A Novel Surface Finish Can Achieve Robustness Against Copper Creep Corrosion for Better Reliability of Printed Circuit Boards (PCBs)

Kunal Shah, Ph.D.
LILOTREE
WA, USA
kunal.shah@lilotree.com

Dem Lee, Jeffrey Lee
iST-Integrated Service Technology Inc.
Hsinchu, Taiwan
dem_lee@istgroup.com; jeffrey_lee@istgroup.com

ABSTRACT
Due to tremendous growth in Information Technology equipment in the Big Data/server applications, 5G-6G-high frequency, Edge Computing, Artificial Intelligent (AI) applications recently, the hardware reliability of these equipment is critical and paid more attention in the industry. With harsh environment and severe air pollution, hardware equipment is subjected to severe corrosion and reduce lifetime. Among various materials used in the electronics assembly, reliability evaluation of surface finishes on printed circuit boards (PCBs) is critical for long terms optimal operation of the equipment. The failure mode due to exposure to long term harsh environment, air pollution, etc. involves creep corrosion which can potentially cause electrical short failure. It is important to evaluate for the robustness against creep corrosion occurrence in the electronic assemblies.

Mixed Flowing-Gas (MFG) test is an environmental stress laboratory test intended to simulate contaminated industrial ambiance. There are many controllable parameters, including temperature, relative humidity, corrosive gases type (e.g. H_2S, Cl_2, NO_2, SO_2, NH_3 and O_3…etc.), concentration and gaseous flowing rate, etc. Because many controllable parameters, complex equipment setup and continuous constant-flowing corrosive gases, MFG test is a popular accelerated corrosion test that has high availability to simulate the field environment corrosion. In order to observe the effective corrosive reactivity within a short period of time, a MFG test condition from International Electronics Manufacturing Initiative (iNEMI) was adopted in this research. iNEMI MFG test condition has high concentration of hydrogen sulfide (H_2S), mixed with multiple corrosive gases that is an effective accelerated condition for corrosion test. Various, surface finishes were evaluated including Electroless Nickel Immersion Gold (ENIG), Immersion Tin (ImmSn), Hot Air Solder Leveling (HASL), Organic Solderable Preservative (OSP)and novel Ni-free surface finish. Creep corrosion tendencies and robustness were compared among various surface finish options and long-term reliability in harsh environmental conditions is evaluated.

Key words: Novel Ni-free surface finish, Reliability, Printed Circuit Boards (PCBs), Creep corrosion, Signal integrity, High frequency PCBs.

BACKGROUND
Due to tremendous growth in Information Technology (IT) equipment in the Big Data/server applications, 5G-6G-high frequency, Edge Computing, Artificial Intelligent (AI) applications recently, the hardware reliability of these equipment is critical and paid more attention in the industry. With harsh environment and severe air pollution, hardware equipment is subjected to severe corrosion and reduce lifetime. Among various materials used in the electronics assembly, reliability evaluation of surface finishes on PCBs is critical for long terms optimal operation of the equipment. The failure mode due to exposure to long term harsh environment, air pollution, etc. involves creep corrosion which can potentially cause electrical short failure. It is important to evaluate for the robustness against creep corrosion occurrence in the electronic assemblies.

Creep corrosion is the corrosion of metallization- typically copper and silver and migration of the corrosion product- typically sulfide-based chemistry of metals across the PCB through laminate and solder mask[1]. In the environments with the high humidity and/or high levels of sulfur-bearing gaseous contaminants, the extent of creep corrosion is high which leads to electrically short circuit scenarios in adjacent pads, traces, etc. leading to malfunctioning of the electronic assemblies. The large growth of electronics in the geographies such as Asia which has high humidity and sulfur-based gaseous contaminants in the air have led to tremendous increase in corrosion based electronic assemblies failure rates. The criticality of various applications including IT equipment, data servers, 5G-G Antennas/assemblies, AI, etc. have warranted to produce better reliability of electronic assemblies which can withstand these harsh environmental for long period of time. The creep corrosion is originated at the metallization surfaces including exposed surface finishes. Understanding various surface finishes' propensity towards creep corrosion and evaluating novel surface finish which can offer robustness against creep corrosion for better reliability of PCB and PCB Assembly (PCBA) are critical. In this paper, we will evaluate conventional surface finishes i.e., ENIG, ImmSn, HASL, OSP, and novel Ni-free surface finish for their robustness against creep corrosion.

The novel Ni-free surface finish involves nano-engineered barrier layer treatment is conducted on bare copper in place of nickel in ENIG, and gold is deposited on the barrier layer (see schematic below) [2]. There is no nickel in this approach and reliability aspect is still upheld through barrier layer treated copper and gold final finish.

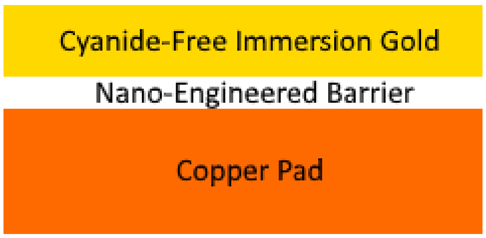


Figure 1. Novel Nickel-free surface finish, which includes a nano-engineered barrier layer instead of the Ni-P layer in ENIG. Layers not to scale.

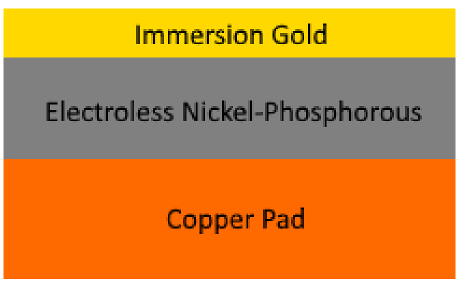


Figure 2. ENIG surface finish, including the problematic nickel-phosphorous (Ni-P) layer. Layers not to scale.

As the frequency increases, the current density is concentrated towards the surface (surface finish) instead of the entire Cu cross-section. Hence the choice of surface finish is critical since it will affect the insertion loss.

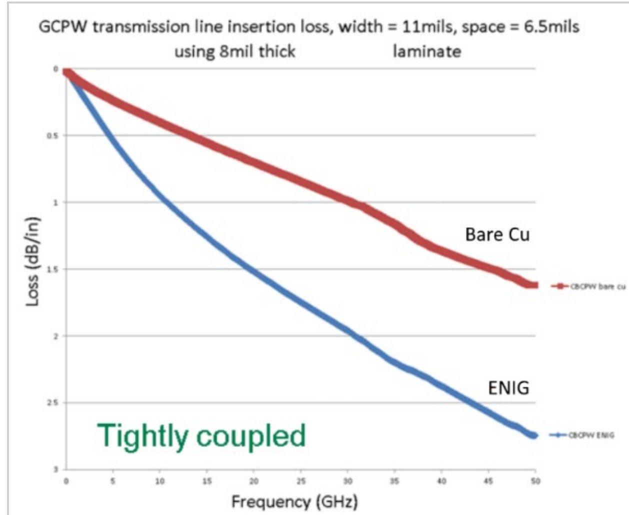


Figure 3. Insertion loss comparison between circuits with bare copper conductors and with ENIG-plated copper conductors, from 0 – 50 GHz [3]

Figure 3 shows increased insertion loss due to ENIG surface finish on copper conductors compared to bare Cu over 0 – 50 GHz range. 5G cellular networks, which are currently in use worldwide, are using millimeter frequency bands at the higher end of that range; for example, Verizon (US) is using a 29 GHz band, and AT&T (US) is using a 39 GHz band. Higher GHz bands are already being discussed for cell networks between 50 – 100 GHz due to the higher throughput of data available at higher frequencies [7], and automotive radar already uses a 76-81 GHz band. This creates an issue that must be addressed not only for fast-approaching future technologies, but also for current devices which still have to contend with the signal losses due to the nickel in ENIG surface finishes. Already, the market is using a number of high-frequency circuit boards, and is one of the fastest-growing areas in the electronics industry [3].

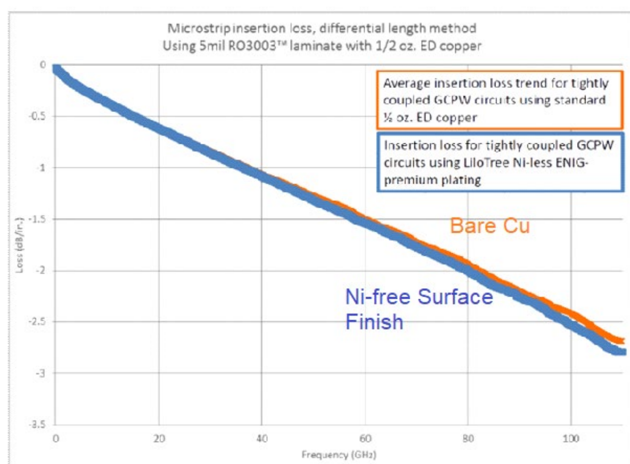


Figure 4. Insertion loss of the Ni-less surface finish (blue) compared to bare standard ½ oz ED copper (orange) from 0 – 100 GHz on tightly coupled GCPW circuits

As shown in the graph above, the insertion loss of the novel Ni-free surface finish is almost exactly identical to the insertion loss of bare copper over the 0 – 100 GHz frequency range. This indicates that the Ni-free surface finish is able to be used in high-frequency applications with hardly any insertion loss increase compared to bare copper. The graphs can also be compared to Figure 1, which shows that ENIG has a loss of around 2.75 dB/in at 50GHz, compared to the values shown in these graphs, about 1.25 dB/in at 50GHz – more than a 50% decrease in insertion loss. Since the novel Ni-free surface finish has such a small difference in insertion loss compared to bare copper, especially when contrasted with ENIG insertion loss, the novel Ni-free surface finish solution is an optimal surface finish for high-frequency applications [3].

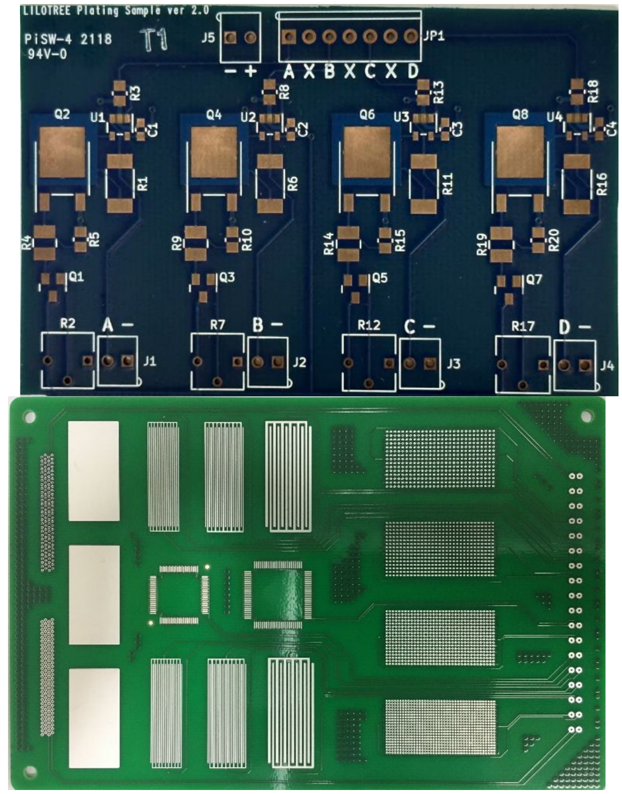
EXPERIMENT

In order to observe the effective corrosive reactivity within a short period of time, the acid-gases based MFG test condition from iNEMI was adopted in this research. [4] iNEMI MFG test condition has high concentration of H_2S, mixed with multiple corrosive gases that is an effective accelerated condition for copper corrosion test. Besides, the corrosion thickness growth of accelerated corrosion test can be satisfied the ANSI/ISA 71.04 G2 severity level compliant to 5 years exposure for Cu corrosion only. [5] Table 1 shows MFG test conditions in this research. After corrosion test, several analytical methods were used in this work, including, Optical Microscope (OM) Inspection, Coulometric Reduction (CR), Cross-section Polisher, (CP), Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX).

Table 1. Description of MFG test conditions

Temp (°C)	**RH (%)**	**H_2S (ppb)**	**SO_2 (ppb)**	**NO_2 (ppb)**	**Cl_2 (ppb)**	**Check Point**
40	75	1,200	200	200	20	G2-5yrs

2 PCBs without flux was selected as test vehicle, one was from Lilotree and the other one was from vendor A. There were various patterns with different fine pitches design on the PCBs. Figure 5 shows the PCB layout of test vehicle. In addition, a novel PCB surface finish material; Novel Ni-free surface finish was tested from Lilotree, and also 4 PCB surface finish materials were tested, including ENIG, ImmSn, HASL, and OSP materials from A vendor. Table 2 listed the Design of Experiment (DOE) matrix with various PCB surface finish materials and vendors in MFG test run. The DOE matrix design not only enables the verification of the effectiveness of anti-creep corrosion capability comparison between the novel Ni-free surface finish and typical ENIG PCB surface finishes, but also makes a robustness ranking for PCB with various surface finish materials in this research.



(a) PCB from Lilotree
(b) PCB from Vendor A
Figure 5. Test vehicle is two PCB with various surface finish materials, and different vendors

Table 2. Description of DOE matrix with various PCB surface finish materials and vendors in MFG test run.

TV #ID	**PCB Vendor**	**Surface Finish**	**Quantity**
01	Lilotree	Novel Ni-free surface finish	1 Pc
02	A	ENIG	1 Pc
03	A	LF-HASL	1 Pc
04	A	ImmSn	1 Pc
05	A	OSP	1 Pc

In this research, a treated silver and copper coupon with 99.95% and 99.99% purity, respectively, both coupons were put into MFG chamber with samples together for corrosion reactivity quantification in this accelerated corrosion test. Therefore, we can know how long test duration we needed. Figure 6 shows the MFG chamber setup in this research.

Figure 6. MFG chamber setups.

Post-exposure metal coupons were used to qualify the silver and copper corrosive reaction rate using Coulometric Reduction (CR) analysis. CR is a kind of cathodic reductions by constant current coulometric technique, the procedures and equipment is defined by the ASTM B825-02. [6] This analytic method is designed to determine the relative quantities of tarnish film on control coupons that result from gaseous environmental tests. Figure 7 shows the CR setup in this research.

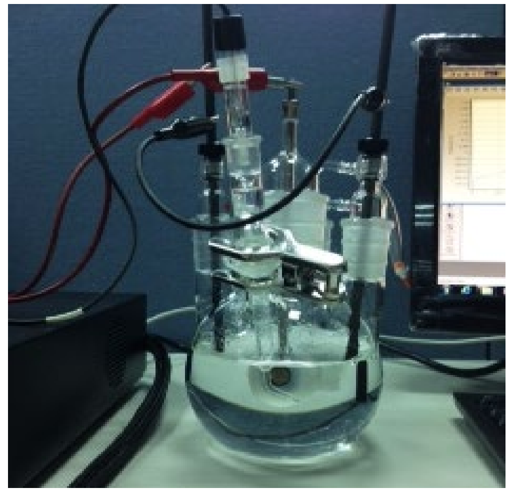


Figure 7. Coulometric reduction setups

Results and Discussion

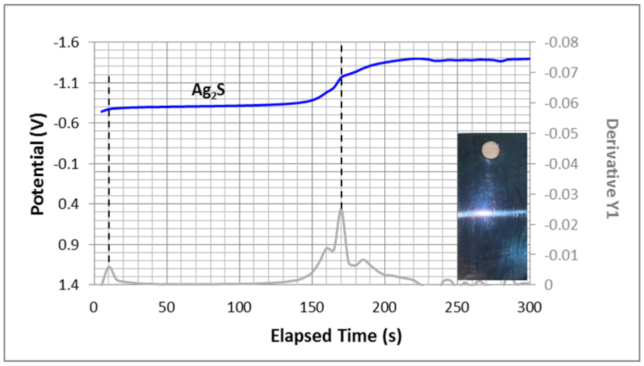
Corrosion Rate Measurement in MFG chamber

Obvious copper corrosion reactivity was observed in this MFG test. The silver and copper corrosion rate was 561 Å/day and 8,988 Å/day, respectively. Table 3 is the corrosion rate results in this MFG test.

Table 3. Summary the testing conditions at MFG test run.

MFG Test	**Temperature; °C**	**Relative Humidity; %RH**	**Corrosive Gases**	**Corrosion Rate, Å/day**	
				Ag	**Cu**
iNEMI	40°C	75%RH	4 Type Acid-Gases	561	8,988

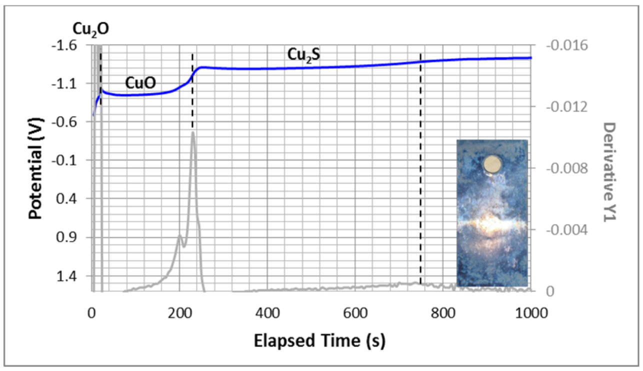
CR results shown silver sulfide (Ag_2S) was obtained from silver coupon and also copper oxide (CuO), cuprous oxide (Cu_2O) and copper sulfide (Cu_2S) were obtained from copper coupon after MFG test. Figure 8 shows the CR analysis for silver and copper coupons after 1 day exposure in MFG chamber. The reduction potential of Ag_2S was about -0.7 V in CR curve. CuO, Cu_2O and Cu_2S were observed at -0.7 V, -0.9 V and -1.2 V, respectively. Reduction current density is -0.2mA/cm^2 and -1.0mA/cm^2 for silver and copper coupon, respectively, and referred to a saturated calomel electrode in 0.1 M KCl electrolyte. The derivative curve was used to determine the reduction region for each corrosive product. It will be easy to calculate the corrosive reaction rate and reduce the errors of artificial judgment for the CR curve.



Silver Coupon

Silver Corrosion Product	Seconds	Thickness, angstroms	Exposure Days	Silver Corrosion Rate, angstroms/day
AgCl	0	0	1	561
Ag_2S	160	561		

* Reduction current density is -0.2mA/cm²



Copper Coupon

Copper Corrosion Product	Seconds	Thickness, angstroms	Exposure Days	Copper Corrosion Rate, angstroms/day
Cu_2O	10	124	1	8988
CuO	210	1352		
Cu_2S	510	7512		

* Reduction current density is -1.0mA/cm²

Figure 8. CR results for silver and copper coupons with pre-treatment after 1day exposure in MFG test run. Reduction current density is -0.2mA/cm^2 and -1.0mA/cm^2 for silver and copper coupon, respectively in this analysis that referred to a saturated calomel electrode in 0.1M KCl electrolyte.

The corrosion thickness growth with 7 days accelerated test can be satisfied the G2 severity level with 0.32-year warranty and 5.24-year warranty for silver and copper, respectively. 7 days test durations was carried out in this MFG test. Therefore, this accelerated test can be satisfied ANSI/ISA 71.04 G2 severity level compliant to 5 years exposure for Cu corrosion only. Table 4 lists accelerated corrosion simulation in this MFG test.

Table 4. listed accelerated corrosion simulation in this MFG test.

ANSI/ISA 71.04 G2 Severity	Expected Corrosion Thickness Growth	
	Silver (Ag)	Copper (Cu)
1-year (12-months) warranty	12,000 Å	12,000 Å
3-years (36-months) warranty	36,000 Å	36,000 Å
5-years (60-months) warranty	60,000 Å	60,000 Å
Accelerated MFG test (7 days)	**3,927 Å**	**62,916 Å**
Assessed simulation time in G2	**0.32 years**	**5.24 years**

<u>Metal Corrosion Resistance Ranking for PCB with Various Surface Finish Materials</u>

Many corrosion feature illustrations, including pore/pitting corrosion, edge corrosion, pad corrosion and creep corrosion were observed in the photo of optical microscope inspection for PCB with various surface finishes after the MFG test. Therefore, the MFG test has enough severe corrosion reactivity that can effectively verify the robustness of PCB with various surface finishes in this research. Figure 9 shows the example of optical microscope inspection for PCB with various surface finishes before/after 7 days of exposure at MFG chamber. HASL PCB has high robustness against corrosion than PCB with others surface finish materials. Basically, the solder finish can fully protect the PCB pad to avoid the corrosion occurrence. However, it will induce loss of solder coverage at the edge of PCB pad by surface tension of melting solder during HASL process. Therefore, there was only slight edge corrosion occurrence on the edge of HASL PCB pad after the MFG test. ImmSn is a metallic coating of tin which is deposited directly over the top copper layer of a PCB using an electroless chemical bath process. ImmSn PCB has good robustness against corrosion, but obvious edge corrosion was still observed on the PCB pad after the MFG test. The corrosion occurrence was limited at the interface of solder mask terminal and copper trace. Therefore, the corrosion occurrence has more relationship to Solder Mask Designed (SMD) area since it will induce less of tin deposition at solder mask undercut of PCB pad during ImmSn process. Others PCBs, including OSP, novel Ni-free surface finish and ENIG materials have obvious pore/pitting corrosion and pad corrosion occurrence after the MFG test. Even obvious creep corrosion feature was observed on ENIG PCB after the MFG test. Therefore, the MFG test was able to effectively discriminate between various surface finish materials of varying degrees of metal corrosion propensity. The metal corrosion propensity ranking is shown as below:

Metal Corrosion Propensity: ENIG > Novel Ni-free Surface Finish > OSP > ImmSn > HASL

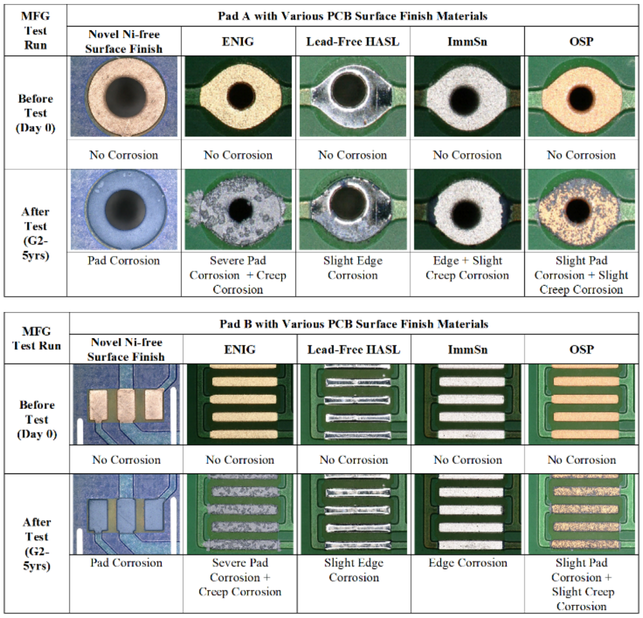
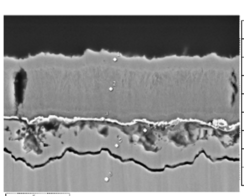


Figure 9. Example of optical microscope inspection for Pad A and B with various surface finishes before/after 7 days of exposure at MFG chamber

Creep Corrosion Resistance Comparison between novel Ni-free surface finish PCB and typical ENIG PCB

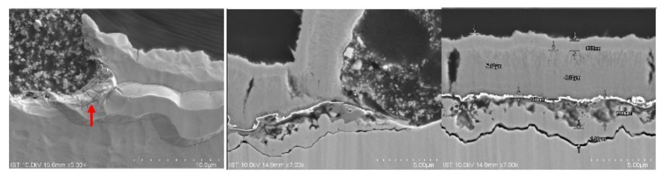
H_2S concentration and metal finish porosity have been mentioned that were key factor to corrosion occurrence on ENIG PCBs. [7] Because of gold and nickel are porosity-based metal materials, and also higher concentration of H_2S was adopted in the MFG test. If the thickness of gold and nickel is not enough, the inner copper based is easily reacted with H_2S to form Cu_2S on the surface of ENIG layer. In general, a gold plating thickness of 5µm has enough protection against the inner copper-based reacted with atmospheric H_2S. [8] But there was only 0.15um thickness of gold plating in this ENIG PCBs. This is a reason why pad corrosion occurrence on the novel Ni-free surface finish and ENIG PCBs after the MFG test. A thick layer of amorphous Cu_2S was observed on PCB pad after the MFG test due to the porosity of gold and nickel plating. The similar results have been published in previous research for ENIG PCBs failure analysis. [9] Figure 10 shows SEM photo and element analysis in a cross-section view for point analysis at Ni-free surface finish PCB after the MFG test.



Spectrum	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5	Spectrum 6
C	4.31	2.95	5.56	5.76	2.49	2.66
O		4.64	4.43	19.21	9.19	0.86
S	27.18	22.91	14.41	7.88		
Cl			0.93			
Ni		0.28	0.82	1.08	0.20	0.26
Cu	68.51	69.22	51.14	58.87	88.12	96.21
Au			22.72	7.20		
Total	100.00	100.00	100.00	100.00	100.00	100.00

Figure 10. SEM photo and element analysis in a cross-section view for point analysis at novel Ni-free surface finish PCB after the MFG test.

Besides, a gap formed between two nickel layers at SMD area of ENIG PCB, and the gap can provide an easy path for copper ion migration and for copper sulfide creep. This is a reason why the creep corrosion occurrence on ENIG PCB. However, no gap existence was observed at the SMD area of novel Ni-free surface finish PCB. Therefore, the nano-engineered barrier layer instead of the Ni-P layer in ENIG that can effectively prevent the gap formation, and eradicate the creep corrosion occurrence on SMD area of PCB. Figure 11 shows SEM photo for the existence of gap identification for (a) SMD area of ENIG PCB and (b) SMD area of novel Ni-free surface finish PCB and gold plating thickness measurement after the MFG test, and Figure 12 shows SEM photo for element analysis in a cross-section view for map analysis at SMD area of novel Ni-free surface finish PCB after the MFG test.



(a) SMD area of ENIG PCB (b) SMD area of novel Ni-free surface finish PCB and Au plating thickness measurement

Figure 11. SEM photo for the existence of gap identification for (a) SMD area of ENIG PCB and (b) SMD area of novel Ni-free surface finish PCB and Au plating thickness measurement after the MFG test

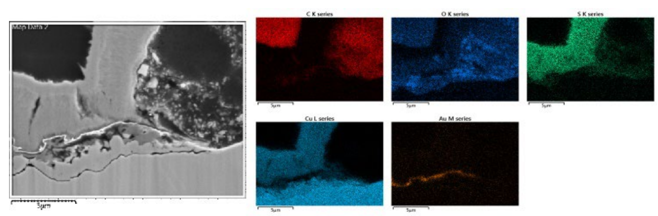


Figure 12. SEM photo for element analysis in a cross-section view for map analysis at SMD area of novel Ni-free surface finish PCB after the MFG test.

Figure 13 shows the example of optical microscope inspection for novel Ni-free surface finish and ENIG PCBs in 7 days of exposure in MFG chamber. Therefore, no obvious creep corrosion feature was observed on novel Ni-free surface finish PCB after the MFG test. The creep corrosion propensity comparison was shown as below:

Creep Corrosion Propensity: ENIG > Novel Ni-free Surface Finish

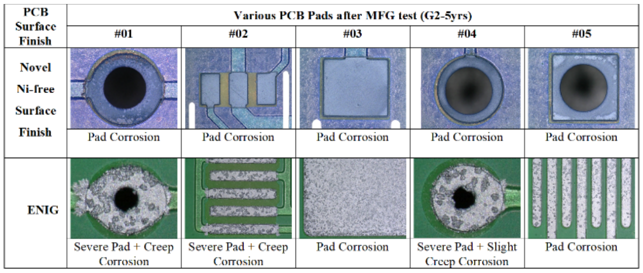


Figure 13. Example of optical microscope inspection for novel Ni-free surface finish and ENIG PCBs before/after 7 days of exposure at MFG chamber

Although novel Ni-free surface finish PCB has not the best robustness against the harsh environmental exposure at the MFG chamber. However, no obvious creep corrosion feature was observed on the PCB pad of novel Ni-free surface finish after MFG test in 7 days of exposure in MFG chamber, especially for SMD area. Besides, the corrosive product was uniformed and the surface is smooth on the PCB pads

CONCLUSIONS

The novel Ni-free surface finish of cyanide-free immersion gold plated onto a nano-engineered barrier layer treated copper is a viable solution for high-frequency-HDI applications. The surface finish was tested for insertion loss and robustness against creep corrosion. The results showed that this surface finish performs better than ENIG in terms of extremely low insertion loss and robustness against creep corrosion after MFG test in 7 days of exposure. This Ni-less surface finish with nano-engineered barrier layer is an optimal solution to the current need for a reliable surface finish for high-frequency, HDI PCB applications.

REFERENCES

[1] P. Singh, et. al., "WHITE PAPER A Cost-Effective & Convenient Approach to Creep Corrosion Testing" iNEMI Aug 2018.

[2] K Shah, "Novel Surface Finish for 5G-mmWave frequency PCB Technologies- How to Achieve Optimum Signal Integrity", IPC APEX 2023.

[3] K. Shah, "Novel Ni-free Surface Finish Next Generation PCB Technologies (RF-Microwave-5G-HDI-High Frequency) Focusing on Performance (Low Insertion Loss) & Better Reliability" IMPACT 2022

[4] Fu H., C. Chen, P. Singh, J. Zhang, A. Kurella, X. chen, X. Jiang, J. Burlingame, S. Lee. "Investigation of factors that influence creep corrosion on printed circuit boards – Part 2, "*SMTA International 2012*.

[5] International Society of Automation (ISA), ANSI/ISA 71.04-2013: ISA Standard "Environmental Conditions for Process Measurement and Control Systems: Airborne Contaminants, 2013.

[6] American Society for Testing and Material, ASTM Designation B825-02: Standard Test Method for Coulometric Reduction of Surface Films on Metallic Test Samples.

[7] T. T. M Tran, C Fiaud, E. M. M Sutter, A Villanova "The atmospheric corrosion of copper by hydrogen sulphide in underground conditions", *Corrosion Science*, Volume 45, Issue 12, December 2003, Pages 2787-2802.

[8] Aleksey Shakhmatov, Robert Badrak , William Howie , and Sergey Kolesov, "Silver braze corrosion in H_2S environment: life assessment and methods of preventing", *Corrosion in the Oil & Gas Industry 2019*.

[9] Fu Haley, P. Singh, A. Kazi, W. Ables, D. Lee and J. Lee, K. Guo, J. Li, S. Lee and G. Tong, "Testing Printed Circuit Boards for Creep Corrosion in Flowers of Sulfur Chamber: Phase 2" *SMTA International 2015*.