

Modelling the Electroplating of Hexavalent Chromium

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Abstract: This project modeled an industrial hard chromium plating process for automotive components. The process was modeled via the COMSOL Multiphysics Electrodeposition module in a two-dimensional space. The simulation examined the effect of solution conductivity (X1), electrode spacing (X2), and anode height (X3) utilizing a factorial design approach. A sensitivity analysis was used to study the effect of these variables on the absolute thickness value at the midpoint (Y1), as well as the non-uniformity of the plated surface (Y2). The results concluded that the three variables selected for this study had a substantial impact on the overall thickness value as well as the non-uniformity. The most to least significant variables were solution conductivity, anode-cathode spacing, and anode height, respectively. The model and factorial design were used to generate a numerical relationship between the variables.

Keywords: Electroplating, chromium, hard plating, electrodeposition, automotives

1. Introduction

Chromium has persistently been used as the coating of choice in light of its several desirable properties that make it suitable for applications in various industries, including the automotive and aerospace industries [1]. Electroplated chromium has good wear resistance and a high hardness value, between 500 and 900 on the Brinell scale [2, 3]. The addition of chromium also results in high corrosion resistance of the material due to the formation of a passive film in the presence of oxygen [4]. The electrodeposition of chromium is an essential process in the production of strut rods and shock rods for automotive applications. This plating ensures the structural integrity of these parts, and thus, the process is scrutinized to ascertain that the throughput is consistent and maintains a high standard of quality.

The plating facility studied for this simulation has been in operation for several decades and the process has remained mostly

unchanged. At the current processing conditions, the thickness is 300% higher than the current requirements for this form of plating. The excess chromium is then ground down in order to meet these technical specifications. This practice is quite expensive, due to increased raw material costs as well as additional costs associated with the plating and grinding processes. The overplating also results in greater strain on the downstream processes. Knowledge of the electrochemistry surrounding this plating operation as well as identification of the key variables is essential in order to initiate process improvement and optimization.

The two main characteristics in a plating operation are: non-uniformity along the height of the cylindrical rod, and the thickness value at the midpoint of the rod.

Non-uniformity along the height is a key characteristic for the plating industry. This is because the limiting factor in this scenario is that the minimum plating thickness occurs at the centre of the cathode. This region must, however, meet the technical specification required. Thus, although the ends of the cathode may have already met this standard, the plating process must continue until the desired thickness is formed at all points on the cathode. The excess amounts at the ends are then ground off, leading to inefficiencies in the form of economic and environmental repercussions. Thus, the non-uniformity of the plating thickness along the cathode length was identified to be a key variable to be optimized in this project.

The second key dependent variable to be studied was the actual thickness of chrome that was plated on the surface of the cathode.

COMSOL Multiphysics and MATLAB were used in order to simulate this process in a two-dimensional space with the chemical reactions at each electrode in order to generate the current distribution and thickness values. The simulation examined the effect of solution conductivity, electrode spacing, and anode height utilizing a factorial design approach. A sensitivity analysis

was used to study the effect of these variables on the absolute thickness value at the midpoint, as well as the non-uniformity of the plated surface.

2. Governing Equations

The electroplating process consists of two main steps: (i) the mass transport of chromium ions through the electrolyte to the surface of the electrode, and (ii) the reduction of chromium ions at the cathode through chemical reactions.

The fundamental equations needed to model the system are:

2.1 Conservation Balances

The conservation of mass must be maintained for each of the species throughout the system, and is expressed as:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_i$$

R_i = Rate of accumulation/removal of species i by electrochemical reactions

It was assumed that electroneutrality was maintained throughout the system, and is expressed as:

$$\sum -z_i C_i = 0$$

2.2 Nernst Planck Equations

The flux of each of the ions in the electrolyte is given by the Nernst-Planck equation as follows:

$$N_i = -D_i \nabla C_i - z_i u_i F C_i \nabla V$$

$$u_i = \frac{D_i}{RT}$$

N_i = Mass transport vector ($\text{mol}/\text{m}^2 \cdot \text{s}$)

D_i = Diffusivity of species i in the electrolyte (m^2/s)

C_i = Concentration of species i in the electrolyte (mol/m^3)

z_i = Charge of species i in the electrolyte

u_i = Mobility of species i in the electrolyte ($\text{mol} \cdot \text{m}^2/\text{J} \cdot \text{s}$)

F = Faraday's constant ($\text{A} \cdot \text{s}/\text{mol}$)

V = Electrolyte potential (V)

2.3 Butler-Volmer Equation

The flux at the model boundaries are determined by the established electrochemical reactions and the Butler-Volmer equation.

$$i = i_o \left[\exp\left(\frac{\alpha_a n_e F \eta}{RT}\right) - \exp\left(\frac{\alpha_c n_e F \eta}{RT}\right) \right]$$

$$\eta = E - E_{eq}$$

$$\frac{dn}{dt} = \frac{1}{n_e F}$$

α_a = Anodic charge transfer coefficient

α_c = Cathodic charge transfer coefficient

E = Electrode potential (V)

E_{eq} = Equilibrium potential (V)

i = Electrode current density (A/m^2)

i_o = Exchange current density (A/m^2)

n_e = Number of electrons involved in the electrode reaction

η = Activation overpotential

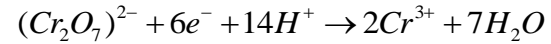
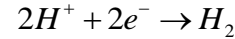
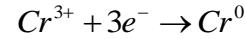
I = Electric current flowing through the system

n = Number of moles of species

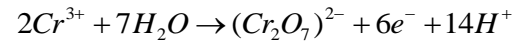
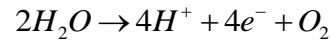
3. Chemical Reactions

The electrochemical reaction for the electrodeposition of chromium can be divided into a collection of half reactions at the anode and cathode, respectively.

The main cathodic reactions include:



The main anodic reactions include:



In this system, the current efficiency of the complete reduction of hexavalent chromium is much lower than that of the other reactions. Hence, the primary reduction reaction is the evolution of hydrogen. Because of the occurrence of gas nucleation at the cathode surface, mass transfer limitations are introduced, which adversely impact the plating rate. However, the purpose of this simulation is to perform only a basic investigation, and thus, these effects have been neglected.

4. Model Development

4.1 Assumptions

A few of the key assumptions that were made in order to generate this model were:

1. The oxidation of trivalent chromium at the anode and the reduction of hex- to tri-chromium at the cathode were in equilibrium.
2. The radial variations in thickness for the cathode are negligible compared to the deviation in thickness along the height of the cathode. Therefore, the system could be modeled in a two dimensional geometry.
3. Mass transfer limitations resulting from the production of gaseous species at the electrodes were negligible.

4.2 Geometry

Although the actual system consisted of multiple anodes and cathodes in a plating bath, the model studied the interaction between one anode, one cathode, and the electrolyte. The configuration is shown in Figure 1 below.

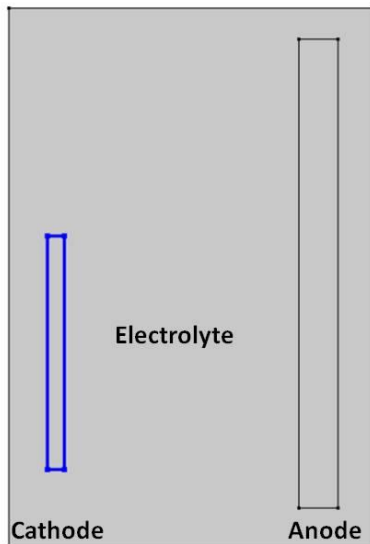


Figure 1: System geometry in two-dimensional space

4.3 Model

The model was developed using the Electrodeposition, Secondary Interface in the Electrodeposition module available in COMSOL Multiphysics. In this interface, the system is assumed to be perfectly mixed, thereby eliminating the effect of mass-transfer.

A constant conductivity of 50 S/m in the electrolyte was used. This was calculated using the molar conductivities and concentrations of the ions present in the electrolyte.

The system is modeled as a stationary problem, thus excluding the time-dependent solvers. This was done in order to reduce the computing power and time needed, as the current distribution was not expected to change with time and the current obtained at each point on the electrode could be easily translated into thickness values using Faraday's law.

The COMSOL model therefore only describes the current and potential distribution in the electrolyte and at the surface of the electrodes. Faraday's law, the properties of the deposited material, and cumulative plating time of the actual electroplating system were then used to compute the thickness of the deposited chrome layer in MATLAB.

5. Results and Discussion

5.1 Current Distribution

As mentioned above, the electrodeposition model of hexavalent chromium for the system provides initialization results in the form of current density across the electrolyte, and on the surfaces of the cathode and anode. The current density values are then imported into MATLAB to solve for the transient (time dependent) step in order to determine the plating thickness over a specified duration. The model has been developed to simulate a batch electrodeposition process in a quiescent tank of chromic acid electrolyte. The current distribution plot is shown in Figure 2 below.

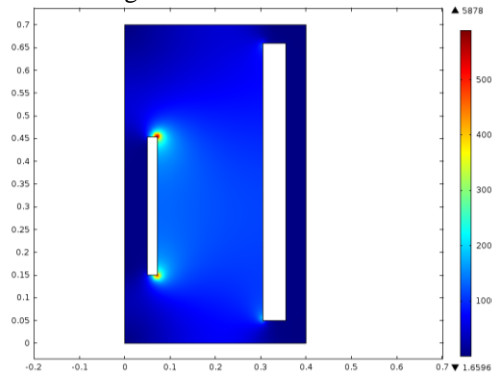


Figure 2: Current density across the system

Based on Figure 2 above, several trends can be noted. The electrolyte between the anode and cathode appeared to have current flowing through it. However, the electrolyte on the opposite side, where the anode and cathode did not face each other, remained relatively inactive. This agreed with theory that the electrons flow through the least resistive or shortest path, i.e. in the region where the electrodes faced each other. This is an important consideration for the plating operation, because the area on the inactive side of the anode and cathode would lead to the creation of dead zones, which would lead to non-uniform plating thickness. This could be improved through the use of a rotating electrode.

The next evident trend is with regards to the non-uniformity of the current across the length of the anode and cathode. Due to the asymmetric geometry, i.e. that the anode is significantly larger than the cathode with respect to length, this leads to an accumulation of current at the top and the bottom of the cathode.

5.2 Effect of Solution Conductivity

The conductivity of the solution is the ease with which current can be transferred across an electrolyte. This is dependent on the type and concentration of ionic species that are present in the system, where an increase in the ionic strength corresponds to a significant increase in current transfer, resulting in a higher plating thickness. See Figure 3.

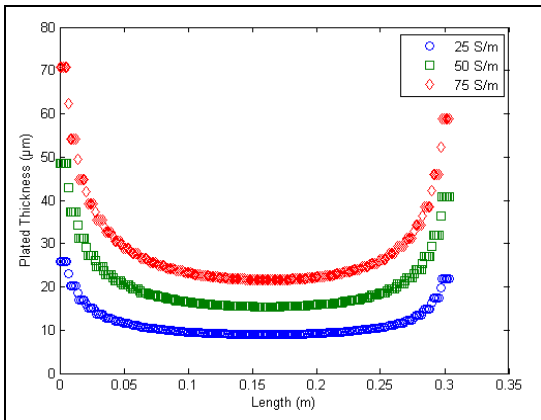


Figure 3: Effect of solution conductivity

5.3 Effect of Anode-Cathode Spacing

The spacing between the electrodes is an important characteristic to take into account with regards to the uniformity of the plated surface. Decreasing the spacing would result in an increase in the non-uniformity, while pulling the electrodes further apart would result in a more uniform surface. See Figure 4.

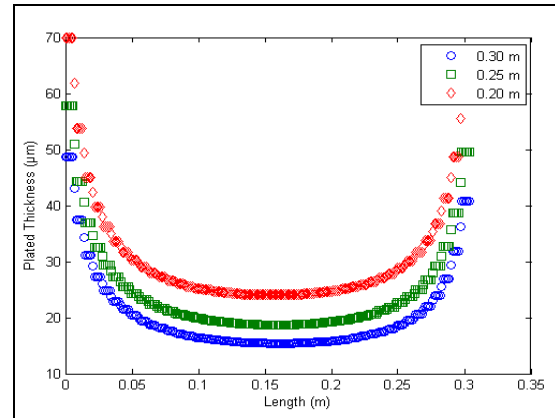


Figure 4: Effect of anode-cathode spacing

5.4 Effect of Anode Height

The accumulation of excess current at the top and bottom of the cathode results from the difference in the height of the two electrodes. If the anode is excessively larger than the cathode, the plated surface will be quite non-uniform. Comparatively, if the cathode and anode are the same height, the plated surface will be more uniform. The model; however, disagreed with this theory, and may need further refinement. See Figure 5.

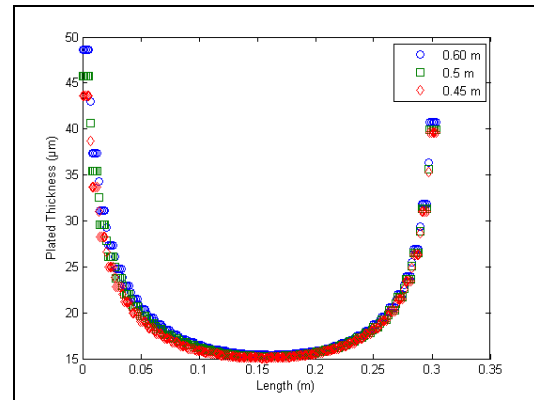


Figure 5: Effect of anode height

6. Factorial Design

The project was used to perform a full factorial experimental design to study the effect of the three selected parameters on the two variables. A sensitivity analysis was conducted on each of the three parameters by choosing a high and low value for each factor. The simulation was then run at a set of combinations of these values. Table 1 summarizes the values selected for each parameter.

Table 1: Full Factorial Design Conditions

Parameter	High	Low
<i>Solution Conductivity</i>	75 S/m	25 S/m
<i>Anode-Cathode Spacing</i>	0.30 meters	0.20 meters
<i>Anode Height</i>	0.60 meters	0.45 meters

The plating thickness was calculated using a total of a 45 minute cycle time, and was evaluated at the midpoint of the cathode. This was selected as the location of interest because, as discussed above, the plating thickness is at a minimum at the midpoint (length-wise). Non-uniformity was estimated using the standard deviation of all plating thickness values across the surface of the cathode.

6.1 Response Models

The preliminary response models were developed for both, uniformity and plating thickness by assuming an additive, linear relationship, as described by principles of a factorial design. The models for each are as follows, where X_1 is the conductivity, X_2 is the anode-cathode spacing, and X_3 is the anode height.

The response model for the midpoint thickness value was:

$$Y_1 = 17.2228 + 14.3433X_1 - 11.3053X_2 + 0.4275X_3$$

The response model for the non-uniformity value was:

$$Y_2 = 8.3610 + 8.3350X_1 - 4.2206X_2 + 1.6113X_3$$

6.2 Effect on Plating Thickness

Based on the equations above, it is evident that the largest factor impacting plating thickness is the conductivity of the solution. As predicted from theory, an increase in the solution conductivity causes an increase in the thickness due to more efficient current transfer. The next most significant factor is the anode-cathode spacing. The model confirms that an increase in the anode-cathode spacing would result in a decrease in the midpoint thickness. This is due to the fact that the electrons would have to travel a larger distance through the electrolyte, resulting in an increase in ohmic losses through the solution. Thus, it is a desired condition to minimize this spacing. Lastly, it was found that the anode height had negligible impact on the plated thickness at the midpoint of the cathode.

6.3 Effect on Non-Uniformity

It is evident that the largest factor contributing to the non-uniformity of the plated surface is the solution conductivity. For this factor, an increase in the conductivity of the solution would cause a greater uniformity. This agrees with theory that an increase in conductivity results in decreased ohmic losses from the electrolyte, allowing for a higher efficiency in current transfer. Thus, the decreased electrical resistance would cause the electrons to travel through the path to the top and bottom more easily, leading to an accumulation of current at these locations. The next factor to consider is the anode-cathode spacing. The model suggests that increasing the spacing between the electrodes would result in decreased non-uniformity, i.e. more uniform plating. Thus, it is desired to maximize the spacing as much as possible; however, as mentioned before, increasing this value results in a decrease in the overall thickness, and therefore, an optimal value must be determined. The last factor to consider is anode height. As evident through the model, increasing the anode height leads to increased non-uniformity. This result appears to be sensible, because the excess current at the top and bottom is generated by the fact that the anode is much longer than the cathode. Since current density is directly proportional to the plating thickness, decreasing this difference between the heights leads to a more uniform plating thickness.

7. Conclusions

The response models developed for the plating thickness (Y1) and non-uniformity (Y2) were developed to predict these values based the operating conditions with respect to the three variables. These models were used to study the impact of the three parameters. The solution conductivity has a large impact on the electron transfer across the electrolyte; thus, increasing this value leads to better operating conditions. Secondly, optimal anode-cathode spacing can be determined such that the plating thickness meets the technical specifications, while maintaining good uniformity. Changes to this spacing would be limited by the existing setup of the plating bath based on the cathode and anode rails, as well as the tank dimensions. Lastly, the anode height should be reduced in order to increase the uniformity of the plated surface.

Although the results obtained from this simulation agreed with theory, further improvements to the model are required to obtain a more accurate simulation of the actual plating process. Improvements to this study would include creating the model in a three-dimensional geometry as well as the inclusion of mass transfer resistances imposed by the production of the gaseous species.

8. References

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9. Acknowledgements

Funding for this study was provided by Ontario Centres of Excellence (OCE) Connections Program. The authors of this work also acknowledge the support of Dr. J. Grove and Dr. M. Pritzker at the University of Waterloo.