The Surface Finish Effect on the Creep Corrosion in PCB

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Abstract

Creep corrosion normally happens in the end system, PCB, connectors and components are widely noted due to the exposure of high sulfur environments under elevated humidity. In this study, the major focus is the investigation of PCBs with 3 different types of surface finish (ImAg, Post-Treatment ImAg, HT-OSP), SMD vs NSMD and non clean organic acid flux residue from simulating wave soldering process under MFG Test (Mixed Flowing Gas Test). The realistic mixed flowing gas (H_2S, SO_2, NO_2, Cl_2) at certain concentration of each and relative humidity are designed to accelerate creep corrosion happening.

One of the purposes in this study is to investigate the effect of the mixed flowing gas with various H_2S concentration (500 ppb, 1000 ppb, 1700 ppb) at 5 days duration on the corrosion rate (nm/day) in the Cu coupon and Ag coupon in order to understand how H_2S drives the corrosion acceleration. The data are also verified by the methods of Weight Gain Analysis and X-Section with SEM/EDX.

The result shows much higher corrosion rates are observed on Cu coupon in both Individual and Mixed Flowing Gas Tests. The corrosion rate of Cu coupon rapidly increases with H_2S concentration above 1000 ppb. Ag coupon have more active corrosion in low H_2S concentration than high H_2S concentration. Flaking corrosion also happens on the Cu coupon with heavy corrosion product in the high H_2S concentration test condition. And more visible creep corrosion is observed on HT-OSP finished circuit boards and SMD, as the residue of organic acid flux residue is not able to prevent corrosion occurrence.

Key Words: Creep Corrosion, Surface Finish, Organic Acid Flux, Mixed Flowing Gas Test (MFG), SMD, NSMD

Introduction

Many volcanoes erupted in Iceland, Japan, Indonesia and the Philippines in the recent two years. There are 2,000 extinct volcanoes and 523 active volcanoes distributed in four major volcanic belts in the world. There are twenty volcanic eruptions at any time and volcanic activity increased significantly since year 2000. This released more sulfides posing a threat to the environment. The general and volcanic gas compositions are shown in Figure 2. H_2O and SO_2 released into the air may cause corrosion after a volcanic eruption.

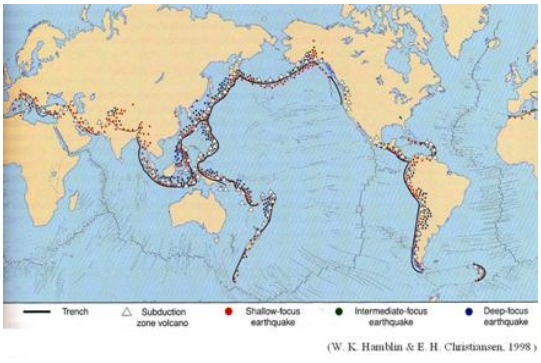


Figure 1. The major volcanic belts in the world.

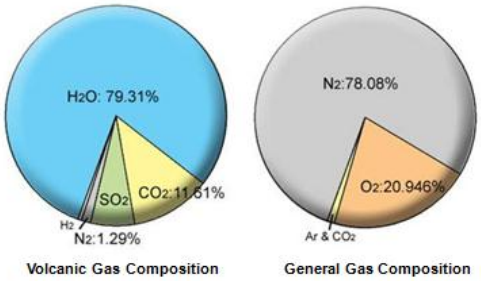


Figure 2. The comparison of general and volcanic gas compositions.

There are many types of active sulfur compounds that are able to cause corrosion. The creep corrosion is the mass transport process where solid corrosion products migrate over a surface without the involvement of an electric field. [1] The comparison among Creep Corrosion, Dendrite, and CAF is shown in Table 1, which illustrate different mechanism to electrical failure. [2]

Table 1. The comparison among Creep Corrosion, Dendrite and CAF. [2]

Comparison	Creep Corrosion	Dendrite	CAF
Substrate	Cu	Cu/Ag/Tin-Lead…	Cu
Corrosion Product	Cu_2S	FO	Cu Oxide/ Hydroxide
Electron Migration	X	Cathode to Anode	Anode to Cathode
Failure Mode	Short / Open	Short	Short
Humidity Requirement	Yes	Yes	Yes
Voltage Requirement	No	Yes	Yes

The mechanism of creep corrosion in Dr. Ping Zhao's previous published paper described the process of **Dissolution → Diffusion → Re-deposition.** The multiple mono-layers of water are adsorbed on the surface under high relative humidity and then the corrosion products dissolve into these water layers. Therefore, they diffuse over the surface in solution down the concentration gradient and re-deposit. The mechanism of creep corrosion is shown in Figure 3. [3]

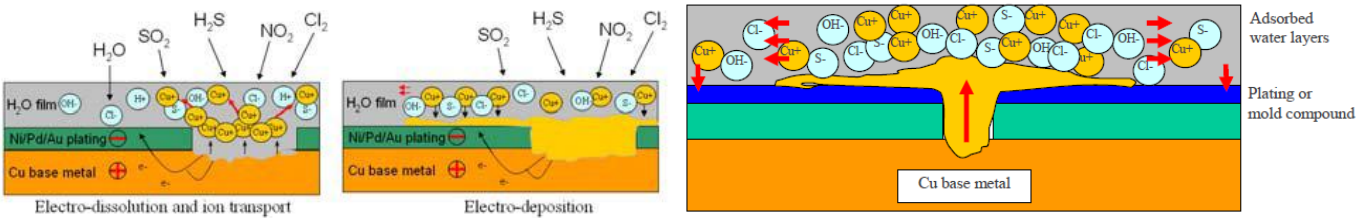


Figure 3. The mechanism of creep corrosion from Dr. Ping Zhao's previous published paper[3]

There are a number of factors that lead to creep corrosion in PCBs, as shown in Table 2. In this paper, the study is focused on the factors of PCB board design (SMD vs NSMD), surface finish, flux residue in wave soldering and MFG test conditions. The creep corrosion on a PCB will induce electrical failure in the electronic product. Obvious corroded PCBs are identified in some locations with elevated level of sulfur-based gases, including paper mills, waste-water treatment plants, landfills, swamps, and exit / entrance ramp, especially in the developing countries. [4]

Table 2. The factors to creep corrosion

Factors to Creep Corrosion		Studied in this paper
1	PCB board design	**v**
2	Surface Finish	**v**
3	Flux residue	**v**
4	Solder Mask Geometry	**v**
5	Solder Paste Coverage	

6	Reflow	
7	Wave Soldering process	
8	MFG Test Conditions	**v**

In the electronic industry, there have been a number of test methods developed to evaluate the corrosion resistance from the view point of PCB materials, PCB assembly process and gas condition. The MFG test method was carried out in 1980's. It's the primary test method used currently in the electronic industry.

The MFG test is a laboratory test where the temperature (℃), relative humidity (%RH), concentration of gaseous pollutants (ppb level), and other critical variables (such as volume exchange rate and airflow rate) are carefully defined, monitored and controlled. [5] The purpose of MFG test is to use the combination of four most common corrosive gases in the environment, H_2S, Cl_2, NO_2, SO_2 to simulate and accelerate atmospheric corrosion due to exposure. Many specific and application-oriented MFG test methods created for industrial applications are shown in Table 3. [6][7][8][9]

But there is still no accepted industry standard created for MFG test to correlate to real service life yet. From the literature published, the critical factor that causes creep corrosion is the concentration of H_2S. IPC 3-11g Corrosion of Metal Finish Task Group also had a draft discussion for setting 1500ppb possibility as the minimum concentration of H_2S in IPC/APEX 2011. Further progress will be updated in the next publication.

Table3. MFG test methods for industrial applications concentration: (unit: ppb) [6][7][8][9]

Condition	Class	H_2S	CL_2	NO_2	$S0_2$	Temp	RH
Telcordia	Indoor	10	10	200	100	30℃	70%
	Outdoor	100	20	200	200	30℃	70%
ALU	Intl.	1500-2000	20	200	200	40℃	70%
Battelle	Class 2	10	10	200	-	30℃	70%
	Class 3	100	20	200	-	30℃	75%
	Class 4	200	50	200	-	50℃	75%
EIA	II	10	10	200	-	30℃	70%
	II A	10	10	200	100	30℃	70%
	III	100	20	200	-	30℃	75%
	IIIA	100	20	200	200	30℃	70%
	IV	200	30	200	-	40℃	75%
IEC	1	100	-	-	500	25℃	75%
	2	10	10	200	-	30℃	70%
	3	100	20	200	-	30℃	75%
	4	10	10	200	200	25℃	75%
IBM		40	3	610	350	30℃	70%

Experiment

1. MFG test set up

a. Chamber feature is shown in figure 4

Yamasaki GH-180-VL/M(JAPAN)

Temperature：25℃~+50℃

Humidity range：70%~95%(RH)

Mode：Single or Mixed flowing gas

Inside dimension：50(W)*50(D)*50(H)/cm

Capacity : According to Volume fraction(1 : 2)

Figure 4. MFG test system in IST's lab.

b. MFG Test Flow

Figure 5 shows the flow chart. 4 kinds of individual gas coming from the bottom side are mixed before getting into the chamber. The gas flow in the chamber is coming from the bottom side. The gas emission coming from the chamber first goes

into Filter Tank for neutralization and then goes to Active Carbon for deodorization. The final gas emission is non-toxic and non-polluting.

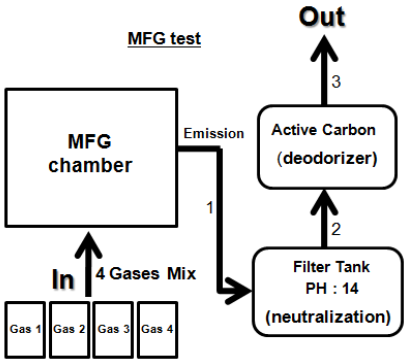


Figure 5. IST MFG test flow chart

c. Uniformity measurement in the MFG chamber

In order to make sure that each board will experience the same test conditions and the test boards installed in the chamber will not be interfere with the gas flow it is necessary to verify the corrosion level in different locations of the chamber. A total of 12 Cu coupons and 12 Ag coupons with 99.99% purity (1 inch x 1 inch) are cleaned through proprietary chemical cleaning procedure and hung in different area of the chamber with some test boards for 5 days exposure with various H_2S concentration (500 ppb, 1000 ppb, 1700 ppb) to understand how H_2S drives the corrosion acceleration. The chamber set up is shown in Figure 6. The weight gain after the test confirms whether the corrosion degrees in different locations of the chamber are all in the reasonable range and make sure the gas concentration inside the chamber is stable and uniform. The weight gain and corrosion product of each coupon is verified by the methods of Weight Gain Analysis, X-Section and u-XPS to define acceptable uniformity.

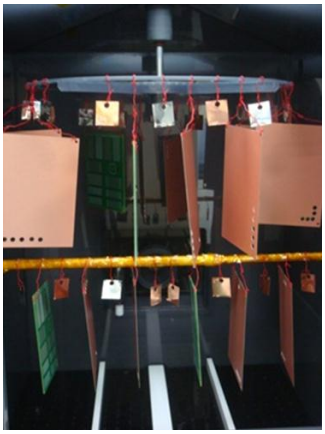


Figure 6. Chamber set up of uniformity test

d. Test condition

The critical factor of creep corrosion is the concentration of H_2S, which has been already been shown in previously published papers. In order to get more visible creep corrosion phenomenon, 1700 ppb is chosen for the concentration of H_2S in this experiment based on the ALU's study. [10] The MFG test condition in this study is shown in Table 4.

Table 4. MFG Test Condition in this experiment (ppb)

H_2S	Cl_2	NO_2	SO_2	Temp.	RH	Duration
1700	20	200	200	40℃	90%	21days

Before MFG test, all of the test boards are reflowed one time. The reflow profile is shown in Figure 7. After reflow, all PCBs are placed in the MFG chamber in figure 8.

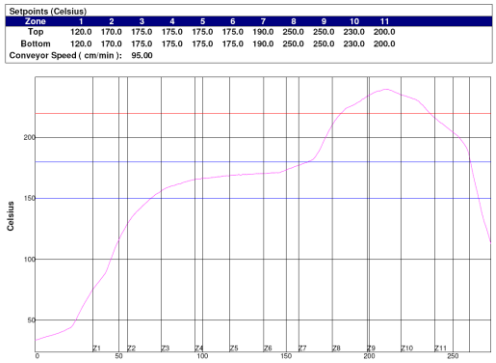


Figure 7. The reflow profile prior to MFG test

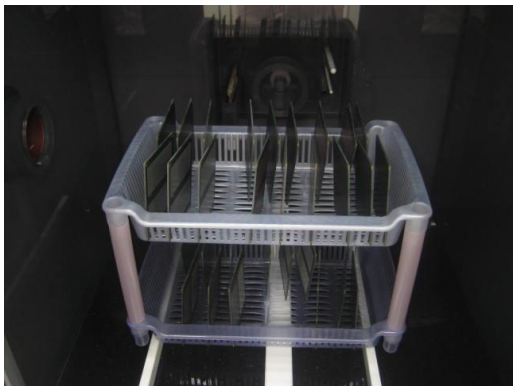


Figure 8. PCB placement for MFG Test

2. PCB design

Table 5 shows the DOE matrix to investigate material, process and design effect on the creep corrosion. Two groups A and B of sample are investigated in this study. Group A is NSMD. (See Figure 9) Group B is Comb-Pattern design. (See Figure 10)

Table 5. Test Vehicle of the DOE matrix

Group	Test Vehicle	Feature	Factors to study
A	HF PCB 80 x 80 mm	NSMD	Surface Finish: 1) ImAg 2) Post-Treatment ImAg 3) HT OSP 1 ; HTOSP 2
B	HF PCB 80 x 80 mm	SMD Comb Line	Flux: Flux 1 ; Flux 2

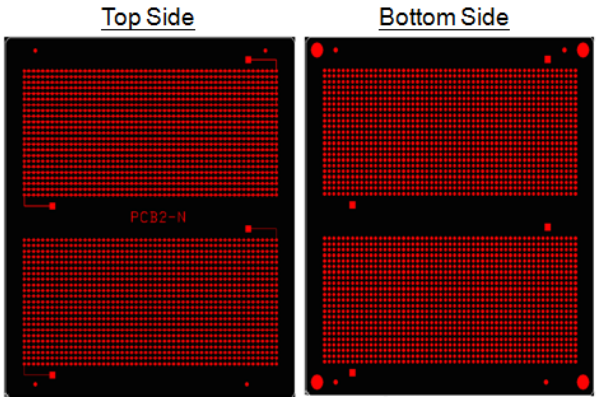


Figure 9: Test board design of Group A

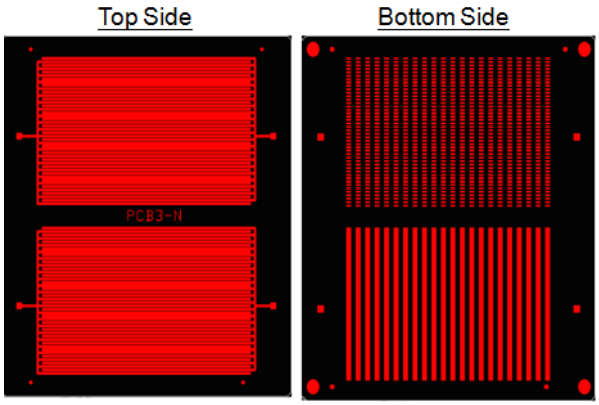


Figure 10: Test board design of Group B

a. SMD vs NSMD is shown in Figure 11

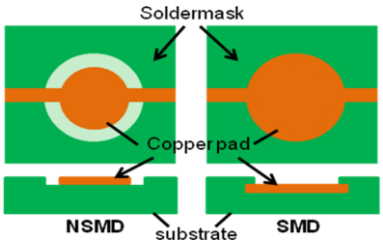


Figure 11. SMD vs NSMD features

b. Surface finish comparison is shown in table 6

Table 6: The description of surface finishes vehicle

Experiment	Surface Finish	Supplier
Group A	ImAg	Vendor 1
	Post-Treatment ImAg	Vendor 2
	HT OSP 1	Vendor 3
	HT OSP 2	Vendor 2
Group B	ImAg	Vendor 1

c. Flux residue in wave soldering

In Group B, two types NC(No Clean) and OA(Organic Acid) Flux are sprayed on PCB with the simulation of wave soldering condition by baking the flux residue on the PCB.

PCBs of Group B are put in the oven at 125℃ for 5 minutes and then at 270℃ for 1 minute after the NC OA Flux are sprayed on it to simulate wave soldering condition and have flux residue remaining on the PCB.

Result and Discussion

a. Uniformity Test

Before and after the uniformity test, 5 weightings are conducted by the microbalance and the average is calculated. After the weight gain, corrosion product is verified by the methods of Weight Gain Analysis, Coulometeric Reduction(CR) and X-Section with SEM/EDS.(See Figure 12 and Figure 13.) The data from the three methods are consistent with each other. It can be defined that the gas inside of the chamber is uniform.

The effect of the mixed flowing gas with various H_2S concentration (500 ppb, 1000 ppb, 1700 ppb) at 5 days duration showed that a much higher corrosion rate is observed on Cu coupons in both the Individual and Mixed Flowing Gas Test.

The corrosion rate of Cu coupons rapidly increases with H_2S concentration after reaching at 1000 ppb. Ag coupons have more active corrosion in lower H_2S concentration than higher H_2S concentration. Flaking corrosion also happens on the Cu coupon with heavy corrosion product in the high H_2S concentration test condition. (See Figure 14, Figure 15, Figure16.)

Ag Coupon	Ag1	Ag2	Ag3	Ag4	Ag5
Ag2S wt gain (angstroms)	630	910	580	1170	720
Ag2S CR (angstroms)	513	538	535	546	636
Cu Coupon	**Cu1**	**Cu2**	**Cu3**	**Cu4**	**Cu5**
Cu corrosion product wt gain (angstroms)	15880	15630	15060	17840	17790
CR (angstroms)	14603	20361	14127	20547	16574

Figure 12. Weight gain analysis by CR [11]

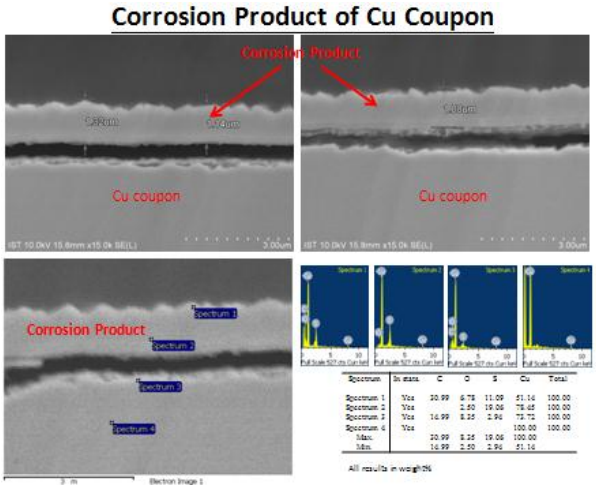


Figure 13. Weight gain analysis by X-Section with SEM/EDS

Thickness of Cu_2S/Ag_2S

H_2S	500 ppb	1000 ppb	1700 ppb
Cu2S Thickness(nm)	935	1787	7425
Ag2S Thickness(nm)	102	50	81

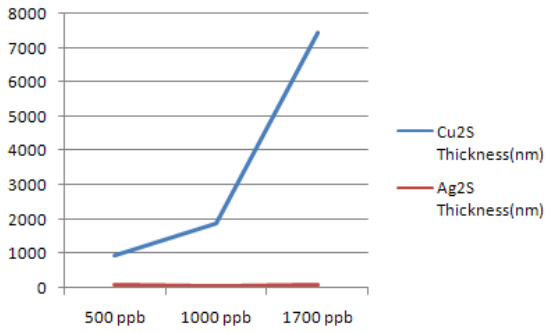


Figure 14. Thickness analysis of Cu_2S/Ag_2S

Gained Weight of Cu/Ag Coupons

H_2S	500 ppb	1000 ppb	1700 ppb
Cu-Gained Weight(g)	0.00106	0.00208	0.00842
Ag-Gained Weight(g)	0.00010	0.00005	0.000007

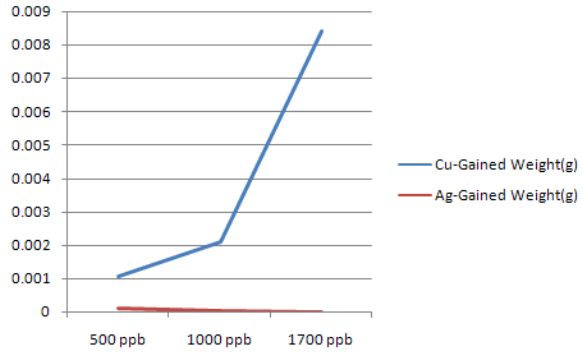


Figure 15. Weight gain analysis of Cu/Ag coupons

Corrosion Rate of Cu/Ag Coupons

H_2S	500 ppb	1000 ppb	1700 ppb
Cu-Corrosion Rate(nm/day)	187	357	1485
Ag-Corrosion Rate(nm/day)	20	10	16

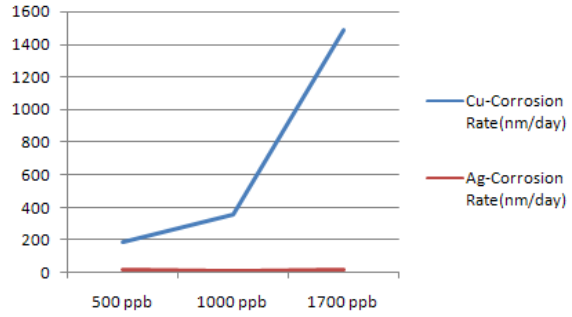


Figure 16. Corrosion Rate of Cu/Ag coupons

b. SMD vs NSMD effect on the creep corrosion

According to previous experiment, creep corrosion can be observed on both SMD and NSMD features. The degree of creep corrosion on SMD board features grows laterally across solder mask and is greater than that at the metal/laminate interface on NSMD board feature. The difference is explained as following discussion, which also refers to some published papers. [11][12]

1) The migration on the laminate around NSMD areas has to overcome the land between Cu pad and solder mask.
2) SMD is a much smoother surface so that the corrosion product can travel much more readily across the planar surface.
3) A gap is made at the interface between soldermask and Cu pad shown in figure 17 and figure 18 due to the poor soldermask processing (exposed Cu at edge of soldermask), so that creep corrosion emanates from SMD features. Figure 19 shows the creep corrosion of SMD and NSMD board features.

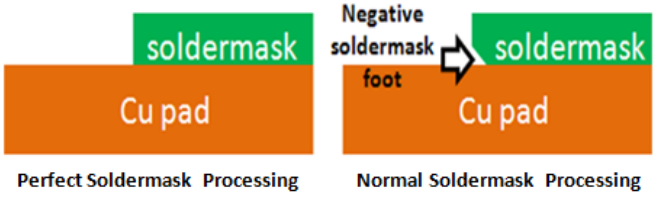


Figure 17. Normal and poor soldermask processing

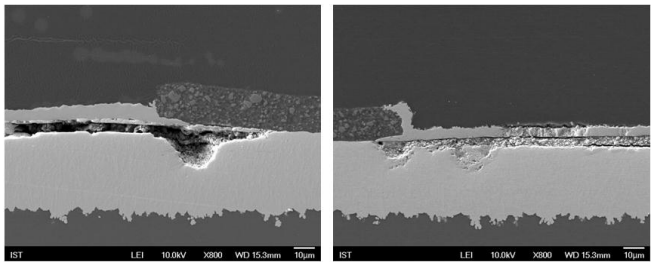


Figure 18. Creep corrosion occurred from the exposed copper at the edge of soldermask.

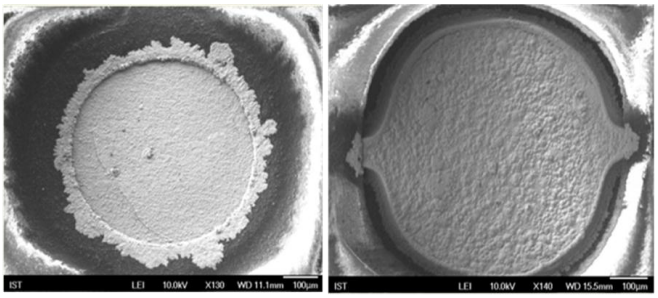


Figure 19. Creep corrosion on SMD and NSMD board features.

c. Surface finish effect on the creep corrosion (Group A)

In the mid of 2006, ROHS legislation has been implemented and the use of lead in electronic products is prohibited. The PCB manufactures are driven to transition from lead coating final finishes to lead free alternatives. The most common lead free surface finishes applied today are ImAg (Immersion Silver) and OSP (Organic Solderability Preservatives) to date based on solder joint reliability validation. With creep corrosion concerns in high reliability product like telecom, network product and so on, the 2 available surface finish were found not to be good candidates to prevent its occurrence. Therefore, one improved ImAg surface finish with post-treatment is designed for comparison besides the above 2 candidates in the creep corrosion resistance study. Group A PCB is NSMD design with 3 different types of surface finish, and Group B PCB is Comb-Pattern design with ImAg surface finish.

Creep corrosion is observed on all the three types of surface finish based on the visual inspection and the analysis through Cross-Section, SEM/EDS and electrical measurement in Table 7.

Table 7. Creep corrosion of different surface finishes

Surface Finish \ Result	Corrosion on pad	Corrosion on Trace	Shorting Occurrence
ImAg	O	O	X
Post-Treatment ImAg	O	X	X
HT OSP 1	O	O	O
HT OSP 2	O	O	O

Finally, the corrosion severity of the three PCB finishes is ranked as below.

OSP > ImAg > Post-Treatment ImAg

The creep corrosion evolution of NSMD is shown in Figure 20.

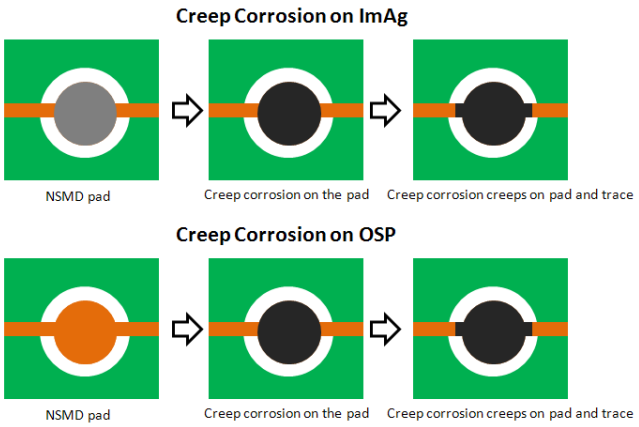
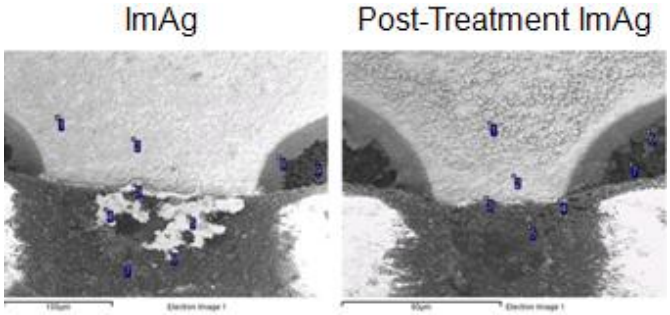


Figure 20: Creep corrosion evolution of NSMD PCB

ImAg and Post-Treatment ImAg

The comparison in SEM/EDS analysis between ImAg and Post-Treatment ImAg coating show that the corrosion rate of ImAg is higher than Post-Treatment ImAg. In figure 21, the corrosion of ImAg creeps onto the trace from pad, but the corrosion of Post-Treatment ImAg only occur on the pad and doesn't creep to the trace. The pad of ImAg has been corroded and flaked as shown in figure 22, therefore, it is concluded Post-Treatment ImAg has the better performance than normal ImAg.



Spectrum	C	O	Al	Si	S	Cu	Ag	Total
1					15.58	76.94	7.48	100.00
2	6.05				15.00	74.07	4.88	100.00
3	21.78	2.31	0.78		9.72	51.40	14.00	100.00
4	49.46	22.75		7.60	3.14	8.49	8.55	100.00
5	23.30				11.62	59.11	5.97	100.00
6	16.15				11.42	31.22	41.22	100.00
7	51.55	30.08	1.17	8.08	2.32		6.80	100.00
8	43.06	56.94						100.00
9	48.05	51.95						100.00
Max.	51.55	56.94	1.17	8.08	15.58	76.94	41.22	
Min.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

Spectrum	C	O	Si	S	Cu	Ag	Total
1				14.41	48.86	36.73	100.00
2				14.08	62.16	23.76	100.00
3	3.77	3.10		14.60	24.88	53.65	100.00
4	5.63			13.53	34.90	45.94	100.00
5	39.61	41.00	18.16		1.23		100.00
6	42.06	44.37	13.57				100.00
7		100.00					100.00
Max.	42.06	100.00	18.16	14.60	62.16	53.65	
Min.	0.00	0.00	0.00	0.00	0.00	0.00	

Figure 21: Top view SEM/EDS analysis

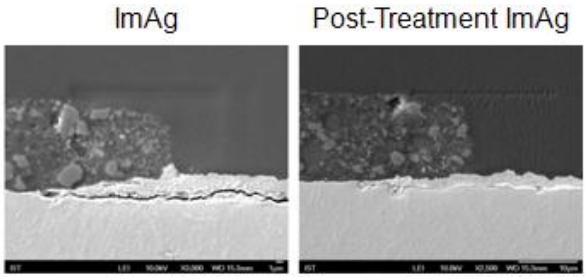


Figure 22: Pad comparison of side view

Porosity in surface finish is an inherent characteristic. When the Cu pad is rougher, it will promote micro-voids. The Post-Treatment is molecular self-assembly Monolayer. The molecule will selectively attach itself to available copper, as shown in Figure 23.

The silver layer is getting denser with better coverage of Cu pad preventing corrosion happening. The Post-Treatment ImAg with more organic preservative is designed to have better performance than ImAg under the corrosive gas exposure. [2]

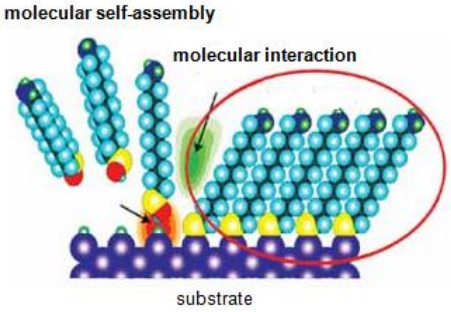


Figure 23: The mechanism of Self-Assembly Monolayer. [2]

The comparison of the 2 HT OSP

Both HT OSP 1 and HT OSP 2 have worse performance than ImAg, but there is not enough evidences to judge which one is the worst. HT OSP 1 has creep and flaking corrosion. The corrosion product on the pad is thinner and smoother. HT OSP 2 has creep corrosion but the pad isn't flaked. The corrosion product on the pad of HT OSP 2 is thicker and rougher as shown in Figure 24. Figure 25 shows the side view of HT OSP 1 and HT OSP 2. Both of them have creep corrosion from pad to the trace and the pad crater. HT OSP 2 has thicker corrosion product on the pad.

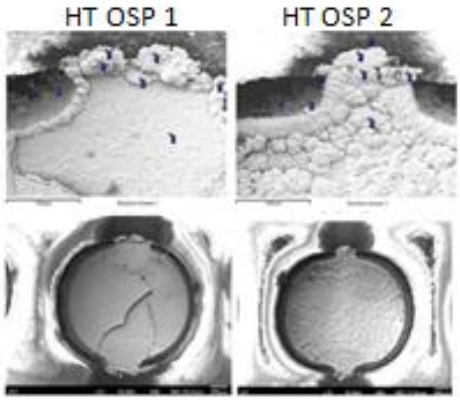


Figure 24: Top view of HT OSP1 and HT OSP2

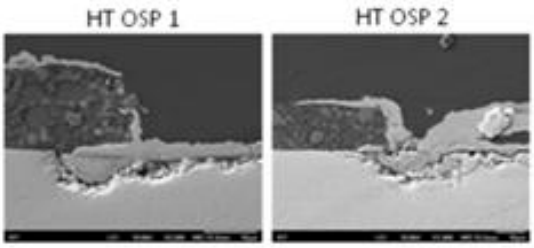


Figure 25: Both HT OSP1 and HT OSP2 have creep corrosion product.

ImAg has a higher porosity ratio than Post-Treatment ImAg and it is assumed that OSP might have higher porosity ratio than ImAg in Figure 26. Currently there are three testing methods for surface finish porosity in the industry. These are Gas Exposure Method, Electrolysis Imaging Method and Salt Spray Test Method. But all of them are not the ideal and reliable test methods to identify quantitatively the porosity.

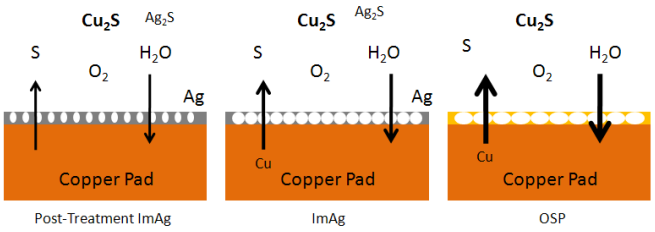


Figure 26: Qualitative comparison of porosity ratio among surface finish

d. u-XPS Analysis

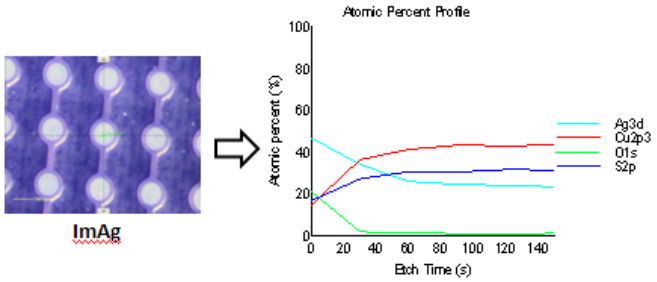


Figure 27: Atomic Percent Profile of ImAg

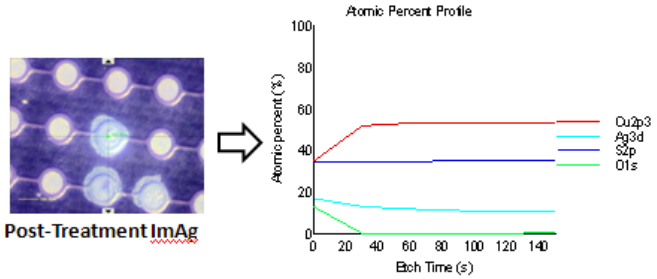


Figure 28: Atomic Percent Profile of Post-Treatment ImAg

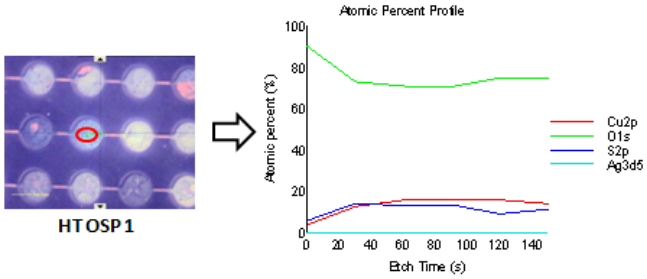


Figure 29: Atomic Percent Profile of HT OSP1

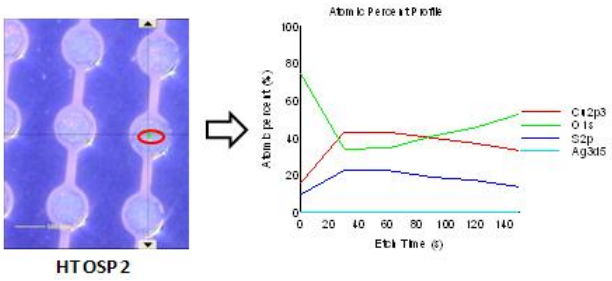


Figure 30: Atomic Percent Profile of HT OSP2

e. Flux Residue effect on the creep corrosion (Group B)

Wave-soldering flux residues can promote creep corrosion and this has been published in Dr. C. Xu's paper. [1][10] It is expected we will get a similar result in this study. The SEM/EDS of corroded pad with flux residue is shown in Figure 31. The creep corrosion is found in Figure 32 with SEM/EDS analysis. Flux residue will cause moisture absorption and the H+ ionic contamination will dissociate Cu oxide and accelerate creep corrosion. [2]

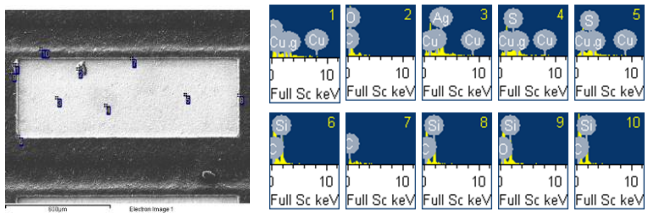


Figure 31: SEM/EDS analysis of corroded Pad

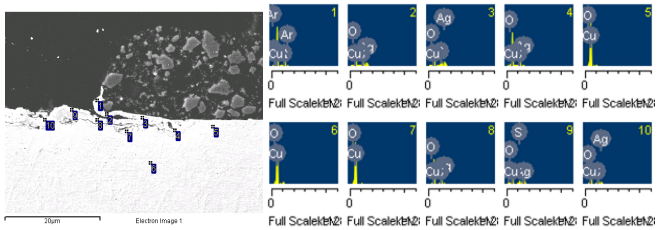


Figure 32: SEM/EDS analysis of creep corrosion

Creep corrosion typically occurs when copper is exposed to an environment containing sulfur. Cu_2S is the primary creep corrosion product. Cu_2S is produced by the attack of the copper at the edge of the soldermask. Cu_2S film can migrate across any surface that it contacts. Creep appears to begin by growth of dendrites. As the corrosion products increase in thickness, the resistance decreases until functional shorting occurs.

Conclusion and Further Research

Creep corrosion can be driven by multiple factors. In addition to environmental factors, such as pollution, temperature, humidity the complicated PCB manufacturing process is also another concern. There might be many potential influences on creep corrosion during the process and not only surface finish, flux, and board design. The corrosion occurrence on the PCB is very sensitive to surface chemical properties. Ionic cleanliness and the roughness and surface chemistry of the soldermask might be other factors that influence the rate of creep corrosion growth. That will be the topic for further study.

References

[1] C. Xu, W. Reents, J. Franey, J. Yaemsiri and Devaney,"Creep Corrosion of OSP and ImAg PWB Finishes" Alcatel-Lucent, Murray Hill, NJ and Raleigh, NC, USA

[2] He Jingqiang, Tu Yunhua, "电子产品的爬行腐蚀失效", Huawei Technologies Co., Ltd. EMAsia-China.com

[3] He Jingqiang, Tu Yunhua, Liu Sang, "PCB Creep Corrosion and Board Design Considerations", Huawei Technologies Co., Ltd. Shenzhen, Guang Dong, P.R. China

[4] Craig Hillman, Joelle Arnold, Seth Binfield, and Jeremy Seppi, " SILVER AND SULFUR: CASE STUDIES, PHYSICS, AND POSSIBLE SOLUTIONS" DfR Solutions, College Park, MD, USA

[5] American Society for Testing and Material, ASTM Designation B845-97: Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts, 1997

[6] International Electro-technical Commission, IEC Standard 68-2-60(second edition) Environmental Testing-Part2: Tests-Flowing mixed gas corrosion test, 1995.

[7] Electronic Industries Association, EIA Standard TP-65A: Mixed Flowing Gas, Jan. 1998

[8] Telcordia GR-63-CORE Issue2, Section 5.5,"Airborne Contaminants Test Methods", Nov. 2000

[9] Chao, J.G., Gore, R.R., "Evaluation of a mixed flowing gas test,"1991 Proceedings of the Thirty Seventh IEEE Holm Conference on Electrical Contacts,pp.216-228, Piscataway, NJ:IEEE,1991.

[10] C. Xu, W. Reents, J. Franey, J. Yaemsiri and J. Devaney,"Creep Corrosion of OSP and ImAg PWB Finishes", Alcatel-Lucent, Murray Hill, NJ and Raleigh, NC, USA

[11] Coulometeric Reduction data is conducted by IBM's Dr. PJ Singh in INEMI Creep Corrosion project

[12] Lenora Toscano, Ernest Long, Ph.D., and Swanson,"CREEP CORROSION ON PCB SURFACES: IMPROVEMENTS OF PREDICTIVE TEST METHODS ANDDEVELOPMENTS REGARDING PREVENTION TECHNIQUES", Mac Dermid, Waterbury, CT,USA

[13] Randy Schueller, Ph.D, "CREEP CORROSION ON LEAD-FREE PRINTED CIRCUIT BOARDS IN HIGH SULFUR ENVIRONMENTS", Dell Inc. Austin, TX, USA

The Surface Finish Effect on the Creep Corrosion in PCB

Presenter : Cherie Chen

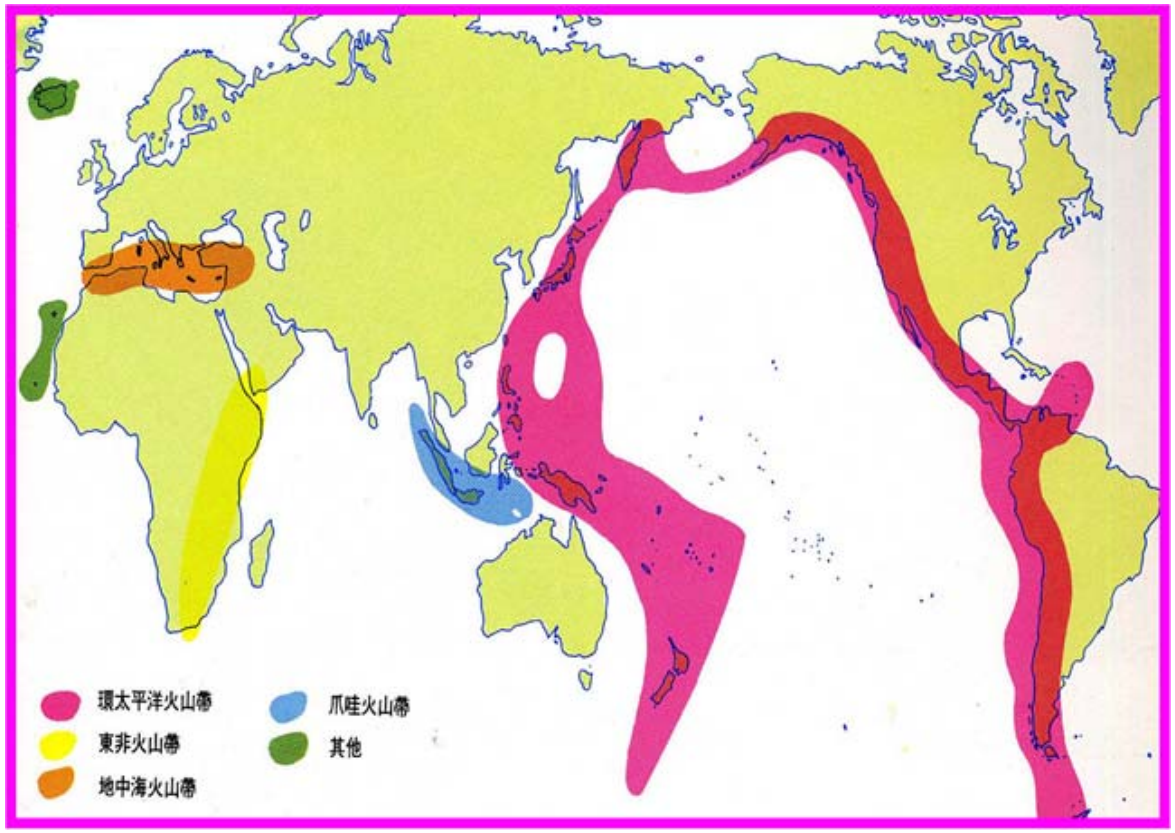
Outline

- Introduction
- Experiment Purpose
- Experiment Design
- Experiment Result
- Conclusion
- Q & A

Introduction

The Major Volcanic Belts in The World

- Pacific Ring of Fire
- East Africa Ring of Fire
- Mediterranean Ring of Fire
- Java Ring of Fire



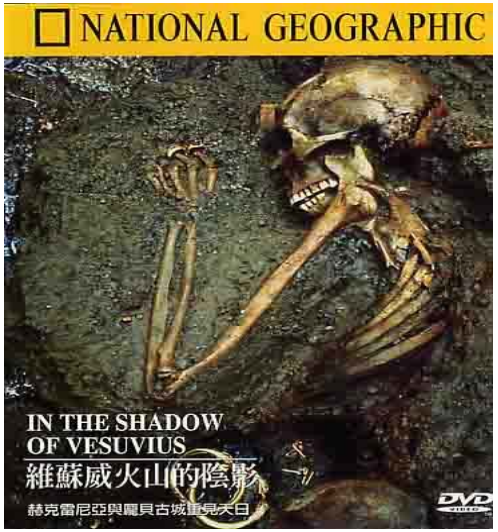
Refer to :新竹市青草湖社区大学网站

Frequent Volcanic Eruptions in Recent Years

Volcanic Eruptions in 2010 ~ 2011		
Time	Volcano	Area
2010.03	Eyjafjallajokull Volcano	Ice Island
2010.10	Merapi Volcano	Indonesia
2011.01	Mount Etha Volcano	Italy
2011.02	Bulusan Volcano	Philippines
2011.03	Kilauea Volcano	Hawaii
2011.03	Shinmoedake Volcano	Japan
2011.03	Kagoshima Volcano	Japan
?	Mount Changbai Volcano	China
?	Mount Tatun Volcano	Taiwan

Geological experts say :

- **20 Volcanic Eruptions any time**
- **Volcanic Activities occur more frequently since 2000.**



Italy Vesuvius Volcanic Eruptions

Crater of Mount Vesuvius

The Silent Mount Before Volcanic Eruptions

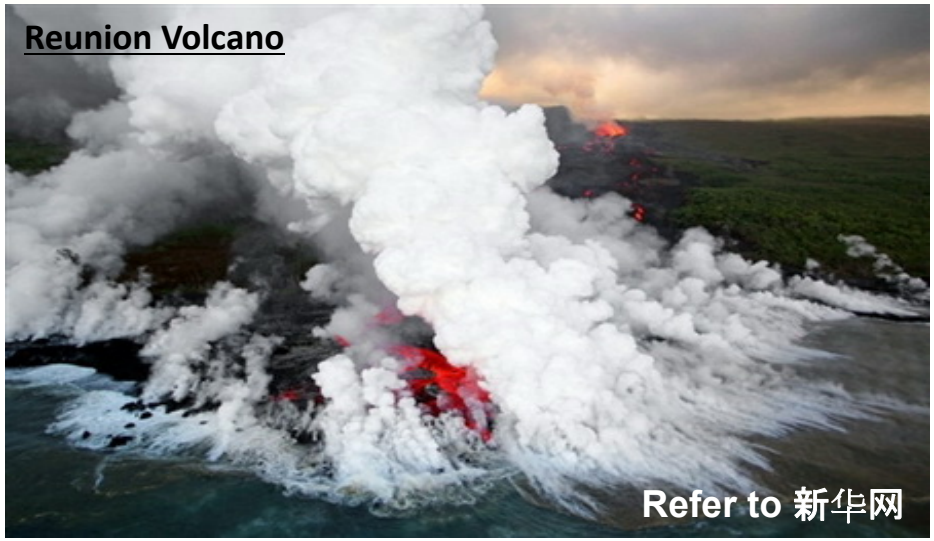
Mount Changbai in China

Mount Tatun in Taiwan

refer to : http://chifoto.blogspot.com/

Volcanic Eruptions

Reunion Volcano



Ice Island Volcano

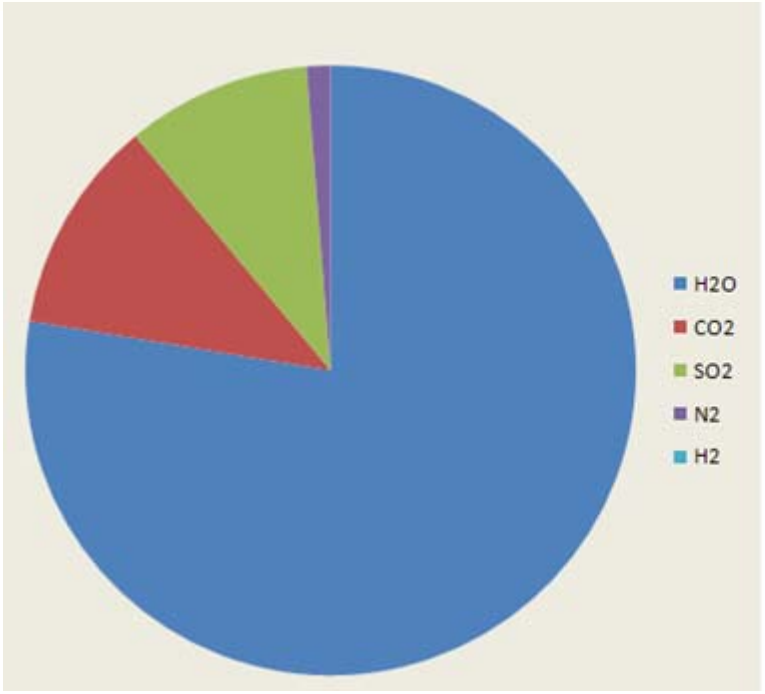
Alaska Volcano

World Geological Park – Mount Yandang

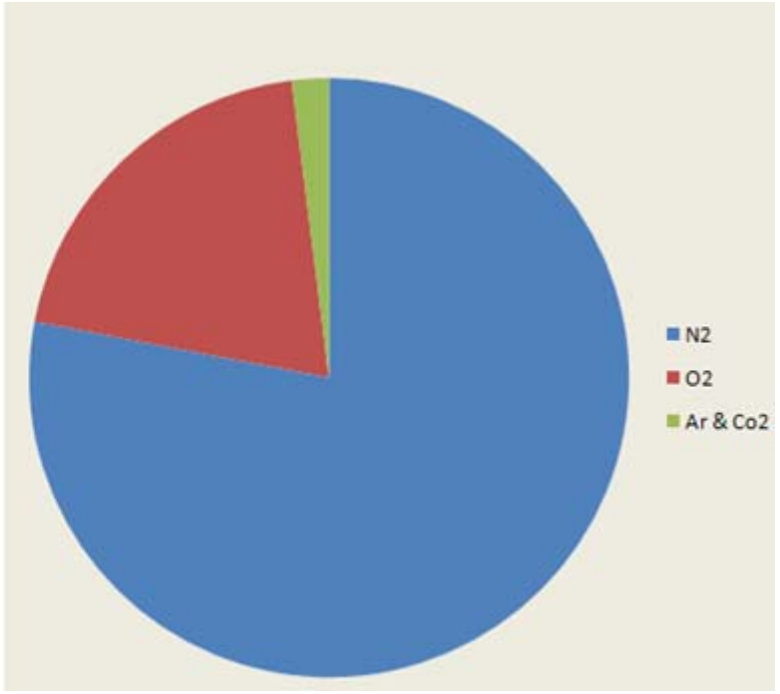
The Product of Volcanic Eruptions ~ Ash

- Diameter is less than 2mm
- Composed of the rocks, minerals and volcanic glass fragments
- From the rock and magma crushed into small particles during the volcanic eruptions
- Different from the soot, hard and insoluble in water
- In addition to the climate impact of volcanic ash, but also on human and animal damage to the respiratory system

The comparison of general and volcanic gas compositions



General Gas Composition



Volcanic Gas Composition

The general gas composition and volcanic gas composition are closely related to exhaust gas of volcanic eruptions.

Refer to 台湾台北科技大学网站

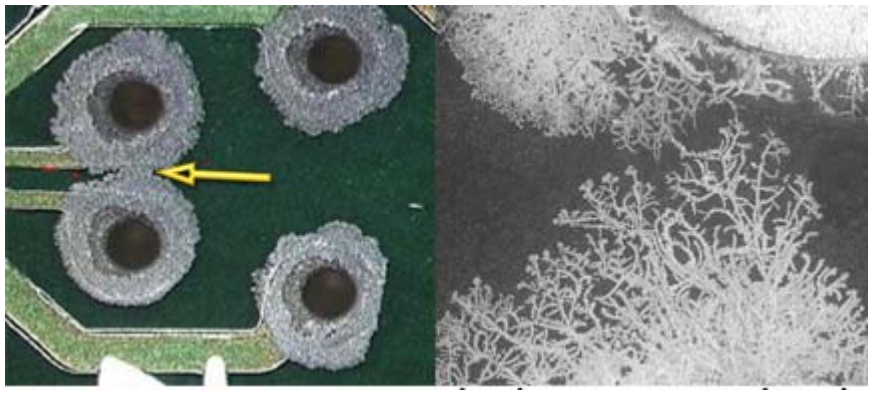
Creep Corrosion

- Creep corrosion typically occurs when copper is exposed to an environment containing sulfur.

- Cu_2S is the primary creep corrosion product. Cu_2S is produced by the attack of the copper at the edge of the soldermask.

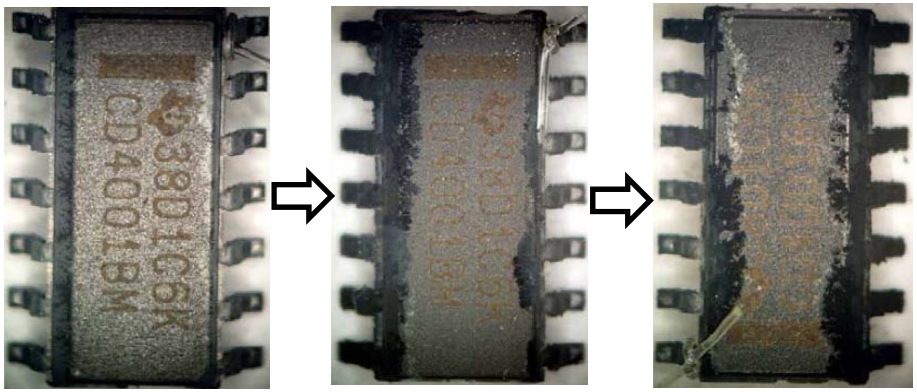
- Creep appears to begin by growth of dendrites. As the corrosion products increase in thickness, the resistance decreases until functional shorting occurs.

Creep Corrosion on PCB



Refer to : Dr. Randy Schueller's published paper

Creep Corrosion on PPF SOIC

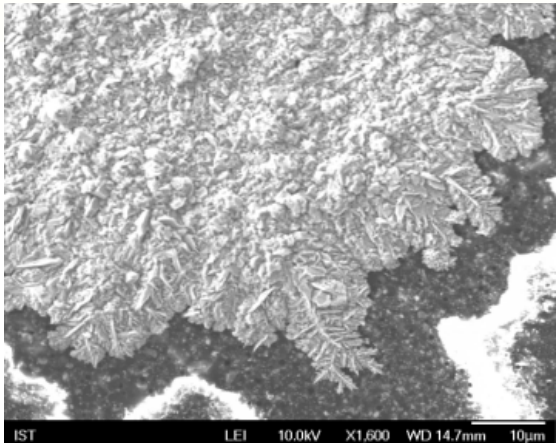


Refer to : the published paper of Maryland University

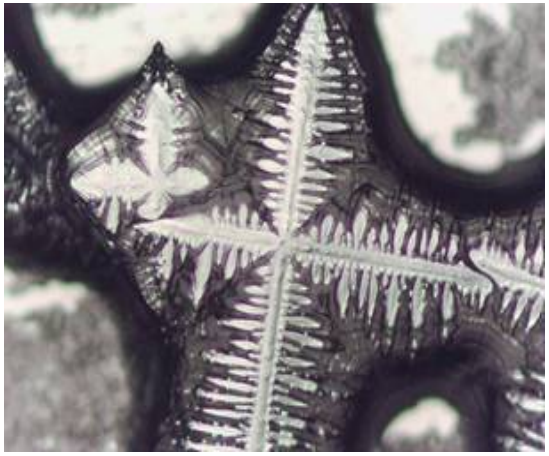
Comparison among Creep Corrosion, Dendrite and CAF

Comparison	Creep Corrosion	Dendrite	CAF
Substrate	Cu	Cu/Ag/Tin-Lead…	Cu
Corrosion Product	Cu_2S	FO	Cu Oxide/ Hydroxide
Electron Migration	X	Cathode to Anode	Anode to Cathode
Failure Mode	Short / Open	Short	Short
Humidity Requirement	Yes	Yes	Yes
Voltage Requirement	No	Yes	Yes

Creep Corrosion

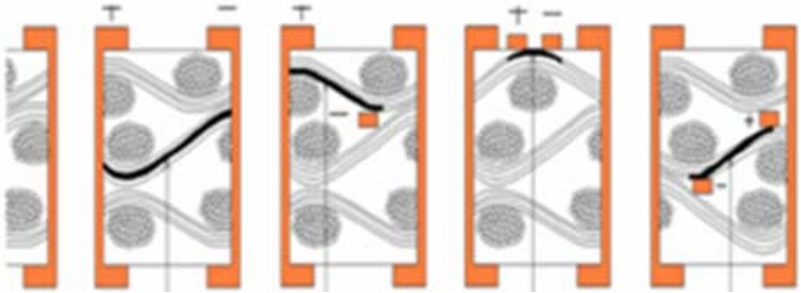


Dendrite



Refer to 北京工业大学现代教育技术中心

CAF

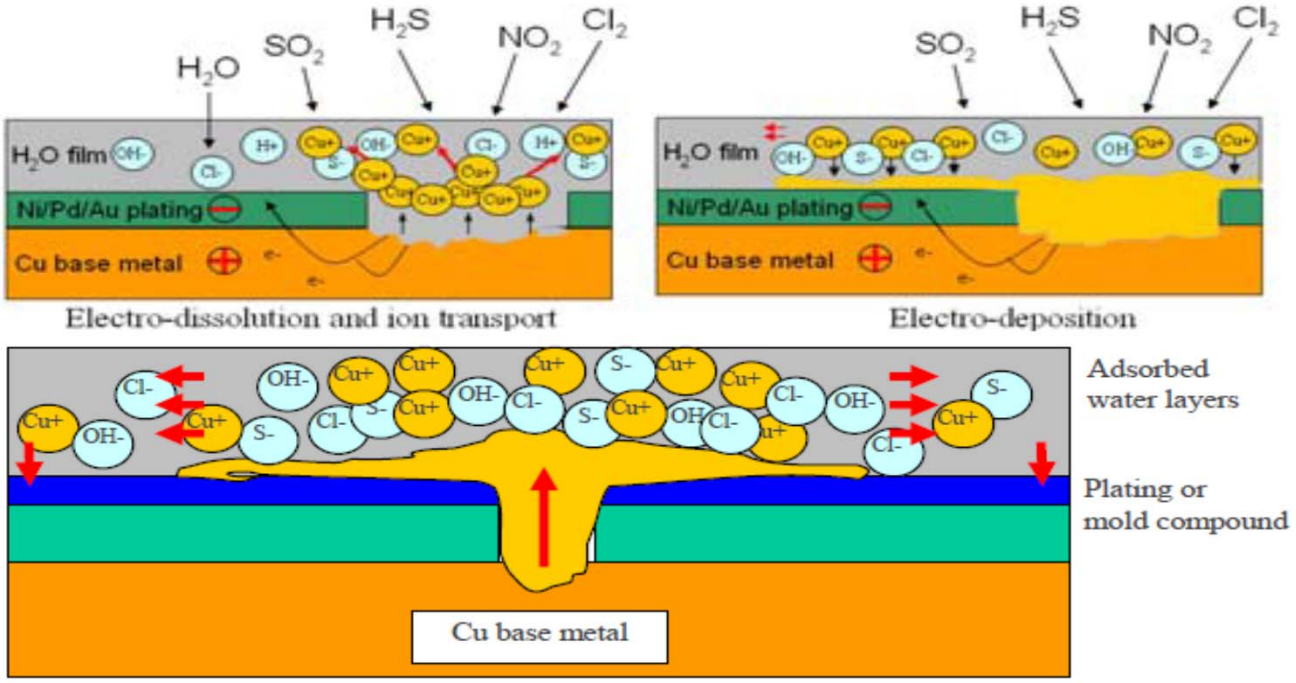


Refer to 中国赛宝实验室可靠性分析中心

The Mechanism of Creep Corrosion

The mechanism of creep corrosion in Dr. Ping Zhao's previous published paper described the process of **Dissolution → Diffusion → Re-deposition**

Creep Corrosion on the Gull-Wing Lead of PSOP



1. The multiple mono-layers of water are adsorbed on the surface under high relative humidity and then the corrosion products dissolve into these water layers.

⇩

2. They diffuse over the surface in solution down the concentration gradient and re-deposit.

The Factors to Creep Corrosion

- PCB Design
- Surface Finish
- Flux Residue
- SMD & NSMD
- Test Condition
- Reflow
- Wave Soldering
- Solder Paste Coverage

MFG Test

MFG(Mixed Flowing Gas) Test

- The MFG test method was carried out in 1980's.

- A laboratory test where the temperature (℃), relative humidity (%RH), concentration of gaseous pollutants (ppb level), and other critical variables (such as volume exchange rate and airflow rate) are carefully defined, monitored and controlled.

- The purpose of MFG test is to use the combination of four most common corrosive gases in the environment, H_2S, Cl_2, NO_2, SO_2 to simulate and accelerate atmospheric corrosion due to exposure.

- Many specific and application-oriented MFG test methods created for industrial applications

- There is still no accepted industry standard created for MFG test to correlate to real service life yet.

Application-oriented MFG test methods

Condition	Class	H_2S	CL_2	NO_2	SO_2	Temp	RH
Telcordia	Indoor	10	10	200	100	30℃	70%
	Outdoor	100	20	200	200	30℃	70%
ALU	Intl.	1500-2000	20	200	200	40℃	70%
Battelle	Class 2	10	10	200	-	30℃	70%
	Class 3	100	20	200	-	30℃	75%
EIA	Class 4	200	50	200	-	50℃	75%
	II	10	10	200	-	30℃	70%
	II A	10	10	200	100	30℃	70%
	III	100	20	200	-	30℃	75%
	IIIA	100	20	200	200	30℃	70%
	IV	200	30	200	-	40℃	75%
IEC	1	100	-	-	500	25℃	75%
	2	10	10	200	-	30℃	70%
	3	100	20	200	-	30℃	75%
	4	10	10	200	200	25℃	75%
IBM		40	3	610	350	30℃	70%

MFG Test System

Brand : Yamasaki

Model : GH-180-VL/M(Japan)

Temperature : 20 ℃ ±50 ℃

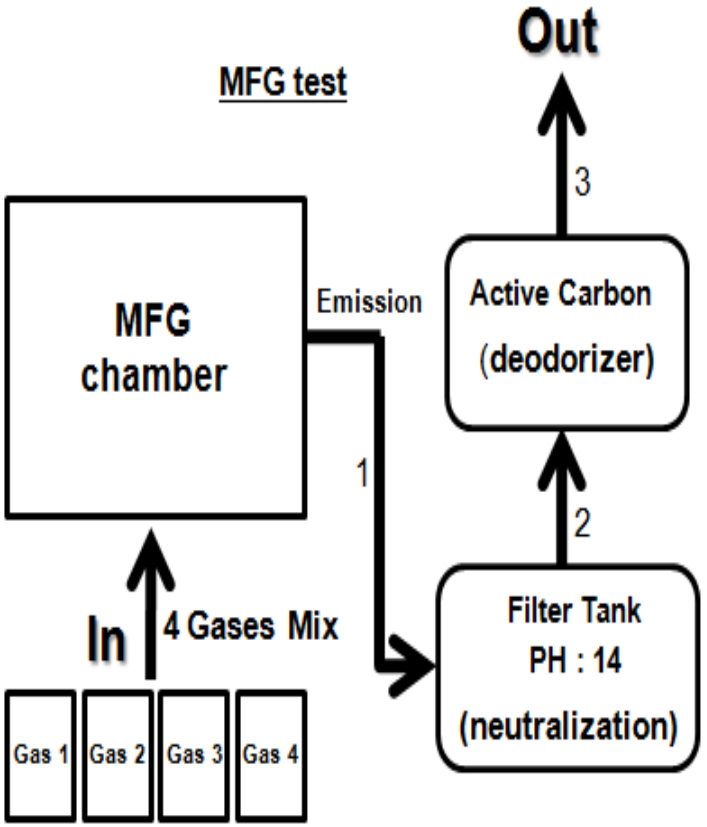
Humidity Range : 70 ~ 95%(RH)

Exchange Rate : 1500 L / hour

Mode : Single or Mixed flowing gas

Inside Dimension :
50 cm (W) x 50 cm (D) x 50 cm (H)

MFG Test System



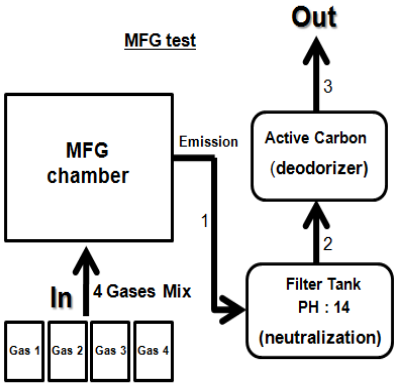
MFG Test Flow

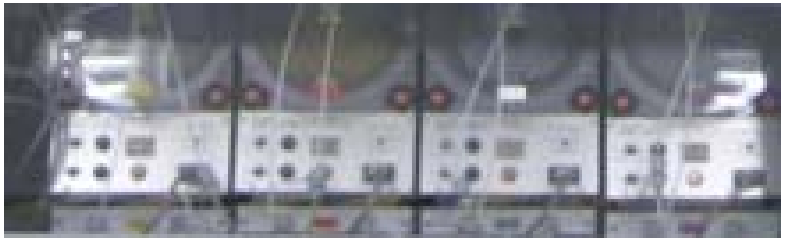
Test Conditions & Gas Concentration Setting

H_2S	NO_2	Cl_2	SO_2	Temp.	RH	Duration(day)
1700 ppb	200ppb	20ppb	200ppb	40℃	90%	21

- Gas concentration is set according to the exchange rate of the chamber

- 1500 Litter gas get into the chamber and 1500 Little gas emission go out





Gas Concentration

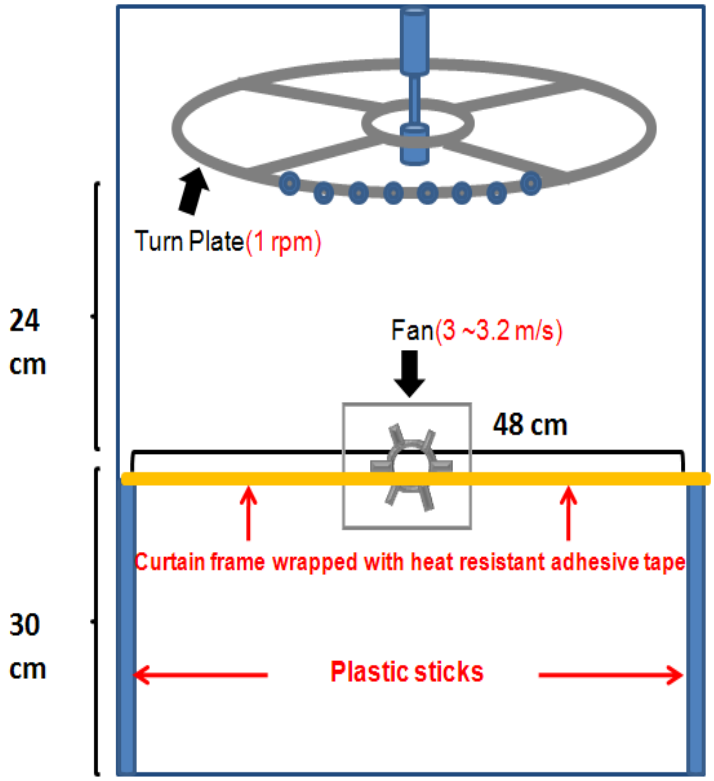
Test Condition				
Gas	H2S	Cl2	SO2	NO2
Concentration	1700 ppb	20 ppb	200 ppb	200 ppb
Gas Cylinder	50000 ppm	100 ppm	1000 ppm	1000 ppm
Chamber Exchange Rate	1500 L/H			
Liter/per hour (L/H)	0.05	0.3	0.3	0.3
Calculation of Exchange Rate				
Gas	**Gas In**	**=**	**Gas Out**	
H2S	1500 L/H x 1.7 ppm		0.05 L/H x 50000 ppm	
Cl2	1500 L/H x 0.02 ppm		0.3 L/H x 100 ppm	
SO2	1500 L/H x 0.2 ppm		0.3 L/H x 1000 ppm	
NO2	1500 L/H x 0.2 ppm		0.3 L/H x 1000 ppm	

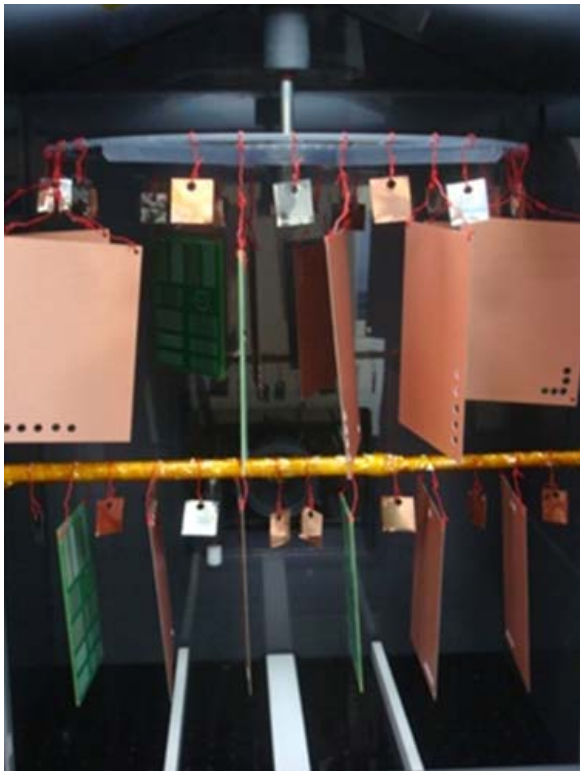
Uniformity Measurement in the MFG chamber

Chamber Set up of Uniformity Test

Test Condition

H_2S	NO_2	Cl_2	SO_2	Temp.	RH	Duration(day)
500/1000/1700 ppb	200ppb	20ppb	200ppb	40℃	75%	5





Weight Gain Analysis

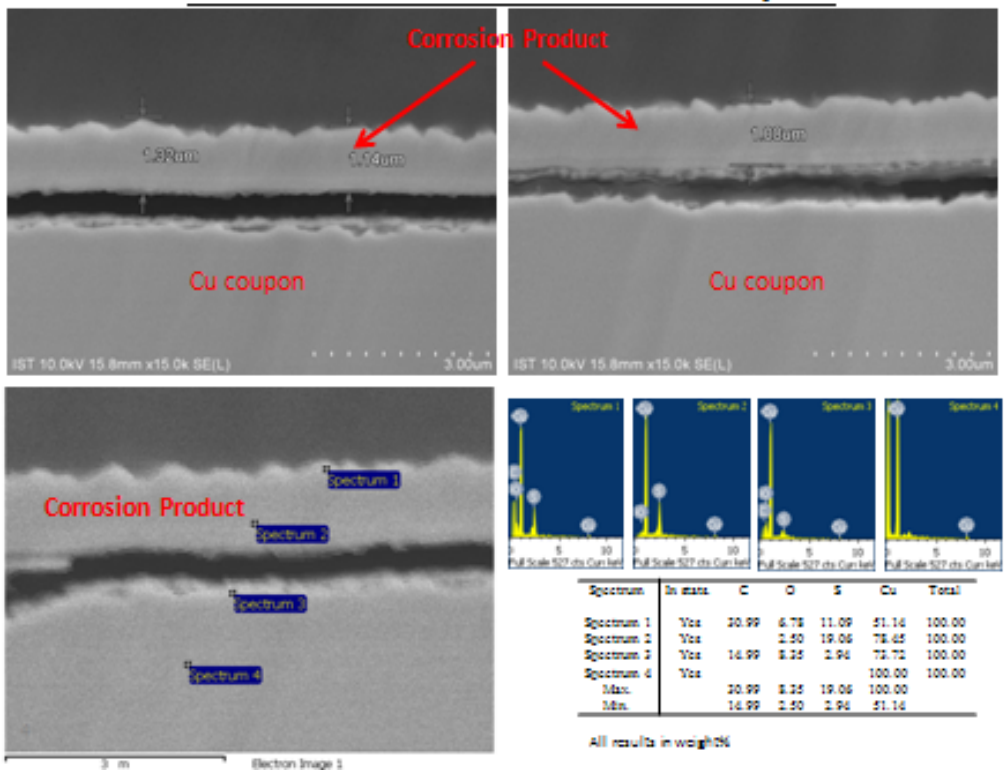
Ag Coupon	Ag1	Ag2	Ag3	Ag4	Ag5
Ag2S wt gain (angstroms)	630	910	580	1170	720
Ag2S CR (angstroms)	513	538	535	546	636
Cu Coupon	**Cu1**	**Cu2**	**Cu3**	**Cu4**	**Cu5**
Cu corrosion product wt gain (angstroms)	15880	15630	15060	17840	17790
CR (angstroms)	14603	20361	14127	20547	16574

- Weight gain analysis methods :

  a. Weight Measurement
  b. Coulometric Reduction(CR)
  c. X-Section with SEM/EDS

- The data of weight gain analysis by the three methods are consistent to each other.

Corrosion Product of Cu Coupon



Spectrum	In stats.	C	O	S	Cu	Total
Spectrum 1	Yes	20.99	6.78	11.09	51.14	100.00
Spectrum 2	Yes		2.50	19.06	78.45	100.00
Spectrum 3	Yes	14.99	8.35	2.96	73.72	100.00
Spectrum 4	Yes				100.00	100.00
Max.		20.99	8.35	19.06	100.00	
Min.		14.99	2.50	2.96	51.14	

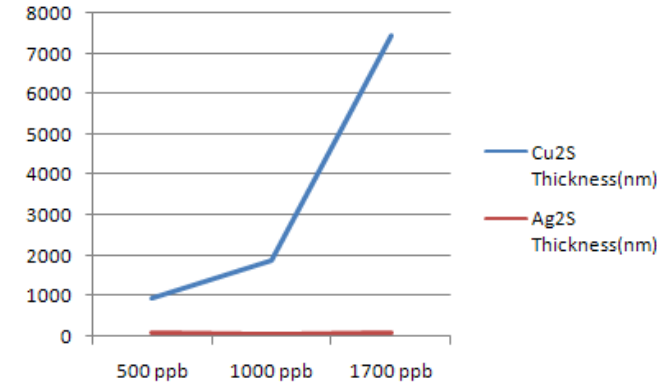
All results in weight%

Weight gain Analysis of Cu/Ag coupons in 3 different concentration of H_2S

- The corrosion rate of Cu coupon rapidly increases while H_2S concentration after reaching at 1000 ppb.
- Ag coupon has more active performance in lower H_2S concentration than higher H_2S concentration.
- Flaking corrosion also happens on the Cu coupon with heavy corrosion product in the high H_2S concentration test condition.

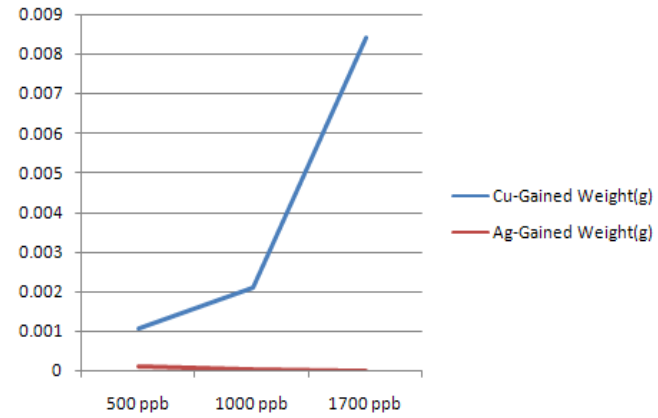
Thickness of Cu_2S/Ag_2S

H_2S	500 ppb	1000 ppb	1700 ppb
Cu2S Thickness(nm)	935	1787	7425
Ag2S Thickness(nm)	102	50	81



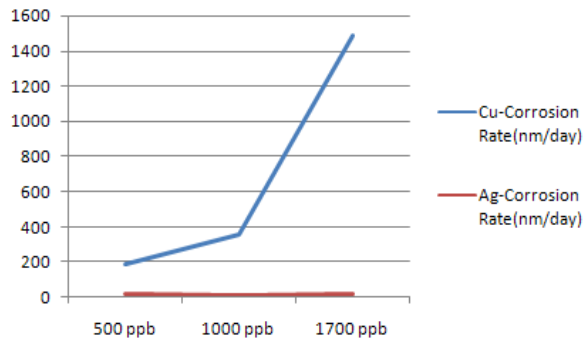
Gained Weight of Cu/Ag Coupons

H_2S	500 ppb	1000 ppb	1700 ppb
Cu-Gained Weight(g)	0.00106	0.00208	0.00842
Ag-Gained Weight(g)	0.00010	0.00005	0.000007



Corrosion Rate of Cu/Ag Coupons

H_2S	500 ppb	1000 ppb	1700 ppb
Cu-Corrosion Rate(nm/day)	187	357	1485
Ag-Corrosion Rate(nm/day)	20	10	16



MFG Test Matrix

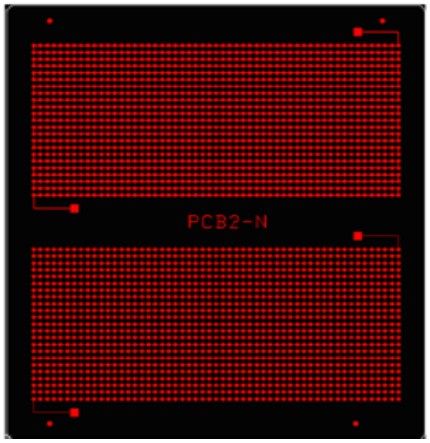
Group	Test Vehicle	Feature	Factors to study
A	HF PCB 80 x 80 mm	NSMD	**Surface Finish**
			1) ImAg
			2) Post-Treatment ImAg
			3) HT OSP1
			4) HT OSP2
B	HF PCB 80 x 80 mm	SMD	**Flux**
		Comb Line	1) NC OA Flux1
			2) NC OA Flux2

- To investigate material, process and design effect on the creep corrosion.
- Two groups(A and B) of test boards are investigated in this study.

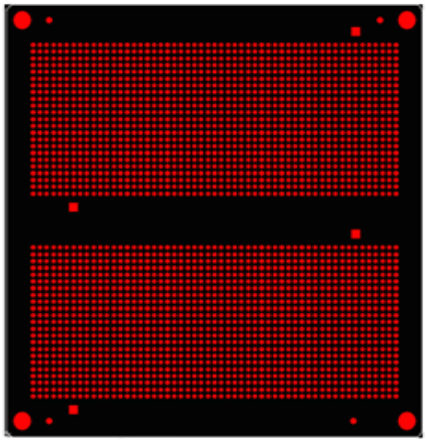
PCB Design & Surface Finish

Group A

Top Side



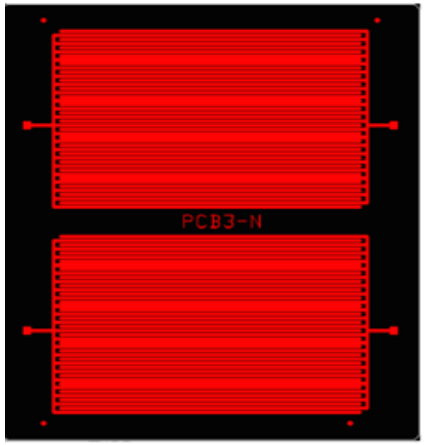
Bottom Side



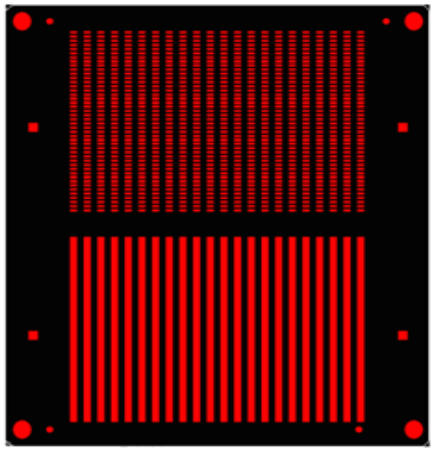
SMD Design

Group B

Top Side

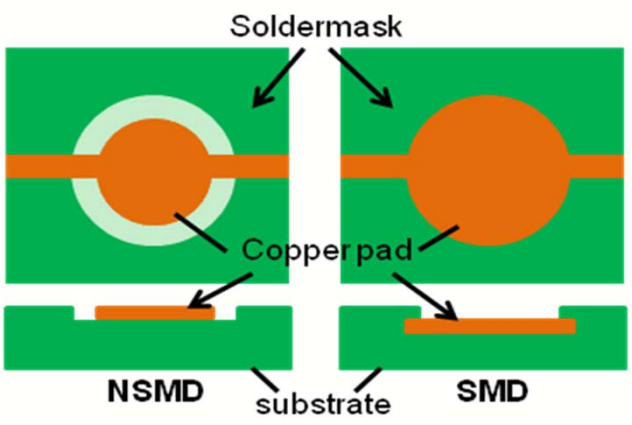


Bottom Side



NSMD Design

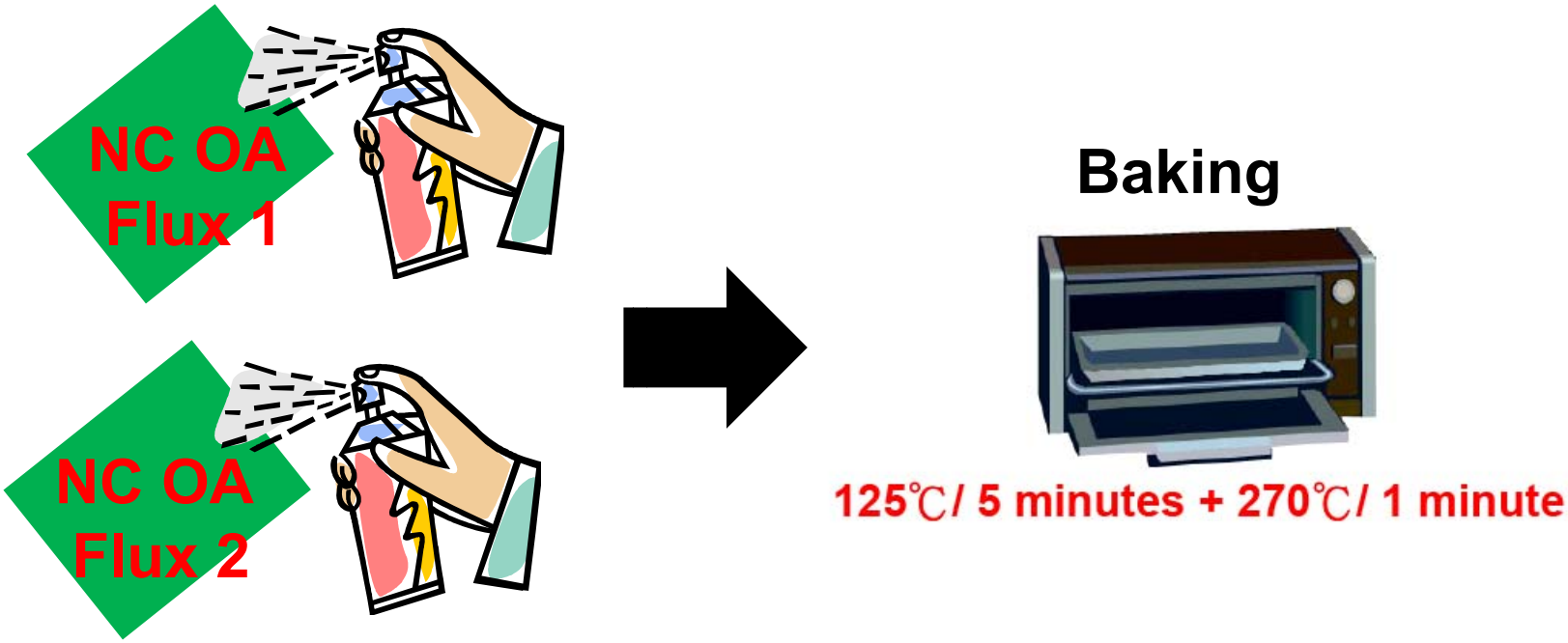
SMD & NSMD Design



Group	Surface Finish	Supplier
Group A	ImAg	Supplier 1
	Post-Treatment ImAg	Supplier 2
	HT OSP 1	Supplier 3
	HT OSP 2	Supplierr 2
Group B	ImAg	Supplier 1

Flux Residue for Wave Soldering Simulation

- Group B
- Spray 2 different types of NC OA Flux on the boards
- The boards with flux are baked at 125℃ for 5 minutes and then 270℃ for 1 minute to simulate the wave soldering process.



MFG Test

- Test Conditions :

H_2S	CL_2	NO_2	SO_2	Temp.	RH	Duration
1700	20	200	200	40℃	90%	21days

- All test boards have one time reflow before MFG test

SMT line & Reflow Profile

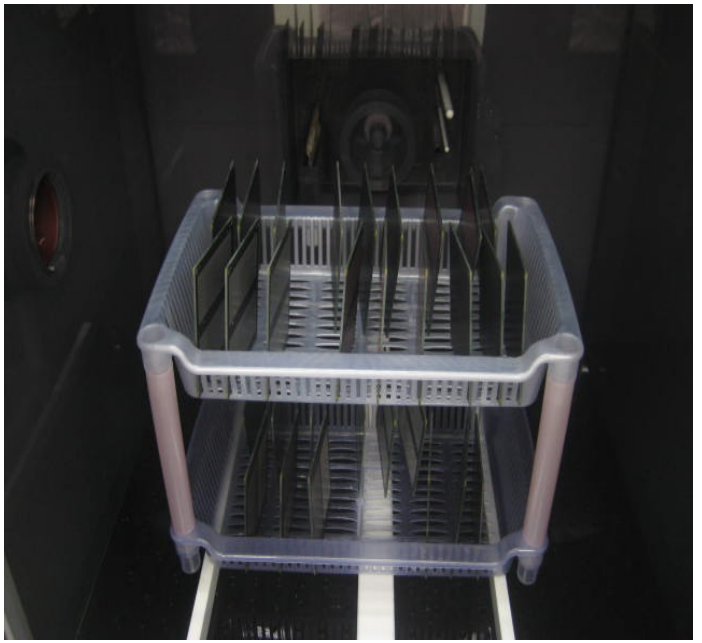
Maker : FURUKAWA

Type : XNJ-1145PT

Upper/lower hot blast fan

Water cool type

Upper Limit : 300℃



Chamber set up

Experiment Result

SMD vs NSMD Effec on Creep Corrosion

- The degree of creep corrosion on SMD board feature grows laterally across solder mask is greater than that at the metal/laminate interface on NSMD board feature.

- The difference is explained as following discussion：

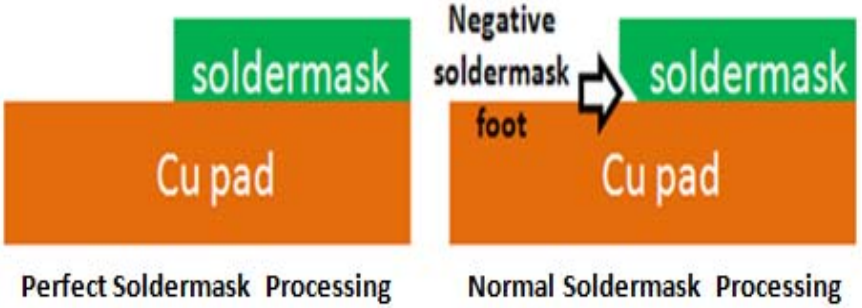
1) The migration on the laminate around NSMD areas has to overcome the land between Cu pad and solder mask.

2) SMD is a much smoother surface so that the corrosion product can travel much more readily across the planar surface.

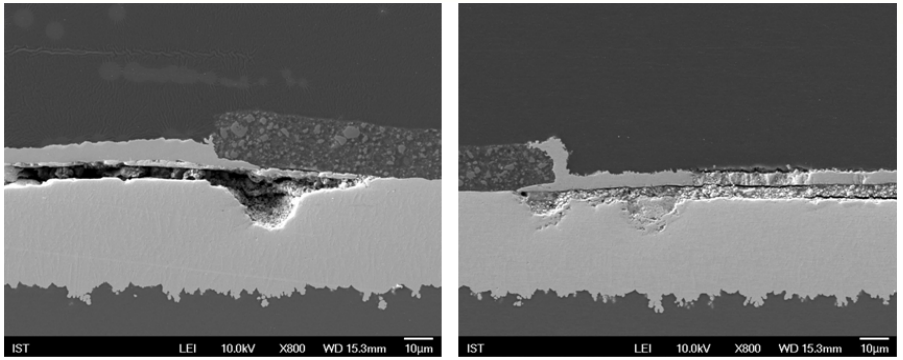
3) A gap is made at the interface between soldermask and Cu pad due to the poor soldermask processing (exposed Cu at edge of soldermask), so that creep corrosion emanate from SMD features.

SMD vs NSMD Effec on Creep Corrosion

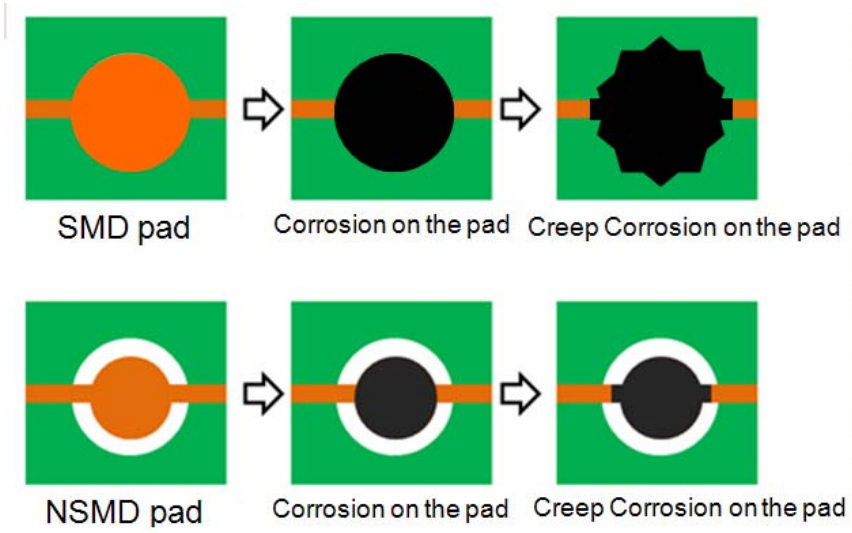
Perfect & Normal soldermask processing



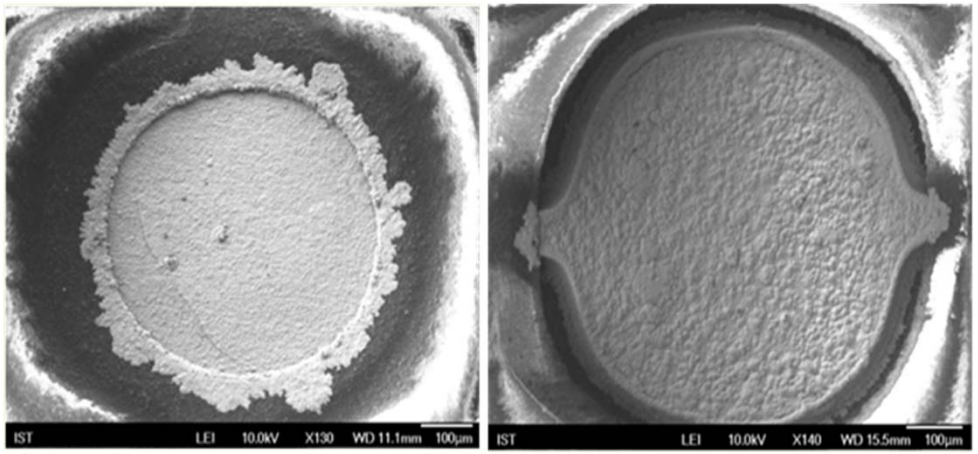
Creep Corrosion occurred from the exposed copper at the edge of soldermask



Creep Corrosion evolution of SMD & NSMD PCB



PCB Creep Corrosion of SMD & NSMD PCB



Surface Finish Effect on Creep Corrosion– Group A

- Creep corrosion is observed on all the three types of surface finish based on the visual inspection and the analysis through Cross-Section, SEM/EDS and electrical measurement. The result show as below.

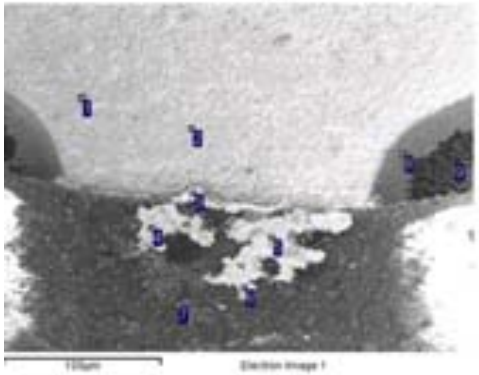
Surface Finish \ Result	Corrosion on pad	Corrosion on Trace	Creep Corrosion	Shorting Occurrence	Rank
ImAg	O	O	O	X	2
Post-Treatment ImAg	O	X	O	X	3
HT OSP 1	O	O	O	O	1
HT OSP 2	O	O	O	O	

- The corrosion severity of the three PCB surface finishes is ranked as below.

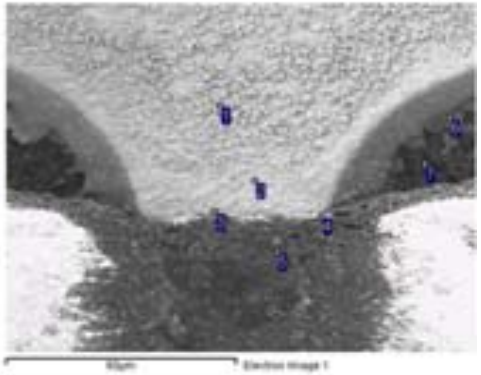
OSP > ImAg > Post-Treatment ImAg

ImAg and Post-Treatment ImAg

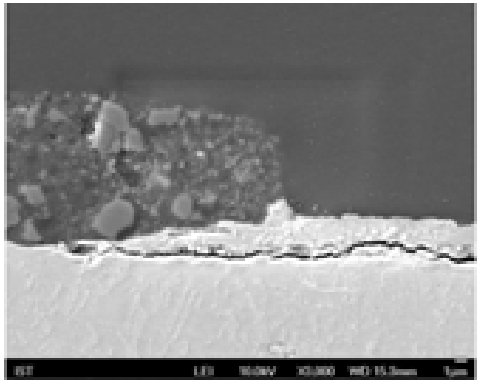
ImAg



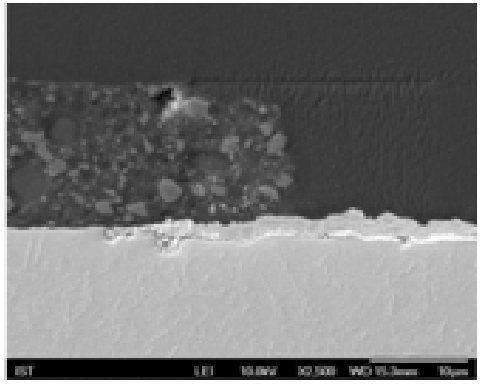
Post-Treatment ImAg

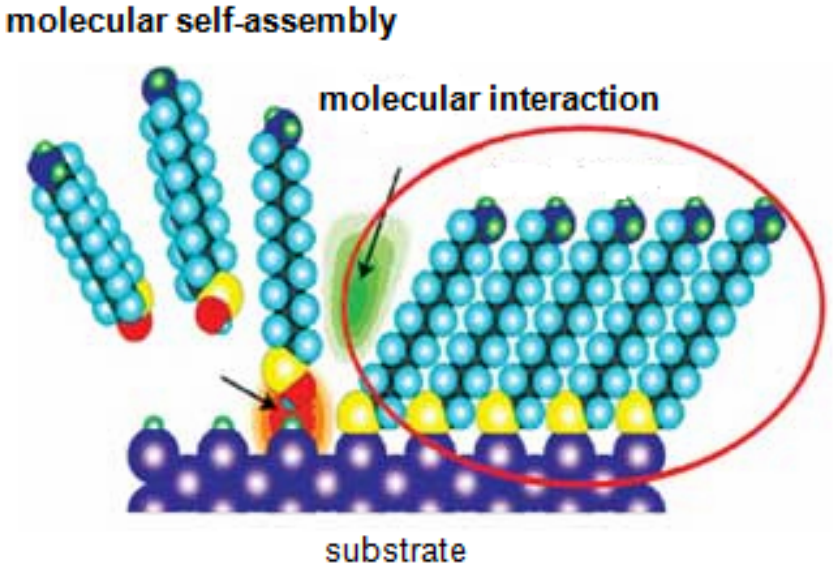


ImAg



Post-Treatment ImAg



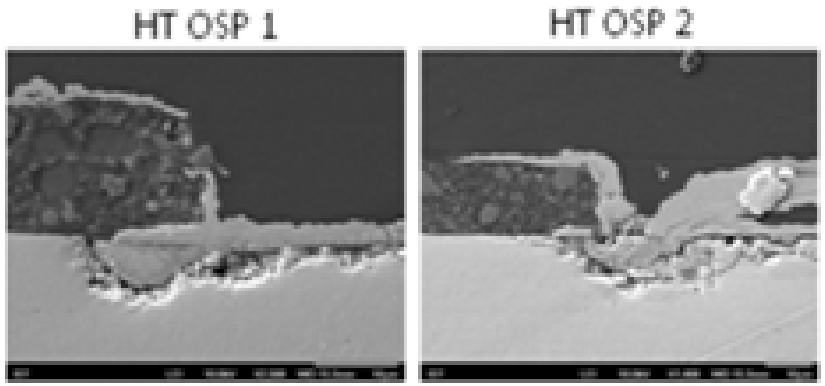


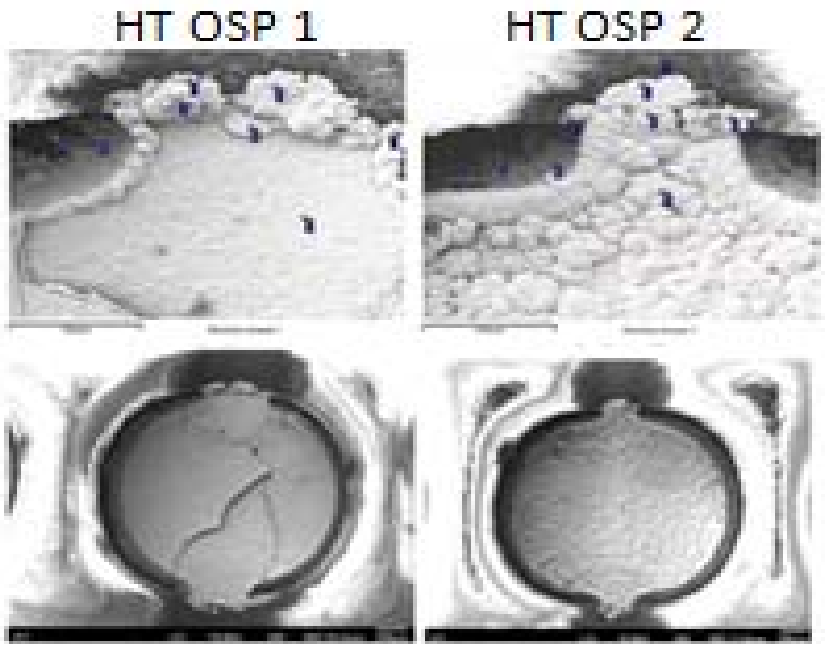
Refer to EMAsia-China.com

Post-Treatment is molecular self-assembly Monolayer. The molecule will selectively attach itself to available copper. The silver layer is getting denser with better coverage of Cu pad to prevent corrosion happening. The Post-Treatment ImAg with more organic preservative is designed to have better performance than ImAg under the corrosive gas exposure.

The Comparison of HT OSP1 & HT OSP2

- Both HT OSP 1 and HT OSP 2 have worse performance than ImAg, but there are no enough evidences to judge which one is the worst.
- HT OSP 1 has creep and flaking corrosion. The corrosion product on the pad is thinner and smoother.
- HT OSP 2 has creep corrosion but the pad isn't flaked. The corrosion product on the pad of HT OSP 2 is thicker and rougher.
- Both of them have creep corrosion from pad to the trace and the pad crater. HT OSP 2 has thicker corrosion product on the pad.

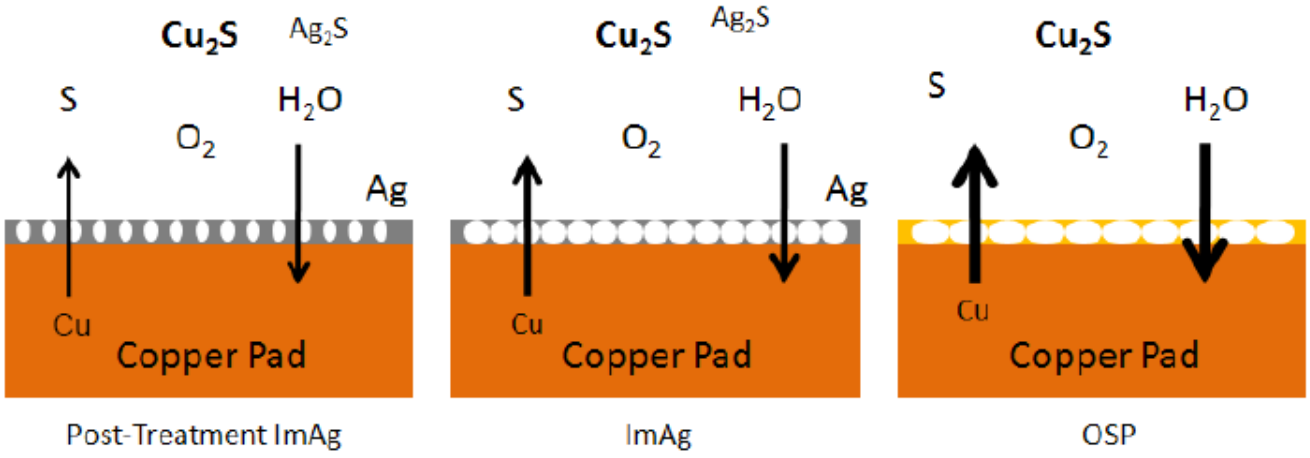




Qualitative Comparison of Porosity Ratio Among Surface Finishes

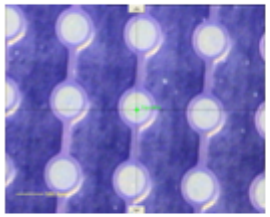
- ImAg has the higher porosity ratio than Post-Treatment ImAg, it is assumed that OSP might have higher porosity ratio than ImAg.

- In Currently there are three testing methods for surface finish porosity test in the industry, which are Gas Exposure Method, Electrolysis Imaging Method and Salt Spray Test Method.
  But all of them are not the ideal and reliable test methods to identify quantitatively the porosity.

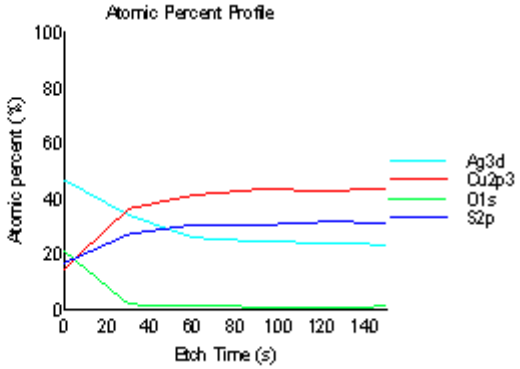


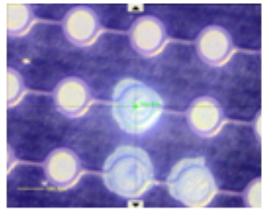
u-XPS Analysis

ImAg vs Post-Treatment ImAg

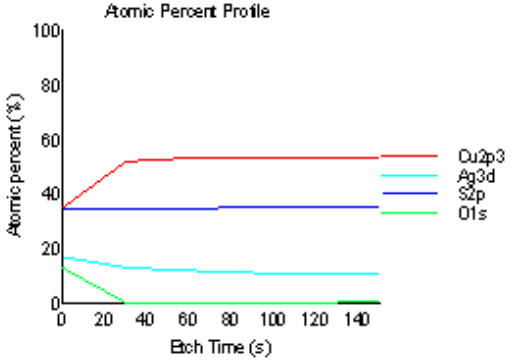


ImAg

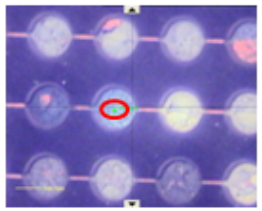




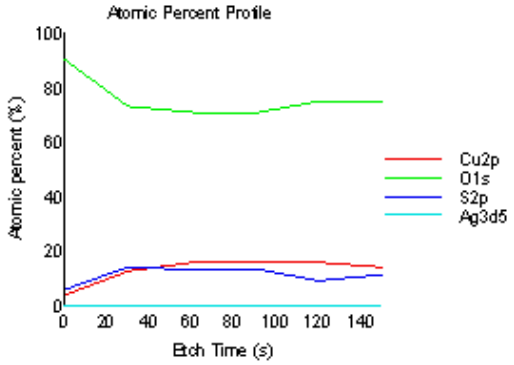
Post-Treatment ImAg

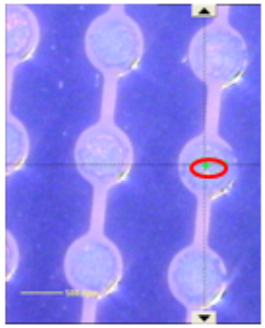


HT OSP1 vs HT OSP2

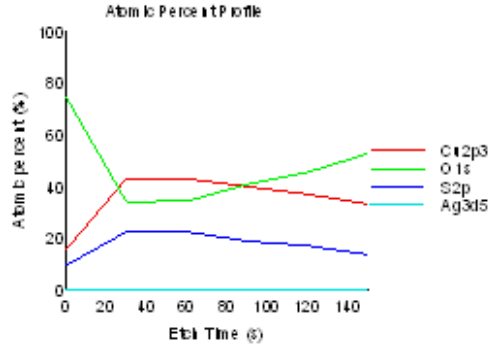


HT OSP 1



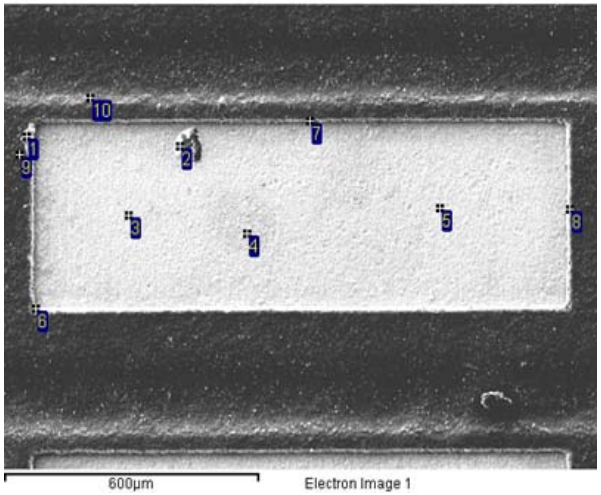


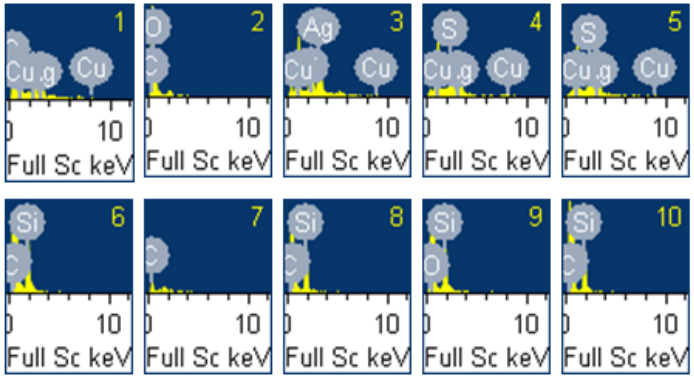
HT OSP 2

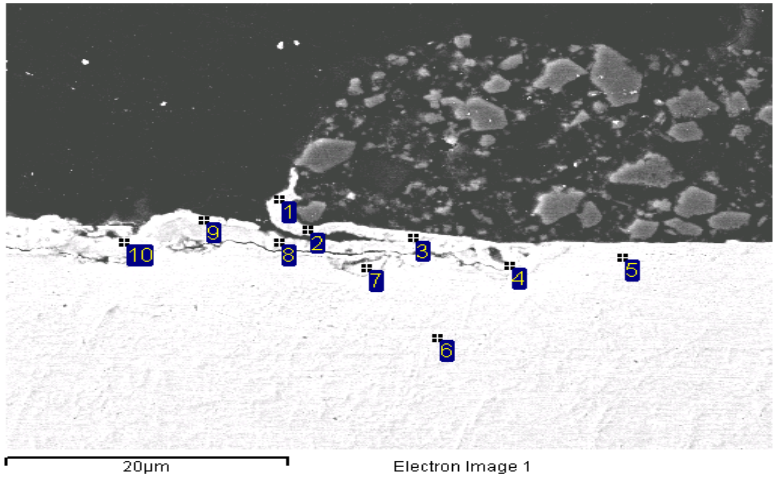


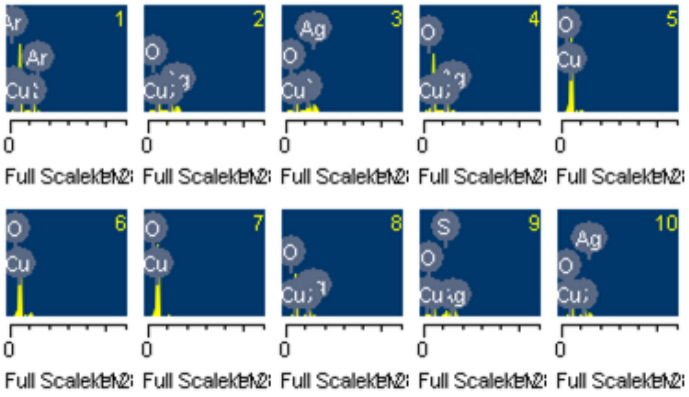
Flux Residue effect on the creep corrosion – Group B

- Flux residue will cause easily moisture absorption and the H+ of ion contamination is helpful to dissociate Cu oxide and accelerate creep corrosion.









Conclusions

- Creep corrosion can be driven by multiple factors.
- Except environmental factors, such as pollution, temperature, humidity, complicated PCB manufacturing process is another concern.
- There might be many potential influences to creep corrosion during the process not only surface finish, flux, and board design.
- The corrosion occurrence on PCB is very sensitive to surface chemical properties. Ionic cleanliness, the roughness and surface chemistry of the soldermask might be other factors to influence the rate of creep corrosion growth.

Welcome your comments !