

UNDERSTANDING CREEP CORROSION FIELD FAILS

Phil Isaacs¹, Jing Zhang² & Terry Munson³
IBM Corporation & Foresite, Inc.

pisaacs@us.ibm.com, jingzhan@us.ibm.com & terry@foresiteinc.com

¹MN, USA, ²NY, USA ³IN, USA

Abstract

Dendrites, Electrochemical Migration (ECM) and parasitic leakage, are usually caused by process related contamination. For example, excess flux, poor handling, extraneous solder, fibers, to name a few. One does not normally relate these fails with environmental causes. However, creep corrosion is a mechanism by which electronic products fail in application, primarily related to sulfur pollution present in the air.¹ The sulfur reacts with exposed silver, and to a lesser extent, exposed copper. This paper will explore various aspects of the creep corrosion chemical reaction:

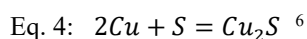
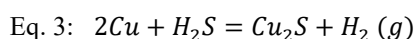
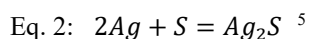
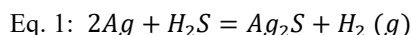
1. What is driving the creep corrosion reaction?
2. Why is drying the product a necessary precursor to obtaining creep corrosion in tests?^{2, 3}
3. Test methods with Flowers of Sulfur, FoS, and sulfur rich clay.
4. Discussion of creep corrosion related field fails.
5. When does creep corrosion become ECM.
6. Sources of sulfur containing pollution.
7. Methods to take to avoid creep corrosion.

While there are places with sulfur containing pollution, creep corrosion will be a factor which will impact reliability. Creep corrosion will need to be understood and handled.

Key words: Creep corrosion, Flower of Sulfur, (FoS), Immersion Silver, (ImAg), Mixed Flowing Gas, (MFG), Sulfur & Hydrogen Sulfide

Introduction:

Sulfur containing pollution is known to have harmful effects on the environment and to humans. Much is known about these effects. Sulfur containing pollution can also have deleterious effects on electronic components and their assemblies.⁴ Some examples can be seen in figures 1 and 2. There are different chemical compounds found in sulfur containing pollution: elemental sulfur, sulfur dioxide and hydrogen sulfide, to name a few, all of which can cause corrosion on PCBAs. The compounds have an oxidizing reaction when they come into contact with metals. In this case, the metals of interest are copper (Cu) and Silver (Ag), as provided in equations 1 – 4.



Chemical reactions 1 - 4 are the chemical reactions which initiate creep corrosion.

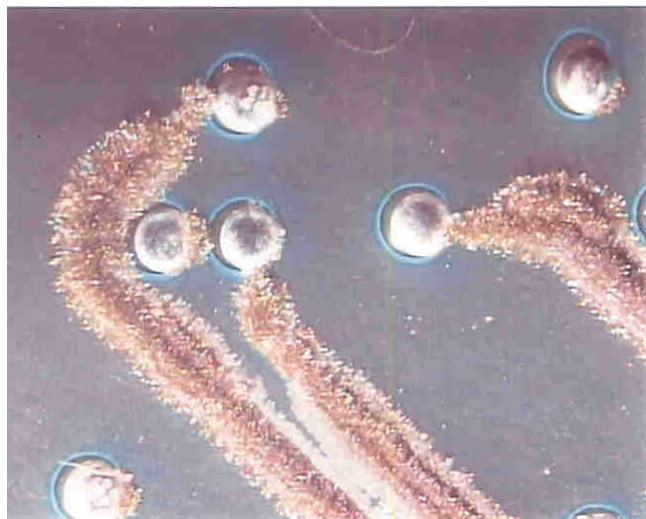


Figure 1: Creep Corrosion on Copper

Much has been written about creep corrosion. However, there is conflicting information in these studies. For example, in some studies, moisture⁷ is required for the reaction to proceed. In other studies, it was noted that for the creep corrosion reaction to occur, the Printed Circuit Board Assemblies (PCBAs) first needs to be dried.⁸ This is a significant disparity between the studies. In this paper, the authors will attempt to explain this disparity and its significance relevant to product testing and use.

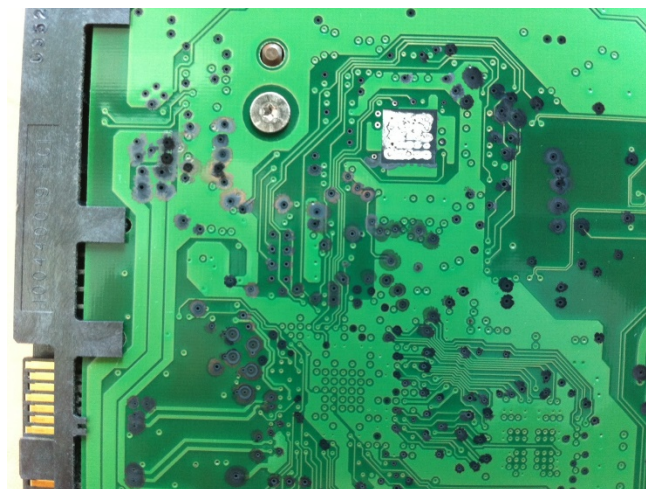
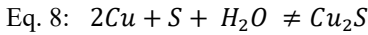
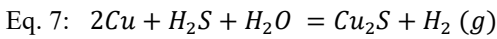
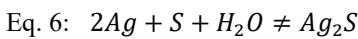
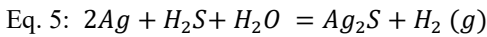


Figure 2: Creep Corrosion on Silver

Background:

There are three test methods used to evaluate a products robustness to different forms of sulfur containing pollution. The first is Mixed Flowing Gas (MFG), which utilizes hydrogen sulfide (H₂S), among other gases, to assess the robustness of the exposed metal against attack by sulfur. The second test is Flowers of Sulfur (FoS) which utilizes the elemental form of sulfur (S). And the third method is exposure to Sulfur Rich Clay (SRC).

In comparing the physical properties of H₂S and S, H₂S is soluble in water,⁹ while S is insoluble¹⁰ in water. We theorize that this may be the reason that samples placed in FoS need to be “dried” prior to testing, otherwise no initiation of creep corrosion will occur. This is demonstrated in equations 5 – 8.



The hypothesis is as follows: there is a boundary layer of moisture adsorbed onto the surface of the circuit traces of the PCBA. This boundary layer prevents contact between elemental sulfur and the underlying metallurgy. This boundary layer of moisture needs to be removed in order for elemental sulfur to come in to contact with the underlying circuitry.

Test:

To verify the hypothesis, three tests will be performed:

1. Mixed Flowing Gas, Class III, 20 days
2. Flowers of Sulfur, 15 days
3. Sulfur Rich Clay,¹¹ 15 days

Tables 1 and 2 define the make-up of each test.

Table 1: Active Components of each Test

Mixed Flowing Gas	Flowers of Sulfur	Sulfur Rich Clay
-Chlorine -Hydrogen sulfide -Nitrogen dioxide -Sulfur dioxide	- Sulfur - NaClO	-Sulfur

Table 2: Test Plan

	Low RH*	Pre-bake**	40/90 C/%RH***
Test	Sample #		
MFG	1-3	11-13	21-23
FoS	4-6	14-16	24-26
S Rich Clay	7-9	17-19	27-29
Control****	10	20	30

*Note: 25 C 0% Relative Humidity (RH).

**Note: Bake at 65C for 24 hours in a cross flow drying oven.

***Note: 40C/90% RH for 72 hours

****Note: Standard Temperature and humidity

Test Vehicle:

A bare copper version of the Umpire 2 test vehicle was selected for this study, see figures 3 and 4. A bare copper test vehicle was selected so that the focus could be on the creep corrosion reaction itself, rather than the secondary galvanic reaction that occurs between the silver and copper.

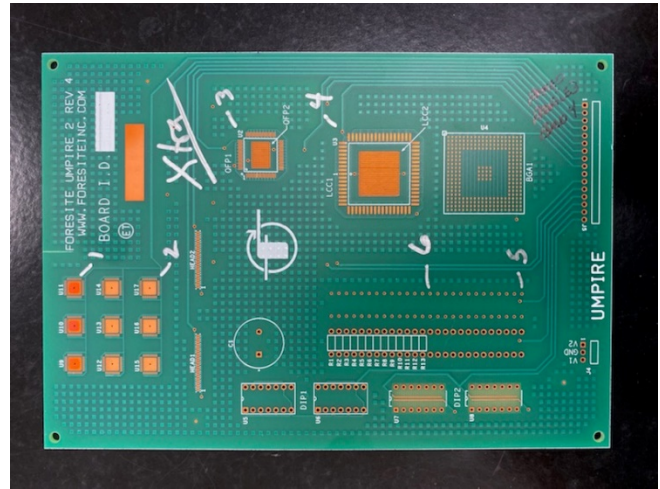


Figure 3: Umpire 2 Test Vehicle, top

The samples were all baked at 65C prior to shipping to the facility that will perform the afore mentioned tests. Each test vehicle was photographed to document the surface condition. The parts were then placed in moisture resistant bags, with the air removed from the bags for shipment to the test house.

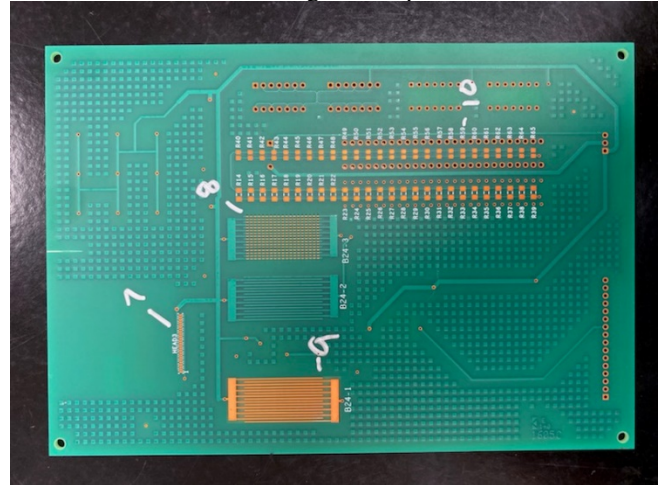


Figure 4: Umpire 2 Test Vehicle, bottom

The test conditions within the MFG test can be found in tables 3 and 4.

Table 3: Gas Concentration prior to mixing in MFG Chamber

H ₂ S/N ₂	Hydrogen sulfide Nitrogen	1000 ppm Balance
Cl ₂ /N ₂	Chlorine Nitrogen	100 ppm Balance
NO ₂ /N ₂	Nitrogen dioxide Nitrogen	1000 ppm Balance

Table 4: Resulting Environment within MFG Chamber

H ₂ S	100 ± 10 ppb
Cl ₂	20 ± 5 ppm
NO ₂	200 ± 25 ppb
SO ₂	200 ± 25 ppb
Relative Humidity	75 ± 2 %
Temperature	30 ± 2 C

Table 5: FoS Humidity and Temperature as a function of Salt used

Days	Salt	%RH	Temp
1-5	MgCl ₂	38	50.2
6-10	NaCl	58	50.2

Table 6: Local Ionics Test for Chloride and Sulfate, µg/in²

Test	MFG		FoS		Sulfur Rich Clay		Control	
	Chloride Level	Sulfate Level	Chloride Level	Sulfate Level	Chloride Level	Sulfate Level	Chloride Level	Sulfate Level
Dry Storage	23.65	39.65	90.65	80.31	5.44	61.07	0.46	0.27
65C Bake	24.61	40.35	90.54	81.95	6.21	59.96		
40C90%RH	24.19	40.09	92.71	83.25	5.98	62.05		
Average	24.15	40.03	91.30	81.84	5.88	61.03	0.46	0.27

response was different, the exposure to different gases and their by-products was the same within a test cell as determined by local ionics testing.

Mixed Flowing Gas Visual Test Results

As can be seen in figure 5, the samples preconditioned with dry storage and the 65C dry bake had far more creep corrosion than the samples preconditioned with the 40C, 90% relative humidity environment.

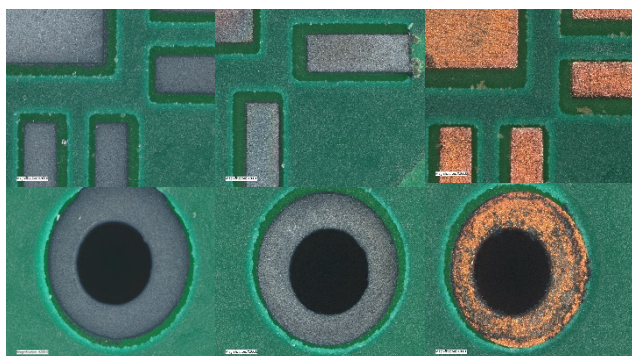


Figure 5: Mixed Flowing Gas Visual Results; Left to Right, Dry Storage, 65C Prebake, 40C/90%RH

The samples preconditioned with 40C and 90% relative humidity have a light salting of creep corrosion, where the samples preconditioned in a dry storage environment visually have much more than a thin film of corrosion products present.

Flowers of Sulfur Visual Test Results

The visual results of the FoS test is very similar to the results found in the MFG test. One difference is the plated-through-holes, PTHs, have much more visual creep corrosion than the corresponding QFN mounting pads.

11-15	KCl	76	50.2
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Test Results:

To assess the extent of the exposure and the reaction to the exposure to the oxidizing environment from each test, localized ionics measurements were taken on the PCBAs. See Table 6 for the results.

As presented in table 6, the amount of ionics present on each test vehicle within a test cell, regardless of the preconditioning, was approximately the same. Even though the visual

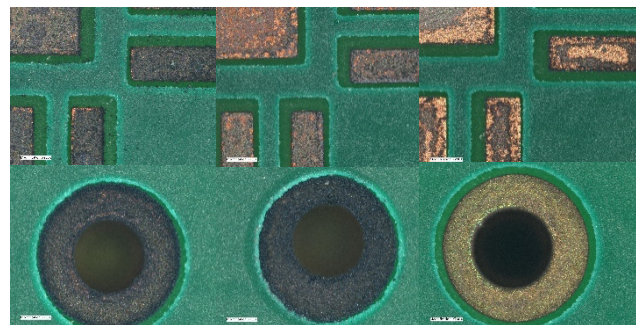


Figure 6: Flowers of Sulfur Visual Test Results; Left to right, Dry storage, 65C Prebake, 40C/90% RH

Another difference is the color of the creep corrosion found on PTH of the 40C and 90% relative humidity sample. It has an olive-green tint to it, indicating that the sodium hypochlorite participated in the reaction, forming cupric chloride. The results can be seen in figure 6.

Sulfur Rich Clay Visual Test Results:

The visual test results for samples exposed to sulfur rich clay are similar to those of samples exposed to MFG and FoS tests. The cleanest samples were those preconditioned with 40C and 90% relative humidity. The results can be seen in figure 7.

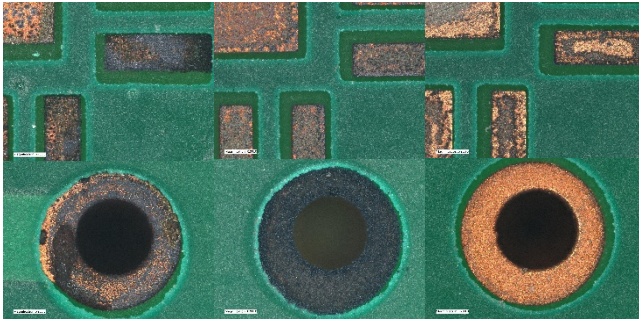


Figure 7: Sulfur Rich Clay Visual test results; Left to Right, Dry storage, 65C Prebake, 40C/90% RH

Control Samples:

The control samples show no visual sign of general corrosion or creep corrosion, as seen in figure 8.

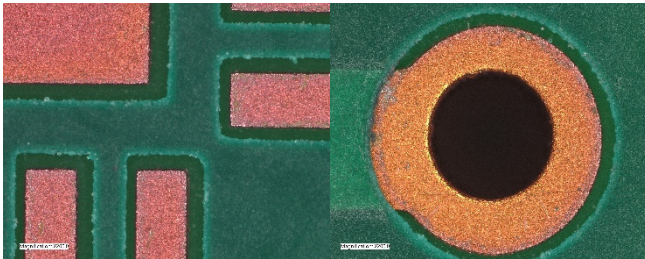


Figure 8: Control Samples, no preconditioning, no test exposure to sulfur

Discussion:

When measured by local ionics testing, the samples exhibit the same levels of ionics present. However, the samples that were exposed to high humidity prior to being exposed to the corrosive gas environments have less reaction to the sulfur exposure for all three testing conditions. There is significant creep corrosion growing on the samples that were exposed to a bake (65C for 24 hours) and samples that were stored in a low humidity (25C/0% RH) condition for three weeks in all three sulfur test conditions (MFG, FoS and Sulfur Rich Clay). But samples exposed to high humidity for 72 hours (40C/90%RH) showed a dramatic reduction in the formation of creep corrosion (copper sulfide crystals) during exposure for all three sulfur rich test conditions (MFG, FoS and Sulfur Rich Clay).

A question may be asked, why do the samples preconditioned with 40 C and 90% relative humidity exhibit the least amount of creep corrosion? It is generally assumed that most corrosion reactions take place in an aqueous or humid environment. Elemental sulfur's hydrophobic nature may explain why the FoS and Sulfur Rich Clay tests did not react, creating a significant amount of creep corrosion. However, this does not explain the lack of reaction in the MFG test which contains hydrogen sulfide and sulfur dioxide, neither of which are hydrophobic.

When copper is exposed to the environment, humidity and air, a passivation layer is formed creating a protective layer which retards other corrosion reactions. Perhaps the 40C and 90% relative humidity accelerated the creation of a passivation layer. This is in general agreement with an observation by a colleague, that test vehicles that have been

stored in standard conditions for two years do not visually exhibit any creep corrosion when exposed to the same corrosive environments.

Field Fails caused by Creep Corrosion

A failure caused by a rubber band left on the surface of the subassembly block holding units together during wave soldering, is presented in figure 9. The rubber band was left on the units and put into the field in a sealed enclosure operating at 60C. As illustrated in figure 9, the creep corrosion was so strong it fractured the thin soldermask and growing crystals the length of the traces bridging in multiple locations. Figure 10 shows the backside of a controller panel mounted on a wall in Canada. The panel was exposed to sulfur rich drywall. The immersion silver bare board finish to a high sulfur environment at ambient temperature and humidity conditions for four months, causing the unit to fail.



Figure 9: Immersion silver trace exposed to a rubber band at Foresite for 48 hours at 60C in sealed bag

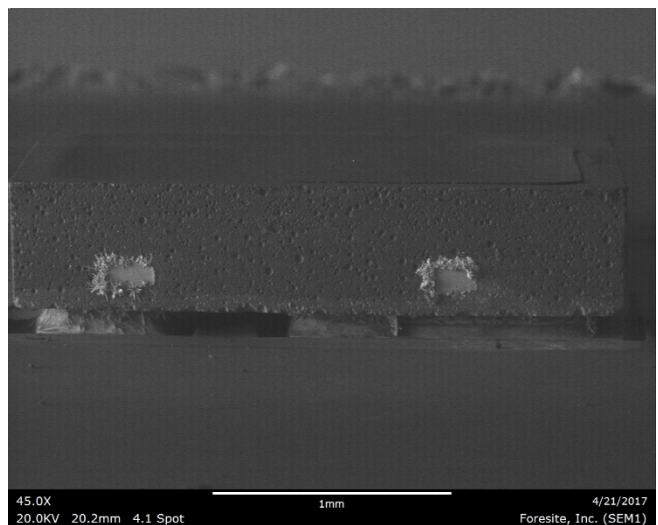


Figure 10: Plastic package with exposed copper silver plated lead frame exposed to sulfur rich air quality

Components with exposed copper or plated finishes such as Electroless Nickel and Gold (ENIG), Immersion Tin (ImSn)

or Immersion Silver (ImAg) all can have exposed copper that can be attacked by sulfur rich sources. It is necessary to understand these sources. Examples are provided in figures 11 – 16.

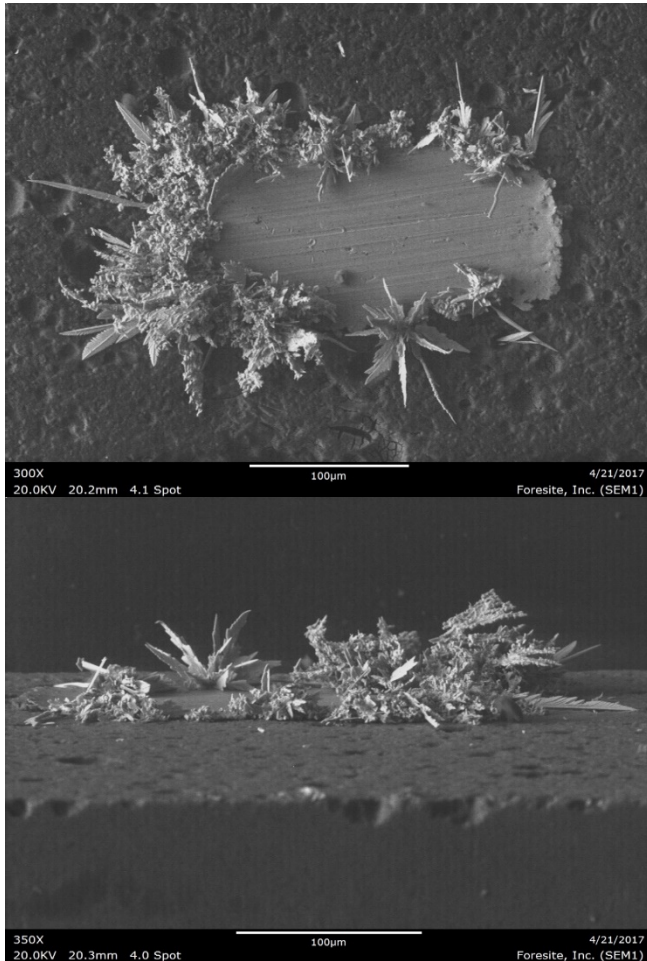


Figure 11/12: Top; plastic package with exposed copper silver plated lead frame exposed to sulfur rich air quality. Bottom; side view.



Figure 13: Flex circuit ENIG finish over copper inside ESD bag next to cardboard separators for 1 year inside box.



Figure 14/15/16: Display in ESD Bag, sample location for EDS elemental analysis which shows sulfur at 16.5 wt% and nothing present in the ESD Bag but at 18.9% in the cardboard separator.

Sources of Sulfur Containing Pollution

There are natural and man-made sources of sulfur containing pollution, such as often there are sulfur crystals forming around the volcanic vents or the smell of sulfur in the air. Of late, the Kilauea caldera has been closed to visitors due to the presence of the toxic gas, hydrogen sulfide. When coal is burned that contains sulfur, the sulfur is burned as well, or oxidized, along with the coal to form sulfur dioxide. When sulfur dioxide is hydrated, it forms sulfurous acid, which is responsible for acid rain. Paper mills are also known for their stench, due at least in part to the sulfur containing bleaching agent, sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$. Sulfur containing pollution has been known to come from a pig feedlot and attributed to creep corrosion leading to system level failures.

In his paper, Paul Mazurkiewicz, mentions field failures specifically caused by several forms of sulfur pollution.¹² These sources include two modelling facilities, where sulfur rich clay is used as the modelling medium. Another source was a geothermal power plant, where sulfur levels are high. In travelling, one may have had the misfortune of experiencing places that have sulfur water. Hydrogen sulfide content in the water causes the water to taste like rotten eggs.

Prevention

Prevention was not needed prior to the advent of RoHS legislation. Before, often tin/lead hot air solder leveling was used, creating an effective barrier between the copper and sulfur containing pollution. Also, more common in the days of tin/lead was the use of rosin-based flux, which also acted as a barrier, preventing corrosion products. Although common practice today is to dry the parts prior to shipping to prevent or retard the formation of corrosion products. It is counter-intuitive, but, this and other works, demonstrate that in the case of creep corrosion this is not only ineffective, it can promote creep corrosion. At the same time, it isn't practical to submit systems to a 40C 90% RH environment. This may be reducing the opportunity for creep corrosion, but it may well provide other pathways for electrochemical migration.

The most obvious solution is, where possible, the source of the sulfur should be removed from the system environment. For example, using carbon filters in air handling equipment. Another solution is to provide a barrier between the pollution and the PCBAs. This can be accomplished by using an appropriate sealed NEMA enclosure.¹³ Conformal coatings suitable to act as a barrier for sulfur, may also be used¹⁴ but verification that the coating does reduce the creep corrosion is necessary. Unlike silicone coatings which are very susceptible to sulfur ingress. Some silicone conformal coating materials have a "gettering" effect, attracting sulfur rather than acting as a barrier.

Conclusion

The preconditioning environment prior to subjecting the parts to a sulfur containing environment made a significant difference in the amount of creep corrosion which grew on the samples.

1. All the samples preconditioned with an 40C, 90% relative humidity environment had far less creep corrosion than their counterparts in the test which were dried prior to exposure.
2. The QFN mounting pads tended to have less creep corrosion than the corresponding PTHs on the same test vehicles.
3. Where the hydrophobic nature of elemental sulfur may explain the lack of creep corrosion that occurred on the samples preconditioned with temperature and humidity, it does not explain why the samples that were submitted to MFG, hydrogen sulfide and sulfur dioxide gases, also had far less creep corrosion than the dried counterparts in the experiment.
4. The parts preconditioned with 40C and 90% R.H. may have accelerated the formation of a copper oxide layer, forming a "passivation" layer, retarding also the corrosion in the MFG test.
5. There are various approaches to prevention of creep corrosion. The most effective methods preclude the contact between the atmospheric sulfur and the printed circuit board assemblies.
6. The results of all three test methods correlate well, regardless of the form of sulfur containing pollution.
7. In the FoS test, the sodium hypochlorite appears to have participated in the reaction on the samples prepped with 40C and 90% R.H., making cupric chloride.

Future work

Our future work will include the investigation of effective barriers to prevent creep corrosion.

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⁸ Singh, P., Palmer L., et al, "Relative Humidity Dependence of Creep Corrosion on Printed Circuit Boards," 2017 ICEP Proceedings.

⁹ Handbook of Chemistry and Physics, p. B-165, 1973, CRC Publishing.

¹⁰ Handbook of Chemistry and Physics, p. B-117, 1973, CRC Publishing.

¹¹ The type of clay used is Chavant type J-525. It contains 30 to 50% elemental sulfur. When the clay is heated to its working temperature, 45 to 55 C, sulfur is readily released.

¹² Mazurkiewicz, Paul., op. cit.

¹³ <https://www.nemaenclosures.com/enclosure-ratings/nema-rated-enclosures.html>

¹⁴ <https://multimedia.3m.com/mws/media/1620403O/corrosion-protection-of-metal-surfaces-from-sulfur-3m-novec-coatings-technical-bulletin.pdf>