Electrodeposited metal matrix nanocomposites as thin films and high aspect ratio microstructures for MEMS

Alonso Lozano Morales
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ELECTRODEPOSITED METAL MATRIX NANOCOMPOSITES AS THIN FILMS AND HIGH ASPECT RATIO MICROSTRUCTURES FOR MEMS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
In
The Gordon A. and Mary Cain Department of Chemical Engineering

By
Alonso Lozano Morales
B.S., Universidad de Sonora, Mexico, 2001
December, 2006
To my parents: Juan Lozano Cardenas and Maria Concepcion Morales Cabrera
To my brothers: Genaro, Gabriel and Juan
And to my wife Sandra
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ABSTRACT

The electrodeposition of metal-matrix nanocomposites as thin film and high aspect ratio microstructures (HARM’s) for MicroElectroMechanical Systems (MEMS) components is examined. The effect of γ-Al₂O₃ nanopowder on copper reduction from acidic and basic electrolytes is examined with rotating disk electrodes (RDE’s). At pH 0.2, regions of copper inhibition and enhancement are identified in the kinetic regime. Low particle loading (12.5 g/L) results in an inhibited copper rate, while, high particle concentration (60 g/L) does both, inhibits the rate at low overpotentials and accelerates it at higher overpotentials, depending on the electrode rotation rate. At pH 8 the presence of particles resulted in an enhancement of the Cu reaction rate, while at pH 10 the reaction rate appeared inhibited. The change of the Cu partial current density was attributed to the change of copper complexed species.

A mathematical model that couples particle mass transport with metal kinetics during Cu-γ-Al₂O₃ electrodeposition from acidic electrolytes was developed. The model, based on convective-diffusion transport and Tafel reaction kinetics, is solved numerically, and the calculated species concentrations at the solution-electrode interface are used to describe the electrode processes. The simulation was in agreement with experimental observations, predicting the influence of experimental variables.

A comparison of Cu-particle nanocomposites electrodeposition into deep recesses from sulfuric acid and ammonia-citrate electrolytes is presented, to provide better understanding of how complexing agents affect the copper-alumina codeposition rate and establish the best operating conditions for useful nanocomposites for HARM’s. Recessed electrodes were prepared using X-ray lithography. Partial current density, current...
efficiency and deposited particle concentration were determined with RDE’s. Cu-γ-Al₂O₃, Cu-CeO₂ and Cu-TiO₂ micropost nanocomposites were successfully performed into 500 µm deep recesses. Particle concentration and uniformity was dependent upon particle and electrolyte type.

The electrodeposition of NiCu composites using nanometric diameter alumina and ceria was examined using the Rotating Cylinder Hull Cell (RCHC). A variation in rotation rate was studied with and without particles. The amount of alumina particles in the alloy composite was much higher than the content of ceria with the same electrolyte loading. Particles altered the deposition rate of Cu and Ni affecting the deposit composition.
CHAPTER 1 INTRODUCTION

Composite electrodeposition refers to electrolysis in which micron or submicron size particles are suspended in the electrolyte; the particles become embedded in the electroformed solid phase, imparting special properties to it depending on the degree and type of particle incorporation.\(^1\) Electrodeposition offers advantages over competing technologies such as physical and chemical vapor deposition since it requires simpler instrumentation and operating conditions, and can be used to deposit onto irregularly shaped geometries and deep recesses.\(^2\)

Electrodeposits find numerous applications as thin films and as three-dimensional, thick structures in microdevices. The properties of interest for both thick and thin films cover a broad range, including corrosion resistance, improved wear resistance, microhardness and strength compared with the corresponding values for pure metal or alloy deposits.\(^3\)-\(^13\) Applications for such composite coatings include dry lubricating (or wear resistance) coatings, corrosion and oxidation resistant coatings or dispersion-hardened coatings. Other applications include materials for printed-circuit boards, micromechanics, sensors, actuators, sacrificial layers for microfabrication, functional coatings, electrical contacts, mold inserts, x-ray absorbers, and slide bearings among others.\(^14\)

At the present time, structural materials present two major shortcomings, loss of strength at elevated temperatures and relatively low elastic moduli.\(^15\) A way to solve these problems is to strengthen materials by the incorporation of high-strength and high-modulus particles or fibers in a metal matrix. Methods, such as powder metallurgy, high pressure bonding, internal oxidation and infiltration present disadvantages in the
production of dispersion strengthened and fiber reinforced composites, due to the high process temperatures and pressures required. In electrodeposition there is no requirement for such high temperatures that can damage the particles or fibers.

With the trend toward miniaturization, electrodeposition has established itself as the manufacturing technology of choice. Electrodeposition also holds great promise to conformably deposit metals and composites for microelectronic fabrication and HARMs (High Aspect Ratio Microdevices). HARM’s are typically hundreds of micrometers in height, with widths ranging from a few micrometers to tens of micrometers, and they can be manufactured from materials such as metals, ceramics and polymers. Large surface areas (tens of square centimeters to square meters) covered with HARM’s have potential applications in a variety of fields, including heat transfer, fluid mechanics, composite materials, bearings, and catalytic systems. The use of nanoparticles in the synthesis of metal matrix composites is of interest for the fabrication of microelectromechanical systems (MEMS). Nanocomposite materials exhibit superior wear, hardness and corrosion resistance for the next generation of microdevices, and as thin films for surface finishing applications. In order to produce devices of micron size, the composite material that the device is constructed from must contain nanometric size particles.

Conventional anisotropic silicon etching used to create recesses for subsequent metal deposition is restricted to crystallographic orientations. Traditional ultraviolet (UV) lithography is limited by the depth of the pattern as a result of the lower energy of the UV beams, resist sensitivity and contrast. On the other hand, deep x-ray lithography, which uses high energy x-rays produced by a synchrotron, is utilized to transfer a pattern onto thick x-ray resists with lateral dimensions on the order of a few microns and with heights
of up to 2 mm, so that tall, three dimensional structures can be produced. The importance of electrodeposition as a fabrication technology in the microelectronics industry is growing. High-resolution lithographic techniques has enabled electronic device integration, with electrodeposits several hundred microns thick.

Electrodeposition or electroplating comprises one step of the high-resolution lithographic LIGA process. LIGA is the German abbreviation of the three major process steps, lithography (Lithographie), electroplating (Galvanoformung) and molding (Abformung).\textsuperscript{20} The LIGA process has important features such as microstructures hundreds of micrometers in height, smooth and flat side walls, aspect ratios on the order of 100:1, and economical manufacture of microstructures by molding. The use of the LIGA process overcomes many drawbacks of other traditional fabrication methods and pattern transfer techniques such as chemical etching, sputter etching, reactive ion etching. As an integral part of the LIGA process, electrodeposition is employed after exposure and development of the resist and is used to build up a complementary pattern onto a metal substrate by filling the empty spaces of the electrically non-conductive resist starting from the electrically conducting base. The metal pattern produced can then be used as the microdevice itself or can serve as a mold for plastic replication.\textsuperscript{21} Thus, x-ray lithography combined with electroforming and molding techniques allow the fabrication of microstructures, several hundred micrometers in depth, with any cross sectional shape with nearly atomic resolution and vertical side-walls.\textsuperscript{19}

Even though composite electrodeposition has been studied for the fabrication of thin films, only a few studies have considered composite plating in recesses. Jakob et al.\textsuperscript{22} have codeposited nanometric TiO$_2$ and Al$_2$O$_3$ along with nickel into microstructures.
Yeh et al.\textsuperscript{23} and Wang\textsuperscript{24} demonstrated the electrodeposition of sub-micron SiC-Ni and Al\textsubscript{2}O\textsubscript{3}-Ni composites, respectively into LIGA electrodes.

Although, a few studies on thin films have observed that the presence of particles in the electrolyte influences the metal deposition rate,\textsuperscript{25-29} no systematic model has been able to comprehensibly explain it, particularly in the metal kinetic reduction regime. Thus, in order to better understand changes in the metal rate due to the presence of the nanoparticles, the Cu-particle nanocomposite systems were investigated with rotating disk electrodes. The parameters of interest include: particle electrolyte concentrations, electrode/electrolyte agitation rates and electrolyte pH. The results of electrodeposition onto unrecessed surfaces were then used for electrodeposition of microdevices into deep recessed surfaces.

The overall goals of the work presented here are to investigate and characterize the effects of the electrolyte and applied current/potential on the electrodeposition of Cu-particle nanocomposites into recessed and onto unrecessed surfaces. Both an experimental and theoretical modeling approach are considered. The main parameters of interest include:

1. The effect of hydrodynamic environment (i.e. rotation rate) in characterizing thin film codeposition.
2. A comparison of results with an adsorption and transport model.
3. The effect of the electrolyte pH on the electrodeposition of Cu-particle nanocomposites on unrecessed and recessed surfaces.
4. The fabrication of high aspect ratio composites with controlled composite composition.
1.1 References


CHAPTER 2 LITERATURE REVIEW

2.1 Composite Materials

Even though the origins of composite electrodeposition lie in the early 1900s, most of the application and modeling developments have been achieved in the last 40 years. Table 2.1 shows some typical uses of electrolytic metal matrix/included particle coatings.\(^1,2\) In 1928 Fink and Prince\(^3\) studied Cu-graphite layers electrodeposited for car engine components. In 1962, a patent was issued for the co-deposition of different types of particles within a metal matrix by means of electrodeposition.\(^4\) In 1966 a new technology emerged, Si-C particles co-deposited within a nickel matrix had its first major industrial use in the coating of trochoid bores in rotary engines.\(^5\) In the late 1960s and throughout the 1970s considerable research in composite electroplating was carried out.\(^6,7\) Composites have been applied to many engineering components, usually by electrolytic deposition strategies. The wear life of cylinder/piston combinations have been considerably extended due to the application of this technology to metal matrix/hard particle inclusion in small engines.\(^6\) Also, during the 1960s, important developments were achieved at BAT Vickers.\(^8\) The use of electrodeposits based on, for example, Ni/SiC or Co/WC, enhanced wear and hardness properties at elevated temperatures. Due to the success of composite electrodeposits, similar technology was applied to electroless deposits. In the late 1960s electroless nickel composites were fabricated in Germany, and then were developed in the Netherlands and the USA in the early 1970s.\(^8,9\) Other electroless baths for composite coatings of Ni-borides, Cu-phenolics, and Co-carbides, also have been used. Thus, a wide range of electrical conductivity, temperature
resistance, corrosion resistance, lubricity, hardness and wear resistance can be realized by utilizing these plating processes and different particles.\textsuperscript{10}

**Table 2.1. Some Typical Uses of Electrolytic Metal/Included Particle Coatings.\textsuperscript{1,2}**

<table>
<thead>
<tr>
<th>Work piece or component</th>
<th>Industrial Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bores in aircraft components</td>
<td>Bores coated to size with Co/CrC to reduce wear and fretting at high temperatures and to help eliminate costly welding and grinding operations.</td>
</tr>
<tr>
<td>Piston rings</td>
<td>Cast iron piston rings coated with Co/CrC on external diameter for improved wear resistance/anti-scuffing.</td>
</tr>
<tr>
<td>Aircraft nose wheel steering body</td>
<td>Coated with Co/CrC in the bore to provide wear resistance in sliding contact with Al alloy pistons</td>
</tr>
<tr>
<td>Automobile shackle pin</td>
<td>EN58 hardened pins coated with Ni plus Al\textsubscript{2}O\textsubscript{3} on outside to provide resistance to wear, corrosion and abrasion.</td>
</tr>
<tr>
<td>Glass moulds</td>
<td>Ni plus Al\textsubscript{2}O\textsubscript{3} deposited onto the face of cast iron moulds to provide oxidation and wear resistance.</td>
</tr>
<tr>
<td>Aerospace air conditioning system pump components</td>
<td>Co/CrC to resist dry rubbing wear and fretting at 500 °C.</td>
</tr>
<tr>
<td>Cutting tools in the semiconductor industry</td>
<td>Ni/diamond coatings to provide a thin layer capable of wafer producing a sharp, wear resistant cutting edge on a conventional substrate, e.g. Al or steels.</td>
</tr>
<tr>
<td>Automotive engine cylinder bores</td>
<td>Cylinder bores coated to size with Ni/SiC to reduce wear at elevated temperatures.</td>
</tr>
<tr>
<td>Rotary engines</td>
<td>Ni/SiC particles used on rotary engines to reduce wear on rotating apex seal of Wankel engines</td>
</tr>
<tr>
<td>Cutting tools for semiconductors</td>
<td>Ni/diamond coatings on stainless steel wire used to cut semiconductors wafers.</td>
</tr>
<tr>
<td>Printed circuit board tracking</td>
<td>Cu-epoxy resin to provide a controlled range of electrical conductivity.</td>
</tr>
<tr>
<td>Heat exchangers</td>
<td>Ni/PTFE to promote dropwise condensation and, hence, more efficient heat transfer than a continuous film.</td>
</tr>
<tr>
<td>Automotive clutch components</td>
<td>Ni/PTFE to control friction.</td>
</tr>
</tbody>
</table>
2.2 Copper-alumina Composites

Alumina is the ceramic considered to be the most cost effective and widely used material; it is a hard and wear resistant material with high strength and stiffness as well as good thermal conductivity. Copper-alumina nanostructured composites can be fabricated by chemical routes\textsuperscript{11,12} powder metallurgy,\textsuperscript{13-18} thermochemical processing\textsuperscript{19} and electrodeposition.\textsuperscript{20-27} Their interest lies in the enhancement of mechanical properties compared to the parent metal,\textsuperscript{18,22} and for their thermal and mechanical stability at elevated temperatures.\textsuperscript{28} Applications include its use in electronic packaging, and as materials for electrodes and contact terminals, such as high-performance electrodes for industrial spot welding.\textsuperscript{29}

During the past forty years copper-alumina codeposition systems have been extensively studied. In 1962 Hoffmann\textsuperscript{30} stated that $\gamma$-alumina could not be codeposited from copper sulphate and fluoroborate baths, but it was easily codeposited from copper pyrophosphate and formate plating baths. Today, Hoffmann’s statement has been disproved and $\gamma$-alumina particles have been effectively codeposited from copper sulphate solutions.\textsuperscript{31-34}

Similarly, in 1963 Sautter\textsuperscript{35} confirmed the impossibility of $\gamma$-alumina to be deposited from acid copper sulphate baths. Brandes\textsuperscript{36} in 1967 reported that the microthrowing power of plating baths was very important in codeposition. Tomaszewski\textsuperscript{37} observed that monovalent cations such as $\text{Tl}^+$, $\text{Cs}^+$, $\text{Na}^+$ and $\text{K}^+$ increase the codeposition of $\alpha$ or $\gamma$-alumina from copper sulphate baths considerably.

Later in 1971, Chen and Sautter\textsuperscript{38} found that what determines the feasibility of codeposition with copper from sulphate baths was the crystallographic structure of
alumina: $\alpha$-alumina can be deposited, but $\gamma$-alumina can not. In addition, they found that by increasing the amount of particles suspended in solution, codeposition increased.

In 1972, Saifullin\textsuperscript{39} demonstrated that $\alpha$-alumina codeposition could be increased by the addition of organic additives like thiourea in copper sulphate baths. Malone\textsuperscript{40}, in 1973 showed that $\gamma$-alumina traces could be codeposited from copper sulphate baths, but monovalent cations did not promote such codeposition. In 1974, the zeta potential of alumina in diluted copper sulphate baths was measured by Foster\textsuperscript{41}, and demonstrated that the zeta potential reached high values in the presence of monovalent cations, without a significant effect on the polarization curve. He also discussed the importance of hydrodynamics in codeposition.

Celis and Roos\textsuperscript{31,32} in 1977, demonstrated the ability to codeposit either $\alpha$- or $\gamma$-alumina from acid copper sulphate plating baths, developing a more satisfactory chemical analysis method,\textsuperscript{42} as the basis of the apparently contradictory result with previous findings. Plating parameters such as concentration of particles suspended, current density, and the use of additives were found to have an identical effect on the codeposition of $\alpha$- and $\gamma$-alumina. But, the major difference was that the amount of $\gamma$-alumina deposited was always much lower than $\alpha$-alumina. Also, they reported a maximum in the amount of $\alpha$- and $\gamma$-alumina codeposited with respect to current densities, which was correlated to the potential at which the copper reduction reaction passes from charge-transfer to transport control.

Buelens,\textsuperscript{43} developed a model, which was based on a statistical approach, allowing the prediction of the amount of alumina particles codeposited at different plating conditions. They also reported the important effect of hydrodynamics.
2.3 Copper-ceria Composites

Cerium oxide is a very promising material, which has potential uses in many applications. CeO$_2$ as a pure compound is a good candidate material for the new generation of resistive-type oxygen sensors.$^{44,45}$ Cerium oxide has been widely used as a catalytic activity promoter for the elimination of toxic exhaust gases in automobiles.$^{46,47}$ Also, cerium oxide based solid solutions have been already considered as possible substitutes for zirconia for fuel cell applications due to their higher ionic conductivity in comparison to zirconia ceramics.$^{48,49}$ Ceria thin films can be used as high refractive index materials and insulating films on semiconductors. Nanoparticles have a higher catalytic activity and better sinterability compared with coarse grained bulk materials.$^{50}$

Ceria composites have useful properties for mechanical,$^{51}$ catalytic and electronic applications,$^{52-56}$ as well as for corrosion protection.$^{57,58}$ Kumar et al.$^{51}$ found that a alumina-ceria ceramic composite cutting tool insert shows improvement in the mechanical properties such as hardness and fracture toughness than the pure alumina ceramic cutting tool insert. In a study of the comparison of Cu-Ceria-SDC (Samaria-Doped Ceria) and Au-Ceria-SDC composites for solid oxide fuel cells (SOFC) anodes, it was found that the addition of ceria plays an important role in improving anode performance in solid oxide fuel cells, either through improved catalytic activity or mixed ion-electronic conductivity.$^{52}$ The characterization and reactivity of nanostructured cerium-copper-oxide composites for environmental catalysis has been studied by Adamopoulos et al.$^{53}$ They synthesized nanophase cerium-copper-oxide composites via a co-precipitation approach, concluding that the temperature-programmed reduction
indicated that cerium-copper-oxide composite has an enhanced oxygen storage capacity compared to CeO$_2$ or pure copper oxide. Akyurtlu et al.$^{54}$ studied the behavior of ceria-copper oxide sorbents under sulfation conditions. They found that in the 723-823 K temperature range combined cerium oxide-copper oxide sorbents had specific sorbent capacities (mass of sulfur removed per unit mass of metal sorbent) and sulfation rates significantly larger than those of cerium oxide or copper oxide sorbents used alone. Cu/CeO$_2$/γ-Al$_2$O$_3$ $^{55}$ and CuO/CeO$_2$-based catalysts$^{56}$ have been used for steam reforming of methanol. In a study of the oxidation of a novel chromium coating with CeO$_2$ dispersions, it was demonstrated that CeO$_2$ particles improved the oxidation resistance of steel.$^{57}$ Nunes et al.$^{58}$ studied the corrosion behavior of alumina-aluminum and silicon carbide-aluminum metal-matrix composites, and found that ceria (CeO$_2$) coatings improved corrosion resistance of such composites.

2.4 Copper-titania Composites

Titania has different applications compared to alumina and ceria, for instance it can be used as a photosensitiser for photovoltaic cells, and can enhance the efficiency of electrolytic splitting of water when used as an electrode coating, also as a photocatalyst to detoxify drinking water,$^{59,60}$ decontaminate industrial wastewater and purify air streams.$^{61}$ Titania can also be used to sense the amount of oxygen (or reducing species) present in the atmosphere. Titania thin coatings exhibit self cleaning and disinfecting properties under exposure to UV radiation (antimicrobial coatings), which makes it a good candidate material for applications such as medical devices, food preparation surfaces, air conditioning filters, and sanitary ware surfaces.$^{62}$
Titania film composites also have useful mechanical\textsuperscript{63-66} and corrosion-resistant properties.\textsuperscript{65} In 1986, Warrier and Rohatgi\textsuperscript{63} synthesized copper titania particulate composites from a powder metallurgy method and studied their mechanical, electrical and electrical contact properties. They found that the density of the composites decreased, while their hardness and electrical resistivity increased with increasing titania content. Concluding that copper composites with a 5 wt. % TiO$_2$ could be a good candidate material for light duty electrical contacts. Fawzy et al.\textsuperscript{64} electroplated Cu-$\alpha$-Al$_2$O$_3$ and Cu-TiO$_2$ composites from acidic baths in 1995. They observed that there was a parallelism between the increase in microhardness and the increase in the $\alpha$-Al$_2$O$_3$ and TiO$_2$ wt. % codeposited with copper. Titania particles have also been incorporated into a different metal matrix, for instance, Li et al.\textsuperscript{65} electrodeposited titaniam-nickel nanocomposite coatings consisting of a nanocrystalline nickel matrix (average grain size: 10 nm) and nanometer-sized titania particles dispersed in a nickel matrix and studied their mechanical and corrosion-resistance performance. They reported that Vickers microhardness and corrosion resistance of the nanocomposite coatings increase with increasing content or decreasing grain size of titania particles in the composite coatings. Walker et al.\textsuperscript{66} electrodeposited good quality coatings of lead from fluoborate and fluosilicate baths, and reported that the hardness and strength of the coatings can be increased by the codeposition of powdered titania.

2.5 Mechanisms in Electrochemical Codeposition

The mechanism of particle codeposition is not well understood. Adsorption and electrophoretic effects have been cited as key parameters. Since the particle composition of a deposit also depends on the rate of metal deposition, both rates of metal and particle
incorporation need to be considered. A review of kinetic and mass transport effects on the coupled particle incorporation rate is presented.

Electrophoresis is related to the migration of charged particles in suspensions, due to an electrical field applied. In 1962 Whiters stated that the movement of positively charged particles towards the negatively charged cathode, due to an electrophoretic effect, could be responsible for the codeposition. He was the first to attempt explaining electrochemical codeposition. However, in most plating baths the ionic strength is high, so transport by electrophoresis tends to be small as a result of the low potential gradient in the electrolyte.

Martin and Williams in 1964 suggested that particles were driven to the surface of the cathode as a result of agitation of the bath. The higher the agitation, the more particles would impact the cathode, as a result codeposition will then be governed by the contacting time of particles with the cathode and the rate of metal deposition.

In 1967 Brandes and Goldthorpe proposed particle codeposition resulted from Van der Waals attractive forces acting between particles and the cathode surface, in such a way that once adsorbed onto the cathode the particles will be incorporated into the growing metal matrix.

In 1968 Saifullin and Khalilova were the first to report a model, which calculates the weight percentage of particles incorporated. This model had to be rejected since it was based on mechanical entrapment only. Bazzard and Boden in 1971 suggested that the particles have to stay at the cathode surface for a certain time after colliding with it due to bath agitation, in order to become occluded. Even though they reported an
equation to calculate the particle weight percentage in the deposits, they stated that it lacked any physical significance.

Guglielmi\textsuperscript{71} in 1972 proposed a mechanism that represented a big step forward to explain the codeposition of solid particles with metals. Basically, this model is based on two consecutive steps: during the first step, a loose physical adsorption of particles approaching the cathode takes place; this loosely adsorbed layer of particles is surrounded by adsorbed ions. In the second step, which is electrochemical in nature, the particles become strongly adsorbed on the cathode, due to an electric field applied at the cathode. As a consequence, the strongly adsorbed particles are occluded by the metal growing layer.

Kariapper and Foster\textsuperscript{72} (1974), based on two experimental observations, proposed a mathematical expression to determine the rate of particle entrapment. The first evidence was that due to an increase in agitation rate, the collision of a particle with the cathode increases, and the second was that the forces acting on particles resting on the cathode surface are influenced by agitation.

In 1987, Celis, Roos and Buelens\textsuperscript{73} attempted to predict the amount of codeposited particles for a given metal-particle system by formulating a model which analyzes the transfer of particles from the bulk solution to the surface of the cathode. They proposed a five-step process for the codeposition of particles with metals. In the first step, particles in the bulk of the solution adsorb ions from the solution, thus, a double layer forms around each particle. In the second step, the particles are transported by convection to the hydrodynamical boundary layer. Then, in the third step, the particles diffuse through the diffusion layer to the surface of the cathode. Finally, similar to the model proposed by
Guglielmi, the particles are incorporated in two steps. Particles surrounded by ions are adsorbed on the cathode, becoming embedded when some of these ions are reduced.

A more general model than that of Celis et al.\textsuperscript{73} was proposed by Hwang and Hwang.\textsuperscript{74} This model, based on Gugliemi’s, states that the codeposition rate of particles is determined by the reduction rate of adsorbed species on the particles, whose rates are determined by kinetic and/or diffusion parameters. Since they investigated the codeposition of Co-SiC, the reduction of H\textsuperscript{+} and Co\textsuperscript{2+} is their starting point. In the reduction of these ions adsorbed on the particles, three different current density regions were distinguished: a low current density region, where only H\textsuperscript{+} can be reduced, an intermediate current density region, where Co\textsuperscript{2+} is reduced and H\textsuperscript{+} has reached its limiting current density, and finally a high current density region, where the reduction rate of both ions is transport limited.

Guo et al.\textsuperscript{75} came up with a model that describes the mass transport by similitude numbers, which are dimensionless and determined by the factors influencing mass transport. The Sherwood number for mass transport of particles to a fixed plate in a dilute suspension was modified for codeposition. Nevertheless, the model may not predict key features like a maximum particle concentration versus current density, due to a limited range of experimental data, and due to the absence of kinetic effects.

In 1987 Valdes and Cheh\textsuperscript{76} reported a model for codeposition of small particles (e.g. on the nanoscale) on a rotating disk electrode (RDE). In this model, they took into account the different ways particles are transported. An equation of continuity was chosen for the particle number concentration based on a differential mass balance. The expression was composed of different mass transport processes such as Brownian
diffusion and convection. They showed that the “perfect sink” model predicts a particle concentration maximum at the limiting current density, contradicting experimental observations. The perfect sink model states that all particles arriving within a critical distance of the electrode surface are captured. Thus, they had to propose a different model based on the assumption that the reduction rate of the ions adsorbed on the particles is the main factor for the electrodeposition of particles, consistent with experimental evidence from the literature.

A different model for micron size particles was developed by Fransaer et al. They developed a particle trajectory model, based on all forces and torques acting on a particle: gravity, electrophoretic force and the double layer force. This model fails close to the electrode surface because it leads to the “perfect sink”. Because of this problem, they introduce the particle-electrode interaction term, introducing a new equation for the probability that a particle at the electrode surface will be incorporated, which gives a good description of the variation of the amount of particles in the deposits as a function of the bath particle concentration. The trajectory model also, does not predict a maximum particle concentration with respect to current density, and it is not applicable to nanosize particles where Brownian motion is expected to dominate.

2.6 LIGA Process

2.6.1 X-ray Lithography

Due to an increase in density of memory, logics and storage, devices were being placed more closely, and as a consequence it became necessary to make the conductors to these devices thicker to maintain low current density and avoid electromigration. Due to the nature of chemical etching it was impossible to place conductors more closely than
twice the thickness of the film from which they were etched. In response to such needs, electroplating through-lithographic mask technology was then explored instead of vapor deposition followed by etching, being first introduced for electronic device fabrication in the IBM T. J. Watson Research Center in the late 1960s. This patterning technology consists of using thin film seed layers, applying thick polymeric resist, patterning the resist with an inverse pattern, electrodepositing the metal into the recesses, and subsequently removing the resist and the thin seed layer, creating a 3D pattern. Romankiw et al. were the first to carry out experiments with thin film seed layers and electroplating of copper conductors through lithographic resist mask, at IBM’s T. J. Watson Research Center.

The most difficult and demanding task during the early days of x-ray lithography was the fabrication of the x-ray masks. It was difficult to obtain x-ray gold absorbers pattern by ion milling. The patterns had fuzzy edge definition, not sharp, and the trenching action of the ions during ion milling or sputter etching of the patterns in gold frequently weakened or punctured the thin diaphragm. Later, the problem was solved by fabricating x-ray masks by using a 50 Å Ti and 300 Å gold conducting seed layer on the diaphragm coated with PMMA. As result, very well-defined features with perfectly vertical walls were achieved, which led to extremely well-defined sharp edges of the patterns. In 1974 the first demonstration of the deep etch patterns generated in PMMA using synchrotron radiation was produced with 60:1 aspect ratio.

The LIGA process was first developed at the Karlsruhe Nuclear Research Center (KfK) in Germany in the late 70s, in addition to IBM in the USA. Not only does LIGA offer a wider selection of materials when compared to techniques such as wet-chemical
etching of single-crystalline silicon,\textsuperscript{81} or dry-etching processes by means of low-pressure plasma,\textsuperscript{82} but also properties like optical transparency, mechanical stiffness and hardness, electrical conductivity and magnetic properties, can be obtained, which opens new opportunities for the fabrication of micro-mechanical, micro-fluidic and micro-optical components. As a result, hybrid systems are being developed and put into the market,\textsuperscript{83} such as “milli” rotational motors, micro-pumps, linear motors, photonic systems, and various analytical devices assembled with high precision LIGA components. The LIGA process can be applied in fields as diverse as sensors for environmental, medical, communication and automotive technologies, chemical and biological analysis.\textsuperscript{84,85}

A typical sequence of the major processing steps involved in the production of microstructures using the LIGA process consists of firstly generating the primary pattern by deep x-ray lithography using synchrotron radiation. Next, manufacturing metal microstructures by electroplating can be the end product or it can be transferred into a robust mold insert. Injection molding or hot embossing are molding techniques that enables cost effective mass production of LIGA parts in materials such as metals, ceramics or polymers. In the first step the absorber pattern on an x-ray mask is transferred into a thick resist layer by shadow printing with synchrotron radiation. Then the resist layer is applied on a conductive substrate, which is used as the cathode in electroplating. Polymethyl methacrylate (PMMA) is the x-ray resist most commonly used. The x-ray photons are absorbed within the irradiated regions, resulting in main chain scission of the PMMA, enhancing the solubility in this section; it can be dissolved completely. Next, by electrodeposition of typical metals such as Cu, Au, Ni, the microstructure pattern is plated-up. Finally, PMMA is dissolved leaving the patterned metal structures as the end
product. Alternatively, a robust mold insert can be produced by extending the electroplating to reach a thickness of several millimeters above the height of the primary structure. Then the mold insert can be replicated by molding techniques, such as injection molding, reaction injection molding or hot embossing into metal, ceramic or polymer materials, offering a way to low cost mass production of LIGA microstructures.\textsuperscript{86,87}

X-ray lithography in combination with electroplating is a technique for the fabrication of High Aspect Ratio Microdevices (HARM’s), which are typically hundreds of micrometers in height, with widths ranging from a few micrometers to tens of micrometers. In 1989, Benecke \textit{et al.}\textsuperscript{88} produced a microactuator, which is based on a bimaterial effect, and used extensively in the fabrication of temperature controlled electrical switches. In 1991, Bley \textit{et al.}\textsuperscript{89} fabricated a microgear made of nickel. Wallrabe \textit{et al.}\textsuperscript{90}, in 1992 fabricated, designed, and tested an electrostatic stepping micromotor successfully using the electrostatic principle. Mohr \textit{et al.}\textsuperscript{91} (1992) used electromagnetic activation to measure the fatigue behavior of micromechanical elements made of electroplated nickel. In 1993, Guckel \textit{et al.}\textsuperscript{92} fabricated a micromotor using four stacked layers based on the electromagnetic principle. Lochel \textit{et al.}\textsuperscript{93} in 1994, demonstrated a three-dimensional micro coil winding made of nickel-iron, the next year (1995), they also demonstrated magnetically driven linear actuators.\textsuperscript{94} In the same year, a microturbine was fabricated at the Center for X-ray Lithography (CXRL) in Wisconsin employing 500-micron thick nickel turbine and a plated copper stator.\textsuperscript{95} In 1996, Acosta \textit{et al.}\textsuperscript{96} designed, fabricated and operated a variable reluctance magnetic motor using permalloy rotors and stators. Also, Doppler \textit{et al.}\textsuperscript{97} have microfabricated gear pumps for viscous fluids. In 1997, Fischer \textit{et al.}\textsuperscript{98} studied two different methods to increase structure heights using the
single layer technique and the multi-layer stacking technique. Because assembly adds a step to batch fabrication along with other alignment and clamping issues and techniques, single layer devices have the advantage of ease of assembly. The disadvantages are long development cycles and electroplating times. Lehr et al.\textsuperscript{99} used microactuators of ferromagnetic materials like Ni and NiFe to make fiber optic switches due to a strong demand for fiber optics in high data transfer. Liu et al.\textsuperscript{100} (1997) fabricated microchannels (made out of nickel) by molding glass onto a 20:1 and 150 µm high pattern. In the following year, Ford et al.\textsuperscript{101} fabricated an integrated microdevice (out of PMMA) comprising of a piezo-driven micropump and a microelectrophoresis device with a fluorescence detector. Leith et al.\textsuperscript{102} in 1999 produced a microgear of nickel iron made by selective etching of iron rich layers, made by modulating the composition using pulsed electrolyte agitation. Also in 1999 Sadler et al.\textsuperscript{103} made an electromagnetic actuator by plating nickel-iron permalloy in the shape of a micromachined horseshoe type inductor and, in 2001, an eddy current sensor\textsuperscript{104} which consisted of coils of nickel-iron permalloy as the magnetic core to fabricate a proximity sensor capable of detecting cracks on the order of a few hundred microns. Bauer et al.\textsuperscript{105} used the LIGA process to produce optical waveguides used in telecommunications by compression molding of PMMA. In 2001, a microfluidic device made by the LIGA process from PMMA and PC to identify genes associated with cancer causing genes, by the ligase detection reactions using either micro-electrophoresis or DNA microarrays was demonstrated by Soper et al.\textsuperscript{106} Katsarakis et al.\textsuperscript{107} in 2002 fabricated a metallic photonic band-gap crystal for use as filters in high-frequency devices; they used square and triangular lattices of nickel posts 800 µm tall in PMMA. Morales et al.\textsuperscript{108} produced complex metal cantilevered
microstructures on multiple levels. In 2003, Oka et al. developed a micro-optical distance sensor using a combination of micromachining and the LIGA process.

2.7 Composite Electrodeposition in Recesses

Even though the deposition of composite coatings on flat and cylindrical geometries has been achieved, very little work exists on their deposition into deep recessed geometries. In 1999, Yeh et al. performed DC electrodeposition of micron and submicron sized SiC and Ni from a nickel sulfamate bath of a hundred microns thick film for MEMS applications. It was found that not only the particulate concentration in the deposit increased with increase in the powder concentration in the electrolyte, but also the internal stress increased. Lower currents yield a decrease in the internal stress in the deposit. With finer particles hardness improved and a smoother surface was obtained. No measurements were done to determine the uniformity of particles in the microstructure. The same year (1999) Wang deposited γ-alumina and nickel from a nickel sulfamate electrolyte with different particle loading at acidic pHs. A horizontal and a vertical electrode setup were investigated. Two distinct regions divided by a slanted boundary were evident in the vertical setup, one with high and the other with lower alumina concentrations. The region at the bottom of the recess had lower alumina concentration than at the top and can be attributed to the weaker agitation deep inside the recess. In a horizontal setup, the distribution was more uniform. The resulting microposts had a high 40-wt % alumina average concentration, due to extremely agglomerated particles in the electrodeposit.

Flores et al. in 2000 deposited Cu and γ-alumina by potentiostatic deposition from a citrate electrolyte at a pH of 4.0 into recesses 500 micron deep. The resulting microstructures contained 3 % by weight of alumina in average, but poor adhesion and
void formation was evident. Conditions were not optimized. In 2000, Jakob et al.\textsuperscript{113} electrodeposited nanometric alumina and titania along with nickel from a Watts bath in microstructures for tribological applications. The recesses were about 50 µm deep. A high concentration of alumina in the electrolyte (5 volume %) was reported. They observed agglomeration of the particles and a height dependent incorporation. In a study of the electrodeposition of Ni-Cu-γ-Al\textsubscript{2}O\textsubscript{3} into deep recesses by Panda and Podlaha,\textsuperscript{114} particles were found to increase the reaction rate of copper in the recesses. No studies about how complexing agents affect the copper-particle codeposition rate have been reported yet.

2.8 References


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CHAPTER 3 EXPERIMENTAL DESIGN

The experimental setup, substrate preparation, and apparatus used for characterization of thin film and microdevice composites are described in this chapter.

3.1 Thin Films

Two and three electrode systems are used to perform the electrodeposition of metal-matrix nanocomposites thin films on cylinder and rotating disk electrodes, respectively. Figure 3.1 shows a schematic diagram of a typical two electrode cell set up. The cathode is the working electrode (WE) on which the nanocomposites are electrodeposited, and the anode is used as the auxiliary or counter electrode (CE). Figure 3.2 shows a schematic diagram of a typical three electrode cell set up. In this set up a third electrode is used to monitor the potential at the WE, the reference electrode (REF); and is placed as close as possible to the cathode to reduce the solution resistance between them and consequently minimize the ohmic drop effects. Current or potential can be controlled by using a galvanostat or potentiostat, respectively.

3.2 Recessed Electrodes

3.2.1 Substrate Preparation

The recessed electrodes were produced by exposing 500 µm thick polymethylmethacrylate (PMMA) sheets attached to copper plates to X-ray radiation at the LSU-CAMD synchrotron facility, following the procedure of Kanigicherla. Square copper plates of 2.5 cm by 2.5 cm and thickness 0.75 mm were used as standard substrates. Each copper plate was mechanically polished and cleaned up with soap, water, and acetone and then rinsed with a 10% sulfuric acid solution for 2 minutes. Finally, it
Figure 3.1. Schematic of a two-electrode cell.

Figure 3.2. Schematic of a three-electrode cell.
was rinsed in deionized water for 3 minutes. Table 3.1 shows the components of the solution used to oxidize the copper surface in order to promote adhesion to the PMMA sheet. After placing the copper plate in the oxidizing solution at a temperature of 95 °C for 20 minutes, it was rinsed in deionized water and dried.

**Table 3.1** Composition of the oxidizing solution used to oxidize copper electrode

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₂</td>
<td>54.26</td>
</tr>
<tr>
<td>NaOH</td>
<td>68.00</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>11.44</td>
</tr>
<tr>
<td>NaCl</td>
<td>4.67</td>
</tr>
</tbody>
</table>

3.2.2 Bonding

The 500µm thick PMMA sheet was cut in the same size as the copper plates, and was bonded to the copper substrates using the bonding solution shown in Table 3.2.

**Table 3.2.** Bonding solution composition used to bond PMMA and Cu/CuOx electrode.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Methacrylate (MMA)</td>
<td>0.919</td>
</tr>
<tr>
<td>Powdered PMMA</td>
<td>0.055</td>
</tr>
<tr>
<td>Benzoil Peroxide (BPO)</td>
<td>0.0164</td>
</tr>
<tr>
<td>Dimethyl Aniline (DMA)</td>
<td>0.011</td>
</tr>
</tbody>
</table>
It is important to take into account the order of mixing: MMA and DMA are mixed together first, followed by the addition of the powders PMMA and BPO. The mixture was magnetically stirred for about 4 hrs. The bonding solution was added on the oxidized copper substrate and the PMMA sheet was affixed on to it. To assure good adhesion, air bubbles trapped between the PMMA sheet and the copper plate, were removed manually. Immediately after, a pressure of about 10 psi was applied to the substrate and was left overnight to let the bonding solution solidify.

3.2.3 Lithography of PMMA

X ray lithography is based on the principle of collimated high energy X rays generated from a synchrotron radiation facility that are incident on a 2-D mask patterned with a high atomic number absorber and a low atomic number membrane or an open area. Figure 3.3 shows a schematic of the exposure. The X rays pass through the membrane or open area of the mask and induce exposure of polymethylmethacrylate (PMMA). During exposure to X rays, the average molecular weight of the PMMA decreases in the irradiated areas due to the scission of long polymers chains. The exposed PMMA becomes soluble and can be removed with a developer (chemical solvents), which preferentially dissolves the lower average molecular weight resist. The removal of the PMMA is called development. The conductive base layer in the developed region is then ready to electroplate any desired metal or composite. The microstructures may be the final product or serve as a mold insert for injection molding and used to reproduce secondary polymer, ceramic, or metal templates nearly identical to the primary PMMA template.
The bonded PMMA/Cu sample was placed behind a tantalum (Ta) mask and exposed to collimated X rays (wavelength 4Å) at XRLM-3 beamline and 1.3 GeV at CAMD. Table 3.3 lists the exposure conditions. In front of the Ta mask an aluminum filter was placed to absorb photons of lower energy so that the appropriate ratio of top dose to bottom dose received by PMMA can be ensured. The dose of exposure at the bottom was 3500 J/cm$^3$, which was enough to ensure complete development. A top to bottom dose not exceeding 7.5 was used with a 0.4 inches scan length and scan speed of 0.5 inch/s. The tantalum mask used was square patterned with 183 x183 µm squares, 75 µm apart. The thickness of the resist was 500 microns.

3.2.4 Development and Rinsing

The next step after x rays exposure was development and rinsing of the PMMA exposed. Here the main goal is to remove the PMMA exposed to x-rays during lithography, which is achieved in a two step process. First, the resist is dissolved using an appropriate developing solution,$^2$ whose components are listed in Table 3.4, followed by a rinsing step, Table 3.5.$^2$ Usually, the rinsing step is longer than the developing one.

The complete removal of the PMMA was achieved in 3 cycles. Each cycle consists of 40 minutes in the developer, 20 minutes in the rinsing solution. Ultrasonic agitation (Branson Model #1510) was used during the developing and rinsing steps to accelerate the removal of the resist.$^3$ It is important to mention that the use of ultrasound results in the production of heat. Prolonged times of ultrasonic agitation resulted in delamination of the resist from the copper oxide and sometimes it broke down. Therefore, it is very important to allow the developing and rinsing solution to cool down between cycles. Finally, right after the development and rinsing process, the sample was left in a beaker.
with deionized water magnetically stirring for 5 minutes to assure complete removal of the developed material.

Figure 3.3. Schematic of the x-ray lithography process.
Table 3.3 Conditions of exposure for 500 µm PMMA at CAMD beamlines.

<table>
<thead>
<tr>
<th>Beamline</th>
<th>Be Filter (µm)</th>
<th>Al Filter (µm)</th>
<th>Energy (MeV)</th>
<th>Dose (mA.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRLM-2</td>
<td>175</td>
<td>16</td>
<td>1.3</td>
<td>11300</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>16</td>
<td>1.45</td>
<td>3878</td>
</tr>
<tr>
<td>XRLM-3</td>
<td>250</td>
<td>16</td>
<td>1.3</td>
<td>3655</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>16</td>
<td>1.45</td>
<td>11808</td>
</tr>
</tbody>
</table>

Table 3.4 Components of the developing solution used to remove the exposed PMMA.

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene glycol butyl ether</td>
<td>600</td>
</tr>
<tr>
<td>Morpholine</td>
<td>200</td>
</tr>
<tr>
<td>2-aminoethanol</td>
<td>50</td>
</tr>
<tr>
<td>Water</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 3.5 Components of the rinsing solution used to remove the PMMA.

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene glycol butyl ether</td>
<td>800</td>
</tr>
<tr>
<td>Water</td>
<td>200</td>
</tr>
</tbody>
</table>
3.2.5 Etching

Etching of the substrate was carried out to remove the copper oxide layer at the bottom of the recess in the developed areas before the electrodeposition process. This was achieved by leaving the substrate for 4 minutes in a beaker containing the etching solution. This will expose the areas of the conductive copper plates covered by the copper oxide layer to the electrolyte, making possible the flow of current. Table 3.6 lists the components used for the etching solution. After etching, the sample was rinsed using deionized water for 5 minutes and finally, it was placed it in the electrode holder for electroplating.

Table 3.6 Components of the etching solution used to remove the copper oxide.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Chloride</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.2.6 Holder Design

The electrode holder consisted of two circular PEEK disks of 5.5 cm in diameter and 1 cm thickness. The disk on the top had the center cut out in a circular form with a 1.5 cm diameter. This is the only section of contact between the substrate and the electrolyte, providing a plating area of approximately $1.58 \text{ cm}^2$. The disk on the top has two concentric O-rings embedded in grooves to completely seal the electrode holder and avoid any contact of the solution with the copper substrate from the outer sides, also to
prevent the solution from seeping in from the inner circular shape. The outer O-ring is separated 1.8 cm from the center and 0.7 cm from the inner O-ring. Twelve equidistant holes of 4 mm where drilled between the outer O-ring and the outer edge of the disk on the top; the same number of screw holes where drilled in the bottom disk.

Figure 3.4 shows a schematic for the electrode holder used in the experiments. A square copper plate of 2.4 by 2.4 cm was embedded into a recess in the center of the bottom disk, so that the entire surface was planar. A hole was drilled through the center of the disk from the backside to provide electrical contact by means of an insulated copper wire of 3.7 mm diameter. The developed recessed electrode was placed on the top of the copper plate in the bottom disk, and the two disks were screwed together with plastic nylon screws. Just before the electrodeposition, the entire holder setup was rinsed with deionized water and placed in an ultrasound bath to ensure that all the air bubbles inside the recesses were removed. The 1 cm recess between the top of the substrate-PMMA electrode and the outer edge of the holder promotes uniform current distribution across the features.

3.3 Plating Cell Setup

3.3.1 Deep Recesses Microelectrodes

A 1000 mL reaction kettle made of Pyrex glass was used to contain the electrochemical cell. The whole electrode assembly is suspended by the insulated copper wire attached to the bottom disk (from the back side) of the electrode holder. A perforated copper plate of 6 by 6 cm was used as the anode, which was affixed to the insulated copper wire supporting the electrode holder. The holes on the anode were 0.7 cm in diameter.
Figure 3.4 Top views of (a) top and (b) bottom of the electrode holder.

The anode was 2 cm above the surface of the electrode holder and parallel to it. A different insulated copper wire was attached to the anode to make electrical contact. The perforations in the anode were made to keep the particles uniformly dispersed. Both, mechanical (Arrow, Model No. 1750) and magnetic (Corning Inc.) agitation were used to keep the electrolyte in uniform suspension and to avoid particle sedimentation and formation of local concentration gradients.

A horizontal face up orientation not only helps the gas bubbles generated during electroplating to escape out of the recesses, but also helps to avoid geometric-dependent distributions, because nanoparticles tend to settle uniformly within the recess. Figure 3.5 shows a schematic of the set up for the electroplating cell used. Trapped water in the
recesses was allowed to diffuse out, and the electrolyte could diffuse in, by allowing the electrode to stand in solution for at least five minutes before any experiment was conducted.

Figure 3.5 Schematic for the set up of a face-up recessed electrode.
3.3.2 Rotating Disk Electrode

The Rotating Disk Electrode (RDE) is typically used for laboratory studies due to its ability to control hydrodynamic conditions; it is the most popular among the electrodes used for electrochemical experiments under controlled mass transfer conditions, because the boundary layer thickness can be derived analytically.

Preliminary studies were performed with RDE’s before proceeding to electroplating into deep recesses. Figure 3.6 shows a schematic of the RDE set up used in the experiments. A three electrode system with a cell volume of 1000 ml was used to perform the experiments; a rotating disk electrode was used as the cathode. The disk was 6 mm in diameter, stainless steel 316 plated with a Au surface layer (Acid gold strike and Orpotem 24 gold solution by Technic Inc.) for improved adhesion. A copper foil with an array of 7 mm holes was used as the anode. The anode was kept stationary and was placed parallel to the working electrode. The holes in the anode helped to avoid accumulation and settling of alumina particles on it, and promote a homogeneous distribution of the particles in the electrolyte. A saturated calomel electrode was used as the reference electrode. Nitrogen was bubbled in the experimental cell prior to the experiments for a period of 20 minutes. Electroplating conditions for deep recesses were based on those used for rotating disk electrode experiments.

3.3.3 Rotating Cylinder Hull Cell (RCHC)

The RCH cell is used to electrodeposit alloy-matrix nanocomposite thin films on Rotating Cylinder Electrodes (RCE’s). The Hull cell is a trapezoidal cell arrangement of the anode and cathode that has been conventionally used for assessing the deposit morphology and composition at different current densities⁴ (Figure 3.7). When reactions
are facile and field effects dominate there is a large current distribution, i.e. primary
current distribution. A shortcoming of the typical Hull cell is the absence of controlled
mass-transport conditions. In addition, particle codeposition requires particles to be kept

![Figure 3.6](image)

Figure 3.6 Schematic for a typical rotating disk electrode (RDE) set up.

in suspension in the electrolyte through either chemical or mechanical means. Simple
mechanical agitation with a control of mass transport of both the metal ions and particles
can be obtained with a Rotating Cylindrical Hull Cell (RCHC) introduced by Landolt et al.,\textsuperscript{5-7} and commercially available by Eco Chemie B.V., Utrecht, The Netherlands.\textsuperscript{8}

\textbf{Figure 3.7} Schematic of a typical Hull cell set up top view. Dimensions in cm.

The RCHC (Figure 3.8) consists of a rotating cylinder electrode and an asymmetrically placed counter electrode. The current is shielded from the electrode with a suitably placed concentric, plastic barrier. It is relatively simple to use without the need of elaborate pumping systems and does not require a large volume of electrolyte. Due to the particular arrangement of the anode and cathode a well controlled non-uniform current distribution is developed along the cathode length. With the RCHC a wide range of metals, alloys or composite materials can be electrodeposited with a control of the electrolyte solution hydrodynamics in a single experiment.
**Figure 3.8.** Schematic of a RCH cell. The cylinder cathode (A) attached to the motor (B), and a concentric Pt anode (C) electrically connected through a copper friction contact (D) meet at output (E) to the RCH cell controller. A plastic shield (F) is placed concentrically with the cylinder cathode. Dimensions in cm.

### 3.4 Composite Characterization Equipment

Figure 3.9 shows a KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF) used to analyze thickness and composition of the deposits along the cylindrical cathodes obtained from the RCE experiments. Particle weight percentage along microdevices and thin film deposits electroplated on RDE’s was analyzed using
Scanning Electron Microscopy (SEM, JEOL JXA-733) with Wavelength-Dispersive X-ray Spectrometer (WDS) (Figure 3.10), the particle concentration calculations were made using the CAF correction method. For topographical information of thin film and microdevice deposits a SEM, JEOL 840A was employed (Figure 11). Transmission electron microscopy (TEM JEOL 100CX) was used to analyze the presence of nanoparticles embedded in the deposits (Figure 12). See Appendix B for sample preparation procedures for SEM and TEM analyses.

**Figure 3.9.** KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF).

**Figure 3.10.** Scanning Electron Microscope equipped with WDS (JEOL JXA-733).
Figure 3.11. Scanning Electron Microscope (JEOL 840A).

Figure 3.12. Transmission Electron Microscope (JEOL 100CX).

3.5 References


CHAPTER 4 EFFECT OF $\text{Al}_2\text{O}_3$ NANOPOWDER ON Cu ELECTRODEPOSITION FROM ACIDIC ELECTROLYTES*

The effect of $\gamma$-$\text{Al}_2\text{O}_3$ nanopowder electrolyte concentration and rotation rate on copper reduction from sulfuric acid electrolytes was examined with rotating disk electrodes. Regions of copper inhibition and enhancement were identified in the kinetic regime, with little change in the mass transport copper limiting current density.

4.1 Introduction

Composite electrodeposition refers to electrolysis in which micron or submicron size particles are suspended in the electrolyte; the particles become embedded in the electroformed solid phase, imparting special properties to it depending on the degree and type of particle incorporation. Some characteristic features of composite deposits are: improved wear resistance, microhardness and strength compared with the corresponding values for pure metal or alloy deposits. Cu-alumina and Ni-alumina composite coatings exhibit higher yield, ultimate tensile strengths and lower ductility than pure copper or nickel deposits. A smaller decrease in hardness and coercivity during annealing was observed for alumina-strengthened nickel samples compared to bulk Ni. The microhardness of copper-$\alpha$-$\text{Al}_2\text{O}_3$ and copper-$\text{TiO}_2$ composites increased when the concentration of $\alpha$-$\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ codeposited with copper was increased.

There are many studies that attempt to predict the degree of particle incorporation into the deposit as a function of the plating variables\textsuperscript{13-31} but none have focused on the effect the particle has on the metal reduction rate. A few studies have observed that the presence of particles in the electrolyte influences the metal rate.\textsuperscript{32-36} Watson and Walters\textsuperscript{32} showed that chromium particles catalyzed nickel electrodeposition from an electrolyte containing 1-2 $\mu$m average diameter particles on rotating cylinder electrodes. In contrast, Webb and Robertson\textsuperscript{33} reported an inhibition of nickel reduction with 0.01 $\mu$m $\gamma$-Al$_2$O$_3$ particles. In their study, using rotating disk electrodes, the nickel polarization curves shifted to more cathodic potentials with an increase in the concentration of alumina particles in the bath. In addition, an increase in the electrolyte alumina particles increased the weight % of alumina incorporated into the solid films. The effect of $\gamma$-Al$_2$O$_3$ particles (50 nm diameter) on copper electrodeposition from a sulfuric acid electrolyte using a rotating cylinder electrode has also been reported by Stojak and Talbot.\textsuperscript{34} The current density decreased with the addition of particles in the kinetically-limited region. Under mass transfer control, with the addition of particles, the limiting current density remained the same at low particle loadings (i.e. 39 and 129 g/l), and was enhanced for higher particle concentrations (i.e.158 g/l). Podlaha and Landolt\textsuperscript{35} observed an inhibition of the cathodic copper current density in citrate electrolytes using rotating cylinder electrodes. The anodic current density was lowered (inhibited), at small current density (from 0 to $\sim$ 40 mA/cm$^2$) but was larger (enhanced) at high applied current densities (from 40 to $\sim$ 100 mA/cm$^2$). In contrast, other studies have shown that there is no change in the metal deposition rate with particle addition to the electrolyte. For example, Hwang and Hwang\textsuperscript{36} have studied the co-electrodeposition of silicon carbide ($\sim$3 $\mu$m diameter particles)
with cobalt. They observed that the particle content (up to 5 g/l) in solution has no effect on the polarization curve.

The main goal of this study was to try to better characterize inhibition and enhancement effects in an uncomplex, simple copper sulfate electrolyte. The effect of different alumina particle electrolyte concentrations on copper electrodeposition at different electrode rotation rates was studied and compared with the deposition of the pure metal.

4.2 Experimental

4.2.1 Solution

Electrolytes were composed of copper sulfate and sulfuric acid, with and without the addition of \(\gamma\)-Al\(_2\)O\(_3\) particles. The content of the copper solution was 0.1 M CuSO\(_4\)•5H\(_2\)O and 1.2 M H\(_2\)SO\(_4\). The pH was adjusted to a value of 0.22 ± 0.02 with sulfuric acid. The \(\gamma\)-Al\(_2\)O\(_3\) particle electrolyte loadings were 0, 12.5, 39 and 60 g/L having an average particle diameter of 32 nm supplied by Nanophase Technologies Corporation, IL, USA. The particles were kept in suspension using a magnetic stirrer. According to Lee and Wan\(^3\), the zeta potential of \(\gamma\)-Al\(_2\)O\(_3\) particles in an acidic copper electrolyte for cupric sulfate concentrations below 0.1 M is negative.

4.2.2 Electrochemical Cell

A three electrode system with a cell volume of 1000 ml was used to perform the experiments; a rotating disk electrode was used as the cathode. The disk was stainless steel 316 plated with a Au surface layer (Acid gold strike and Orpotem 24 gold solution by Technic Inc.) for improved adhesion. A copper foil with an array of 7 mm holes was used as the anode. The anode was kept stationary and was placed parallel to the working
electrode. The holes in the anode helped to avoid accumulation and settling of alumina particles on it, and promote a homogeneous distribution of the particles in the electrolyte. A saturated calomel electrode was used as the reference electrode. Nitrogen was bubbled in the experimental cell prior to the experiments for a period of 20 minutes.

4.2.3 Procedure

A computer controlled potentiostat and impedance system (Zahner IM6e) were used to measure polarization curves, ohmic resistance and for Cu-alumina plating. Polarization curves were measured without and with particles for electrode rotation rates of 900, 1600, 2500 and 3600 rpm (laminar flow regime). All polarization scans were performed by increasing the cell potential from the open circuit value (200 mV vs SCE) to –1.2V at a scan rate of 5 mV/s. The frequency range used for the impedance spectra was of 1 MHz to 100 mHz. The constant net plating charge used was 27 C/cm² for each deposit. The agitation of the suspension was controlled by the rotating electrode hydrodynamics by keeping the agitation due to the magnetic stir bar at the bottom of the cell to a minimum. The mass of the copper thin films was determined by stripping analysis in a 1.2 M H₂SO₄ solution using a Bipotentiostat Model AFCBP1 (PINE Instrument Company). The current efficiency was calculated taking the ratio of the total stripping charge to the total charge applied for each deposit.

4.2.4 Composition Analyses

The alumina weight percentage was analyzed using a WDS electron microprobe (Superprobe 733, Jeol). Four points chosen randomly were analyzed for each sample calculating an average value; the standard deviation is shown as error bars in the corresponding figures. Alumina concentration was determined by the stoichiometric ratio
of oxygen to aluminum, as Al₂O₃. The conditions used for the analysis were: a beam current of 10 nA and a magnification of 6000. A scanning electron microscope (Jeol, JSM-840A) was used to observe the surface roughness of deposits with different amount of alumina particles; all the micrographs were taken with a magnification of 500. Also, transmission electron microscopy (TEM-JEOL 100CX) was employed to analyze the presence of alumina particles in the deposits at 200 KeV and a point to point resolution of 23 nm to produce the optical and bright-field images. See Appendix B for sample preparation procedures for SEM and TEM analyses.

4.3 Results and Discussions

4.3.1 Current-potential Relationship

The effect of particle loading on the current-potential relationship is shown from Figure 4.1a through Figure 4.1d at different electrode rotational rates. At an electrode rotational rate of 900 rpm, Figure 4.1a, there is almost no effect on the polarization curve for a particle loading of 12.5 g/L. At both 39 and 60 g/L, the current density decreases for a given potential from the kinetically-controlled region to the mass transfer region. It is important to point out that there is a bigger inhibition in the current density for a particle loading of 39 than for 60 g/L, which is unexpected if a simple electrode blocking mechanism by particles is assumed. The electrode rotation rates of 1600, 2500 and 3600 rpm are shown in Figures 4.1b through 4.1d, respectively, for each of the four electrolytes. The figures are similar to the polarization curves at 900 rpm, except for the polarization curve corresponding to 60 g/L, which shows both inhibition (< ~ -0.17 V) and enhancement (> ~ -0.17 V). At 1600 rpm, inhibition of the total polarization is observed at low current densities and then makes a transition at –0.16 V becoming
enhanced. The electrode rotational rates of 2500 rpm (Figure 4.1c) and 3600 rpm (Figure 4.1d), show an enhancement in the total polarization. In contrast to the effects observed in the kinetically-controlled region due to the presence of particles in the electrolyte, there is almost no significant effect in the mass transfer region for a particle loading up to 60 g/L, as shown in the Levich plot (Fig. 4.2), of the apparent limiting current density as

**Figure 4.1.** Effect of particle loading on polarization scans at different electrode rotation rates: (a) 900, (b) 1600, (c) 2500, and (d) 3600 rpm.
a linear function of the square root of the electrode rotation rate. The apparent limiting current density region reflects the limiting current density of copper and the side reactions. The current density plateau was not always apparent. Therefore, the value interpolated from the inflection point was used as the limiting current density. The slopes of the Levich plots with and without particles are the same $(8.6 \pm 0.2 \text{ mA s}^{1/2} \text{ cm}^{-2} \text{ rad}^{-1/2})$.

![Graph showing the effect of particle concentration on the limiting current density (iL).](image)

**Figure 4.2.** Effect of particle concentration on the limiting current density ($i_L$).

### 4.3.2 Weight Percent of $\gamma$-Al$_2$O$_3$ Particles

The weight percent of alumina in the deposit at different particle electrolyte concentration at 900 rpm is shown in Figure 4.3. At a particle loading of 12.5 g/L the weight percent of alumina decreases with increasing cathodic potentials. Particle loading of 39 and 60 g/L result in alumina content that is relatively insensitive to the potential.
The higher the particle loading in the electrolyte the larger is the weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposits. This behavior has also been documented previously for other systems in the literature.$^{10,13,33,38,39}$

![Graph showing the weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit at different particle loading and an electrode rotational rate of 900 rpm.](image)

**Figure 4.3.** Weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit at different particle loading, and an electrode rotational rate of 900 rpm.

Also, the larger the amount of $\gamma$-Al$_2$O$_3$ particles in the deposit, the larger the standard deviation, as represented by the error bars. The increased dispersion in the data was attributed to less precision in the microprobe analysis due to an increase in undesirable
charging effects as a consequence of the non-conductive nature of alumina manifested at high deposit concentration.

Figures 4.4a through 4.4d show SEM micrographs of how the surface roughness of the deposits is affected due to the presence of alumina, at a cathodic constant current density of 60 mA/cm² for a period of time of 7.5 minutes, and electrode rotation rate of 900 rpm. The conditions of deposition corresponded to the case where the copper reduction is inhibited in all electrolytes. Changes in surface roughness did not correlate to the degree of inhibition. Figure 4a shows the surface of plated elemental copper. Nodules, of uniform size, 4.8 ± 0.7 µm with a confidence level of 95%, are well distributed in the deposit. However, the morphology changes when particles are added to the electrolyte, (Figures 4.4b to Figure 4.4d). For a particle loading of 12.5 g/L the surface is rougher than that of pure copper (Figure 4.4b) having an average nodule size of 10.8 ± 2.4 µm. At 39 g/L alumina loading there is a transition from a bigger nodule size to a smaller one (Figure 4.4c), Figure 4.4d corresponds to a deposit obtained from a 60 g/L particle loading. This micrograph shows the most uniform microstructure, similar to the elemental deposit without alumina, with a nodule size much smaller than those in Figures 4b and 4c.

At higher magnifications the same pattern in surface morphology is observed in Figures 4a-d, thus the results point to a variation in microstructure with alumina electrolyte concentration that changes from a rough deposit to a smooth one. The particle concentration in the deposit also increases with electrolyte composition as noted in Figure 4.3. At 12.5 g/L the surface is rough, exhibiting a larger apparent surface area, but the polarization curves of the composite electrolyte are nearly the same as the elemental
Figure 4.4. SEM micrographs of a (a) pure copper deposit, and γ-Al₂O₃-Cu composites obtained from a (b) 12.5, (c) 39, and (d) 60 g/L particle loadings, at 900 rpm, 60 mA/cm² and deposition time of 7.5 min.

deposition (Figure 4.1a). The rough morphology may arise due to growth between particles, as the particles are expected to block part of the electrode surface. The rough morphology may suggest an increased surface area available for reaction. But since there is no change in the polarization curve, then any increase in active area is negated by the area covered by the particles. With a much larger amount of particles in the solution, 60 g/L, and thus in the deposit, a leveling effect also accompanies the blocking effect of the particles, yielding smoother deposits. In other words, the additional particles at the
surface position themselves at the highest peaks, expected from a particle diffusion control. There is a greater inhibition of the copper reaction rate at a constant potential compared to the 12.5 g/L case. The largest copper inhibition occurs in the intermediate electrolyte containing 39 g/L particles. In these deposits, the surface is smoother than the 12.5 g/L case, and more particles are present in the deposit. Thus both factors would contribute to a more pronounced blocking effect, as observed for Cu reduction. The deposit morphology from the 60 g/L particle electrolyte is the smoothest and has the greatest amount of particles in the deposit. Based on the decrease of apparent surface area and increase of blocking particles, a further reduction of the copper rate would be expected at a constant potential, but experimentally, it is not (Figure 4.1a). There is only a modest inhibition of the copper rate. Therefore, a mechanism that involves solely blocking and changes in surface area cannot explain the experimental data. Another effect, such as an enhancement or catalytic phenomenon, must also be governing the copper reaction rate.

Figure 4.5 shows the weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit from a bath containing 12.5 g/L particles as a function of potential and electrode rotational rate. There is no significant influence of the potential on the weight percent of alumina for each rotation rate and there is no effect of the deposit alumina concentration with rotation rate. Figure 4.6 shows the weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit from a bath containing 60 g/L particles as a function of potential and electrode rotational rate. There is no significant influence of the potential on the weight percent of alumina for each rotation rate. Likewise, there is little effect of the deposit alumina concentration with rotation rate, with the exception of the lowest rotation rate at 900 rpm. At 900 rpm, the
**Figure 4.5.** Weight percent of $\gamma$-$\text{Al}_2\text{O}_3$ particles in the deposit at different electrode rotational rates, and particle loading of 12.5 g/L.

**Figure 4.6.** Weight percent of $\gamma$-$\text{Al}_2\text{O}_3$ particles in the deposit at different electrode rotational rates, and particle loading of 60 g/L.
Figure 4.7. SEM micrographs of a γ-Al₂O₃-Cu composite obtained from a 60 g/L particle loading at different electrode rotation rates: (a) 1600, (b) 2500, and (c) 3600 rpm, 60 mA/cm² and deposition time of 7.5 min.

polarization curve at 60 g/L is inhibited, while at the other extreme 2500 and 3600 rpm the polarization curve is enhanced. Figures 4.7a through 4.7c show the morphology of the deposits obtained at 60 g/L particle concentration at different electrode rotation rates (e.g. 1600, 2500 and 3600 rpm) where current enhancement is observed in the polarization curves. The deposits were fabricated at a constant current density with the same plating conditions as the deposits shown Figure 4.4. Their surface roughness is alike and smoother than the one corresponding to the 900 rpm deposit (Figure 4.4d) obtained from
the same electrolyte. Thus, the enhancement phenomenon is not due to a local increase in surface area, supporting a catalytic approach.

4.3.3 Current Efficiency and Partial Current Densities

Figure 4.8a shows the current efficiency of copper and copper-\(\gamma\)-Al\(_2\)O\(_3\) deposition, respectively, as a function of the potential and particle loading 900 rpm. The current efficiency was above 80% for all particle loadings, but the highest average current efficiency occurred for the particle-free bath. Figure 4.8b shows a comparison between the total current density and the partial current density for different particle loadings at the electrode rotation rate of 900 rpm.

![Figure 4.8(a).](image)

**Figure 4.8(a).** Current efficiency of copper and copper-\(\gamma\)-Al\(_2\)O\(_3\), at different particle loadings, and at an electrode rotational rate of 900 rpm.

The inhibition of the copper partial current density is observed. Thus, due to the relatively high current efficiency, the inhibition of the total polarization (see Figures 4.1a
to 4.1d) is indicative of the inhibition of the copper reduction reaction. Some data points, however, do show smaller differences between the copper partial current densities compared to the polarization curve than what is implied in the current efficiency. This is due to the differences in the two types of experiments. The polarization curve at 5 mV/s is not ideally at steady state, and during the electrolysis experiments the surface area can change with a concomitant shift in potential.

Figure 4.9 shows the copper and copper-\(\gamma\)-Al\(_2\)O\(_3\) current efficiency as a function of the potential and rotation rate for films deposited from a particle free electrolyte (Figure 4.9a) and a bath containing 12.5 g/L alumina (Figure 4.9b).

![Graph](image)

**Figure 4.8(b).** Comparison of the total current density (solid lines) and the copper partial current density (discrete points) for different particle loadings, at an electrode rotation rate of 900 rpm: (X) no particles, (\(\triangle\)) 12.5, (\(\Box\)) 39 and (\(\triangleup\)) 60 g/L.
Figure 4.9(a). Current efficiency of copper at different electrode rotational rates, from a particle free electrolyte.

Figure 4.9(b). Current efficiency of copper-γ-Al₂O₃, at different electrode rotational rates, at a particle loading of 12.5g/L.

Figure 4.9a shows that the copper current efficiency was high and above 80% for all rotation rates, without any significant effect due to potential. Figure 4.9b shows that the
copper-γ-Al2O3 current efficiency was about the same as Figure 4.9a, without particles, for all rotation rates, which confirms the insensitivity of the copper reduction rate for a particle loading of 12.5 g/L with rotation rate.

Figure 4.10a shows the copper and copper-γ-Al2O3 current efficiency as a function of the potential and rotation rate for films deposited from the bath containing 60 g/L. The current efficiency was also above 80 % for all rotation rates; in general it increases with more negative potential for each rotation rate.

![Graph](image)

**Figure 4.10(a).** Current efficiency of copper and copper-γ-Al2O3, at different electrode rotational rates, at a particle loading of 60g/L.

In Figure 4.10b the copper partial current density is shown and compared to the total current density for different electrode rotation rates at 60 g/L. The copper partial current density is shifted to more positive potential values by increasing the electrode rotational rate, i.e. it is more enhanced. Similar results with nickel were observed by
Webb and Robertson\textsuperscript{33} for the Ni-\(\gamma\)-Al\(_2\)O\(_3\) system. Also, due to the relatively high current efficiency, the enhancement of the total polarization for 1600, 2500 and 3600 rpm is indicative of the enhancement of the copper reduction reaction (see Figures 4.1b to 4.1c). The slight drop in current efficiency with rotation rate is therefore due to an enhancement of the side reaction.

![Graph showing current density vs potential for different rotation rates.]

**Figure 4.10(b).** Comparison of the total current density (solid lines) and the copper partial current density (discrete points) for a particle loading of 60 g/L at different electrode rotation rates: (O) 900 rpm, (X) 1600 rpm, (Δ) 2500 rpm, (□) 3600 rpm.

Figure 4.11 shows a TEM micrograph of \(\gamma\)-Al\(_2\)O\(_3\) particles incorporated in the composite plated from a bath containing 39 g/L of particles at an electrode rotational rate of 900 rpm and a current density of –30 mA/cm\(^2\). The micrograph shows \(\gamma\)-Al\(_2\)O\(_3\)
particles in the bath that vary in size between 10 and 100 nm. No attempt has been made to eliminate particle agglomeration as surfactants for this purpose may also affect the metal reduction rate.

Figure 4.11. TEM micrograph for a 7.4 wt % γ-Al₂O₃-cooper composite obtained from a bath containing 39 g/L particles at a constant cathodic current density of 30 mA/cm².

The inhibition of copper reduction can be described by a blocking mechanism, having its fundamental basis in the Guglielmi [13] approach. Other models have incorporated a similar adsorption approach [22, 31, 36, 40]. To our knowledge, there has not been any model that describes an enhancement of the metal reduction rate. It is observed here that the enhancement occurs only when a large amount of particles are present in the electrolyte and included into the deposit. Therefore, a mathematical description of the reaction rate should include the coupled mass transport of particles with the metal kinetic rate expression, presented in next chapter.
4.4 Summary

Both Cu inhibition and enhancement occurs when alumina nanoparticles are in suspension. The kinetic region of the copper reaction rate was dependent on both particles concentration and electrode rotation rate. At all rotation rates, at a particle loading of 12.5 g/L, there is almost no change in the copper kinetic behavior. In contrast, the Cu reduction is inhibited when 39 g/L particles are added to the electrolyte, at all rotation rates. A particle concentration of 60 g/L, exhibits both Cu inhibition (< ~ -0.17 V) and enhancement (> ~ -0.17 V) at 1600 rpm, and only enhancement for electrode rotation rates of 2500 and 3600 rpm. Surface roughness of the deposits was affected due to the presence of particles in suspension, resulting in a variation in microstructure that changes from a rough deposit to a smooth one as the amount of electrolyte particle loading is increased.

4.5 References


CHAPTER 5 MATHEMATICAL MODEL FOR THE EFFECT OF AL₂O₃ NANOPowDER ON Cu ELECTRODEPOSITION FROM ACIDIC ELECTROLYTES

A mathematical model that couples particle mass transport with metal kinetics during Cu-γ-Al₂O₃ electrodeposition from acidic electrolytes was developed. The model which is based on convective-diffusion transport and Tafel reaction kinetics is solved numerically, and the calculated species concentrations at the solution-electrode interface are used to describe the electrode processes.

5.1 Introduction

Celis et al.¹ reported a survey and trends on the understanding of the mechanism of electrolytic composite plating, as well as the mathematical models developed over the years by other people to describe the incorporation of particles in electrodeposited metal-matrixes. Hovestad et al.² also reported a survey on electrochemical codeposition of inert particles in a metallic matrix and models to predict the codeposition rate. Fitted parameters models have succeeded partly to predict the amount of particles in the deposit from experimental conditions. Yet, the mechanism of particle codeposition is not well understood. Therefore, there are many studies that attempt to predict the degree of particle incorporation into the deposit as a function of the plating variables,³-²⁴ but none has focused on the effect the particle has on the metal reduction rate. Only a few studies have observed experimentally that the presence of particles in the electrolyte influences the metal rate.³,²⁵-²⁹ In general, the metal reaction rate can be inhibited, enhanced or unaffected, depending on the particle loading, type and size as well as on the electrolyte. Stojak and Talbot²⁵ reported that under mass transfer control, with the addition of particles, the limiting current density remained the same at low particle loadings (39 and
129 g/L), and was enhanced for higher particle concentrations (158 g/L). Podlaha and Landolt\textsuperscript{26} observed an inhibition of the cathodic copper current density in citrate electrolytes using rotating cylinder electrodes due to the presence of alumina nanoparticles. Hwang and Hwang\textsuperscript{11} observed that SiC particle content (up to 5 g/L) in solution has no effect on the polarization curve. Fawzy \textit{et al.}\textsuperscript{3} reported both, inhibition and enhancement for particle loadings up to 20 g/L with either $\alpha$-Al$_2$O$_3$ or TiO$_2$ particles suspended in the bath. Watson and Walters\textsuperscript{27} showed that chromium particles catalyzed nickel electrodeposition from an electrolyte containing 1-2 $\mu$m average diameter particles on rotating cylinder electrodes. Webb and Robertson\textsuperscript{28} reported an inhibition of nickel reduction with 0.01 $\mu$m $\gamma$-Al$_2$O$_3$ particle loadings (up to 20 g/L) using rotating disk electrodes. In the work presented here a model to describe both enhancement and inhibition of copper from acidic electrolytes due to the presence of alumina nanoparticles will be developed to predict our experimental results.\textsuperscript{29}

By incorporating Guglielmi’s\textsuperscript{8} approach of a blocking mechanism, the inhibition of copper reduction can be predicted, a similar adsorption approach has been incorporated by other models.\textsuperscript{8-14,30} To our knowledge, there has not been any model that describes an enhancement of the metal reduction rate. In this work, a mathematical description of the reaction rate includes the coupled mass transport of particles with the metal kinetic rate expression, since it is observed that the enhancement occurs only when a large amount of particles are present in the electrolyte and included into the deposit.

\textbf{5.2 Mathematical Model}

A mathematical model of the Cu-$\gamma$-Al$_2$O$_3$ system codeposition onto a rotating disk electrode (RDE) from a simple sulfuric electrolyte is presented. This model couples mass
transport of particles with metal kinetics. Prior models\textsuperscript{3-24} do not predict a change in the metal rate during codeposition. The species of interest are: Cu\textsuperscript{+2}, H\textsuperscript{+}, OH\textsuperscript{-} and alumina nanoparticle (P). The corresponding material balance equation for species i can be written as

\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_i \quad [5.1]
\]

where \( R_i \) denotes the homogeneous reaction. In this case, the only homogeneous reaction considered is

\[
H_2O \leftrightarrow H^+ + OH^- \quad [5.2]
\]

and it is assumed to be infinitely fast such that equilibrium is reached. The system is treated as a one-dimensional problem, neglecting radial variations, which is a good approximation for a small disk, in the presence of well-supported electrolyte and mass-transfer and kinetic overpotentials\textsuperscript{31}.

### 5.2.1 Model Assumptions

The model assumes that electrochemical reactions occur on the surface not covered by adsorbed species. Alumina particles are treated as being able to adsorb onto the electrode surface prior to incorporation, \( P_{ads} \). The fractional coverage of these species is designated as \( \theta = P_{ads} \). The model includes hydrogen ion reduction and water reduction as the main side reactions. The model also assumes steady-state conditions in an isothermal and isobaric system. Concentration gradients are restricted to a thin boundary layer near the electrode surface, in which mass transport is governed by diffusion. The Nernst diffusion layer approach is applied and migration effects are considered to be negligible.
Interaction between solute species are absent since a dilute solution approach was taken. Finally, a Cartesian coordinate system is considered.

5.2.2 Model Equations

At steady-state and taking into account the homogeneous dissociation reaction of water, the material balance equations in the diffusion layer, $0 < X < \delta$, for species $\text{Cu}^{+2}$, $\text{P}$, $\text{H}^+$, and $\text{OH}^-$, respectively, are:

$$\nabla \cdot N_{\text{Cu}^{+2}} = 0$$  \[5.3\]

$$\nabla \cdot N_{\text{P}} = 0$$  \[5.4\]

$$\nabla \cdot N_{\text{H}^+} = \nabla \cdot N_{\text{OH}^-}$$  \[5.5\]

where mass transfer is governed by diffusion $N = -D \frac{\partial C}{\partial X}$, assuming a constant diffusion coefficient, $D$. The water equilibrium reaction is

$$K_w = C_{\text{OH}^-} C_{\text{H}^+}$$  \[5.6\]

The intermediate species $\theta$ exists only at the electrode surface so that its concentration is zero within the boundary layer and the bulk solution. Equations [5.3]-[5.6] are the four equations to solve for the four species of interest.

5.2.3 Boundary Conditions

There are three overall reactions at the electrode surface: hydrogen evolution and particle and copper metal deposition. Hydrogen can be produced by hydrogen ion reduction and at higher potentials by reduction of water

$$\text{H}^+ + e^- \overset{\kappa_2}{\longrightarrow} \frac{1}{2}\text{H}_2$$  \[5.7\]

$$\text{H}_2\text{O} + e^- \overset{\kappa_3}{\longrightarrow} \frac{1}{2}\text{H}_2 + \text{OH}^-$$  \[5.8\]
It is assumed that hydrogen is dissolved in the solution, and the flow field is not affected. Copper metal and particles are allowed to deposit from their metal ions and inert particles, respectively:

$$\text{Cu}^{2+} + 2e^- \xrightarrow{K_{\text{ads}}} \text{Cu}_{(s)}$$  \hspace{1cm} [5.9]

$$P \xleftarrow{K_{\text{ads}}} P_{\text{ads}}$$  \hspace{1cm} [5.10]

$$P_{\text{ads}} \xrightarrow{K_p} P_{\text{inc}}$$  \hspace{1cm} [5.11]

Thus, at the electrode surface $X = 0$, the partial current densities are related to the fluxes.

$$N_{\text{Cu}^{2+}} - \frac{i_{\text{Cu}^{2+}}}{2F} = 0$$  \hspace{1cm} [5.12]

$$N_p + V_p = 0$$  \hspace{1cm} [5.13]

$$N_{H^+} - \frac{i_{H^+}}{F} = N_{OH^-}$$  \hspace{1cm} [5.14]

where $V_p$ is the rate of deposition of particles in units of mol/(cm$^2$·s). At a distance $\delta$ from the cathode $X = \delta$, the species concentrations are equal to their bulk values

$$C_i = C_i^b$$  \hspace{1cm} [5.15]

The thickness of the Nernst diffusion layer ($\delta$) for a rotating disk electrode (RDE) depends on the electrode rotation rate and is given by the Levich Eq.

$$\delta_N = 1.61D_i^{1/3} \omega^{-1/2} v^{1/6}$$  \hspace{1cm} [5.16]

where $D_i$ is the smallest diffusion coefficient of species $i$ (cm$^2$/s), $\omega$ is the electrode rotation rate (rad/s) and $v$ ($= 0.01$ cm$^2$/s) is the kinematic viscosity.
Charge-transfer kinetics at the electrode surface are assumed to obey the Tafel equation, a modification of the Butler-Volmer expression. The partial current densities, $i_j$, can be expressed as a function of the kinetic constants, $k_j [\text{with } k_j = k_j^\circ \exp (-b_j E)]$, for each reaction, $j$, the inverse Tafel slope, $b_j$, the surface concentrations, $C_i$, the adsorption coverage, $\theta_i$, and the potential $E$ (taken with respect to the normal hydrogen electrode). Copper and alumina deposition and hydrogen evolution occurs only in the regions not covered by the intermediates, $1 - \theta$. Then, in the Tafel region, the corresponding electrochemical rate expressions are

\[
i_{\text{Cu}} = -2Fk_{\text{Cu}^2+}^\circ C_{\text{Cu}^2+}^\circ (1 - \theta) \exp (-b_{\text{Cu}^2+} E) \tag{5.17}
\]

\[
i_{\text{H}_2} = -Fk_{\text{H}^+}^\circ C_{\text{H}^+}^\circ (1 - \theta) \exp (-b_{\text{H}^+} E) - Fk_{\text{H}_2}^\circ (1 - \theta) \exp (-b_{\text{H}_2} E) \tag{5.18}
\]

where:

\[
b_j = \frac{n_j \alpha_j F}{RT} \tag{5.19}
\]

\[
\theta = \frac{K_{\text{ADS}}^2 C_{\text{p}}^\circ}{1 + \frac{K_{\text{p}}}{k_{\text{p}}} + K_{\text{ADS}}^2 C_{\text{p}}^\circ} \quad K_{\text{ADS}} = \frac{k_{\text{p}}}{k_{-\text{p}}} \tag{5.20}
\]

The expression for $\theta$ is derived by a mass balance at steady state, assuming Langmuir adsorption. The deposition rate of particle can be represented as

\[
V_p = K_p \theta \tag{5.21}
\]

where $V_p$ is the deposition rate of particles, mol/s; $K_p$ is the rate constant of particle deposition.
5.2.4 Numerical method

The partial current densities were calculated by solving the concentration distribution for the unknowns $Cu^{+2}$, $H^+$ and the surface coverage, $\theta$ at a given applied cathodic potential, $E$, electrode rotation speed and electrolyte particle loading. The solution of PDE’s was carried out using Newman’s Band subroutine for a three-point finite difference technique. In the domain, central differences were employed, and forward and backward differences at $X=0$ and $X=\delta$, respectively. Since the flux boundary conditions, Eq. [5.12]-[5.14], depend on the surface concentration of species as seen in Eq. [5.17]-[5.18], a concentration profile of the species is assumed to begin an iteration scheme, which calculates the boundary conditions and after calculating the species concentrations, it compares them with the assumed values until a convergence is attained.

The partial current densities were determined at each applied potential. The total current density is the sum of the partial current densities.

$$i_T = \sum_j i_j$$ \hspace{1cm} [5.22]

The current efficiency, $\epsilon$, for metal deposition is equal to the partial current density of copper $i_{Cu}$, divided by the total current density.

$$\epsilon = \frac{i_{Cu}}{i_T}$$ \hspace{1cm} [5.23]

The weight percentage of the copper, $w_{Cu}$, and alumina $w_{Al_2O_3}$ in the composite is calculated as follows:

$$w_{Cu} = \frac{i_{Cu}MW_{Cu}}{i_{Cu}MW_{Cu}/2F + V_pMW_p} \times 100$$ \hspace{1cm} [5.24]
\[
W_{Al_0} = \frac{V_pMW_p}{i_{Cu}MW_{Cu}/2F + V_pMW_p} \times 100 \tag{5.25}
\]

where MW is the molecular weight.

### 5.2.5 Model parameters

The kinetic parameters and dissociation constants are given in Table 5.1. A list of the bath composition and diffusion coefficients used for the calculations is listed in Table 5.2. The kinetic and transport properties were measured, taken from the literature or fitted to approximate experimental results. The fitted rate constants \(k_{Cu^{2+}}^0, K_p, K_{ADS}, k_{H^+}, k_w^0\) and the Tafel constants \(\alpha_{Cu^{2+}}, \alpha_{H^+}, \alpha_w\) were chosen to approximate the experimental results for copper electrodeposition and hydrogen side reaction, but have not been optimized. These kinetic parameters were determined by matching the theoretical results to the experimental polarization curves, measured current efficiencies and particle weight percentage, simultaneously. \(k_{Cu^{2+}}^0, \alpha_{Cu^{2+}}, 33\) and \(k_w^0, \alpha_w, k_{H^+}, \alpha_{H^+}, 34\) were slightly varied from literature to match the experimental polarization curve results for the particle-free electrolyte at 900 rpm with an average relative error of 0.07. These values were subsequently used to predict the tendencies for different rotation rates. \(K_p\) and \(K_{ADS}\) were fitted to the experimental polarization curve results for a particle loading of 12.5 g/L at 900 rpm with an average relative error of 0.09. The diffusion coefficient of copper ions was determined from the slope of Figure 4.2 for the case when no particles are present in suspension, a plot of the limiting current density vs. the electrode rotation rate (rad/sec) to the 0.5 power. The particle diffusion coefficient (\(D_p\)) was calculated using Stokes’ Law of particle settling in suspension.
\[ D_p = \frac{kT}{6\Pi \mu r} \]  

where \( k \) is the Boltzman constant, \( T \) is the temperature (K), \( \mu \) is the viscosity and \( r \) is the particle radius. The diffusion coefficients \( D_{H^+}, D_{OH^-} \) were taken from the literature. The same set of parameters was used in all mathematical simulations, except for \( \alpha_{Cu^{2+}} \) and \( \alpha_w \) which were changed with rotation rate at 60 g/L, in order to predict both inhibition and enhancement.

**Table 5.1.** Dissociation constants and kinetic parameters

<table>
<thead>
<tr>
<th></th>
<th>( Cu^{2+} )</th>
<th>( P )</th>
<th>( \theta = P_{ads} )</th>
<th>( H^+ )</th>
<th>( H_2O )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{diss} ) ( (cm^3/mol)^2 )</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>( 1.0 \times 10^{-20} )</td>
</tr>
<tr>
<td>( k_i (cm/s) )</td>
<td>( 3.15 \times 10^5 )</td>
<td>( 1.2 \times 10^{-6} )</td>
<td>( 8.0 \times 10^5 )</td>
<td>( 2.5 \times 10^{-11} )</td>
<td>( 1.2 \times 10^{-11} )</td>
</tr>
<tr>
<td>( \alpha_i )</td>
<td>0.32*</td>
<td>–</td>
<td>–</td>
<td>0.11</td>
<td>0.45*</td>
</tr>
</tbody>
</table>

* Values for \( C_p \leq 39 \text{ g/L} \)

\( \alpha_{Cu^{2+}} = 2 \times 10^{-8} \omega^2 (\text{rpm}) + 2 \times 10^{-5} \omega + 0.3195 \);

\( \alpha_{H_2O} = 2 \times 10^{-8} \omega^2 (\text{rpm}) - 7 \times 10^{-6} \omega + 0.4826 \) for \( C_p = 60 \text{ g/L} \).

**Table 5.2.** Bath composition and transport parameters

<table>
<thead>
<tr>
<th></th>
<th>( Cu^{2+} )</th>
<th>( P )</th>
<th>( \theta = P_{ads} )</th>
<th>( H^+ )</th>
<th>( OH^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_i (mol/cm^3) )</td>
<td>( 0.1 \times 10^{-3} )</td>
<td>( (0.12-0.59) \times 10^{-3} )</td>
<td>( 1.0 \times 10^{-13} )</td>
<td>( 0.63 \times 10^{-5} )</td>
<td>( 1.6 \times 10^{-17} )</td>
</tr>
<tr>
<td>( D_i (cm^2/s) )</td>
<td>( 6.0 \times 10^{-6} )</td>
<td>( 6.9 \times 10^{-7} )</td>
<td>–</td>
<td>( 1.0 \times 10^{-4} )</td>
<td>( 5.5 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
5.2.6 Simulation

The results of the model will be compared with four sets of experimental data, presented in Chapter 4.

The model results of the particle loading effect on polarization scans at different electrode rotation rates is shown in Figure 5.1: (a) 900, (b) 1600, (c) 2500, and (d) 3600 rpm. Figure 5.1(a) is in qualitative agreement with the experimental data, since it shows that there is almost no effect on the polarization curve for a particle loading of 12.5 g/L, and the current density decreases for a given potential from the kinetically-controlled region to the mass transfer region, at both 39 and 60 g/L. The model also predicts a bigger inhibition in the current density for a particle loading of 39 than for 60 g/L.

![Figure 5.1(a)](image)

**Figure 5.1(a).** Model correlations of the particle loading effect on polarization scans at 900 rpm.

The results for current densities at electrode rotation rates of 1600, 2500 and 3600 rpm are shown in Figures 5.1(b) through 5.1(d) respectively for different particle
loadings. The model results capture the kinetic region of the copper reduction rate as a function of particle loading between -0.05 to -0.4 V and are similar to the polarization curves at 900 rpm, except for the polarization curve corresponding to 60 g/L, which shows both inhibition and enhancement. At 1600 rpm, inhibition of the total polarization is observed at low current densities and then makes a transition at approximately –0.16 V becoming enhanced.

![Graph showing polarization curves with different particle loadings.](image)

**Figure 5.1(b).** Model correlations of particle loading effect on polarization scans at 1600 rpm.

Furthermore, the electrode rotational rates of 2500 rpm (Figure 5.1c) and 3600 rpm (Figure 5.1d), show an enhancement in the total polarization. As observed from the polarization curve results, even though the presence of particles in the electrolyte affects the kinetically-controlled region, there is almost no significant effect in the mass transfer region for a particle loading up to 60 g/L.
**Figure 5.1(c).** Model correlations of particle loading effect on polarization scans at 2500 rpm.

**Figure 5.1(d).** Model correlations of particle loading effect on polarization scans at 3600 rpm.
The weight percent of the deposit concentration at different particle electrolyte concentration of the model at 900 rpm is shown in Figure 5.2. The model does not exactly match the experimental data, but shows qualitative trends and gives the correct order of magnitude of particle concentration. At all particle loadings the weight percent of alumina decreases with increasing cathodic potentials. The higher the particle loading in the electrolyte the larger is the weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposits for all potential values, following the same trend as the experimental data (Figure 4.3). This behavior has also been documented previously for other systems in the literature.$^{8,28,35-37}$ This model predicts a decrease of wt. % alumina with potential for all particle loadings, which is in good agreement with the experimental data for the 12.5 g/L case, but not for the 39 and 60 g/L ones, which remain almost constant with potential.

**Figure 5.2.** Calculated weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit at different particle loading, and an electrode rotational rate of 900 rpm.
Figure 5.3 shows the calculated weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit from a bath containing 60 g/L particles as a function of potential and electrode rotational rate. Similar to the experimental results (Figure 4.6), the model predicts little effect of the deposited alumina concentration with rotation rate. The model predicts a small influence of the potential on the weight percent of alumina for each rotation rate at low potential values, vanishing at higher cathodic potentials. Also in this case, the wt. % alumina range predicted by the model at different rpm’s is in agreement with the experimental observations. The prediction of the wt. % alumina decreasing with potential differs from the experimental data, which remains constant with potential.

![Graph showing wt % Alumina vs Potential](image)

**Figure 5.3.** Calculated weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit at different electrode rotational rates, and particle loading of 60 g/l.

Figure 5.4 shows the current efficiency of copper and copper-$\gamma$-Al$_2$O$_3$ deposition, respectively, as a function of the cathode potential and particle loading 900 rpm. Current efficiencies near 100 % are predicted for all particle loadings at low potential values,
Figure 5.4. Calculated current efficiency of copper and copper-\(\gamma\)-Al\(_2\)O\(_3\), at different particle loadings, and at an electrode rotational rate of 900 rpm.

Figure 5.5. Calculated current efficiency of copper and copper-\(\gamma\)-Al\(_2\)O\(_3\), at different electrode rotational rates, at a particle loading of 60g/l.
typical for copper electrodeposition from acidic baths, decreasing slightly at high potential values at which the water reduction side reaction takes place. Figure 5.5 shows the copper and copper-\(\gamma\)-\(\text{Al}_2\text{O}_3\) current efficiency as a function of the potential and rotation rate for films deposited from the bath containing 60 g/L. The current efficiency was also near 100 % for all rotation rates, decreasing slightly at high potential values.

5.3 Summary

The electrodeposition of Cu-\(\gamma\)-\(\text{Al}_2\text{O}_3\) composites from acidic electrolytes was used as a model for the theoretical study of the effect of particles on copper kinetics. A mathematical model that couples particle mass transport with metal kinetics during codeposition was developed. The mathematical model successfully predicts polarization behavior, composite composition and current efficiency as a function of applied potential, electrolyte particle loading and electrode rotation rate. The model predicts inhibition and enhancement of copper rates at different particle loadings, a decrease in wt. % alumina with increasing cathodic potentials and an increase with higher particle loadings in the electrolyte. The model also predicts little effect of the deposit alumina concentration with rotation rate, and current efficiencies near 100 %, all of which were observed experimentally.

5.4 References

CHAPTER 6 ELECTRODEPOSITION OF Cu-Al₂O₃ THIN FILMS AND MICROPOSTS IN AMMONIA-CITRATE ELECTROLYTES*

The electrodeposition of Cu-γ-Al₂O₃ nanocomposites as thin films and into recessed electrodes prepared with x-ray lithography was examined in ammonia-citrate electrolytes. Partial current density, current efficiency and deposit particle concentration were determined with a rotating disk electrode.

6.1 Introduction

Metal matrix nanocomposites consist of two phases where at least one phase is restricted to the nanoregime. Copper-alumina can be fabricated by chemical routes¹,² powder metallurgy,³⁴⁻⁸ thermochemical processing⁹ and electrodeposition.¹⁰⁻¹⁷ Their interest lies in the enhancement of mechanical properties compared to the parent metal,⁸,¹² and for their thermal and mechanical stability at elevated temperatures.¹⁸ Applications include their use in electronic packaging, and as materials for electrodes and contact terminals, such as high-performance electrodes for industrial spot welding.¹⁹ The advantage of the electrodeposition fabrication method over others is in depositing material into deep recessed microstructures for microelectromechanical system (MEMS) components. There are only a few studies of composite deposition into deep recesses. Jakob et al.²⁰ have codeposited nanometric TiO₂ and Al₂O₃ along with nickel into microstructures. Yeh et al.²¹ demonstrated the electrodeposition of sub-micron SiC-Ni into lithographic recessed electrodes. Wang²² and Goods²³ reported conditions for Ni-

Al₂O₃ composites into deep recesses prepared by X-ray lithography. Panda and Podlaha\textsuperscript{24} reported NiCu-γ-Al₂O₃ micropost arrays electrodeposited from a pH 8 ammonia-citrate electrolyte. In this paper, we present the operating conditions to electrodeposit Cu-γ-Al₂O₃ into deep recessed geometries.

It is advantageous to understand how the particles affect the metal deposition rate and current efficiency in order to judiciously select electrodeposition conditions to deposit metal matrix composites into recessed structures. Low current efficiency, with associated gas evolution and local pH changes, can be detrimental to depositing into micro-patterned, recessed substrates due to the blockage of the electrode surface by gas bubbles or unwanted solid products. The decrease of the copper reduction partial current density due to the presence of alumina particles has been observed by Stojak \textit{et al.}\textsuperscript{14} in sulfuric acid electrolytes, and Podlaha and Landolt\textsuperscript{15} in an acidic citrate electrolyte. Lozano-Morales and Podlaha\textsuperscript{17} identified regions of copper inhibition and enhancement in the kinetic regime, in sulfuric acid electrolytes. Fawzy \textit{et al.}\textsuperscript{11} studied the effect of α-Al₂O₃ and TiO₂ particles on copper electrodeposition from acidic baths. Both, inhibition and enhancement were observed for particle loadings up to 20 g/L with either particle type. In this paper the effect of the particle on the Cu partial current density is explored for basic ammonia-citrate electrolytes.

Electrodeposition of Cu-γ-Al₂O₃ nanocomposites both as thin films and high aspect ratio structures are presented here. Cu can be plated at and near the limiting current density from citrate electrolytes with smooth morphologies,\textsuperscript{25-26} however typical electrolytes in acidic conditions can be unstable.\textsuperscript{27} Here an ammonia-citrate bath is examined at pH 8 and 10 with γ-alumina nanoparticles onto a rotating disk electrode.
Partial current density, current efficiency and deposit particle concentration are presented. The most promising electrolyte results were used to deposit nanocomposite microposts into 500 micron recessed arrays of microposts.

6.2 Experimental

6.2.1 Solution

The electrolytes were composed of copper sulfate and sodium citrate, with the addition of $\gamma$-Al$_2$O$_3$ particles (12.5 g/L), and without particles. The particles have an average particle diameter of 32 nm with a specific surface area of 30-60 m$^2$g$^{-1}$ supplied by Nanophase Technologies Corporation, IL, USA. Two electrolytes were examined: (1) 0.25 M CuSO$_4$, and 0.3 M Na$_3$C$_6$H$_5$O$_7$ at different pH values, and (2) 1.0 M CuSO$_4$, and 1.2 M Na$_3$C$_6$H$_5$O$_7$ at pH 8. The pH was adjusted with ammonium hydroxide (NH$_4$OH). The low copper concentration electrolyte with 0.25 M CuSO$_4$ and 0.3 M Na$_3$C$_6$H$_5$O$_7$ required 0.11 M of ammonium hydroxide to reach pH 8 and 0.56 M ammonium hydroxide for pH 10. The addition of particles to these electrolytes slightly altered the amount of ammonium hydroxide needed to establish the pH; for pH 8 and 10 with particles the amount of ammonium hydroxide required was 0.13 M and 0.59 M, respectively. The concentrated electrolyte with 1.0 M CuSO$_4$ and 1.2 M Na$_3$C$_6$H$_5$O$_7$ required 0.60 M of ammonium hydroxide and with particles 0.62 M ammonium hydroxide.

6.2.2 Electrochemical Cell

Deposition experiments were performed on rotating disk electrodes (RDE’s) and recessed microelectrodes 500 $\mu$m thick. The particles were kept in suspension by mechanical agitation by the RDE and in the case of the recessed electrodes both
mechanical (Arrow, Model No. 1750) and magnetic (Corning Inc.) agitation were used to keep the electrolyte in uniform suspension and to avoid particle sedimentation and formation of local concentration gradients. A three-electrode system was used to perform polarization experiments with the RDE. The disk area was 1.5 cm$^2$, and was machined from 316 stainless steel. A Au surface layer was electrodeposited onto the stainless steel disk for improved adhesion of the composite film (Acid gold strike and Orotemp 24 gold solution, Technic Inc.). A platinum mesh was used as the anode. A saturated calomel electrode was the reference electrode. The main side reaction is considered to be water reduction; nitrogen was bubbled in the experimental cell prior to experiments to remove dissolved oxygen and thus eliminate the oxygen reduction side reaction. All the experiments were performed at a room temperature of 25 ± 1 °C.

The recessed electrodes were produced by exposing 500 µm thick polymethylmethacrylate (PMMA) sheets attached to copper plates to X-ray radiation at the LSU-CAMD synchrotron facility, following the procedure of Kanigicherla. See chapter 3 for details about microrecessed electrodes substrate preparation.

6.2.3 Procedure

A computer controlled potentiostat and impedance system (Zahner IM6e) were used to measure polarization curves, ohmic resistance and for Cu-alumina deposition. Polarization curves were measured with and without particles for electrode rotation rates of 400, 900, 1600, and 2500 rpm (laminar flow regime). All polarization scans were performed by increasing the cell potential from the open circuit value (-0.22 mV vs SCE) to –1.2 V at a scan rate of 2 mV/s. The frequency range used for the impedance spectra was of 100 mHz to 1 MHz. Ten deposits at different current densities were analyzed for
each rotation rate in the kinetically-controlled region, at a constant deposition time of 33.3 min. Pulsed galvanostatic control was employed in the electrodeposition into recessed electrodes. An EG&G PARC Potentiostat/Galvanostat (Model 363) coupled with an EG&G PARC function generator (Model 175) was used.

6.2.4 Composition Analyses

A KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF) was used to analyze the alumina weight percentage of the composites obtained from the RDE experiments. Ten points were analyzed for each sample and the average value was presented here. Scanning Electron Microscopy (SEM, JEOL JXA-733) with Wavelength-Dispersive X-ray Spectrometer (WDS) was used to quantify the deposit composition distribution. Composition analysis using a linescan with 16 µm intervals was performed along the length of the post using WDS. The spot size of the analyzed area of the sample was 10 µm in diameter and the quantification for each measurement is an average over this area. For topographical information a SEM, JEOL 840A was employed. See Appendix B for sample preparation procedures for SEM and TEM analyses.

6.3 Results and Discussion

6.3.1 Chemical Equilibria

Table 6.1 shows the list of equilibrium chemical reactions and the corresponding stability constants, adapted from Rodes et al., for the non-ammonia case and augmented to include the copper-ammonia species. The concentration of twenty-four species was determined at different pHs for the electrolytes prepared with 0.114 M and 0.56 M ammonium hydroxide. The equilibrium equations given in Table 6.1, with the following
material balances, were used to solve for the species concentrations, under the constraint that the species satisfy electroneutrality.

All copper species sum to the total concentration of copper added to the electrolyte,
\[[\text{Cu}^{+2}] + [\text{CuOH}]^+ + [\text{Cu(OH)}_2] + [\text{Cu(OH)}_3]^+ + [\text{Cu(OH)}_4]^{-2} + [\text{CuNH}_3]^{+2} + [\text{Cu(NH}_3)_2]^{+2} + [\text{Cu(NH}_3)_3]^{+2} + [\text{Cu(NH}_3)_4]^{+2} + 2[\text{Cu}_2(\text{AOH})_2]^{-2} + [\text{CuHAOH}] + 2[\text{Cu}_2(\text{AO})_2]^{-4} + 2[\text{Cu}_2(\text{AOAOH})]^{-3} + 2[\text{Cu}_2\text{AO}] = \text{total copper concentration} \quad [6.1]\]

and all citrate species, where A = C_6O_6H_4, are equal to the total concentration of citrate in the electrolyte,
\[2[\text{Cu}_2(\text{AOH})_2]^{-2} + [\text{CuHAOH}] + 2[\text{Cu}_2(\text{AO})_2]^{-4} + 2[\text{Cu}_2(\text{AOAOH})]^{-3} + [\text{Cu}_2\text{AO}] + [\text{AOH}]^{-3} + [\text{HAOH}]^{-2} + [\text{H}_2\text{AOH}]^- + [\text{H}_3\text{AOH}] = \text{total citrate concentration} \quad [6.2]\]

The sum of the nitrogen containing species is given as:
\[[\text{NH}_4]^+ + [\text{NH}_3] + [\text{CuNH}_3]^{+2} + 2[\text{Cu(NH}_3)_2]^{+2} + 3[\text{Cu(NH}_3)_3]^{+2} + 4[\text{Cu(NH}_3)_4]^{+2} = \text{total ammonium hydroxide concentration} \quad [6.3]\]

The material balance of sodium and sulfate is taken to be equal to the concentration of the added salts,
\[[\text{Na}^+] = 3 \text{ (total citrate concentration)} \quad [6.4]\]
\[[\text{SO}_4]^{-2} = \text{total copper concentration} \quad [6.5]\]

Electroneutrality must also be satisfied (anions = cations):
\[2\text{SO}_4^{-2} + \text{OH}^- + 2[\text{HAOH}]^{-2} + 3[\text{AOH}]^{-3} + [\text{H}_2\text{AOH}]^- + 2[\text{Cu}_2\text{AOH}_2]^{-2} + 4[\text{Cu}_2\text{AO}]^{-4} + 3[\text{Cu}_2(\text{AOAOH})]^{-3} + [\text{Cu(OH)}_3]^+ + 2[\text{CuOH}_4]^{-2} - (\text{Na}^+ + \text{H}^+ + 2\text{Cu}^{+2} + 2[\text{Cu(NH}_3)]^{+2} + 2[\text{Cu(NH}_3)_2]^{+2} + 2[\text{Cu(NH}_3)_3]^{+2} + 2[\text{Cu(NH}_3)_4]^{+2} ) = 0 \quad [6.6]\]
<table>
<thead>
<tr>
<th>Reactions</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}^{2+} + \text{OH}^- = \text{CuOH}^+$</td>
<td>$10^{6.3} = \frac{[\text{CuOH}^+]}{[\text{OH}^-][\text{Cu}^{2+}]}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2\text{OH}^- = \text{CuOH}_2^-$</td>
<td>$10^{12.8} = \frac{[\text{CuOH}_2^-]}{[\text{OH}^-][\text{Cu}^{2+}]}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 3\text{OH}^- = \text{CuOH}_3^-$</td>
<td>$10^{14.5} = \frac{[\text{CuOH}_3^-]}{[\text{OH}^-][\text{Cu}^{2+}]}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 4\text{OH}^- = \text{CuOH}_4^{2-}$</td>
<td>$10^{15.6} = \frac{[\text{CuOH}_4^{2-}]}{[\text{OH}^-][\text{Cu}^{2+}]}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + \text{NH}_3=\text{CuNH}_3^{2+}$</td>
<td>$10^{4.12} = \frac{[\text{CuNH}_3^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2\text{NH}_3=\text{Cu(NH}_3)_2^{2+}$</td>
<td>$10^{7.63} = \frac{[\text{Cu(NH}_3)_2^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^2}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 3\text{NH}_3=\text{Cu(NH}_3)_3^{+2}$</td>
<td>$10^{10.51} = \frac{[\text{Cu(NH}_3)_3^{+2}]}{[\text{Cu}^{2+}][\text{NH}_3]^3}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 4\text{NH}_3=\text{Cu(NH}_3)_4^{+2}$</td>
<td>$10^{12.61} = \frac{[\text{Cu(NH}_3)_4^{+2}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{NH}_3 = \text{NH}_4^+$</td>
<td>$10^{9.4} = \frac{[\text{NH}_4^+]}{[\text{H}^+][\text{NH}_3]}$</td>
</tr>
<tr>
<td>$2\text{Cu}^{2+} + 2\text{AOH}^- = \text{Cu}_2(\text{AOH})_2^{2-}$</td>
<td>$10^{14.43} = \frac{[\text{Cu}_2(\text{AOH})_2^{2-}]}{[\text{Cu}^{2+}]^2[\text{AOH}^-]^2}$</td>
</tr>
</tbody>
</table>
| $\text{Cu}^{2+} + \text{AOH}^- + \text{H}^+ = \text{CuH}(\text{AOH})$ | $10^{9.55} = \frac{[\text{CuH}(\text{AOH})]}{[\text{Cu}^{2+}][\text{AOH}^-][\text{H}^+]}$ | (Table continued)
\[2Cu^{+2} + 2AOH^{-3} = Cu_2(OA)_2^{-4} + 2H^+ \quad 10^{5.87} = \frac{[H^+]^2[Cu_2(OA)_2^{-4}]}{[Cu^{+2}]^2[AOH^{-3}]} \]  

\[2Cu^{+2} + 2AOH^{-3} = Cu_2(AOAOH)^{-3} + H^+ \quad 10^{10.85} = \frac{[H^+][Cu_2(AOAOH)^{-3}]}{[Cu^{+2}]^2[AOH^{-3}]^2} \]  

\[2Cu^{+2} + AOH^{-3} = Cu_2AO + H^+ \quad 10^{4.92} = \frac{[H^+][Cu_2(AO)]}{[Cu^{+2}]^2[AOH^{-3}]} \]  

\[HAOH^2 = H^+ + AOH^{-3} \quad 10^{6.3} = \frac{[H^+][AOH^{-3}]}{[HAOH^2]} \]  

\[H_2AOH^- = H^+ + HAOH^{-2} \quad 10^{-4.34} = \frac{[H^+][HAOH^{-2}]}{[H_2AOH^-]} \]  

\[H_3AOH = H^+ + H_2AOH^- \quad 10^{-2.92} = \frac{[H^+][H_2AOH^-]}{[H_3AOH]} \]  

\[H_2O = H^+ + OH^- \quad 10^{-13.9} = \frac{[H^+][OH^-]}{[H_2O]} \]  

Figure 6.1 is a plot of the dominant species in the different electrolytes over a range of pH. The species concentrations in Figure 6.1 (a-b) are those found in the electrolyte containing 0.25 M copper sulfate and 0.3 M sodium citrate with (a) 0.11 M and (b) 0.56 M ammonium hydroxide, used for the RDE studies. Figure 6.1(c) presents the species distribution at a higher concentration of copper sulfate (1.0 M) and sodium citrate (1.2 M), used for deep recess deposition. In Fig 6.1(a), the species in highest concentration for pH values lower than 9.4 is the copper-citrate complex followed by ammonium ions, free citrate, and ammonia, \( Cu_2(AO)_2^{-4} > NH_4^+ > AOH^{-3} > NH_3 \), where \( A = C_6O_6H_4 \). The \( Cu(NH_3)_4^{+2} \) concentration is not shown since its concentration is less than 0.001 M. At pH values greater than 9.4 the order of the ammonium ions and ammonia is reversed. By
Figure 6.1(a). Concentration of species in electrolyte containing 0.25 M copper sulfate, 0.3 sodium citrate and 0.11 M ammonium hydroxide.

Figure 6.1(b). Concentration of species in electrolyte containing 0.25 M copper sulfate, 0.3 sodium citrate and 0.56 M ammonium hydroxide.
Figure 6.1(c). Concentration of species in electrolyte containing 1.0 M copper sulfate, 1.2 M sodium citrate and 0.6 M ammonium hydroxide.

increasing the amount of ammonium hydroxide in the electrolyte to 0.56 M, Fig 6.1 (b), the dominant species are the ammonium ions and the species’ concentration follows the order: $\text{NH}_4^+ > \text{Cu}_2(\text{AO})_2^{-4} > \text{AOH}^{-3} > \text{NH}_3 > \text{Cu}(\text{NH}_3)_4^{+2}$. Also in this case, for pH values greater than 9.4 the order of the ammonium ions and ammonia is reversed. In the more concentrated electrolyte, Figure 6.1 (c) the amount of added ammonium hydroxide was 0.6 M. The species in highest concentration follow the same order as in Figure 6.1(b), $\text{NH}_4^+ > \text{Cu}_2(\text{AO})_2^{-4} > \text{AOH}^{-3} > \text{NH}_3 > \text{Cu}(\text{NH}_3)_4^{+2}$ differing only in the concentration of the species.

6.3.2 RDE Experiments

The effect of pH by the addition of ammonium hydroxide on the current-potential relationship is shown in Figure 6.2 at an electrode rotation rate of 2500 rpm, and in the
Figure 6.2. Polarization scans with increasing ammonia additions to alter the solution pH at an electrode rotation rate of 2500 rpm and 12.5 g/L particle loading. (By Jill Fitzgerald)

low copper concentration electrolyte: 0.25 M CuSO₄, 0.3 M Na₃C₆H₅O₇ and 12.5 g/L alumina particles. The limiting current density of Cu is above 0.1 A/cm² (not shown). At pH 3.79 (0 M NH₄OH) the electrolyte was unstable and precipitated over time, so no further analysis was taken. With the addition of ammonium hydroxide to the electrolyte and consequently changing the solution pH from 3.79 to 8 (0.11 M NH₄OH), the copper partial reduction rate shifts to more negative potentials. Further addition of ammonium hydroxide to the solution until pH 10 is reached (0.56 M NH₄OH) resulted in a polarization curve with a shift in the opposite direction. These shifts in polarization observations are consistent with copper-citrate particle free electrolytes reported by Chassaign et al. The change in the polarization curves may reflect a change in the type of Cu complexed species. At high pHs with ammonium hydroxide, Cu(I) intermediate species are stable and the limiting current density of this first electron transfer is captured in the polarization curve at pH 10, Figure 2, between –0.5 and –0.6 V.
**Figure 6.3(a).** Cu partial current densities for a particle-free electrolyte, pH 8, at different electrode rotation rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)

**Figure 6.3(b).** Cu partial current densities for a 12.5 g/L particle loading, pH 8, at different electrode rotation rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)
The copper partial current density for a particle-free electrolyte at different electrode rotation rates and at a pH value of 8 is shown in Figure 6.3 (a) for the low copper concentration electrolyte. The rotation rate has no significant effect on the reaction rate confirming the kinetically-limited region. Figure 6.3 (b) shows a large increase in the copper partial current density with the presence of particles (e.g. 12.5 g/L).

Figure 6.4. Weight percentage of $\gamma$-Al$_2$O$_3$ particles in the deposit at different electrode rotational rates: (x) 400, (△) 900, (□) 1600, (◇) 2500 rpm, pH 8 and particle loading of 12.5 g/L. (Error bars represent the standard deviation). (By Jill Fitzgerald)

The weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit from the low copper concentration electrolyte at pH 8 containing particles is shown in Figure 6.4. The alumina weight percent is highest at the low current densities (20 wt %) and decreases to a steady value near 0.015 A/cm$^2$, depending on the rotation rate. At 1600 and 2500 rpm there is more
alumina deposited into the copper matrix compared to 400 and 900 rpm, when the current density exceeds 0.015 A/cm². The standard deviation of the alumina weight percentage was higher for the rotation rates of 1600 and 2500 rpm compared to lower values of rotation rates as shown by the error bars. The current efficiency is shown in Figure 6.5 for the low copper concentration electrolyte at pH 8 for the (a) particle-free electrolyte and (b) the electrolyte with particles. There is an increase in the current efficiency when particles are present. There is also a difference in the current efficiency behavior with applied current density. In the particle-free electrolyte the current efficiency decreases significantly with current density at all rotation rates, except for the highest rotation rate of 2500 rpm, while in the electrolyte with particles there is a relatively constant value at a given rotation rate. In the particle electrolyte, higher efficiency is observed for the lower rotation rates (e.g. 400 and 900 rpm), which also corresponds to the condition with the smallest amount of alumina incorporated into the deposit (Fig 6.4). Also, the data becomes more scattered at high rotation rates compared to low ones as a result of the wide particle wt. % distribution range at rotation rates higher than 1600 rpm as seen in Figure 6.4. Figure 6.6 shows the copper partial current density for the low copper concentration electrolyte at a pH of 10 in a (a) particle-free electrolyte and (b) with particles, at different electrode rotation rates. There is a steeper rise in the copper partial current density compared to the pH 8 case, both with and without particles, indicative of a change of the copper reacting species to the predominately complexed copper-ammonia species. The addition of particles to the electrolyte shifts the copper applied current density approximately 200 mV to less noble potentials, inhibiting the copper reduction rate. This observation is in direct contrast to that observed in the pH 8 electrolyte.
Figure 6.5(a). Current efficiency of a particle-free electrolyte, pH 8, at different electrode rotational rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)

Figure 6.5(b). Current efficiency of a 12.5 g/L particle loading electrolyte, pH 8, at different electrode rotational rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)
Figure 6.6(a). Cu partial current densities for a particle-free electrolyte, pH 10, and at different electrode rotation rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)

Figure 6.6(b). Cu partial current densities for a 12.5 g/L particle loading electrolyte, pH 10, and at different electrode rotation rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)
Figure 6.7 shows the weight percent of $\gamma$-Al$_2$O$_3$ particles in the deposit from the pH 10 electrolyte. In general, the amount of alumina particles in the deposits is much lower compared to the pH 8 electrolyte. The data ranges from 1 to 4 wt % alumina in the pH 10 electrolyte, in contrast to the large particle deposit concentration in the pH 8 electrolyte (Fig 6.4). The standard deviation of the alumina weight percentage was smaller in general, except at the high current density region where the deposits are rougher. The current efficiency for the low concentration electrolyte at pH 10 is shown in Figure 6.8 for the (a) particle-free electrolyte and (b) with particles. The values are significantly lower, less than 50 %, compared to the values at pH of 8 (Fig 6.5) over the entire range of applied current densities for all electrode rotation rates.

![Graph showing Al$_2$O$_3$ composition vs. Current density](image)

**Figure 6.7.** Wt. % of $\gamma$-Al$_2$O$_3$ particles in the deposit at different electrode rotational rates: (x) 400, (△) 900, (□) 1600, (◇) 2500 rpm, pH 10 and particle loading of 12.5 g/L. (Error bars represent the standard deviation). (By Jill Fitzgerald)
Figure 6.8(a). Current efficiency for a particle-free electrolyte, pH 10, at different electrode rotational rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)

Figure 6.8(b). Current efficiency for a 12.5 g/L particle loading electrolyte pH 10, at different electrode rotational rates: (*) 400, (△) 900, (□) 1600, (◇) 2500 rpm. (By Jill Fitzgerald)
The qualitative observations between the two different pH electrolytes are summarized in Table 6.2. The copper species in the particle-free electrolyte changes with pH. There is a larger \( \text{Cu}_2(\text{AO})_2^{-4} / \text{Cu} (\text{NH}_3)_4^{2+} \) ratio at pH 8 compared to pH 10. At pH 8 the copper partial current density is enhanced and the current efficiency increases with the addition of particles. There is a large range of particle concentration found in the deposit, but large values up to 20 wt % is possible. The more particles in the deposit (achieved at the higher rotation rates) the lower is the current efficiency. In contrast, at pH 10, there is an observed inhibition of the copper partial current density with the addition of particles, with significantly lower amounts of alumina (1-4 wt %) incorporated into the deposit for rotation rates \( \geq 1600 \text{ rpm} \) accompanied with a low current efficiency.

Inhibition of reduction reactions in alloy codeposition and in elemental deposition with additives have been associated with the loss of active surface area by adsorbed species\textsuperscript{34-35}.

**Table 6.2. Qualitative observations in the low copper concentration electrolyte**

<table>
<thead>
<tr>
<th></th>
<th>pH 8</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}_2(\text{AO})_2^{-4} / \text{Cu} (\text{NH}_3)_4^{2+} ) (particle-free electrolyte)</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Behavior of ( i_{\text{Cu}} )</td>
<td>Enhanced</td>
<td>Inhibited</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 ) wt % in deposit</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Current efficiency, %</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

Since particles have been modeled as adsorbing onto the electrode surface\textsuperscript{36-37} their blocking of the electrode area may explain the lower Cu partial current density in the pH 10 electrolyte, though it does not explain the apparent enhancement behavior in the pH 8
electrolyte. Modeling endeavors that predict particle incorporation have linked the incorporation rate to the metal deposition kinetics, suggesting that the type of reacting species or electrolyte environment may affect the particle wt % in the deposit. During the reduction of Cu from a copper-citrate complex, there is an adsorbed Cu intermediate at the electrode surface, though copper-ammonia intermediate species are soluble. Since there is a larger particle wt % in the deposit at pH 8 (e.g. rotation rates ≥ 1600 rpm) when more copper-citrate species are present compared to pH 10, then the adsorbed Cu intermediate may be an important factor in determining the amount of particle incorporation. However, high alumina deposit content in copper electrodeposited from sulfuric acid electrolytes, without any complexing agent, has also been observed, and is typical of a soluble copper intermediate during reduction. Thus, the species intermediate type alone is not a sufficient predictor of particle incorporation.

As pointed out by the seminal work of Guglielmi the particle must be adsorbed to the electrode surface in order for it to be retained in the growing deposit, governed by electrokinetics, suggesting that the point of zero charge is an important factor. The pH where the point of zero charge (PZC) occurs for alumina particles in non-complexing electrolytes has been reported to be between 8.3-8.6. For pH values higher than the PZC, alumina particles are negatively charged, whereas for pH values lower than PZC, they are positively charged. Thus, the very low amount of alumina in the deposit in the pH 10 electrolyte is consistent with a repulsive electrokinetic effect due to an unfavorable negative particle charge.

Furthermore, the copper partial reduction rate is enhanced in the presence of particles at pH 8, whereas for the pH 10 electrolyte, it is inhibited. An example is shown
in Fig. 6.9 for the partial current densities at 2500 rpm. A change in the complexing equilibria with the addition of particles can explain the change in the copper partial current density. At pH 8 the copper species is predominately complexed with citrate, Cu$_2$(AO)$_2$$^{-4}$, as opposed to ammonia. If more Cu(NH$_3$)$_4$$^{+2}$ species become available, then the copper partial current density is expected to shift to more noble potentials, resulting in an apparent enhancement effect. In contrast, at pH 10 if there is a change in the ratio of Cu$_2$(AO)$_2$$^{-4}$ / Cu(NH$_3$)$_4$$^{+2}$ generating more Cu$_2$(AO)$_2$$^{-4}$ compared to Cu(NH$_3$)$_4$$^{+2}$ species, then the copper partial current density is expected to shift to more negative potentials, resulting in an apparent inhibition effect. The alumina particle surface charge has been identified to be positive at pH 8 and negative at pH 10 in noncomplexing systems, and thus the particles would have different adsorption affinities at pH 8 or 10. At pH 8 the citrate anions are expected to be adsorbed to the alumina particles and therefore will alter the complexing of copper ions, favoring the formation of Cu(NH$_3$)$_4$$^{+2}$. Luther et al.$^{46}$ have shown that at pH $\geq$ 3 citrate ions are specifically adsorbed onto the surface of alumina in the presence of ammonia. At pH 10, ammonium ions are expected to be adsorbed onto the alumina, resulting in an excess of citrate ions available for an increase in the formation of Cu$_2$(AO)$_2$$^{-4}$ species.

6.3.3 Deep Recess Experiments

Ideally, electrodeposition by application of constant current or potential is desirable. Several constant current depositions were attempted ranging from 10 to 16 mA/cm$^2$, in micro-recessed electrodes. Electrodeposition of Cu-alumina microposts was very limited, primarily due to the hydrogen evolution side reaction caused by water and/or hydrogen ions reduction. The hydrogen bubbles are also liable to adhere to the surface resulting in
non-uniform current distributions. In addition, it also leads to a more brittle and structurally weaker deposit due to hydrogen embrittlement. Thus, as a result of the side reaction, the concentration of hydroxyl ions (OH⁻) accumulates at the electrode surface, which leads to a rather steep increase in the local pH at the electrode surface, increasing precipitation due to the formation of the insoluble hydroxide of Cu. Precipitation blocks the passage of current into the recess, leading to non-uniform distribution of current over the pattern.

![Graph showing Cu partial current densities at different pH levels with and without particles, electrode rotation rate 2500 rpm.](image)

**Figure 6.9.** Cu partial current densities at both pH 8 and 10 with and without particles, electrode rotation rate 2500 rpm.

Due to hydrogen gas blocking the electrode surface and local surface pH changes, the hydrogen evolution side reaction can be problematic in deep recess plating. A pulse scheme with long relaxation times was adopted to avoid these drawbacks. The relaxation time (zero current) enables reacting species to be supplied again within the recess and allows the products of side reactions to diffuse out of the recess. Pulsing of current was
considered in an attempt to overcome the problems of direct current electrodeposition. The pulsing of current can be more easily controlled than potential by holding one step at zero current, thereby ensuring that not net reaction takes place. It of course dictates a constant total reaction rate of deposition.

The most promising electrolyte for plating into deep recesses studied here (citrate-ammonia electrolytes) with high efficiency and particle incorporation is the pH 8 case. However, since the current efficiency is not 100%, hydrogen gas can block the electrode surface. Therefore, a pulse scheme with long relaxation times was adopted to avoid this drawback. Also, due to the increased diffusion path a higher Cu concentration (1 M) was used to raise the limiting current density, thus, the citrate concentration was also augmented (1.2 M) to keep the same copper/citrate ratio as with the less concentrated electrolyte.

Figure 6.10 shows the top view of a SEM micrograph of an array of Cu-γ-Al₂O₃ microposts from the composite plating bath electroformed by pulsing; the insert shows the cross sectional view of a single 500 µm tall micropost. The optimum operating conditions found for this system were an applied cathodic current density of 0.016 A/cm² with an on time of 10 s and off time of 60 s. The applied current density was chosen so that at the bottom of the recess the applied current density is lower than the steady-state copper limiting current density, calculated as 0.018 A/cm², assuming a diffusion coefficient of 4.5 x 10⁻⁶ cm²/s and a boundary layer thickness that was equal to the recess depth, 500 µm. After 6 1/2 days the deposit reached the surface of the recess, and produced mushroom-like deposits at the recess mouth (overplate).
Figure 6.10. SEM micrographs for Cu-$\gamma$-Al$_2$O$_3$ microposts from a composite plating bath containing 12.5 g/L particles, 1 M CuSO$_4$, 1.2 M sodium citrate, pH 8 at a pulsed cathodic current density of 0.016 A/cm$^2$, with an On and Off times of 10 and 60 s respectively.

Figure 6.11. Al$_2$O$_3$ wt. % along three representative microposts electroplated at a pulsed cathodic current density of 0.016 A/cm$^2$, with an On and Off times of 10 and 60 s respectively, from an electrolyte containing a particle loading of 12.5 g/L, 1 M CuSO$_4$, 1.2 M sodium citrate, and a pH value of 8.
Figure 11 shows the weight percentage of Al₂O₃ along the height of three representative microposts electroplated at a constant current density of 0.016 A/cm² in a bath containing a particle loading of 12.5 g/L and a pH value of 8. The alumina weight percentage along each post is uniform, varying slightly in concentration from post to post. The range of the average alumina weight percentage among the three posts is between 7.5 - 7.9 wt. %.

6.4 Summary

The electrodeposition of Cu-γ-Al₂O₃ nanocomposites as thin films and into recessed electrodes prepared with x-ray lithography was examined in ammonia-citrate electrolytes. At pH 8 the presence of particles resulted in an enhancement of the Cu reaction rate, while at pH 10 the reaction rate appeared inhibited. The change of the Cu partial current density was attributed to the change of the copper complexed species. The amount of alumina particles in the deposit and current efficiency was greater at pH 8 than pH 10, making the pH 8 solution a more promising electrolyte to electroplate into 500 µm deep recesses for MEMS composite components. High aspect ratio microstructures of electrodeposited copper-γ-Al₂O₃ nanocomposites were successfully performed into deep recesses with uniform concentration of alumina along the length of the microposts.

6.5 References


CHAPTER 7 ELECTRODEPOSITED Cu-MATRIX HIGH ASPECT RATIO MICROSTRUCTURE (HARM) COMPOSITES USING X-RAY LITHOGRAPHY

Since Cu-$\gamma$-Al$_2$O$_3$ high aspect ratio micropost composites were fabricated from citrate-ammonia electrolytes (Chapter 6), the next goal was to study different particle types and electrolyte. A study comparing the effect of surface morphology, composition gradients and particle agglomeration along the electrodeposit microposts was carried out with three different particle types from sulfuric acid electrolytes, to have a better understanding of how complexing agents affect the Cu-particle codeposition rate, which to the author’s knowledge has not been reported yet.

Electrodeposition of Cu-$\gamma$-Al$_2$O$_3$, Cu-CeO$_2$ and Cu-TiO$_2$ as thin films and High Aspect Ratio Microstructures (HARM’s) was examined from acidic electrolytes. Recessed electrodes were prepared using X-ray lithography. Partial current density, current efficiency and deposit particle concentration were determined with a rotating disk electrode. The concentration of particles in Cu-matrix thin film composites, as well as the particle distribution along the microposts were dependent upon the particle type.

7.1 Introduction

Metal matrix composites can have different engineering applications, depending on the degree and type of particle that is dispersed into the metal. Even though, different methods such as surface oxidation,$^1$ mechanical mixing,$^2$ co-precipitation,$^3$ powder metallurgy$^4$ and gel precipitation,$^5$ have been used to incorporate oxide particles to strengthen the copper matrix, electrodeposition offers advantages over these competing technologies and chemical vapor deposition since it requires simpler instrumentation and operating conditions, besides it can be used to deposit onto irregularly shaped geometries
and into deep recess. The electrodeposition of different copper composites have been studied in the search for new engineering applications.\textsuperscript{6-10} For instance, copper has a very high electrical conductivity and it is one of its most useful properties. But, because copper has poor tensile and creep strengths, even at moderate temperature, it has to be combined with oxide particles to strengthen the copper matrix in order to avoid design problems arising when used in electrical applications.\textsuperscript{11} Refractoriness, hardness, strength, wear and corrosion resistance are only a few properties desired in copper composite materials. Warrier and Rohatgi\textsuperscript{4} studied mechanical, electrical and electrical contact properties of Cu-TiO\textsubscript{2} composites containing 5-20 wt. %. They found that the density of the composites decreased, while their hardness and electrical resistivity increased with increasing titania content. Concluding that copper composites with a 5 wt. % TiO\textsubscript{2} could be a good candidate material for light duty electrical contacts. In another study, Fawzy \textit{et al.}\textsuperscript{8} electroplated Cu-\(\alpha\)-Al\textsubscript{2}O\textsubscript{3} and Cu-TiO\textsubscript{2} composites from acidic baths. They observed that there was a parallelism between the increase in microhardness and the increase in the \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} wt. % codeposited with copper.

Cu-Al\textsubscript{2}O\textsubscript{3} composite materials are of interest because of the enhanced mechanical properties compared to the metal matrix\textsuperscript{12, 13} and for their thermal and mechanical stability at elevated temperatures.\textsuperscript{14} Applications include their use in electronic packaging; and as materials for electrodes and contact terminals, such as high-performance electrodes for industrial spot welding.\textsuperscript{15}

Ceria and doped ceria are one of the most important ceramic materials, since they have important and different catalysis uses, such as an important component of the three way automotive catalyst,\textsuperscript{16} as an ionic conductor,\textsuperscript{17} as a gas sensor,\textsuperscript{18} and as an electrolyte
material of solid oxide fuel cells.\textsuperscript{19} Cerium oxide particles have also been combined with metal matrixes, since ceria films have useful properties for catalytic and electronic applications,\textsuperscript{20} as well as for corrosion protection.\textsuperscript{21} It has been demonstrated that CeO\textsubscript{2} particles improve the oxidation resistance of steel in a study of the oxidation of a novel chromium coating with CeO\textsubscript{2} dispersions. Ceria thin films have also found uses as high refractive index materials and insulating films on semiconductors.\textsuperscript{22}

Electrodeposition is the key technology that can be used to deposit metal matrix structures into deep recesses. The challenge in fabricating metal matrix composites for MEMS includes restricting the second phase material to the nanoscale and controlling the composition distribution of the deposit. In this work, copper has been selected as a model system to electroplate Cu-\(\gamma\)-Al\textsubscript{2}O\textsubscript{3}, Cu-CeO\textsubscript{2} and Cu-TiO\textsubscript{2} composites as thin film and High Aspect Ratio Microstructures (HARM’s) from acidic electrolytes.

7.2 Experimental

7.2.1 Solution

Acid and basic electrolytes with and without the addition of particles were examined. Acid and basic electrolytes were adjusted to a pH of 0.2 and 8.0 with sulfuric acid and ammonium hydroxide, respectively. The composition for thin film electrodeposition was 0.25 M CuSO\textsubscript{4}\cdot5H\textsubscript{2}O, and 1.2 M H\textsubscript{2}SO\textsubscript{4} for acid baths, and 0.25 M CuSO\textsubscript{4}, and 0.3 M Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7} for basic baths. For microposts electrodeposition, acid baths composed of 1.0 M CuSO\textsubscript{4}\cdot5H\textsubscript{2}O, and 1.2 M H\textsubscript{2}SO\textsubscript{4} were used, whereas basic baths were composed of 1.0 M CuSO\textsubscript{4}, and 1.2 M Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}. Three types of particles were examined: \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} having an average diameter of 32 nm, supplied by Nanophase Technologies Corporation, IL, USA, CeO\textsubscript{2} and TiO\textsubscript{2} both with a reported diameter size of
9-15 nm, supplied by Alfa Aesar, MA, USA. The particle electrolyte loading was 12.5 g/L for each particle type.

7.2.2 Electrochemical Cell

Deposition experiments were performed on rotating disk electrodes (RDE’s) and recessed microelectrodes 500 µm thick. The particles were kept in suspension using a magnetic stirrer during thin film electrodeposition. The agitation of the suspension was controlled by the rotating electrode hydrodynamics by keeping the agitation due to the magnetic stir bar at the bottom of the cell to a minimum. In the case of the recessed electrodes both, mechanical (Arrow, Model No. 1750) and magnetic (Corning Inc.) agitation were used to keep the electrolyte in uniform suspension and to avoid particle sedimentation and formation of local concentration gradients. A three-electrode system was used to perform polarization experiments with the RDE. The disk area was 1.5 cm², and was machined from 316 stainless steel. A Au surface layer was electrodeposited onto the stainless steel disk for improved adhesion of the composite film (Acid gold strike and Orotemp 24 gold solution, Technic Inc.). A copper foil with an array of 7 mm holes was used as the anode. The anode was kept stationary and was placed parallel to the working electrode. The holes in the anode helped to avoid accumulation and settling of alumina particles on it, and promote a homogeneous distribution of the particles in the electrolyte. A saturated calomel electrode was the reference electrode. Nitrogen was bubbled in the experimental cell prior to experiments.

The recessed electrodes were produced by exposing 500 µm thick polymethylmethacrylate (PMMA) sheets attached to copper plates to X-ray radiation at
the LSU-CAMD synchrotron facility, following the procedure of Kanigicherla [23], see chapter 3 for details about microrecessed electrodes substrate preparation.

### 7.2.3 Procedure

A computer controlled potentiostat and impedance system (Zahner IM6e) were used to measure polarization curves, ohmic resistance and for Cu-particle thin film deposition. Polarization curves were measured with and without particles for an electrode rotation rate of 1600 (laminar flow regime). All polarization scans were performed by increasing the cell potential from the open circuit value (-0.22 mV vs SCE) to –1.2 V at a scan rate of 2 mV s⁻¹. The frequency range used for the impedance spectra was from 100 mHz to 1 MHz. Five deposits at different current densities were analyzed for the 1600 rpm rotation rate in the kinetically-controlled region. The constant net plating charge used was 27 C/cm² for each deposit. Pulsed galvanostatic control was employed in the electrodeposition into recessed electrodes. A PINE Bipotentiostat Model AFCBP1 (PINE Instrument Company) coupled with an AMEL function generator (Model 568) was used.

### 7.2.4 Composition Analyses

The particle weight percentage was analyzed using Scanning Electron Microscopy (SEM, JEOL JXA-733) with Wavelength-Dispersive X-ray Spectrometer (WDS). For thin film deposits five points chosen randomly were analyzed for each sample calculating an average value; the standard deviation is shown as error bars in the corresponding figures. 30 points along the microposts from bottom to top were analyzed to determine the particle composition distribution. The size of the interaction volume of the electron beam and the sample was 10 μm in diameter and the quantization for each measurement is an average over this area. The alumina concentration was determined by the
stoichiometric ratio of oxygen to aluminum, Al₂O₃, and the same method was used for ceria and titania concentration. SEM (Jeol, JSM-840A) was used to obtain topographical information of thin film deposits, as well as of microposts. Transmission electron microscopy (TEM JEOL 100CX) was used to analyze the presence of nanoparticles embedded in the microposts. See Appendix B for sample preparation procedures.

7.3 Results and Discussions

Figure 7.1 shows the effect of different particle types on the copper partial current density from an acidic electrolyte in the kinetically-controlled region. In the case where no particles and alumina particles are present the copper reduction rate increases in a linear fashion versus potential. The addition of alumina particles to the electrolyte does not have a significant effect on the copper kinetics. For the cases where ceria and titania particles are present in the electrolyte, the copper partial current density is enhanced for all potential values. There is an average variation of 0.95 and 0.15 % of the Cu partial current density when ceria and titania particles are present, respectively, thus the enhancement observed at the lowest and highest potential values is significant. The largest enhancement is observed when ceria particles are in the electrolyte.

The variation of weight percentage of the three different particles on the composites versus current density and potential is shown in Figure 7.2. In all the cases, the alumina, titania and ceria weight percentage decreases when current density increases (Figure 7.2a) and correspondingly when the voltage increases (Figure 7.2b). Of all three different particles in the composites, the alumina weight percentage is the highest, with a maximum of 6 wt. % around a potential value of -0.15 V (-40 mA/cm²). Titania in the
Cu-TiO$_2$ composites varies from 3.2 to 1 wt. %. In the Cu-CeO$_2$ composites, ceria varies from 3.3 to 0.7 wt. %.

**Figure 7.1.** Effect of different particle types on the variation of the copper partial current density with potential, from a particle loading of 12.5 g/L, at 1600 rpm.

The effect of the codeposition of different particle types on the variation of the copper current efficiency with potential and current density, from electrolytes containing 12.5 g/L particle loadings at 1600 rpm is shown in Figure 7.3. In general, high current efficiencies were achieved with and without the presence of particles in the electrolytes. In each case the current efficiency increases with potential (Figure 7.3a) or current density (Figure 7.3b). Current efficiencies from 83 to 100 % in the case where alumina particles were present in the electrolyte, 85 to 100 % for alumina, and 90 to 100 % were obtained when ceria particles were present. And in the case where no particles were present the current efficiencies varied from 86 to 93%. Figure 7.4 shows the surface morphology of a pure copper deposit (Figure 7.4a) and three different composites: Cu-$\gamma$-Al$_2$O$_3$ (Figure 7.4b), Cu-CeO$_2$ (Figure 7.4c), and Cu-TiO$_2$ (Figure 7.4d), obtained from
their corresponding electrolytes with a particle loading of 12.5 g/L. The current density and time of electrodeposition were 80 mA/cm² and 5.6 minutes respectively, at an electrode rotation rate of 1600 rpm. At these conditions the particle weight percentage in each composit was almost the same as shown in Figure 7.2a.

![Figure 7.2](image-url)

**Figure 7.2.** Variation of the weight percent in the deposit of different particle types with (a) current density and (b) potential, at an electrode rotational rate of 1600 rpm and particle loading of 12.5 g/L.
Figure 7.3. Effect of the codeposition of different particle types on the variation of the copper current efficiency with (a) potential and (b) current density, from electrolytes containing 12.5 g/L particle loadings at 1600 rpm.

The composite micrographs show that the presence of particles in the composites affect the surface morphology of the pure copper deposit in different ways. Even though, the formation of a few new nodules is observed in the copper-alumina and copper-ceria
Figure 7.4. SEM micrographs of a) pure copper deposit and b) Cu-γ-Al$_2$O$_3$, c) Cu-CeO$_2$, d) Cu-TiO$_2$ composites obtained from a 12.5 g/L particle loading, at 1600 rpm, -80 mA/cm$^2$ and deposition time of 5.6 min.

deposits compared to Cu-TiO$_2$ composites, the presence of particles have little effect on the pure copper surface morphology. In the Cu-titania composite (Figure 7.4d) the nodules increase, which may suggest a correlation between the enhancement of the copper reduction rate and an increase in surface area when titania particles are present. But, on the other hand, the surface morphology of the deposit with ceria looks the same
Figure 7.5. SEM micrographs of a) pure copper deposit and b) Cu-γ-Al₂O₃, c) Cu-CeO₂, d) Cu-TiO₂ composites obtained from a 12.5 g/L particle loading, at 1600 rpm, -40 mA/cm² and deposition time of 11.25 min.

similar to the copper and copper-alumina deposits despite an enhancement in the copper reduction rate. Thus, the relation of enhancement due to an increase in surface area does not hold. The surface morphology of a pure copper deposit (Figure 7.5a) and three composites: Cu-γ-Al₂O₃ (Figure 7.5b), Cu-CeO₂ (Figure 7.5c), and Cu-TiO₂ (Figure 7.5d), were analyzed at a current density of 40 mA/cm² where the particle weight percentage in
each composite is different (Figure 7.2a). In all cases when particles are present in the composites the surface morphologies are similar and seem smoother than the pure copper deposit.

The variation of the particle weight percentage along three different 500 µm tall microposts from Cu-γ-Al₂O₃, Cu-CeO₂ and Cu-TiO₂ microstructure composites is shown in Figure 7.6. For all the cases the microstructures were fabricated by pulsing DC current, with On and Off times of 10 and 50 s respectively, using in each case a particle loading of 12.5 g/L. Similar to the case of thin films, the Al₂O₃ content in the microposts was about the same (Figure 7.6a). The distribution of alumina weight percentage along each micropost shows some variability. The amount of alumina near the base of the microposts was found to be around 1 wt. %, reaching values of up to 5 wt. % at the top with some scattered points of 15 wt. %. Dramatically lower amounts of ceria and titania were observed in the microposts. For ceria the weight % was less than 1 wt. % and remained constant along the microposts (Figure 7.6b). The lowest amount of particles detected was titania, from the Cu-TiO₂ composites. Less than 0.1 wt. % was observed, even though isolated points of up to 0.3 and 1 wt. % were detected (Figure 7.6c). Figure 7.7 shows a TEM micrograph of (a) Cu-γ-Al₂O₃ and (b) Cu-CeO₂ micropost composites obtained pulsing a constant cathodic current density of 16 mA/cm², using a duty cycle of 0.167, from simple acidic electrolytes with a particle loading of 12.5 g/L. The non-uniformity of alumina particles along the microposts can be due to agglomeration of nanoparticles in specific areas (lighter area) as observed in Figure 7.7(a). Figure 7.7(b) shows isolated ceria nanoparticles embedded in Cu microposts. Ceria particles are distributed more
Figure 7.6. Particle wt. % variation along the length of three different a) Cu-Al₂O₃, b) Cu-CeO₂ and c) Cu-TiO₂ micropost composites, obtained pulsing DC current with On and Off times of 10 and 50 s respectively, from 12.5 g/L particle loading electrolytes.
Figure 7.7. TEM micrographs for (a) Cu-γ-Al₂O₃ and (b) Cu-CeO₂ micropost composites obtained by pulsing a constant cathodic current density of 16 mA/cm² for 10 s, with a duty cycle equal to 0.167.
Figure 7.8. Top view of SEM micrographs of a) Cu-$\gamma$-Al$_2$O$_3$, b) Cu-CeO$_2$, c) Cu-TiO$_2$ microposts obtained from a 12.5 g/L particle loading, at a pulsed cathodic current density of 0.016 A/cm$^2$, with an On and Off times of 10 and 50 s respectively.
uniformly along the microposts (Figure 7.6b) compared to alumina particles (Figure 7.6a).

During deep recess electroplating the amount of titania and ceria particles were significantly lower than in thin films. Since the boundary layer is much bigger in micropost deposition, 500 µm, compared to a 10 µm boundary layer for thin film electrodeposition on a rotating disk electrode at 1600 rpm, there can be a change in species mass transport. The alumina concentration is little affected in a micropost, so it is expected that the difference in the titania and ceria deposit content may be due to a local pH rise, or in other words a high mass transport resistance of hydroxyl ions.

Even though electroplating occurs under acidic electrolytes, the local pH at the electrode surface may rise as a consequence of hydrogen ion reduction. Since the point of zero charge (PZC) is lower for titania and ceria compared to alumina the local pH change can affect the particle charge. The pH at which the PZC occurs for titania is $\text{pH}_{(\text{PZC})} \cong 6$ and for ceria $\text{pH}_{(\text{PZC})} \cong 6.75^{24}$ compared to a value of 8.5 for alumina.$^{25}$ A pH rise can cause the ceria and titania surface to have a negative net charge, provoking an electrostatic repulsion between particles on the electrode surface, reducing the amount of particles incorporated in the copper matrix. If the local pH is below its PZC then the particle would have a net positive charge and is expected to be attracted to the electrode surface. Thus, the pH rise at the surface is most probably below 8.5 which is consistent with the high concentration of alumina in the micropost.

The top views of three different composite microposts: Cu-$\gamma$-Al$_2$O$_3$ (Figure 7.8a), Cu-CeO$_2$ (Figure 7.8b), and Cu-TiO$_2$ (Figure 7.8c) are shown in Figure 7.8. Even though the particle weight percentage is different in all cases at the top of the microposts, the
morphology of the top view in all three cases seems to be unaltered by the type and amount of particles.

7.4 Summary

Cu-γ-Al₂O₃, Cu-CeO₂, and Cu-TiO₂ composites were successfully obtained as thin films and HARM’s. The addition of alumina particles to the electrolyte did not have a significant effect on the copper kinetics. Whereas ceria and titania particles enhanced the copper partial current density for potential values between -0.1 to -0.15 V. The presence of particles in the composites affects the surface morphology of the pure copper deposit thin film. On the other hand the type of particle did not affect the surface morphology of the micropost composites. The highest particle concentration in thin film and HARM composites was achieved in the Cu-Al₂O₃ system. Cu-TiO₂ and Cu-CeO₂ microposts resulted in drastic reduction in particle composition, which may be attributed to a local pH rise, or in other words a high mass transport resistance of hydroxyl ions.

7.5 References

CHAPTER 8 ELECTRODEPOSITION OF NiCu-MATRIX NANOCOMPOSITES USING A ROTATING CYLINDER HULL CELL

Alloy-matrix composites were also studied. The electrodeposition of NiCu composites using nanometric diameter alumina and ceria was examined using the Rotating Cylinder Hull Cell (RCHC). A variation in rotation rate was studied with and without the presence of particles. Both the alumina and ceria weight percentage did not vary with applied current density. The amount of alumina particles in the alloy composite was much higher than the content of ceria with the same electrolyte loading. Particles altered the deposition rate of both Cu and Ni affecting the deposit composition.

8.1 Introduction

The electrodeposition of alloys\textsuperscript{1,2} and composite\textsuperscript{3-6} materials has been of particular interest due to the unique and often superior properties compared to their constituent components. For example, the micro-hardness values of short $\delta$-Al$_2$O$_3$ fibers in aluminum alloy composites were higher than that of the aluminum alloys.\textsuperscript{7} Berkh et al.\textsuperscript{8} studied the codeposition of Al$_2$O$_3$ particles with a Cr-Ni alloy (4-90 wt. % Cr) from a trivalent N,N-dimethylformamide electrolyte.\textsuperscript{9} They found that Al$_2$O$_3$ particle codeposition with Cr-Ni alloy matrix resulted in a reduction of surface roughness, residual stresses and wear resistance; microhardness remained unaffected at about HV 7000.

Nickel-copper alloy materials are well known for their good corrosion resistance,\textsuperscript{2,10-14} thermoelectrical,\textsuperscript{15,16} catalytic,\textsuperscript{17-19} mechanical\textsuperscript{20-22} and magnetic\textsuperscript{16,23,24} properties. NiCu alloys have a high thermoelectric power, which allows the fabrication of very sensitive heat-flux sensors with the composition of Constantin (solid solution with 35 to 50 wt. % of Ni in Cu).\textsuperscript{15} These materials have been also employed in different
applications such as catalysts, for instance in the electric-oxidation of small organic molecules,\textsuperscript{17} and the hydrogenation of benzene and n-hexane.\textsuperscript{18}

The electrodeposition of alumina composites has also been widely studied\textsuperscript{4,25-27} in metal-matrix composites because alumina improves not only their mechanical properties,\textsuperscript{4,25} but also their thermal and mechanical stability at elevated temperatures [26]. There are few works related to the electrodeposition of NiCu matrix-composites. Fawzy \textit{et al.}\textsuperscript{21} found that during electrodeposition of NiCu alloys with $\alpha$-Al$_2$O$_3$ and TiO$_2$, there was a decrease in the cathodic polarization. They observed that the higher a superimposed a.c. density and the lower its frequency the greater was the depolarizing effect. The microhardness of the alloy was improved by the presence of $\alpha$-Al$_2$O$_3$ and TiO$_2$ particles in the composites. Panda and Podlaha\textsuperscript{28} studied the NiCu-$\gamma$-Al$_2$O$_3$ system on both recessed and unrecessed surfaces. In microrecesses the inclusion of alumina nanoparticulates in solution, even in small quantities, help to enhance mass-transport. Whereas, in the electrodeposition of thin films using a RCE there was not an effect of alumina altering the metal rate at 1000 rpm. In another study, NiCu-carbon fibre composites were obtained showing that the bonding and flexural strength of the composite were significantly increased.\textsuperscript{22} In this work the effect of nanometer size alumina particles on the copper and nickel deposition is studied with copper under diffusion control and the nickel kinetically controlled.

The NiCu-CeO$_2$ will represent the first time, to our knowledge, that such a composite has been deposited. Ceria films have useful properties for chemical,\textsuperscript{29} catalytic and electronic applications,\textsuperscript{30} and corrosion protection.\textsuperscript{31} In a study of the oxidation of a novel chromium coating with CeO$_2$ dispersions, it was demonstrated that CeO$_2$ particles
improved the oxidation resistance of steel.\textsuperscript{31} Also, the addition of ceria plays an important role in improving anode performance in solid oxide fuel cells, either through improved catalytic activity or mixed ion-electronic conductivity.\textsuperscript{30} Here, the effect of ceria particles on the copper and nickel deposition is explored.

The Rotating Cylindrical Hull Cell (RCHC) is a tool that can be used to readily assess the variation in composition and thickness of a deposit over a wide range of applied current density. Madore and Landolt\textsuperscript{32} presented design conditions for obtaining a large variation in current distribution in the NiCu system. They demonstrated the deconvolution of partial current densities in a NiCu alloy by mapping the current distribution to a polarization curve. This work will represent the first demonstration of the use of the RCHC to composite deposition.

\textbf{8.2 Experimental}

\textbf{8.2.1 Solution}

Citrate electrolytes were composed of 0.025 M CuSO\textsubscript{4}, 0.7 M NiSO\textsubscript{4} and 0.25 M Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7} with and without particles, at a pH of 4.5. Two types of particles were examined: \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} having an average diameter of 32 nm, supplied by Nanophase Technologies Corporation, IL, USA, and CeO\textsubscript{2}, with a reported diameter size of 9-15 nm, supplied by Alfa Aesar, MA, USA.

\textbf{8.2.2 Electrochemical Cell}

The RCHC system (Echo Chemie B.V., RHC70006) was used to perform the experiments; the rotating cylindrical cathode was a 410 stainless steel rod with a 0.6 cm in diameter and 8 cm in length, and the anode was a platinum mesh.
8.2.3 Procedure

All the deposits were obtained using an average current density of -13 mA/cm² for a period of 29 minutes. A computer controlled potentiostat and impedance system (Zahner IM6e) were used to measure polarization curves and ohmic resistance. Polarization curves were measured with and without particles for a rotating cylinder electrode (RCE) rotation rate of 540 rpm (turbulent flow regime), a saturated calomel electrode was used as the reference electrode. All polarization scans were performed by increasing the cell potential from the open circuit value at a scan rate of 2 mV/s. The frequency range used for the impedance spectra was 100 mHz to 1 MHz. The agitation of the suspension was controlled by the rotating electrode hydrodynamics.

8.2.4 Composition Analyses

A KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF) was used to analyze the thickness and composition of the deposits. Scanning Electron Microscopy (SEM, JEOL JXA-733) with Wavelength-Dispersive X-ray Spectrometer (WDS) was used to double check the ceria weight percentage with probe size of 10 µm, probe current of 10 nA and acceleration voltage of 15 KV. Thirty points were analyzed along each of the cylindrical cathodes. The partial current densities of Cu and Ni were obtained from the composition and thickness analysis. See Appendix B for sample preparation procedures for SEM analyses.

8.3 Results and Discussion

A comparison of polarization curves obtained from the electrodeposition of a NiCu alloy for a particle free electrolyte and for particle loadings of 12.5 g/L alumina and ceria at rotating cylinder electrode (RCE) of 540 rpm is shown in Figure 8.1. When ceria
particles are present in the electrolyte the total current density is inhibited in the whole potential range, whereas when alumina particles are present, the total current density is not affected until the potential is more negative than \(-0.7\) V, where it is enhanced. Inspection of the partial current densities that govern the total current density was carried out by the RCHC.

![Polarization curve](image)

**Figure 8.1.** Polarization curves from the electrodeposition of a NiCu alloy for a particle free electrolyte and with the presence of particle loadings of 12.5 g/L alumina and ceria at 540 rpm.

A primary current distribution approach was taken to interpret the data. In order to evaluate the validity of using such an approach, the Wagner number was determined for the average current density employed in the RCHC. The conductivity measured for the electrolyte with no particles was of 0.04 S/cm. From the polarization curve a slope of 22 mV/(mA/cm\(^2\)) was measured in the region where both copper and nickel deposit. The length of the cylinder used during the RCHC experiments was 8.0 cm. The corresponding
Figure 8.2(a). Variation in thickness and composition for a nickel-copper alloy along the cylinder cathode obtained at 540 rpm from a particle free electrolyte.

Figure 8.2(b). Variation in thickness and composition for a nickel-copper alloy along the cylinder cathode obtained at 540 rpm from a 12.5 g/L alumina particle loading.
Figure 8.2(c). Variation in thickness and composition for a nickel-copper alloy along the cylinder cathode obtained at 540 rpm from a 12.5 g/L ceria particle loading.

Wagner number under these conditions is 0.1. Therefore, the Ni current distribution is almost primary.

Figure 8.2 shows the variation in thickness and alloy composition with and without particles at 540 rpm. Figure 8.2(a) shows the results from a particle free electrolyte. The deposit thickness increased from 0.6 to 4.0 microns with increasing current density and the corresponding variation in composition was 96 weight percent Cu to 37 weight percent copper. Figure 8.2(b) and 8.2(c) show the composition and thickness distribution when a particle loading of 12.5 g/L of alumina and ceria particles were added to the electrolyte. In the case where alumina particles were present in the electrolyte, the deposit thickness was nearly the same as when no particles were present; it increased
from 0.6 to 3.9 μm with increasing current density. The amount of alumina in the deposits varied from 2 to 6 wt. % and the corresponding copper composition variation was 90 to 20 percent (Figure 8.2b), the copper composition was lowered by up to 6 percent in the low current density region and up to 46 percent in the high current density region, due to the presence of alumina particles. When ceria particles were present, the deposit thickness increased from 1.0 to 3.4 μm with increasing current density (Figure 8.2c), which was slightly higher at the bottom of the cylinder cathode, but lower at the top than that obtained from a particle free electrolyte or when alumina particles were added to the electrolyte. The amount of ceria in the deposits was lower than 1 %, and it varied from 0.8 to 0.1 wt. % with current density. The corresponding copper composition variation was between 94 to 23 wt. %. In this case, the ceria particles lowered the copper composition by up to 2 percent in the low current density region and up to 38 percent in the high current density region. The type of particle used has little effect in the thickness of the deposits, but it has an important effect in the alloy composition along the cylinder cathode.

The particles may alter the diffusion layer thickness or the metal kinetics. Stojak and Talbot\textsuperscript{33} did not observe any effect in the limiting conditions for copper electrodeposition for alumina particles loading below 120 g L\textsuperscript{−1}, but a particle loading of 158 g/L was found to increase the limiting conditions by 32 %. Panda and Podlaha\textsuperscript{28} concluded that the inclusion of nanoparticulates in solution, even in small quantities, help to enhance mass-transport in recessed electrodes. A previous study of the effect of Al\textsubscript{2}O\textsubscript{3} nanopowder on Cu electrodeposition\textsuperscript{27} showed that alumina particles changed the copper reduction rate, regions of copper inhibition and enhancement were identified in the
kinetic regime, with little change in the mass transport copper limiting current density. Thus, the partial current densities are examined.

The effect of different particles on the copper using a 12.5 g/L particle loading of alumina and ceria at an electrode rotation rate of 540 rpm is shown in Figure 8.3. The copper partial current density remains constant and equal to its mass transfer-limited value for each case over the entire potential range. The copper partial current density is inhibited when particles (either Al₂O₃ or CeO₂) are present in the electrolyte as shown in Figure 8.3. The copper partial current density is less inhibited when ceria particles are present in the electrolyte.

Figure 8.3. Effect of different particles on the copper limiting current density along the potential region using a 12.5 g/L particle loading of alumina and ceria at an electrode rotation rate of 540 rpm.
Verification of mass transport control of the copper reaction was carried out by varying the rotation rate. The value of the copper current density at -0.5 V was determined at different rotation rates with and without the presence of particles (Table 1) in the electrolyte using the RCHC. According to the empirical expression by Eisenberg et al. (10) the limiting current density follows

\[ i_L = 0.01nFC^bD^{0.644}ν^{-0.344}S^{0.7}d_i^{0.4} \]

where \( n \) is the number of electrons transferred, \( F \) is Faraday’s constant, \( C^b \) is the copper bulk concentration, \( D \) is the copper diffusion coefficient, \( ν \) is the kinematic viscosity, \( S \) is the rotation speed (in rpm) and \( d_i \) is the cathode diameter. Table 8.1 shows that there is a change in the copper partial current density with rotation rate so that a transport control is occurring. The diffusion coefficients of copper in a particle-free electrolyte was determined from the slope of a plot of the reciprocal of the limiting current density vs. the electrode rotation rate to the -0.7 power (Figure 8.4). The copper diffusion coefficient was \( 1.1 \times 10^{-6} \) cm\(^2\) s\(^{-1}\) similar to the value reported by Madore and Landlot (6) for the same electrolyte without particles. In the presence of particles, the copper partial current density does not change significantly with rotation rate, not indicative of a mass transport-limited behavior. Thus, at -0.5 V the copper rate is still under kinetic control, indicative of an inhibition of the copper rate by particles.

<table>
<thead>
<tr>
<th>rpm</th>
<th>( i_{Cu} ) (mA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No particle</td>
</tr>
<tr>
<td>200</td>
<td>0.8</td>
</tr>
<tr>
<td>365</td>
<td>1.0</td>
</tr>
<tr>
<td>540</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Figure 8.4. Determination of the diffusion coefficient of copper according to the Eisenberg correlation. The slope was determined from a line which fits the experimental data.

Figure 8.5. Effect of different particles on the nickel partial current density along the potential region using a 12.5 g/L particle loading of alumina and ceria at an electrode rotation rate of 540 rpm.
The nickel partial current density increases with potential in the kinetically-controlled region in all cases at an electrode rotation rate of 540 rpm (Figure 8.5). In this case, the partial current density of nickel is also inhibited when ceria particles are present in the electrolyte, but there is a clear enhancement with the presence of alumina particles as shown. Table 2 lists the values of the nickel charge transfer coefficients from electrolytes with and without the presence of particles at 540 rpm, which were calculated from the slopes of Tafel plots. The Tafel slopes were calculated from high potentials (e.g. from -0.9 to -1.3 V) where nickel primary current distribution dominates. In the absence of particles in the electrolyte, a nickel charge transfer coefficient was found to be equal to 0.21, similar to the value reported by Hessami and Tobias. The presence of alumina particles in the electrolyte did not have a large effect on the nickel charge transfer value of 0.25, but with the presence of ceria particles in the electrolyte the nickel charge transfer decreased to 0.15.

Table 8.2. Nickel charge-transfer coefficients with and without particles

<table>
<thead>
<tr>
<th>Tafel slope / V⁻¹</th>
<th>αN\text{c}_{i}</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Particles</td>
<td>16.1</td>
</tr>
<tr>
<td>Alumina</td>
<td>19.3</td>
</tr>
<tr>
<td>Ceria</td>
<td>11.5</td>
</tr>
</tbody>
</table>

The variation of the side reaction and current efficiency with potential during the electrodeposition of NiCu alloys and NiCu-particle composites at 540 rpm is shown in Figures 8.6(a)-(b). In Figure 8.6(a) the side reaction remains almost constant with potential in the region where copper deposition occurs, but at higher potentials (e.g. > -0.7 V) it increases exponentially, as expected for water reduction. The side reactions are highest when alumina particles are present in the electrolyte, and lowest with ceria. The
Figure 8.6. Variation of a) side reaction and b) current efficiency with potential during the electrodeposition of NiCu alloys and NiCu-particle composites at 540 rpm and 12.5 g/L particle loading.
corresponding current efficiencies for the electrodeposition of NiCu alloys and NiCu-particle composites are shown in Figure 8.6(b). In all cases the current efficiency decreases exponentially with potential. There is little change in current efficiency with the presence of particles, despite a change in the side reaction, because of the associated change in the metal partial current densities.

8.4. Summary

NiCu-alumina and ceria composites were examined using the Rotating Cylinder Hull Cell. Particles did alter Cu deposition. The limiting current density of copper was decreased with the presence of particles in the electrolyte. On the other hand, both inhibition and enhancement of the Ni current density occur in the presence of ceria and alumina particles in the electrolyte, respectively. The type of particle used had little effect in the thickness of the deposits, but it had an important effect in the alloy composition along the cylinder cathode.

8.5 References


CHAPTER 9 CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

Both Cu inhibition and enhancement occurs when alumina nanoparticles are in suspension. The kinetic region of the copper reaction rate was dependent on both particles concentration and electrode rotation rate. At all rotation rates, at a particle loading of 12.5 g/L, there is almost no change in the copper kinetic behavior. In contrast, the Cu reduction is inhibited when 39 g/L particles are added to the electrolyte, at all rotation rates. A particle concentration of 60 g/L, exhibits both Cu inhibition (< ~ -0.17 V) and enhancement (> ~ -0.17 V) at 1600 rpm, and only enhancement for electrode rotation rates of 2500 and 3600 rpm. Surface roughness of the deposits was affected due to the presence of particles in suspension, resulting in a variation in microstructure that changes from a rough deposit to a smooth one as the amount of electrolyte particle loading is increased.

The electrodeposition of Cu-γ-Al₂O₃ composites from acidic electrolytes was used as a model for the theoretical study of the effect of particles on copper kinetics. A mathematical model that couples particle mass transport with metal kinetics during codeposition was developed. The mathematical model successfully predicts polarization behavior, composite composition and current efficiency as a function of applied potential, electrolyte particle loading and electrode rotation rate. The model predicts inhibition and enhancement of copper rates at different particle loadings, a decrease in wt. % alumina with increasing cathodic potentials and an increase with higher particle loadings in the electrolyte. The model also predicts little effect of the deposit alumina concentration with
rotation rate, and current efficiencies near 100 %, all of which were observed experimentally.

The electrodeposition of Cu-$\gamma$-Al$_2$O$_3$ nanocomposites as thin films and into recessed electrodes prepared with x-ray lithography was examined in ammonia-citrate electrolytes. At pH 8 the presence of particles resulted in an enhancement of the Cu reaction rate, while at pH 10 the reaction rate appeared inhibited. The change of the Cu partial current density was attributed to the change of the copper complexed species. The amount of particles in the deposit and current efficiency was larger for pH 8 than pH 10, making the pH 8 solution a more promising electrolyte to electroplate into 500 $\mu$m deep recesses for MEMS composite components. High aspect ratio microstructures of electrodeposited copper-$\gamma$-Al$_2$O$_3$ nanocomposites were successfully performed into deep recesses with uniform concentration of alumina along the length of the microposts.

Cu-$\gamma$-Al$_2$O$_3$, Cu-CeO$_2$, and Cu-TiO$_2$ composites were successfully obtained as thin films and HARM’s. The addition of alumina particles to the electrolyte did not have a significant effect on the copper kinetics. Whereas ceria and titania particles enhanced the copper partial current density for potential values between -0.1 to -0.15 V. The presence of particles in the composites affects the surface morphology of the pure copper deposit thin film. On the other hand the type of particle did not affect the surface morphology of the micropost composites. The highest particle concentration in thin film and HARM composites was achieved in the Cu-Al$_2$O$_3$ system. Cu-TiO$_2$ and Cu-CeO$_2$ microposts resulted in drastic reduction in particle composition, which may be attributed to a local pH rise, or in other words a high mass transport resistance of hydroxyl ions.
NiCu-alumina and ceria composites were examined using the Rotating Cylinder Hull Cell. Particles did alter Cu deposition. The limiting current density of copper was decreased with the presence of particles in the electrolyte. On the other hand, both inhibition and enhancement of the Ni current density occur in the presence of ceria and alumina particles in the electrolyte, respectively. The type of particle used had little effect in the thickness of the deposits, but it had an important effect in the alloy composition along the cylinder cathode.

9.2 Future Work

Cu-γ-Al₂O₃, Cu-TiO₂, and Cu-CeO₂ microposts have been fabricated by pulsing a constant cathodic current from sulfuric acid electrolytes, but only Cu-γ-Al₂O₃ microdevies were fabricated from citrate-ammonia electrolytes. In order to prove the methodology, different particle types such as CeO₂ and TiO₂ can be studied from basic baths as well. Longer relaxation times are needed from basic electrolytes in order to grow microposts, since the current efficiencies are lower compared to acid electrolytes. By doing so, more knowledge about how complexing agents can affect metal-particle deposition rate can be gained.

Even though Cu-TiO₂ and Cu-CeO₂ microposts were fabricated from acidic electrolytes, the weight percentage of particles embedded in the copper matrix decreased dramatically an order of magnitude compared to the Cu-γ-Al₂O₃ system. Thus, the next step is to increase the amount of CeO₂ and TiO₂ particles embedded in copper. A pulse reverse technique approach can concentrate the amount of particles embedded in the metal-matrix according to Podlaho et al. In a study of pulse-reverse plating of
nanocomposite thin films, they reported that this method permits the enhancement of particles concentration in a metal matrix.

The mathematical model presented in Chapter 5 to describe the effect of alumina nanoparticles on copper electrodeposition from acidic electrolytes, should be expanded to include the chemical equilibria for citrate-ammonia electrolytes and predict the copper reduction rate enhancement and inhibition at pH 8 and 10, respectively, as well as particle weight percentage and current efficiencies reported in Chapter 6.

9.3 References


# NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_i$</td>
<td>concentration of species $j$, mol cm$^{-3}$</td>
</tr>
<tr>
<td>$d$</td>
<td>cylinder electrode diameter, cm</td>
</tr>
<tr>
<td>$D_i$</td>
<td>diffusion coefficient of species $i$, cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_p$</td>
<td>diffusion coefficient of particle, cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$e$</td>
<td>electronic charge, C</td>
</tr>
<tr>
<td>$E$</td>
<td>potential, V</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant, 96487 C equiv$^{-1}$</td>
</tr>
<tr>
<td>$i_j$</td>
<td>current density of species $j$, mA cm$^{-2}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant, 1.38 x $10^{-23}$ J K$^{-1}$</td>
</tr>
<tr>
<td>$k_j$</td>
<td>reaction rate constant of species $i$, cm s$^{-1}$</td>
</tr>
<tr>
<td>$K_{W}$</td>
<td>water dissociation constant, 1 x $10^{-20}$ mol$^2$ cm$^{-6}$</td>
</tr>
<tr>
<td>$K_i$</td>
<td>equilibrium constant of species $i$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molecular weight of species $i$, g mol$^{-1}$</td>
</tr>
<tr>
<td>$n_i$</td>
<td>number of electrons transferred in the reduction of $i$</td>
</tr>
<tr>
<td>$N_i$</td>
<td>flux of species $i$, mol cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$N_p$</td>
<td>flux of particles, mol cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of particle, cm</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$R_i$</td>
<td>homogeneous reaction of species $i$</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature, 298 K</td>
</tr>
<tr>
<td>$x$</td>
<td>distance from electrode surface, cm</td>
</tr>
</tbody>
</table>
Indices

- ads: adsorbed
- b: bulk
- i, j: species
- inc: incorporated
- p: particle
- side: side reaction
- T: total
- w: water

Greek

- $\alpha_i$: transfer coefficient of species $i$
- $\delta$: diffusion layer thickness, $\mu$m
- $\rho_p$: density of particle, g cm$^{-3}$
- $\rho_s$: density of solution, g cm$^{-3}$
- $\varepsilon$: current efficiency, %
- $\nu$: kinematic viscosity, cm$^2$ s$^{-1}$
- $\omega$: rotation rate, rpm
- $\mu$: fluid viscosity, kg m$^{-1}$ s$^{-1}$
- $\theta$: adsorption coverage
APPENDIX A: REPRODUCIBILITY OF EXPERIMENTAL DATA

The reproducibility of experimental data is shown in this section. Figure A.1 shows the variation of alumina weight % in a copper matrix composite with potential, obtained from an acidic electrolyte at 900 rpm. In all experiments each point represents an average value of at least four different measurements with a standard deviation represented by error bars. The results are reproducible within 1.6 to 0.05 wt. % alumina over the potential range. There is a larger variation at the more positive potentials compared to the more negative potentials, where the Cu rate is higher. The same procedure was applied for some experimental data points at critical regions in this work.

![Graph showing reproducibility of experimental wt. % alumina in a Cu-alumina composite obtained from a sulfuric acid electrolyte at 900 rpm and 12.5 g/L particle loading.](image)

**Figure A.1.** Reproducibility of experimental wt. % alumina in a Cu-alumina composite obtained from a sulfuric acid electrolyte at 900 rpm and 12.5 g/L particle loading.
The reproducibility of experimental polarization curves is shown Figure A.2, which shows the variation of total current density with potential, obtained from a particle-free acidic electrolyte at 900 rpm. The average relative error is 0.05 over the entire potential range. Polarization curves were recorded at least twice to prove data reproducibility for all cases in this work.

**Figure A.2.** Reproducibility of experimental polarization curves for copper reduction from a particle-free sulfuric acid electrolyte at 900 rpm.
APPENDIX B: SAMPLE PREPARATION PROCEDURES FOR SEM AND TEM ANALYSES

Thin Film Preparation Procedure for SEM Analysis

Since the composite is plated on a stainless steel disk electrode, the sample is conductive and ready to be analyzed using SEM. No additional preparation method is required.

Microposts preparation procedure for SEM-WDS analysis

Cross-sectional SEM-WDS analysis requires the following procedure.
1. Once the PMMA is dissolved in acetone and the microposts are free standing, the sample is mounted in epoxy.
2. The sample embedded in epoxy is then cut using an Accutom-5 with a 356-CA diamond cutting saw.
3. Then, it is polished using SiC grinding paper (HV 30-800), grits 500, 1200 and 4000.
4. A 200 Å carbon film was evaporated (Benton 502 carbon coater) onto the epoxy-mounted sample for analyses of the microposts.

Thin Film Preparation Procedure for TEM Analysis

TEM preparation is a more involve process compared to SEM. The film must be thin enough for electrons to pass through it. As an alternative to ion milling, the sample analysis was carried out at the edge of cut pieces of the deposit. The following presents the procedure used.
1. Strip off the Cu-matrix composite thin film from the disk electrode.
2. Scrape a few flakes off the thin film.
3. Place the flakes in eppendorf tubes filled with water and shake them using a Vortex Jr. Mixer.
4. Repeat step two with ethyl alcohol.

5. Finally, the thin slices of the metal-matrix composite are picked up with a Cu-grid to be analyzed with the TEM.

**Micropost Preparation Procedure for TEM Analysis**

Micropost preparation for nanoparticle imaging requires the following procedure.

1. Strip off a few microposts from the copper substrate under an optical microscope.

2. Put the microposts in eppendorf tubes filled with water and shake them using a mixer, Vortex Jr. Mixer, to separate the microposts.

3. Repeat step two with ethyl alcohol, leaving a small amount of alcohol at the end.

4. Add a small amount of LR White Resin (hard grade acrylic resin) and shake the eppendorf tube again.

5. Aspirate the remaining alcohol in the tube.

6. Repeat steps 4-5 until there is no alcohol left in the tube.

7. Place the plastic tube in a vacuum oven (not heated), to reduce the pressure to remove any bubbles present.

8. Embed the resin with the microposts in small aluminum foil containers.

9. Using an optical microscope make sure the microposts are spread out on the resin.

10. Place a second aluminum foil container on top of the first one, to prevent oxygen entering the container, so that the resin can polymerize and get hard.

11. Put the container in a vacuum oven at 60 °C overnight.

12. Once the resin is hard, cut with a saw a piece of resin with an embedded micropost.

13. Place the piece of resin in a MT 5000 Sorval Ultra Microtome, DuPont, to get very thin slices of metal (60 nm thick).
14. Finally, the thin slices of the metal-matrix composite micropost are placed on a Cu-grid to be analyzed with the TEM.
VITA

Mr. Alonso Lozano Morales was born in Nueva Italia, Michoacan, Mexico, on August 31, 1978, the son of Mr. Juan Lozano Cardenas and Mrs. Maria Concepcion Morales Cabrera. Mr. Lozano Morales has three elder brothers: Genaro, Gabriel and Juan. He completed his high school education in Nacozari de Garcia, Sonora, Mexico, in 1996. Mr. Lozano Morales was accepted to the Departamento de Ingenieria Quimica y Metalurgia at the Universidad de Sonora (USON), Mexico. During his senior year in college, he went to the University of Waterloo (UofW), Canada, as an exchange student for one year, enrolling in courses of his specialty as process engineer. He graduated as the top student and received his Bachelor of Science degree from USON with honors in 2001. Then, he joined the doctoral program at Louisiana State University (LSU) in January 2002. Mr. Lozano Morales, a doctoral candidate, will receive the degree of Doctor of Philosophy at the December 2006 commencement. All the above degrees are and will be from the Department of Chemical Engineering.