The Effect of Copper Plating Processes and Chemistries on Copper Dissolution

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Abstract
Implementation of lead-free assembly processes results in higher copper dissolution rate than traditional SnPb alloys. The rate at which copper is dissolved could be dependent on many factors, such as solder alloy, contact time, solder temperature, flow rate, copper plating processes, copper grain structure, etc. The effect of assembly processes and process parameters on copper dissolution is well known and published. However, there is limited study on the influence of PCB (printed circuit board) fabrication processes and chemistries on copper dissolution.

This paper focuses on the effect of copper plating processes and chemistries on copper dissolution. Different Cu plating methods and chemistries were studied and compared. The paper will discuss the impact of Cu plating processes (direct current plating vs. pulse reverse plating), current density, plating chemistries and rectifiers on dissolution rate. The Cu microstructure from different plating methods is discussed.

Keywords: Lead-free, SnAgCu, Copper Dissolution, Copper Plating Processes.

Introduction
Copper dissolution is a natural metallurgical reaction through which copper dissolves in a tin-rich liquid. Copper dissolution is not a new phenomenon. It happens during the tin-lead soldering process; however, copper dissolution becomes more pronounced during lead-free assembly due to the high tin content of lead-free alloys (SAC305/405), higher solder pot temperature and longer contact time. It is a real process challenge for lead-free pin through-hole (PTH) component rework.

There are many studies on the effects of assembly process parameters on copper dissolution.[1-5] It is well known that the assembly process parameters such as contact time, pot temperature, solder alloy, nozzle design and wave turbulence, etc. significantly influence the copper dissolution rate.[1-3] Longer contact time and higher pot temperatures resulted in higher copper dissolution.[1-2] Alternative lead-free alloys (such as SnCuNi and SnCuNiGe) have been reported to reduce the rate of copper dissolution.[4-5]

There are very limited studies on the effects of the copper plating processes on copper dissolution[5-6]. A previous internal study compared nineteen different plated coppers using various industry chemistries, plating parameters, and bath lives. Results found some coppers dissolve more than twice as fast as others. [6]

This paper discusses the critical copper plating variables that affect the copper dissolution. It also compares the copper dissolution rate variation due to the copper plating processes and assembly processes. .

Test Vehicle
Flextronics lead-free test vehicle was used during this study (Figure 1). The board dimension was 225mm x 150mm x 1.67mm. The board surface finish was OSP. The copper coupon and pin header locations were used for the copper dissolution study.

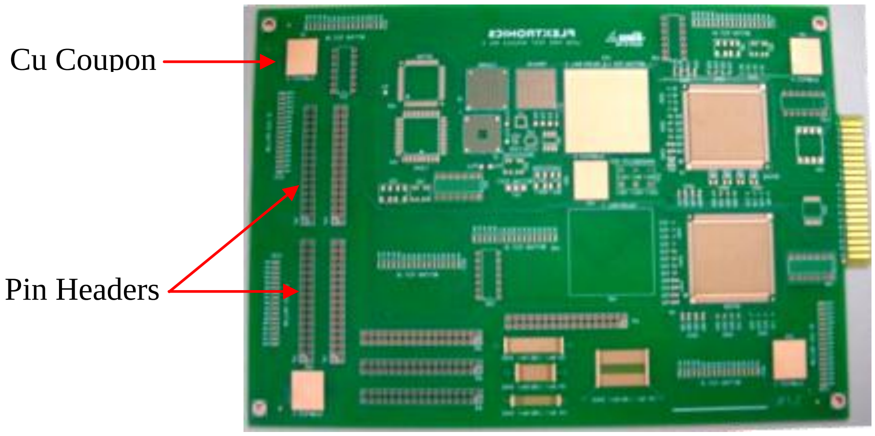


Figure 1 – Flextronics Lead-Free Test Vehicle.

Effect of Plating Processes on Copper Dissolution

Variables

There are many process variables in the copper plating processes, and the most common and critical factors were included in this study. Different copper plating processes (Table 1) were studied, such as direct current plating (DC), pulse reverse plating (PRP), vertical DC and horizontal pulse. The effects of current density, plating chemistry and type of rectifier on copper dissolution rate were also investigated (Tables 1 & 2).

Table 1 - Copper Plating Process Variables

Copper Plating Variables	Levels
Copper plating processes	Direct Current Plating (DC) vs. Pulse Reverse Plating (PRP)
	Vertical DC vs. Horizontal pulse
Current density	Low, High
Chemistry	Chemistry 1, Chemistry 2
Type of rectifiers	Rectifier 1, Rectifier 2

Table 2 - Copper Plating Methods

Marking	Plating Methods
Plating 1	Vertical DC, Low Current Density
Plating 2	Vertical DC, High Current Density
Plating 3	Horizontal Pulse, Chemistry 1
Plating 4	Horizontal Pulse, Chemistry 2
Plating 5	Pulse, rectifier 1
Plating 6	Pulse, rectifier 2

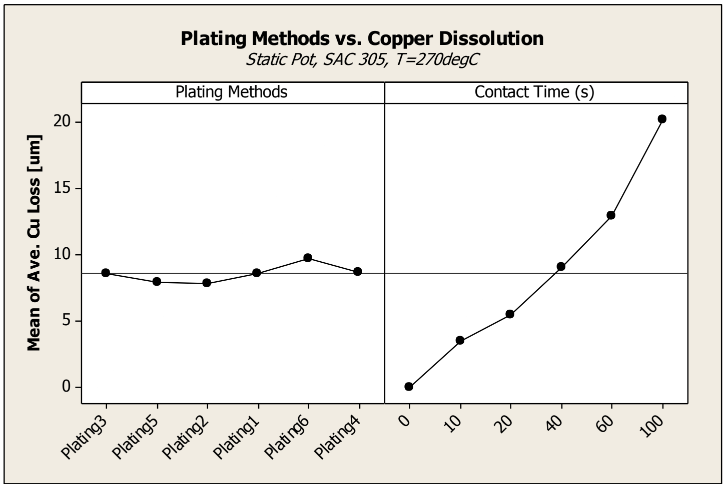
On the assembly side, different contact times (0s, 10s, 20s, 40s, 60s, and 100s) were included for each copper plating method. A static pot of Sn3.0Ag0.5Cu alloy was used in the experiment, and the pot temperature was kept constant at 270ºC (Table 3).

Table 3 - Assembly Process Variables.

Assembly Process Variables	Levels
Contact time	0s, 10s, 20s, 40s, 60s, 100s
Pot temperature	270ºC

Results and Discussions

Statistically speaking, both plating methods and contact time significantly affected the copper dissolution rate [Figure 2]. The results showed that plating #2 resulted in the least copper loss, and plating #6 resulted in a higher dissolution rate. It was noticed that the copper loss due to the contact time was more significant than the copper loss due to the copper plating methods [Figure 2, 3 and 4]. The current density and type of rectifier affected the copper dissolution rate. Higher current density resulted in less copper dissolution [Figure 3]. Rectifier 1 caused less copper loss than Rectifier 2 [Figure 4].

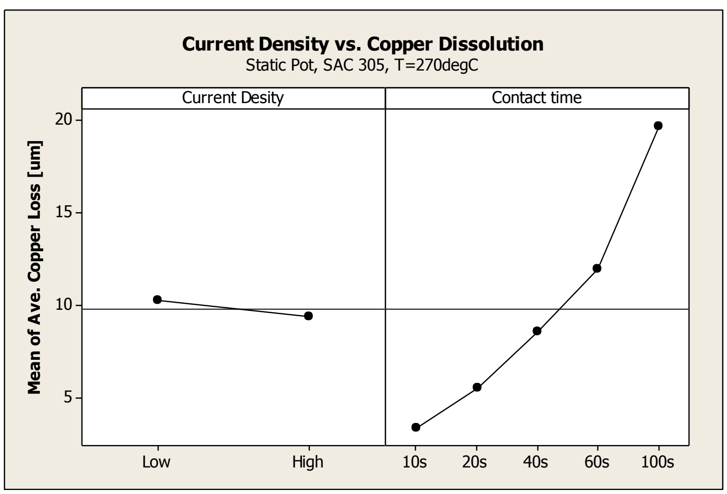


Analysis of Variance for Ave. Cu Loss [um], using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Plating Methods	5	12.78	12.78	2.56	3.83	0.010
Contact Time (s)	5	1569.32	1569.32	313.86	469.84	0.000
Error	25	16.70	16.70	0.67		
Total	35	1598.81				

S = 0.817327   R-Sq = 98.96%   R-Sq(adj) = 98.54%

Figure 2 - Effect of Plating Methods and Contact Time on Copper Dissolution

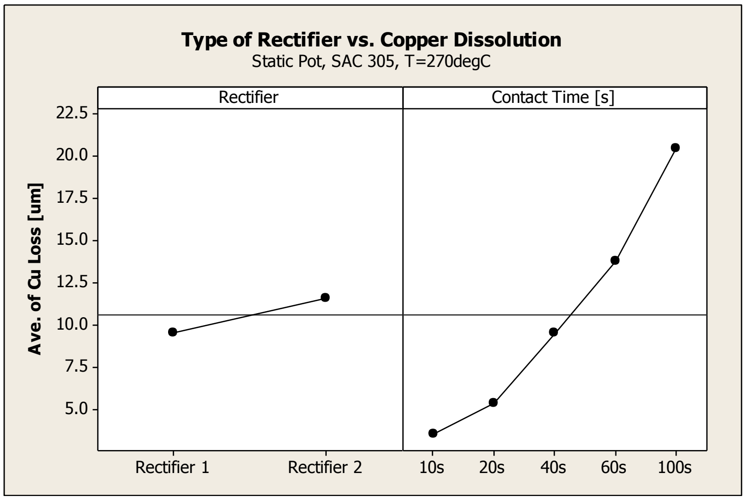


Analysis of Variance for Ave. Cu Loss [um], using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Current Density	1	1.756	1.756	1.756	16.04	0.016
Contact time	4	321.870	321.870	80.467	735.13	0.000
Error	4	0.438	0.438	0.109		
Total	9	324.063				

S = 0.330847   R-Sq = 99.86%   R-Sq(adj) = 99.70%

Figure 3 - Effect of Current Density on Copper Dissolution



Analysis of Variance for Ave. of Cu Loss [um], using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Rectifier	1	10.609	10.609	10.609	7.22	0.055
Contact Time [s]	4	370.548	370.548	92.637	63.08	0.001
Error	4	5.875	5.875	1.469		
Total	9	387.032				

S = 1.21188 R-Sq = 98.48% R-Sq(adj) = 96.58%

Figure 4 - Effect of Rectifier on Copper Dissolution

There was no difference in the copper dissolution rate using plating chemistry 1 or plating chemistry 2 in our study [Figure 5]. There was a very small difference in the copper dissolution rate between the direct current plating (DC) process and the pulse reverse plating (PRP) process [Figure 6]. The difference in the copper loss between the horizontal pulse process and the vertical DC process was not significant [Figure 6].

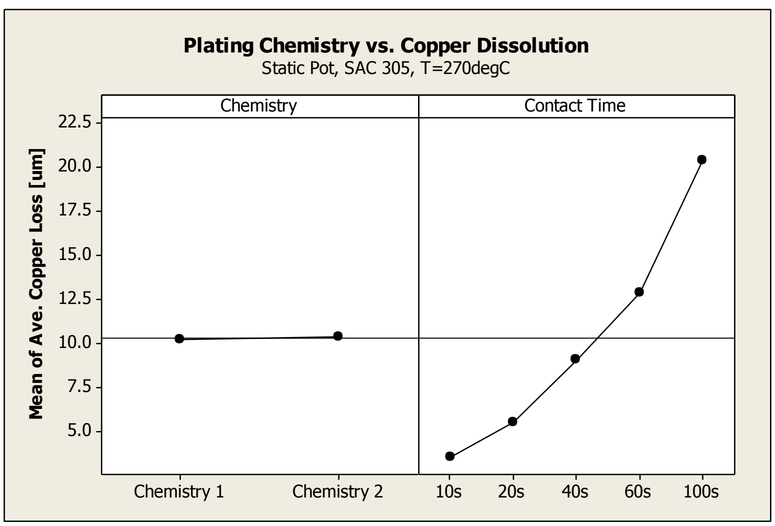


Figure 5 - Effect of Plating Chemistry on Copper Dissolution

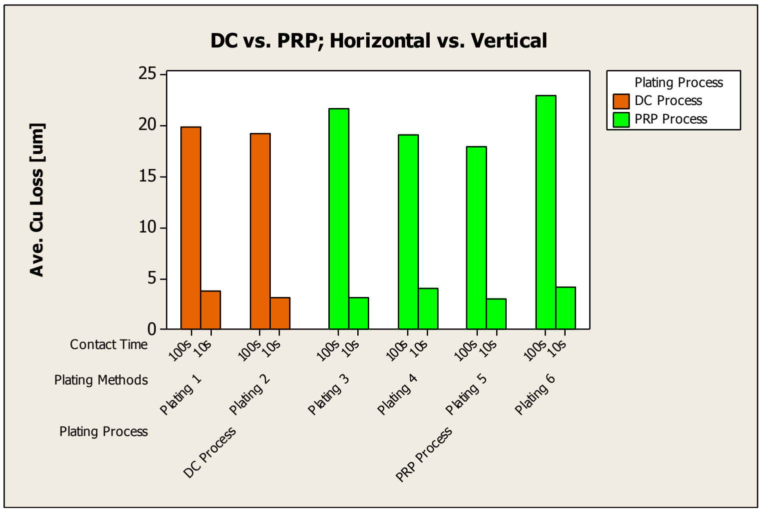
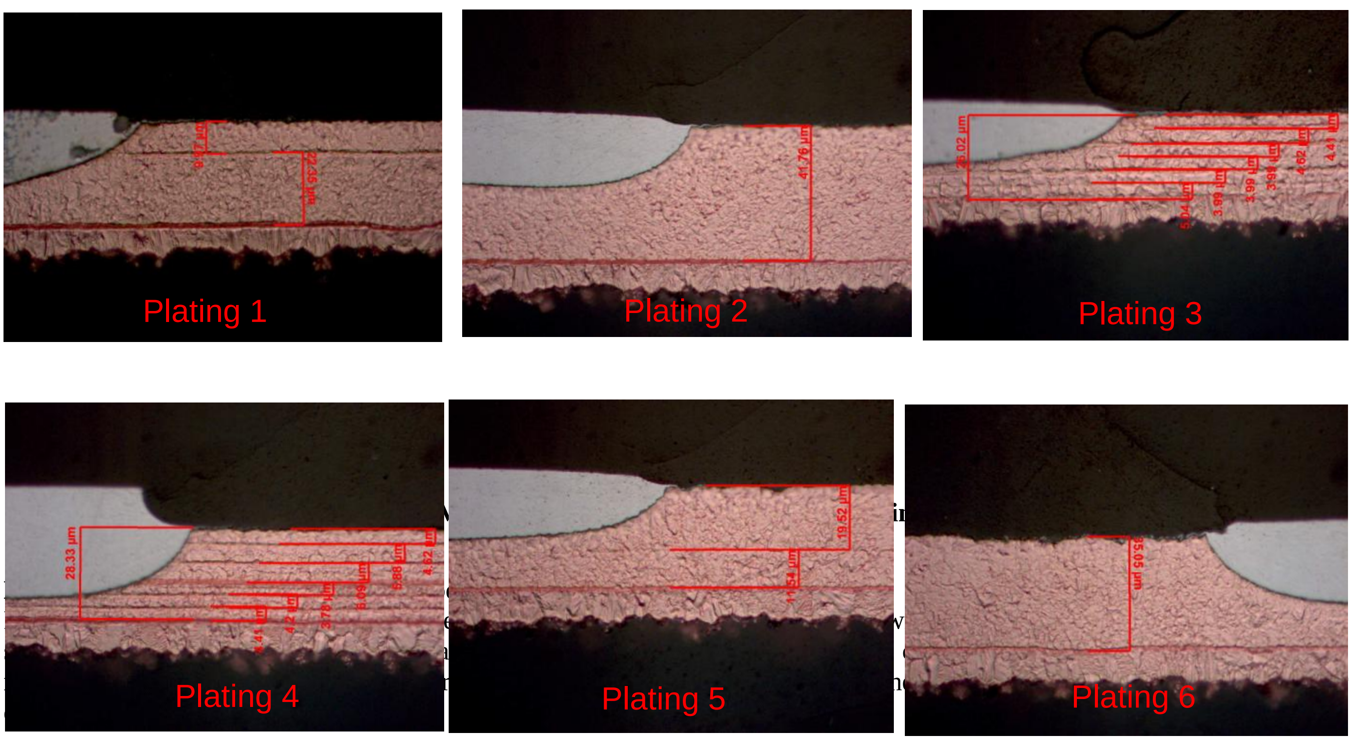


Figure 6 - DC vs. PRP

Copper Microstructure

The copper microstructures from the various plating methods are shown in Figure 7. Different plating methods resulted in different layered structures. However, there was no correlation between the copper microstructure and the copper dissolution rate in this study. Plating #2 resulted in the least copper dissolution, and plating #6 resulted in the most copper dissolution; however their microstructure appeared similar under high magnification microscope.



A further study was conducted for plating # 2 and plating #6 using a dynamic minipot rework environment. As expected, the knee of the PTH barrel was seen to dissolve at a faster rate than other locations of the barrels. The copper at the knee was dissolved on average five times faster than at the middle of the barrel and three times as fast as at the annular ring location, at the contact time of 20s and the pot temperature of 270ºC. Diffusion and proximity to the solder flow explain this phenomenon.[1-2] Similar phenomenon has been reported elsewhere.[1-2]

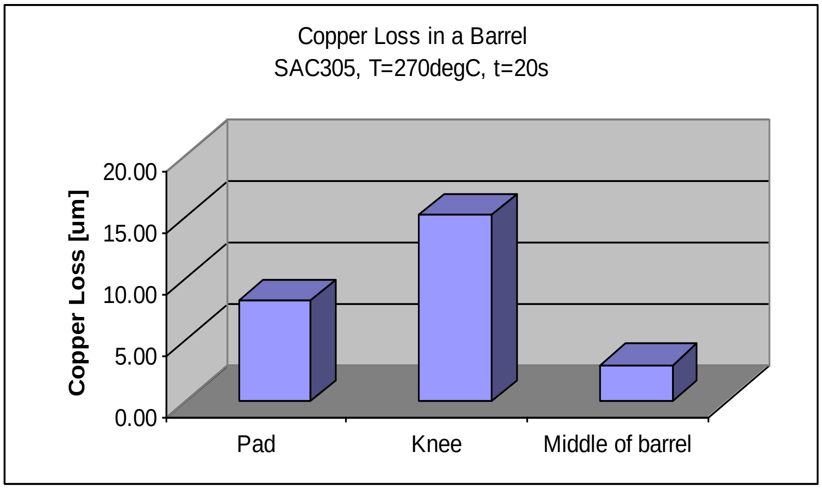


Figure 8 - Average Copper Loss in the barrel. SAC 305; T=270°C; t=20s

The presence of the component helped to slow the Cu dissolution rate. Smaller copper loss was seen at the knee of barrel loaded with a component as compared to the barrel without the component [Figure 9]. The component lead helped to reduce the solder flow turbulence and slow the erosion effect. This is consistent with previous publications that the flow rate and solder turbulence had a significant impact on the copper dissolution rate.[1,3] Variation in the copper dissolution rate from barrel to barrel within a connector was also seen in this study. The barrels that were closer to the center of the nozzle typically experienced higher copper dissolution than the barrels located at the outer edges because there was more turbulence at the middle of the nozzle than at the outer edge. [3] In our experiment, the left knee position resulted in higher copper loss than at the right knee [Figure 9]. The solder flowed from the center of the nozzle to the left or the right, but the wave was seen stronger on the left side.

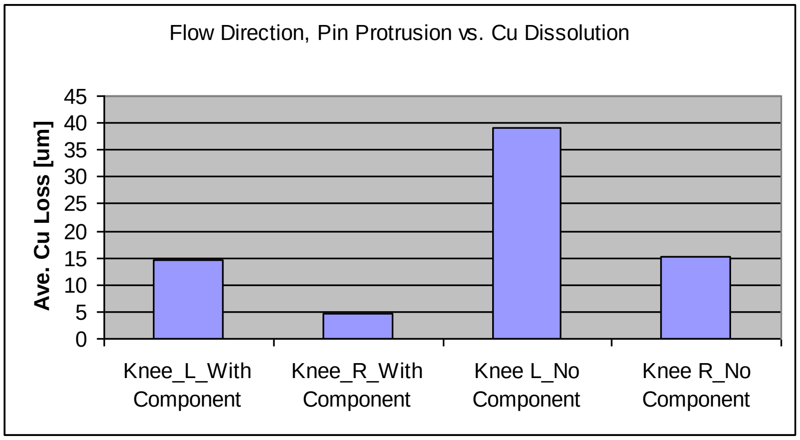


Figure 9 – Component, Pin Protrusion vs. Cu Dissolution. SAC 305; T=270°C; t=20s

As seen in the static flow experiment, the copper plating #2 resulted in less copper dissolution than the copper plating #6 in the dynamic flow minipot experiment [Figure 10]. However, the copper loss variation due to the copper plating methods was relatively small as compared to the copper loss variation due to the assembly processes such as contact time, flow direction, barrel location, pin protrusion, etc. [Figure 11]

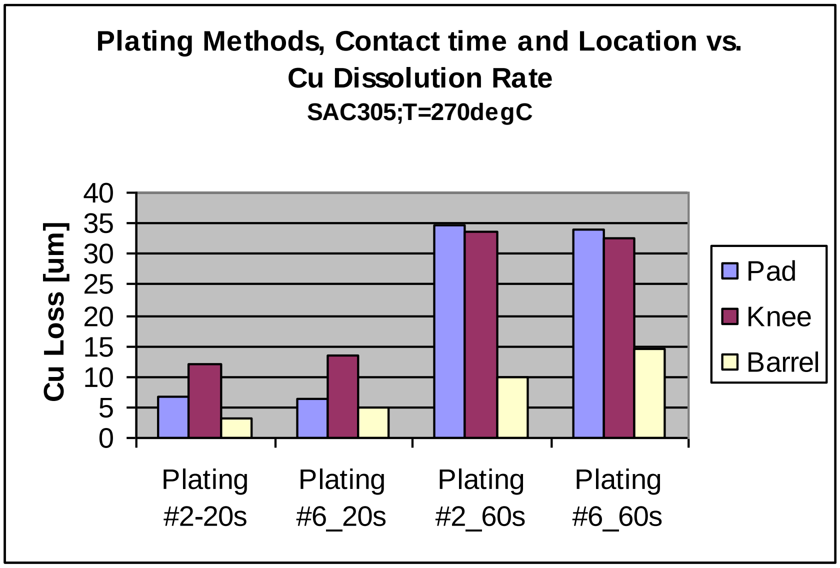


Figure 10 – Plating Methods and Contact Time vs. Copper Dissolution

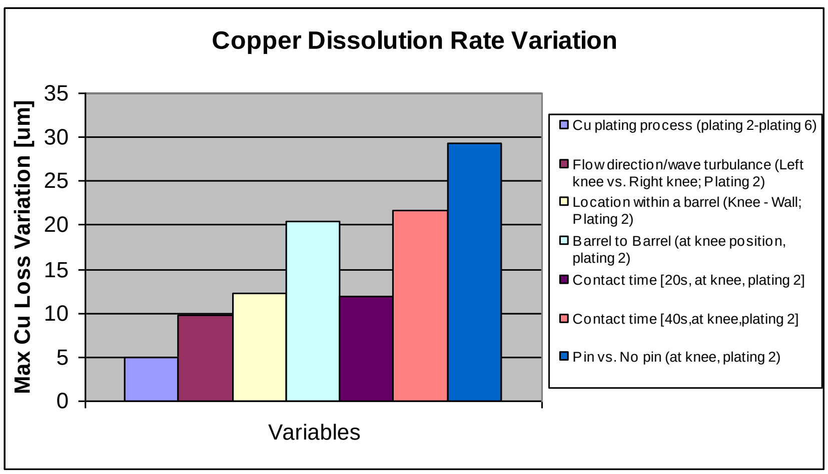


Figure 11 – Copper Dissolution Rate Variation Due to Copper Plating and Assembly Processes.

Conclusions

Assembly process variables such as alloy, contact time, pin protrusion, flow direction and wave turbulence, etc. predominantly affect the Cu dissolution rate. Therefore, for the current study, the effect of copper plating processes and chemistries on Cu dissolution becomes relatively small as compared to the assembly process effect. The difference in the copper loss between DC and PRP processes was small. There was no significant difference in the copper dissolution rate between Vertical DC and Horizontal Pulse processes. No significant difference in the copper dissolution rate was detected between Chemistry 1 and Chemistry 2 as additive. For the Vertical DC process, higher current density resulted in a lower copper dissolution rate. Plating 2 resulted in less copper loss than plating 6. Copper plating can help with the dissolution rate. Process optimization and solder alloy still play an important role in mitigating copper dissolution. Further research on other plating process variables is needed. A study on the PTH solder joint reliability of various remaining copper thicknesses is recommended.

Acknowledgements

The authors would like to thank Teresita Villavert and Tu Tran for cross-section samples in the dynamic flow experiment.

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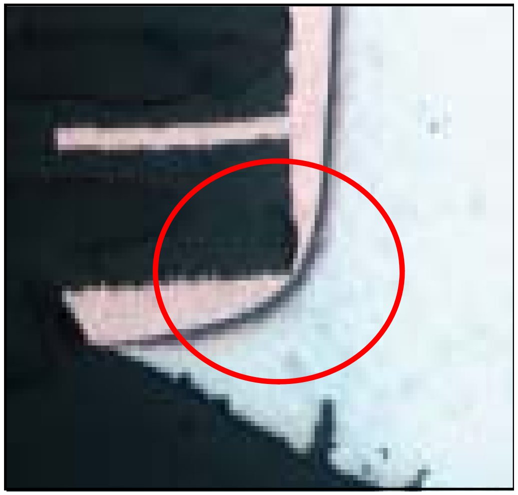
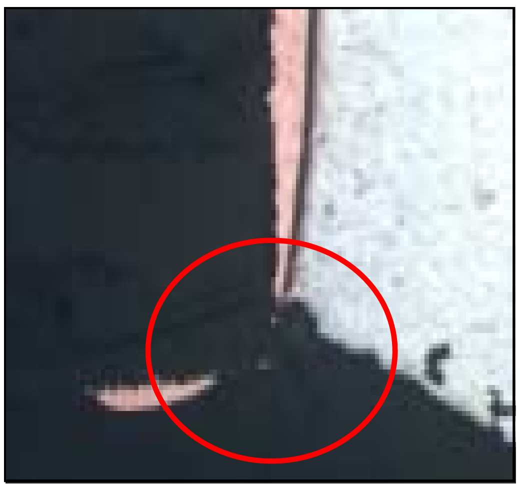
Flextronics International

Outlines

- Introduction
- Test Vehicles
- Plating Process Variables
- Results and Discussions
  - Copper Microstructure
  - Effects of Assembly Processes
- Conclusions

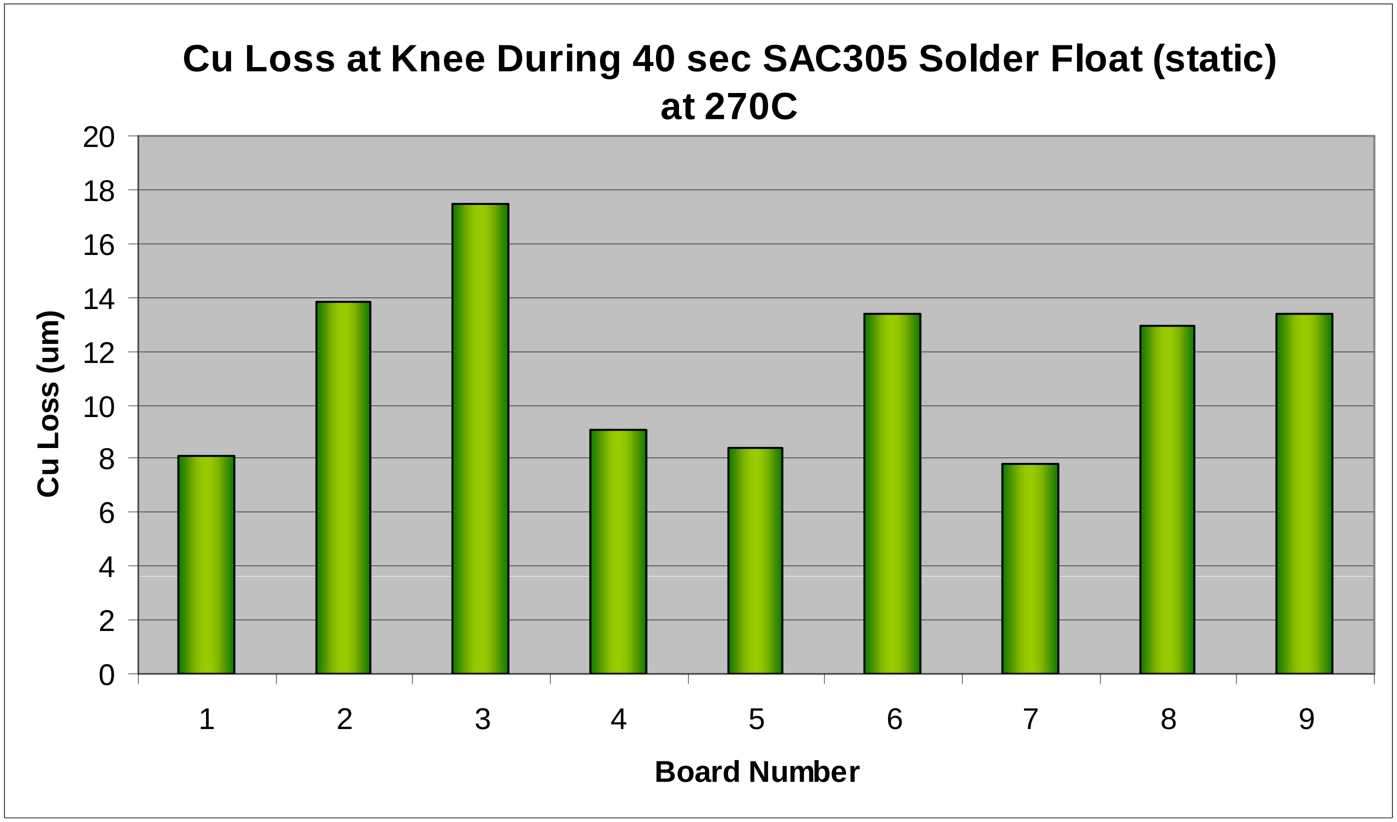
Introduction





- Cu dissolution is a metallurgical reaction where the copper (Cu) dissolves into a tin-rich liquid (SAC305).
  - This reaction occurs at wave solder & PTH rework.
- Cu dissolution can vary between adjacent PTHs.
- Cu dissolution is a function of:
  - Solder alloy (Sn%)
  - Solder temperature
    (lower temperature = less dissolution)
  - Solder dwell / contact time
    (less contact time = less dissolution)
  - Solder flow rate & direction
    (lower flow = less dissolution/erosion)
  - Other factors (plating chemistry & processes, batch variation, etc…).

Introduction (Cont'd)



1 - Supplier 1, Location 1
2 - Supplier 1, Location 1
3 - Supplier 1, Location 1
4 - Supplier 1, Location 1
5 - Supplier 2, Location 1
6 - Supplier 2, Location 2
7 - Supplier 3, Location 1
8 - Supplier 3, Location 2
9 - Supplier 4, Location 1

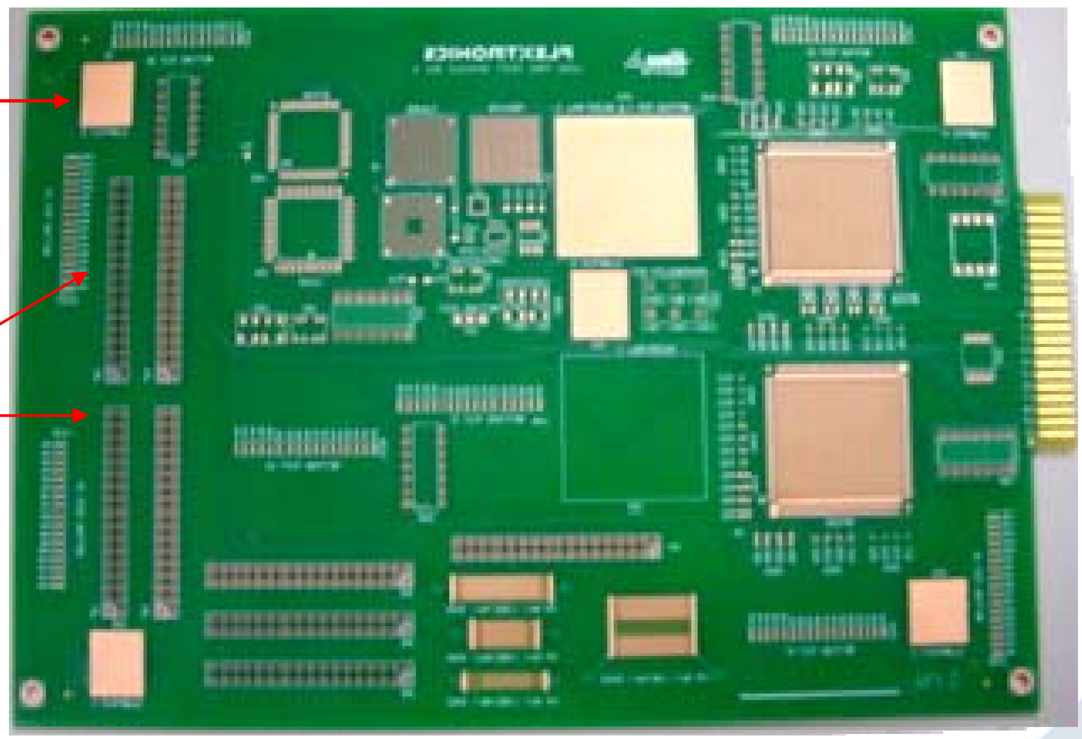
- Variation in dissolution rate was seen for boards from different suppliers/locations/batches.

Test Vehicle

- Flextronics LF Test Vehicle, Rev. 5
- Board surface finish: OSP
- Board dimension: 225mm x 150mm x 1.67mm

Cu Coupon

Pin Headers



Variables

- Copper Plating Process Variables

Copper Plating Variables	Levels
Copper plating processes	Direct Current Plating (DC) vs. Pulse Reverse Plating (PRP)
	Vertical DC vs. Horizontal pulse
Current density	Low, High
Chemistry	Chemistry 1, Chemistry 2
Type of rectifiers	Rectifier 1, Rectifier 2

- Assembly Process Variables

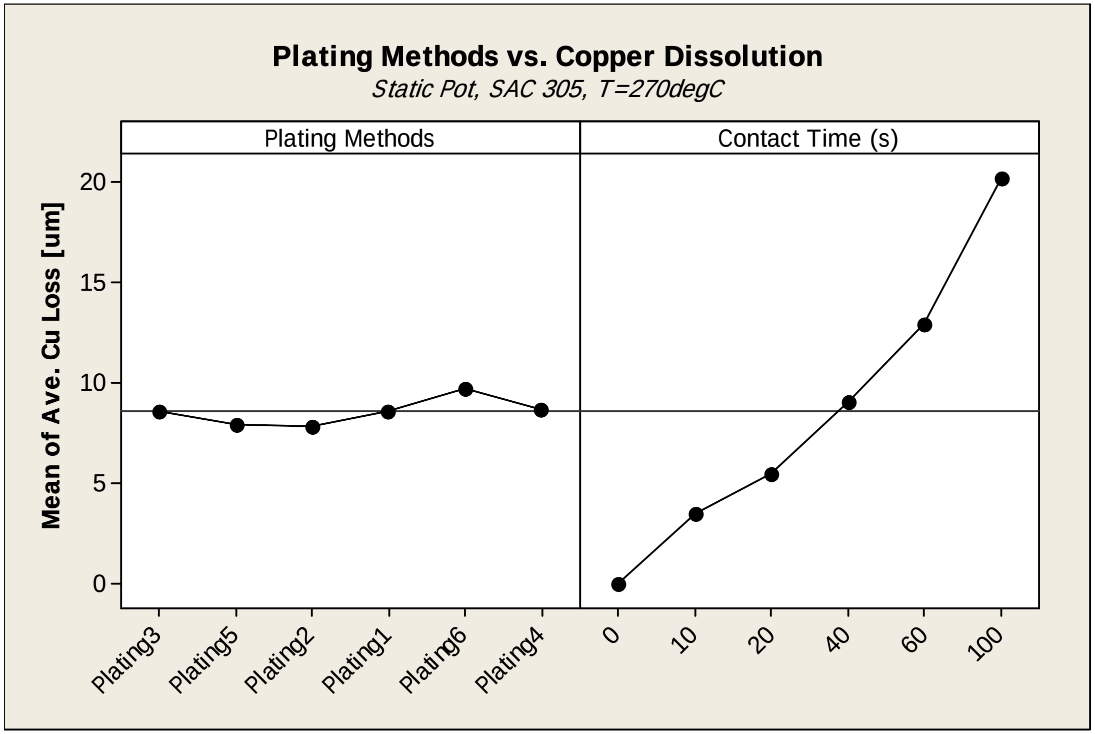
Assembly Process Variables	Levels
Contact time	0s, 10s, 20s, 40s, 60s, 100s

- Constant Factors
  - Alloy: Sn3.0Ag0.5Cu
  - Pot Temperature: 270ºC

Copper Plating Methods

Marking	Plating Methods
Plating 1	Vertical DC, Low Current Density
Plating 2	Vertical DC, High Current Density
Plating 3	Horizontal Pulse, Chemistry 1
Plating 4	Horizontal Pulse, Chemistry 2
Plating 5	Pulse, rectifier 1
Plating 6	Pulse, rectifier 2

Effect of Plating Methods and Contact Time



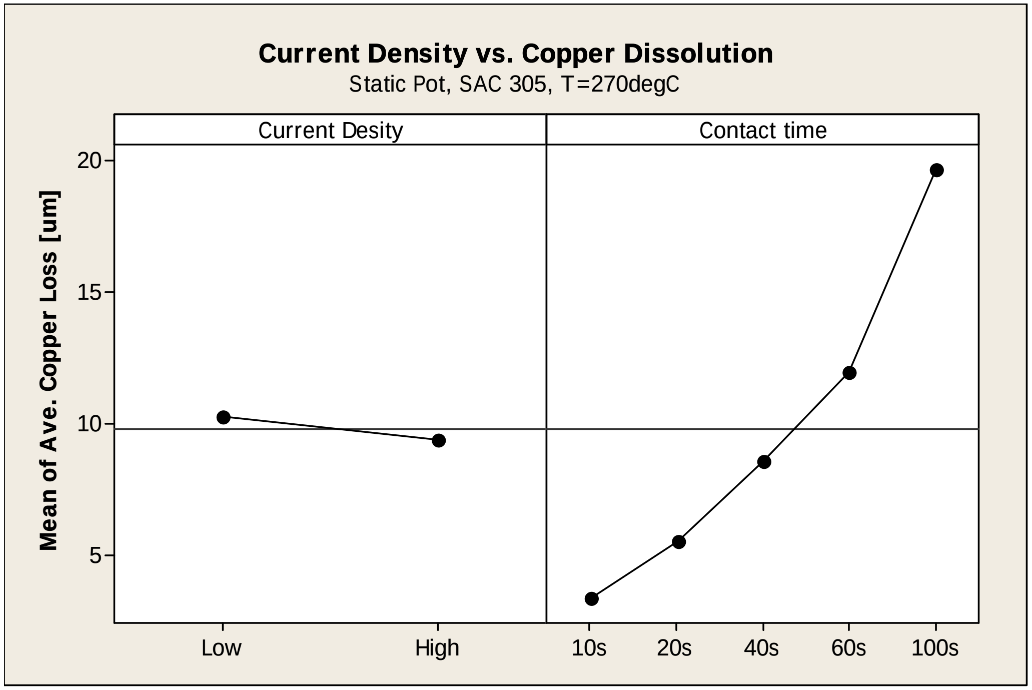
Analysis of Variance for Ave. Cu Loss [um], using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Plating Methods	5	12.78	12.78	2.56	3.83	0.010
Contact Time (s)	5	1569.32	1569.32	313.86	469.84	0.000

S = 0.817327   R-Sq = 98.96%   R-Sq(adj) = 98.54%

- Statistically speaking, both plating method and contact time significantly affected Cu dissolution.
- Contact time was the dominant factor.

Effect of Current Density



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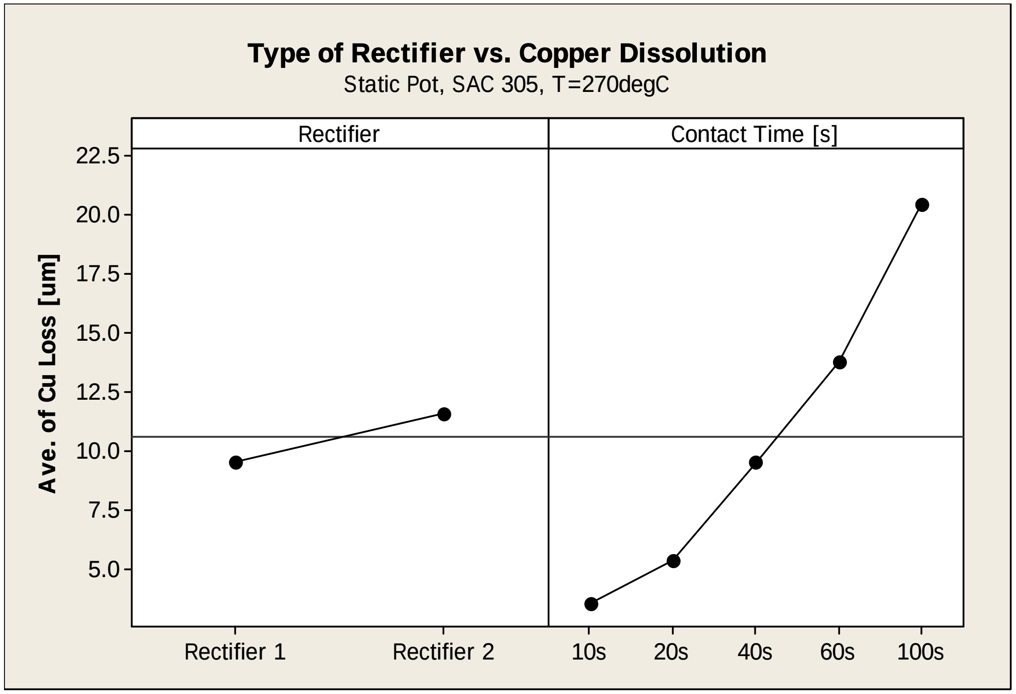
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Current Density	1	1.756	1.756	1.756	16.04	0.016
Contact time	4	321.870	321.870	80.467	735.13	0.000

S = 0.330847 R-Sq = 99.86% R-Sq(adj) = 99.70%

- Higher current density resulted in less copper loss.
- The difference in current density was statistically significant.
- However, contact time was the most significant factor that affected Cu dissolution. The change in copper dissolution rate due to current density became relatively small as compared to contact time effect.

Effect of Rectifier



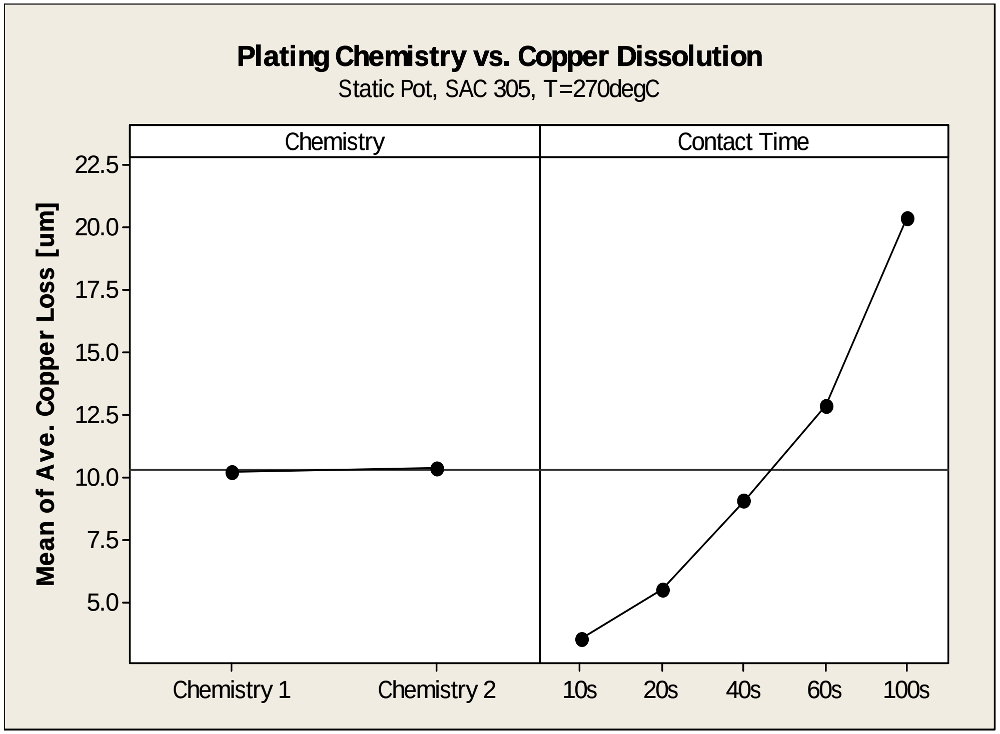
Analysis of Variance for Ave. of Cu Loss [um], using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Rectifier	1	10.609	10.609	10.609	7.22	0.055
Contact Time [s]	4	370.548	370.548	92.637	63.08	0.001

S = 1.21188 R-Sq = 98.48% R-Sq(adj) = 96.58%

- Rectifier 2 resulted in higher dissolution rate than rectifier 1.
- The difference in Cu loss due to rectifier type was much less significant as compared to the Cu loss due to contact time.

Effect of Plating Chemistry



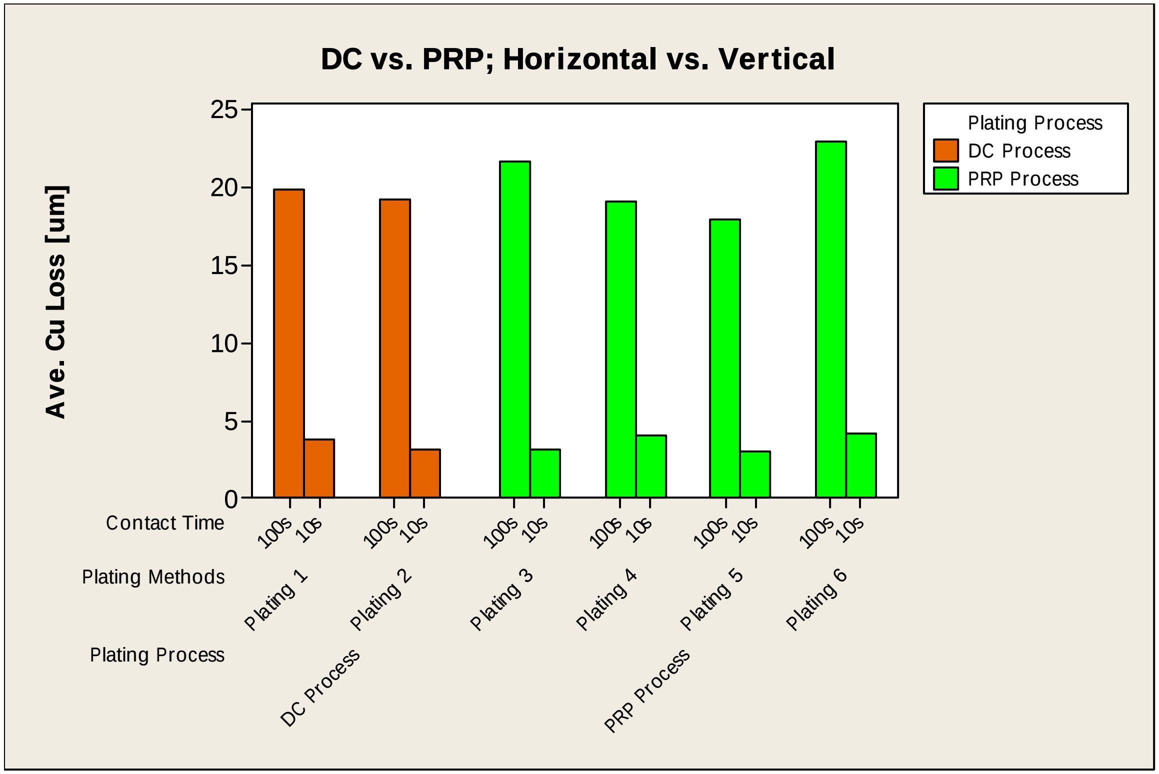
Analysis of Variance for Ave. Cu Loss [um], using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Chemistry	1	0.027	0.027	0.027	0.02	0.894
Contact Time	4	356.100	356.100	89.025	66.73	0.001

S = 1.15505 R-Sq = 98.52% R-Sq(adj) = 96.68%

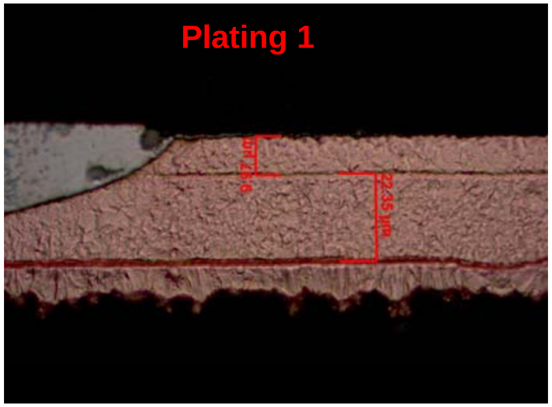
- There was no difference in copper dissolution using Chemistry 1 or Chemistry 2.

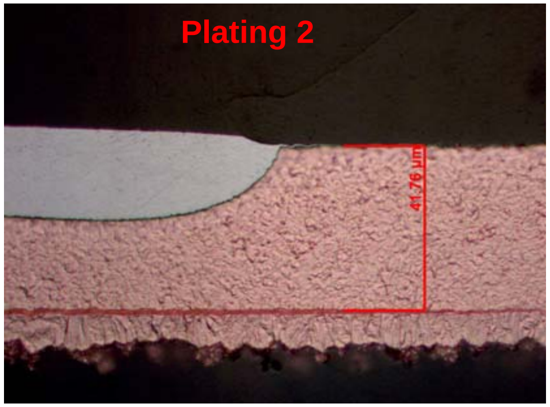
Direct Current Plating vs. Pulse Reverse Plating

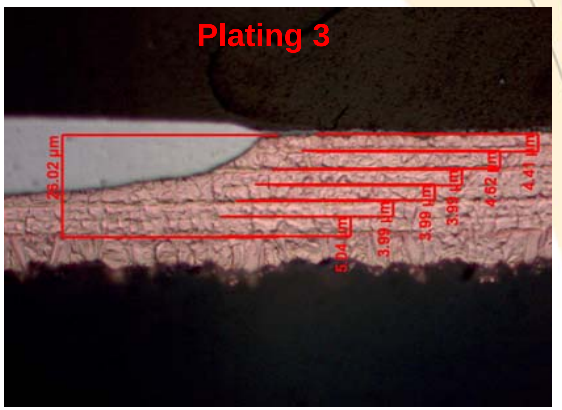


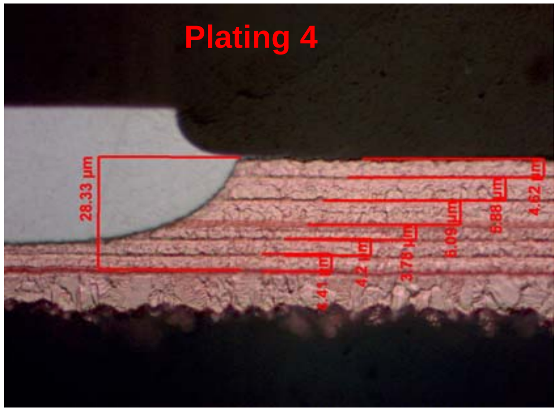
- The difference in Cu loss between DC and PRP process was small.
- There was no significant difference in Cu loss between Vertical DC and Horizontal Pulse Process.

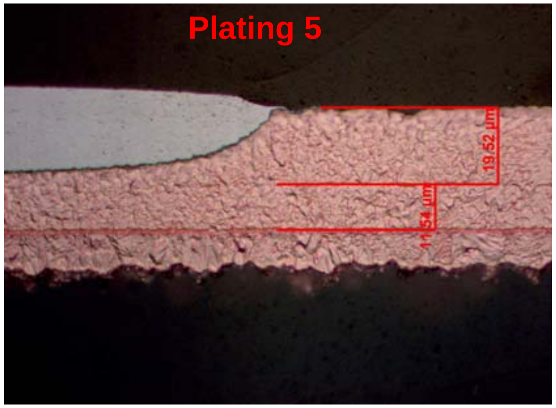
Copper Microstructure

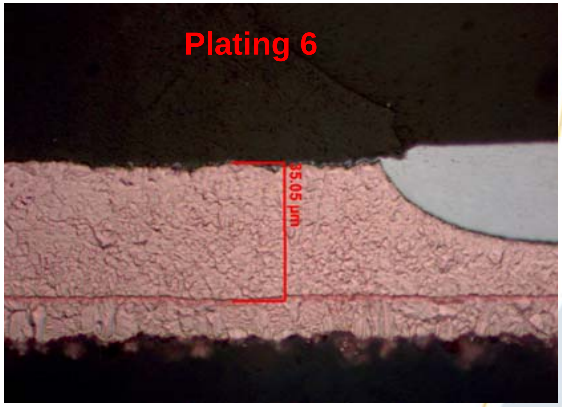






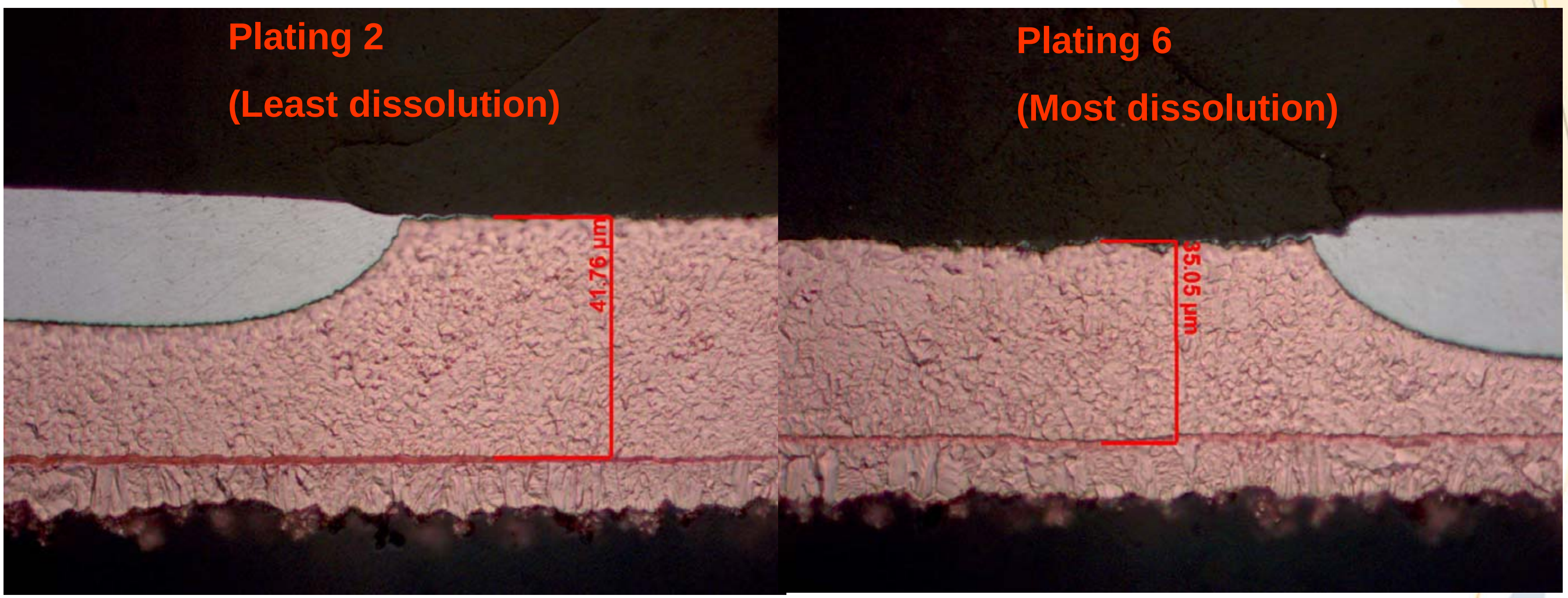






- Different plating methods resulted in different layered structure.

Cu Microstructure (Cont'd)

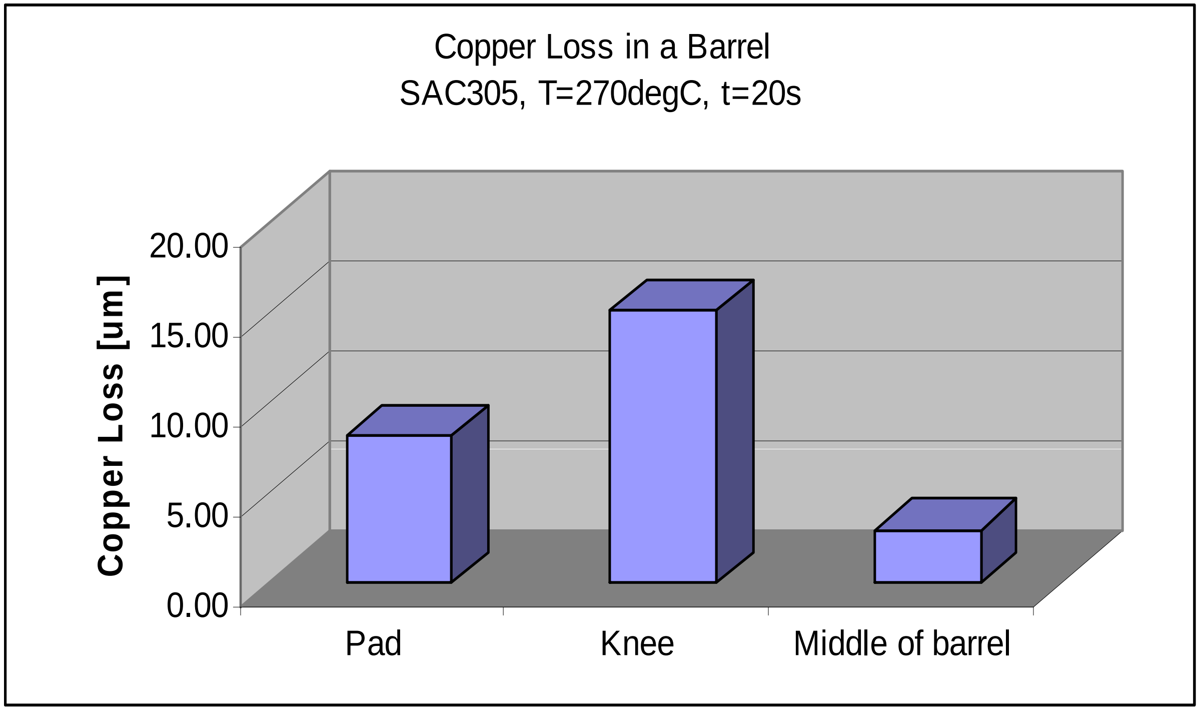


• There was no correlation between copper microstructure and copper dissolution rate.

Effect of Assembly Processes on Copper Dissolution

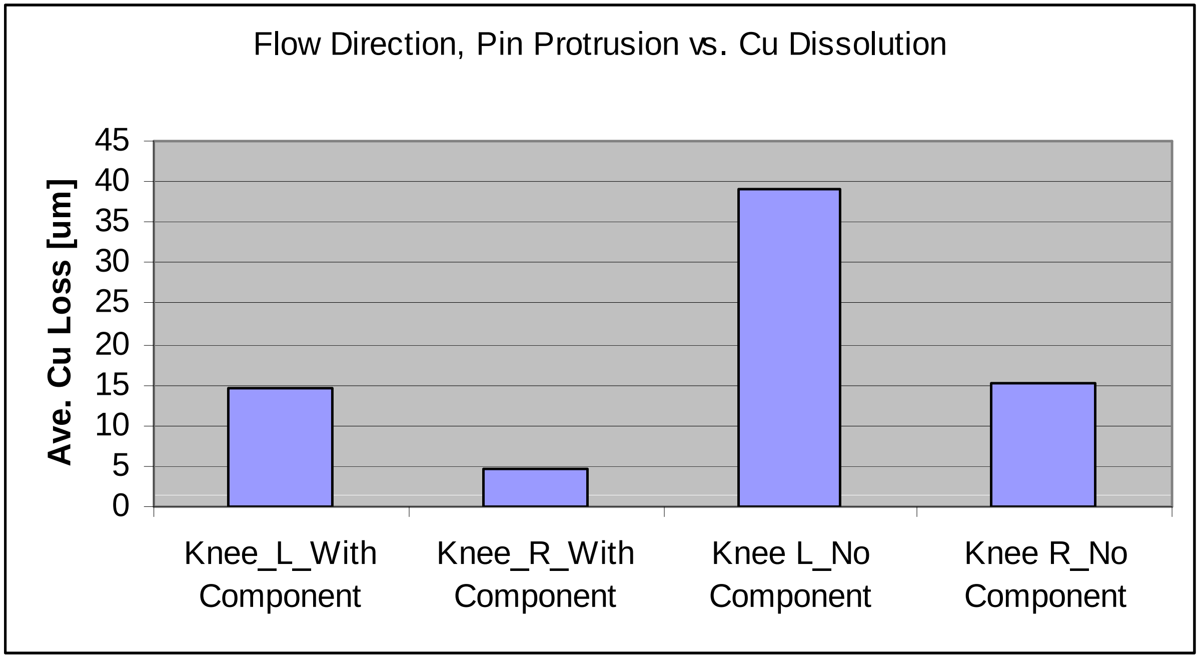
- Further study was performed for plating 2 (least dissolution) and plating 6 (most dissolution) using dynamic minipot rework environment.

Effect of Copper Location in the Barrel



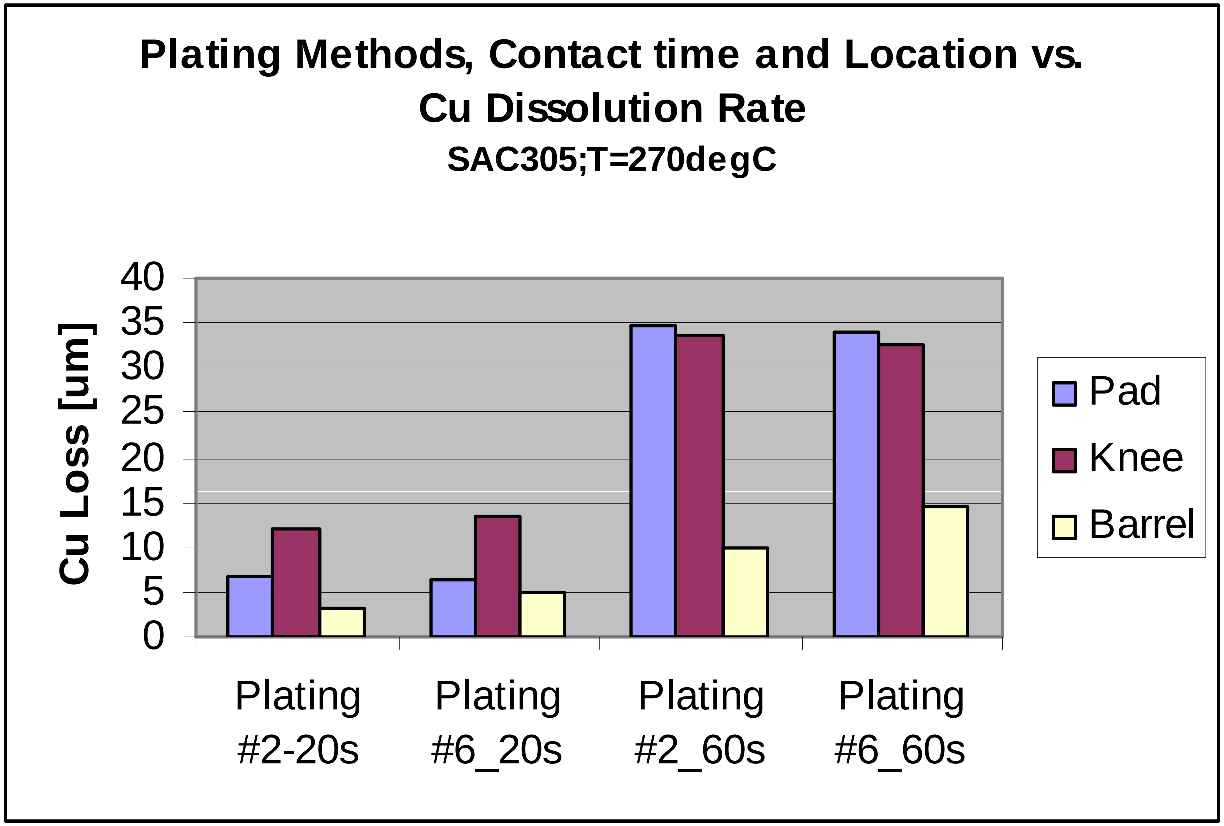
• Copper dissolution at the knee position > at the pad position> at barrel wall.

Effect of Solder Flow Rate and Direction



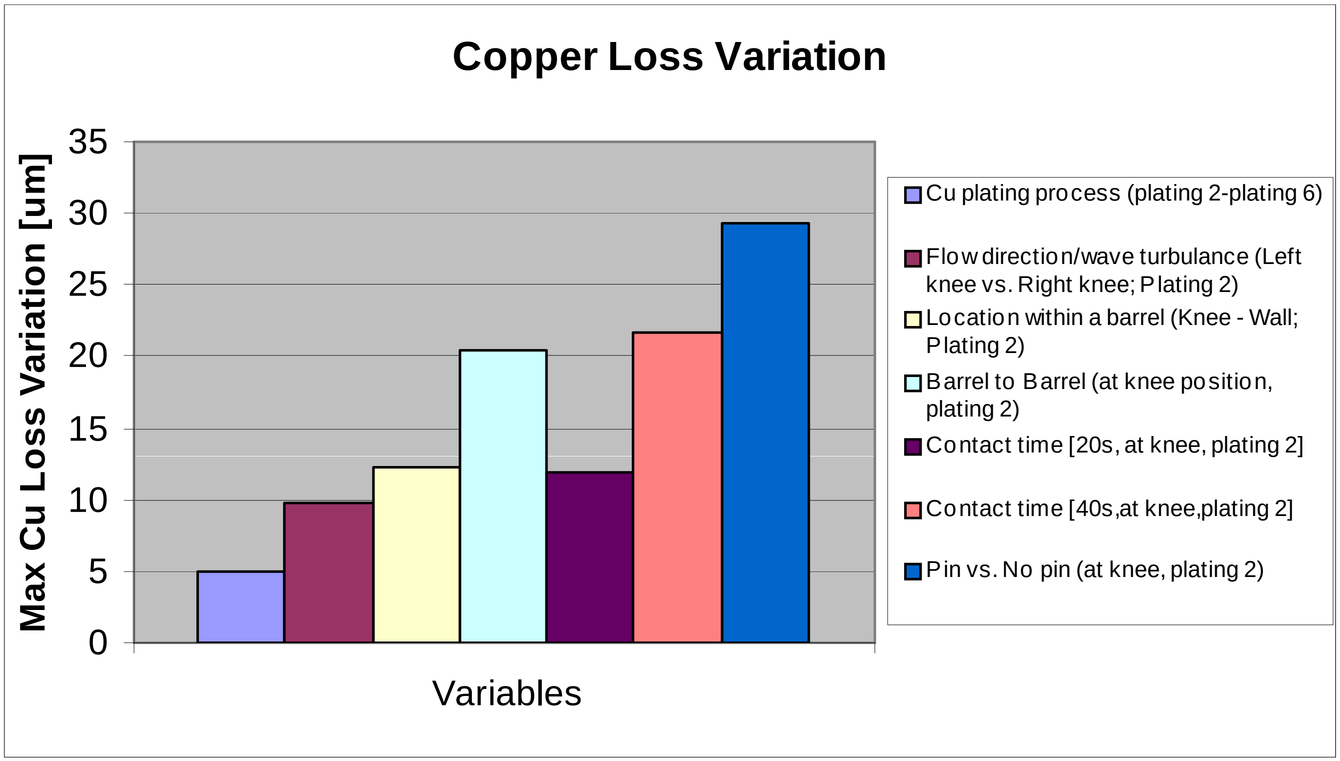
• The presence of the component helped to slow the Cu dissolution.
• In our experiment, the left knee position resulted in higher copper loss than at the right knee. The solder flowed from the center of the nozzle to the left or the right, but the wave was seen stronger on the left side.

Copper Dissolution Variation



• As the contact time increased, the effect of the assembly process variables on copper dissolution became more significant.

Copper Dissolution Variation (Cont'd)



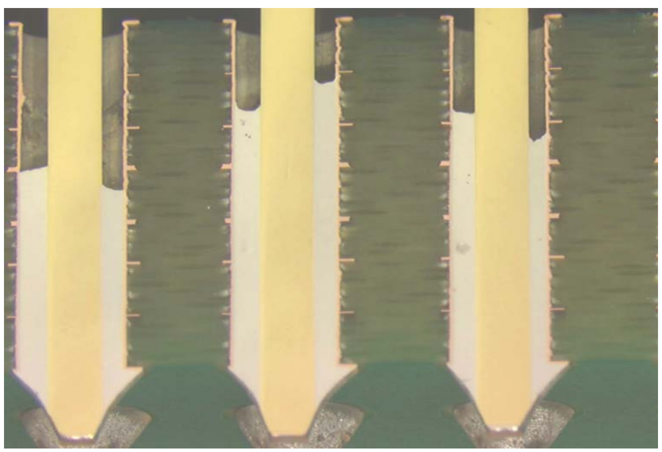
• Copper dissolution rate difference due to copper plating processes was much smaller than the variation due to assembly processes.

Hole-Fill vs. Cu Dissolution

• For achieving better hole fill, higher pot temperature and longer contact time should be used.

• However, higher temperature and longer contact time result in more copper dissolution.

• Dissolution and wetting behavior go hand-in-hand and have related effects. Additive elements (such as Ni, Ge, Sb, etc…) added to the solder alloy that will inhibit dissolution, may also inhibit wetting of the solder to the PTH.



Summary

- The difference in Cu loss between DC and PRP process was small. There was no significant difference between Vertical DC and Horizontal Pulse process.
- There was no difference in copper dissolution using Chemistry 1 or Chemistry 2 as additive.
- For Vertical DC process, higher current density resulted in less Cu loss. The difference in current density was statistically significant, but the loss was relatively small as compared to the copper loss due to contact time.
- Different plating methods resulted in different layered structure. However, there was no correlation between copper microstructure and copper dissolution rate.

Summary (Cont'd)

- Assembly process variables such as alloy, contact time, pin protrusion, flow direction and wave turbulence, etc. predominantly affect the Cu dissolution rate. Therefore, for the current study, the effect of copper plating processes and chemistries on Cu dissolution becomes relatively small as compared to the assembly process effect.
  - For the PTH rework process that requires long contact time, solder alloy and process optimization play a dominant role in copper dissolution.
  - For the PTH wave soldering process that requires short contact time, the effect of copper plating can still be significant.

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Thank You