ELECTROCHEMICAL CORROSION MEASURMENTS ON METAL ALLOYS EXPOSED TO EAC CLEANING AGENTS

As presented at SMTA International 2019

ABSTRACT

Electronic devices are essential to the reliable operation of the products that employ them. Miniaturization necessitates a fundamental change in how materials and processes are selected to ensure reliability. Solder is a critical component engineered for specific applications. Numerous factors require consideration including board finishes, solder alloy, reflow temperatures, and operating temperature. When process residues are cleaned, the interaction of the cleaning agent with exposed metals must also be considered.

Engineered aqueous cleaning agents are multifunctional cleaners designed to achieve many seemingly contradictory goals. To penetrate, wet and flow under low profile components, the wash solution must exhibit a low surface tension. Once the cleaning agent has successfully removed the residue set, the wash fluid must be rinsed out using high surface tension rinse water.

The robust nature of the cleaning agent requires its effectiveness at removing a wide range of contaminants off of Printed Circuit Board Assemblies (PCBAs). These factors need a broad spectrum approach while not damaging polymers or corroding metals; being able to clean and protect metals at low cleaning agent concentrations while being able to dissolve large quantities of contamination (high contaminate to cleaning agent ratios).

Historical approaches to cleaning agent-metal compatibility have been limited mainly towards visual and qualitative methods. Occasionally, there has been work that uses quantitative test methods, such as weight loss. Electrochemical determination of the corrosion potential and corrosion rate offers a more comprehensive approach towards creating a cleaning process that is as advanced and reliable as the PCBAs cleaned in it. This paper aims to quantify the impact that engineered aqueous cleaning agents have on the materials used in the manufacturing highly-reliability electronics.

INTRODUCTION

The material sets used in the high-reliability electronics industry are rapidly changing due to the increased demands placed on PCBAs. In addition to the demands of increasing complexity and decreasing size, new environmental demands, both extrinsic and intrinsic to the PCBA, are occurring. First, PCBAs must endure harsher extrinsic environments than ever before, such as at the bottom of an oil well or in space, where environmental factors are external to the PCBA design and manufacturing process. PCBAs are no longer expected to function in harsh environments, they are *required* to function. These are environmental factors which are controlled directly by the PCBA design and manufacturing process. Secondly, PCBAs now have an added intrinsic environmental demand: they must leave less of an environmental impact than before. The phasing out of lead-based solders is the classic example of this, although events such as the elimination of chlorofluorocarbons (CFCs) can be considered another intrinsic environmental demand.

With these demands and limitations placed on electronic devices, the well-established material sets have been disrupted, and newer materials are required. Again, the classic example being the change from eutectic tin-lead solder to lead-free materials, such as the SAC solder systems. These new materials have different chemical and physical properties than the materials they are replacing as well as require different associated material sets (e.g. flux chemistry, or cleaning process) and have less historical data to rely upon.

In addition to the material set changes, the increased complexity, density, and reliability of PCBAs is making cleaning more important. With the reduction in component size comes an increase in the electric field between two conductors of different polarity. This causes ions, which come from contamination, to migrate and potentially participate in chemical reactions. The migration of ions can cause an increase in leakage current, signal degradation, or can cause short circuits. Since the conductor spacing is much smaller, much less contamination is required to cause problems.

In recent history, many high-reliability PCBAs began using no-clean solder flux, due to the advertised lack of a necessary cleaning process. These no-clean fluxes were designed to use volatile weak organic acids (WOAs) and/or undergo polymerization during the reflow process. The rationale behind them was to either remove, decompose, or entrap ionic contamination. When ionic contaminants combined with water from the environment and a DC bias, from either the circuits on the PCBA or a galvanic cell from the materials used, can cause premature failure.

The demands being placed on PCBAs rapidly called for smaller pitches on devices, lower standoff heights, and in some cases larger overall package areas. This has invalidated some of the rationales behind using no-clean fluxes. For instance, while many WOAs used in no-clean fluxes readily volatilize or decompose at temperatures below common reflow temperatures, the process takes time. The amount of acid, both in terms of mass and the number of acid groups found in residue, does not decrease as much as one would expect [1]. Additionally, components now have much lower standoff heights. This causes three distinct problems with regards to cleanliness. First, it reduces the ability of the WOAs to volatilize and outgas during the reflow process.

Secondly, the reduced standoff height causes flux residues to be drawn farther underneath components due to capillary forces, making it more challenging to volatilize the WOAs. Third, cleaning agents have a lower surface tension than water and can combat these two effects. However, cleaning agents must be rinsed out from under components, lest they become contamination themselves. The lower standoff height increases this challenge as water no longer has a low enough surface tension to reliably penetrate underneath the components.

But what is corrosion? Corrosion is an irreversible reaction of a material, most commonly metals, which results in the consumption of the material or the dissolution of the material into its environment [2]. Corrosion is a wide and complex topic, and as such much of the fundamentals cannot be discussed here, and the authors suggest the text by Stansbury as a starting point for electrochemical corrosion basics [3]. While there has been, and still is significant effort in characterizing these newer materials in the end-use environment, less attention has been paid towards characterizing these newer materials, and in many cases even the older materials, in the cleaning process.

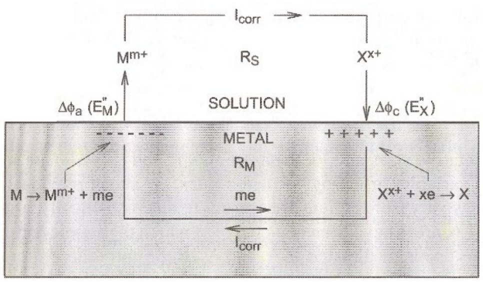


Figure 1. *Corrosion Circuit (Modified from [3])*

In the few previous papers that have studied corrosion in the cleaning process, two approaches were used. The first approach is using Pourbaix diagrams, the second is using weight loss measurements. Pourbaix diagrams are a plot of potential v. pH and are a useful tool in summarizing large amounts of data. However, Pourbaix diagrams can only tell what *might* happen, not what *is* happening. They are strictly based on thermodynamic quantities of the system which they are calculated for. They do not consider the kinetics of corrosion, meaning that while a reaction may be thermodynamically favorable, it's kinetics could be slow enough that it does not occur. Also, the most commonly published Pourbaix diagrams are for a pure metallic element in water. In some cases, it is possible to find Pourbaix diagrams for alloys or for simple aqueous solutions with some common ions (such as chloride).

Cleaning agents are complex systems with many different ionic components and even nonionic components which may influence the corrosion process. Additionally, virtually all aqueous-based cleaning agents on the market, regardless of pH contain some type of corrosion inhibitor. These corrosion inhibitors greatly shift and change Pourbaix diagrams. Corrosion inhibitors primarily act by changing the available kinetic pathways available to the corrosion process. As noted above, Pourbaix diagrams are blind towards kinetic effects. Pourbaix diagrams are known to lead to incorrect conclusions based on the previously mentioned reasons, in addition to others. However, they can be a useful guide.

The other method that has been used to determine corrosion in the cleaning process is through weight loss [4]. In this method, test coupons of the metal to be studied are: cleaned, weighted, exposed to the cleaning process, cleaned of any corrosion products, and weighed again [5]. This method will, theoretically, produce the most accurate measurement of corrosion rate. However, this is only practical when the corrosion rates are significant or when corrosion rates are low, a prolonged exposure period is needed, as a considerable quantity of metal must be removed to get a measurable difference. Additionally, the removal of the corrosion products at the end can introduce substantial error if any of the uncorroded metal is removed. Modern cleaning agents are designed to have very low corrosion rates, and as such weight loss measurement is not an ideal method. What is needed is a new approach to corrosion in the cleaning process. The corrosion process during cleaning *must* be better understood.

In the corrosion process, one or more chemical species loses an electron(s) or oxidizes, while some other species gains electron(s), or reduces. Due to the conservation of charge these reduction and oxidation reactions occur together and are termed *redox* reactions. Equation (1) gives a generalized oxidation reaction and equation (2) gives a generalized reduction reaction.

$$M \rightarrow M^{n+} + ne^{-} \qquad (1)$$

$$X^{n+} + ne^{-} \rightarrow X \qquad (2)$$

As a result of the release or consumption of electrons in each of these reactions, an electrical potential develops, and then current can flow. These reactions occur at different sites, with the site of the oxidation reaction being called the anode or anodic site, and the reduction site being called the cathode or cathodic site. Due to historical reasons, there is a wide range of terms, signs, and conventions that are different between the fields of electrical engineering, electrochemistry, and corrosion science. For this paper, the Stockholm sign invariant convention is used [6]. In this convention positive potentials, with respect to E_{corr}, which is the potential at which corrosion is occurring at the highest rate, are defined as oxidation potentials and negative potentials are reduction potentials; the currents resulting from the oxidation reaction is called the anodic current and has a positive sign, and the reduction reaction causes a cathodic current, which has a negative polarity. Figure 1, shows the generalized reactions, potentials ($\Delta\phi$), and currents.

Fundamentally, all electrochemical corrosion methods are just different permutations of measurement and/or control of potential or current. To limit the scope of this paper, only certain key methods and variables will be presented, in limited depth, and with many omissions for clarity purposes. To measure the corrosion rate, the corrosion current (i_{corr}) must be determined. Since the corrosion process releases and consumes electrons, the number of electrons transferred per second indicates the rate of the chemical reactions. If the number of electrons transferred for a given oxidation reaction is known, then this current is proportional to the corrosion rate, as governed by Faraday's Law (3), where:

- c is a unit conversion factor whose value depends on the units of the other terms
- I_{corr} is the corrosion density (typically µA/cm^2)
- $E.W.$ is the equivalent weight (mass change of an element per electron transferred)
- A is the electrode area
- ρ is the density.

However, i_{corr} cannot be measured directly and must be determined via calculations.

$$\text{Corrosion Rate} = \frac{cI_{corr}E.W}{A\rho} \qquad (3)$$

There are many different ways to determine I_{corr}, but the traditional way is a method called *polarization* *resistance* or *linear polarization resistance* [7]. In this method a potential, with respect to a reference electrode, is applied to a working electrode made of the material of interest, causing a current to flow to/from an inert third electrode, *counter electrode*. The resulting current is measured as a function of the applied potential. For relatively small applied potentials (typically±20 mV), the change in current is typically linear and the Stern-Geary Equation (4) holds true [8].

$$i_{corr} = \frac{\beta_A \beta_C}{2.3(\beta_A + \beta_C)} \frac{\Delta i}{\Delta E} = \frac{B}{R_p} \qquad (4)$$

The terms $\beta_{a,c}$ correspond to the anodic and cathodic Tafel constants, respectively. Sometimes these Tafel constants are combined into a proportionality constant B. This better illustrates that corrosion rate will be inversely proportional to the polarization resistance, all other things being held constant. Tafel constants must be determined either via an independent experiment which sweeps over a larger potential range or via additional analysis of the polarization curve [9], the former method was used. Because the large potential range used to determine the Tafel constants accelerates corrosion, and therefore may change the surface of the material chemically and/or physically, this method is done after determining the last term. The last term of (4), $\Delta i/\Delta E$, is equivalent to the inverse of the *polarization resistance* (R_p) which is a resistor that does not always obey Ohm's Law. There are other methods of determining R_p, such as Electrochemical Impedance Spectroscopy (EIS), which was conducted during this study but is beyond the scope of the current paper.

The prior discussion assumes, among other things, that the diffusion of the active species is not the rate-limiting step in the corrosion process. If this is not the case, the corrosion system is called *diffusion-limited*, meaning that the corrosion rate could be much higher than under the conditions measured. In this case then as the diffusion-limited Tafel constant (β_{diff}) becomes very large (4) becomes dominated by the smaller Tafel constant and reduces to (5) where β is the non-diffusion limited Tafel constant [10].

$$i_{corr} = \frac{1}{R_p}\left[\frac{\beta_{diff}\beta}{2.3(\beta_{diff} + \beta)}\right]_{\beta_{diff}\to\infty} = \frac{1}{R_p}\frac{\beta}{2.3} \qquad (5)$$

METHODS

To study the electrochemical corrosion of common materials used in PCBA manufacturing samples of four common metals: copper, SAC305 solder, high lead solder, and eutectic solder were obtained from commercial sources. Table 1, shows the nominal chemical composition of the various materials.

Table 1. Nominal Alloy Composition (wt.%)

	Cu 110	SAC 305	High Lead	Eutectic
Cu	100.0%	0.5%	-	-
Pb	-	-	-	37.0%
Sn	-	96.5%	5.0%	63.0%
Ag	-	3.0%	95.0%	-

The solder alloys used were obtained in the form of solder bars, and the copper was a standard bar. The metal samples were cut to a smaller size. The electrochemical cell used was a 3-electrode cell that was modified to permit the cleaning agent to be circulated in a closed-loop. The reference electrode was a Hg/HgO type, filled with 20% potassium hydroxide [11]. The cleaning agent was run at a nominal concentration of 14.0 wt%. The temperature was measured every minute during the data collection. The ambient temperature was 25±5 °C, and no corrections were applied for temperature.

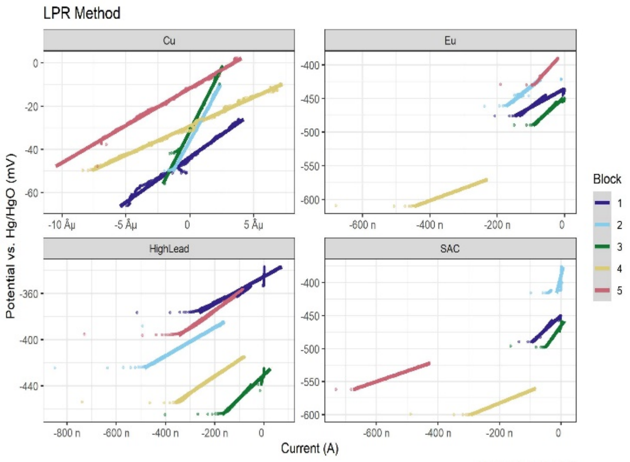
The open-circuit potential (OCP) was measured every second until the electrode drift was deemed to be stable, with a drift rate of 0.5 mV/min. Once that stabilized, a potentiostat EIS spectrum was obtained from 100 kHz to 10 mHz with a peak to peak voltage of 10 mV vs. OCP, which will be used in an upcoming paper. Next, a linear polarization resistance measurement was made over the range of OCP ±20 mV with a scan rate of 0.166 mV/s, which is a typical scan rate. Next a Tafel plot was generated over the range of OCP ± 250 mV in order to determine the Tafel constants.

The DOE itself was a randomized complete block design with five (5) replicates. Each block was one "batch" of diluted cleaning agent and contained one sample of each metal run in a randomized order.

At the start of each block, a fresh batch of diluted cleaning agent was prepared and allowed to stir for 30 minutes to allow the phase distribution of the cleaning agent components to equilibrate. Next, the four test samples (one of each metal) were progressively ground from 240, 320, and 400 grit silicon carbide. Immediately prior to testing the coupon was then ground with 600 grit silicon carbide abrasive and rinsed with acetone. After the 30-minute equilibration was completed, the system was filled with the cleaning agent solution and the first metal sample was placed in the corrosion cell. After each sample was completed, the metal was changed without draining the system, meaning all the metal samples within the block were tested with the same sample of cleaning agent. Between blocks, the complete electrochemical system was drained, rinsed several times with DI water, and then rinsed with acetone and allowed to dry.

RESULTS/CONCLUSION

Figure 3 shows the linear polarization data used in calculating the corrosion rates. As shown in (4) the slope of these lines is the polarization resistance of the corrosion system, and is inversely proportional to the corrosion rate.



Line represents linear fit

Figure 3. Polarization resistance plots for all metals. Top: copper (left), eutectic solder (right). Bottom: high lead solder (left), SAC305 solder (right)

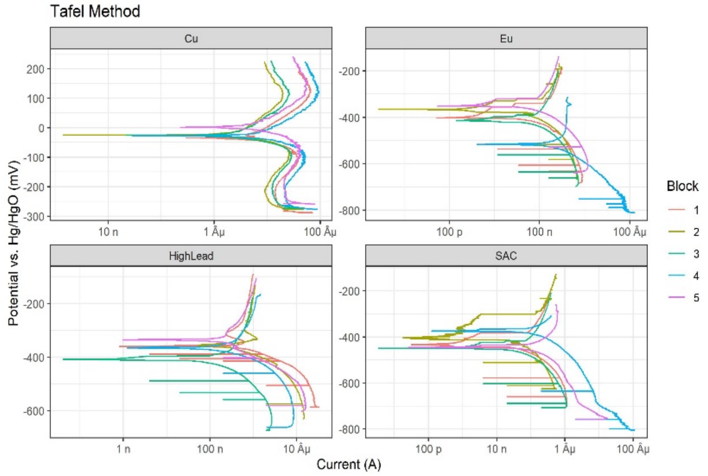


***Figure 2.** Tafel Plots for All Samples*

In reviewing the Tafel plots there was evidence that the corrosion process could be under cathode diffusion control, as indicated by a short, nonlinear cathodic portion of the Tafel plot. This could also be caused by oxidation of species in the cleaning agent, a highly capacitive electrochemical cell, noise or surface finish effects which will be studied in future works. The corrosion rates were calculated for the diffusion limited process of equation (5).

Basic summary statistics of the corrosion rates are presented as Table 2. Copper has a substantially higher corrosion rate than the other metals, at nearly an order of magnitude higher than the solder alloys. shows the individual corrosion rates for all of the metals, along with the mean and 95% confidence interval.

Table 2. Corrosion Rate Basic Statistics

Metal	N	Corrosion Rate (mm/yr)	Std. Dev.	Standard Error	95% CI
Cu	5	3.04E-04	1.72E-04	7.71E-05	2.14E-04
Eutectic	5	8.13E-06	1.30E-06	5.82E-07	1.61E-06
High Lead	5	3.63E-05	1.13E-05	5.07E-06	1.41E-05
SAC 305	5	1.26E-05	6.45E-06	2.88E-06	8.01E-06

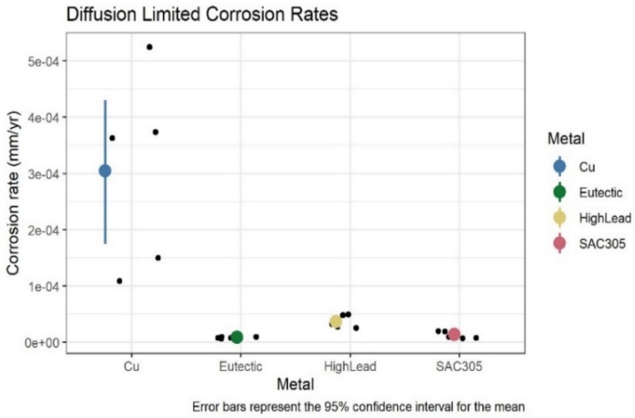


***Figure 4**. Plots of Corrosion Rates*

For the statistical analysis of the corrosion rates, the data was found to follow a lognormal distribution, which is not unusual for this type of data [12]. The logarithm of the corrosion rate was used for subsequent data analysis. The cleaning agent had an actual concentration of 14.01±0.19%. As this was close to the target concentration of 14%, no additional considerations were given to controlling for variations in concentration. A one-way ANOVA was used without the block as a factor, as it was found to be statistically insignificant.

Table 3. Pairwise Comparisons on Transformed Corrosion Rates

Metal 1	Metal 2	Mean Dif.	Std. Error	t-value	p
SAC 305	Cu	1.36	0.116	8.3	≤0.001
SAC 305	Eutectic	-0.15	0.073	1.44	0.529
SAC 305	High Lead	0.488	0.082	4.22	0.036
Cu	Eutectic	-1.51	0.095	11.2	0.004
Cu	High Lead	-0.869	0.101	6.06	0.015
Eutectic	High Lead	0.638	0.048	9.36	≤0.001

Subsequently, a *post hoc* analysis was used to determine the difference in the corrosion rates between metals, Table 3. Figure 5 shows the results of the post hoc analysis graphically. The only pair of metals which had a statistically insignificant difference in the corrosion rate was SAC 305 and tin lead eutectic solder. Referring back to **Table 1,** it is not surprising that those solder alloys are similar with respect to corrosion rate as they are both predominantly tin.

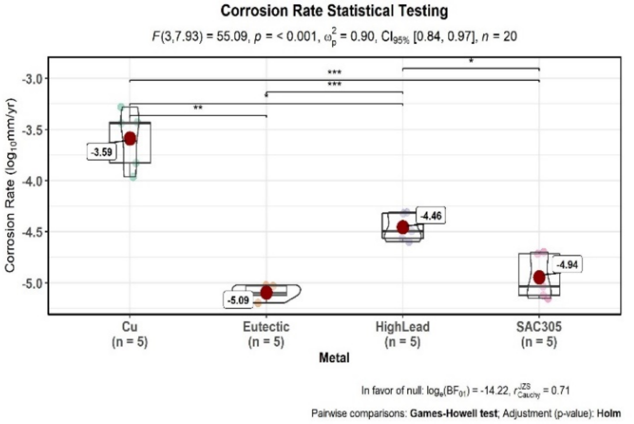


***Figure 5.** Post Hoc Analysis of the Corrosion Rates of Metals*

FUTURE WORK

As noted in the introduction, there has not been a comprehensive *experimental* analysis of the corrosion of metals in the wash process of high reliability electronics. This experiment was only a first step into better understanding the impact of the wash process on the reliability of PCBAs. Future work will further investigate the impact that diffusion has on the corrosion process. In addition, the cleaning process will be better simulated by introducing the effects that elevated contamination and temperature. Additionally attempts will be made to better understand the corrosion mechanism in the cleaning process.

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