Corrosion Resistance of PWB Final Finishes

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Abstract
As the electronic industry is moving to lead-free PWB final finishes and high density circuit boards, the widely used PWB finish, SnPb HASL, has to be replaced with a lead-free and coplanar PWB finish. This transition has already occurred for many commercial products as of July, 2006. Long-term, high reliability products such as in the Telecom industry are still evaluating the reliability of these lead-free finishes. The popular choices for replacing HASL are OSP, ImAg, ENIG, and ImSn. Among these lead-free finishes, ImAg and OSP are the preferred finishes for many applications, while ImSn and ENIG are used for niche applications. Extensive testing and reliability assessments have been performed on the four lead-free PWB finishes. However, very little attention has been paid to the corrosion resistance of the lead-free PWB finishes once they are field deployed. This is partly due to the fact that the traditional board finish, HASL, has excellent corrosion resistance due to its thick coating and inherent corrosion resistance. In this work, the corrosion resistance of the lead-free PWB finishes has been evaluated using a highly accelerated mixed flowing gas test. We have correlated the extent of corrosion after test to samples kept in field locations around the world for several years, with emphasis on understanding impact of corrosive field conditions on lead-free PWB finishes, especially for telecommunication products with expected service life of 10-20+ years. Not surprisingly, currently used accelerated corrosion test conditions have been shown to be inadequate to challenge products in harsher environments. A comparison will be made between current testing standards and our test conditions. For severe corrosion conditions, several new failure modes associated with the lead-free PWB finishes will be reported and their relevance to field deployed product will be discussed. The impact of the corrosion on the long-term reliability of the electronic devices will also be discussed.

Introduction
Printed wiring board final finishes were developed with the primary design objective of providing a solderable and coplanar surface for the component attachment during electronic circuit's assembly. While the short-term corrosion resistance of the board finishes is important for the purpose of maintaining shelf-life up to 12 months, long-term corrosion resistance was not required nor considered [1-3]. The long-term corrosion resistance in the field during the service life of the device has not been an issue for the traditional board finish HASL, as it has excellent corrosion resistance due to its thick coating and inherent corrosion resistance of SnPb. As the commercial electronic industry has moved to lead-free processes, ImAg, OSP, ENIG and ImSn are exclusively used as the PWB finishes. This transition will occur for the higher reliability products once more detailed and longer-term reliability studies have been completed. One of the key features associated with these lead-free board finishes is the coplanarity of the finish due to its thin coating, which brings reduced corrosion resistance with it. For ImAg, the coating material itself can also corrode in more aggressive environments with sulfur-containing compounds. There is clearly a need to understand the behavior of these lead-free board finishes in these aggressive environmental conditions throughout the current worldwide marketplace.

Several testing methods have been developed for corrosion resistance assessment of various materials. The most comprehensive and widely used corrosion test for electronic devices is probably the mixed flowing gas test, which utilizes a combination of corrosive gases to simulate the field condition and allows the accelerated test to be performed on the electronic device in the lab [4-5]. For correlating the exposure in the MFG chamber with the exposure in various field conditions, carefully prepared Cu coupons are often used. Based on the weight gain of copper coupons, a set of environmental corrosion classes was defined by Battelle, ISA and others to allow comparisons among field locations and corrosion test chambers. Table 1 compares the classification by Battelle [4] and ISA [6].

Table 1 - Corrosive Environment Classes, based on Cu2S growth on coupons

Battelle		ISA	
Severity Class	**1 Year Film Thickness**	**ISA Severity Class**	**1 Year Film Thickness**
I	**<35 nm**	**G1 (mild)**	**<360 nm**
II	**40 to 70 nm**	**G2 (moderate)**	**<1200 nm**
III	**80 to 400 nm**	**G3 (harsh)**	**<2400 nm**
IV	**> 500 nm**	**GX (severe)**	**>2400 nm**

The Battelle class system is one among many, but may be the most widely used for describing the effects of corrosion on electronic equipment. The classes set up by Battelle have been claimed to provide 1 year of equivalent field service in two

days of chamber exposure [7]. It is important to point out that this correlation is based on Cu coupons deployed in the field at room temperature. The equipment, on the other hand, is exposed to a higher temperature due to the heat generated during operation. This would create a significantly higher corrosion rate for the field-deployed electronic devices compared to the Cu coupons at room temperature. Thus, the Battelle accelerated test conditions may under-estimate the actual corrosion of equipment in the field.

The highest levels encountered in North America are generally Class II, except in special industrial situations such as chemical plants or paper factories. On the other hand, class III environments are often seen in other areas of the world and, in some of the areas, even class IV conditions occur [9-11]. Each Battelle class has an associated recipe for the test chamber conditions. The substantial variations in the definition of the classes must be seen as an indicator of the reliability of any acceleration factor for MFG tests. In its Network Environment Building Standard (NEBSTM) GR-63-CORE, Telcordia [8] provides two MFG condition sets, one for equipment inside controlled building environments (60-90nm/year) and a harsher set for equipment in enclosed outdoor installations (180-270nm/year). Both of these standards were developed for equipment deployed in North America and are considered to provide accelerated aging conditions for deployment there. No acceleration factor is given by Telcordia. There is now, in 2006, sufficient information on environmental situations elsewhere in the world to understand that the NEBSTM conditions may not provide an accelerated condition when compared to deployment in more corrosive environments. It may, in fact, be decelerated, when compared with some real, more corrosive environments [9-11].

Veale [12] of Rockwell Automation has studied the corrosion resistance of OSP, ImAg, ENIG and ImSn using MFG test and concluded that none of these coatings can be considered immune from failure in an ISA G3 environment, but ImSn and OSP could be expected to survive an ISA G2 environment. However, based on the Cu coupon corrosion rate provided by the paper (350nm/day), the MFG condition was actually an ISA G1 (or Battelle class III) rather than ISA G3. This would mean that none of these coatings can be considered immune from failure in Battelle class III environment and ImSn and OSP could be expected to survive Battelle class II environment.

Mazurkiewicz [13] of HP has reported field failure of computers with ImAg coated circuit boards in harsh industrial environment containing high levels of reduced sulfur gases. In some of the cases, products failed within a few months after installation.

Given the varying environmental conditions in the current world marketplace [9-11], we feel that there is a need to understand how the lead-free PWB finishes (OSP, ImAg, ENIG and ImSn) would behave during the service life of equipment deployed in harsh environments containing high levels of corrosive gases. In this work, the corrosion test results using a highly accelerated mixed flowing gas test will be reported. We have correlated the extent of corrosion after test to samples kept in field locations around the world for several years, with emphasis on understanding impact of corrosive field conditions on lead-free PWB finishes. For severe corrosion conditions, several new failure modes associated with the lead-free PWB finishes will be reported and their relevance to field deployed product will be discussed. The impact of the corrosion on the long-term reliability of the electronic devices will also be discussed.

Experimental

Based on literature survey and extensive internal testing within Alcatel-Lucent both in the field and the lab, the parameters of mixed flowing gas test were chosen to simulate the worst field conditions which can be encountered in the current worldwide marketplace. This test condition represents Battelle class IV and ISA class G2. The concentration of corrosive gases is summarized in Table 2. The temperature was 40^{o}C and the humidity was 69% RH. To further simulate the operating condition, half of the samples were also biased at 10V with a current limit control at 4mA. The corrosion rate was monitored using Cu coupon weight gain and was determined to be ~600 nm/day, averaged over 28 samples installed at various locations inside the MFG chamber. Similar thickness of corrosion products have been observed for Cu coupons deployed for one year in some field locations [9-11].

Table 2 - Concentration of corrosive gases in MFG chamber

Gas	Concentration (ppb)
H_2S	1700
NO_2	200
Cl_2	20
SO_2	200

An IPC B25 comb structure with 1.0 oz finished copper was used as test vehicle. The width of the copper lines was 0.01 inch and the spacing between adjacent lines is 0.013 inch. Coupons both with HASL and without finishes were purchased from SUNSTONE CIRCUITS INC. The test vehicle was then distributed to several major PWB finish chemistry suppliers to be coated with OSP, ImAg, ImSn and ENIG. The finished samples were then placed in Static Intercept® bags to prevent corrosion during shipment. The samples underwent two cycles of reflow using typical lead-free reflow profile (peak temperature was ~250°C and time above liquidius was ~90s) and then placed in the MFG chamber for corrosion testing.

Results

Hot Air Solder Leveling (HASL) and Cu

As reference samples, both HASL (SnPb) finish coupons and coupons with bare Cu-lines were included in the matrix. As expected, HASL showed only minor discoloration after 10 days of MFG test conditions, while Cu was severely corroded after only 2 days exposure. Figure 1 shows typical pictures of Cu samples after 2 days MFG test. The corrosion products, consisting primarily of Cu_2S and Cu_2O, flake readily. It is noteworthy that the flakes of the corrosion products are highly conductive and can cause short circuit between adjacent conductive lines. These shorts can be brief and temporary, leading to intermittent failures in products.

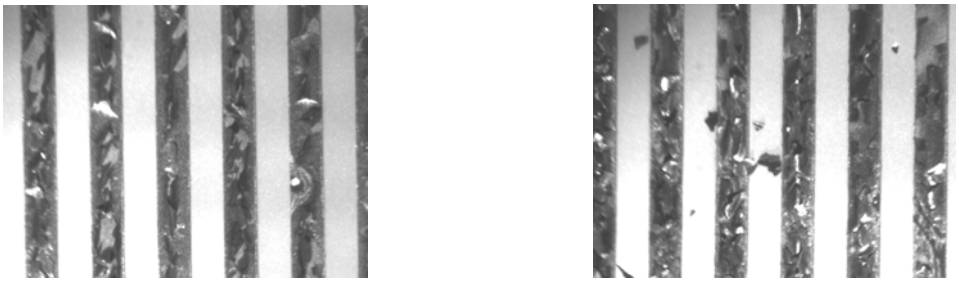

Figure 1 – Coupons without final finishes after 2 days MFG

Immersion Ag (ImAg)

Seven different ImAg processes from several suppliers were tested in this experiment. After two days MFG exposure, all the ImAg surfaces are covered with grayish corrosion products, primarily due to Cu_2S. However, creep corrosion across the laminate was seen only at one location in a single sample. This is shown in Figure2. This rather localized creep corrosion is most likely due to local contamination, probably due to a droplet of some kind of liquid as indicated by the shape of creep corrosion.

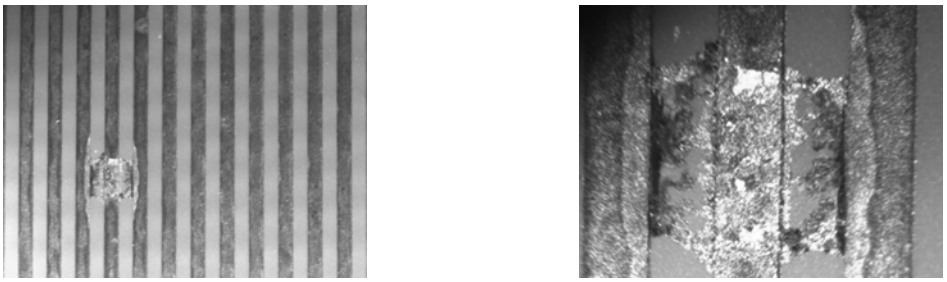

Figure 2 - Short due to creep corrosion

For the biased samples, an electrical short of 26 kΩ was detected on one sample after 2 days MFG exposure. The short was traced back to a foreign object (filament) across the adjacent lines. The filament was then removed for EDS analysis, which was done at various locations of the filament. Figure3 shows the SEM image of this filament and EDS result for one location. As one can see from Figure3, the filament is partially covered with a metallic film. EDS analysis shows that the metallic layer consists of Cu, Ag, S and Cl. The EDS analysis on the area without metallic film reveals only C and O, indicating a polymer fiber, most likely introduced during sample handling. It is also interesting to note that the metallic layer extends from positive biased Cu-line to negative biased Cu line. This is very similar to the widely studied phenomena of conductive anodic filament (CAF) formation, which occurs on glass fiber imbedded in the laminate and also has the characteristic of the metallic film growing from anode to cathode. In the case of ordinary electrochemical migration (ECM), the growth of the metallic filament occurs typically from cathode to anode. To differentiate this phenomenon from the CAF and ECM, we term it as fiber-assisted electrochemical migration (FAEM). Apparently, the laminate surface of our coupons is very clean/inert and does not allow the electrochemical migration to occur. On the other hand, the inadvertently introduced fibers have picked up enough moisture or corrosive gases to allow electrochemical migration to occur over it. The implication of this result is two-fold. First, the fibers, which can be introduced into the equipment from various sources, could potentially introduce a

permanent or intermittent short circuit. The intermittent short circuit failure mode is difficult to pin-point in the real world and can often lead to a no-trouble-found failure report since it often is destroyed upon causing a failure. Secondly, any contamination on the surface or imperfection of the materials could provide a pathway for electrochemical migration on a circuit board with ImAg as PWB finish.

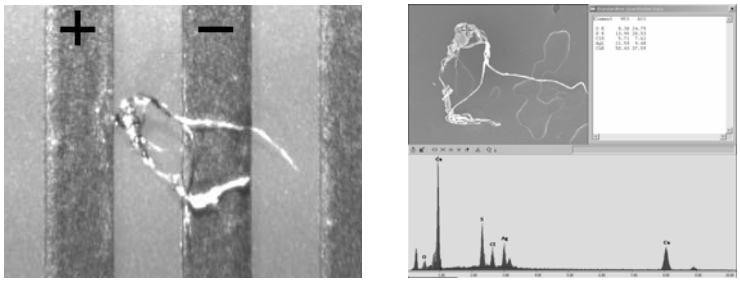

Figure 3 - Short due to fiber assisted electrochemical migration after 2 days MFG

After 5 days MFG exposure, four out of seven ImAg finishes show fiber-assisted electrochemical migration (FAEM). After 15 days MFG exposure, two additional ImAg chemistries show FAEM. Only one ImAg does not show FAEM, even after MFG exposure for 40 days. However, for this latter chemistry, creep corrosion along the fiber (Fiber-Assisted Creep Corrosion, FACC) was observed, which was also seen on a second ImAg chemistry. On the other five ImAg, no FACC was seen. In Figure4, FAEM on ImAg after 5 days MFG test (left) and after 10 days MFG test (middle) was shown. In the right picture of Figure4, a case of FACC is seen.

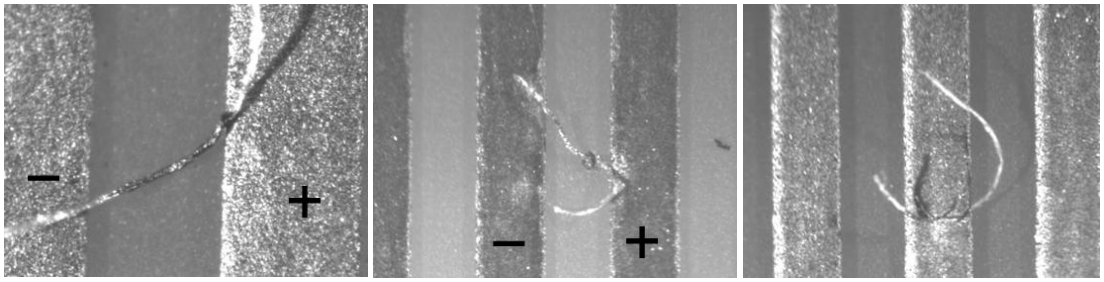

Fig.4 FAEM after 5 days (left) and 10 days (middle). FACC

A second issue associated with ImAg is the blistering or peeling of the conductive corrosion products from the surfaces. After 10 days MFG test, most of the samples only show minor blistering. Peeling and flaking were only observed after 40 days MFG exposure. However, a qualitative adhesion test using 3M "Post-it®" paper can be used as a deliberately weak standard adhesive. When applied to samples after 15 days MFG exposure, the corrosion products can be easily removed by the adhesive on post-it paper, thus proving they are only weakly attached to the substrate. This is true for all seven ImAg PWB finishes tested in this work. Figure 5 shows pictures for three of the seven ImAg chemistries. In all three pictures, the left part shows the post-it paper with corrosion products, while the right part is the substrate surface after adhesion test.

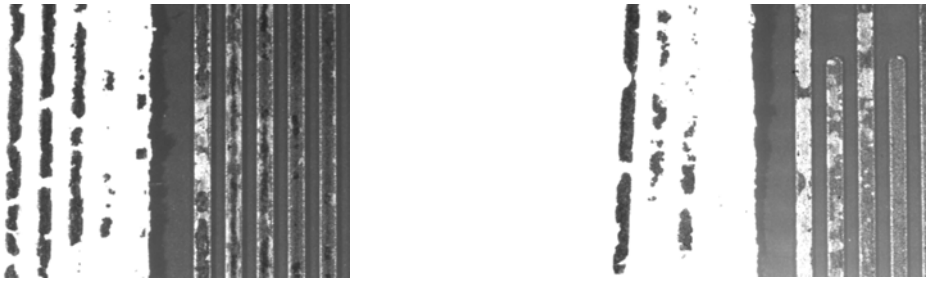

Fig.5 Three ImAg samples after adhesion test: post-it paper (left part) and substrate (right)

Organic Solderability Preservatives (OSP)

5 different OSP processes from various suppliers have been tested in this experiment. After 2 days and 5 days MFG exposure, varying degrees of corrosion is observed on the surface. No creep corrosion or electrochemical migration is seen on the laminate surface or on the fibers between adjacent leads.

After 10 days MFG exposure, either flaking or sliver formation are observed on all the samples. Both flakes and slivers are due to conductive corrosion products and can cause short circuit between the adjacent leads. As matter of fact, the first electrical short (26 Ω) was detected after 6 days MFG exposure and was attributed to peeled films of the corrosion product bridging adjacent lines (See Figure6). EDS analyses on the flakes indicate that it consists primarily of Cu_2S.

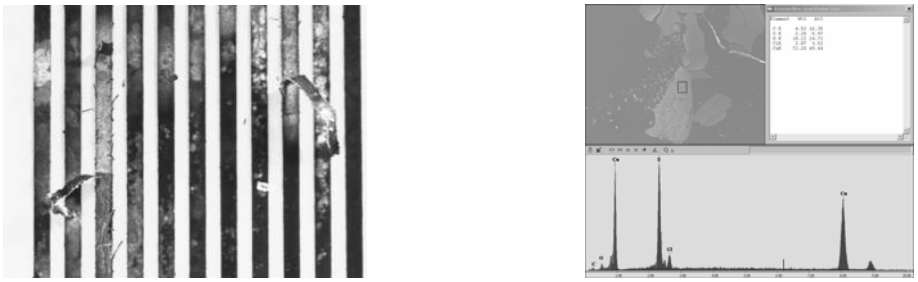

Fig.6 - Short circuit due to the flakes of corrosion products (Cu_2S) bridging to the adjacent lines.

Several high resistance shorts in the range of several kΩ to few hundred kΩ were also detected and have been found to be due to bridging across adjacent leads by conductive slivers. Figure 7 illustrates the short circuit due to the slivers.

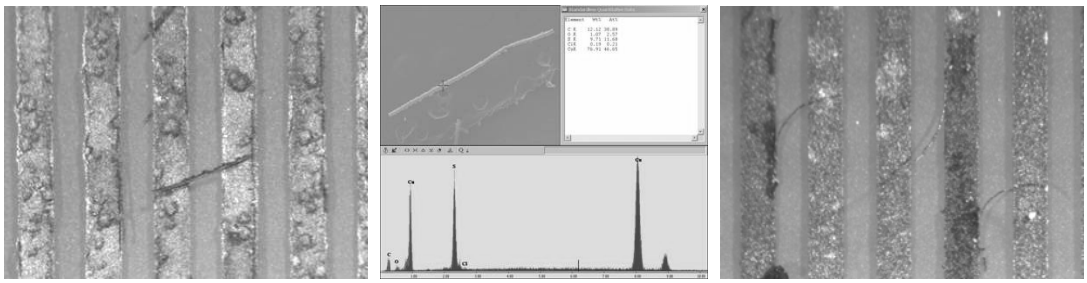

Fig.7 - High resistance short due to sliver formation on OSP.

EDS analysis performed on the sliver shows that it consists primarily of Cu_2S. Apparently, there is extensive corrosion along the edge of the Cu lines and results in the corrosion products detaching from the edge to form conductive slivers.

FAEM was also observed on three of the five OSP chemistries, with the first after 15 days MFG exposure. FACC was also seen on one sample after 40 days MFG exposure. Similar to ImAg, significant creep corrosion was not seen on any laminate surfaces, except on samples after 40 days MFG test. This is rather different than the work by Veale [12], where severe creep corrosion was observed after 20 days MFG exposure at less corrosive conditions than those used in this work.

Electroless Ni and Immersion Au (ENIG)

Three different ENIG processes were tested in our work. For two of the ENIG processes, the corrosion occurs preferentially through pores in the finish, while the third process shows corrosion preferentially occurring at the edge of lines. After 10 days MFG exposure, the corrosion products cover the majority of the surface. However, spontaneous flaking is observed only after 15 days MFG exposure. Again, both flaking of the corrosion products and sliver formation were observed (See Figure 8). FAEM was observed on two of the three ENIG chemistries after 15 days MFG exposure. The third ENIG sample showed FAEM first after 40 days MFG exposure. FACC was also seen on two samples after 40 days MFG exposure.

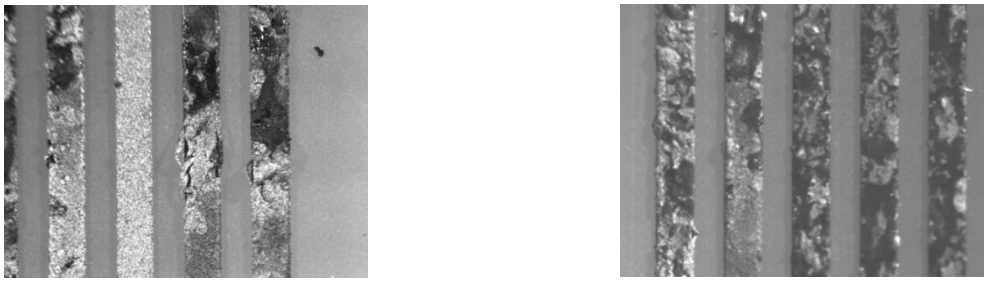

Fig.8 - ENIG after 15 days MFG test.

Immersion Tin (ImSn)

Three different ImSn processes were tested in this experiment. No significant corrosion was observed on samples after 2 and 5 days MFG test. Samples after 10 days MFG test start to show corrosion due to porosity. Figure 9 shows optical images of samples after 20 days MFG exposure. However, no reliability concern associated with corrosion is seen on ImSn, even after 40 days MFG exposure.

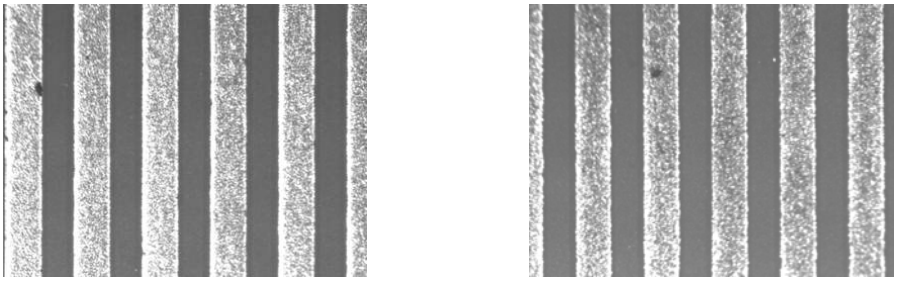

Fig.9 - ImSn after 20 days MFG test.

Discussion

The two key findings of this work are fiber-assisted electrochemical migration (FAEM) and flaking of conductive corrosion products. Both can cause electrical short circuits and pose a reliability concern for electronic devices. Albeit to different degrees, ImAg, OSP and ENIG are all susceptible to these two failure mechanisms when they are exposed to a corrosive environment such as Battelle class IV or ISA class G2. However, these finishes may still be used for less corrosive environment such as Battelle class II. Even for Battelle class III, these finishes may provide adequate protection for equipment with short expected service life (2-5 years) against attack by corrosive gases. For equipment with long expected service life (10 to 20 years) deployed in more corrosive environment such as Battelle class IV or ISA class G2, ImAg, OSP and ENIG may not provide adequate corrosion protection during the service life of the equipment. For equipment deployed in those harsh environments, additional protection, such as conformal coating or use of solder paste to cover entire lead-free surface finishes, may be required.

Ag is notorious for its propensity to undergo electrochemical migration and, because of this, has been removed from electrical contacts in electronic devices. Since ImAg was introduced as PWB finish for printed circuit boards, extensive testing has been done under various temperature-humidity-bias conditions. It was concluded that the thin Ag film of ImAg behaves rather differently from the thick electroplated Ag films and is not prone to electrochemical migration. To our knowledge, no test has been done in a corrosive environment containing corrosive gases such as H_2S, SO_2, Cl_2 etc during the qualification of ImAg as a PWB finish. The behavior of ImAg under such conditions remains largely unknown. Only recently, works [12-13] of corrosion test on lead-free PWB finishes start to appear in the literature. This is also true for OSP, ENIG and ImSn. In Veale's work [12], severe creep corrosion and dendritic growth were observed after 20 days MFG test. In this work, significant creep corrosion across dielectric surface was first observed only after 40 days MFG exposure, even though the condition in this work is more corrosive than those in Veale's work. However, it is demonstrated in this work that creep corrosion and electrochemical migration can occur at much shorter MFG exposure times, if proper pathways are created by either surface contaminations or presence of foreign materials (such as fiber assisted processes).

Migration of ions under electrical field has been widely studied and is well understood. There are three key steps involved:

1) anodic metal dissolution:
   $M \longrightarrow M^{n+} + ne^-$
2) ionic migration from anode to cathode and inter-electrode deposition/precipitation:
   migration in the electrical field
   $M^{n+} + mX \longrightarrow MX_m$
3) cathodic reaction (reduction and deposition):
   $M^{n+} + ne^- \longrightarrow M$
   $M^{n+} + mX \longrightarrow MX_m$

While step one can be greatly accelerated by the presence of corrosive gases, step two depends strongly on humidity and the formation of an electrolyte layer on the surface. The competition of the two processes in step 2 will eventually determine the growth direction. If the ionic migration dominates, metal ions will migrate to the cathode and dendrites will grow from cathode towards anode. This is the case for electrochemical migration of many metals (Ag, Cu, Sn etc) under condensing or high humidity conditions. On the other hand, if deposition or precipitation dominates in the step 2, the growth of metal compounds (oxide, sulfide etc) would occur from anode toward cathode. This is the case for CAF and Cu electrochemical migration in presence of Cl under condensing or high humidity conditions. The fiber-assisted electrochemical migration

(FAEM) observed in this work falls also under this category. As the fiber is typically only weakly attached to the circuit board, it could cause intermittent electrical short as well as no-trouble-found type of failure in the field.

The second key finding in this work is the ability of corrosion products to cause electrical shorts through either flaking or sliver formation. Although cupric oxide is an insulator, cuprous oxide is a semiconductor with a band gap of 2.0eV. The bonding in copper sulfides cannot be correctly described in terms of a simple oxidation state formalism because the Cu-S bonds are more covalent than ionic in character and have a high degree of delocalization, resulting in complicated electronic band structures. The majority of its members are semiconductors. Several nonstoichiometric compounds with Cu:S ratios between 1.0 and 1.4 also contain both monosulfide as well as disulfide ions. Depending on their composition, these copper sulfides are either semiconductor or metallic conductors. Furthermore, the EDS analysis also showed presence of metallic Cu in the flakes and slivers, which further contributes to the conductivity of the peeled films.

From corrosion resistance standpoint, ImSn is the only lead-free PWB final finish which could survive Battelle class IV and ISA class G2. However, the tin whisker issue has to be better understood if ImSn is to be used for fine-pitch application.

Conclusion

Although OSP, ImAg and ENIG are the preferred PWB surfaces for Battelle class II environment and electronic devices with short expected service life (few years), they may not be suited for long service life equipment deployed in harsh environment such as Battelle class IV or ISA class G2 seen in some areas of the current worldwide marketplace. Fiber-assisted electrochemical migration and flakes/sliver formation of conductive corrosion products could lead possible failure for electronic devices deployed in those areas. ImSn provides acceptable corrosion protection and may be used for equipments deployed in such harsh environments, if tin whisker formation is not an issue. Continued work is needed to understand corrosion susceptibility of these lead-free finishes for longer-life, high reliability products for continued customer satisfaction.

Acknowledgements

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