SPECTROELECTROCHEMICAL INVESTIGATION OF PASSIVE LAYERS FORMED ON ELECTRODE SURFACES

BY

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DISSEbATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate College of the University of Illinois at Urbana-Champaign, 2012

Urbana, Illinois

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Corrosion, broadly defined as environmental damage to materials (usually metallic), is an important concern for maintaining infrastructure and for many manufacturing and transport processes. Corrosion is typically prevented or controlled by formation of a passivating layer that prevents diffusion of oxidative elements that might attack the base material, either by a passive oxide formed by sacrificial agents in the material or by use of organic inhibitors.

Various electrochemical techniques are used to compare the relative efficacy of these passivation layers, including linear sweep voltammetry, which gives the breakdown potentials and corrosion currents, and AC impedance, from which film resistance and inhibition efficacy can be determined. Although voltammetry gives an idea of whether a film successfully passivates a metal surface, it gives little insight into the mechanism of inhibition and chemical interactions that take place between the film and metal surface. Shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) allows interrogation of the electrode-electrolyte interface where corrosion occurs.

Benzotriazole (BTA) is the prototypical inhibitor used in both plating baths and for the chemical mechanical planarization in the microprocessor manufacturing. It forms a film that allows uniform removal of the electrodeposited copper to result in smooth surfaces. It has face dependent protection efficiency which has been studied by various surface sensitive techniques including scanning tunneling microscopy (STM), surface enhanced Raman spectroscopy (SERS), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and sum frequency generation (SFG). It is a good test for the viability of shell-isolated nanoparticle enhanced Raman (SHINERS) particles in investigating surface film formation on single crystal
Cu. SHINERS did not reproduce the face dependent behavior found in STM and SFG experiments but did confirm difference between polycrystalline and single crystalline surfaces noted but not previously explained in literature.

Rhodanine (RD) is common subunit in many pharmaceutical agents. It has been demonstrated to chelate metal ions, most notably Ag(I), and Cu (I) and Cu(II). It is has been studied as a corrosion inhibitor for Cu. In this dissertation, SERS was used to characterize the time dependent and potential dependent interactions of RD with Cu electrode surfaces to better elucidate the mechanism for inhibition. RD has greater corrosion inhibition than BTA at the same concentration, and this protection increases with time. The time dependent SERS spectra showed a marked decrease in intensity after 1 h which is attributed to formation of thick films opaque to the laser line. Atomic force microscopy (AFM) showed that films were 100 nm thick after 1-2 h incubation time.

Levelers are used in electrodeposition of Cu to promote bottom up fill of features created on Si chips to connect devices. They work by passivating the surface thus promoting deposition within features rather outside. In the best case, leveler concentration is used to tune the plating potential. Previous work showed that pH 1 benzyldimethylhexadecyl ammonium chloride (BDAC) best served this function of tuning potential when compared to two other candidates, dodecyltrimethyl ammonium bromide (DTAB), and thonzonium bromide (ThonB). At pH 3, however, ThonB is best at tuning the plating potential with concentration. Using SHINERS we show that potential dependent behavior is observed for ThonB at low concentration whereas there is little to no corresponding behavior of DTAB or BDAC. BDAC strongly at both low and high concentrations whereas DTAB does not interact strongly with Cu surface at any of the three the concentrations used.
Ni superalloys are typically used in aggressive environments (high temperatures and pressures, corrosive liquids such as those present for jet turbines, chemical processing plants, and in ductwork and heat exchangers for nuclear plants). They form a scale in high temperature oxidizing environment composed mostly of Cr and the other oxophilic elements in the alloy that protects the bulk alloy from oxidative damage. Investigating how long term heat treatment affects the electrochemical behavior and speciation has implications towards their use in nuclear reactor components. Heat treatment positively affected the corrosion resistance which corresponded with different product speciation, specifically with regards to the appearance of reduced Cr species.
To my parents
ACKNOWLEDGEMENTS

The completion of this dissertation would not have been possible without the guidance of my advisor Professor Andrew A. Gewirth. He gave me inspiration for my projects, offered advice when I was stuck, and allowed me to circuitously end up with my thesis research.

I thank my former labmates Karen Stewart, Scott Shaw, Andrew Campbell, Jeremy Hatch, Matt Thorum, and Matt Thorseth (the final countdown) for showing me the ropes around lab and being open to discussing all sorts of things during lunch. I know now for instance, that it usually helps to press the ‘on’ button when I want the potentiostat to work.

I thank Joe Buthker for politely enduring my daily nattering about this, that and the other thing. Without your calming influence I doubt I would have survived for long at my desk. I also enjoyed sharing my grad school journey with Brandon Long and Dennis Butcher.

Of course I appreciate Claire Tornow for becoming my friend after that initial year of distrust. Her cheery nature and can do attitude were critical to my maintaining a semblance of sanity. Thanks for listening to the rant and ravings of a near lunatic. I loved being introduced to the world of fiber arts; stitching and bitching was a definite good experience. I also felt somewhat helpful when answering the occasional question about instrumental setup. You definitely made me feel welcome at your desk, despite my many hours of bugging you. I appreciate it.

Thank you Adele, Laura and Jen for upping the female-to-male ratio. It’s great to have estrogen in lab. I hope you continue the trend. I also appreciated Professor Gulfeza Kardas who infused joy and productivity into what otherwise would be a relatively uneventful summer.
I also thank my Suslick lab compatriots Rachel, Brad, John, Sandra, Maryam, and Jin Rui. I’ve enjoyed our many hours of witty or banal banter.

MRL staff made learning about new instrumental skills easy and enjoyable. Their insights were invaluable for my projects.

My boyfriend Matthew Small listened to all my trials and tribulations with my research and injected my life with a bit of rationality. He is one of my role models, and I will always be envious of his ability to focus on research and come up with his own pet projects, all the while doing endurance events with Jessica Klinkenberg.

My parents support provided me with the grounding I required to stay the course for grad school and my brothers allowed me to view grad school from a different perspective.
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CHAPTER 1: GENERAL INTRODUCTION

Techniques used to investigate corrosion

Corrosion inhibition is important for maintenance of infrastructure (primarily piping for liquid transport and structural materials) and in the microelectronics industry. It is typically achieved through formation of passivating films on the metallic surface that prevents oxidation of a bulk metal, either by formation of an oxide from sacrificial agents in an alloy, or by deposition. In the US $276 billion is spent each year controlling corrosion damage.\(^1\) Corrosion damage generally falls under two categories: uniform or localized corrosion. In uniform corrosion, the material does not form a passive layer in its environment and is freely oxidizing. Localized corrosion happens when the passive layer is non-uniform and the less protected areas are attacked.\(^2\) This initial attack can be self propagating and result in pit and crevice formation on the surface of the material which can further propagate until the material fails.\(^2\) Stress corrosion cracking is a synergistic affect where stresses to the material, combined with environmental factors, initialize local corrosion forming pits or crevices.\(^2\)

One way to investigate corrosion inhibition is with electrochemical measurements. These typically involve a three-electrode setup with a working, counter and reference electrode. Linear sweep voltammetry, wherein a linear ramp of potential is applied to the working electrode relative to the reference electrode and the current response between the working and counter electrode is measured, allows for determination of the electrochemical window of passivation with anodic (oxidative) and cathodic (hydrogen evolution for aqueous solution) breakdown of the passivation layer occurring at the end potentials.\(^3\) Dampened current densities and more positive anodic oxidation potentials are the desired characteristics for a passive layer.\(^4\)
AC Impedance, a sinusoidal potential wave is applied to the working electrode and the current response measured, allows one to model the passive layer as an electrical circuit with resistors representing the electrode polarization resistance and solution resistance and a capacitor from the film and electric double layer. These values allow for determination of the resistivity and capacitance of the film, which give an idea of surface coverage as well as film thickness. Inhibition efficiency, shown in equation 1.1, is determined from the resistance of a passivated electrode relative to that of an unprotected electrode. It along with, film resistance, anodic corrosion current and potential are the typical figures of merit for passivation films.

\[ \eta \% = \left( \frac{R_p'}{R_p} \right) \times 100 \]  

(1.1)

Where \( \eta \% \) is the inhibition efficiency, \( R_p' \) is the polarization resistance of a passivated electrode and \( R_p \) is the polarization resistance of an unprotected electrode.

**Figure 1.1.** Equivalent circuit diagram for electrical double layer.

Although electrochemical experiments give one an idea of the protective ability of the passivating film, it does not allow for determination of the chemical composition of the film nor the mechanism of film formation. Surface Enhanced Raman Spectroscopy allows one to obtain vibrational information of analytes at or near the electrode surface in aqueous solutions. Interrogation of film behavior, before and after cathodic or anodic breakdown potentials, is then possible.
Raman spectroscopy involves exciting a sample with monochromatic light and collecting the inelastically scattered light (typically Stokes shift). The selection rule for Raman scattering is a change in polarizability (equation 1.2). Since the typical scattering coefficient for molecules is very small (~$10^{-30}$-$10^{-25}$ cm$^2$/molecule), normal Raman is only useful for very concentrated samples, not the low concentrations (ppm) typically used for corrosion inhibition.

Also, the molecules of interest are associated at or near the electrode surface, meaning that probing the solution will have limited significance. Therefore, enhancement of signal at or near the electrode surface is necessary to probe the electrode electrolyte interface and thus interrogate passivating film formation.

$$\alpha = \frac{\mu_i}{E}$$  \hspace{1cm} (1.2)

Where $\alpha$ is polarizability of a bond, $\mu_i$ is the induced dipole moment, and $E$ is the electric field.

When a coinage metal (Ag, Au, Cu) has features smaller than the wavelength of scattered light, the localized surface plasmon can be excited which produces an enhancement of the signal corresponding to molecular vibrations occurring at or near the feature surface (eqn 1.3 and 1.4). There is also a two-fold enhancement from direct chemical bonding of the molecule of interest to the substrate. Since the enhancement from both contributions are confined near the surface of the metal, probing of the electronic double layer is guaranteed.

$$|E_{out}|^2 = E_0^2 [1 - g^2 + 3 \cos^2 \theta (2 \text{Re}(g) + |g|^2)]$$  \hspace{1cm} (1.3)

Where Raman intensity is $|E_{out}|^2$, $\theta$ is the angle between the incident field vector and that of a molecule at the surface of a particle.
\[ g = \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + 2\varepsilon_{out}} \]  

(1.4)

Where \( \varepsilon_{in} \) is the dielectric constant of the metal particle and \( \varepsilon_{out} \) is the dielectric constant of the outside environment. Maximum enhancement occurs when the denominator of \( g \) approaches 0.

There are many surfaces of interest related to corrosion that are not coinage metals and examining films on unaltered materials would give valuable information to corrosion mechanisms at single crystal faces. Strategies commonly used to obtain enhancement from non-enhancing substrates include: deposit surface of interest onto nanostructured SERS substrate (difficult and there is contribution from SERS substrate due to limitation of thin deposition as signal drops off exponentially with distance), deposition of coinage metal particles onto surface of interest (which can give confounding signals), and tip–enhanced Raman (TERS) in which a nanoparticle is used as the Raman probe and can simultaneously give topographical information. Of these strategies, TERS is most desirable because of the dual modes; however, a few challenges prevent wide use of the technique. One is that the signal is very small. Many models have been used to predict the field of enhancement; however, and promise with the three-dimensional finite difference time-domain (3D-FDTD) method in particular. \(^{13-14}\) Another is that producing tips that give reproducible signal enhancement is difficult. Once a reliable tip is produced it is susceptible to fouling as is already a problem for STM or AFM measurements. Taguchi et al have had moderate success coating Si tips with Al\(_2\)O\(_3\) to examine crystal violet and adenine.\(^{15}\)

Tian developed a technique called Shell-Isolated Nanoparticle Enhanced Raman Spectroscopy (SHINERS) which expands upon the TERS concept.\(^7\) Au\(^7\) or Ag\(^14\) nanoparticles
serve as ‘probes’ and are coated with a thin layer of metal oxide consisting of SiO$_2$, AlO$_3$, or MnO$_2$ that prevents direct contact with the electrode and analyte of interest. Using these particles allows for investigation of atomically flat electrodes and the signal from the particles in amplified by the number of particles. Spectra of pyridine, thiosulfate, and carbon monoxide at various single crystal faces have been obtained using SHINERS. A scheme of SHINERS setup is pictured in Figure 1.1. This opens up a new range of systems that can be studied with Raman spectroscopy.

![Figure 1.2. Cartoon of Shell Isolated Nanoparticle Enhanced Raman at a Cu(111) face electrode with Benzotriazole-Cu(I) dimer adsorbed.](image-url)
**Benzotriazole**

1,2,3-Benzotriazole (BTA) is a common corrosion inhibitor for Cu and Cu alloys.\(^{17}\) It is used in the microelectronics industry for chemical-mechanical planarization slurries as well as in Cu plating baths.\(^{18}\) Cotton first researched BTA as a viable corrosion inhibitor in the 1960’s and expected the BTA worked as a physical barrier when complexed with Cu and Poling confirmed the proposed structure of the film with IR (BTA-Cu(I)).\(^{19-20}\) BTA has a protection efficiency of about 90\% in concentrated sulfuric acid solutions; protection efficiency increases with increasing pH.\(^{17}\) The general understanding gathered from FTIR,\(^{20-23}\) SERS,\(^{22, 24-40}\) X-ray photoelectron spectroscopy (XPS),\(^{41-48}\) and quartz crystal microbalance (QCM),\(^{49-52}\) for the mechanism of film formation of BTA is that BTA forms a stable adlayer spontaneously when exposed to Cu surfaces. When Cu ions are released from the surface, BTA may also form an organometallic layer that prevents diffusion of oxidants to the Cu surface.

Calculations have shown that deprotonated BTA forms a more stable adlayer than the neutral BTAH which correlates well with its increased inhibition efficacy at higher pH (BTA has a pK\(_a\) of 8.2), also deprotonated BTA\(^{-}\) competes with Cl\(^{-}\) for surface sites.\(^{48, 53-54}\) Calculations also show that the organometallic complex of BTA with Cu forms even more stable adlayers on the Cu than the deprotonated monomer along with forming a densely packed layer that protects the Cu surface from chemical attack.\(^{52-55}\)

Mayanna and Setty demonstrated that BTA also has face dependent efficiency\(^{56}\) in the order 100>110>111. This trend corresponds to the relative disorder of BTA adlayers formed on Cu(111) versus Cu(100) shown in STM\(^{57-60}\) and verified with sum frequency generation (SFG) by Schultz et al.\(^{61}\) Although the PMIRRAS spectra show no difference between the crystal faces, the spectra showed that the BTA films formed by anodic polarization of the Cu electrode were
irreversible even at potentials where hydrogen evolution occurs which physically disrupts the film.\textsuperscript{21} This contradicted SERS studies by Chan and Weaver who observed electrochemically reversible features in spectra.\textsuperscript{30}

**Rhodanine (RD)**

Rhodanine (RD, 4-thiazolidinone-2-thione) is a sulfur-containing N,O-heterocycle which, when derivatized, serves many manufacturing and pharmaceutical purposes.\textsuperscript{62-64} It chelates metal ions\textsuperscript{65} and has been used to detect heavy metals in solution.\textsuperscript{66} RD has two thiol groups and an amino group which are both known to interact strongly with metal surfaces. This along with its ability to chelate metal ions makes it a great candidate as a corrosion inhibitor.

![Rhodanine structure](image)

**Figure 1.3.** Rhodanine structure.

RD has been demonstrated to have good corrosion protection for mild steel\textsuperscript{67-68} and Cu\textsuperscript{69-70} and was patented for use as a leveler in 1952.\textsuperscript{71} Although there have been many structural studies for RD\textsuperscript{72-77} (due to its pharmaceutical benefits) few studies have been performed examining the RD metal interaction\textsuperscript{78-79} and none have investigated the influence of potential on the vibrational modes of RD.

**Levelers in the standard Cu plating acid bath**
Electrodeposition is currently used to create Cu interconnects which connect devices on Si chips.\textsuperscript{80-81} The standard plating bath consists of an aqueous solution of sulfuric acid which imparts sufficient conductivity to the solution and removes oxide from the electrode surface, CuSO$_4$ as the Cu ion source, chloride which reduces the anode polarization and acts in conjunction with the suppressor and accelerator systems, and organic additives.\textsuperscript{80, 82-83} There are three types of organic additives used in plating bath solutions for optimal Cu deposition to create interconnects that fill features on the wafer: 1) suppressors (or carriers) which are polyethylene glycols; 2) accelerators (or brighteners) containing thiol or disulfide groups and sulfonic acid groups; and 3) levelers generally surfactants with amine functionality.\textsuperscript{84} Accelerators are thought to enhance deposition at the bottom of features in the presence of levelers and allow for high aspect ratio feature filling also known as superconformal filling.\textsuperscript{85-92} Carriers and levelers promote even plating across the field of the chip by increasing the electrodeposition overvoltage.\textsuperscript{81} Levelers prevent overfill bumps by associating with the surface and competing with the accelerators promoting an even deposit across the plane of the chip.\textsuperscript{80, 82-83, 93-94} This three component system allows for the efficient void-free filling of features, and generally results in a relatively flat coating that requires minimal processing after electrodeposition of interconnects.

It is important to know how these different additives interact with the electrode surface in order to engineer additives with superior plating performance. SERS and SHINERS offer a convenient, non-intrusive way to conduct \textit{in-situ} monitoring of surface specific interactions and gives an idea of how these additives orient with respect to the electrode surface and facilitate - or impede - Cu plating. SERS has been used to investigate interaction of additives with Cu surfaces both with and without the presence of Cu ions.\textsuperscript{94-105} Previously, it was determined that potential
induced orientation of quaternary ammonium salts (referred to as “quat salts”) at low concentration corresponded to the ability to tune the Cu plating potential with concentration of the leveler.\textsuperscript{94} Janus Green B is a typical leveler used in the damascene process and is known to undergo potential driven orientation.\textsuperscript{97, 106-107}

**Passive oxide formation on Ni based alloys**

Generation IV nuclear reactors such as the Very High Temperature Reactors (VHTR) present a materials challenge because they will utilize higher temperatures and pressures for increased efficiency in electricity production.\textsuperscript{108-109} Reactors that run at higher temperatures will also have the capacity for thermochemical water splitting to produce hydrogen which is (currently) easier and cheaper to store than electricity.\textsuperscript{109-110} Electrochemical and thermochemical water splitting can utilize the excess heat of high temperature reactors to generate H\textsubscript{2}.

Because thermochemical systems only require heat to proceed, they are the more favorable candidates for H\textsubscript{2} generation with nuclear generators.\textsuperscript{109} The sulfur-iodine cycle, in which SO\textsubscript{2} and I\textsubscript{2} are used to spilt water, is a favorable candidate because of the simplicity of separating the H\textsubscript{2} and O\textsubscript{2} evolving components and recyclability of inputs.\textsuperscript{109} Stress corrosion cracking (SCC) is a major concern for failure because of the high temperatures and pressures required for the reactors to run.\textsuperscript{111-114}

Haynes 617 (Ni-Cr-Co-Mo) and Haynes 230 (Ni-Cr-W-Mo) are solid-solution strengthened Ni-based alloys developed as high temperature and corrosion resistant materials.\textsuperscript{115-117} They currently under consideration for use in components of generation IV reactors such as tubing and heat exchangers.\textsuperscript{116, 118-120} Corrosion resistance is imparted on the alloy through
formation of a passive oxide composed primarily of \(\text{Cr}_2\text{O}_3\). The effect of high temperature on the alloys’ electrochemical behavior has important implications for use in components for VHTRs.

References

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CHAPTER 2: EXPERIMENTAL

Reagents

Chemicals were reagent grade and used as received. All solutions were prepared using ultrapure water (Milli-Q UV plus, Millipore Inc., 18.2 MΩ cm) and H$_2$SO$_4$ (Ultrex II, J. T. Baker). Corrosion inhibitors were rhodanine (RD) (99%, Sigma Aldrich) and Benzotriazole (BTA) (98%, Sigma Aldrich). Leveler solutions were made with dodecyltrimethyl ammonium bromide (DTAB), thonzonium bromide (ThonB) and benzyltrimethylhexadecyl ammonium chloride (BDAC), and Na$_2$SO$_4$ (99.999%) and CuSO$_4$ (99.999%) from Sigma Aldrich.

Raman experiments

Raman experiments were performed using an in-situ cell described previously.$^1$ Potential control was maintained with a CV-27 potentiostat (BAS). The He–Ne laser (λ=632.8 nm) was projected onto the sample at ~45° incidence. Scattered radiation was collected with F/4 focusing lens and focused at the entrance slit of a monochromator. A 1200 grooves/mm grating dispersed radiation onto a cooled charge-coupled device (CCD, Andor). Typical acquisition time was 30 s.

Electrodes for Surface Enhanced Raman Spectroscopy (SERS) measurements were polycrystalline Cu disks (1 cm diameter, Monocrystals Inc.) prepared by polishing to 0.3 um grit Al$_2$O$_3$ and then electrochemically roughening in 0.1 M KCl with a Au wire counter electrode and Ag/AgCl reference electrode. After roughening, electrodes were held at -0.56 V and then rinsed with copious amounts of ultrapure water. $^2$ Raman cell setup was described previously. $^1$ Potential was controlled with a CHI 760D potentiostat (CH Instruments). The He–Ne laser (λ = 632.8 nm) was projected onto the sample at 45° incidence. Scattered radiation was collected with an f /4 focusing lens and focused at the entrance slit of a monochromator. A 1200 grooves/mm
grating dispersed the radiation onto a cooled charge coupled device (CCD, Andor). The typical acquisition time was 30 s.

Shell-isolated nanoparticle enhanced Raman preparation

Silica-coated gold sols were synthesized as described in the literature,\(^3\text{-}^5\) a brief explanation follows. A gold sol with 18 nm diameter particles was synthesized by using sodium citrate reduction. The particles were coated with (3-Aminopropyl)trimethoxysilane (APS) and a 1-2 nm film of silica on the gold particles was created by immersing the APS-coated particles in an aqueous solution containing 0.54 wt% sodium silicate that left stirring for 2-3 days. Excess reagents and side products were removed by dialysis. TEM confirms the gold particles have an average diameter of 18 nm with 1-2 nm thick silica shell. [insert tem]

SHINERS measurements were performed at room temperature using an in-situ cell described previously\(^6\) with a Au wire counter electrode and Ag/AgCl reference electrode. The excitation line was a HeNe laser (632.8) impinging the surface at a 45° angle. Scattered light was collected with an air cooled CCD. Typical acquisition time was 30 s.

Preparation of single and polycrystalline Cu disks for SHINERS experiments

The working electrodes were 1 cm diameter Cu(111) and Cu(100) single crystals (Monocrystals Co.). Surface orientation of the crystals was verified by four-circle XRD. Crystals were mechanically polished to a 0.25 μm grit size (Metadi Supreme diamond suspension, Buehler) and electropolished in 50% w/v phosphoric acid at 2 V versus a Pt counter electrode for 30 s. After electropolishing, the crystals were rinsed with Millipore water and dried under Ar. A film of SiO\(_2\)-coated gold particles was made by drop casting 50 μL of the suspended
particles onto the crystal and drying under Ar. Polycrystalline Cu disks were also used as working electrodes. They were prepared as above except the electropolishing solution was 85% w/v phosphoric acid. For comparison, the polished disks were also electrochemically roughened as described in Chan and Weaver.\(^2\) Alternatively, polished disks were used for shiners experiments without the electropolishing step for leveler study.

**Preparation of Inconel 617 and Haynes 230 disks**

Plates of alloy 617 and alloy 230 (made by were hot working and solution treatment at 1177 °C) were supplied by Haynes International.\(^7\) Composition of the as-received alloys are described in Mo et al.\(^7\) Discs (2-3 mm thick) were cut from plates. Some plates were aged in laboratory air at temperatures of 900 °C and 1000 °C for 3000 h. The disks were used as the working electrodes and were polished to mirror finish with 0.3 um Al\(_2\)O\(_3\) and were sonicated in ultrapure water then rinsed with copious amounts of ultrapure water before use in experiments.

**Electrochemical experiment setup**

Electrochemical experiments were performed using a CHI 760D potentiostat (CH Instruments) with a two component cell, Pt gauze counter electrode, and “no leak” Ag/AgCl reference electrode (Cypress). Working electrodes were held in place with Kel-F collets screwed into a rotating disk shaft connect to a modulated speed rotator (Pine Research Instrumentation). Electrochemistry was performed using a CHI760C or CHI 760D potentiostat (CH Instruments). Electrochemistry was performed in a two-compartment glass cell with Au wire counter electrode separated from working electrode compartment by glass frit and a Ag/AgCl “no-leak” (Cypress) reference electrode connected to working electrode compartment by Luggin capillary.
Electrochemical measurements were performed in a three electrode cell using a CHI760C or CHI 760D potentiostat (CH Instruments). A ~1 cm Cu (poly) disk (Monocrystals Inc.) was used as the working electrode for cyclic voltammetry, impedance versus potential measurements, and plating experiments. A carbon rod was used as the counter electrode and a Ag/AgCl electrode connected via a salt bridge was used as the reference. Solutions were purged with Ar before use for 1 h, and an Ar atmosphere was maintained in the cell during all electrochemical measurements. The electrodes were maintained in the hanging meniscus configuration. Plating experiments were performed with the crystal attached via a collet to a rotator (Pine Instruments MSRX Speed Control) and performed at a rotation rate of 120 rpm.

**X-ray photoelectron spectroscopy (XPS)**

XPS experiments were performed with an Axis ULTRA spectrometer (Kratos Analytical). A monochromatic Al X-ray source was used with a 150 W source power, a 1000 meV step energy, and a 100 ms dwell time for two sweeps. Data were calibrated to a C 1s peak.

**Atomic force microscopy (AFM)**

AFM images were obtained in acoustic mode using a PicoSPM 300 (Molecular Imaging) device controlled by a Nanoscope E controller (Digital Instruments). Si probes with a resonant frequency of 300 kHz and force constant of 40 N/m were used for both imaging and scraping (Tap300Al-G, Budget Sensors). Images were collected at a scan rate of 2.98 Hz and were further analyzed with WSxM 3.0 (Nanotec Electronica) and OriginPro 8.5 (OriginLab). For AFM film thickness measurements, the inhibitor film was formed by immersing the Cu(111) crystals in a solution of 10 mM rhodanine and 0.5 M H₂SO₄. At the desired incubation time, a Cu crystal was
removed from the solution and immediately placed in the AFM cell for imaging. A solution of 0.5 M H$_2$SO$_4$ was used for imaging to prevent the surface film from reforming. The surface was first imaged *in situ* in acoustic mode to find a smooth area. Moving into a smaller area, the surface was then scraped in contact mode for several minutes to remove the Cu-inhibitor film. An image of the scraped area was obtained again in acoustic mode and the depth of the film measured directly by using available bearing analysis software.

**Calculations**

Optimal geometries for three oxidation states of rhodanine with water solvation were constructed by using the Spartan 08 program (Wavefunction, Inc) using a restricted Hartree-Fock SCF calculation with Pulay DIIS and Geometric Direct Minimization method and a 3-21G* basis set. After energy minimization, the Spartan program was utilized to find the normal modes and frequencies for the anion, cation and neutral rhodanine molecules.

**References**

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CHAPTER 3: SHELL-ISOLATED NANOPARTICLE ENHANCED RAMAN SPECTROSCOPY OF BENZOTRIAZOLE FILM FORMATION ON Cu(100), Cu(111) AND Cu(POLY)

Introduction

Corrosion inhibition is important in processing metals submersed in oxidizing solutions. 1,2,3-Benzotriazole (BTAH) is a common additive in polishing slurries and plating baths because of its ability to inhibit corrosion of Cu and its alloys.\(^1\) The general understanding of the mechanism of inhibition gathered from FTIR\(^2\)\(^-\)\(^3\) and SERS\(^4\)\(^-\)\(^6\) is that when Cu ions are released from the surface, a coordination polymer of Cu(I) and BTA\(^-\) forms that prevents further oxidation.

Benzotriazole exhibits face dependent corrosion efficiency that goes in the order 100>110>111.\(^7\) In aqueous sulfuric acid solutions, STM\(^8\)\(^-\)\(^10\) studies have shown that a sulfate layer forms on the Cu surface that serves a template for BTAH adsorption. The BTAH layer on the Cu(100) face is highly ordered whereas the BTAH layer on Cu(111) is highly disordered. The disorder of the BTAH film is attributed with decreased corrosion inhibition on the 111 face.

One major issue regarding the BTA film concerns the reversibility of its formation. On this

\(^1\)This chapter appeared in its entirety in the Journal of Raman Spectroscopy as Honesty, N. R.; Gewirth, A. A. “Shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) investigation of benzotriazole film formation on Cu(100), Cu(111), and Cu(poly)” \textit{J. Raman Spectrosc.} \textbf{2011}, \textit{43} (1), 46-50. Copyright 2011, John Wiley & Sons, Ltd. This article is reprinted with the permission of the publisher and is available from \url{http://onlinelibrary.wiley.com} and using DOI: 10.1002/jrs.2989. This work was funded by the National Science Foundation.
issue, SFG$^{11}$ and IRRAS$^2$ measurements, along with the QCM$^{12,13}$ all agree that the BTA film formation is irreversible. Such is not the case with numerous SERS studies, obtained from polycrystalline Cu, which exhibit reversible BTA film formation.

Reversible BTAH physisorption$^{14,15}$ is known to occur at concentrations below 0.17 mM which is the critical concentration for effective inhibition, however the studies mentioned above use concentrations well above this concentration. Concentration of BTAH also affects the corrosion mechanism. When polycrystalline Cu electrodes are anodically polarized in NaCl solutions, intergranular corrosion occurs at low BTAH concentrations (1 mM) and pitting occurs at greater concentrations of BTAH.$^{16}$

One reason that SERS measurements might show reversible behavior while those from IRRAS and SFG do not is that the SERS measurements are performed on polycrystalline materials while the former use single crystals. The use of single crystals in a SERS experiment is difficult, since the plasmon mode giving rise to the SERS single is enhanced on a roughened surface. The roughened surface also raises issues regarding the origin of the SERS signal, as asperities (“hot spots”) where the $E$ field is high might behave differently from the balance of the surface. In 2011, Tian reported an elegant way to study single crystal surfaces called Shell-Isolated Nanoparticle Enhanced Raman Spectroscopy (SHINERS).$^{17,18}$ With SHINERS the signal enhancement comes from silica-encapsulated gold particles deposited onto the surface of interest. The gold particles provide the enhancement, while the silica shell performs prevents agglomeration of the particles and direct interaction of the gold with the surface of interest. This eliminates the need for the surface to be SERS active and allows for the direct investigation of single crystal electrodes. We revisit BTA film formation to ascertain whether this process is reversible or irreversible in Raman measurements.
Results and Discussion

In voltammetry, although there are minimal differences for the onset hydrogen evolution on different faces,\textsuperscript{2, 19} crystallographic orientation has no significant effect on kinetics of Cu dissolution in BTAH containing H\textsubscript{2}SO\textsubscript{4} solutions.\textsuperscript{8} Figure 3.1 shows the cyclic voltammograms of particle coated single crystal copper surfaces. The particle coating does not appear to affect the onset of hydrogen evolution or Cu dissolution relative to literature.\textsuperscript{8, 10, 19}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{voltammograms.png}
\caption{Cyclic voltammograms of particle-coated Cu(100), Cu(111), Cu(poly), and roughened Cu(poly) in 75 mM BTAH, 0.1 M H\textsubscript{2}SO\textsubscript{4} at a 50 mV s\textsuperscript{-1} scan rate. Raman spectra from solid BTAH, an aqueous solution consisting of, 0.75 mM BTAH + 0.1 M H\textsubscript{2}SO\textsubscript{4}, SERS of Cu(poly) and SHINERS from Cu(111), Cu(100) and Cu(poly) are displayed in.}
\end{figure}
Figure 3.2. These spectra display a number of peaks which match those assigned by Chan and Weaver\textsuperscript{4} (Table 3.1). Differences between the SERS obtained from the solid surfaces and aqueous and solid BTAH are similar to those described previously.\textsuperscript{4-6, 20-23} The spectra obtained from single crystalline Cu strongly resemble that of polycrystalline Cu, except for the relative intensity of the modes between 1100 cm\textsuperscript{-1} and 1200 cm\textsuperscript{-1} and the breathing modes at 785 cm\textsuperscript{-1} and 1390 cm\textsuperscript{-1}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Raman spectrum, of solid BTAH, 75 mM BTAH, 0.1 M H\textsubscript{2}SO\textsubscript{4}, 75 mM BTAH, 0.1 M H\textsubscript{2}SO\textsubscript{4} on Cu (100) at -0.7 V vs. Ag/AgCl, same on Cu(111), same on polycrystalline Cu, and the same on roughened polycrystalline Cu. Intensities are normalized to the 785 cm\textsuperscript{-1} mode.}
\end{figure}
Table 3.1. Peaks (cm\(^{-1}\)) and their assignments for spectra shown in Figure 1.

<table>
<thead>
<tr>
<th>Vibrational frequencies/cm(^{-1})</th>
<th>solid BTAH</th>
<th>solution BTAH</th>
<th>Cu(100)</th>
<th>Cu(111)</th>
<th>Cu(poly)</th>
<th>roughened Cu(poly)</th>
<th>Chan and Weaver(^d)</th>
<th>Band Assignments(^{4,6})</th>
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<td>235</td>
<td></td>
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<td></td>
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<td>428</td>
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<td>549</td>
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</tr>
<tr>
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<td>627</td>
<td>626</td>
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<td>785</td>
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<td>993</td>
<td>978</td>
<td>976</td>
<td>982</td>
<td>974</td>
<td></td>
<td></td>
<td>SO(_4) symmetric stretch</td>
</tr>
<tr>
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<td>1013</td>
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<td>1019</td>
<td>1010</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>1045</td>
<td>1046</td>
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<td></td>
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<td>1148</td>
<td>1134</td>
<td>1145</td>
<td>1140</td>
<td></td>
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<td>1193</td>
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<td>1190</td>
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<td>1286</td>
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</tr>
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<td>1370</td>
<td></td>
<td>F. R. with 1385</td>
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<td>1385</td>
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<tr>
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<td></td>
<td>1443</td>
<td>1444</td>
<td>1444</td>
<td>1440</td>
<td></td>
<td></td>
<td>skeletal stretch</td>
</tr>
</tbody>
</table>
Figure 3.3 shows potential dependent spectra obtained for all three of the surfaces considered. The spectra display the same peaks for all surfaces at roughly the same energy and respond similarly to potential changes. As the potential is swept in the anodic direction, the 1020 cm\(^{-1}\) mode and 1190 cm\(^{-1}\) mode increase in intensity relative to neighboring peaks. This difference in intensity remains as the scan changes direction for the single crystal faces but disappears for the polycrystalline Cu. For better comparison of the surfaces Figure 3.4 has an overlay of spectra obtained from the three surfaces considered here at three different potentials: the starting potential of -0.7 V, a potential where dissolution of Cu is prevalent at 0 V, and back to -0.7 V after the cathodic sweep. The spectra from the three surfaces are similar except for differences in relative intensity in the 1100-1200 cm\(^{-1}\) region where three peaks have been assigned by Chan and Weaver: 1140 cm\(^{-1}\) which is a NH in-plane bending mode assigned by Youda et al\(^6\), 1160 cm\(^{-1}\) associated with a combination of the asymmetric triazole stretching and NH bending modes, and 1190 cm\(^{-1}\) the combination mode associated with deprotonation of BTAH.\(^{22}\) The 1140 cm\(^{-1}\) mode is typically associated only with surface associated BTAH, while the 1190 cm\(^{-1}\) mode is associated with the BTA-Cu film arising as a consequence of anodic oxidation of BTA on Cu.\(^6,23\) When the potential is swept in the anodic direction, the 1190 cm\(^{-1}\) peak increases in intensity relative to neighboring peaks for all three surfaces. As the potential is swept in the cathodic direction the 1190 cm\(^{-1}\) peak continues to increase in intensity for the 111 and 100 faces but decreases for the polycrystalline face.
Figure 3.4. Potential dependent spectra for Cu(100), Cu(111), and polycrystalline Cu in 75 mM BTAH, 0.1 M H₂SO₄ for the anodic sweep (a), (c), (e), and (g) and the cathodic sweep (b), (d), (f), and (h). Spectra are offset for clarity. Arrows indicate scan direction.
Figure 3.5. Potential dependent Raman spectra obtained on Cu(100) (a), Cu(111) (b), polycrystalline Cu (c), and roughened polycrystalline Cu (d) in 75 mM BTAH, 0.1M H₂SO₄ at -0.7 V on the cathodic sweep (top), 0 V vs. Ag/AgCl (middle) and -0.7 V vs. Ag/AgCl on the anodic sweep (bottom). Spectra are offset for clarity.
Figure 3.6 displays the relative peak intensity of the 1190 cm$^{-1}$ mode versus the 1140 cm$^{-1}$ mode. The 1190 cm$^{-1}$ mode is associated with deprotonated BTA, whereas the 1140 cm$^{-1}$ mode is assigned to the NH bending mode of adsorbed BTAH. An increase in the 1190/1140 ratio is thus associated with growth of the BTA(Cu$^+$) film. Fig. 5 shows that this ratio increases for both single crystals surfaces from start of potential scanning at -0.7 V to the anodic limit of the scan. The ratio stops increasing on the Cu(100) face at about -0.2 V and remains constant as the potential is swept in the cathodic direction. However, the ratio for Cu(111) continues increasing as the potential is swept in the cathodic direction until -0.3 V when it plateaus. The ratio for polycrystalline surface does not start increasing until -0.3 V, grows substantially until the anodic limit of the scan, remains stable as the potential is swept in the negative direction, and then falls after -0.4 V to the initial ratio. Thus, all three surfaces exhibit different film growth behavior.
**Figure 3.6.** Potential dependent ratio of peak intensities for 1190 cm$^{-1}$/1140 cm$^{-1}$ for Cu(100) (a), Cu(111) (b), Cu(poly) (c), and roughened Cu(poly) in 75 mM BTAH, 0.1 M H$_2$SO$_4$. 
The behavior displayed in the SHINERS of the BTA film formed on single crystal Cu here matches that found in other in-situ studies using Cu single crystals. STM,\textsuperscript{8,10} IRRAS,\textsuperscript{2} and SFG\textsuperscript{11} all show that the BTA film persists on the cathodic sweep, while film formation on the polycrystalline surface in sulfuric acid -- as measured in SERS -- is reversible.\textsuperscript{4,6} Thus reversible BTA film formation observed in SERS on Cu seems to be intrinsic to the polycrystalline material used previously\textsuperscript{4,6}.

Why should the SERS signal show reversibility of the film on polycrystalline Cu? First, Cl\textsuperscript{−} -- introduced during roughening of the Cu surface -- could change properties of the BTA film. Many studies have shown that adding Cl\textsuperscript{−}, which competes for surface sites and coordinates to the BTA-Cu film, will promote reversibility.\textsuperscript{2,5,11,24} However, other SERS studies on polycrystalline Cu explicitly avoid roughening in Cl\textsuperscript{−} - containing solution, yet the reversibility persists.\textsuperscript{6} Second, the large number of grain boundaries present on the polycrystalline material might affect the BTA fi lm. Calculations of monomeric BTA and BTA-Cu oligomer chains show that the BTA-Cu chains adsorb more strongly to the Cu surface than monomeric BTA, thus allowing dissolution of the film from defect sites at grain boundaries.\textsuperscript{25-27} Tian suggests that negative potentials both reduce the size of the oligomers and attract sufficient H\textsuperscript{+} to reprotonate coordinated BTA.\textsuperscript{5,24} A similar mechanism is suggested to occur with BTA films with ionic liquids as the solvent.\textsuperscript{28} Disruption at grain boundaries could allow reprotonation to occur on BTA-Cu films formed on polycrystalline Cu.

**Conclusions**
We showed that film formation depend on the face of the Cu crystal exposed. More generally, the SHINERS technique allows information about growth on single crystal surfaces to be obtained.

References

1. Finsgar, M.; Milosev, I., Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. Corros. Sci. 2010, 52 (9), 2737.
15. Jin-Hua, C., Zhi-Cheng, L., Shu, C., Li-Hua, N., Shou-Zhuo, Y., An xps and baw sensor study of the structure and real-time growth behavior of a complex surface film on copper in


CHAPTER 4: SURFACE ENHANCED RAMAN INVESTIGATION OF RHODANINE FILM FORMATION ON COPPER ELECTRODES

Introduction

Rhodanine (RD) is a member of the thiozolidine group which has many industrial and pharmacological applications including dyes\(^1\), antimicrobials\(^2-3\), and as a drug scaffold.\(^4\) Many RD derivatives readily forms complexes with Ag and Cu ions in solution and also forms a film on Ag colloid surfaces.\(^5-7\) Abdallah and others have shown it to have protective capabilities for Cu.\(^8-9\) The protection of the films is attributed to the thiol group which adsorbs strongly to metal surfaces.\(^9\)

Many structural studies of RD have been performed including single crystal x-ray diffraction,\(^10-11\) FTIR,\(^12-15\) Raman spectroscopy\(^5-6, 13\), and DFT calculations.\(^5-6, 13, 16\) It has 11 tautomers, 5 of which are pictured in Figure 4.1. A few SERS studies investigating the adsorption RD on Ag colloids have been undertaken. It was found that RD can make a RD-Ag(I) organometallic complex\(^6\) or a dimerize\(^5\) on the Ag surface.

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\(^{2}\)Work was performed with help from Professor Gülfeza Kardaş and her group at Cukurova University which performed the fitting and interpretation of electrochemical data in Figures 4.2-4.6 as well as the idea for the project.
Although many structural studies have been undertaken with RD and RD complexes, there are few which examine the interaction between RD and metallic surfaces. As of yet, no spectroelectrochemical experiments for RD have been published. In this chapter, we interrogate the electrochemical behavior of RD with roughened Cu and use Surface Enhanced Raman Spectroscopy (SERS) to study RD film formation on the electrode surface. SERS allows for vibrational information from electrode-electrolyte interface to be gathered.

**Electrochemical impedance spectroscopy (EIS) measurements**

Fig. 4.2 shows Nyquist plots for copper in 0.5 M H₂SO₄ solution with and without 10 mM RD and 10 mM BTAH at 0 time. It is clear that the impedance response of copper has significantly changed after immersing in RD and BTAH solutions for 0 min.
Figure 4.2. Anodic polarization curves of Cu electrode recorded in 0.5 M H₂SO₄ solution (▲) and containing 10 mM BTAH (○), 10.0 mM RD (●).

The Nyquist plot of bare copper measured in 0.5 M H₂SO₄ solution displayed an obvious two capacitive loops in high and low frequency regions. The first resistance ($R_1$) corresponds to the oxidation of the metal, after oxidation a copper oxide film forms. When RD and BTAH are added the corrosive media, two capacitive loops were seen in high and low frequencies at beginning of the immersion time. All impedance plots are analyzed in terms of the equivalent circuits shown in Fig. 4.3. Generally these circuits fall into the classical parallel capacitor and resistor combination with the series resistance being that of the bulk solution. $R_s$ represents the uncompensated solution resistance, $R_1$ represents the oxidation of the copper and $R_2$ corresponds
to the copper oxides film resistance for copper in 0.5 M H₂SO₄ solution. In Fig. 5, \( R_f \): oxide (\( R_{ox} \)) and/or film resistance (\( R_f \)), \( R_p \): pore resistance (\( R_{por} = R_{ct} + R_d + R_a \)), \( R_p = R_1 + R_2 \). \( R_p \): polarization resistance, \( R_{ct} \): charge transfer resistance, \( R_d \): diffuse layer resistance, \( R_a \): resistance of accumulated species, \( CPE1 \): oxide/film capacitance, \( CPE2 \): double layer capacitance. \( n \) shows the phase shift which can be explained as the degree of surface inhomogeneity or surface roughness.\(^{17}\) The value of \( n \) is between 0 and 1 (0≤\( n \)≤1). This is related to deviation from the ideal capacitive behavior. \( CPE \) represents a constant phase element to replace a double layer capacitance (\( C_{dl} \)) in order to give a more accurate fit to the experimental results.\(^{18-19}\) The impedance parameters obtained by fitting the EIS data to the equivalent circuit are listed in Table 1. In this case, the inhibition efficiency (\( \eta \)) can be calculated from the polarization resistance using the following formula;

\[
\eta \% = \left( \frac{R_p' - R_p}{R_p} \right) \times 100
\]

(4.1)

Where \( R_p \) and \( R_p' \) are uninhibited and inhibited polarization resistances, respectively.

**Figure 4.3.** The equivalent circuit model for corrosion process of the Cu absence and presence inhibitors. \( R_p = R_1 + R_2 \). \( R_s \): uncompensated solution resistance, \( R_p \): polarization resistance, \( RL \): film resistance (\( R_f \)), \( R2 \): pore resistance (\( R_{por} = R_{ct} + R_d + R_a \)), \( R_{ct} \): charge transfer resistance, \( R_d \): diffuse layer resistance, \( R_a \): resistance of accumulated species, \( CPE1 \): oxide/film capacitance, \( CPE2 \): double layer capacitance.
diffuse layer resistance, $R_a$: resistance of accumulated species, $CPE_1$: film capacitance, $CPE_2$: double layer capacitance.

It is clear that the corrosion of copper is inhibited by the presence of RD or BTAH. As the inhibitor added to 0.5 M H$_2$SO$_4$ solution, the CPE values tend to decrease while the $R_p$ value and inhibition efficiency increase. This suggests that inhibitor molecules are adsorbed on the copper surface, which protects it from corrosion. The inhibition efficiency and surface coverage are 93.8 % and 0.93 for RD respectively.

**Table 4.1.** Electrochemical parameters for Cu electrode corresponding to the EIS data in 0.5 M H$_2$SO$_4$ solution in the absence and presence of 10 Mm BTAH and 10.0 mM RD at 0 min.

<table>
<thead>
<tr>
<th>inhibitor</th>
<th>$R_1$ (Ω)</th>
<th>$n_1$</th>
<th>$CPE_{dl-1}$ ($10^{-6}$)</th>
<th>$R_2$ (Ω)</th>
<th>$n_2$</th>
<th>$CPE_{dl-2}$ ($10^{-6}$)</th>
<th>$R_p$ (Ω)</th>
<th>$\eta$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>10.2</td>
<td>0.76</td>
<td>325.3</td>
<td>10.8</td>
<td>0.58</td>
<td>7542.8</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>BTAH</td>
<td>100</td>
<td>0.72</td>
<td>90.0</td>
<td>57</td>
<td>0.60</td>
<td>2628.4</td>
<td>157.0</td>
<td>80.9</td>
</tr>
<tr>
<td>RD</td>
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<td>363</td>
<td>0.48</td>
<td>652.21</td>
<td>480.0</td>
<td>93.8</td>
</tr>
</tbody>
</table>

In order to examine effect of short immersion time on the corrosion behavior of Cu in 0.5 M H$_2$SO$_4$ solution with the addition of 10 mM RD and 10 mM BTAH, EIS technique was used. Therefore, more reliable results can be obtained from this technique. From short immersion times, it is possible to characterize the surface layer modification, i.e., formation and growth of inhibitor film. Fig. 4.4 and 4.5 show the Nyquist diagrams of Cu in inhibited solutions after
exposure times ranging from 0 to 2 h. The insets correspond to a magnification of high frequencies region. Impedance diagrams obtained in 0.5 M H₂SO₄ were fit to the electrical equivalent circuit presented in Fig. 4.5. The related electrochemical data are collected in Table 4.2. It is apparent from Fig. 4.4, at the high frequency regions, a weak depressed semicircle and at the low frequency regions, a large depressed semicircle is observed in the Nyquist plots of RD or BTAH. The first loop was related to the pore resistance \( R_{por} \), and the second one was attributed to the film resistance \( R_f \). The film resistance becomes the dominant contribution resistances as the formation of the protective RD and BTAH film progresses. After 100 min of immersion in a solution of RD, the high frequency loop disappears and only one capacitive loop is observed in the Nyquist plot. This behavior may suggest the formation of a protective inhibitor film on the copper surface. In presence of RD or BTAH in corrosive media, after 60 min, the polarization resistances for inhibitors were increased to 940 Ω and 1625 Ω from 480 Ω and 157 Ω for RD and BTAH, respectively. The \( R_p \) values increased significantly, which indicated the continuous growth of the surface film with time and the approach in the perfect coverage of the surface film on the metal at the end of the 120 min. The growth of this layer enhanced the corrosion resistance of the metal. The values of film capacitance \( (CPE1) \) and double layer capacitance \( (CPE2) \) decreased with increasing with immersion times for inhibitors. The decrease in \( CPE1 \) is probably due to a decrease in local dielectric constant and/or an increase in the thickness of a protective layer at electrode surface, enhancing therefore the corrosion resistance of the studied copper. The thickness of the protective layer \( (d) \) is related to \( Cdl \) according to the following equation

\[
C_{dl} = \frac{\varepsilon \varepsilon_0}{d}
\]  

\[(4.2)\]
where $\varepsilon$ is the dielectric constant of the protective layer and $\varepsilon_0$ is the permittivity of free space.

**Figure 4.4.** Nyquist plots of Cu electrode obtained in 0.5 M H$_2$SO$_4$ solution (+) and containing 10.0 mM RD (●), 10.0 mM BTAH (Δ) (solid lines show fitted results, the inset corresponds to a magnification of high frequencies region).
Figure 4.5. Nyquist plots of Cu electrodes in 0.5 M H$_2$SO$_4$ solution in the presence of 10.0 mM RD after 0, 60, 80, 100 and 120 min exposure time (solid lines show fitted results, the inset corresponds to a magnification of high frequencies region).
Figure 4.6. Nyquist plots of Cu electrodes in 0.5 M H$_2$SO$_4$ solution in the presence of 10.0 mM BTAH after 0, 60, 80, 100 and 120 min exposure time (solid lines show fitted results, the inset corresponds to a magnification of high frequencies region).
Table 4.2. Electrochemical parameters for Cu electrode corresponding to the EIS data in 0.5 M H₂SO₄ solution in the presence of 10 Mm BTAH and 10.0 mM RD after different immersion time at 25 °C.

<table>
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<tr>
<th>inhibitor</th>
<th>Time (min)</th>
<th>R₁ (Ω)</th>
<th>n₁</th>
<th>CPE₁ (10⁻⁶) Y₀ / 10⁶ sⁿ Ω⁻¹</th>
<th>R₂ (Ω)</th>
<th>n₂</th>
<th>CPE₂ (10⁻⁶) Y₀ / 10⁶ sⁿ Ω⁻¹</th>
<th>Rₚ (Ω)</th>
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<td>29.35</td>
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<td>0.48</td>
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It is apparent from the results that RD and BTAH inhibit the corrosion of copper in 0.5 M H$_2$SO$_4$ solution at 10 mM concentration used in this study. The $R_p$ values were seen to increase continuously with increasing the immersion time for both inhibitors as well (Table 4.2). Better performance is seen in the case of RD, particularly 100 and 120 min immersion times.

**Surface Enhanced Raman Spectroscopy (SERS) investigation of film composition**

Table 4.3 shows Raman peaks from DFT calculation in comparison to calculations done by Jabeen *et al.*\(^{13}\). Spartan calculations the cation, neutral, and anion forms of RD solvated by water were performed to investigate the effect of oxidation state of the inhibitor has on the Raman spectrum.
Table 4.3. Calculations for oxidation states of RD NH tautomer with peak assignments.

<table>
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<tr>
<th>RD+ DFT RB3LYP 6-31G*</th>
<th>RD DFT RB3LYP 6-31G*</th>
<th>RD DFT RB3LP 6-31G*</th>
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<td>117</td>
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<td>A’</td>
<td>out-of-plane ring deformation</td>
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<tr>
<td>71</td>
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<td>158</td>
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<td>out-of-plane ring deformation</td>
</tr>
<tr>
<td>280</td>
<td>251</td>
<td>245</td>
<td>260</td>
<td>A’</td>
<td>C=O, C=S out-of-plane deformation</td>
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<tr>
<td>450</td>
<td>415</td>
<td>408</td>
<td>411</td>
<td>A’</td>
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</tr>
<tr>
<td>504</td>
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<td>C=O stretch C-S stretch C=S stretch in-plane deformation</td>
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<td>547</td>
<td>534</td>
<td>527</td>
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47
Table 4.4. Simulated spectra of RD tautomer A and experimental data.

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<th>RD(^+) DFT RB3LYP 6-31G(^*)</th>
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<th>RD DFT RB3LYP 6-31G(^*)</th>
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48
Figure 4.7 displays SERS results of Cu crystals that were immersed in 0.5 M H₂SO₄ or 10 mM RD and 0.5 M H₂SO₄ for ~1-2 hrs then removed from solution. The spectra for solid RD powder is added to the overlay for comparison. The spectra of Cu disk immersed in H₂SO₄ has a sharp peak at 980 cm⁻¹ assigned to the symmetric stretching of SO₄²⁻ some broad peaks between 200 and 600 are most likely due to Cu oxides as Cu(I) oxides peaks occur at 620, 532, and 445 cm⁻¹ in acidic and neutral solutions²⁴⁻²⁵ The spectra of a Cu disk immersed in a solution RD has an intense peak 1196 cm⁻¹ which has been assigned S=C stretch²⁰, coincident with some modes in RD. RD film formation begins immediately once Cu is introduced as evidenced by intense spectra at time 0 hr.

Figure 4.7. Ex-situ Raman of Cu that were immersed in 0.5 M H₂SO₄ or 10 mM Rd and 0.5 M H₂SO₄ for ~1-2 hrs then removed from solution and solid Rd spectra for comparison.
Figure 4.8 shows the SERS of Cu electrode in 10 mM Rd 0.5 M H\textsubscript{2}SO\textsubscript{4} after 0, 1, and 2 hr. Peaks shown in Table 4.4 coincide with RD peaks found by Ag SERS measurements done by Jabeen et al and Marzec et al.\textsuperscript{5,6} Peaks at 295 and 1216 cm\textsuperscript{-1} indicate formation of Cu-S bonds (Liao et al 247 Cu(II) stretch, 369 Cu(I)-S stretch, 1202 C-S stretch)\textsuperscript{20}. The intensity of all peaks drops dramatically after an hour and even further at 2 hours. Two possible reasons for this drop in intensity are that a thick film develops that is opaque to laser line and thus scattering is unenhanced or surface restructuring removes the asperities that cause enhancement.

Figure 4.8. SERS of Cu electrode in 10 mM Rd 0.5 M H\textsubscript{2}SO\textsubscript{4} after 0, 1, and 2 hr. Intensity is adjusted for comparison in the graph, inset shows unadjusted spectra.
Figure 4.9 shows SERS of a Cu electrode in 10 mM RD 0.5 M H\textsubscript{2}SO\textsubscript{4} as it is anodically polarized. Additional peaks form as surface potential goes above 0.1 V vs Ag/AgCl. In particular an intense sharp peak at 919 cm\textsuperscript{-1} and peaks at 1122 cm\textsuperscript{-1} at 1309 cm\textsuperscript{-1} which the first two are associated with an out-of-plane deformation of C=O, and in-plane deformation of C=O. This is most likely due to RD molecules interacting with Cu ions. RD can chelate Cu\textsuperscript{2+} ions to form a Cu(I)RD species. Formation of the complex is associated with a downshift in the NH and C=O stretches (from 3080 to 2980 cm\textsuperscript{-1} and 1775 to 1765 cm\textsuperscript{-1} respectively) and the appearance of new C=S stretches at 724 and 710 cm\textsuperscript{-1}.\textsuperscript{7} In addition, Kong and Jang found new peaks appeared at 1560 and 1650 associated with C=N and C=C stretching respectively when RD forms a polymer with Ag(I).\textsuperscript{3} The polarization curve displayed in Figure 4.2 shows that the RD film breaks down around 0.25 V, a marked increase in current density occurs at this potential.
**Figure 4.9.** SERS of Cu electrode in 10 mM RD 0.5 M H$_2$SO$_4$ that is anodically polarized with spectral window of 300-1500 cm$^{-1}$.
Table 4.4 shows the calculated spectra for three potential oxidation states of RD along with peaks from RD adsorbed onto Ag for comparison. Certain peaks are lowered in energy with relation to the neural RD molecule so it is reasonable to suggest that some RD exists in a deprotonated state and thus forms a coordination polymer on the Cu surface analogous to that formed on Ag colloidal suspensions. Possible film composition is of organic dimmers or polymers\(^5\), an organometallic oligomer as forms on Ag colloids\(^6\), or a combination of both. A
peak at 1600 would indicate dimer formation but it is not apparent from either the time
dependent or potential dependent spectra.

**Film thickness determination with AFM**

The thickness of the films on the Cu surfaces was calculated from AFM images in which
the tip was used to mechanically remove the film using contact mode. Figure 4.10 shows AFM
images taken in acoustic mode. The dark square region in the middle of the images is where the
film has been removed down to the Cu surface. The ridges at the edges of the squares are most
likely from the deposition of insoluble material removed during the scratching process. The
smooth regions beyond the ridges are considered the surface of the film. The film thickness for
the Cu crystals incubated for both 1 and 2 hours are calculated to have thicknesses near or
exceeding 200 nm. The difference between the thicknesses of the films formed for 1 and 2 hours
is not statistically significant.

![AFM images](image1.jpg)

**Figure 4.11.** Representative AFM images of Cu electrode in 10 mM Rd 0.5 M H₂SO₄ after 1,
and 2 hr
Conclusions

RD is a good corrosion inhibitor relative to BTA with film resistance and protection efficiency that improve with time. This enhancement with time corresponds to a decay in SERS intensity and is attributed to the thick films found to be ~100 nm by AFM.


CHAPTER 5: INTERACTION OF LEVELERS WITH COPPER SURFACE IN PH 3 SULFATE SOLUTION

Introduction

Electrodeposition of Cu is used to make interconnects for microelectronics because of its lower line resistance, better electromigration characteristics, and ease of feature filling compared to Al and Al-alloy metallization.\textsuperscript{1-3} The typical Cu plating bath is composed of $\text{H}_2\text{SO}_4$, $\text{CuSO}_4$ and organic agents termed suppressors, accelerators, and levelers which work in concert for uniform plating and feature filling across the chip.\textsuperscript{1}

Levelers are used to control overfill bumps that occur during electrodeposition and also serve to reduce the rate Cu growth on the field (outside of features).\textsuperscript{1,4-6} The prototypical leveler is a quaternary ammonium salt. Functionalization of head group and altering the chain length counter ion can affect the plating behavior.\textsuperscript{7} Bozzini et al. showed that Janus Green B, a leveler used for Cu plating, undergoes potential driven orientation changes.\textsuperscript{8-9} Previously, Hatch et al. showed that this reorientation is linked with ability to tune the plating potential with concentration.\textsuperscript{10}

A ‘low acid’ bath with high Cu concentration has many benefits with regards to electrodeposition. It decreases the conductivity of the solution which improves uniformity of deposit. It also decreases roughness while enhancing the Cu transport rate to the surface which should enhance via filling.\textsuperscript{11} In this chapter, we will investigate the effect of varying the concentration with dodecyltrimethyl ammonium bromide (DTAB), thonzonium bromide (ThonB) and benzyldimethylhexadecyl ammonium chloride (BDAC) has on Cu plating potentials in pH 3 sulfate solutions. Potential dependent Shell Isolated Spectroscopy will be used

\textsuperscript{3} Experiments were performed with support provided by Novellus Systems Inc.
to investigate the orientation of the levelers at various potentials which may give insight into the Cu plating behavior.

**Results and Discussion**

Figure 5.2 shows slow scan rate voltammetry obtained from a rotating Cu electrode in a solution containing 10 g/L K₂SO₄ (0.1 M) and 40 g/L CuSO₄ (0.15 M) adjusted to pH 3 with H₂SO₄ with the addition of 0, 10, 25, and 50 ppm of leveler.

**Dodecyltrimethyl Ammonium Bromide (DTAB)**

![Chemical structure of DTAB](image)

**Benzylidimethylhexadecyl Ammonium Chloride (BDAC)**

![Chemical structure of BDAC](image)

**Thonzonium Bromide (ThonB)**

![Chemical structure of ThonB](image)

*Figure 5.1* Chemical structures of DTAB, BDAC, and ThonB.
Figure 5.2. Cyclic voltammogram (10 mV/s scan rate) of rotating (200 rpm) Cu(poly) working electrode in a solution containing 0.16 M CuSO$_4$ and 0.1 M K$_2$SO$_4$ adjusted to pH 3 with H$_2$SO$_4$ with various concentrations of a) CTAB, b) BDAC and c) ThonB.
Absent leveler, bulk Cu deposition begins at 10 mV vs. Ag/AgCl and the current is nearly proportional to applied voltage as has been reported previously, both at pH 3 and at lower pH values. Addition of 10 ppm of DTAB (Fig. 5.2A) inhibits the onset of Cu deposition to approximately -50 mV. The reverse scan shows some hysteresis, which indicates that reformation of the inhibiting DTAB layer is slow relative to the Cu plating event. With the addition of higher concentrations of DTAB, the Cu deposition onset potential shifts to ca. -100 mV and the deposition wave does not exhibit the hysteresis seen with the lower DTAB concentration. This indicates that the inhibition layer remains on the surface on both the forward and reverse voltammetric scans.

Fig. 5.2B shows the effect of addition of 10 ppm of BDAC to the blank plating solution. BDAC at this concentration inhibits the onset of bulk Cu deposition to -200 mV. The forward sweep shows that partial breakdown of the inhibiting BDAC layer occurs, because the deposition current initially does not reach the level of the voltammogram of the blank. However, at the reversal potential (-0.5 V) the current approaches that of the blank, and the reverse sweep basically traces the inhibitor-free voltammogram.

With addition of 25 ppm of BDAC, bulk deposition is inhibited until a potential of -220 mV. The return sweep displays hysteresis but Cu deposition remains inhibited as compared to the leveler free case. With addition of 50 ppm BDAC, there are two regions of the cathodic sweep with negative current starting at around -40 mV which gradually increases until bulk deposition occurring at around -250 mV. Cu deposition is impeded compared with the 25 ppm case until about -400 mV wherein the two voltammograms overlay.
Adding 10 ppm of ThonBr to the plating solution inhibits the onset of deposition to -230 mV as shown in Fig. 5.2C. The current on the forward scan approaches that of the blank solution at ca. -450 mV and the return sweep displays a large hysteresis. 25 ppm ThonB inhibits onset further to -270 mV, but the current is not as high as that found with the lower concentration of inhibitor. Finally, with addition of 50 ppm Thon B, Cu deposition is further inhibited to -340 mV, but again the current attained at -500 mV is substantially less than that found with the BDAC-free case.

Figure 5.3 displays cyclic voltammograms of a Cu electrode without Cu in solution and overlay of impedance versus potential plots for 10, 25, and 50 ppm of leveler. In the presence of DTAB, concentration has little effect on the electrochemical behavior of the electrode. Both cyclic voltametry and impedance vs potential plots are indistinguishable at the 10, 25, and 50 ppm. BDAC, however, does have concentration dependent behavior. As the concentration of BDAC increases, the trench for capacitance shifts to more negative potentials. At 10 ppm, BDAC has some adsorption phenomena occur between -0.5 V and 0.8 V that does not occur at higher concentrations. ThonB has a much larger capacitance trench than in other cases and but cyclic voltammetry and capacity versus potential plots show little variance will concentration increase. An reductive peak occurs at ~-1 V vs Ag/AgCl which is where the reduction of Cu⁺ to Cu⁰ occurs in neutral sulfate solutions.¹²
Figure 5.3. Cyclic voltammograms (2 mV/s scan rate) and impedance versus potential measurements (excitation frequency $\omega = 25$ Hz and an amplitude of 10 mV) with a Cu electrode and levelers at 10 ppm, 25 ppm, and 50 ppm in 0.1 M $K_2SO_4$ pH adjusted to 3 with H$_2$SO$_4$. 

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Figures 5.4 displays the potential dependent SHINERS for pH 3 sulfate solutions with 10 ppm of DTAB, BDAC, and ThonB. DTAB has no potential dependent behavior which corresponds well with its electrochemical behavior (it does not tune the plating potential with concentration).

BDAC has peaks at the start of the scan (0 mV) and remain over the course of the scan. Some peaks (Peaks I, J, and M all associated with amino deformation modes along with some CH modes of the chain) increase with intensity reach a max at -600 mV and then decrease in intensity. Other peaks keep a relatively constant intensity until about -1000 mV whereupon they exhibit a small decrease in intensity associated with competition between BDAC and adsorbed H.

ThonB exhibits potential dependent behavior different than the other two cases. At 0 mV the spectra exhibit three peaks: B, assigned to the benzyl in plane ring deformation, CH₃-O-C rocking, C-C symmetric stretch, I assigned terminal C-C-C stretch and K assigned symmetric SO₄²⁻ stretch. Peaks I and K are convoluted together. Then as the scan progresses in the cathodic direction peaks O and U which are assigned to CHCH wagging modes appear at -200 mV. At -400 mV Peak K increases in intensity. Peaks D, E, F, N, P, R, S, X, and Y associated with the head group appear along with peaks H, Q, and V associated with the tail. At -800 and -1000 mV peak I, L, U, X and Y have very large intensities. At -1200 mV there is a reduced intensity for all peaks associated with completion with H evolution.
Figure 5.4. SHINERS spectra of 10 ppm leveler in pH 3 K$_2$SO$_4$. Potential versus Ag/AgCl.
Figure 5.5 displays the potential dependent SHINERS for 50 ppm of DTAB, BDAC, and Thon B in pH 3 sulfate solution. Tables 5.1-5.3 are the peak assignments for the potential dependent spectra shown in Figures 5.4 and 5.6.

Unlike in the 10 ppm case, DTAB displays some potential dependent behavior for peaks E end of tail C-C stretch and F methylene chain rotation. There is also potential dependent behavior for peaks M and N associated with the head group. For the 50 ppm BDAC peaks C, I, K P and R at all potentials gradual increase in intensity until -600 mV then decrease in intensity at more negative potentials. For spectra of 50 ppm, ThonB peaks are very intense until -1000 mV when a reduction in intensity occurs due to competition with H adsorption. In particular, G and N associated with the head group and J, O, and V associated with C-C and C-H modes of the tail group.
Figure 5.5. SHINERS spectra of 50 ppm leveler in pH 3 K₂SO₄. Potential versus Ag/AgCl.
### Tables 5.1 Peaks and assignments for DTAB.

<table>
<thead>
<tr>
<th></th>
<th>Assignments</th>
<th>Calculation</th>
<th>pH 1 10 ppm</th>
<th>pH 3 10 ppm</th>
<th>pH 3 50 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Symmetric stretch N-((CH_x)) + (CC)</td>
<td></td>
<td>615</td>
<td>624</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Symmetric stretch N-((CH_x)) + (CC)</td>
<td></td>
<td>641</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Symmetric stretch C-N</td>
<td></td>
<td>713</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Tail CH rocking, C-C rotation</td>
<td></td>
<td>736</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>End of tail C-C stretch</td>
<td></td>
<td>760</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Methylene chain rotation</td>
<td>789</td>
<td>762</td>
<td>788</td>
<td>789</td>
</tr>
<tr>
<td>G</td>
<td>S-O symmetric stretch</td>
<td></td>
<td>980</td>
<td>981</td>
<td>976</td>
</tr>
<tr>
<td>H</td>
<td>C-C asymmetric stretch</td>
<td>1052</td>
<td>1048</td>
<td>1029</td>
<td>1020</td>
</tr>
<tr>
<td>I</td>
<td></td>
<td></td>
<td>1129</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td></td>
<td></td>
<td>1198</td>
<td>1192</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
<td></td>
<td>1301</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td></td>
<td></td>
<td>1372</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td>1390</td>
<td>1390</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Combined N-(CH) asymmetric stretch and chain C-H wag</td>
<td>1444</td>
<td>1443</td>
<td>1445</td>
<td>1440</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td>1588</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td>1592</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>H₂O bend</td>
<td></td>
<td>1636</td>
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Table 5.2. Peaks and assignments for BDAC.

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Calculation</th>
<th>pH 1 peaks(^0)</th>
<th>10 ppm</th>
<th>50 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Benzyl ring deformation</td>
<td>541</td>
<td>542</td>
<td>552</td>
</tr>
<tr>
<td>B</td>
<td>Benzyl ring out of plane bend</td>
<td>604</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Benzyl ring in plane bend</td>
<td>689</td>
<td>652</td>
<td>631</td>
</tr>
<tr>
<td>D</td>
<td>Benzyl ring in plane bend</td>
<td>710</td>
<td>745</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Combined benzyl ring deformation + N-(CHx) breathing mode</td>
<td>781</td>
<td>835</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Chain (C-C) asymmetric stretch</td>
<td>979</td>
<td>979</td>
<td>977</td>
</tr>
<tr>
<td>G</td>
<td>Combined chain (C-C) asymmetric stretch + chain (C-H) rotation/torsion</td>
<td>991</td>
<td>996</td>
<td>995</td>
</tr>
<tr>
<td>H</td>
<td>Combined chain (C-C) asymmetric stretch + chain (C-H) rotation/torsion</td>
<td>1013</td>
<td>1009</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Chain (C-C) asymmetric stretch</td>
<td>1037</td>
<td>1036</td>
<td>1017</td>
</tr>
<tr>
<td>J</td>
<td>Tail rocking, benzene out of plane deformation, N-CH(_3) rocking</td>
<td>1199</td>
<td>1199</td>
<td>1193</td>
</tr>
<tr>
<td>K</td>
<td>Combined benzyl-H in plane bend + N (CH) rotation + Chain (C-H) torsion</td>
<td>1221</td>
<td>1220</td>
<td>1209</td>
</tr>
<tr>
<td>L</td>
<td>Combined methylene spacer (C-H) wagging + (H-C-H) scissoring on N</td>
<td>1591</td>
<td>1590</td>
<td>1568</td>
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Table 5.3. Peaks and assignments for ThonB.

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Calculation$^{10}$</th>
<th>pH 1 10 ppm$^{10}$</th>
<th>pH 3 10 ppm</th>
<th>pH 3 50 ppm</th>
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</thead>
<tbody>
<tr>
<td>A  Benzyl ring deformation</td>
<td>518</td>
<td>526</td>
<td>526</td>
<td></td>
</tr>
<tr>
<td>benzyl in plane ring deformation, CH$_3$-O-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rocking, C-C symmetric stretch</td>
<td>614</td>
<td>627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_{\text{amino}}$(CH$_2$) scissoring/pyrimidyl ring in plane stretch</td>
<td>635</td>
<td>633</td>
<td>635</td>
<td>634</td>
</tr>
<tr>
<td>N$_{\text{amino}}$(CH$_2$) scissoring/pyrimidyl ring in plane stretch</td>
<td>581</td>
<td>608</td>
<td>612</td>
<td></td>
</tr>
<tr>
<td>C  Symmetric stretch (N-CH$_2$) + (CH$_2$-CH$_2$-N) + N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C-C) in plane bending (C-C) out of plane bend</td>
<td>711</td>
<td>708</td>
<td></td>
<td></td>
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<tr>
<td>N (C-C) in plane bend + asymmetric stretch (C-O/C-CH$_2$)</td>
<td>734</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_{\text{quat}}$-CH symmetric stretch</td>
<td>785</td>
<td>782</td>
<td></td>
<td></td>
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<tr>
<td>Benzyl ring in plane stretch</td>
<td>798</td>
<td>825</td>
<td>815</td>
<td>813</td>
</tr>
<tr>
<td>Chain (CH) wagging</td>
<td>854</td>
<td>852</td>
<td>853</td>
<td>843</td>
</tr>
<tr>
<td>Chain terminal C-C-C symmetric stretch</td>
<td>962</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfate symmetric stretch</td>
<td>979</td>
<td>978</td>
<td>975</td>
<td></td>
</tr>
<tr>
<td>Chain (CH) wagging</td>
<td>981</td>
<td>988</td>
<td>978</td>
<td></td>
</tr>
<tr>
<td>1027</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M  Combined pyrimidyl ring deformation + benzyl</td>
<td>1054</td>
<td>1077</td>
<td>1073</td>
<td></td>
</tr>
<tr>
<td>methylene (C-H) rotation</td>
<td>1060</td>
<td>1065</td>
<td>1081</td>
<td></td>
</tr>
<tr>
<td>Chain (CH) wagging</td>
<td>1180</td>
<td>1183</td>
<td>1177</td>
<td>1171</td>
</tr>
<tr>
<td>Pyrimidyl ring out of plane deformation</td>
<td>1215</td>
<td>1215</td>
<td>1203</td>
<td></td>
</tr>
<tr>
<td>Tail C-C symmetric stretch</td>
<td>1255</td>
<td>1236</td>
<td>1243</td>
<td></td>
</tr>
<tr>
<td>N-(CH$_2$) rocking</td>
<td>1273</td>
<td>1270</td>
<td>1298</td>
<td>1297</td>
</tr>
<tr>
<td>C$<em>{\text{chain}}$-H wagging nearest N$</em>{\text{quat}}$</td>
<td>1309</td>
<td>1310</td>
<td>1303</td>
<td></td>
</tr>
<tr>
<td>N$_{\text{methoxy}}$(CH$_3$) rocking</td>
<td>1347</td>
<td>1355</td>
<td>1350</td>
<td>1341</td>
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<tr>
<td>Chain (CH) wagging</td>
<td>1392</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1440</td>
<td></td>
<td></td>
<td>1434</td>
<td></td>
</tr>
<tr>
<td>W  Chain (CH) wagging</td>
<td>1440</td>
<td>1442</td>
<td>1441</td>
<td>1434</td>
</tr>
<tr>
<td>1455</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X  N$_{\text{amino}}$(CH$_2$) symmetric stretch</td>
<td>1588</td>
<td>1591</td>
<td>1608</td>
<td>1603</td>
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<tr>
<td>N$_{\text{quat}}$ methyl (C-H) scissoring</td>
<td>1620</td>
<td>1620</td>
<td>1621</td>
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</tr>
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</table>
In comparison to pH 1 data, DTAB has less change in behavior with regards to concentration and much less hysteresis with regards to plating behavior at pH 3.

For the BDAC case, the behavior is similar, increased concentration increases the overpotential for Cu deposition; however, there is slightly less hysteresis in the pH 3 case.

For the ThonB case the plating voltammetry is completely different than in pH 1 case in which all plots overlay. The peak in current density is much lower with increased concentration of leveler: at 10 ppm peak is the same as leveler case where as the 25 and 50 ppm concentrations have peak current density to about 5 mA/cm$^2$. Since pKa of pyrimidines is fairly acidic at ~1, the ThonB is probably deprotonated at higher pH.$^{13-14}$ This deprotonation promotes reorientation of the ThonBr head group at low concentration.

Conclusions

ThonB has optimal Cu plating characteristics that do not correspond to the leveler only electrochemistry or differential capacity. ThonB exhibits potential dependent behavior at 10 ppm concentrations and exhibits a strong interaction with Cu at 50 ppm in SHINERS spectra. Since potential induced reorganization was attributed to the tuning ability of BDAC at pH 1,$^{10}$ it is reasonable to infer that this potential induced reorientation is what allows ThonBr to tune the electroplating potential of Cu at higher pH.
References

3. Ritzdorf, T., Challenges and opportunities for electrochemical processing in microelectronics. ECS Trans. 2007, 6 (8), 1.
7. Luehn, O.; Celis, J.-P.; Van Hoof, C.; Baert, K.; Ruythooren, W., Leveling of microvias by electroplating for wafer level packaging. ECS Trans. 2007, 6 (8), 123.
CHAPTER 6: EFFECT OF HEAT TREATMENT ON ELECTROCHEMICAL BEHAVIOR AND OXIDATION PRODUCTS OF ALLOYS 617 AND 230

Introduction

Very high temperature reactors (VHTR) with the dual capacity of electricity generation and hydrogen production are promising candidates for future nuclear generators.\(^1\) Two routes currently under consideration are electrochemical or thermochemical water splitting. Of these two options, thermochemical water splitting is preferred because it only requires heat. The sulfur-iodine cycle is a promising candidate because it is relatively efficient at H\(_2\) production at temperatures achievable with VHTR reactors, between 900 and 1000 °C and only requires manipulation of gaseous and liquid phases.\(^2\) Haynes 617 (Ni-Cr-Co-Mo) and Haynes 230 (Ni-Cr-W-Mo) are solid-solution strengthened Ni-based alloys developed as high temperature and corrosion resistance materials currently under consideration for use in components of next generation reactors.\(^1\),\(^3\)-\(^5\) The effect of ageing at high temperature on the alloys’ electrochemical behavior has important implications for use in components for VHTRs.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>B</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>617</td>
<td>1.03</td>
<td>&lt;0.002</td>
<td>0.08</td>
<td>12.2</td>
<td>22.1</td>
<td>0.017</td>
<td>1.104</td>
<td>--</td>
</tr>
<tr>
<td>230</td>
<td>0.38</td>
<td>0.004</td>
<td>0.11</td>
<td>0.29</td>
<td>21.7</td>
<td>0.04</td>
<td>1.4</td>
<td>0.014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ti</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>617</td>
<td>0.064</td>
<td>9.46</td>
<td>52.86</td>
<td>0.002</td>
<td>&lt;0.002</td>
<td>0.05</td>
<td>0.39</td>
<td>--</td>
</tr>
<tr>
<td>230</td>
<td>0.46</td>
<td>1.75</td>
<td>BAL</td>
<td>0.005</td>
<td>&lt;0.002</td>
<td>0.4</td>
<td>&lt;0.01</td>
<td>13.89</td>
</tr>
</tbody>
</table>

Table 6.1. Elemental composition of alloys in average weight percent from Mo et al.\(^1\)
Ni, Cr, and Ni-Cr alloys are known to undergo transpassive dissolution, electron-mediated formation of soluble species from an oxide layer, at sufficiently anodic potentials in aqueous solutions.\textsuperscript{6-11} Ring-disk polarization and AC impedance\textsuperscript{6-9} as well as \textit{in situ} x-ray photoelectron spectroscopy\textsuperscript{12} (XPS) and x-ray absorption near edge spectroscopy\textsuperscript{13} (XANES) of binary (Ni-Cr) alloys show that the main product of transpassive dissolution are soluble Cr(VI) species.

Typical corrosion failure of austenitic Ni alloys in nuclear applications has been attributed to stress corrosion cracking in which a combination of mechanical stress and corrosive elements in the environment cause failure of the passive layer to form pits and cracks on the material’s surface which mechanically weaken the overall structure.\textsuperscript{12-17} Raman spectroscopy and surface-enhanced Raman spectroscopy (SERS) have both been used to investigate the effect of pressurized water reactors on Ni alloys (Alloy 600 and Alloy 690) in which a Cr(III) rich phase determined to be $\alpha$-Cr$_2$O$_3$.\textsuperscript{12-17} Devine’s group has used \textit{in situ} Surface-Enhanced Raman Spectroscopy with electrodeposited gold to investigate the passive layer that forms on austenitic nickel samples exposed to Cl$^-$ in various pHs. In HCl solutions they found the passive layer of alloy C22 (Ni-Cr-Mo-W) to be composed of a combination of MoO$_3$, MoO$_2$, and amorphous Cr(III) oxide species at low potentials and evidence for Cr$_2$O$_3$ at transpassive potentials.\textsuperscript{18}

Although in-situ techniques have been used to characterize the passive layer in ambient conditions and with high temperature and pressure solutions, the effect of heat treatment has not been fully investigated\textsuperscript{1,4-5,19} Unknown is whether heat aging changes the distribution of surface species that form during transpassive dissolution in sulfuric acid. Herein we demonstrate the use of Shell Isolated Surface Enhanced Raman Spectroscopy (SHINERS) to interrogate the
speciation of surface species that form in the anodic potentials for Haynes 617 and Haynes 230 that have been aged at high temperature in air and compare to the as-received alloy.

**Results and Discussion**

Figure 6.1 displays both anodic and cathodic polarization curves obtained in 0.1 M H$_2$SO$_4$ for the various alloy materials considered here. Transpassive dissolution of the passive layer on Cr is sulfate anion-assisted$^{7-9}$ so the electrode was rotated at 1000 rpm in order to facilitate comparison to the literature.
Figure 6.1. Polarization curves of alloys in 0.1 M H₂SO₄ with 10 mV/s scan rate and 1000 rpm rotation.
The polarization curves for Alloy 617 as-received and after heat treatment are reported in Fig. 6.1. The anodic scan shows that the passive region begins at -0.24 ± 0.04 V for all samples, suggesting that both the as-received and heat treated materials will have similar pitting behavior as they share the same critical pitting potential. The current density for the samples at 1.0 V are 1.4 ± 0.4 mA/cm² for the as-received case, 0.70 ± 0.1 mA/cm² for alloy 617 heat-treated at 900 °C, and 0.74 ± 0.3 mA/cm² for alloy 617 heat-treated at 1000 °C. Heat treatment makes the alloy 617 more corrosion resistant as the current density is reduced. Additionally, the as-received alloy 617 exhibits an anodic current in the transpassive region ca. 1.6 times higher than that of heat treated samples, suggesting more easily oxidizable material forms on the surface absent the heat treatment.

The cathodic potential sweep, also shown in Figure 6.1, displays reduced current density relative for all three samples to the anodic sweep, likely originating from the formation of a thicker Cr layer on the anodic sweep. The figure also displays an exponential rise in current at more cathodic potentials for all samples with the as-received Alloy 617 exhibiting a higher cathodic current than the heat treated samples.

The polarization curves for various treatments of Alloy 230 are also shown in Figure 6.1. Onset of heat treated samples more positive than for as-received case at 0.19 V ± 0.04 V vs Ag/AgCl. The current density for the samples at 1.0 V are 0.28 ± 0.05 mA/cm² for the as-received alloy 230, 0.08 ± 0.05 mA/cm² for alloy 230 heat-treated at 900 °C, and 0.07 ± 0.05 mA/cm² for alloy 230 heat-treated at 1000 °C. The heat treatment reduces the current density at 1.0 V versus the untreated case. The as-received sample has a higher anodic current density than that of heat treated samples, again suggesting the presence of more easily oxidizable material on
the surface prior to heat treatment. Return sweep is similar to alloy 617 case with as-received having more cathodic current than the heat treated samples.

Our observation of something with regard to the transpassive region on heat treatment has precedence in the literature. For example, Kewther et al. showed that Alloy 617 used in gas turbines for 37,000 h could become more corrosion resistant with heat treatment 1-2 hr at 1174 °C under inert gas; heat treatment made alloy 617 samples 100 mV more noble in a solution containing 0.05 M H$_2$SO$_4$ + 0.005 M NaCl. Alternatively, heating in air causes carbide precipitate to form alongside grain boundaries and a passive oxide composed of Cr$_2$O$_3$ to form on top of the bulk alloy with a thinner Al$_2$O$_3$ layer underneath. However, heating did not affect grain size distribution. Carbide deposition arising from heating also increases the rate of anodic dissolution of Ni-Cr-Mo alloys in boiling 10% H$_2$SO$_4$. Segregation of Cr in the carbide phase also causes embrittlement of alloy. According to the Pourbaix diagram, in aqueous solution Cr(III) should be dominant species in passivation layer and Cr(VI) species are formed at transpassive potentials.

With regards to electrochemical passivation, in situ XPS measurements of Ni-Cr alloys confirm that the passive layer in the double region is composed of Cr(III) and Ni(II) and thin (1-2 nm) whereas the transpassive region (starting at 1.0 V vs SHE) was composed of a mixture Cr(III) and Cr(VI). Jabs et al. showed that Ni-Cr alloys with 20 weight percent Cr develop an hydroxide layer as evidence by an peak at 577 eV in the XPS after stepping the potential above 0.4 vs SHE. The electrochemical behavior of Alloy 230 in 25-98% H$_2$SO$_4$ has been studied with solution temperatures ranging 25 to 75 °C; however, the effect of heat aging of the alloy on electrochemistry has not been examined. The delayed onset and reduced current density observed here shows that heat treatment makes both alloys more resistant to oxidation. Overall
our results show that Alloy 230 is more corrosion resistant than Alloy 617, a result also found in the literature.

In order to interrogate the species present on both the as-received and heat-treated alloy surfaces, we performed \textit{in situ} SHINERS on both the alloy 617 and alloy 230 materials in both the anodic and cathodic directions. Figure 6.2 shows potential dependent SHINERS obtained from as-received and heat-treated alloy 617 in aqueous 0.1 M H₂SO₄. Table 6.1 provides a listing of peaks and their assignments.

\textbf{Table 6.2.} Peaks and assignments for spectra.

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 800</td>
<td>adsorbed CrO₄²⁻</td>
<td>24-25</td>
</tr>
<tr>
<td>B 810-840</td>
<td>CrO₄²⁻</td>
<td>24-25</td>
</tr>
<tr>
<td>C 850-920</td>
<td>Mixed Cr(III/VI) oxide (MoO₄²⁻ and WO₄²⁻)</td>
<td>26-27</td>
</tr>
<tr>
<td>D 960-980</td>
<td>Cr₂O₇²⁻</td>
<td>24-25</td>
</tr>
<tr>
<td>E 980</td>
<td>SO₄²⁻ symmetric stretch</td>
<td>28</td>
</tr>
<tr>
<td>F 1020</td>
<td>HSO₄⁻ assymetric stretch</td>
<td>28</td>
</tr>
</tbody>
</table>

For the as-received alloy 617 as the potential is swept from -0.4 V to 0.9 V only peaks from the electrolyte are observed. Specifically, a peak at 977 cm⁻¹ (peak E) assigned as the symmetric SO₄²⁻ stretch.²₈ At 0.95 V a group of peaks with large intensities appear at 783 cm⁻¹ (peak A) and 943 cm⁻¹ (peak D) which are assigned adsorbed CrO₄²⁻ and Cr₂O₇²⁻ respectively.²₄-²₅ At 1.0 V, peaks A and D increase in intensity (and shift to higher wavenumbers) with peak A developing a shoulder at 833 cm⁻¹ (Peak B, assigned as free CrO₄²⁻). On the cathodic sweep peaks A and D continue increases in intensity until 0.4 V after which the peaks decrease in intensity. At 0 V a peak centered at 862 cm⁻¹ (peak C) appears and is assigned a mixed oxide Cr(III/VI).²₆-²₇ The region where peak C occurs is also where MoO₄²⁻ (876 cm⁻¹ respectively)
appear when adsorbed onto a Ag colloid. As the potential is swept from 0 to -0.4 V, the intensity of peak C decreases in intensity. Interestingly there is no feature observed at 898 cm⁻¹ that could be associated with HCrO₄⁻.26-27

For the anodic sweep with the 900 °C treated alloy 617 between -0.4 V to 0.8 V only electrolyte peaks, peak E and broad peak centered at 1020 cm⁻¹ (peak F) assigned to HSO₄⁻ are observed.28 At 0.8 V a peak at 867 cm⁻¹ (peak C) appears. At 0.9 V an intense peak at 793 cm⁻¹ (peak A) appears with a shoulder at 970 cm⁻¹ (peak D). All peaks increase in intensity after reaching the switching potential of 1.0V. On the cathodic sweep, peak A reaches maximum intensity at about 0.9 V, the while peaks C and D reach maximum intensity at around 0 V vs Ag/AgCl.

Similar to the other two cases, in spectra obtained from the 1000 °C treated alloy 617 only electrolyte peaks (E and F) are observed from -0.4 to 0.8 V. At 0.8 V a peak at 875 cm⁻¹ (peak C) and at 0.95 V a peak at 800 cm⁻¹ (peak A) appears while peak D has increased in intensity. At 1.0 V, peak A and peak C have increased in intensity while a peak at 960 cm⁻¹ (peak D) has appeared. On the cathodic sweep, peak A reaches its maximum intensity at 0.8 V while peaks C and D reach a maximum between 0.2 V and -0.2 V before decreasing in intensity.
Figure 6.2. Potential dependent spectra of Ni alloys in 0.1 M H$_2$SO$_4$. Spectra offset for clarity.
Figure 6.3 shows the peak intensity for the Cr species on Alloy 617 samples relative to their maximum peak intensity to better interpret the change in Cr speciation with potential. The onset for peak A -- associated with adsorbed \( \text{CrO}_4^{2-} \) -- on the anodic sweep is similar for the three samples. On cathodic sweep the maximum intensity for peak A is reached 0.2 V earlier for the heat-treated Alloy 617 samples relative to the as-received sample. On the cathodic sweep, the maximum intensity for peaks C and D are delayed for 0.2 V for the heat-treated Alloy 617 samples relative to the as-received Alloy 617. Thus heat treatment controls both the nature of the Cr overlayer and its potential dependent development.

Figure 6.3. Relative peak intensity versus potential plot for a) \( \text{CrO}_4^{2-} \), b) mixed oxide, c) \( \text{Cr}_2\text{O}_7^{2-} \).

Our observation that peaks assigned to Cr(VI) species appear at anodic potentials suggests that Cr(VI) is the major product formed in the transpassive region, a result which has consistent with the literature.\(^6\)-\(^7\),\(^21\) There is no clear evidence for \( \text{Cr}_2\text{O}_3 \) formation, which is the major product when either Alloy 230 or Alloy 617 is heated in air;\(^1\) however, the mixed Cr(II)/Cr(VI) species is observed on the cathodic sweep. We note that Cr(III) species have a
smaller scattering cross-section relative to Cr(VI) peaks for spectra produced by roughened or colloidal samples of Ag, Au, and Cu.\textsuperscript{24-25, 29} SERS spectra of Alloy 22 a Ni-Cr-Mo alloy in HCl display broad peaks at 430 and 490 cm\textsuperscript{-1} attributed to an amorphous Cr(III) species.\textsuperscript{18} There are some low intensity features at that region for some of the spectra.

The other interesting aspect of the spectra reported above concerns the delayed potential associated with the formation of peaks associated with Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} and mixed oxide and accelerated potential of the appearance of peak A, associated with CrO\textsubscript{4}\textsuperscript{2-} in the heat treated samples. We suggest that the heat treatment produces more fully oxidized Cr material relative to Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-}, the consequences of which are seen spectroscopically. Interestingly, the Pourbaix diagram for Cr shows that HCrO\textsubscript{4}\textsuperscript{-} rather than chromate should be stable in the potential region interrogated (at pH 1), so the presence of CrO\textsubscript{4}\textsuperscript{2-} suggests a less acidic environment overall. Correspondingly, we note that heat treatment leads to an increase in corrosion resistance.

Figure 6.4 and Figure 6.5 present spectra and intensity vs. potential curves, respectively, for the three Cr species observed from heat treated and as received Alloy 230 samples.

For the as-received Alloy 230 sample, as the potential is swept from -0.4 V to 0.9 V, only electrolyte peaks (E and F) are observed. From 0.85 to 0.9 V, a peak centered at 800 cm\textsuperscript{-1} (peak A) appears and grows in intensity while shifting to 801 cm\textsuperscript{-1}. At 1.0 V peak A develops a shoulder at 847 cm\textsuperscript{-1} (peak B) and a peak at 978 cm\textsuperscript{-1} appears (peak D). On the cathodic sweep, both A and D increase in intensity down to 0.9 V then rapidly decrease in intensity by 0.8 V and continue a gradual decrease in intensity until the end of the scan at -0.4 V.

Similar to the as received case, only electrolyte peaks (E and F) are observed on the 900 °C-treated Alloy 230 sample, as the potential is swept from -0.4 V to 0.4 V. At 0.8 V, a peak centered at 882 cm\textsuperscript{-1} (peak C) appears. At 0.95 V two other peaks at 792 cm\textsuperscript{-1} (peak A) and 975
cm\(^{-1}\) appear (peak D). All three peaks increase in intensity and shift to higher frequencies (800, 888, and 964 cm\(^{-1}\)) until 1.05 V. On the cathodic sweep, peak A increases in intensity until 0.8 V then decreases as the potential is swept to more negative values. Peaks C and D remain at the same intensity until 0 V, where peak C shifts to 920 cm\(^{-1}\) and increases in intensity until -0.4 V the end of the cathodic sweep. This region is where adsorbed MoO\(_4^{2-}\) and WO\(_4^{2-}\) (876 cm\(^{-1}\) and 912 cm\(^{-1}\) respectively) would also occur.\(^{24}\)

For the 1000 °C treated Alloy 230, as the potential is swept from -0.4 to 0.95 only the electrolyte (E and F) are observed. At 1.0 V a peak centered a 795 cm\(^{-1}\) (peak A) appears and grows in intensity at 1.05 V. On the cathodic sweep, peak A increases in intensity, reaches a maximum at 0.8 V and slowly decreases in intensity as the potential is swept to more negative values until 0 V. After 0 V, a peak at 911 cm\(^{-1}\) (peak C) appears and grows in intensity for the rest of the cathodic sweep. This region is where adsorbed MoO\(_4^{2-}\) and WO\(_4^{2-}\) (876 cm\(^{-1}\) and 912 cm\(^{-1}\) respectively) would also occur.\(^{24}\)
Figure 6.4. Potential dependent spectra of 230 alloys in 0.1 M H\textsubscript{2}SO\textsubscript{4}. Spectra offset for clarity.
As in the Alloy 617 case, spectra for alloy 230 samples show no HCrO$_4^-$ peak. Heat treated samples show a delayed onset of CrO$_4^{2-}$ peak and development of a mixed oxide peak during transpassive dissolution.

Heat treated alloy 617 and 230 have different onsets for the mixed oxide peak, alloy 617 having a greater relative peak intensity of the mixed alloy phase to the CrO$_4^{2-}$ peak on the anodic sweep. The Cr$_2$O$_7^{2-}$ peak reaches a maximum intensity at 0 V on 617 whereas it reaches maximum intensity at -0.4 V on the heat treated 230 samples. The as received 230 does not appear to have a mixed oxide phase that develops at cathodic potential.

*Ex situ* XPS was performed on both alloy 230 and alloy 617 after two complete electrochemical cycles between -0.4 and 1.0 V followed by emersion at -0.4 V. XPS obtained from the Cr region are shown in Figure 6.6 and exhibit two peaks at 577 eV and 588 eV. These peaks are assigned as Cr(III/VI) mixed oxide because the energies match that of the 2p peaks for
oxidized Cr. The peaks for Cr(III) are at 577 and 586-8 eV, \(^{30}\) while the peak for Cr (VI) is 578.75 eV. \(^{21}\)
Figure 6.6. *Ex situ* XPS of Ni alloys after potential cycling. Spectra are offset for clarity.
Table 6.3 is a summary of the relative amounts of the most abundant elements in the alloys (Ni, Cr, Mo, Co, and W) before and after oxidation determined from low resolution survey scans. Samples were oxidized by applying a potential of 1.1 V vs Ag/AgCl to the Ni sample for 60 s. The as received and heat treated alloy 617 samples exhibit the same behavior; the percentage of Cr increases, Ni and Co decrease, and Mo remains the same after electrochemical oxidation. For the alloy 230 sample, the percentage of Cr and W increases, while Ni and Mo decrease. The as received 230 has a higher fraction of W compared to the heat treated samples. Heat treatment has a minimal affect on the oxidation state and relative amount of Cr found ex situ for the Ni samples before and after corrosion in 0.1 M H₂SO₄.

**Table 6.3.** Relative atomic % of 5 major elements: Ni, Cr, Mo, W, Co before and after oxidizing at 1.1 V for 60 sec.

<table>
<thead>
<tr>
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<th>alloy 617</th>
<th>alloy 617</th>
<th>alloy 617</th>
</tr>
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<td>900 °C</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Ni</td>
<td>Before</td>
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<tr>
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<td>20</td>
<td>0.1</td>
<td>20</td>
</tr>
</tbody>
</table>

|          | alloy 230  | alloy 230  | alloy 230  |
|          | as received| 900 °C     | 1000 °C    |
| Ni       | Before     | After      | Before     | After      | Before     | After      |
| Ni       | 36         | --         | 45         | 14         | 58         | 14         |
| Cr       | 9          | 29         | 51         | 75         | 35         | 46         |
| Mo       | 53         | 4          | 5          | 4          | 3          | --         |
| W        | 2          | 67         | --         | 7          | 4          | 40         |
Conclusion

We show there is a correlation between transpassive current density and observation of surface Cr species in the Raman spectra. Delayed transpassive dissolution is associated with early onset of Cr(VI) species in spectra. The difference between transpassive current densities from 217 and 630 suggest the two alloys have different corrosion susceptibility and indeed the 230 is more corrosion resistant. In both alloys, heat treatment resulted in delayed onset of the transpassive region, likely because the heat treatment makes more Cr available to the surface. An increase in the relative intensity of the mixed oxide phase occurs with heat treatment.\(^4\)

Finally, we examine reasons that heat treated Alloy 230 and Alloy 617 exhibit greater corrosion resistance relative to the as-received material. The XPS measurements show that oxidation is associated with increased Cr content at the surface and speciation of the Cr to form protective oxides is well-known to increase the passivity of electrode surfaces.\(^6\)\(^-\)\(^11\) It is also understood that the average grain size grows and distribution of sizes increases after heating in furnace,\(^31\) thus leading to the presence of fewer reactive grain boundaries.

There are other possible contributory factors to increased corrosion resistance with the heat treated materials. Al\(_2\)O\(_3\) is known to form as a consequence of internal oxidation;\(^31\)\(^-\)\(^32\) this Al\(_2\)O\(_3\) might contribute to increased corrosion resistance. Formation of a surface layer of MnCr\(_2\)O\(_4\) (spinel) imparts 230 with better corrosion resistance than 617 (as Alloy 230 contains twice as much Mn) at 900 C; however, both undergo spallation and volatilization of Cr\(_2\)O\(_3\) layer at 1100 C.\(^32\) A study involving surface segregation in Haynes 230 showed that while S, P, and Si remained at the surface at 875 C, no change in Ni or Cr content was observed.\(^33\)

Interestingly we found less intense Cr signals in the Raman spectra from the 1000 C treated samples of both 230 and 617. This decrease relative to the samples heat treated at lower
temperatures might be due the formation of volatile CrO$_3$ from Cr$_2$O$_3$ at temperatures above 950 C. \textsuperscript{31} We note, however, that a decrease in Cr content following electrochemical oxidation was not observed in the XPS.

References


Currently copper is used to make interconnects on microprocessors, particularly when feature-filling is required because of its lower line resistance and better electromigration performance as compared to Al.\(^1\) Bis(3-sulfopropyl)-disulfide (SPS) is an accelerator used to promote bottom-up fill of features in the standard Cu acid plating bath by increasing the rate of Cu deposition within features relative to that at the plane above the features.\(^1-6\) It consists of a disulfide bridge and a sulfonate head group. It may bind to the Cu surface through the sulfide group and can undergo reductive bond cleavage at the Cu surface. The sulfonate head group is thought to repel suppressors and levelers (both work by increasing the overpotential of Cu deposition and result in slow growth at the top plane of the chip) thus facilitating Cu deposition. When used in conjunction with Cl\(^-\), SPS and is monomer mercaptopropane sulfonate (MPS) act to reduce the overpotential for Cu deposition.\(^1\)

There are many models under consideration to explain the accelerant effect of SPS.\(^7-12\) The curvature enhanced adsorbate coverage model (CEAC model) proposed by Moffat links the kinetics determined from electrochemical experiments on planar electrodes to that of shape-change simulations of feature filling correctly predicts the appearance of overfill bumps when only a suppresser and accelerator complexes are present.\(^13-14\)

Figure A.1 displays the SHINERS of a solution of 5 mM SPS, 2 mM KCl, 10 mM CuSO\(_4\) and 0.1 M H\(_2\)SO\(_4\) on a Cu(111) electrode. At 0 V some peaks attributed to SPS are present, however they are low intensity. As the potential is stepped to -0.4 V, the SPS as well as Cu-Cl peaks increase in intensity. As the potential is stepped to -0.5 V the SPS peaks continue to grow in intensity. At -0.6 V the SPS peaks exhibit a decrease in intensity.
Figure A.2 displays the SHINERS of a solution of 5 mM SPS, 2 mM KCl, 10 mM CuSO$_4$ and 0.1 M H$_2$SO$_4$ on a Cu(100) electrode. At 0 V the SPS peaks are more distinguishable from the background than in the Cu(111) case. As the potential is swept in the cathodic direction there is a gradual increase in the intensity of all peaks, especially that of peaks A, D and K assigned to Cu-Cl, a combination mode of CH-S stretch and S-O stretch, and a symmetric S-O stretch from the sulfonate group respectively.
Figure A.1. Potential dependent SHINERS of the cathodic sweep in an aqueous solution of 5 mM SPS, 2 mM KCl, 10 mM CuSO$_4$ and 0.1 M H$_2$SO$_4$ on a Cu(111) electrode.
Figure A.2. Potential dependent SHINERS of the cathodic sweep in an aqueous solution of 5 mM SPS, 2 mM KCl, 10 mM CuSO$_4$ and 0.1 M H$_2$SO$_4$ on a Cu(100) electrode.
Table A.1. Peaks and assignments for SPS near Cu.

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<th>Cu(111) (-0.5 V)</th>
<th>Cu(100) (-0.3 V)</th>
<th>Assignments&lt;sup&gt;15&lt;/sup&gt;</th>
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References

APPENDIX B: CARBON DIOXIDE ELECTROREDUCTION ON GOLD

As the end product of all combustion processes, CO$_2$ is an abundant source of carbon. By electrochemical reduction, it can be transformed into relevant - and lucrative - products such as carbon monoxide, methanol and ethylene. These can be used as fuels or as feedstock materials for pharmaceuticals and polymers\textsuperscript{1-6}. There are currently four problems impeding progress in electrochemical CO$_2$ reduction: (1) large overpotentials, (2) simultaneous production of hydrogen along with CO$_2$ reduction, (3) electrode poisoning with the concomitant decrease in efficiency over time and (4) potentially a wide distribution of products.

The study of electrochemical CO$_2$ reduction began with fundamental voltammetry experiments using aqueous solutions on metals with high hydrogen overvoltages (e.g. Hg and Zn)\textsuperscript{7}. These metals are able to reduce hydrogen at potentials much more negative than the thermodynamic equilibrium potential and, thus, reduces the amount of hydrogen evolution. Eyring proposed a mechanism for reduction at Hg electrodes based Tafel plots (Figure B.1)\textsuperscript{7}.

\[
\begin{array}{c}
\text{O}==\text{C}==\text{O} \quad e^- \\
\text{H}_2\text{O}, e^- \quad \text{HCOO}^- + \text{OH}^-
\end{array}
\]

\textbf{Figure B.1.} Proposed mechanism for reduction CO$_2$ to formate.

The general understanding is that the reaction proceeds with two consecutive one electron transfers. The first transfer creates a radical anion that pulls a proton from water and is then
further reduced with another electron to formic acid\textsuperscript{8}. The multiple electron reduction products of CO\textsubscript{2} reduction (e.g., methanol and methane) thermodynamically favorable with equilibrium potentials of around 0.1 V vs the reference hydrogen electrode (RHE) at pH 7 and 25 °C\textsuperscript{3,8-9}. 

\textbf{Table B.1.} Thermodynamic Equilibrium Values for CO\textsubscript{2} Reduction\textsuperscript{10}.

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<th>Electrons</th>
<th>Product</th>
<th>Potential (pH 7, V vs RHE)</th>
<th>ΔG (kJ mol\textsuperscript{-1})</th>
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<td>-CO\textsuperscript{2-}</td>
<td>-2.31</td>
<td>202.1</td>
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<tr>
<td>2</td>
<td>CO</td>
<td>-0.104</td>
<td>19.9</td>
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<tr>
<td>2</td>
<td>HCOOH</td>
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<td>38.4</td>
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<tr>
<td>4</td>
<td>HCOH</td>
<td>-0.072</td>
<td>27.5</td>
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<tr>
<td>6</td>
<td>CH\textsubscript{3}OH</td>
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<tr>
<td>8</td>
<td>CH\textsubscript{4}</td>
<td>0.17</td>
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</table>

Reduction of CO\textsubscript{2} has been attempted on most of the elements of the periodic table. Unfortunately, there is no periodic trend for the efficiency of CO\textsubscript{2} reduction; instead metals are generally categorized by the products they produce\textsuperscript{8,11}. Metals with high hydrogen evolution overpotentials (Pb, Hg, Bi, and other heavy metals) form formic acid at relatively high faradaic efficiency (but also high overpotentials due to the unstabilized CO\textsubscript{2} radical anion). Metals with moderate hydrogen overpotentials bind the CO\textsubscript{2} and form carbon monoxide. However, since hydrogen evolution has similar thermodynamic potentials, Faradaic efficiency (where the product distribution contains mostly C products) is only achieved in nonprotic solvents or by using additives which impede hydrogen evolution in protic solvents. Over time the reaction efficiency of CO\textsubscript{2} decreases. There are two theories of cause: continual deposition over time of heavy metal impurities in the electrolyte\textsuperscript{12}, or the formation of a carbon layer from reduced adsorbates that blocks catalytically active sites\textsuperscript{13-17}. 

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Spectroscopic studies have been performed to further elucidate the reduction mechanism by identifying surface intermediates. Infrared (IRAS) and Raman (SERS) studies confirm the presence of adsorbed CO on Cu, Ag, Pt, Pd and Ni\textsuperscript{18-31}. Oda et al. found that, in CO\textsubscript{2} saturated solutions of 0.1 M KCl, peaks attributed to carbon monoxide appear at around -1.4 V vs the standard hydrogen electrode (SHE) on Cu and -1.0 V on Ag. Since chloride adsorbs strongly to these surfaces, the CO\textsubscript{2} only displaces the M-Cl bonds at potentials negative enough to repel the Cl\textsuperscript{-} ions. Studies have also been performed on these metals in 0.1 M KHCO\textsubscript{3} which is a standard electrolyte for CO\textsubscript{2} reduction. They also had characteristic CO stretches and CO\textsubscript{3}\textsuperscript{2-} stretches were found on Cu.

In this chapter, we performed SERS of electroreduction of CO\textsubscript{2} in basic carbonate solutions to further elucidate the mechanism of CO\textsubscript{2} reduction on Au. Figure B.2 displays the potential dependent SERS spectra of 0.1 M K\textsubscript{2}CO\textsubscript{3} sparged with CO\textsubscript{2}. At open circuit potential there is a prominent peak at 1590 cm\textsuperscript{-1} attributed to water bending and a carbonate symmetric stretching mode. As the potential is stepped in the cathodic direction, a peak at 2080 cm\textsuperscript{-1} attributed to CO stretch appears at -800 mV vs Ag/AgCl. The water bending mode exhibits a slight decrease in intensity with more negative polarization of the Au electrode. When the potential scan is reversed to the anodic direction, the CO peak decreases in intensity and disappears by 400 mV. To further investigate the potential dependent behavior of the CO peak, Figure B.3 displays the integrated peak height of the CO mode was plotted versus potential and overlayed on the Au electrochemistry in CO\textsubscript{2} saturated carbonate buffer.

Figure B.4 displays the potential dependent behavior of a D\textsubscript{2}O solution of K\textsubscript{2}CO\textsubscript{3} sparged with CO\textsubscript{2}. At open circuit potential, there are two prominent peaks attributed to the electrolyte, one at 1200 cm\textsuperscript{-1} assigned to the D\textsubscript{2}O bending mode and one at 1360 cm\textsuperscript{-1} assigned to CO\textsubscript{3}\textsuperscript{2-}. As
the potential is swept in the cathodic direction, a peak at 2080 cm\(^{-1}\) assigned to the CO stretch at -1000 mV. It remains as the potential is swept to -1200 mV. On the reverse sweep the CO peak persists until 400 mV after which it disappears. Figure B.5 overlays the CO peak intensity with the cyclic voltammogram of Au in CO\(_2\) saturated 0.1 K\(_2\)CO\(_3\) in D\(_2\)O. The disappearance of the CO peak coincides with an anodic desorption event at 0 mV in the voltammogram.
Figure B.2. Potential dependent SERS spectra of aqueous solution of 0.1 M K$_2$CO$_3$ bubbled with CO$_2$. Spectra offset for clarity.
Figure B.3. Cyclic voltammagram of Au electrode in aqueous solution of K$_2$CO$_3$ sparged with CO$_2$ overlayed with peak height versus potential of CO peak.
Figure B.4. Potential controlled Raman spectra of D₂O solution of 0.1 M K₂CO₃ sparged with CO₂. Spectra offset for clarity.
Figure B.5. Cyclic voltammogram of Au electrode in D₂O solution of K₂CO₃ sparged with CO₂ overlayed with peak height versus potential of CO peak.
References


