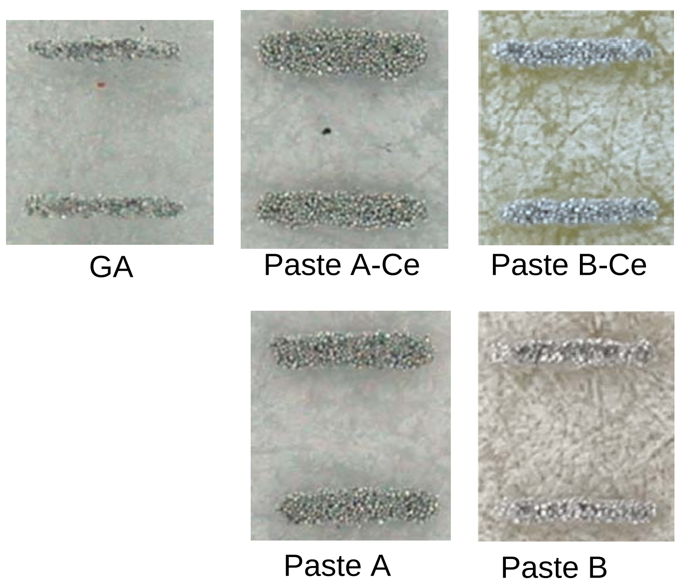


Figure 13 - Comparison of first print of horizontal aperture after 4 hours pause.

2. Slump

All pastes showed no slump at 150ºC, as shown in **Figure 14.**

3. Wetting (Dewetting)

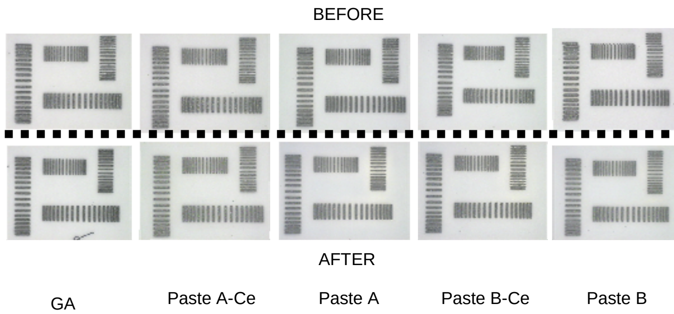


Figure 14 - Solder paste slump samples after conditioned at 150ºC for 10 minutes.

4. Wetting (Dewetting)

1). Short Profile
The dewetting behavior on OSP using short profile is shown in **Figure 15**. Other than the GA sample, the Ce-system showed full wetting as SAC system. About 15% area showed dewetting in GA sample.

Similar dewetting behavior of GA sample using short profile is also observed on ImAg and ImSn samples, as shown in **Figure 16** and **Figure 17**, respectively. Under the same condition, all other pastes showed full wetting on ImAg and ImSn, indicating that Ce has no effect on dewetting under these conditions.

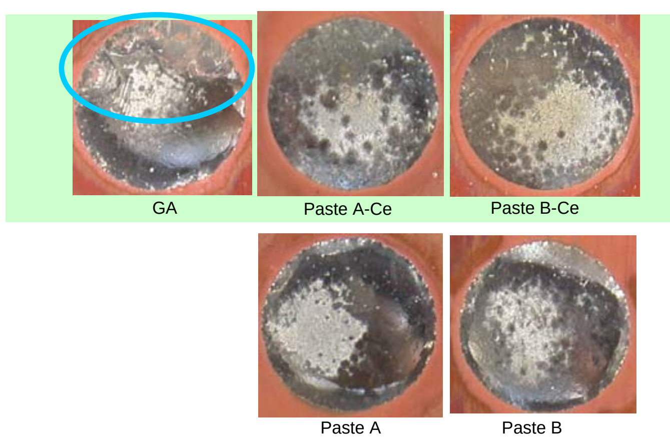


Figure 15 - Dewetting behavior of solder pastes on OSP using short profile.

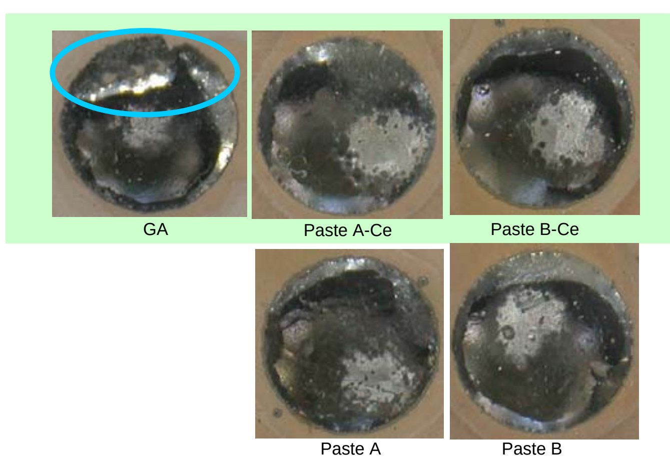


Figure 16 - Dewetting behavior of solder pastes on ImAg using short profile.

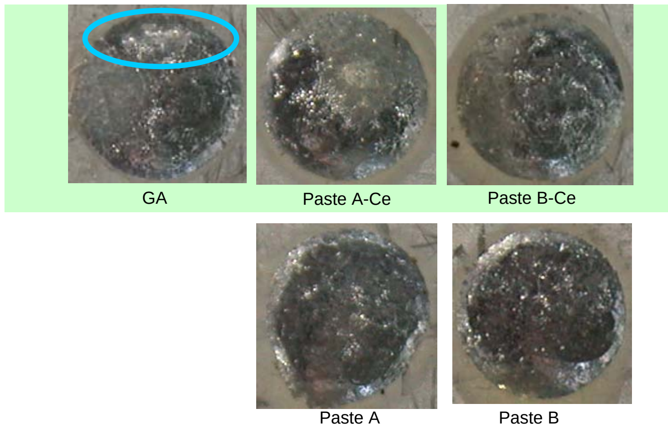


Figure 17 - Dewetting behavior of solder pastes on ImSn using short profile.

No dewetting can be discerned in ENIG samples. GA showed slightly less spreading than the other pastes, as shown in **Figure 18**.

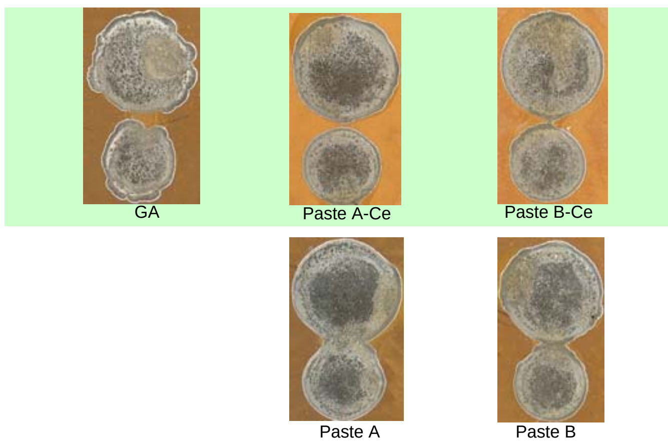


Figure 18 - Dewetting behavior of solder pastes on ENIG using short profile.

2). Medium Profile

The dewetting behavior on OSP using medium profile is shown in **Figure 19**. Other than the GA sample, the Ce-system showed full wetting as SAC system. GA sample showed about 20% dewetted area.

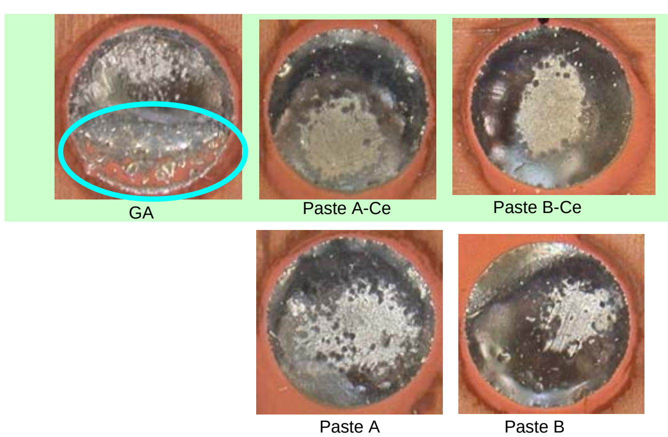


Figure 19 - Dewetting behavior of solder pastes on OSP using medium profile.

Similar dewetting behavior of GA sample using medium profile is also observed on ImAg and ImSn samples, as shown in **Figure 20** and **Figure 21**, respectively. Under the same condition, all other pastes showed full wetting on ImAg and ImSn, indicating that Ce has no effect on dewetting under these conditions.

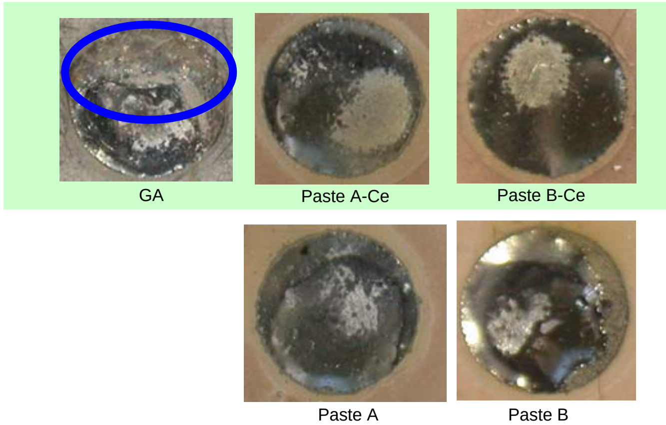


Figure 20 - Dewetting behavior of solder pastes on ImAg using medium profile.

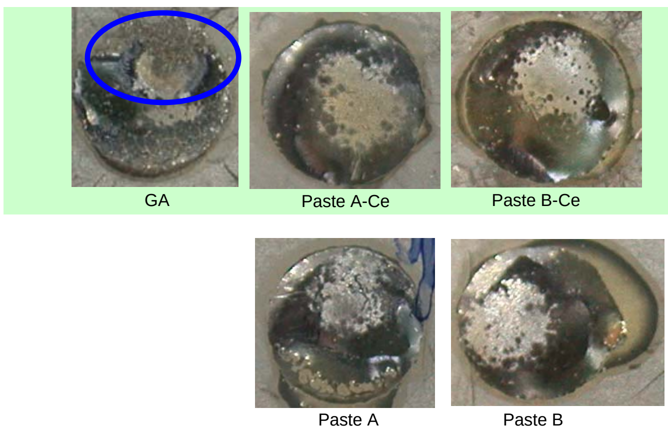


Figure 21 - Dewetting behavior of solder pastes on ImSn using medium profile.

Again, no dewetting can be discerned in ENIG samples, as shown in **Figure 22**. GA showed considerable less spreading than the rest.

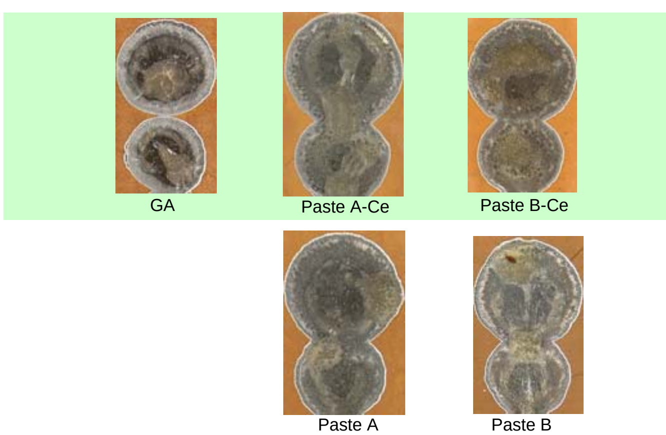


Figure 22 - Dewetting behavior of solder pastes on ENIG using medium profile.

3). Long Profile

The dewetting behavior on OSP using long profile is shown in **Figure 23**. Other than the GA sample, the Ce-system showed slightly less wetting than SAC system, as reflected by the rough edge of solder circles. GA sample showed about 30% deweted area.

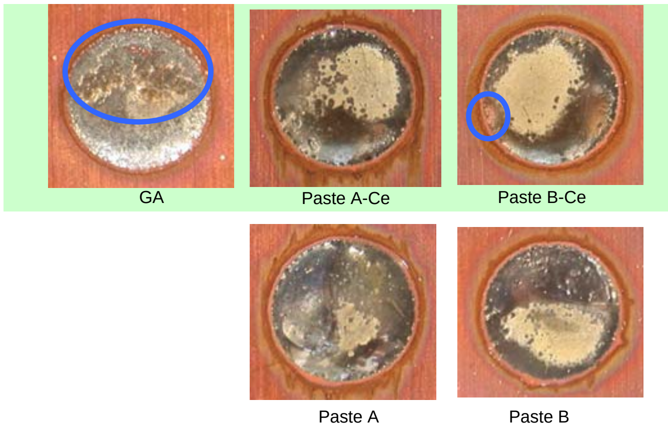


Figure 23 - Dewetting behavior of solder pastes on OSP using long profile.

On ImAg samples, as shown in **Figure 24**, Ce-system showed dewetting on some corners, thus wet poorer than SAC system at long profile. GA showed the most dewetting, with about 40% area dewetted.

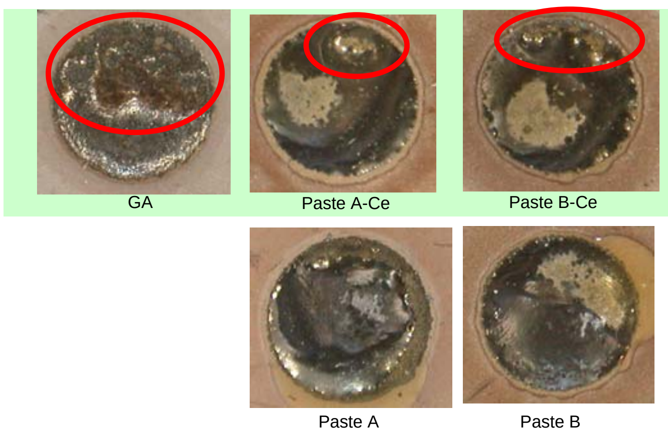


Figure 24 - Dewetting behavior of solder pastes on ImAg using long profile.

On ImSn samples, as shown in **Figure 25**, Ce-system showed more dewetting, thus wet poorer than SAC system at long profile. GA showed the most dewetting, with about 40% area dewetted.

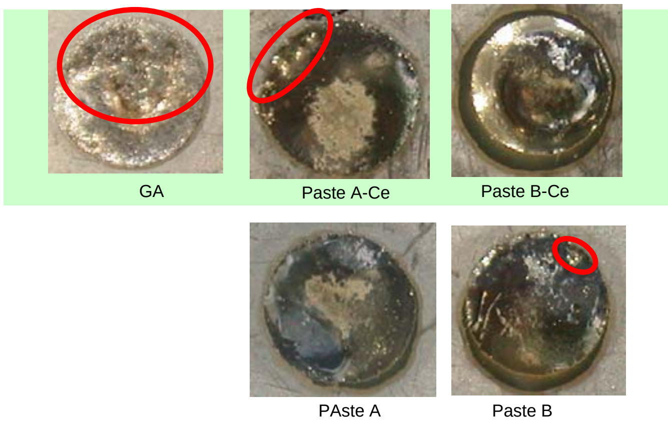


Figure 25 - Dewetting behavior of solder pastes on ImSn using long profile.

Again, no dewetting can be discerned in ENIG samples, as shown in **Figure 26**. Also, the spreading difference between GA and the rest of the pastes diminished in the long profile.

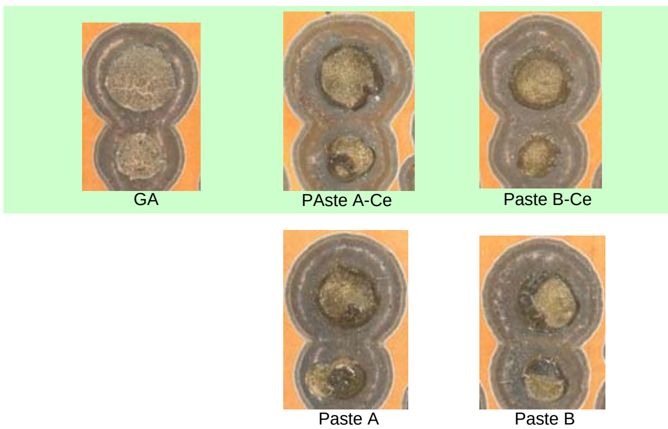


Figure 26 - **Dewetting behavior of solder pastes on ENIG using long profile.**

In summary, Ce induced some dewetting under harsh reflow conditions. This effect is more significant on ImAg, and noticeable on OSP and ImSn. GA showed severe dewetting behavior on ImAg and ImSn, and particularly on OSP.

5. Wetting (Spreading)

No significant difference between Ce-system and SAC system when using short profile, as shown in **Figure 27**.

Ce-system wetted slightly poorer than SAC system when using medium profile, as shown in **Figure 28**. GA wetted the poorest on OSP, ImAg, and ImSn.

When using long profile, Ce-system wetted slightly poorer than SAC system, as shown in **Figure 29**. GA wetted much poorer on OSP and ImSn.

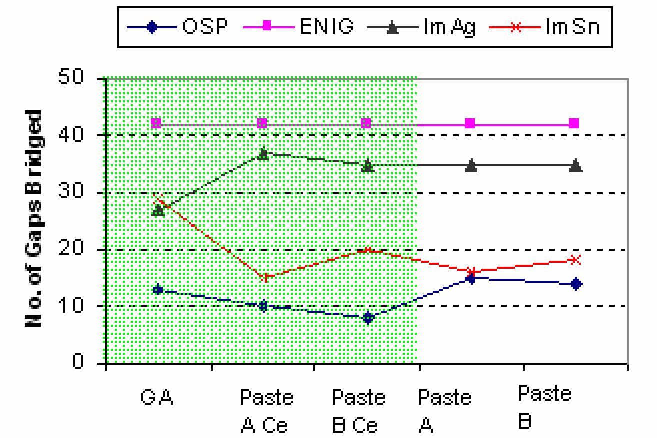


Figure 27 - Wetting (spreading) behavior of solder pastes using short profile.

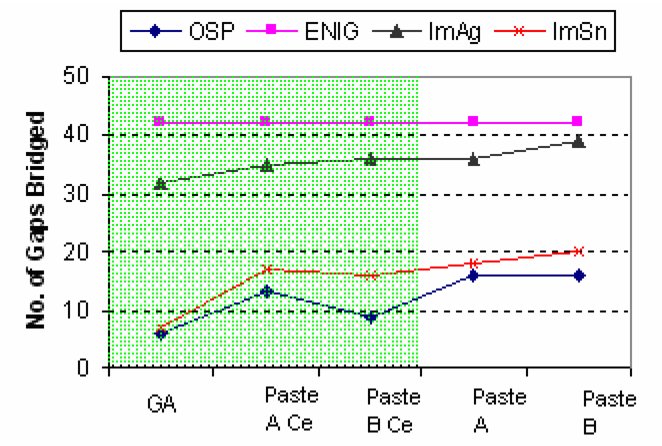


Figure 28 - Wetting (spreading) behavior of solder pastes using medium profile.

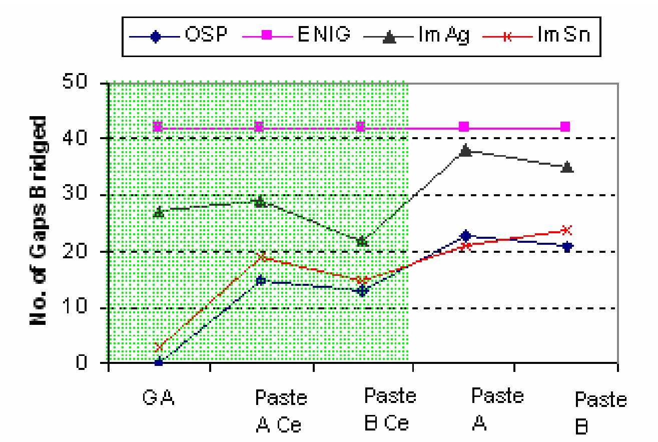


Figure 29 - Wetting (spreading) behavior of solder pastes using long profile.

In summary, Ce-system wet slightly poorer than SAC system under harsh conditions for OSP, ImAg, and ImSn. GA is acceptable under short profile, but is poorer under longer profiles, and is much poorer on OSP and ImSn.

6. Solder Balling

1). Short Profile

At short profile, all pastes showed good solder balling, as shown in **Figure 30**.

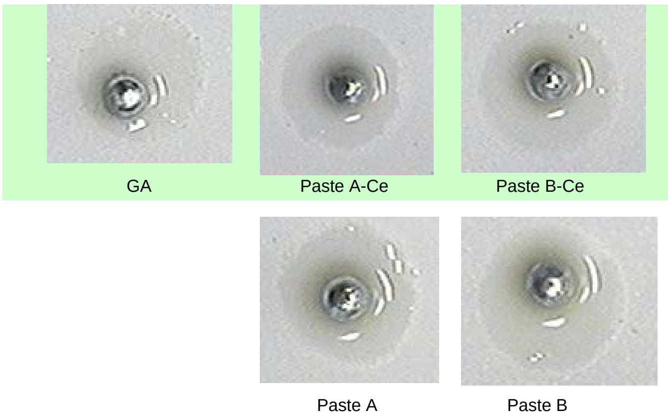


Figure 30 - Solder balling behavior of solder pastes reflowed under short profile.

2). Medium Profile

At medium profile, Ce system showed slightly more solder balling than SAC system, as shown in **Figure 31**. GA showed the most solder balling.

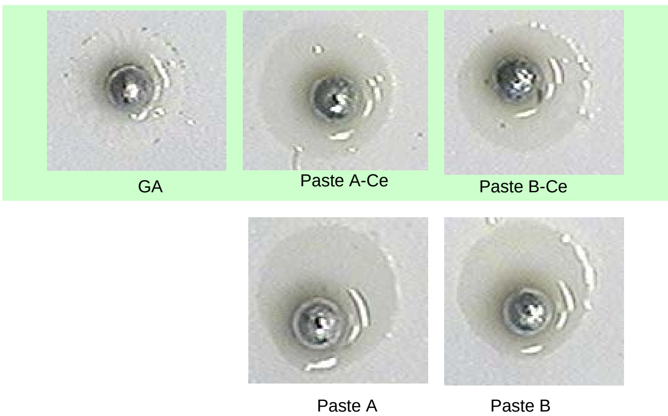


Figure 31 - Solder balling behavior of solder pastes reflowed under medium profile.

3). Long Profile

At long profile, the Ce-system showed considerably more solder balling than SAC system, as shown in **Figure 32.** GA showed the most severe solder balling.

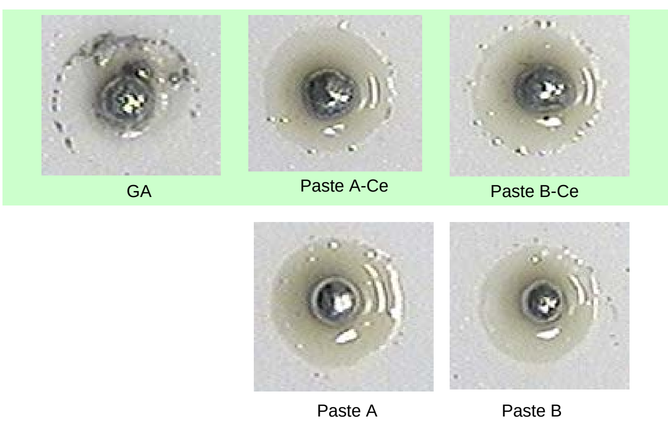


Figure 32 - Solder balling behavior of solder pastes reflowed under long profile.

4. Voiding

The voiding behavior of the solder pastes is exemplified by the partial X-ray images of the solder joints for each of the solder pastes, as shown in **Figure 33**.

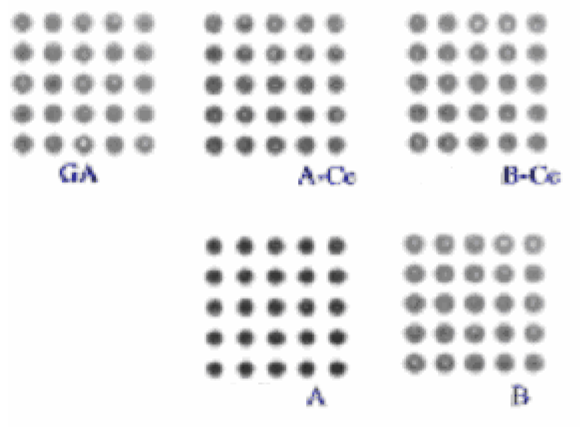


Figure 33 - Partial X-ray images of solder joints for each of the solder pastes.

Figure 34 shows the maximum, mean value, and standard deviation results of voiding analysis for each of the solder pastes. For Paste A flux, Ce showed slightly lower mean value in voiding than SAC, while for Paste B flux, the opposite relation was observed. In other words, no trend can be deduced on the effect of Ce on voiding of Sac system, and the minute difference in mean value is attributable to data scattering. The minute difference in mean value between GA sample and Paste A-Ce and Paste B-Ce is also insignificant. This is particularly true when the maximum voiding value is also considered.

Overall, Ce showed no significant effect on voiding, and the three fluxes tested - GA, A, and B are comparable in voiding performance as well,

Figure **34** Voiding analysis results of solder joints for the five lead-free solder pastes.

7. Solder Beading

The solder beading behavior of solder pastes is shown in **Figure 35**. Ce-system appears to be slightly lower in solder beading rate than SAC system. However, the difference is really insignificant.

GA flux exhibits the lowest solder beading rate, followed by B flux, with A being the highest.

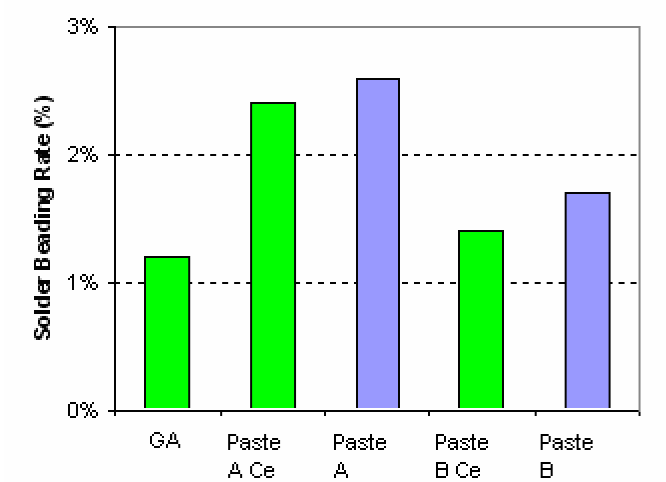


Figure 35 - Solder beading behavior of solder pastes.

8. Tombstoning

Ce-system showed considerably higher tombstoning rate than SAC system, as shown in **Fig. 36**. GA showed the highest tombstoning rate.

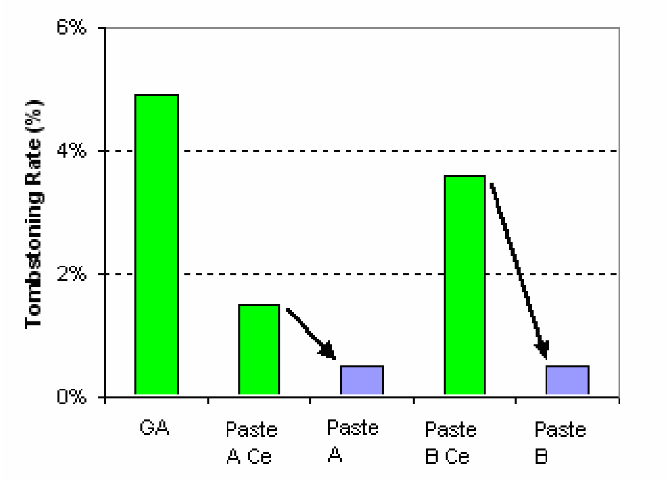


Figure 36 - Tombstoning results of lead-free solder pastes.

9. Probe Testability

Ce has no impact on probe testability, as shown by the insignificant difference between Ce-system and SAC system in **Fig. 37**. On the other hand, GA showed much poorer in-circuit probe test capability than Indium pastes.

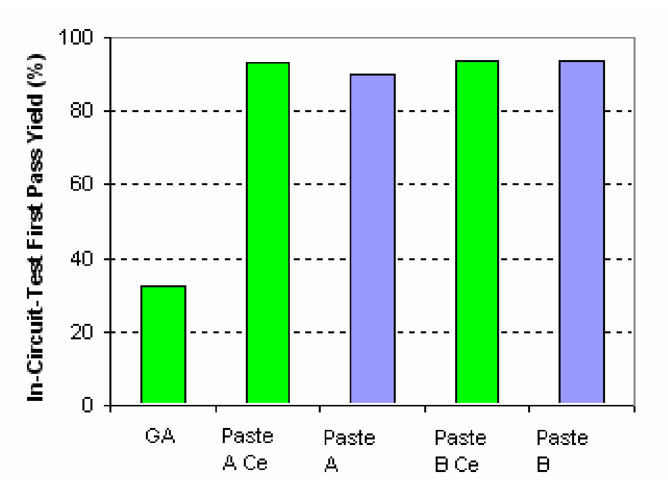


Figure 37 - The in-circuit test first pass rate of lead-free solder pastes.

10. Intermetallic Formation

1). Cu Substrate

The formation of intermetallic compounds (IMC) at solder joint interface on copper substrate as a function of aging time at 150ºC is shown in **Fig. 38** for both SAC solder paste and SACCe solder paste. Two layers of IMC are formed, with Sn-rich layer on solder side and Cu-rich layer on copper side. Examples of the elemental compositions of each IMC layer for samples aged at 150ºC for 20 days are shown in **Table 2**. No Ce can be discerned within either IMC layer.

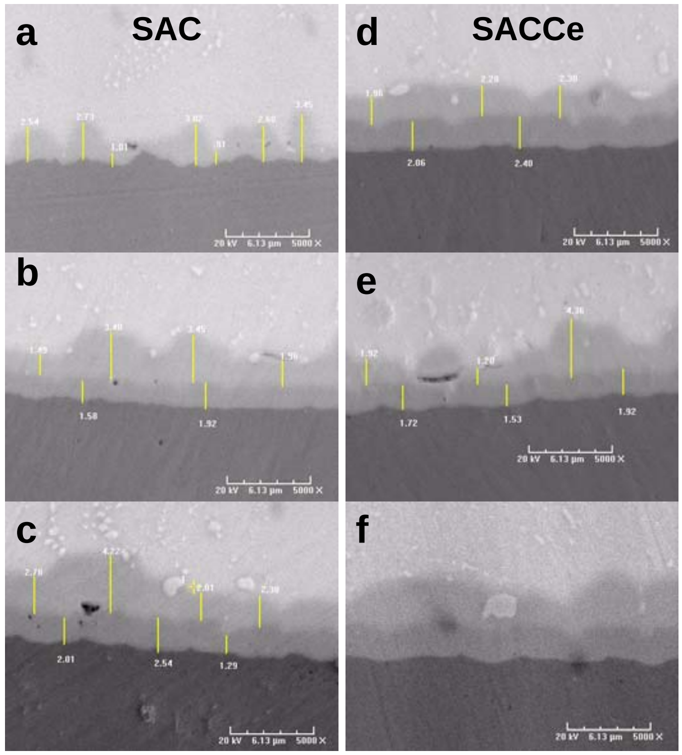


Figure 38 - SEM images of cross-sectioned solder joints on copper substrate. (a) SAC305 as reflowed, (b) SAC305 after aging at 150ºC for 10 days, (c) SAC305 after aging at 150ºC for 20 days, (d) SACCe as reflowed, (e) SACCe after aging at 150ºC for 10 days, (f) SACCe after aging at 150ºC for 20 days,

Table 2 - Examples of elemental composition (atomic %) of intermetallic layers formed on copper for samples aged at 150ºC for 20 days.

Element	SACCe		SAC305	
	Sn-rich	Cu-rich	Sn-rich	Cu-rich
Sn	54.8	28.10	72.62	31.25
Ag	0.00	0.00	0.06	0.00
Cu	45.2	71.90	27.33	68.75
Ce	0.00	0.00	0.00	0.00

The growth rate of IMC layer for joints aged at 150ºC is shown in **Fig. 39** for Sn-rich layer and in **Fig. 40** for Cu-rich layer. The thickness of the Sn-rich layer was virtually unchanged through the thermal aging process, although a very slight increase may be discerned for SAC305 system. However, for the Cu-rich IMC layer, the thickness increased readily with increasing aging time. The effect of Ce on IMC growth rate on Cu is not significant.

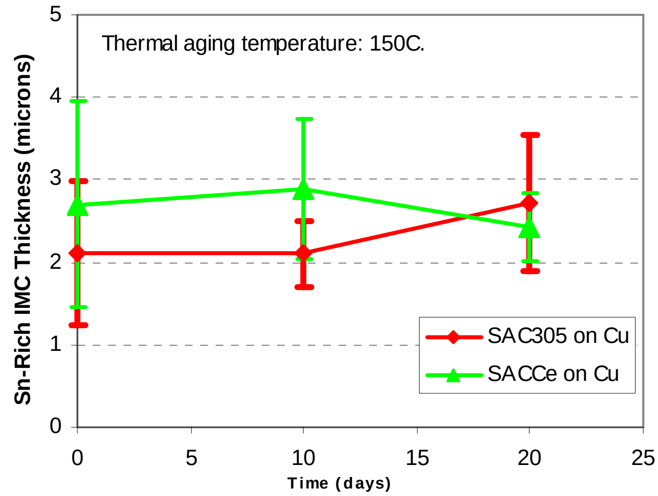


Figure 39 - Growth rate of Sn-rich IMC layer for joints of SAC305 and SACCe alloys on Cu substrate aged at 150ºC.

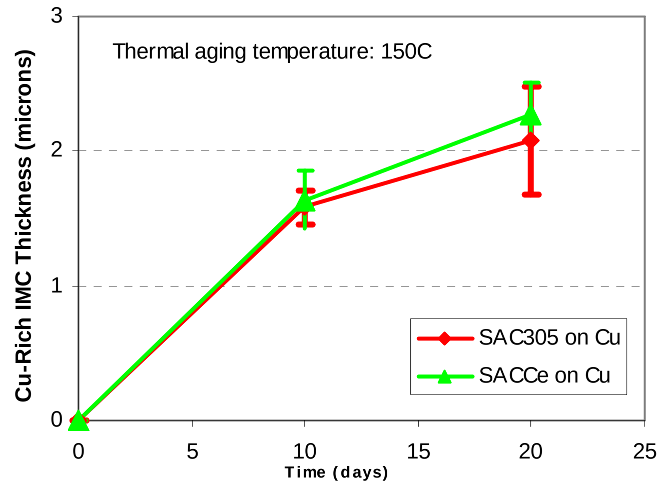


Figure 40 - Growth rate of Cu-rich IMC layer for joints of SAC305 and SACCe alloys on Cu substrate aged at 150ºC.

2). NiAu Substrate

The formation of intermetallic compounds (IMC) at solder joint interface on NiAu substrate as a function of aging time at 150ºC is shown in **Fig. 41** for both SAC solder paste and SACCe solder paste. The elemental compositions of the IMC layer for samples aged at 150ºC for 10 days are shown in **Table 3**. Again, no Ce can be discerned within the IMC layer.

The growth rate of IMC layer for joints aged at 150ºC is shown in **Fig. 42**. The thickness of the IMC layer was virtually unchanged through the thermal aging process. The effect of Ce on IMC growth rate on NiAu is also not significant.

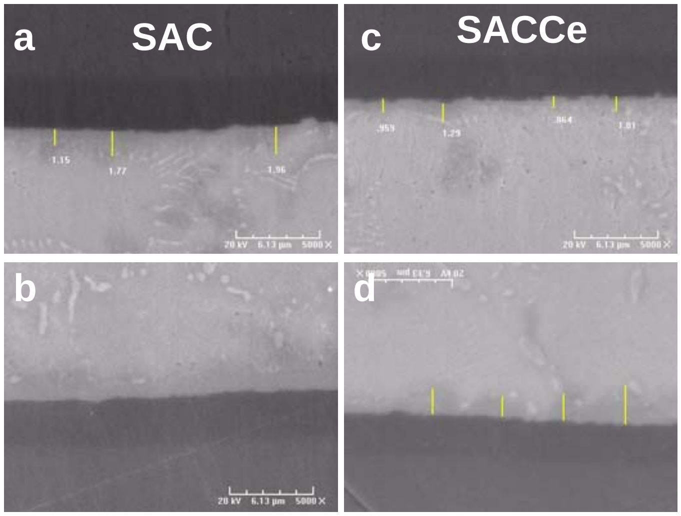


Figure 41 - SEM images of cross-sectioned solder joints on NiAu substrate. (a) SAC305 as reflowed, (b) SAC305 after aging at 150ºC for 10 days, (c) SACCe as reflowed, (d) SACCe after aging at 150ºC for 10 days,

Table 3 - Examples of elemental composition (atomic %) of intermetallic layer formed on NiAu for samples aged at 150ºC for 10 days.

Element	SACCe		SAC305	
	Site 1	Site 2	Site 1	Site 2
Sn	55.50	65.66	66.87	64.12
Ag	0.50	0.00	1.13	0.00
Cu	22.02	11.88	4.96	20.63
Ce	0.00	0.00	0.00	0.00
Ni	21.19	13.91	26.36	14.39
Au	0.79	1.52	0.68	0.87

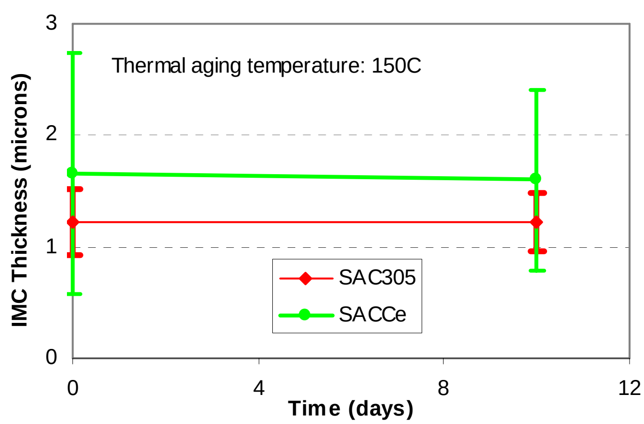


Figure 42 - Growth rate of IMC layer for joints of SAC305 and SACCe alloys on NiAu substrate aged at 150ºC. In summary, Ce has negligible effect on IMC structure and growth rate for joints formed on either Cu or NiAu.

DISCUSSION

1. The China alloy SACCe exhibits a slightly lower solder beading rate, but a considerably higher tombstoning rate than SAC. Both phenomena suggest SACCe wet faster than SAC [3]. This could be explained if addition of Ce results in a lower surface tension. A lower surface tension allows an easier and faster wetting, therefore a higher tombstoning rate. A faster wetting also often results in a lower activation temperature in wetting, and accordingly promises a lower solder beading rate.
2. On the other hand, SACCe exhibit a poorer wetting and solder balling under harsh reflow conditions.

3. The poor solder balling and wetting under harsh reflow conditions might be caused by a poorer quality in solder powder. The powder used in Indium pastes was produced in small scale, thus might not be optimized in manufacturing process, and consequently may be poorer in quality than the main stream high volume SAC powder used by industry. The powder in China paste was probably produced in small scale as well. Since Ce content is merely 0.019%, the impact on manufacturability is estimated to be very small. As a result, the probability of a poor Ce-powder manufacturing process should be small.
4. A more likely cause for the poor solder balling and wetting of Ce-system under harsh reflow conditions is that the SACCe may be more prone to oxidation than SAC alloy. Hypothetically, Ce may preferentially be present at the surface of solder. On one hand, it may result in a lower surface tension. On the other hand, it may be more prone to oxidation, and result in vulnerability toward harsh reflow conditions.

CONCLUSION

Work on assisting China's Ministry of Information Industry (MII) to assess the performance of a solder paste, Gold Arrow, using the China alloy Sn3.0Ag0.5Cu0.019Ce (SACCe) was completed. Two Indium fluxes were incorporated as controls. Ce showed no effect on paste printing, slump, or probe testability on flux residue for SAC system. The difference between SACCe and SAC mainly resides in soldering. SACCe exhibits a slightly lower solder beading rate, comparable voiding, a considerably higher tombstoning rate, and is more prone to oxidation hence wets poorer under harsh reflow conditions. No difference in IMC structure or growth rate can be discerned for joints formed on either Cu or NiAu. Overall, China alloy is acceptable in reflow applications. The flux exhibits a poorer print and a considerably narrower reflow window than both Indium flux controls.

REFERENCE

1. Ning-Cheng Lee, "Critical Parameters in Voiding Control at Reflow Soldering", Chip Scale Review, August-September 2005.
2. Hyoryoon Jo, Benjamin E. Nieman, and Ning-Cheng Lee, "Voiding of Lead-Free Soldering at Microvia", IMAPS, Denver, CO, September 4-6, 2002
3. Ning-Cheng Lee, "Reflow soldering processes and troubleshooting: SMT, BGA, CSP, and flip chip technologies", published by Newnes, an imprint of Butterworth-Heinemann, pp.270, 2002.

Performance of China Alloy SnAgCuCe in Reflow Soldering

Dr. Yan Liu, Paul Bachorik, Geoffrey Beckwith,
Lee Kresge, Matthew Long, William Manning,
Dr. Runsheng Mao, Benjamin Nieman, &
Dr. Ning-Cheng Lee

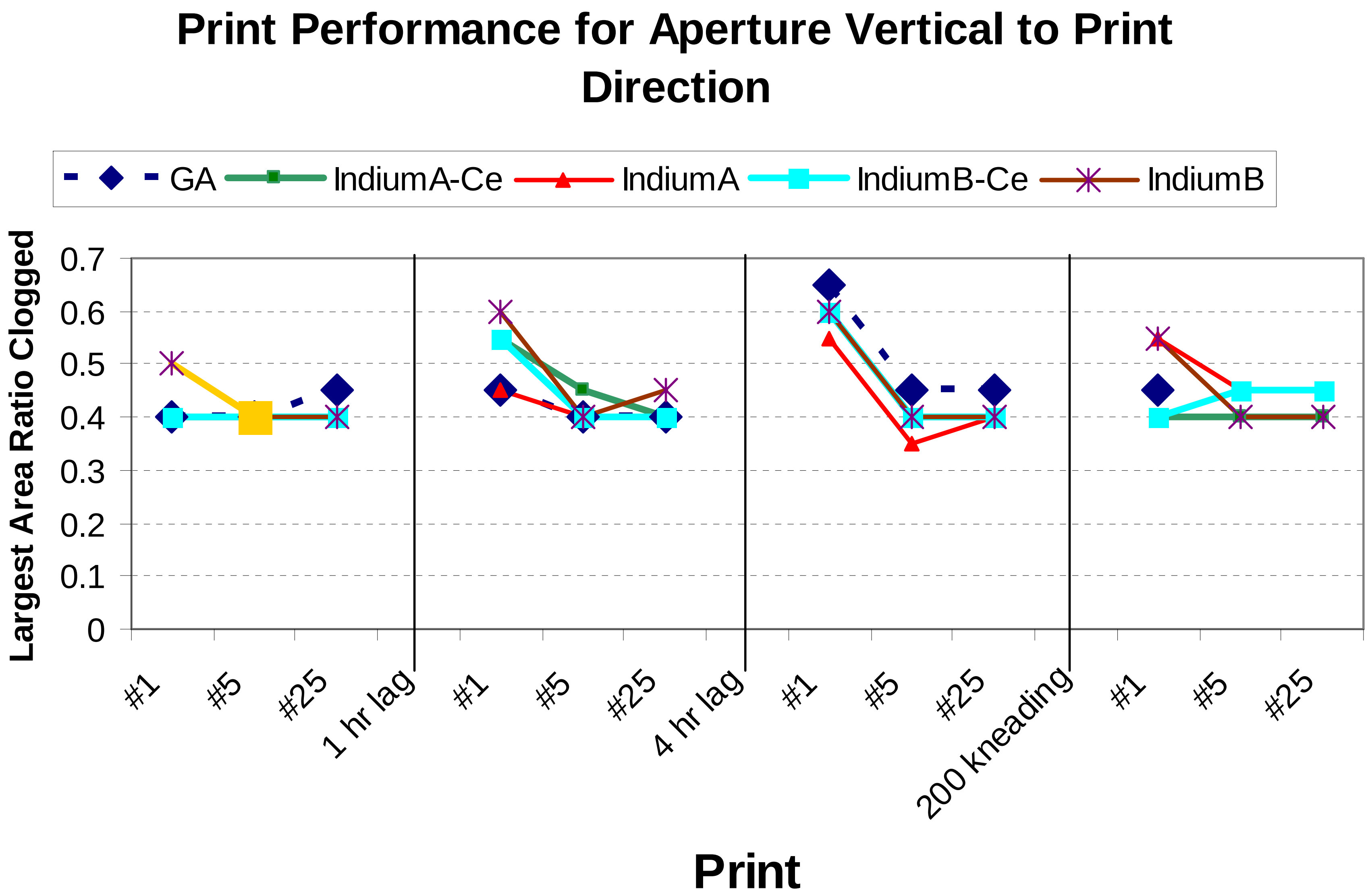
Indium Corporation of America

Methodology

- The performance of SACCe solder paste (Gold Arrow) is benchmarked against SAC solder paste.
- To eliminate flux factor, two Indium fluxes with different chemistries (IndiumA & IndiumB) are used for both SACCe and SAC alloys. Ce effect can be confirmed when effect is observed for both A & B paste chemistries.
- The difference of SACCe and SAC can be assessed by comparing pastes with the same flux but different in alloys.
- The difference between Gold Arrow and Indium fluxes is also assessed by comparing Gold Arrow with Indium pastes using SACCe alloy.

Solder Pastes Evaluated

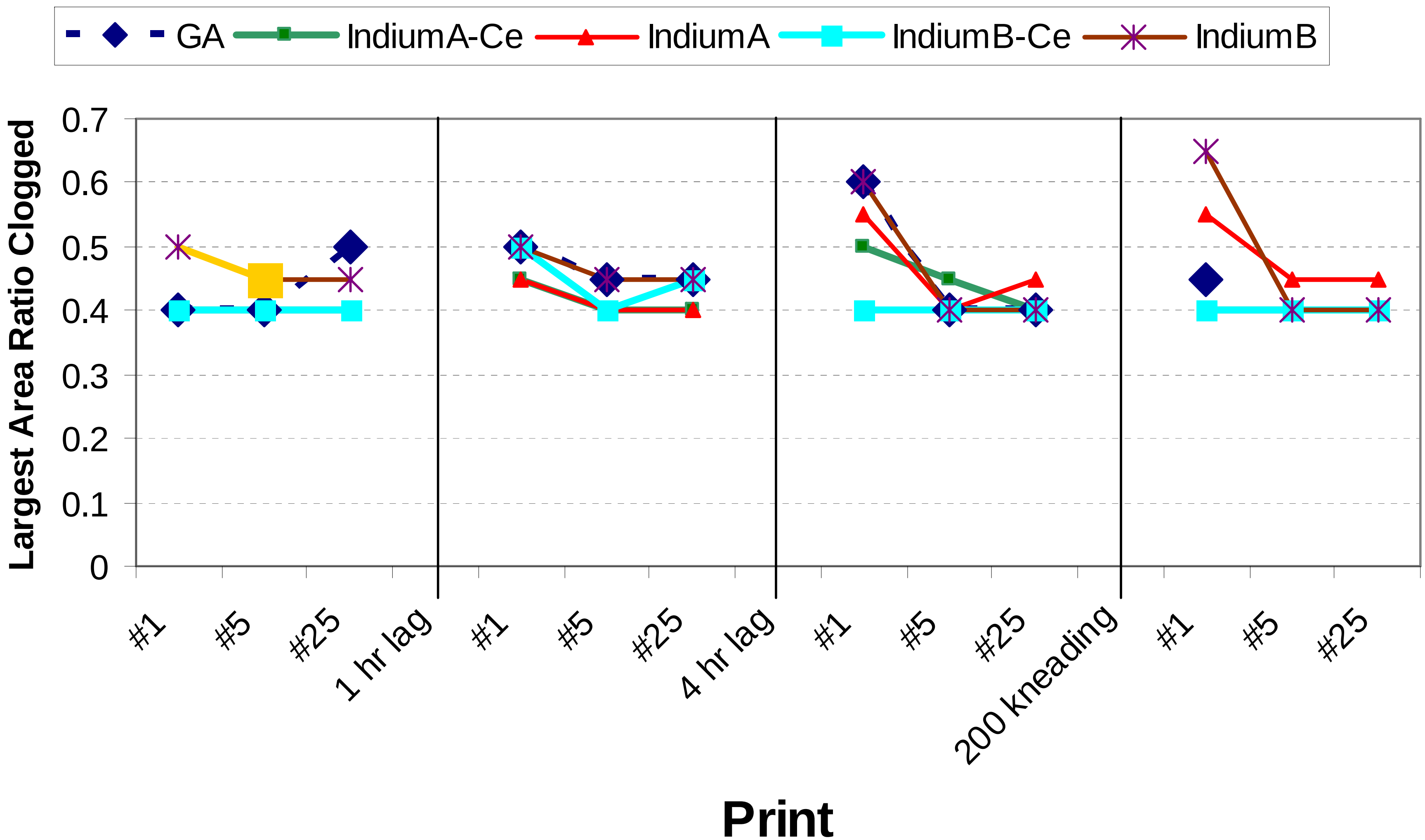
Solder Paste	Code	Alloy	Powder Type	Metal Load
Gold Arrow	GA	96.5Sn3Ag0.5Cu0.019 Ce	3	89.5
Indium A (No-Clean)	IndiumA-Ce	96.5Sn3Ag0.5Cu0.019 Ce	3	89
Indium A (No Clean)	IndiumA	96.5Sn3Ag0.5Cu	3	89
Indium B (No Clean)	IndiumB-Ce	96.5Sn3Ag0.5Cu0.019 Ce	3	89
Indium B (No Clean)	IndiumB	96.5Sn3Ag0.5Cu	3	89



Ce-system is comparable with SAC-system.

GA most sensitive to 4 hr pause. Need more than 5 prints to recover.

Print Performance for Round Aperture



Ce-system is comparable with SAC-system.

GA most sensitive to 4 hr pause.

Example of Printability

Location: H. 1st print after 4 hr pause.

Ce has negligible effect on printability of SAC system.

GA stencil release degraded considerably after 4 hrs pause.

GA

IndiumA-Ce

IndiumB-Ce

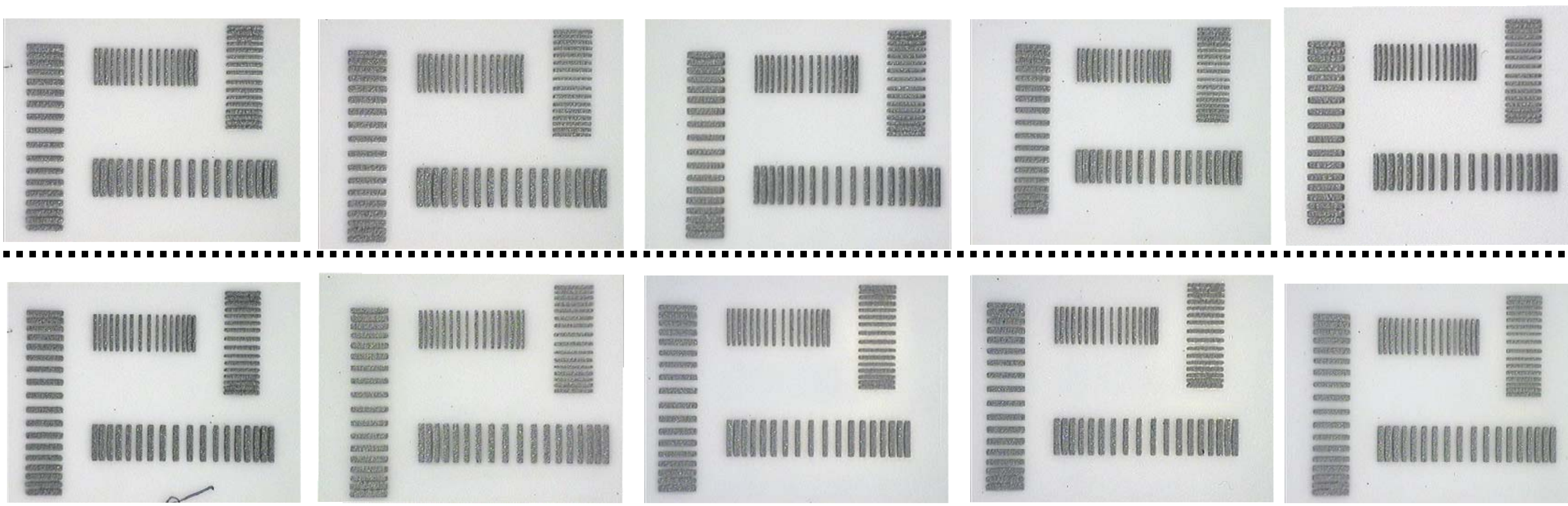
IndiumA

IndiumB

Slump Test of Lead-Free Solder Pastes

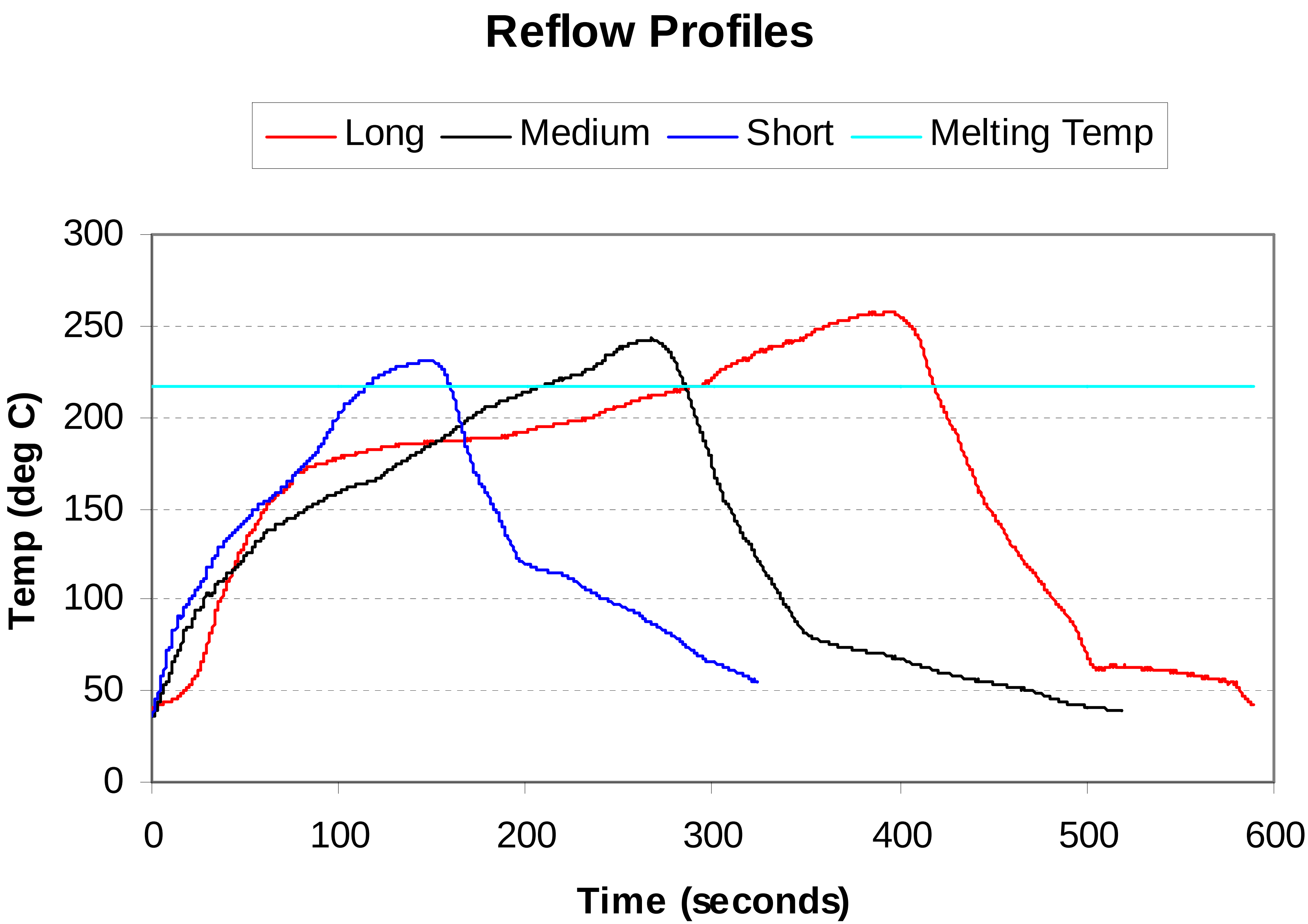
All pastes tested showed no slump at 150C.

BEFORE



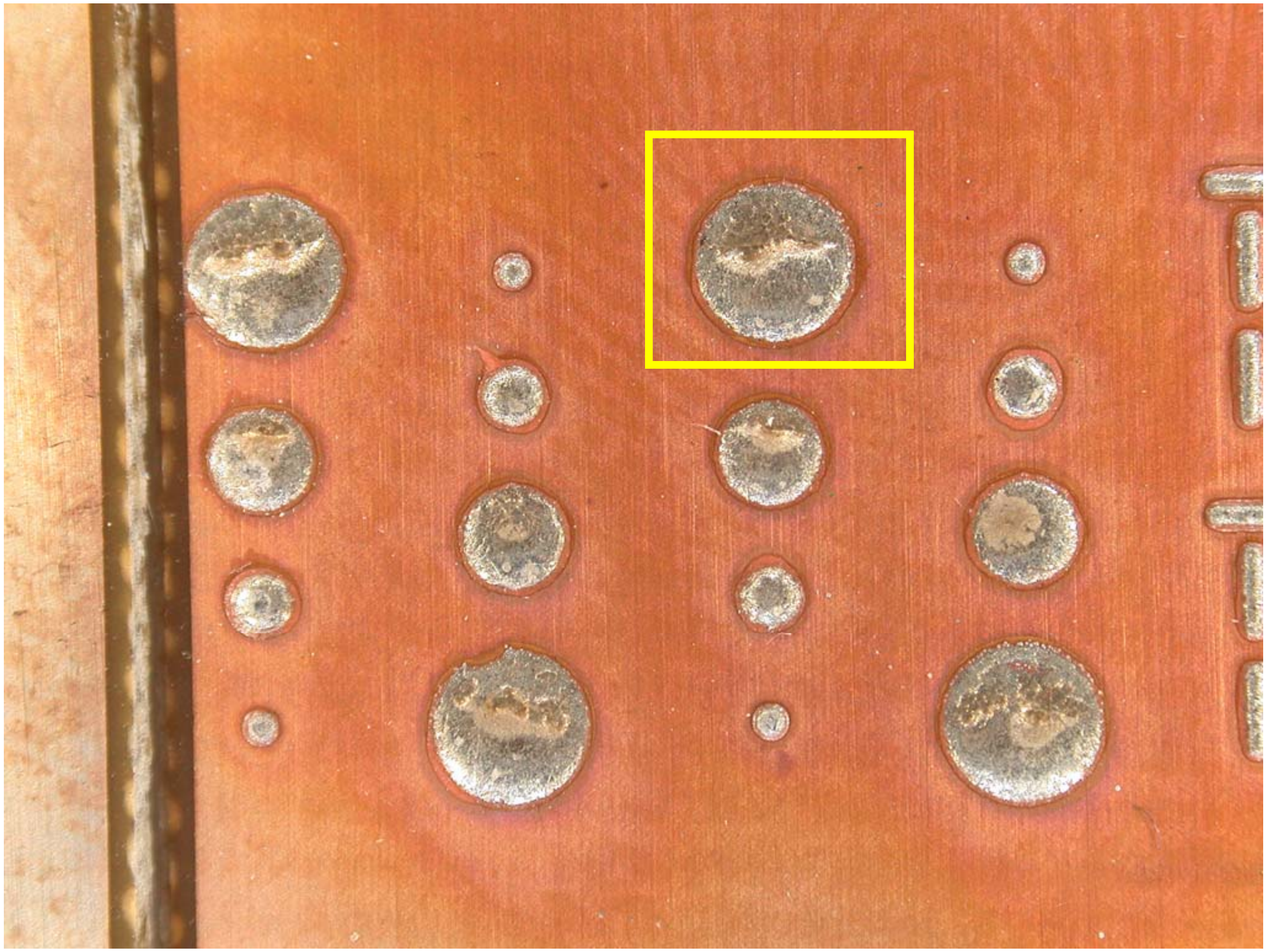
AFTER

GA IndiumA-Ce IndiumA IndiumB-Ce IndiumB


Reflow Profiles
Long
Medium
Short
Melting Temp
Temp (deg C)
0
50
100
150
200
250
300
Time (seconds)
0
100
200
300
400
500
600

Wetting (Dewetting) Stencil Pattern

The circle in yellow bracket is used to exemplify the dewetting behavior in solder paste comparison.



Wetting (Dewetting) on OSP

Short profile

GA

IndiumA-Ce

IndiumB-Ce

At short profile, other than the GA sample, the Ce-system showed comparable full wetting as SAC system.

IndiumA

IndiumB

Wetting (Dewetting) on ImAg

Short profile

GA

IndiumA-Ce

IndiumB-Ce

At short profile, other than the GA sample, the Ce-system showed comparable full wetting as SAC system.

GA showed dewetting.

IndiumA

IndiumB

Wetting (Dewetting) on ImSn

Short profile

GA

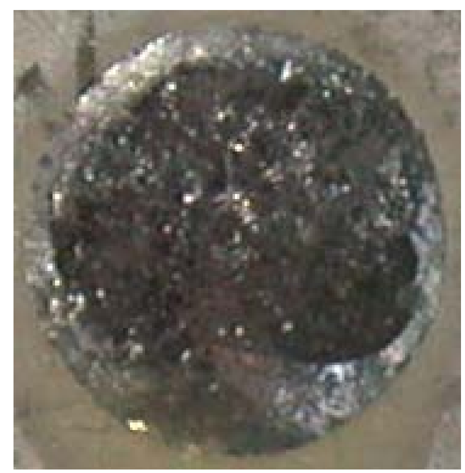
IndiumA-Ce

IndiumB-Ce

At short profile, the Ce-system showed comparable full wetting as SAC system.

GA showed some dewetting.

IndiumA



IndiumB

Wetting (Dewetting) on ENIG

Short profile

GA

IndiumA-Ce

IndiumB-Ce

At short profile, the Ce-system showed slightly less spreading than SAC system.

IndiumA

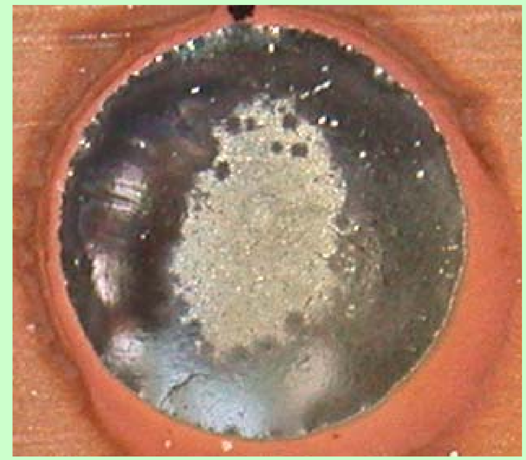
IndiumB

Wetting (Dewetting) on OSP

Medium profile

GA

IndiumA-Ce



IndiumB-Ce

At medium profile, other than the GA sample, the Ce-system showed comparable full wetting as SAC system.

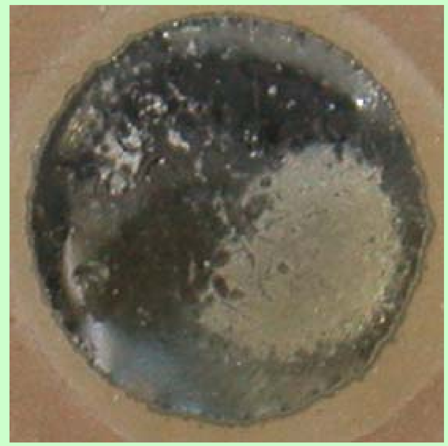
IndiumA

IndiumB

Wetting (Dewetting) on ImAg

Medium profile

GA

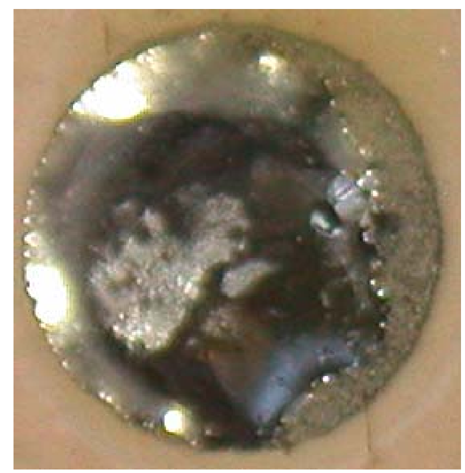


IndiumA-Ce

IndiumB-Ce

At medium profile, the Ce-system showed comparable full wetting as SAC system.

IndiumA



IndiumB

Wetting (Dewetting) on ImSn

Medium profile

GA

IndiumA-Ce

IndiumB-Ce

At medium profile, the Ce-system showed comparable full wetting as SAC system.

IndiumA

IndiumB

Wetting (Dewetting) on ENIG

Medium profile

GA

IndiumA-Ce

IndiumB-Ce

At medium profile, the Ce-system showed comparable full wetting as SAC system.

GA showed considerable less spreading than the rest

IndiumA

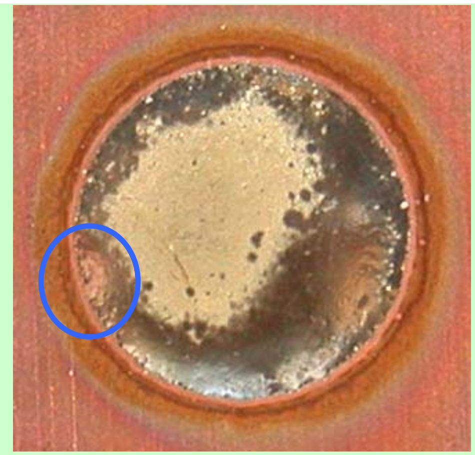
IndiumB

Wetting (Dewetting) on OSP

Long profile

GA

IndiumA-Ce



IndiumB-Ce

At long profile, other than the GA sample, the Ce-system showed comparable full wetting as SAC system.

IndiumA

IndiumB

Wetting (Dewetting) on ImAg

Long profile

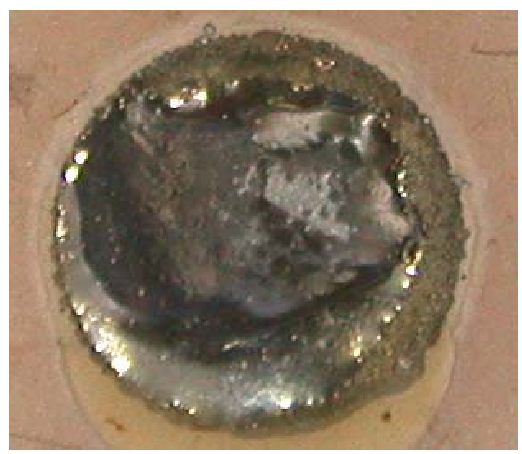
GA

IndiumA-Ce

IndiumB-Ce

At long profile, Ce-system showed dewetting, thus wet poorer than SAC system.

GA showed most dewetting.



IndiumA

IndiumB

Wetting (Dewetting) on ImSn

Long profile

GA

IndiumA-Ce

IndiumB-Ce

At long profile, the Ce-system showed slightly more dewetting as SAC system.

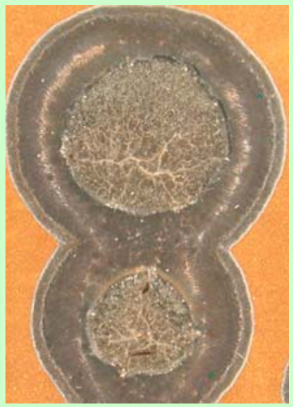
GA showed significant dewetting.

IndiumA

IndiumB

Wetting (Dewetting) on ENIG

Long profile



GA

IndiumA-Ce

IndiumB-Ce

At long profile, the Ce-system showed comparable full wetting as SAC system.

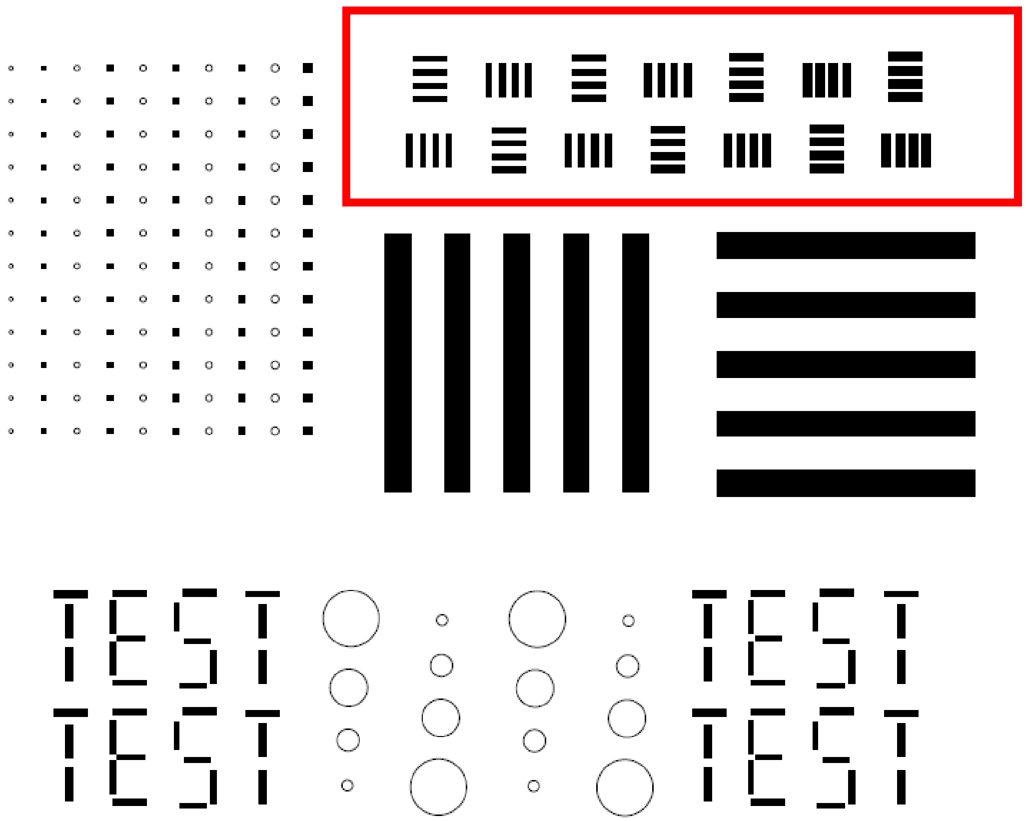
GA shows less flux coverage than other pastes.

IndiumA

IndiumB

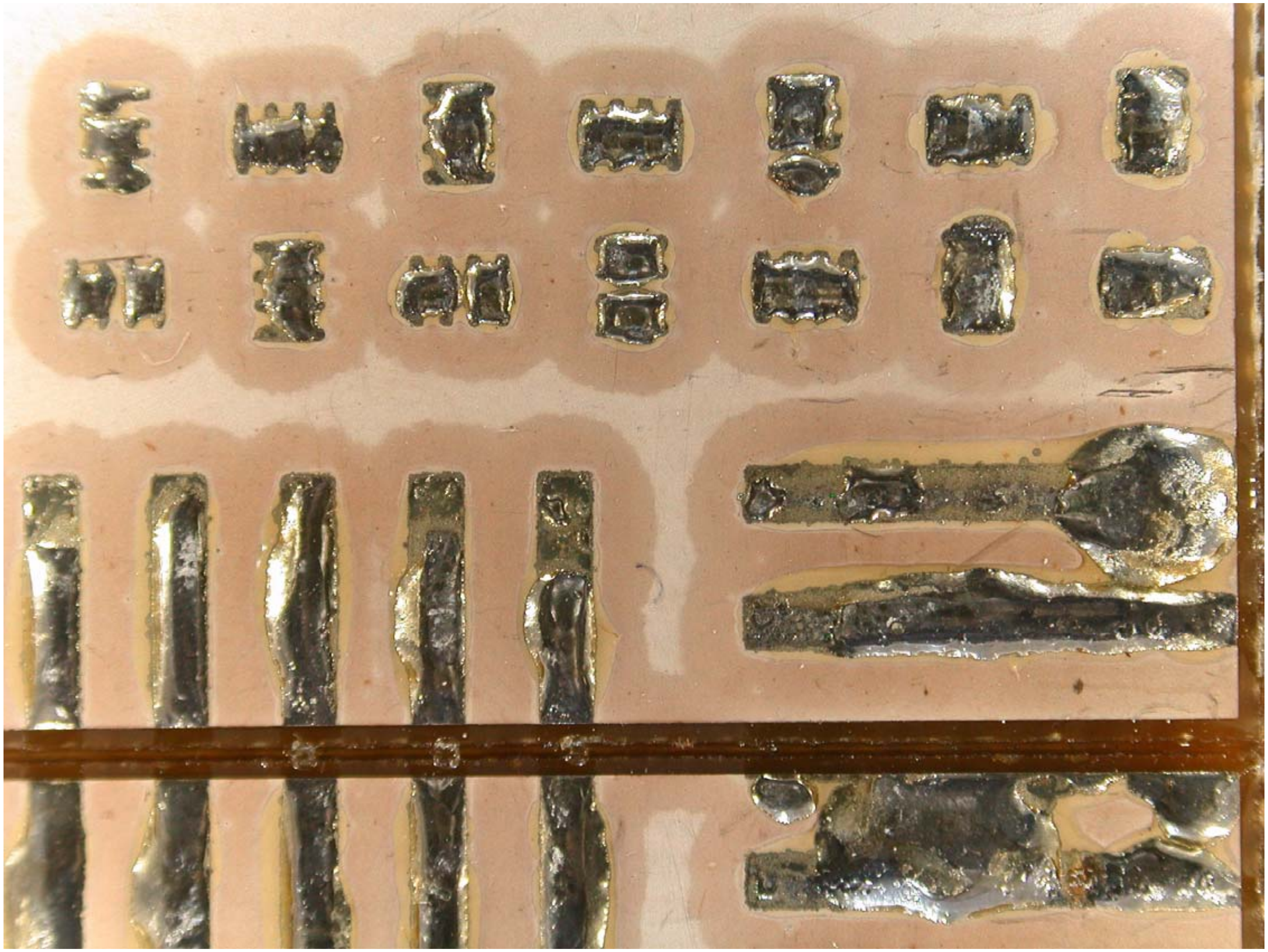
Wetting (Spread Test) Stencil Pattern

Stencil pattern in red bracket is used for wetting (spread) evaluation. The line pattern exhibits a gradual increasing spacing. At reflow, the total bridges formed within the red bracket is used to represent the wetting capability. The more the bridges formed, the better the wetting.



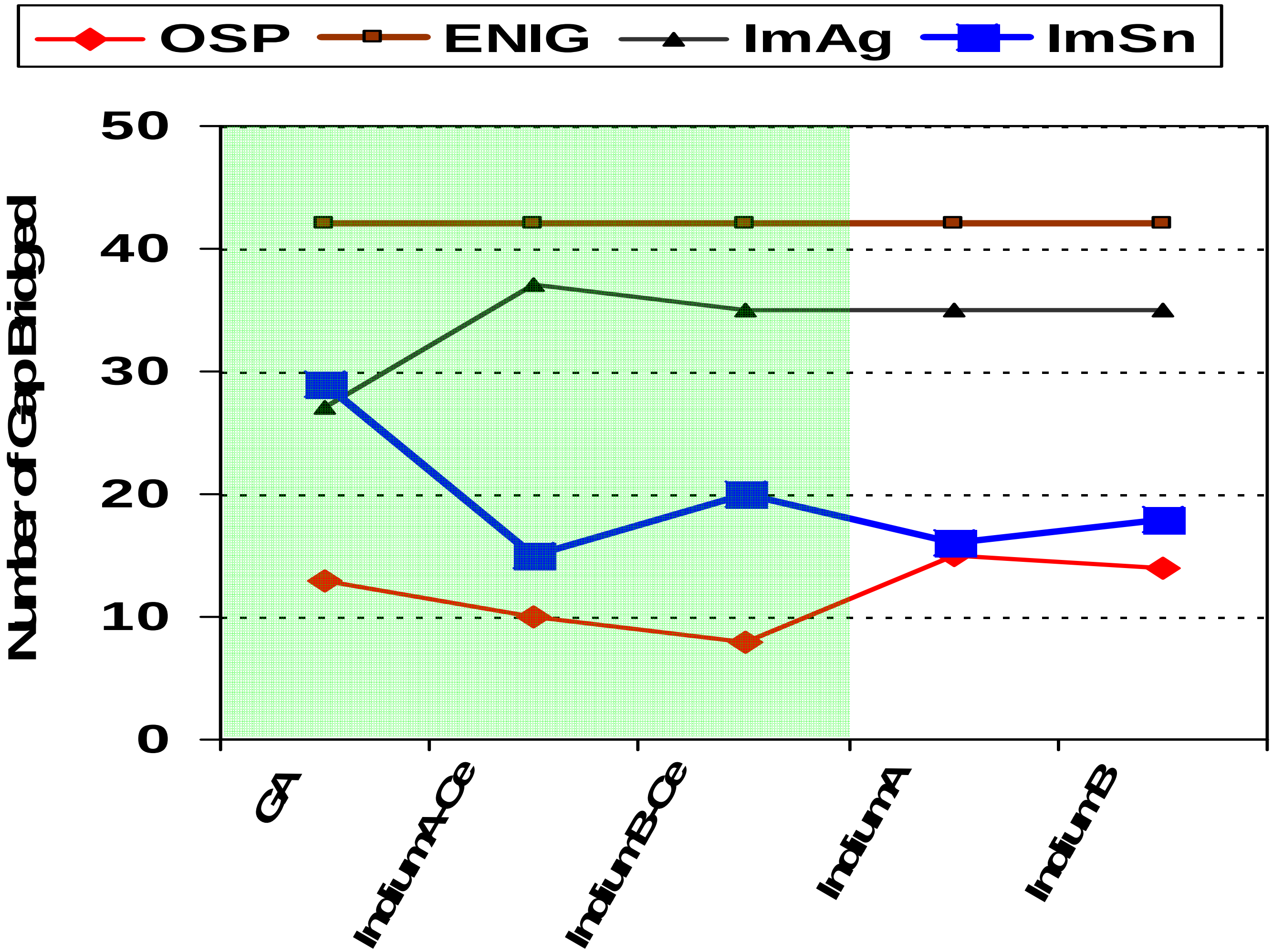
Wetting (Spread)

Example of bridges formed at reflow.



Wetting (Spread)
short profile

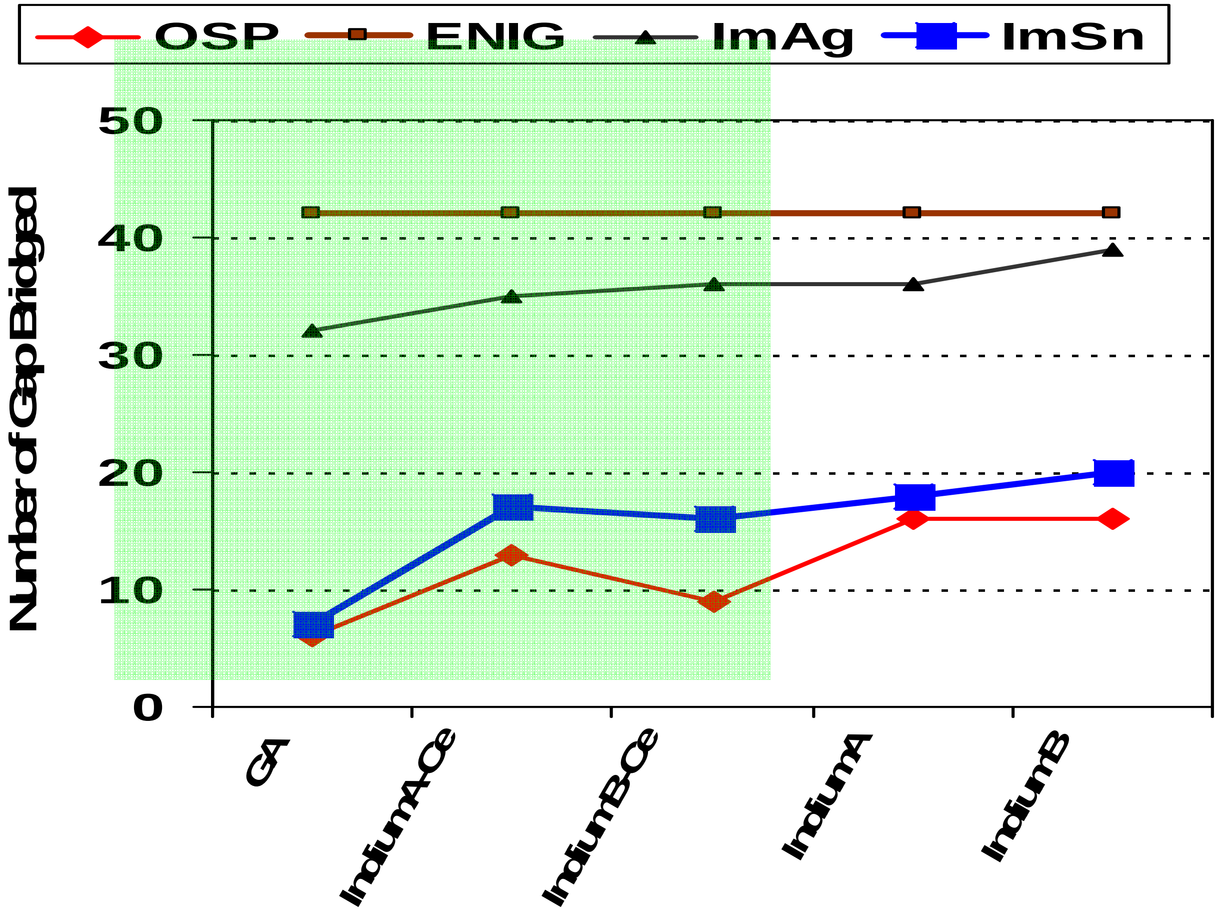
No significant difference between Ce-system & SAC system.



Wetting (Spread)

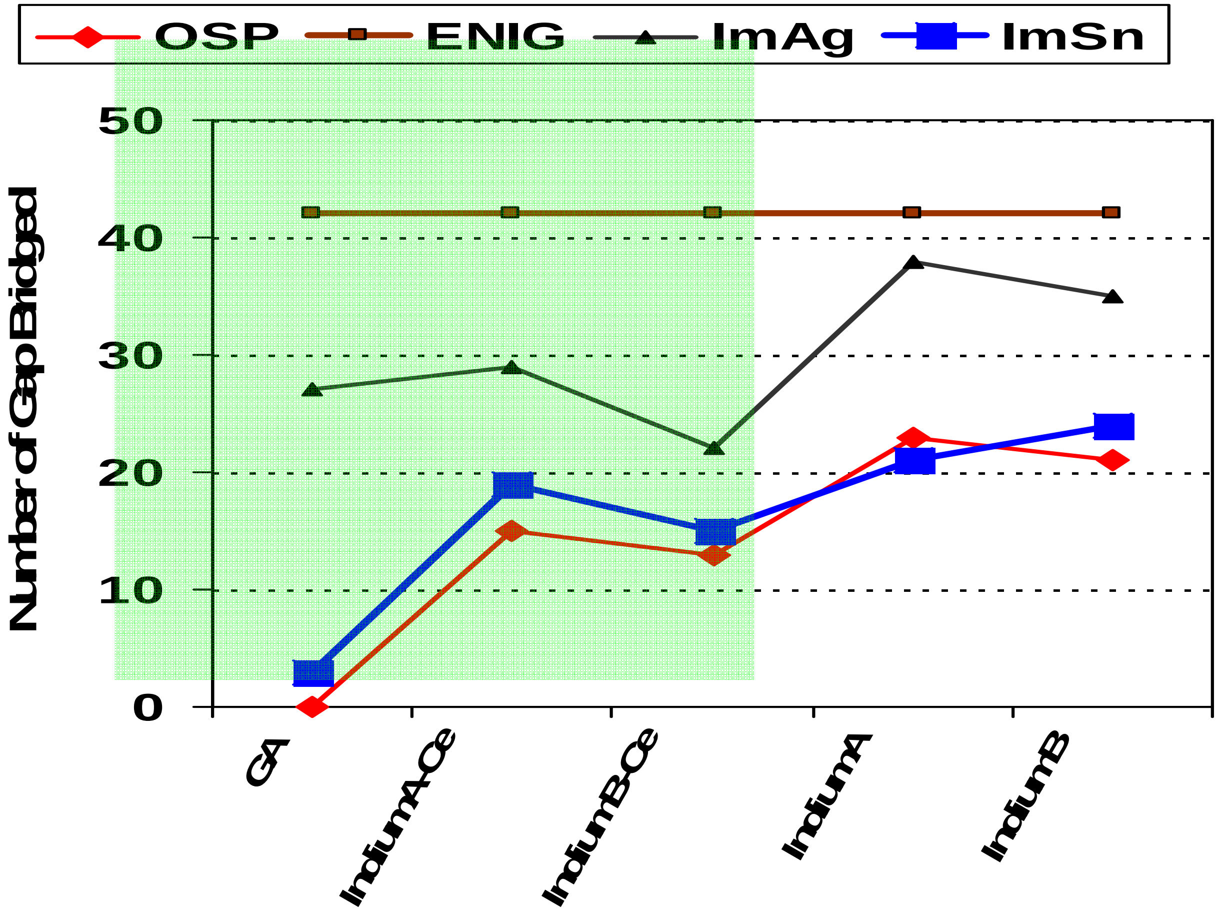
medium profile

Ce-system wet slightly poorer than SAC system. GA poorest on OSP, ImAg & ImSn.



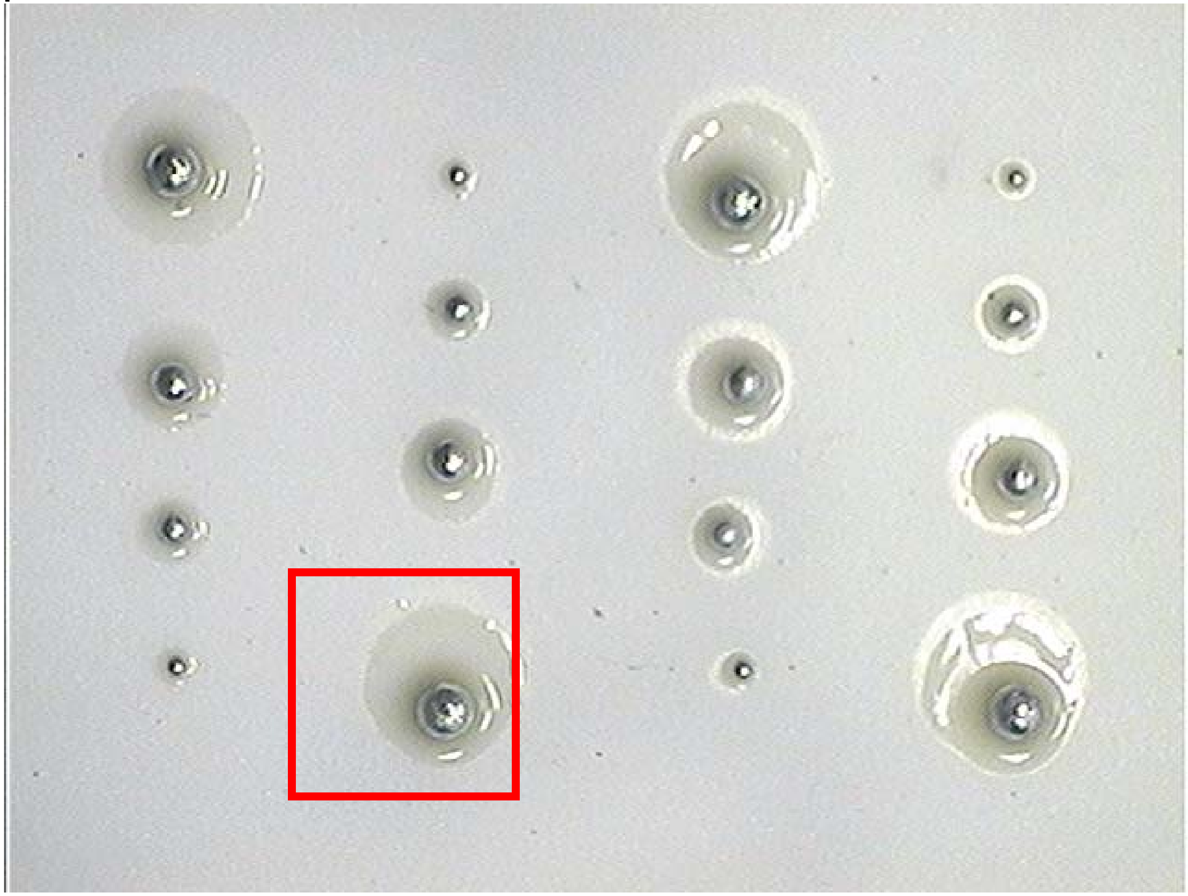
Wetting (Spread)
long profile

Ce-system wet slightly poorer than SAC system. GA much poorer on OSP & ImSn.



Solder Balling

Solder balling was evaluated with the following test pattern. The image in red bracket is used to exemplify the performance in paste comparison.



Solder Balling

Short profile

GA

IndiumA-Ce

IndiumB-Ce

At short profile, all pastes showed good solder balling.

IndiumA

IndiumB

Solder Balling

Medium profile

GA

IndiumA-Ce

IndiumB-Ce

At medium profile, Ce system showed slightly more solder balling than SAC system.

GA showed most solder balling.

IndiumA

IndiumB

Solder Balling

Long profile

GA

IndiumA-Ce

IndiumB-Ce

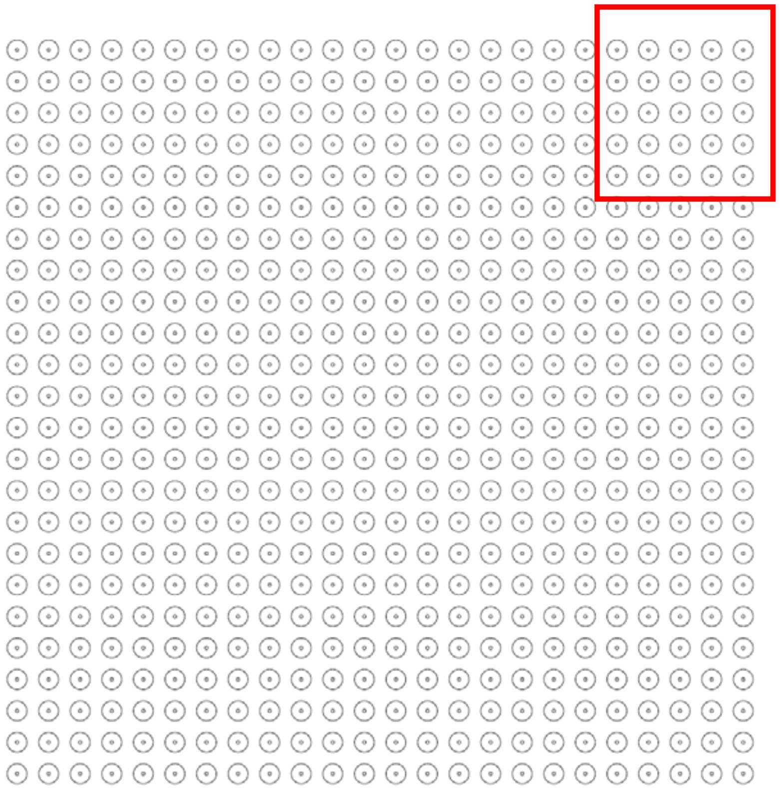
At long profile, the Ce-system showed considerably more solder balling than SAC system.

GA showed most severe solder balling.

IndiumA

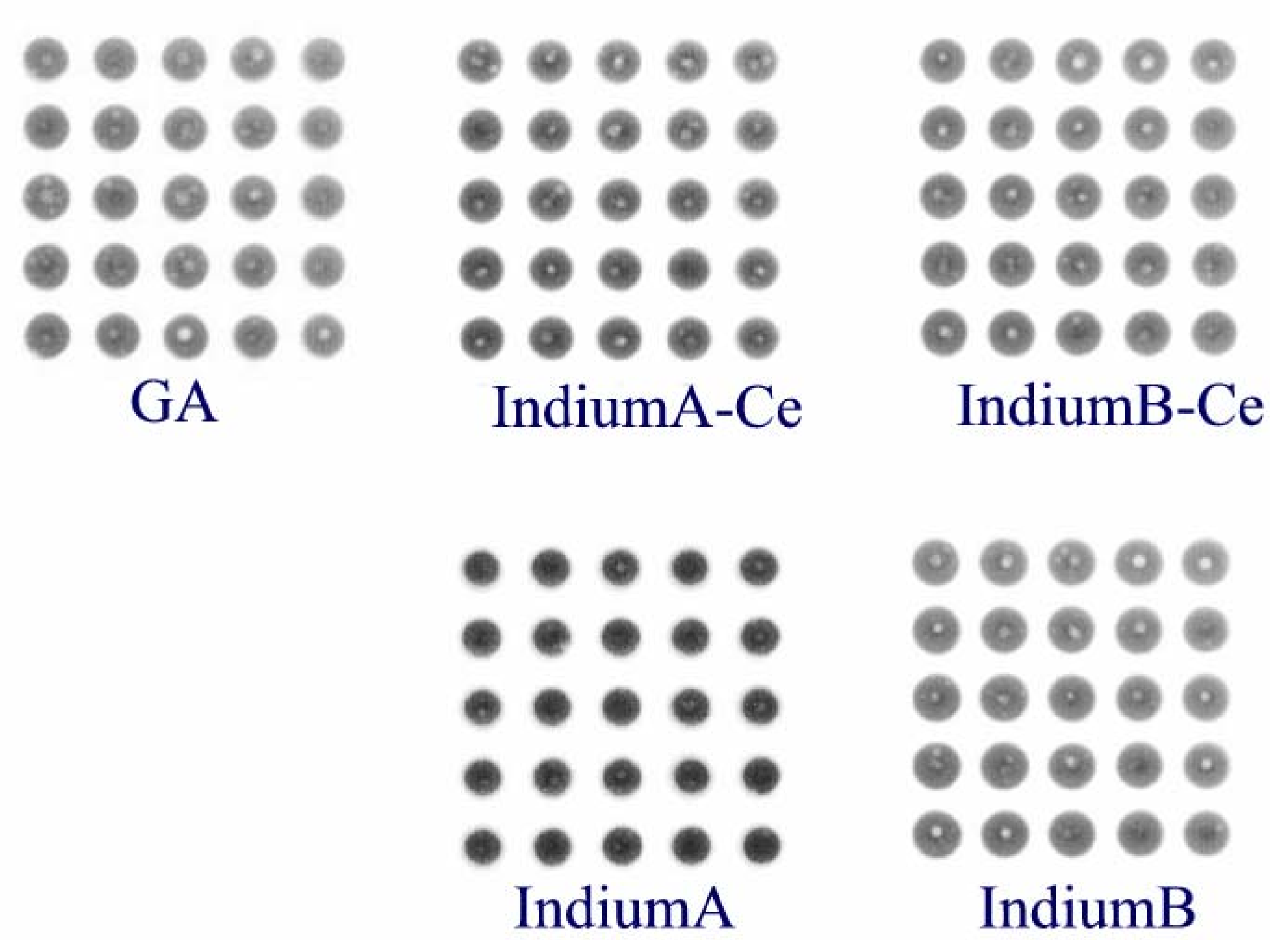
IndiumB

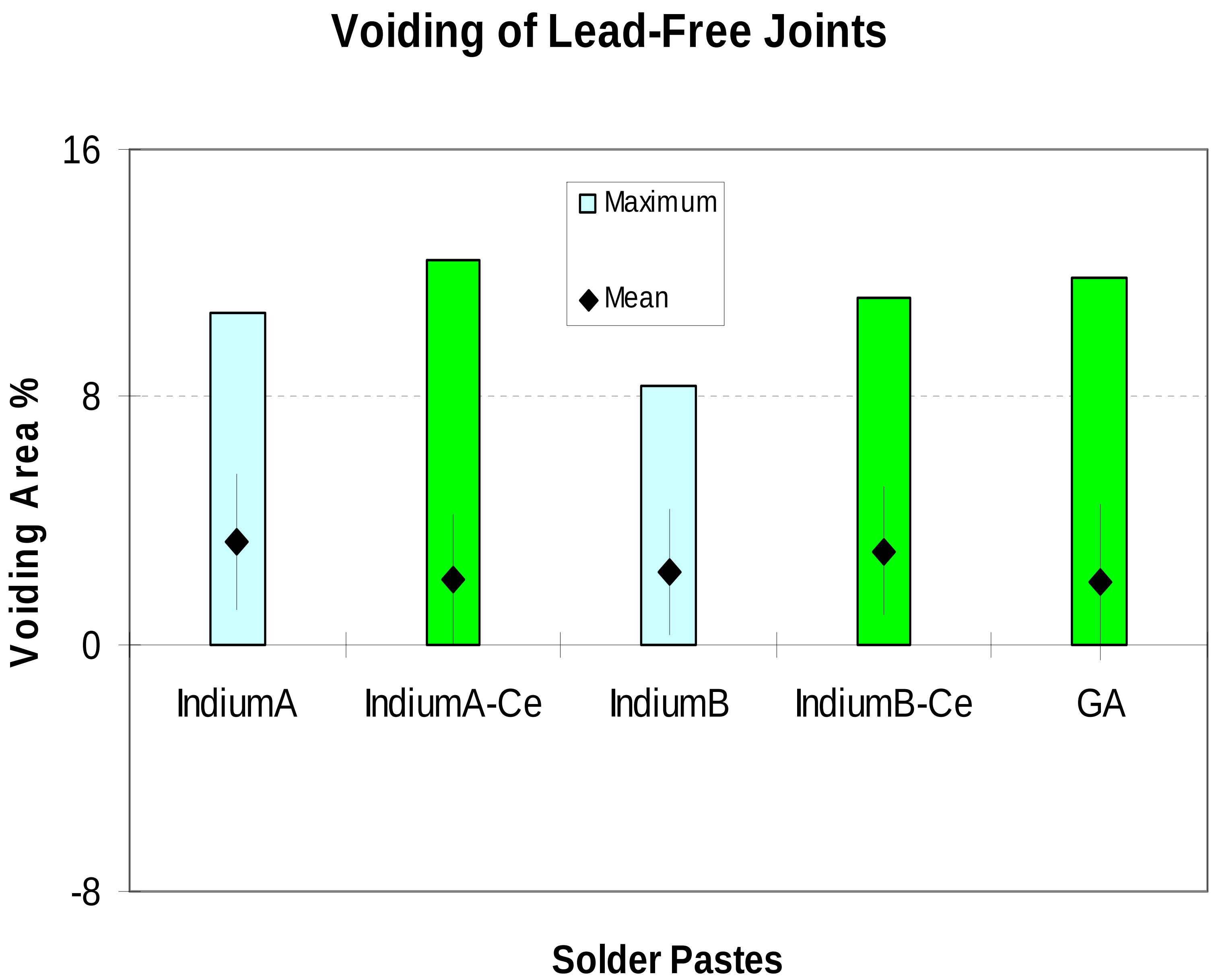
Voiding Test Design



- BGA 24x24 with 40 mil pitch, 25 mil OSP pad diameter, 26 mil SAC387 ball diameter.
- Microvia 4 mil diameter, 4 mil depth.
- BGA mounted with solder paste printed with 4 mil stencil.
- Reflow profile – short profile.
- Voiding examined with X-ray for all joints.

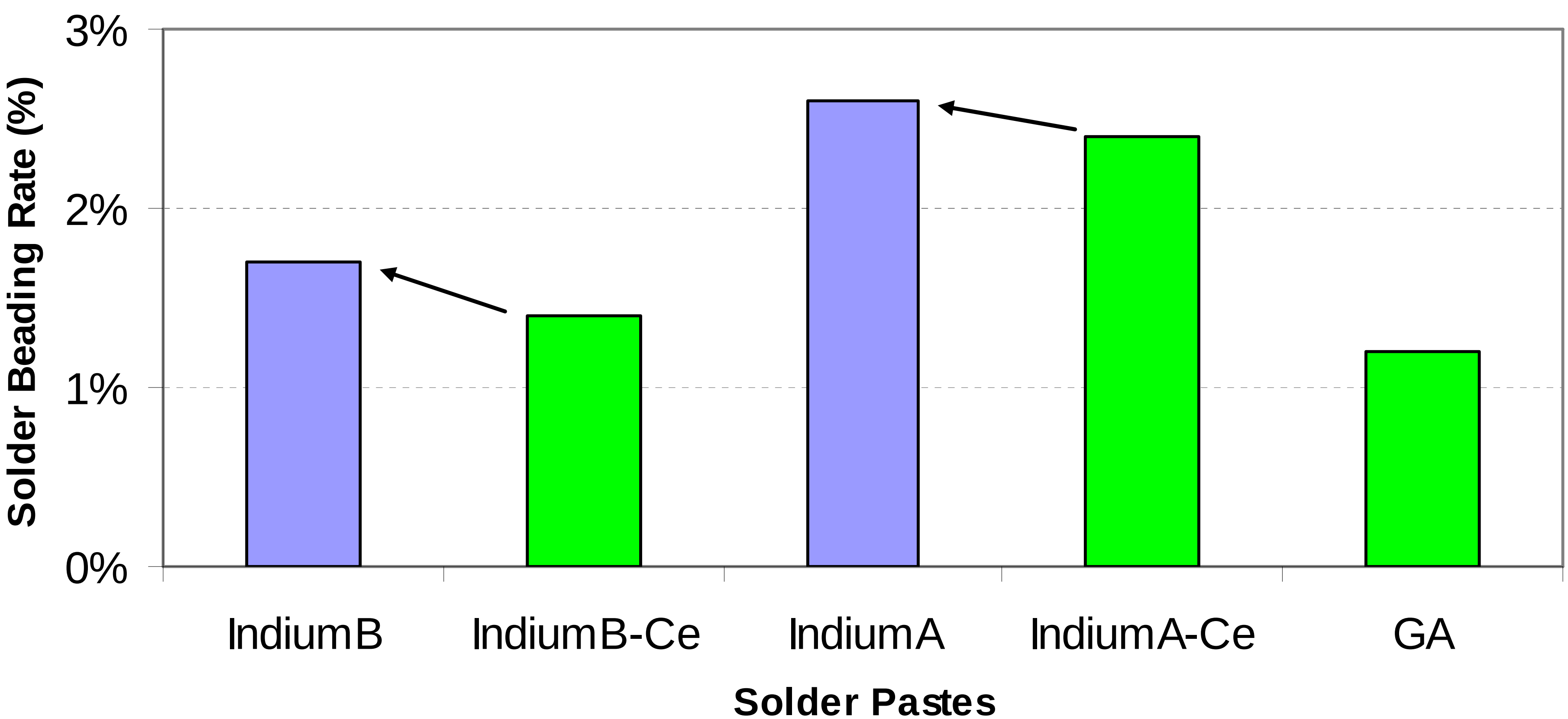
Exemplified Voiding of Joints of Lead-Free Solder Pastes





The effect of Ce on voiding of SAC system is not significant.

Solder Beading of Lead-Free Solder Pastes

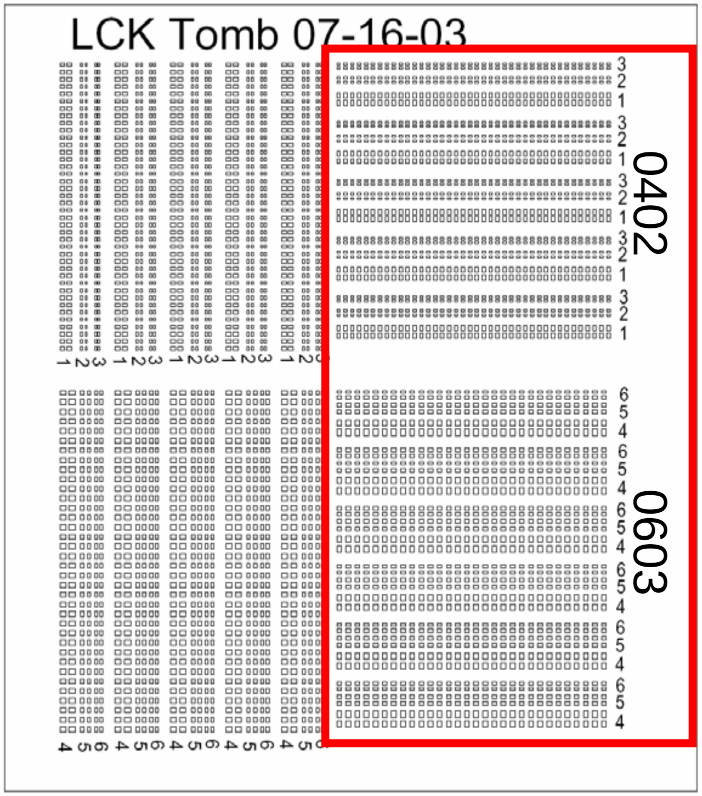


Ce-system showed slightly lower solder beading rate than SAC system.

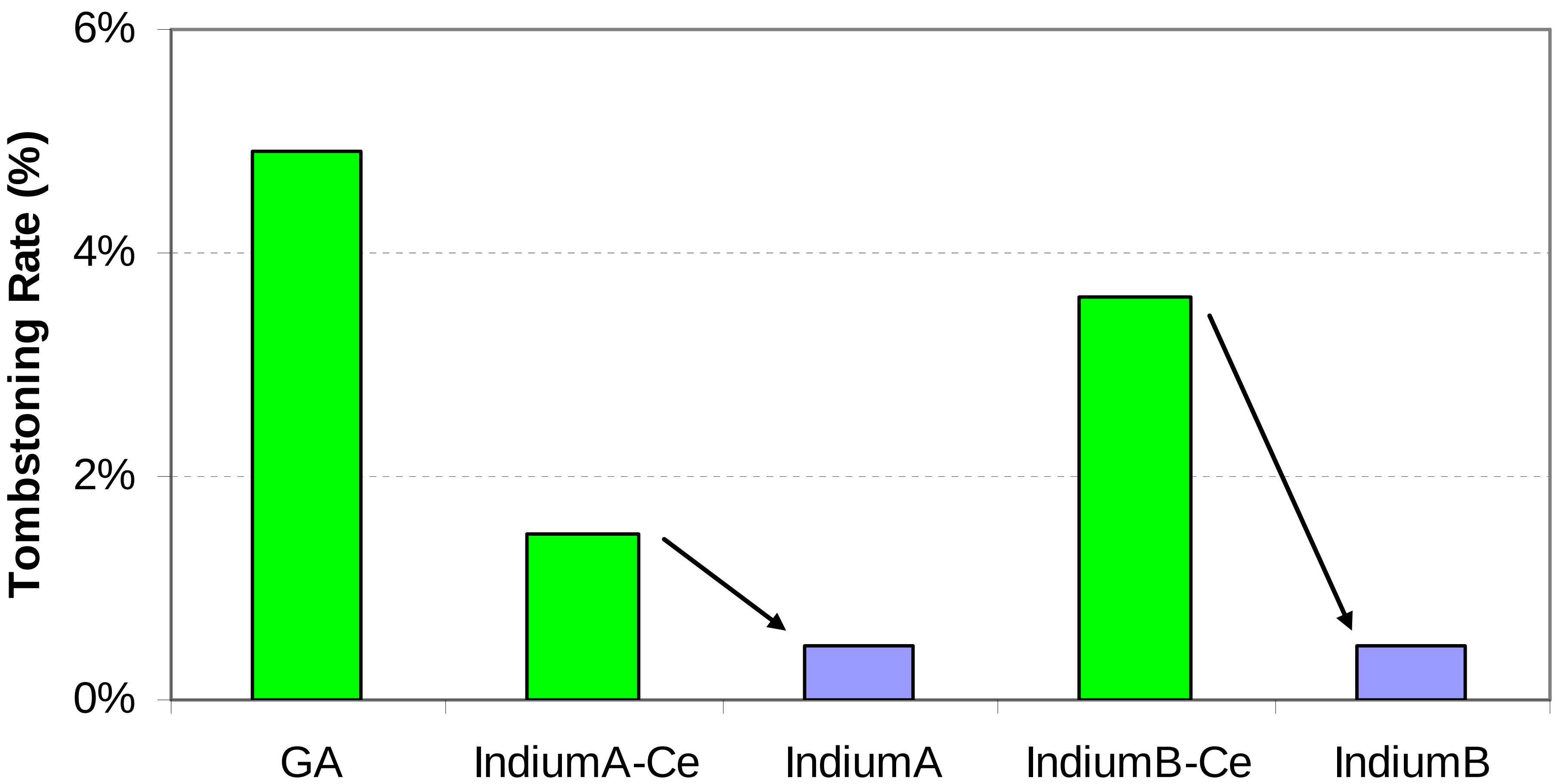
GA showed the lowest solder beading rate.

Tombstoning Test Design

- Chip capacitor 0603 (179 /PCB) and chip capacitor 0402 (240/PCB) are placed onto the red bracket region. Stencil thickness 5 mil.
- Reflowed in vapor phase reflow oven in order to magnify the defect rate. The fluid boiling is 255-260ºC.
- The tombstoning rate is expressed as percentage of all chips tested.



Tombstoning Rate of Lead-Free Solder Pastes

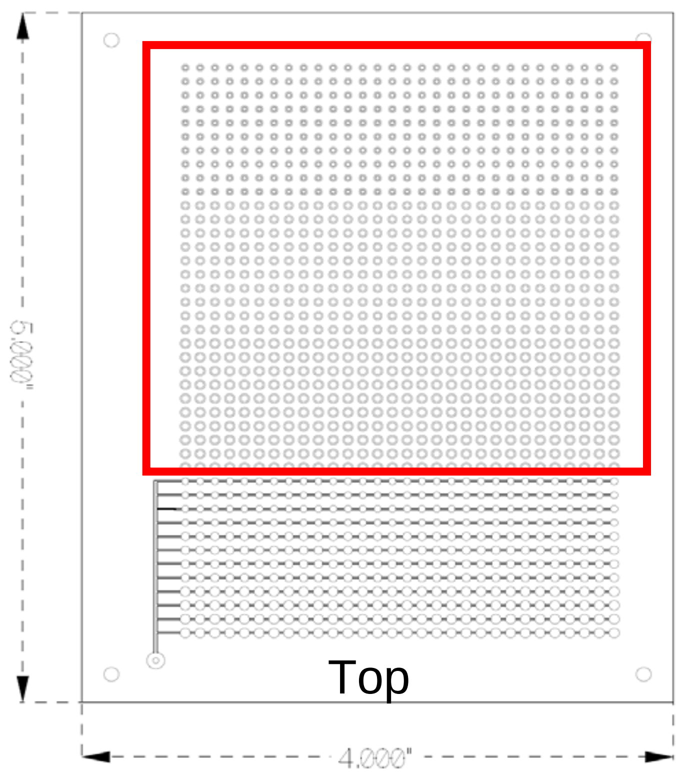


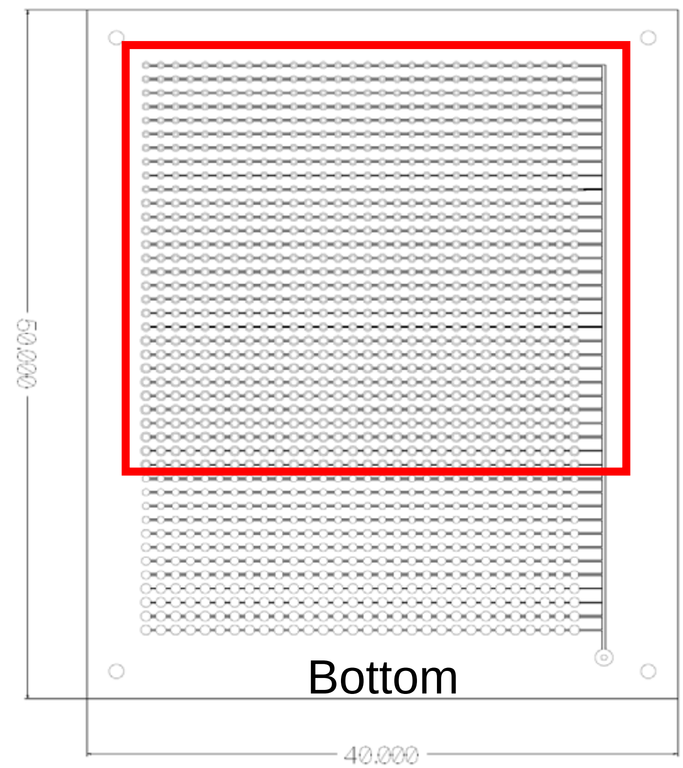
Ce-system showed higher tombstoning rate than SAC system.

GA showed the highest tombstoning rate.

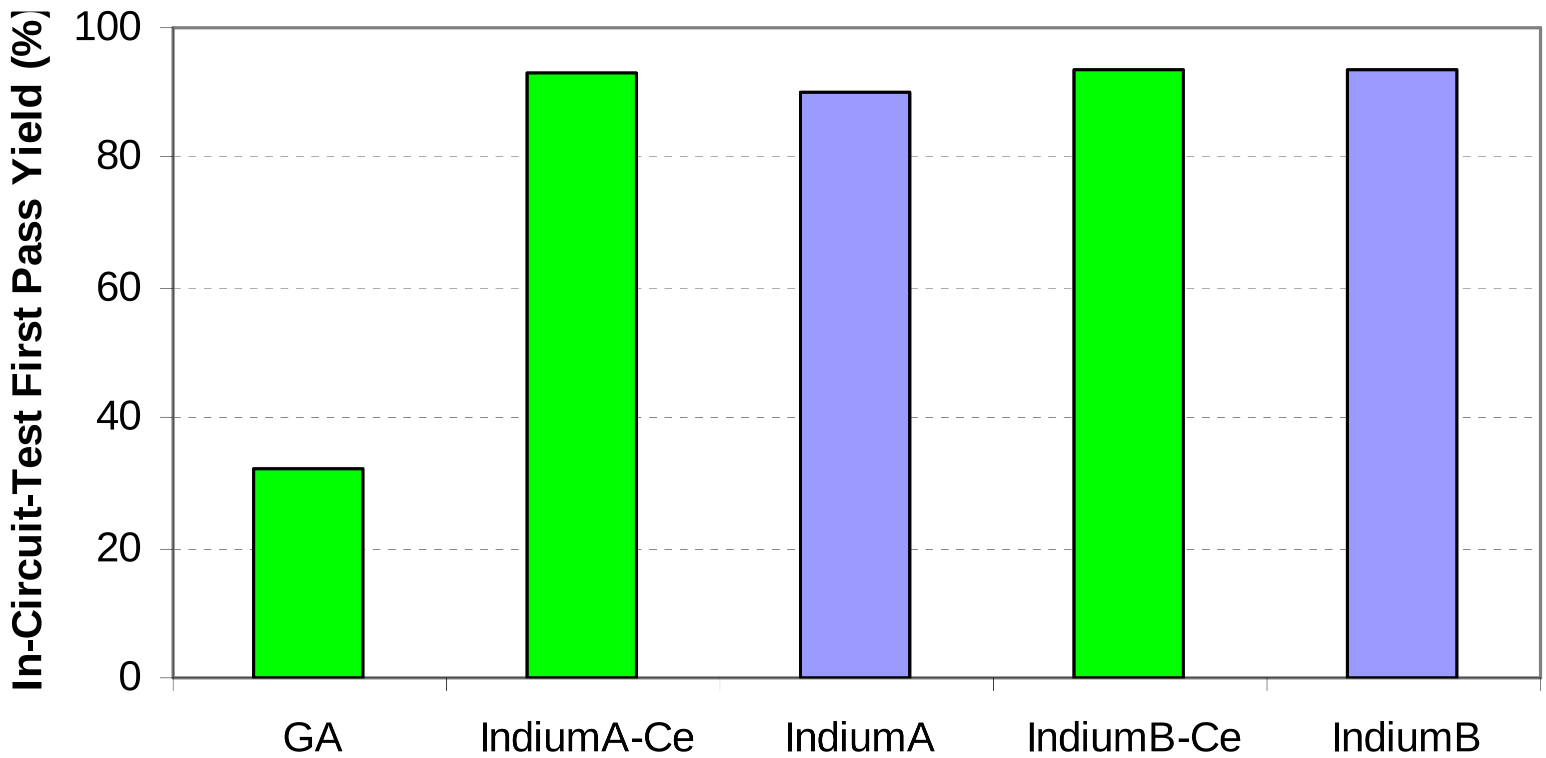
Probe Testing Design

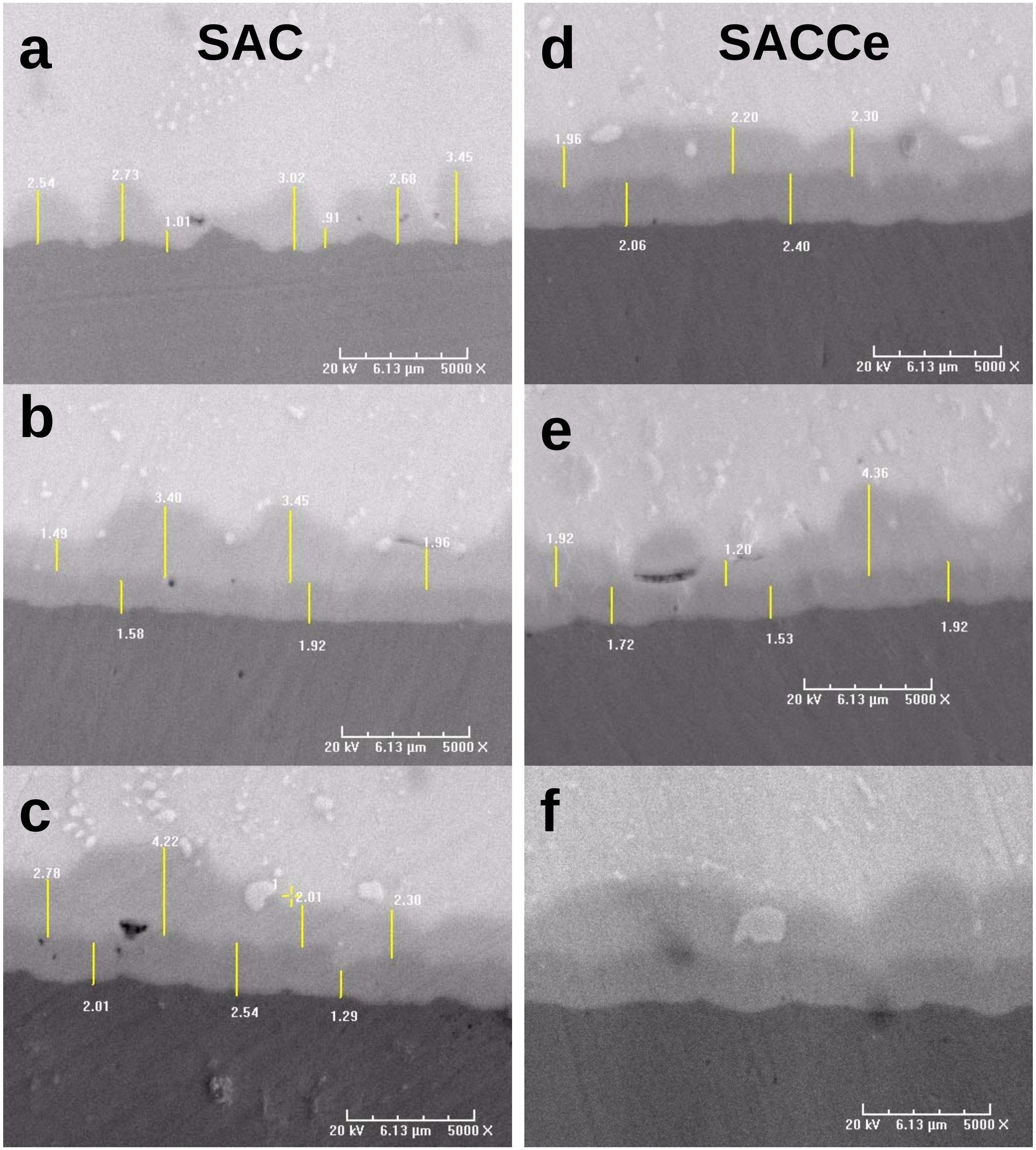
- The test board for probe testing is shown below: top view (left) and bottom view (right)
- Paste printed onto top side of board using 10 mil thick stencil, reflowed with medium profile. Put aside for 24 hrs. Then probe the through-hole pads (enclosed by red brackets) with spear probe for continuity.
- Both sides are probed, with 900 test spots for each side.
- The average of first pass rate of front side and back side is reported as Probing 1st pass rate.





Probe Testing First Pass Yield





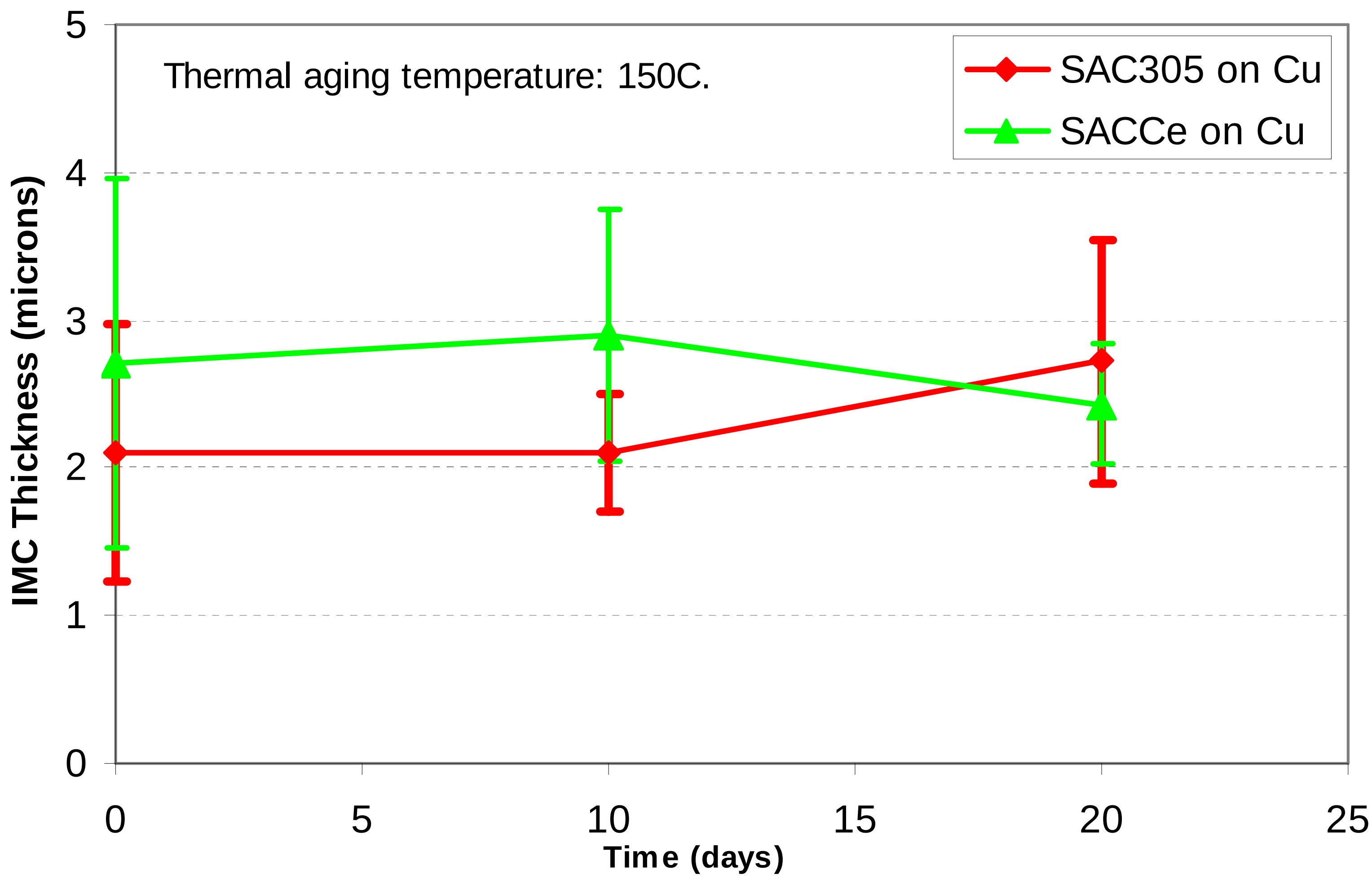
Cu/150ºC

0 day

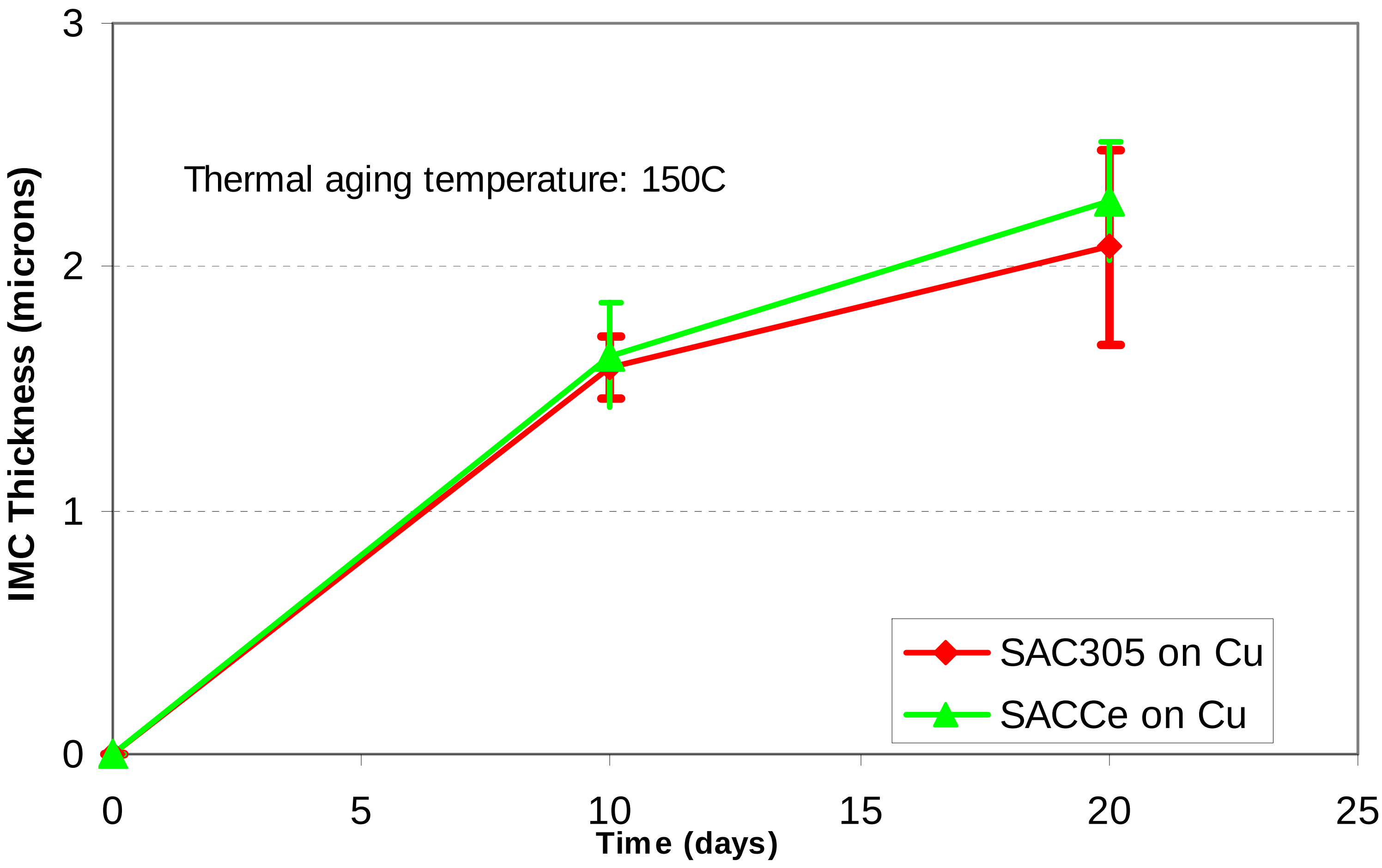
10 days

20 days

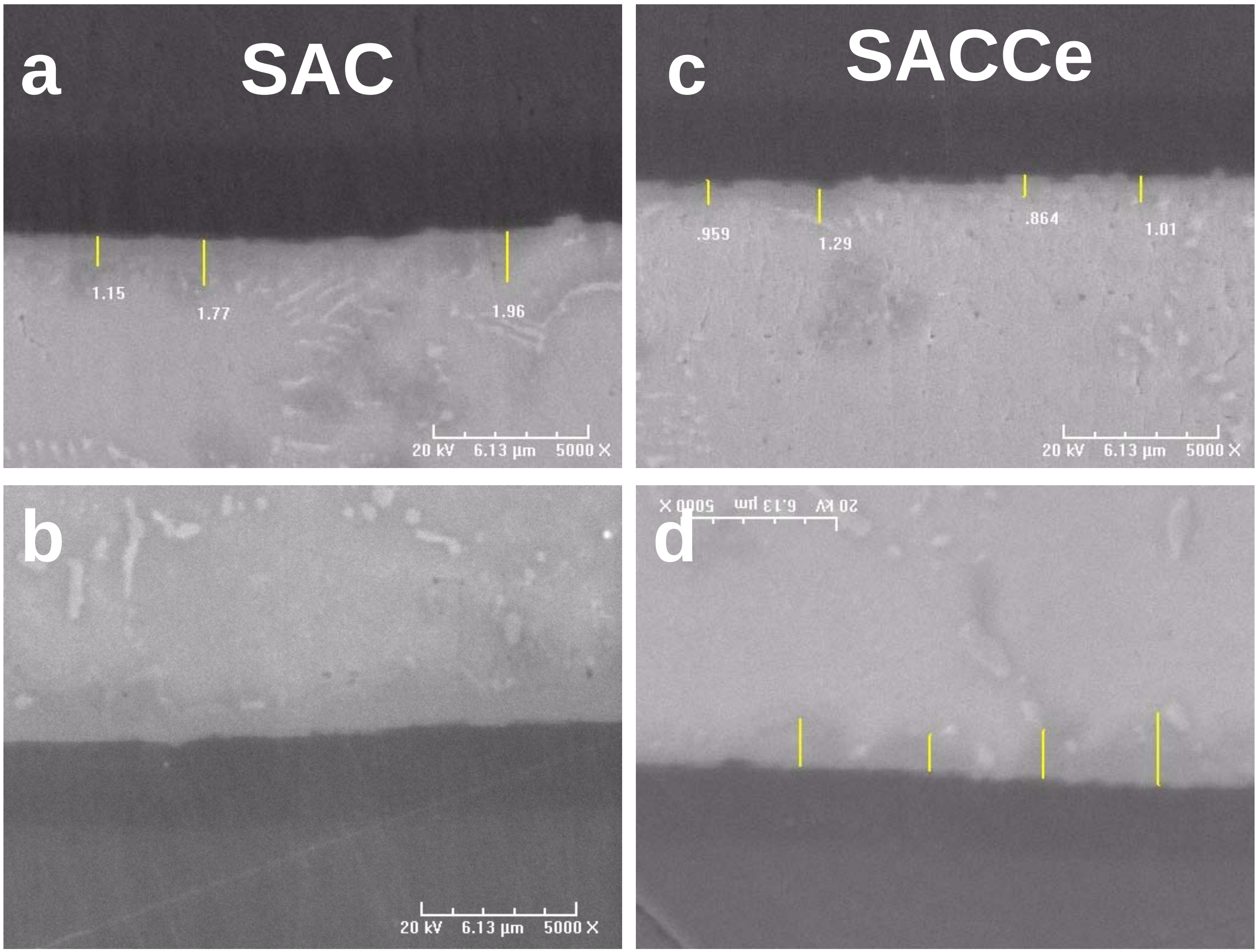
Growth Rate of Sn-Rich IMC Layer in Joints of Lead-Free Solders on Cu at 150°C



Growth Rate of Cu-Rich IMC Layer in Joints of Lead-Free Solders on Cu at 150ºC



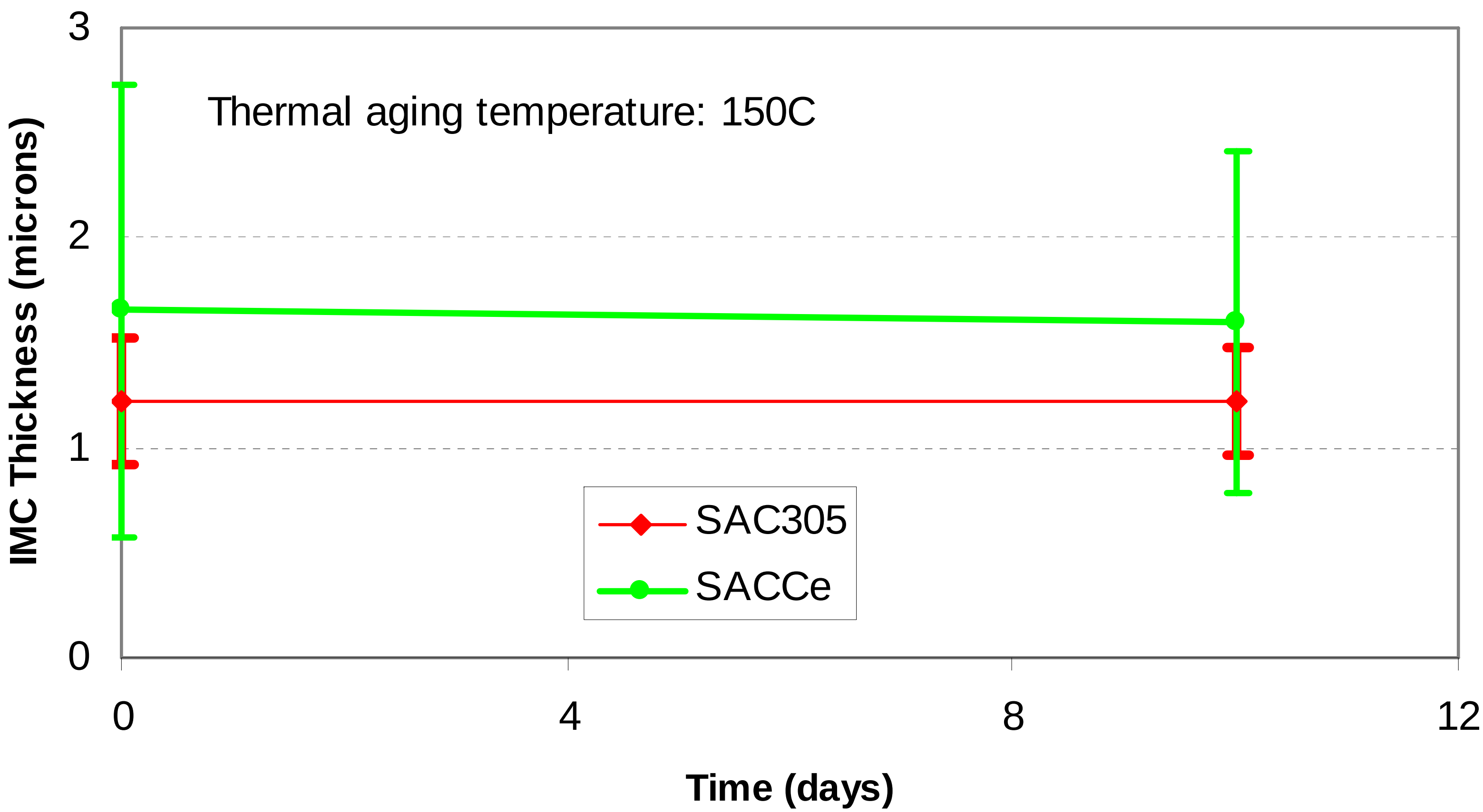
SEM of Joints on NiAu



0 D / 150ºC

10 D / 150ºC

IMC Growth Rate of Lead-Free Joints on NiAu at 150^{o}C



Conclusion

- Ce caused slightly less solder beading than SAC system
- Ce has no effect on printability, slump, probe testability, voiding.
- Ce impede wetting and cause more solder balling. The effect is more noticeable under harsh reflow condition. Ce also induce more tombstoning.
- Ce has no significant effect on IMC structure and growth rate.
- Gold Arrow flux showed significant limitation than Indium flux controls at reflow soldering and probe testing.