Eliminating Ni Corrosion in ENIG/ENEPIG Using Reduction-Assisted Immersion Gold in Place of Standard Immersion Gold

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INTRODUCTION

Nickel corrosion in ENIG and ENEPIG is occasionally reported; when encountered at assembly it manifests as soldering failures in ENIG and wire bond lifts in ENEPIG. Although not common, it can be highly disruptive, resulting in missed deliver schedules, supply chain disruption, failure analysis investigations, and liability - all very costly.

In an effort to highlight and mitigate nickel corrosion defects, The IPC Plating Committee 4-14 has undertaken a revision of the original IPC–4552 Specification (issued 2002). IPC ENIG Specification 4552-Rev A was issued in 2017, and revised again in 2019 (Rev B). Rev B is in final draft; awaiting final ballot. When released, corrosion inspection would become mandatory.

The objective of the second revision, IPC 4552 Rev B, is to eliminate nickel corrosion by focusing attention on the defect. Suppliers will have to offer more robust processes, and manufacturers would have to install tighter process control.

One supplier's attempt to eliminate nickel corrosion is the introduction of Reduction Assisted Immersion Gold (RAIG). This paper addresses the role of RAIG in eliminating corrosion, first in ENIG and then in ENEPIG.

Chemical non-electrolytic gold deposition/plating is the result of reduction of the gold ion in solution to the gold metal. Reduction occurs thru the supply of electrons. Electrons may be supplied by different methods:

Immersion Gold IG
In this displacement reaction, the substrate supplies the electrons needed to reduce the ionic gold to metal. Immersion reaction is limited in deposit thickness capability as the substrate becomes less available. Under non-ideal conditions, immersion gold will corrode the underlying nickel.

Autocatalytic Gold AG deposition
The electrons needed to reduce the gold ions to metal are supplied by a reducing agent component in the bath. This requires an underlayer of immersion gold to initiate. This option is non-aggressive, will not corrode the substrate, and has unlimited thickness potential.

Reduction-Assisted Immersion RAI Gold Deposition
RAIG is a mixed reaction bath. Both immersion and autocatalytic reactions start simultaneously. As the substrate becomes less accessible, the immersion reaction will diminish and the autocatalytic reaction will dominate. It is non-aggressive, will not produce substrate corrosion, and is capable of depositing 4-6 uins of gold in a single step.

- RAIG is non-corrosive, and eliminates Ni corrosion in ENIG and ENEPIG finishes.
- Economic, one gold bath
- Capable of depositing higher thickness of gold (up to 7 µins), if desired.

This is in contrast with fully autocatalytic (electroless) gold, which requires 2 gold baths, including one for the deposition of an initial immersion gold layer prior to the autocatalytic deposition.

$Au^{+2} + 2e \rightarrow Au$

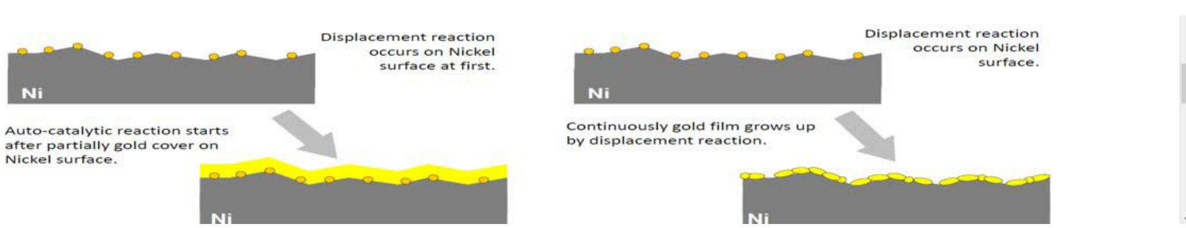

Figure 1 Graphic presentation of immersion gold vs. Reduction-Assisted Immersion Gold

ENIG and Reduction-Assisted Immersion Gold
Nickel corrosion occurs during the immersion gold deposition step. It occurs when the nickel deposit is compromised (uneven with deep crevices) in combination with an extended dwell time in an aggressive (low in gold content, high in acidity) immersion gold bath.

Process control and reduced dwell time in the immersion gold bath are the primary mitigating methods used to date.

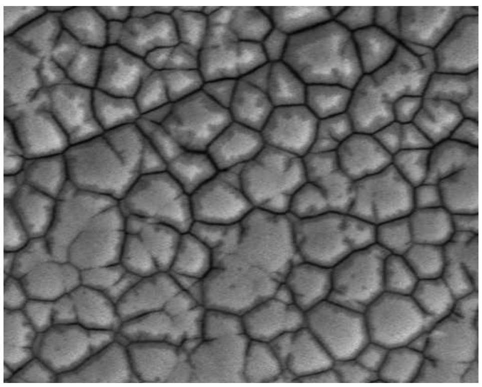

Figure 2 SEM of Ni corrosion

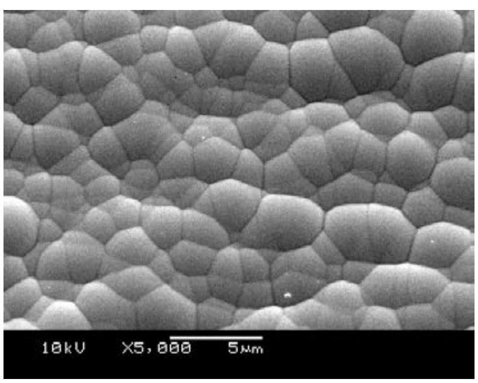

Figure 3 SEM Ni, no corrosion

Table 1, Process sequence & dwell time in minutes

	Control	Sample 1	Sample 2
Cleaner	5	5	5
Micro-etch	2	2	2
Catalyst	1	1	1
Electroless Ni	24	22	22
Immersion Gold IG	9		
RAIG		11	25

Fig 2 shows a 5000X SEM micrograph of a corroded nickel surface after gold stripping. An irregular topography with distinct crevices between the domains is where corrosion initiates and causes black pad.

Fig. 3 shows a 5000X SEM micrograph of a non-corroded nickel surface after gold stripping. The nickel deposit exhibits an even topography. This nickel deposit will never produce a black pad.

A new approach to the elimination of corrosion is the use of RAIG. The RAIG mode of action does not rely on the displacement/corrosion step as a standard immersion gold does; its autocatalytic deposition mode does not create corrosion.

In addition, RAIG can deposit higher thicknesses of gold (3-5 μins). Some product designs prefer a thickness exceeding the recommended thickness of 1.6-2.8 μins. Since the nickel corrosion occurs during the gold deposition step, what is the role of the gold bath (if any) in creating the defect? Ideally, for every atom of nickel metal oxidized to nickel ion, two gold atoms are reduced to gold metal. Investigating RAIG as a means to eliminate corrosion in ENIG follows.

Experimental Design
To demonstrate the capability of the RAIG bath, sample coupons were prepared and run on 2 production lines. The first line used a standard immersion gold bath. This sample was used as reference/ control. The control sample was plated in standard immersion gold for 9 minutes to a thickness of 2.8 μins. All the plating was done using plating chemicals commercially available from C. Uyemura & Co.

The second line used an RAIG bath. The coupons in the RAIG bath had dwell times of 11 minutes and 25 minutes, respectively. Traditionally, extended dwell time in the gold bath produced corrosion. The extended dwell time answered 2 questions: *will corrosion occur?* and *what thickness of gold can be deposited with RAI gold?*

RESULTS AND DISCUSSION

Control

Examination of the deposit cross-section at 1000X as specified in the revised IPC 4552, (figure 4) reveals a low level of corrosion spikes. Based on the classification, the spikes indicate Level 1 or Level 2 corrosion, with a Product Rating of “Level 1” per the proposed IPC 4552 Rev B. Although this is not cause for rejection, it is a process indicator that implies that higher levels of corrosion are possible.

Sample 1

Sample 1 was plated in an RAIG bath for 11 minutes. The gold thickness achieved was 3.12 uin. Refer to Table 2 for thickness values. Examination at 1000 X per IPC 4552 Rev A and proposed Rev B show level “0” corrosion (Product Rating Level 0”). Figure 5 shows three micrographs at 1000 X magnification from sample 1.

Table 2
XRF Readings for Sample 1

n=	1	Au 1 =	3.16 μ"	NiP 2=	175.9 μ"
n=	2	Au 1 =	3.17 μ"	NiP 2=	176.0 μ"
n=	3	Au 1 =	3.08 μ"	NiP 2=	168.4 μ"
n=	4	Au 1 =	3.15 μ"	NiP 2=	177.7 μ"
n=	5	Au 1 =	3.15 μ"	NiP 2=	180.1 μ"
n=	6	Au 1 =	3.14 μ"	NiP 2=	175.7 μ"
n=	7	Au 1 =	3.17 μ"	NiP 2=	178.6 μ"
n=	8	Au 1 =	3.10 μ"	NiP 2=	171.5 μ"
n=	9	Au 1 =	3.20 μ"	NiP 2=	178.5 μ"
n=	10	Au 1 =	3.06 μ"	NiP 2=	176.8 μ"
n=	11	Au 1 =	3.11 μ"	NiP 2=	172.8 μ"
n=	12	Au 1 =	3.08 μ"	NiP 2=	169.4 μ"
n=	13	Au 1 =	3.12 μ"	NiP 2=	167.5 μ"
n=	14	Au 1 =	3.10 μ"	NiP 2=	171.0 μ"
n=	15	Au 1 =	3.23 μ"	NiP 2=	177.7 μ"
n=	16	Au 1 =	3.10 μ"	NiP 2=	168.2 μ"
n=	17	Au 1 =	3.13 μ"	NiP 2=	176.2 μ"
n=	18	Au 1 =	3.15 μ"	NiP 2=	169.5 μ"
n=	19	Au 1 =	3.07 μ"	NiP 2=	169.0 μ"
n=	20	Au 1 =	3.10 μ"	NiP 2=	174.5 μ"

	Au 1 μ"	NiP 2 μ"
Mean	3.128	173.8
Standard deviation	0.044	4.096
CoV (%)	1.41	2.36
Range	0.163	12.6
Number of readings	20	20
Measuring time	30 sec	

Sample 2

For sample 2, the dwell time in the RAIG bath was increased to 25 minutes. This was done to see if extended dwell time in the gold bath would lead to nickel corrosion, and to determine whether higher gold thickness was achievable.

See Table 3 for XRF values. It is not uncommon for designers to specify higher gold thickness. Examination here also showed no corrosion or Level ‘0”. Refer to Figure 6.

Table 3
XRF Readings for Sample 2

n=	1	Au 1 =	5.35 μ"	NiP 2=	156.9 μ"
n=	2	Au 1 =	5.07 μ"	NiP 2=	159.1 μ"
n=	3	Au 1 =	5.19 μ"	NiP 2=	160.4 μ"
n=	4	Au 1 =	5.26 μ"	NiP 2=	161.2 μ"
n=	5	Au 1 =	5.22 μ"	NiP 2=	159.1 μ"
n=	6	Au 1 =	5.08 μ"	NiP 2=	158.7 μ"
n=	7	Au 1 =	5.22 μ"	NiP 2=	157.5 μ"
n=	8	Au 1 =	5.13 μ"	NiP 2=	160.9 μ"
n=	9	Au 1 =	5.17 μ"	NiP 2=	160.6 μ"
n=	10	Au 1 =	5.22 μ"	NiP 2=	158.8 μ"
n=	11	Au 1 =	5.39 μ"	NiP 2=	166.4 μ"
n=	12	Au 1 =	5.35 μ"	NiP 2=	164.7 μ"
n=	13	Au 1 =	5.32 μ"	NiP 2=	166.2 μ"
n=	14	Au 1 =	5.12 μ"	NiP 2=	160.0 μ"
n=	15	Au 1 =	5.31 μ"	NiP 2=	163.4 μ"
n=	16	Au 1 =	5.36 μ"	NiP 2=	165.9 μ"
n=	17	Au 1 =	6.81 μ"	NiP 2=	158.4 μ"
n=	18	Au 1 =	6.62 μ"	NiP 2=	161.5 μ"
n=	19	Au 1 =	6.41 μ"	NiP 2=	164.9 μ"
n=	20	Au 1 =	6.01 μ"	NiP 2=	164.4 μ"

	Au 1 μ"	NiP 2 μ"
Mean	5.480	161.[illegible]
Standard deviation	0.531	3.05[illegible]
CoV (%)	9.68	1.89
Range	1.74	9.50
Number of readings	20	20
Measuring time	40 sec	

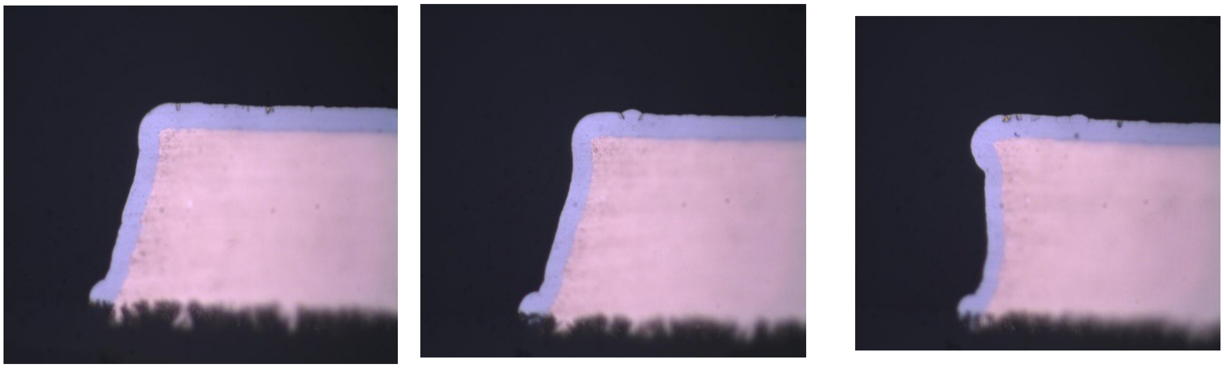

Figure 4, Control sample 3 micrographs in standard immersion gold with low level corrosion

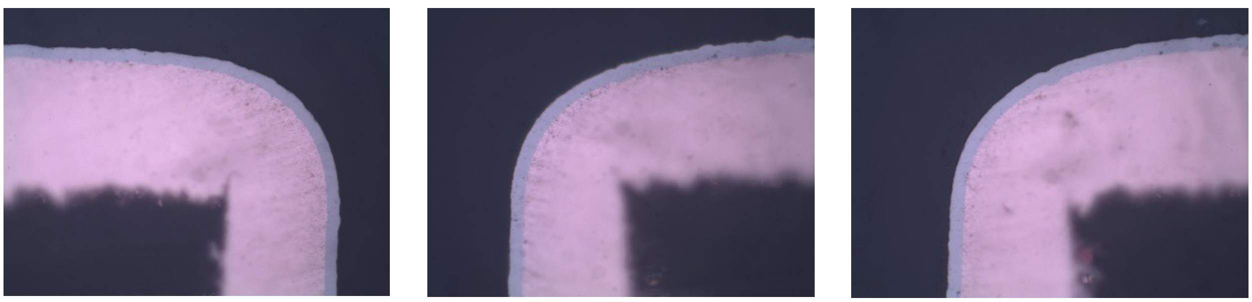

Figure 5, Sample 1 RAI gold 3.12 µins. No corrosion, Level 0 Product Rating

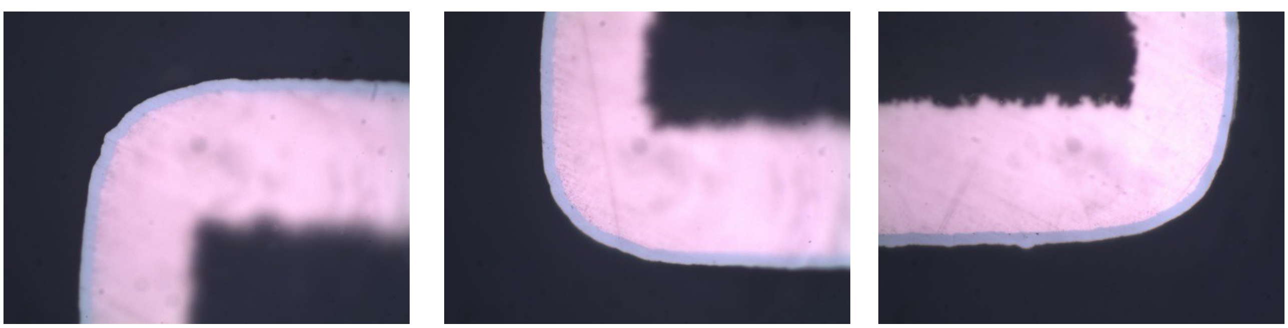

Figure 6, Sample 2 RAI gold (25 minutes dwell time) 5.48 µins gold. No corrosion, Level 0 Product Rating

ENEPIG and RAIG

A comparison was done using standard immersion gold vs. RAI gold.

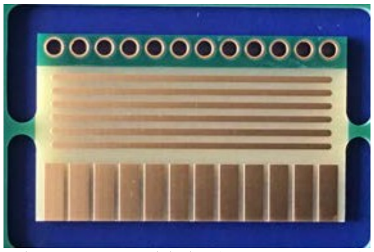

Fig 7 Test Vehicle (2.4 X 1.5 cm)

Experimental Design

The test vehicle (fig 7) used in this study consisted of a a double-sided, copper-clad laminated substrate which was copper plated to a thickness of 20 µm using an acid copper electroplating process. ENEPIG was deposited on the test vehicle using electroless palladium with two different types of gold. The nickel deposit (7-8 % phosphorous) was a single source, deposited at a fixed thickness of 225 -275 µin (5.6 – 6.9 µm). The electroless palladium was a phos Pd with ~ 4.0% P in the deposit.

Two different gold baths were chosen for this investigation. The first was a standard immersion gold bath that ran at a mildly acidic pH of ~5.5 at a temperature of 180^{O}f; the second was a "Reduction Assisted Immersion Gold" bath also known as a "mixed reaction" bath. All the plating was done using plating chemicals commercially available from C. Uyemura & Co.

The thickness of the Pd deposit was varied by changing the dwell time in the baths, and the rate of deposition over time was recorded. The different thickness Ni-Pd layers were individually placed in the immersion gold bath for an exaggerated dwell time of 30 minutes.

Table 4. Thickness of the different coupons for Test 1 with Phos Palladium

Minutes In EP bath	EN µin/µm	EP µin/µm	IG µin/µm
1	272/6.8	2.0/0.05	4.0/0.1
2	272/6.8	3.2/0.08	3.2/0.08
4	272/6.8	4.8/0.12	2.8/0.07
6	272/6.8	5.2/0.13	2.4/0.06
8	272/6.8	6.4/0.16	2.0/0.05
10	272/6.8	8.8/0.22	2.0/0.05

Fig 7 is a graphic presentation of the data from Table 4.

The exaggerated dwell in the gold bath was by design to ensure that some level of Ni corrosion would occur and there would be a way to evaluate the difference that the thickness of the Pd layer would play in Ni corrosion.

TEST #1

Varying thickness of palladium with standard immersion gold.

TEST #2

Varying thickness of palladium with Reduction Assisted Immersion Gold

After each test, a cross-section thru the ENEPIG layer, at different palladium thicknesses, was evaluated for Ni corrosion using a Seiko SEA-5120 Element Monitor MX XRF. The cross-section images of the pads were observed using a JEOL JSM-6010LA SEM.

Table 5, Process Sequence

Process Step	Dwell Time minutes	Test #1	*Test #2*
Cleaner	5	O	O
Microetch	1	O	O
Activator	2	O	O
E'less Ni	20	O	O
E'less P-Pd(1)	1,2,4,5,6,10	O	O
IG Standard(3)	30	O	X
IG Mixed Rxn(4)	30	X	O

Test #1 Phos Palladium/immersion Gold

Test #1 followed the process sequence outlined in Table 5. Six solder test coupons were plated in electroless nickel to fixed dwell time and nickel thickness. This was followed by electroless phos-palladium. The dwell times in the EP bath were 1, 2, 4, 6, 8, and 10 minutes, producing EP thicknesses from 2 - 8.8 µin.

The data shows that the gold thickness at the lower EP thickness was as high as 4.0 µin (0.1µm) and diminished as the thickness of the EP increased. It was limited to 2 µin (0.05 µm) when the thickness of the EP was 8 µin (0.20 µm) or greater.

The explanation is that the gold ions, at the lower EP thickness, had access to the underlying nickel and deposited at an accelerated rate, producing nickel corrosion. Lacking access to the underlying nickel, the immersion gold reaction with phos palladium becomes self-limiting to 2 µin (0.05 µm).

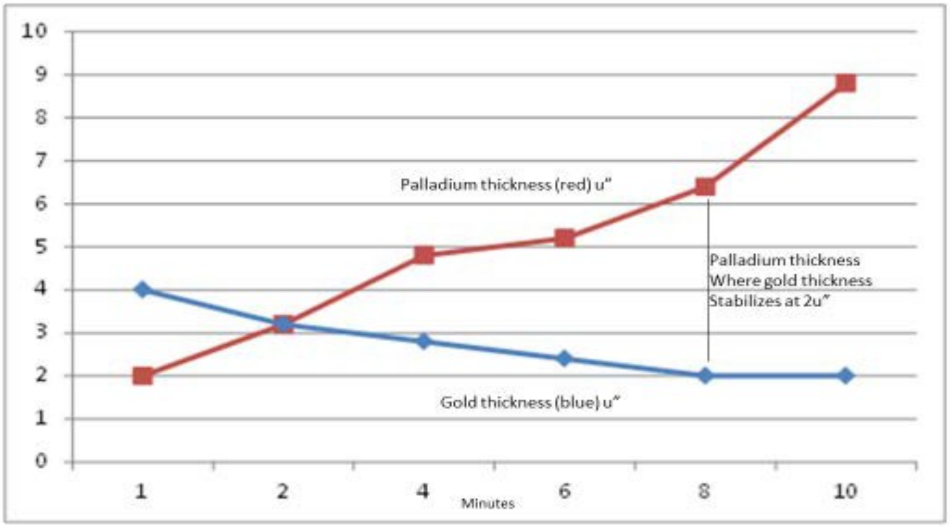

Figure 7, Graphic presentation of data in Table 4

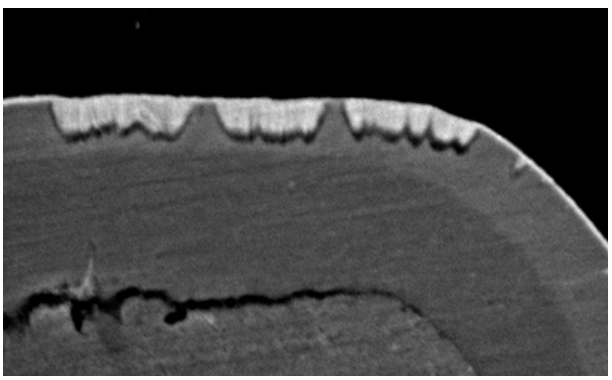

Fig 8 Ni corrosion at 2 µin (0.05µm) of phos palladium. Corrosion was extensive and shallow.

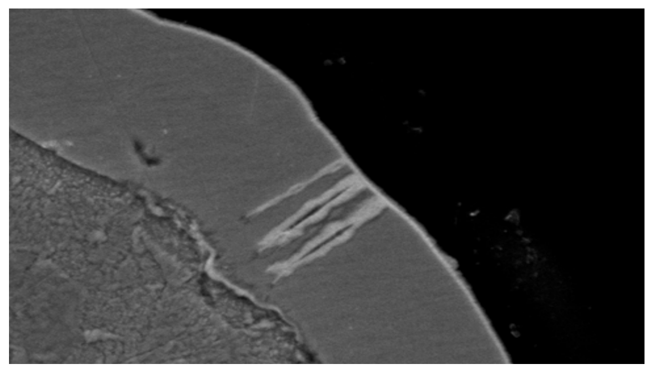

Fig 9 Ni corrosion at 4.8 µin (0.12 µm) of phos palladium. Few intermittent deep corrosion spikes.

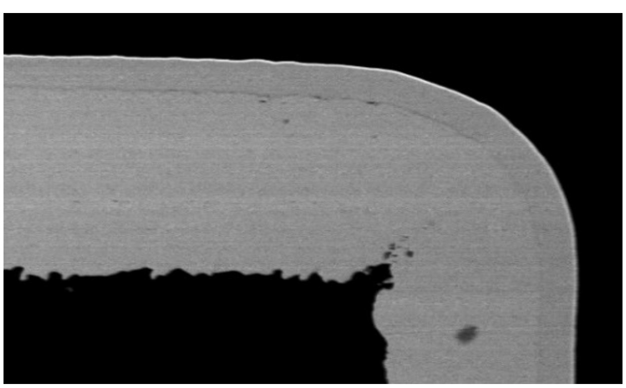

Fig 10. No corrosion at 8.8 µin (0.22 µm) of phos palladium. No corrosion was found.

Figures, 8, 9 and 10 are SEM micrographs depicting the level and type of corrosion at different levels of Phos palladium thickness.

Fig 8 shows shallow extensive corrosion and a thicker gold deposit.

Fig 9 shows intermittent deep corrosion spikes and a gold thickness of 2.8 µin (0.05 µm).

Fig 10 has no corrosion spikes; however the gold thickness was limited to 2 µin (0.05 µm).

Test #2 Phos Palladium/RAI Gold
The results of Test #2 were dramatically different from Test #1. The thickness of the gold was consistently high regardless of the thickness of the deposited palladium. A cross-section examined at 1000 X showed no corrosion at 2 µins of electroless palladium.

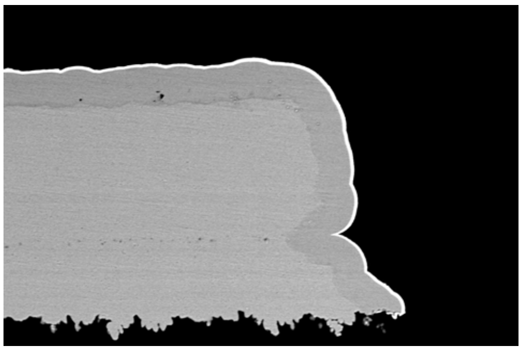

Fig 11. Phos palladium at 2 µins with Reduction Assisted Immersion Gold. Level "0" Corrosion.

The thickness data shown in Table 6 shows that the gold thickness of the reduction assisted or mixed reaction immersion gold was virtually independent of the phos-palladium thickness. Gold continued to deposit at a high rate when the phos-palladium thickness was as low as 2.0 µins.

No signs of nickel corrosion was found at any level of palladium thickness; see Fig 11.

Mitigation of Nickel Corrosion:
The data clearly indicates that corrosion occurred when the palladium layer was less than 4 uins. Increasing the thickness of the EP layer in the range of 6-8 uins would go a long way toward minimizing nickel corrosion in ENEPIG.
Presently the IPC-4556 Specification for ENEPIG specifies 2-12 µin (0.05– 0.3 µm) for the EP layer and 1.2 -2.8 µin (0.03 –0.07 µm) for IG.

Table 6. Phos-Pd with Reduction Assisted Immersion Gold

Minutes in Non-Phos Palladium	EN µin/µm	EP µin/µm	IG µin/µm
1	255/6.4	1.5/0.04	8.73/0.22
2	255/6.4	2.1/0.05	8.05/0.20
4	255/6.4	3.6/0.09	7.28/0.18
6	255/6.4	4.9/0.12	7.24/0.18
8	255/6.4	6.5/0.17	7.30/0.18
10	255/6.4	7.7/0.19	6.96/0.17

The use of RAIG opens the process window to the extent that no corrosion was evident even when the palladium layer was as low as 2.0 uins.

CONCLUSION

The ability of Reduction Assisted Immersion Gold to eliminate corrosion in ENIG and ENEPIG was clearly demonstrated. A side benefit is that RAIG will also deposit a thicker layer of gold for both ENIG and ENEPIG. This is becoming important today as some newer designs call for >3.0 µins of gold for ENIG and ENEPIG. ENIG approaching 3.0 µins of immersion gold would run the risk of creating nickel corrosion.

For ENEPIG, the immersion gold on palladium is very limited (<2.0 µins); higher thickness are not achievable. If ENEPIG is designed for wire bonding applications, a thicker layer of gold (>3.0 µins) can be readily deposited on the palladium using RAI gold. The thicker gold layer opens the wire bonding process window. Reduction Assisted Immersion Gold also prevents nickel corrosion.