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A Review of Models for Time-to-Failure Due to Metallic Migration Mechanisms

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I. Introduction

Electrochemical migration (ECM) is defined as the growth of conductive metal filaments across a printed circuit board (PCB) in the presence of an electrolytic solution and a DC voltage bias [1]. ECM, also known as dendritic growth, is a critical issue in the electronics industry because the intermittent failure behavior of ECM is a likely root-cause of the high occurrence of field failures identified as no trouble found (NTF)/could not duplicate (CND)[2,3].

The dendrites that form due to ECM are extremely fragile tree-like growths. Once the dendrites have bridged the gap between adjacent conductors, a sudden drop in resistance will occur, often leading to system faults. However, if the cross-sectional area of the dendrite is small and the current density is high, then the dendrite may burn out due to high heat dissipation[1]. This leads to intermittent failure behavior and impedes identification of root-cause.

The primary method for controlling ECM is through aggressive control of board-level cleanliness, specifically halides such as bromides and chlorides. As component pitch reduces in size, the use of leadless packages increase, and high density/ high impedance design becomes more commonplace the occurrence of ECM can be expected to rise. Proactive approaches to prevent ECM have included process guidelines and the use of qualification tests. However, the value of the qualification tests, such as IPC TM-650 2.6.14.1 [4] and Telcordia GR-78 [5], is limited without an established time-to-failure (TTF) model. A validated TTF model should be able to provide an acceleration factor that could be used to relate field conditions to the test environment and develop an appropriate test time.

The best practice to establishing a TTF model is through the use of a physics of failure (PoF) based approach. The PoF approach to electronics products is founded on the fact that failure mechanisms are governed by fundamental mechanical, electrical, thermal, and chemical processes. Establishment of a PoF based TTF model requires an understanding of the drivers and physical mechanisms for electrochemical migration and failure models that in the current literature.

ECM occurs in three stages: path formation, initiation, and dendritic growth. ECM requires a path of electrolytic solution. Initiation transpires through the dissolution of the metal at one conductor, the transport of the metal through the electrolytic solution, and deposition of the metal at an oppositely biased conductor. Dendrites grow through the repeated deposition of metal ions.

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[1] $P = j^2R$, where j is the current density and R is the resistance

II. Factors Affecting Electrochemical Migration

Several factors have an influence on ECM including temperature, relative humidity, voltage bias, conductor material, conductor spacing, contamination type, and contamination amount.

A. Temperature

The temperature range for ECM to initiate is between 0°C and 100°C, assuming the electrolytic solution is aqueous[2]. Outside this temperature range, other types of migration behavior that require no electrolytic solution may occur, such as the migration of silver at 150°C [6]. Studies have demonstrated that the propagation rate of dendrites will tend to increase as a function of temperature [7, 8].

Temperature has been associated with ECM through the chemical reaction rate defined by the Arrhenius equation. Because the initiation of ECM is a chemical oxidation-reduction reaction, it follows that the rate of initiation may have an Arrhenius dependence. While this dependence has been established in other corrosion-based failure mechanisms that afflict electronics, such as aluminum corrosion on silicon die, it has not been demonstrated conclusively for ECM on printed circuit board assemblies (PCBAs).

B. Relative Humidity

Relative humidity (RH) is the ratio of the mole fraction of water vapor in the air at a specific temperature to the maximum amount that the air could hold at that temperature, expressed as a percentage. Water vapor can attach to the printed circuit board (PCB) by hydrogen bonding, providing the electrolytic solution that is needed for ECM to occur [9]. Once the relative humidity is high enough for water to adsorb to the PCB, there is a critical moisture level on the surface needed for ECM to occur. This water level is expressed as number of monolayers of water. This critical layer of water is reported to be approximately 20 monolayers thick [10].

The relationship between the critical number of monolayers necessary for migration to occur and the ambient relative humidity is dependent upon the moisture adsorption characteristics of the PCB surface. This adsorption behavior is influenced by the choice of solder mask and the quantity and type of contamination present on the surface. Usually, the higher the relative humidity, the faster the onset of initiation of ECM [11].

The dew point temperature is the temperature where water vapor may condense on the surface is a film, providing a bulk liquid formation and almost instantaneous path formation. If the temperature drops below the dew point, the time for path formation will be much shorter than the time for the other stages of ECM and the time-to-failure might be greatly reduced. For example, water drop tests can demonstrate dendritic growth in seconds; non-condensing ECM tests require hours before failure occurs.

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[2] Broader temperature ranges may apply to electrolytic solutions based on other liquids.

C. Voltage Bias and Voltage Gradient

Voltage bias must be present for ECM to occur. Voltage bias is the difference in voltage between the anode and cathode. This electric field drives ionic migration by causing the positive ions to travel along the field lines from the anode to the cathode through an ion transport path provided by the aqueous medium [12]. A higher bias increases the rate of propagation and may increase the chance of catastrophic failure (i.e. fire, total loss of assembly) [11].

Some studies have suggested that there is a critical voltage bias range, outside which surface ECM will not occur [13]. The lower end of this range is considered to be approximately 2 VDC, due to the need for the bias to be higher than the electrochemical potential of the metal. Values for the electrochemical potential of common electronic materials include 0.13 V for tin/lead solder, 0.25 V for nickel, 0.34 V for copper, 0.8 V for silver, and 1.5 V for gold. This minimum voltage is also dependent upon the environmental conditions, as changes in the surface pH will increase or decrease the electrochemical potential. This behavior is detailed through Pourbaix diagrams. The upper voltage limit is speculated to be approximately 100 volts. Above this voltage the failure mechanism tends to change from surface ECM to other migration failures, such as CFF, or dielectric breakdown.

The effect of voltage gradient, which is voltage bias divided by conductor spacing, was studied by Zou and Hunt [14]. They concluded that the probability of dendrite formation increases as voltage gradient increases.

D. Conductor Spacing

Conductor spacing refers to the distance between two oppositely charged conductors. As this distance decreases, time-to-failure will decrease assuming that the rate of dendrite propagation stays constant. Other factors can also increase the frequency of failure with finer pitch spacings. Smaller spacings tend to be more difficult to clean, potentially resulting in a build up of contaminants. Smaller spacings, at the same voltage, will also result in a higher electric field. As indicated previously, some studies have experimentally determined that the occurrence of ECM is strongly driven by the electric field strength [14,15]. Some of the narrower conductor spacings in electronics packaging can be found in Table 1.

Table 1: Conductor spacings

Parameter	Spacing	Reference
Peripheral Flip Chip Solder Bumps	120 μm	[16]
Thin Shrink Small Outline Package (TSSOP) Leads	170 μm	[17]
PCB External Traces (low voltage line)	100 μm	[18]
BGA Substrate Traces	48 μm	[16]

E. Contamination Type and Concentration

Increased levels of contamination due to poor cleanliness can have a dual effect on ECM behavior. Some contaminants can lower the relative humidity threshold for water to adsorb to the PCB [9]. Contamination may also increase the electrical conductivity of the electrolytic solution, thus decreasing the amount of time it takes for ions to migrate through the solution [9]. Extensive case studies have shown that halide ions, primarily chlorine and bromine ions, tend to be the most harmful contaminants [19].

Table 2: Maximum contamination levels recommended by various sources

	Pauls [19]	Appliance Manufacturer [20]	NDCEE[3] [21]	IPC[4] [22, 23]	DoD [24]	ACI [25]
Chloride ($\mu g/in^2$)	2	3.5	4.5	6.1[5]	6.1[6]	10
Bromide ($\mu g/in^2$)	20	10	15	7.8[7]	7.8	15

F. Conductor Material

As discussed previously in relation to electrochemical potential, conductor materials can also influence electrochemical migration [27]. The most common conductor material is currently eutectic solder (63SnPb). Eutectic solder either comes in the form of the solder interconnect or as hot air solder level (HASL). HASL is an eutectic tin/lead solder layer applied by solder dipping or wave and then leveled with high velocity hot air. HASL has the ideal solderability characteristics of tin/lead alloy and good material compatibility with other finishes and solders.

Other finishes are being used and investigated because of issues with HASL in regards to environmental and technological limitations. As trace spacing decreases to below 2 mil and planarity requirements for surface mount components become more stringent, continued use of HASL is becoming more difficult. The recent interest in Pb-free electronics has increased this transition away from HASL and towards alternative platings, such as electroless nickel immersion gold (ENIG), immersion silver (ImAg), and immersion tin (ImSn).

The influence of the alternative platings will be relatively limited within a most product. Most current and future boards designs with alternative platings will be soldermask over bare copper (SMOBC). In this situation, the exposed conductor materials will primarily consist of the bare copper under the solder mask and the solder material above the solder mask. Within a nominal reflow process, the alternative platings will be designed to be completely consumed within the solder interconnect. Exceptions to this case will include designs with tented vias and designs that require separable connections, such as those with stud bumped area array devices or edge card connectors. A concern with immersion silver may arise from silver's propensity to migrate under humid conditions due the solubility of silver oxides and hydroxides in water. However, current chemistries yield ImAg that is more resistant than original ImAg chemistries.

ENIG tends to be more resistant to ECM due to the nobility of the gold. However, if the relatively thin gold layer is removed for any reason (e.g., scratches), then the more reactive nickel layer would be exposed, this may result in the higher likelihood of migration. A concern with ImAg may arise from silver's propensity to migrate under humid conditions due the solubility of silver oxides and hydroxides in water. However, current chemistries incorporating organic compounds have tended to yield ImAg that is more resistant than traditional silver plating chemistries. Information on the ECM behavior of ImSn is less definitive, as most available test results tend to show no dendritic growth. All alternative platings do have the potential initiate ECM when areas of copper are exposed due to process control issues.

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[3] For water-soluble flux

[4] IPC-6012 defines cleanliness before solder mask operation [24]; IPC J-STD-001 defines cleanliness after the assembly process [25]

[5] IPC defines contamination levels as per equivalent 10 μg/in2 of NaCl [24, 25].

[6] DoD requires a resistivity of less than 2 MΩ, which is equivalent to 10 μg/in2 of NaCl [26]

[7] The conductivity of NaBr (λ_{Br} = 78.1 x 10-4 m2S/mol-1) is roughly equivalent to NaCl (λ_{Cl} = 76.3 x 10-4 m2S/mol)[28]

III. Models

The phenomenon of electrochemical migration (ECM) might be described mathematically as a function of the variables listed above. However, the inclusion of every term that influences ECM in the model could make it unmanageable, and perhaps even impractical.

In spite of this, it is valuable to understand the models that are presented here in terms of their strengths and deficiencies with regard to ECM, and whether or not these models are applicable for industry use. Current models involving electrochemical theory, general chemical stress, dendritic growth, conductive filament formation, migration in plastic encapsulated microcircuits, and metallization corrosion will be presented. Their strengths and deficiencies with regards to being viable life models for ECM will be discussed.

The first two models described in this paper, the Arrhenius and Eyring equations, are derived from constructs around elastic collisions and transition states to describe reaction rate kinetics. Since ECM involves several electrochemical reactions, the relevancy of these two equations is quite clear. The next two models, Barton/Bockris and DiGiacomo, are based upon experimental observations of dendritic growths, but in environments removed from the printed circuit board surface. The last three models are based upon experimental observations of different failure mechanisms that are fundamentally dependent upon the same oxidation/reduction/dissolution processes.

A. The Arrhenius Model

The Arrhenius model is perhaps the most widely used model for chemical reaction rate behavior. The model is defined as

$$t_f = A\exp\left(\frac{\Delta H}{kT}\right) \qquad \textbf{(1)}$$

where t_f is the time to failure, A is a scaling constant, ΔH is the activation energy (eV), k is Boltzmann's constant (8.617 x10-5 eV/K), and T is the temperature (K). While there is much data in the literature supporting the validity of this equation, it has several drawbacks for its sole use for modeling ECM. The inclusion of stresses other than temperature is not considered. This also implies that any synergistic effects of temperature with other stresses cannot be considered.

Hornung [28] proposed a mathematical model for dendritic growth based on Arrhenius behavior, where

$$t_f = \frac{\alpha G}{V}\exp\left(\frac{\Delta H}{kT}\right) \qquad \textbf{(2)}$$

where α is a proportionality constant, G is the spacing between electrodes, V is the applied voltage, ΔH is the activation energy, k is Boltzman’s constant and T is the applied temperature. Hornung measured the dendritic growth of silver through borosilicate glass under an applied electric field. The activation energy for this process was determined to be 1.15±0.15 eV and the growth rate was found to have an approximately linear dependence on the applied electric field.

Hornung's model is appropriate for estimating time-to-failure and acceleration factors, but it does not take into account relative humidity, and therefore is not truly an electrochemical migration model. It also does not take into account ionic contamination, which is one of the primary drivers for ECM in circuit card assemblies. The proportionality constant must also be empirically determined through experimental testing.

B. The Eyring Model

The Eyring model expands upon the Arrhenius equation, adding terms for other stresses as necessary.

$$t_f = AT^{\alpha} \exp\left\{\frac{\Delta H}{kT} + \left(B + \frac{C}{T}\right)S_1 + \left(D + \frac{E}{T}\right)S_2 + \Lambda\right\} \qquad \textbf{(3)}$$

where *A* is a scaling constant, ΔH is activation energy (in eV), *k* is Boltzmann's constant (8.617 x10-5 eV/K), *T* is temperature (K), α, B, C, D, E are constants determining stress interaction, and S_1, S_2, etc., are stresses, such as humidity or voltage. This model is presented in the *IPC Surface Insulation Resistance Handbook* [29] for determination of the acceleration factors associated with this test. The Eyring model corrects the multiple stress and synergism problems of the Arrhenius model, but not without some drawbacks. The complexity of the Eyring model increases dramatically with every added stress, as the number of unknowns increases twice as fast as the number of stresses. In addition, the stress functions are undefined. The stress could be a natural log, exponential, or some other function.

C. The Barton and Bockris Model [30]

Barton and Bockris conducted investigations into the growth of dendrites in electrolytic solutions. In 1962 they published the model

$$v_{\max} = \left[\frac{F^2 D c_\infty}{8\gamma RT}\right]\eta^2 \qquad \textbf{(4)}$$
$$as\ i \to \infty$$

where *i* is the current density at the dendrite tip, v_{max} is the maximum velocity of dendrite growth, *F* is Faraday's constant, *T* is the temperature, *D* is the diffusion coefficient, *R* is the universal gas constant, c_∞ is metal ion concentration, γ is the interfacial energy between the metal and solution and η is the overpotential.

The Barton and Bockris model provides a good general model for dendritic growth. However, unless dendritic growth is the rate limiting step, the model would have to be improved upon to include terms for path formation, electrodissolution, and ion transport. The influence of ionic contamination on the various parameters, such as the interfacial energy, would have to determined theoretically or measured through experimentation.

D. The DiGiacomo Model [8]

DiGiacomo investigated the migration behavior of silver in encapsulated packages and developed the model

$$t_f = \frac{Q_c}{\beta J_{tip}} \qquad \textbf{(5)}$$

where *Qc* is the critical amount of metal ions that must migrate to achieve dendritic growth across a gap, β is the degree of oxidation or fraction of active surface, changes from metal to metal, J_{tip} is the current density at the dendrite tip.

This model was derived from use of the Butler-Volmer equation, which relates electrode potential to current density [31]. However, the inclusion of current density at the dendrite tip makes this model more interesting for academic investigation than for application by industry. Changing the point of focus of the model from current density at the dendrite tip to factors that influence current density would yield a model that evolves from the behavior of the physical mechanism, but incorporate measurable quantities. Current density is a function of conductance and electric field. Conductance is function of contamination and relative humidity. Therefore, failure behavior can be described in terms of contamination, relative humidity, and e-field.

E. **The Peck Model** [32]

The Peck model was developed from a statistical review of time to failure experiments designed to initiate electrolytic corrosion in plastic encapsulated microcircuits (PEMs). Based on the results of temperature/humidity/bias (THB) testing, the model details the corrosion process as

$$t_f = A_0 RH^{-n} f(v) \exp\left(\frac{-\Delta H}{kT}\right) \qquad \textbf{(6)}$$

where t_f is time to failure, A_0 is a material dependent constant, *RH* is relative humidity, *n* is an empirically determined constant, ΔH is activation energy, *k* is Boltzmann's constant, *T* is temperature, and *f(v)* is an undetermined function of voltage. Peck's model is based on the Eyring equation, with stress terms for relative humidity and voltage.

While the Peck model is based on a different failure site (aluminum bond pad vs. printed board surface) and different failure mechanisms (electrolytic corrosion vs. dendritic growth), the underlying oxidation/reduction/dissolution reactions and the relevant environmental stressors (temperature, humidity, voltage) are similar to classical ECM. This may suggest that the experimentally determined constants, such as 2.66 for the humidity exponent[8], may be different for ECM, but the overall behavior prediction may have some validity.

There are limitations to the Peck model. The voltage effect is provided in an undefined state, though some references have indicated a power law effect, with an exponent close to 1.5 [34]. Peck's model also fails to normalize voltage through use of electric field strength, which is probably the more fundamental driver of migration-based phenomenon. Peck's model is strictly based upon experimental observations and is therefore not a true physics-of-failure based model like DiGiacomo. The Peck model does directly take into consideration ionic contamination levels, though decreases in impurity levels followed by increases in activation energy suggest a correlation which has not yet been quantified. Finally, most critically, the Peck model fails to address the potential for critical stress limitations, below which corrosion-based mechanisms will not initiate.

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[8] Later work by Peck and Halberg [35] found the humidity exponent to be closer to 3.

F. The Howard Model [35]

Another model for metallization corrosion is Howard's model, where,

$$t_f = \frac{wlhndF}{MV}\frac{\rho}{t} \qquad (7)$$

where t_f is the time to failure, w is conductor width, l is conductor length, h is conductor thickness, n is valence of conductor, d is density of conductor, F is Faraday's constant, M is atomic weight of conductor, V is voltage bias, ρ is resistivity of electrolyte, and t is electrolyte thickness.

The derivation of this model from Faraday's Law makes it sound from an electrochemical standpoint, but the exclusion of other primary factors such as temperature and relative humidity is not sound. This model was also developed for metallization corrosion leading to open circuits, not short circuits due to migration. It is therefore not applicable to electrochemical migration.

G. The CALCE Model [36]

The Rudra, Pecht, and Jennings model is for conductive filament formation (CFF). CFF is the migration of copper filaments along the epoxy-fiber bundle within the printed wiring board. The model presented here is empirical, based on tests conducted for different laminate types, surface conditions, temperatures, relative humidities, voltages, spacing between conductors, and geometry of the conductors. The predicted time to failure behavior, in hours, is described as

$$t_f = \frac{a\,f\left(1000L_{eff}\right)^n}{V^m\left(M - M_t\right)}, M > M_t \qquad (8)$$

where a is the filament formation acceleration factor, f is a multiplayer correction factor, n is a geometry acceleration factor, V is the applied voltage bias in volts, m is a voltage acceleration factor, M is the percentage moisture content, and M_t is the percentage threshold moisture content. Leff is given by

$$L_{eff} = kL \qquad (9)$$

where Leff is the effective length between conductors, k is a shape factor, and L is the spacing between conductors in inches.

This model predicts the failure due to CFF and has been recently verified [37]. The usefulness and limitations of this model are similar to the Peck model. In both instances, the failure sites and mechanisms differ from classical ECM, but the basic principles are still valid. The CALCE model improves upon the Peck model through its acknowledgement of a critical moisture level. There are two additional limitations to the CALCE model. First, the model couples the relative humidity and temperature through the use of a moisture content term. Moisture content is relevant for a bulk phenomenon such as CFF, but is somewhat of limited value for surface mechanisms such as ECM. In addition, the rate-limiting step with CFF tends to be the time for path formation to occur. With electrochemical migration, the path formation can occur almost instantaneously at elevated relative humidities (above 70%) [38].

IV. Discussions

All of the models mentioned previously require the addition of at least one term, and in some cases more, to account for the primary factors of electrochemical migration given in the literature (temperature, relative humidity, voltage/electric field, contamination). An appropriate PoF based model would be founded on electrochemical principles such as Faraday's Law and the Butler-Volmer equation, and take into account the primary drivers for ECM in a manner that would allow for lifetime prediction by reliability and test engineers. There are number of difficulties preventing the development of this universal model. The primary limitation is determining the rate limiting step within the ECM process and identifying if this step is a growth-defined or a nucleation-defined phenomenon.

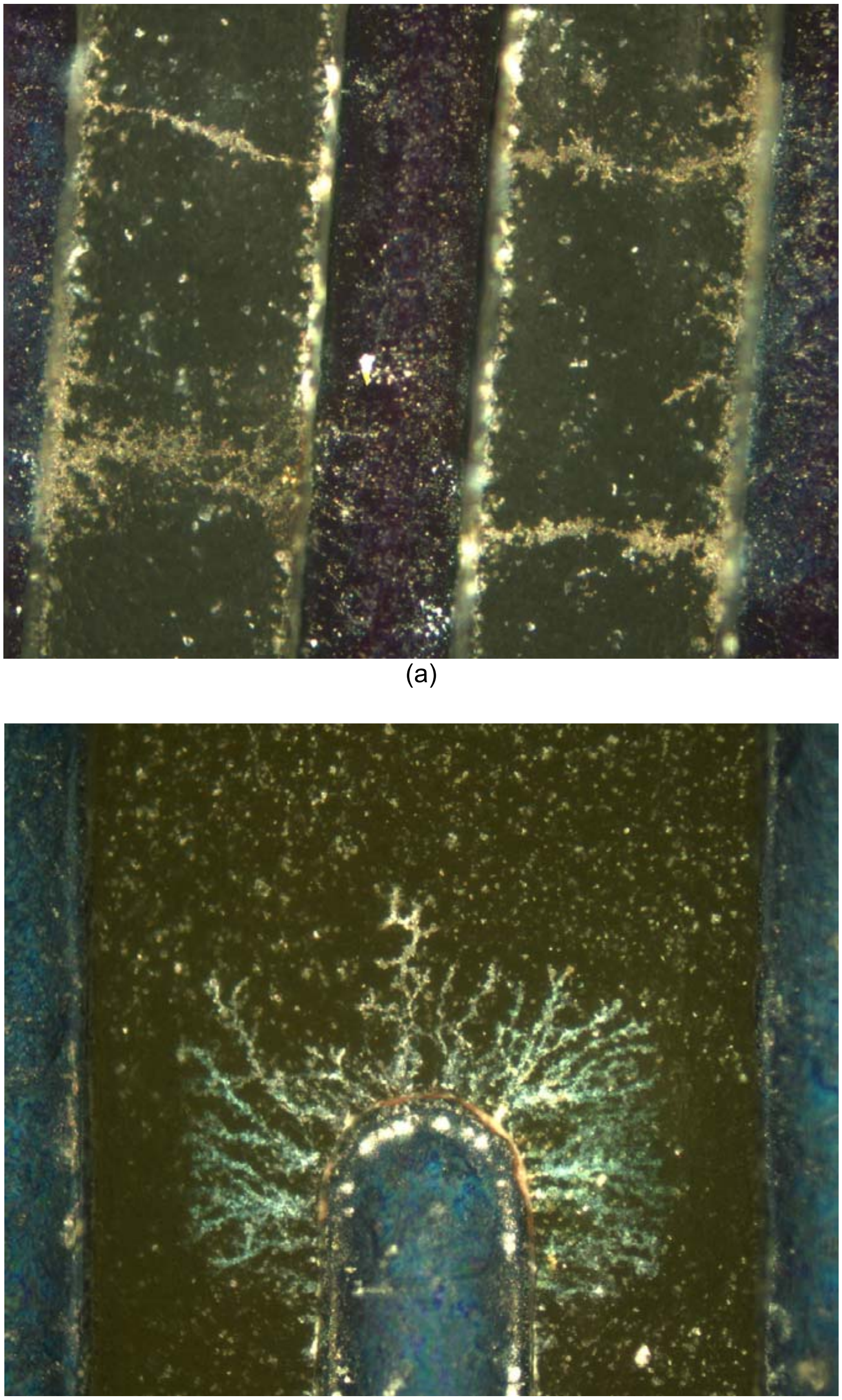
ECM is a multistage process. The first stage, path formation, is the time required for the thickness of the electrolytic solution, usually water molecules adsorbing to the surface of the substrate, to be sufficient to transport metal ions. The second stage in ECM is initiation, which is characterized by three steps. Electrodissolution, the first step, occurs when the metal at a conductor is stripped of an electron(s) and becomes a positive ion (oxidation). The ions are then transported through the electrolytic solution by migration, diffusion, and/or convection during the process known as ion transport. When the ion arrives at the oppositely biased conductor, it attaches through the acquisition of an electron (reduction). This is known as electrodeposition. Electrodeposition is largely diffusion controlled and its rate therefore depends on the metal ion concentration in the aqueous medium. The third and final stage is the growth of dendrites back to the anode (ground, positive).

Time to failure models provide a good approach if the rate-limiting step is time-dependent, such as the transport of ions from anode to cathode or the reciprocal growth of dendrites back from cathode to anode. Historical industry test specifications that require long test times of 500 to 1000 hours, such as IPC Electrochemical Migration Resistance Test [4] and the JIS Testing Method for Soldering Fluxes [39], seem to support this approach. More recent investigations provide some contrary evidence. Surface insulation resistance testing at a higher frequency than the traditional 24-hours seemed to show that most resistance drops associated with dendritic growth occurred within 72 hours of test startup [40]. In addition, as displayed in Figure 1, optical observations of dendritic growth on 'seeded' boards have sometimes shown contradictory behavior. Some conditions trigger dendrites in areas of the highest electric field strength, suggesting time-dependent behavior, and some conditions trigger dendrites periodically throughout the comb structure, potentially suggesting heterogeneous nucleation behavior.

An additional limitation is the difficulty of describing critical stress limits within the construct of the models. The critical number of monolayers necessary to induce ECM has been identified [10], but this finding is not incorporated into any of the models discussed previously. In addition, little work has been performed to relate how various flux chemistries and printed board surfaces interact with relative humidity to produce this critical monolayer level. Another concern is of the role of temperature in ECM. The influence of temperature may be more complex than through classic Arrhenius or Fickian behavior. Sohn and Ray [41] determined that 85°C may be too harsh of an environment for some weak organic acids (WOAs), causing them to break down or volatize. Elevated temperatures, however, can be necessary to induce the diffusion of board-based contaminants, such as bromides used for epoxy flame retardancy or process residues trapped under the solder mask, in a reasonable period of time.

V. Conclusion

There are a number of physics-of-failure (PoF) and empirically-based formulas available for scientists and engineers to use to describe electrochemical migration behavior on the surface of printed circuit boards. All of these formulas can be used for time to failure prediction if the users are aware of the limitations inherent within each model, whether it is because the model fails to include a critical failure driver or if model is derived from a different failure mechanism. The eventual development of a unified model for ECM will most likely require an evolution of the traditional ‘shake and bake’ approach and incorporation of more fundamental techniques, such as potentiostatic measurements and ellipsometry to measure surface monolayers of water, so that the true physical processes can be characterized and related to the phenomenon observed. If nucleation-dependent processes are found to be the critical indicator of ECM, future industry specifications should most likely be steered away from temperature/humidity/bias (THB) testing and towards more rigorous characterization of flux chemistry, plating material, board surface and their interactions.



(a)

(b)

Figure 1: Optical micrographs of a comb pattern on printed circuit boards seeded with either chloride solution (a) or no-clean flux residues (b) and then exposed to 85C/85%RH environmental conditions with an applied bias.

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