

## Modeling Electrodeposition for LIGA Microdevice Fabrication

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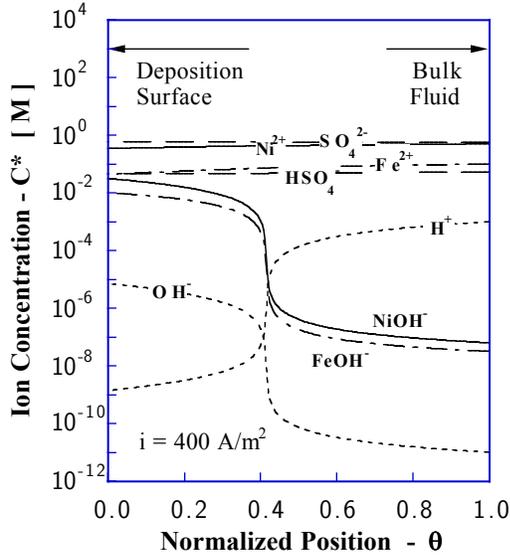
Traditional electroplating practices have not proven very effective in filling the deep holes and trenches characteristic of LIGA molds. Large-scale voids in the deposited metal occur frequently and often without apparent cause. Similarly, local deposition rates within a mold vary widely depending on local feature sizes and on the macro-scale geometry of collections of features. Such local variations in deposition rate lead to uneven mold filling and, eventually, to regions of the mold that cannot be filled completely. These nonuniformities likely result from diffusion transport limitations that arise because the electrolyte in deep mold features remains nearly stagnant, despite bath stirring. In such a diffusion-limited growth process, the deposition surface will typically roughen and become unstable as deposition rates are increased and ion depletion becomes significant. Hydrogen gases may also be generated when ion depletion is significant, leading to a second mechanism for anomalies in the deposition surface. Although it is often possible to avoid these nonuniformities by reducing deposition rates, this would extend plating times beyond the days that are typically required to fill deep molds.

To better understand these transport limitations and to optimize the LIGA deposition process, we have undertaken a combined theoretical and experimental program. The theoretical model describes the quasi-steady electric field within and outside the mold, multispecies ion transport within the mold, and the kinetics of electrode reactions. This model is used to numerically calculate spatial variations in ion concentrations and associated surface deposition rates based on bath chemistry, mold geometry, and plating current or voltage. The complementary experimental program provides fundamental information regarding reaction kinetics as well as qualitative and quantitative insights into rate limiting mechanisms. By observing the deposit morphology for various mold depths, aspect ratios and plating currents, it is possible to map out the boundaries between acceptable and unacceptable regions of the parameter space. Comparison of these observations with theoretical calculations helps to explain the origin of these rate limitations and permits application to other plating conditions. Ultimately, the model will be used to identify optimum conditions for producing high-quality LIGA parts in the minimum time.

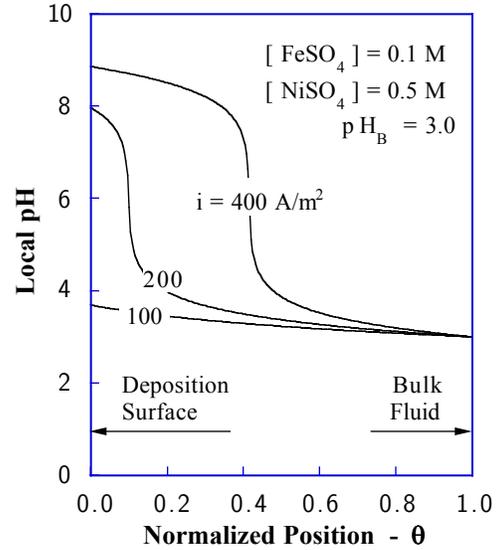
The theoretical model is implemented within a numerical framework that is readily adapted to any specifications of bath composition, dissociation reactions, and electrode kinetics. To date we have focused on an eight-species model describing the simultaneous deposition of nickel and iron from a plating bath containing sulfuric acid and sulfates of both nickel and iron. The eight species included in the model are  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NiOH}^-$ ,  $\text{FeOH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{H}^+$ , and  $\text{OH}^-$ . Transport of these ion species to the mold bottom is governed by diffusion, electromigration, and the homogeneous reactions between species as they move toward the deposition surface. This particular model, closely paralleling that by Grande and Talbot [1], can be used to describe the deposition of either nickel or iron, as well as the codeposition of both species to produce various permalloy compositions.

In addition to ion transport, the mathematical model describes the quasi-steady electric field within the mold and local deposition at the mold bottom. Electric potentials are computed by solving the Poisson-Boltzmann equation relating the field gradient to the local charge density. The Arrhenius kinetics of the electrode reactions are incorporated through Butler-Volmer equations relating the ion current density (equivalent to the deposition rate) to the electrode overpotential, temperature, and reaction pre-exponential constants for each ion species. These equations are strongly coupled to the transport equations because electrode reaction rates depend not only on the ion fluxes but also on local ion concentrations at the electrode surface.

Since electrodeposition inside LIGA molds is nearly one dimensional and quasi-steady, the electric field and species transport equations may be written as second-order ordinary differential equations



**Fig. 1.** Computed spatial distribution of ion species concentrations for nickel and iron codeposition. Bath pH is 3.

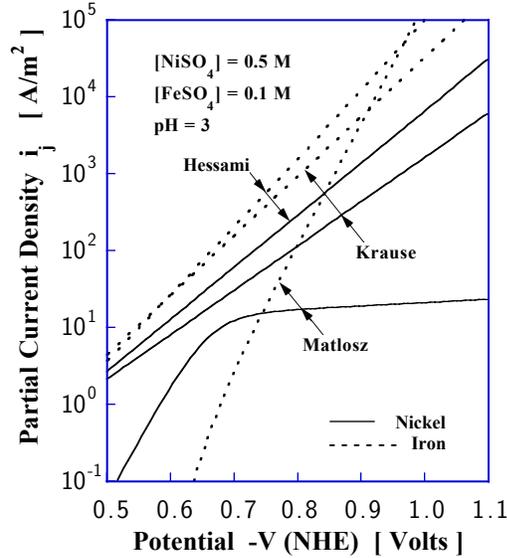


**Fig. 2.** Computed spatial distribution of pH for nickel-iron codeposition at various areal current densities.

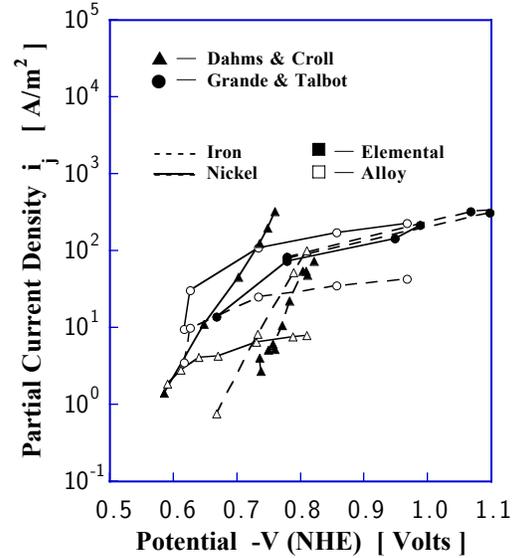
in the spatial position along the mold. These equations are implicitly coupled through the requirement that equilibrium must be maintained for all of the homogeneous dissociation reactions among the transported species. The resulting system of differential equations and algebraic constraints is integrated numerically using DASSL, a stiff ODE and algebraic solver specifically designed for problems of this type. Integration is begun from the top of the mold using bath concentrations that satisfy the equilibrium dissociation relations and the electroneutrality condition. A multi-parameter shooting technique is employed to satisfy the mixed boundary conditions at the deposition surface. The three shooting parameters are the nickel, iron, and hydrogen ion currents, and the three targets are the Butler-Volmer equations relating the ion fluxes to the ion concentrations and deposition kinetics.

Numerical results are shown in Figs. 1 and 2 for the codeposition of nickel and iron from a 0.5 M  $\text{NiSO}_4$  and 0.1 M  $\text{FeSO}_4$  bath at a bath pH of 3. As this problem was previously solved by Grande and Talbot [1], it serves as a check of our numerical calculations. Fig. 1 displays computed ion species concentrations for a 100  $\mu\text{m}$  deep mold at a total current of 400  $\text{A/m}^2$ . This result shows that hydroxide species concentrations increase dramatically from the bath through the mold thickness when currents are large, even though the nickel and iron ion concentrations do not show significant depletion. Thus hydrogen bubble formation may also occur before any noticeable decline in deposition efficiency. Moreover, because metals may be deposited either from the bivalent metal ions or from hydroxides of the metallic species, this increase in hydroxide concentrations may alter the composition and morphology of the deposited material. Fig. 2 further illustrates how strongly the plating surface pH increases with current density. Since surface pH may affect deposition morphology as well as hydrogen evolution, it may be a useful indicator of desirable operating conditions for LIGA.

Although ion transport mechanisms and related material properties are fairly well understood, there is considerable uncertainty in defining the nature and kinetics of electrode reactions. In recent years Hessami and Tobias [2], Matlosz [3], and Krause et. al. [4] have formulated alternative reaction mechanisms, including associated kinetics equations, intended to explain anomalous codeposition of nickel and iron. Each of these models is conceptually distinct, each is consistent with a limited subset of data, yet none can explain all of the data. As seen in Fig. 3, even the qualitative behavior of these three models is quite different when all three are applied to the same plating



**Fig. 3.** Calculated partial current densities for three different models of electrode reaction processes and associated kinetics.



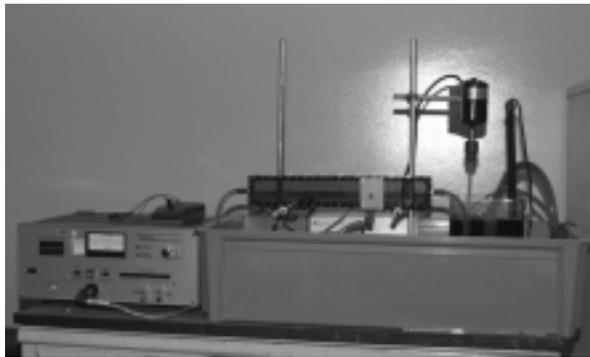
**Fig. 4.** Measured partial current densities for deposition of elemental nickel, elemental iron, and nickel-iron alloy.

conditions. Although all three models indicate increasing dominance of iron at high voltage, the slopes and crossover points differ significantly among the models.

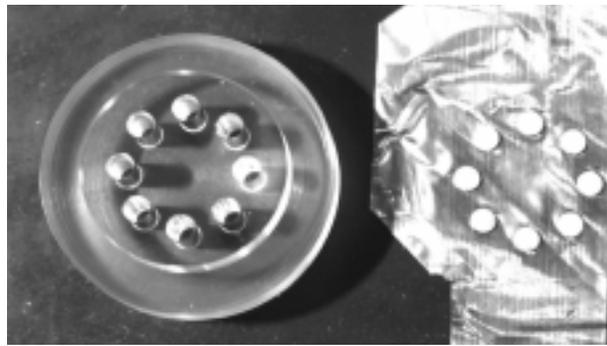
Experimental data for deposition of nickel and iron are equally inconsistent. Fig. 4 reveals nearly an order of magnitude variation in deposition rates and factor-of-two differences in the Tafel slopes for elemental deposition of nickel in the absence of iron. Moreover, the data of Grande and Talbot [1] indicates that nickel deposition increases in the presence of iron, whereas that of Dahms and Croll [5] suggests just the opposite. We are currently seeking to explain some of these apparent inconsistencies by a model that recognizes the dependence of deposition kinetics on the alloy composition of the plating surface. At the same time we are collecting laboratory data that will help to resolve both transport and kinetics issues important to production of LIGA parts.

Our experiments are intended to explore essential features of LIGA-like metal deposition under well characterized conditions that can be compared with theoretical calculations. The apparatus shown in Fig. 5 consists of a transparent Lucite channel about 0.4 m long having a 20 by 50 mm rectangular cross-section. Electroplating solution is pumped from a temperature-controlled reservoir through this channel at a prescribed flow rate. A cathode, analogous to a LIGA mold, and an anode, appropriate to the metal being deposited, are mounted in opposite walls of the flow channel with faces parallel to the flow and flush with the internal surfaces. As seen in the detailed view of Fig. 6, a typical cathode mold consists of a PMMA disc having several identical drill-holes in which metal is deposited. A copper foil on the back of the mold serves as a common cathode for all of the holes. Following deposition, the foil is removed to permit extraction and weighing of deposits and visual examination of the deposition surface. The transparent mold also allows the observation of hydrogen bubble formation during plating. By varying the hole diameter and mold thickness, a wide range of aspect ratios can be easily obtained. This design yields redundant deposition samples from a single mold and enables the uses of multiple molds on a single experiment.

Initial experiments were conducted using a commercial nickel plating solution at a nominal temperature of 38 C. Current densities varying from 11 to 130 A/m<sup>2</sup> were applied to a number of molds over approximately 24 hour periods to produce metal deposits in holes having a diameter of 3 mm and a depth of 12 to 24 mm. The enlarged photos of Fig. 7 illustrate a severe degradation of surface morphology with increasing current density. Although smooth, uniform deposits were produced at 11 A/m<sup>2</sup>, several obvious defects were observed at 65 A/m<sup>2</sup>, and the deposition morphology became clearly unacceptable at 130 A/m<sup>2</sup>. These current densities are considerably



**Fig. 5.** Recessed-cathode electroplating apparatus.



**Fig. 6.** Detail of recessed cathode mold. Mold shown has 3 mm by 12 mm cavities.



7A. 11 A/m<sup>2</sup>



7B. 65 A/m<sup>2</sup>



7C. 130 A/m<sup>2</sup>

**Fig. 7.** Effect of areal current density on deposition surface morphology. Increasing currents lead to pitting and roughening of the deposition surface

smaller than the 200 to 300 A/m<sup>2</sup> commonly used to plate nickel on flat surfaces in well agitated baths, suggesting that the poor morphology is caused by accumulation of hydrogen and depletion of metal ions in the deep, relatively stagnant holes of the molds. The large voids in the plating surface have smooth concave surfaces that could easily conform with hydrogen bubbles generated by electrolysis of water, while smaller scale roughness may be associated with depletion of metal ions. In more recent experiments we have decreased the diameter of the deposition holes both to inhibit convection in the holes and to explore conditions more typical of LIGA.

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