

Copper Alloy Corrosion Inhibition and Considerations for Component Processing

by

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ABSTRACT

This paper deals with the largely undiscussed and frequently misunderstood area of base metal corrosion inhibition. The effects of selected electronic connector/component processing steps on the inhibition films as well as the effects of this film on surface sensitive processes will be reviewed. Measurement techniques for determining the thickness and uniformity of these sub-micron inhibitor films will be presented. Examples of component handling, storage and processing which defeat the corrosion inhibition by this film will also be presented. Conclusions will be drawn on the necessity of base metal corrosion inhibition and the necessity of component processing designs which take into account surface film changes after each processing step.

Introduction to Copper Corrosion and Inhibition

Copper metal surfaces can undergo oxidation when in contact with a gas, a liquid or a solid oxidizer. The process of metal loss due to oxidation is also called corrosion. Corrosion of base metal contacts, before and during the fabrication cycle can have negative consequences on performance, plating, appearance and in extreme cases result in component failure and costly reclaiming operations.

There are many types of corrosion depending upon the oxidizer type and phase. Some of these corrosion processes have specific names. For example, contact of a copper metal surface with dry air will cause a thin film of Cu_2O to form⁽¹⁾. Due to the formation of the adherent product Cu_2O , the rate of reaction (corrosion) slows to an imperceptible rate after the film thickens to about 25Å. This is due to the slow rate at which oxygen and copper diffuse through this film at ambient conditions. The process of forming this 25Å

thin corrosion film is called production of a native or natural oxide. This natural corrosion barrier is termed a kinetic barrier. If for any reason, this thin film barrier is removed chemically or mechanically, the corrosion reaction rate will reestablish until again, the native oxide is produced. Thus, in a desert environment, this type of corrosion would dominate and give adequate protection.

Other thick film kinetic barriers exist. For example, paint, tar, oil, wax or other coatings act as diffusion barriers. Also, thicker films of Cu_2O can be grown electrochemically⁽³⁾⁽⁴⁾. Even adventitious carbon can be a kinetic diffusion barrier.

Kinetic barriers such as BTA films are corrosion inhibitors as long as the films are intact. However, if the humidity of the ambient air reaches a point whereby a water film can form on the surface of copper, or a copper surface is placed into contact with liquid water, new corrosion processes are added to the list of competing corrosion reactions. In aqueous solution, the stable chemical species can

change; the products of a specific reaction can be different than in gaseous corrosion. For example, the most stable oxide of copper in dry air is Cu_2O , but in aqueous solution is CuO ⁽⁵⁾. Also thermodynamics are more complicated because reactions depend not on just the species present but also on the pH, the ionic strength and the solubility of the products (and reactants) in water. This complicates kinetic measurements as well as predictions of mechanisms. Thin water films can cause corrosion nightmares, such as variations in appearance, dimensions, performance, surface cleanliness and component processability: The amount and extent of these variations are functions of changes in surface coverage, pH, ionic strength and solubilities when water rapidly evaporates or is absorbed (by deliquescent components).

Other surface effects can also dominate corrosion. For example, surface wettability of metals and surface tension of liquids can change with pH and ionic strength, i.e. are a function of evaporation rate. In turn the evaporation rate is a function of temperature and humidity. It is no wonder that controlled experiments in a laboratory at a constant temperature and humidity may not be directly relatable to data taken at ambient conditions.

Having this model for corrosion of copper, how does one make or select an inhibitor for copper corrosion? In general, any coating or process which slows corrosion can be called an inhibitor. Kinetic barriers are inhibitors, surface wettability modifiers are inhibitors if they don't allow water to wet a surface. Closed loop systems of buffers, (i.e. pH modifiers), surface wetting modifiers, barrier repair mixtures and solutions are commercially available where each addition slows or modifies one of the above corrosion reaction paths. Cooling tower closed loop systems, boiler closed loop systems, radiator closed loop systems are all examples of inhibitor systems.

The best non-closed loop system of inhibitors is the mixed barrier coating. The best example of a single barrier coating for ambient conditions is Teflon™, due to its non-wetting character, its pH inertness, its ambient temperature stability. However, the same properties that make it perfect for a general corrosion inhibitor cause it to lack the most important inhibitor property. It needs to have an adherent, chemically stable bond which seals all contact of ambient compounds from the copper surface. Teflon™ doesn't chemically bond to copper. Copper oxides are not good barrier coatings in the presence of liquid water, though their films are adherent to the base copper. They dissolve in acids and bases especially in the presence of oxidizers.

Adherent thick film protection is available for finished pans. However, for electronic components, not at their final point of manufacturing, thick film inhibitors will complicate processing. Thus, during all stages of manufacturing, from the base copper metal to the finished product, the surface of the copper must be either protected from corrosion or corrosion must be inhibited (slowed to an acceptable rate).

The only way to protect copper from corrosion is to remove all contact with oxidizers. This can be done by sealing the metal in a vacuum or oxidizer-free environment such as a bag with pure N_2 gas. Neither of these methods is cost effective and/or time effective. There are commercially available⁽⁶⁾, oxidizer removal papers which can be placed with parts to scavenge oxidizers after the bag has been sealed. This approximates an oxidizer-free environment or at least an oxidizer-reduced environment. The cost of using this technology must be weighed verses inhibitor technology. It should be noted that each of these techniques, vacuum and/or gas purge would also have the added benefit of water removal. Water removal simplifies corrosion and allows the natural corrosion barrier of Cu_2O to inhibit the parts if vacuum processing or gas purge processing failed to remove all

the oxidizers but was able to reduce the water content to the point where liquid water could not form.

The other method to keep corrosion of copper at bay is to inhibit the surface. A cost effective, commercially available inhibitor is Benzotriazole (BTA).

Current Theory of Triazole Deposition

Triazoles have been known to inhibit copper corrosion for over 100 years⁽⁷⁾. Triazoles have been commercially available for 45 years⁽⁸⁾. Triazoles have been used very successfully as inhibitors for copper because they possess all the properties necessary for a good inhibitor. These thin films adhere well to copper, they have good stability over a wide pH range, they are thermally very stable and no adverse effects have been found for processing of electronic components⁽⁷⁾.

Research has been conducted to probe each of these attributes. Cohen et al⁽⁹⁾ found that BTA adherently bonds to copper, Cu₂O and CuO covered surfaces. Walker⁽¹⁰⁾ shows the pH range in which triazoles can be reproducibly used varies from pH 3 to 12. Walker has also studied the thermal stability of triazoles⁽¹¹⁻¹³⁾. Current research at Brush Wellman shows BTA gives some amount of surface non-wettability also. This will be discussed later in this paper.

The current model for BTA inhibition depicts the inhibition film to be made up of a Cu-BTA complex which under normal processing conditions grows to about 40-100Å, in the reproducible pH range⁽⁴⁾. To make the Cu-BTA complex, a source of Cu ions must be available near the surface of copper. In most cases this is provided by the Cu₂O native oxide layer⁽¹⁴⁾. Cohen et al⁽⁹⁾ found that an oxidizer added to the BTA (in this case FeCl₃) released sufficient Cu ions into the near surface region to form the multiple layered Cu-BTA complex⁽⁹⁾. If a source of Cu ions is not released into the solution near the copper

surface during complex formation, only a monolayer of Cu-BTA is formed⁽⁹⁾. This extremely thin film does not afford the best possible corrosion barrier obtainable from BTA. Thus, to form the best possible corrosion barrier from BTA, the deposition steps must include production of sufficient Cu₂O or include an oxidizer to provide sufficient Cu ions and include sufficient time-at-temperature to form the thickest possible heterogeneous inhibition structures.

One should note that gas phase BTA application should only form a monolayer initially, since without water, copper ions can not be released to form the multilayered complex. The extra copper needed to form further layers can only come from subsequent decomposition and/or diffusion. Since copper diffusion through the native oxide and/or Cu₂O decomposition is very slow at room temperature, the multiple layer structure can't be formed immediately. Kinetic theory suggests that the hotter the substrate, the faster the multiple layered Cu-BTA complex will form from vapor phase BTA. Thus ambient temperature and humidity variations can cause process/corrosion protection variations when triazoles are deposited via this method. However, if shelf life is short between manufacturing steps, this method of inhibition may be adequate.

Proposed Model System for Cu/Cu₂O/Cu-BTA

After a rigorous review of the literature, a model system for BTA inhibition which incorporates most of the observations of previous investigations was constructed (Figure 1).

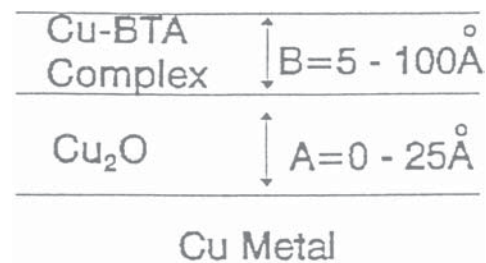


Figure 1. Proposed model system for Cu/Cu₂O/Cu-BTA

The copper surface can be covered by some thickness [A] of Cu_2O . The thickness can vary from total removal as seen by Ishida and Johnson⁽⁵⁾ to no removal as in the case of vapor phase BTA addition. However, thicker than native oxide thicknesses of Cu_2O films can be grown artificially or via corrosion which would modify this model. The minimum thickness of Cu-BTA complex [B] which could be formed is one monolayer. Cohen et al⁽⁹⁾ measured a monolayer of Cu-BTA to be 5Å. Notoya and Poling⁽⁴⁾ suggest that in the normal range of pH's where the highest quality Cu-BTA films are grown, the total of A + B is < 100Å. Thus, the thickest Cu-BTA films would be 75-100Å depending on [A]. By comparison, most product literature from BTA manufacturers quote 50Å⁽⁷⁾ of Cu-BTA as normal. This wide variation in total film thickness, which can change by a factor of 20, may explain the importance of sample preparation to obtain reproducible surfaces suggested by Brown⁽⁷⁾. Brown also warns the reader that films that are too thin to see optically will be a problem for optimization of deposition since changes in bath parameters and/or time-at-temperature would not immediately be measurable. The authors of previous studies on Cu-BTA used a number of techniques to measure their film thicknesses^(2-5,9,14-15) such as: Fourier Transform Infra-Red (FTIR) spectrometry, Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS), ellipsometry, multiple reflection Infra-Red (IR) and Surface Enhanced Raman Scattering (SERS) spectroscopy. Each of these surface sensitive techniques has its strengths and weaknesses but data from all are consistent with the proposed model for inhibition of copper by BTA. Many of these techniques are available in commercial surface analytical laboratories for contract analysis. Some are low enough in price to justify purchase for plant site analytical labs, so the fear that, "If I can't see a change with my eye, I can't optimize or understand my process" can be alleviated.

Surface Wettability Results and Discussion

Brush Wellman uses the XPS technique to optimize and understand its copper alloy inhibitor deposition processes. In an effort to optimize and understand the uniformity of inhibitor deposition, Brush Wellman initialized a surface wettability study. One of the findings of this study reveals an undiscovered feature of BTA. Two samples of our normal inhibited product were obtained and prepared. One was degreased and forced air dried to remove any organic films accumulated during storage, shipment and handling prior to the analysis. The other identical sample was degreased and pickled in 20% H_2SO_4 /3% H_2O_2 to remove all traces of surface deposits (BTA) by dissolution of the underlying alloy, rinsed in deionized water and forced air dried. The surface wettability results of these two samples can be seen in Table 1.

Sample	Cycle	Contact Angle (deg.)	Cos Θ (%)
Pickled Surface	Advancing	56.0	56
Pickled Surface	Receding	14.4	97
Cu BTA Surface	Advancing	99.3	0
Cu BTA Surface	Receding	0	100

The cleaned copper alloy native oxide surface has limited ability to resist wetting by water as indicated by the % wettability above 50% in the advancing cycle. Once the surface has been totally wet, receding cycle, the surface oxide contributes no inhibition due to surface forces, as demonstrated by the near 100% wettability. Note, there is still a kinetic barrier which will give some protection. The BTA inhibited copper alloy surface has excellent ability to resist wetting by water as indicated by the 0% wettability in the advancing cycle. This is the first indication that Cu-BTA may have the ability to protect against ultra thin

water films which form at humidities as low as 50%⁽¹⁶⁾ on some metals. However, when thicker films of water are present, due to heavy condensation or submersion into liquid water and the surface forces are overcome, the receding cycle indicates that this inhibition of wettability due to surface forces is totally lost. This may give some clue as to some of the shipping and handling problems associated with inhibited copper alloys. For example, coils of copper alloys can sit in a humid warehouse environment for more than two years⁽¹⁷⁾ and show no visible signs of corrosion. But ship the same, well inhibited coil in a wet cardboard box which is in contact with the metal, or spill coffee down the wraps of the coil or mop the floor around a coil where the water can rise into the coil due to capillary forces between coil wraps and corrosion will be evident in a very short time on a copper surface having the highest quality BTA coating.

Damage

The surface films can undergo three types of damage in the ambient environment. One type is physical damage such as temperatures in excess of 300 C, which will destroy the Cu-BTA complex. The second type of damage is chemical damage due to humidity, acids, bases, complexing agents, oxidizers and/or solvents. The last is mechanical damage during processing such as stamping, coining, machining, slitting and any operation where abrasive contact takes place. These types of damage may be minimized when the manufacturing operations design specifications include corrosion protection as a design goal.

Each individual operation may have multiple opportunities to damage or totally remove the corrosion inhibition layers. The process of welding, hot tin dip and heat treatment steps can totally remove the Cu-BTA complex due to excessive temperature alone. Solder fluxes and plating pretreatment steps can chemically remove the inhibition films. By definition,

machining would totally remove the copper protection by mechanical damage. Subsequent protection of copper, following these operations, is necessary to eliminate corrosion induced failure modes. Corrosion can induce three types of failure modes. Corrosion can induce failures due to changes in appearance. Corrosion can induce failures due to dimensional changes. Corrosion can induce failures due to inducing performance limitations. Brush Wellman has two types of inhibitors for its copper alloys: BTA inhibition for all chemically cleaned surfaces or degreased surfaces and rolling oil inhibition on rolled products. These inhibitors are applied to meet appearance and performance specifications by our customers.

Removal

One can use the model system of Cu-BTA to predict how to remove the inhibitor layers if they have a detrimental effect on some surface composition sensitive processing steps. In most cases elevated temperatures, though they can be used to remove Cu-BTA, may cause bulk changes in copper alloys and also may generate excess surface oxides which could influence processing or cause a failure in an appearance specification. Mechanical abrasion is efficient in removing Cu-BTA films but complex shaped parts or stamped geometries preclude using this method. Thus, chemical removal is necessary in many cases.

The most cost effective Cu-BTA removal media would be an environmentally safe complexing agent, which would be water soluble and have a pH near that of pure water. Luckily, nature has provided one: citric acid. This nitrogen terminated chelating compound competes with the BTA for the copper ions, which hold the Cu-BTA complex together. At elevated temperatures, the citric acid rapidly extracts the copper ions as a copper citrate complex. Since the BTA is only present in small amounts, it is rapidly lost due to dilution into the citric acid and the Cu-BTA complex

can not reform. The higher the temperature of the citric acid, the faster the removal of BTA. One only needs to choose a temperature and concentration of citric acid to match the automated line speed of the manufacturing operation. Citric acid will also remove excess copper oxides but at a slower rate than the removal of the BTA. The cost effectiveness of this technique for removal of Cu_2O must be checked for each specific operation.

Conclusions

Oxidizers such as O_2 , H_2S , Cl_2 , O_3 in the ambient environment can corrode copper. Exposure to these oxidizers forms passivated surfaces of native oxides, sulfides, chlorides which, due to kinetic barriers, are self limiting. However, the exposure to these oxidizers in the presence of liquid water would quickly cause excessive corrosion induced variations in color, roughness and processability. The added kinetic barrier of the Cu-BTA complex has been shown to give added shelf life to copper exposed to ambient conditions.

Handling, storage, packaging and processing practices can cause failures of the Cu-BTA by thermal, chemical or mechanical damage and the benefit of the Cu-BTA surface wettability barrier may be lost if contact with liquid water is allowed. Thus, component processing designs should include, an analysis of the influence of each proposed process step on current inhibitors in place or selective use of inhibitors and removal of inhibitors to produce the most cost effective, waste free, corrosion free manufacturing processes possible. However, the best components are only as good as their storage, handling, packaging, shipping and receiving practices.

Biography

Dr. Terence M. Thomas is a Senior Surface Chemist in the R & D Division of Brush Wellman. Previously he was a Staff Surface Chemist for 7 years at the Solar Energy

Research Institute. He received his Ph.D. in Inorganic Chemistry in 1980 from the University of Tennessee and conducted his dissertation research at Oak Ridge National Laboratory. He received his M.S. degree in Physical Chemistry from Colorado State University in 1976. He received his BA. degree from Benedictine College in 1974. His current areas of research are in oxidation/reduction reaction mechanisms at gas/solid and liquid/solid interfaces of beryllium containing alloys.

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