Modelling and Optimization of Copper Electroplating Adhesion Strength

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Abstract. In this paper, Response surface methodology (RSM) was utilized to design the experiments at the settings of \( \text{CuSO}_4 \) and \( \text{H}_2\text{SO}_4 \) concentrations and current densities. It also used for modelling and optimize the parameters on the adhesion strength of austenitic stainless steel substrate. The adhesion strength was investigated by the Teer ST-30 tester, and the structure of the samples investigated by using scanning electron microscopy (SEM). The modelling approach adopted in the present investigation can be used to predict the adhesion strength of the copper coatings on stainless steel substrate of electroplating parameters in ranges of \( \text{CuSO}_4 \) 100 to 200 g/L, \( \text{H}_2\text{SO}_4 \) 100 to 200 g/L and current density 40 to 80 mA/cm\(^2\). The results showed that, operating condition should be controlled at 200 g/L \( \text{CuSO}_4 \), 100 g/L \( \text{H}_2\text{SO}_4 \) and 80 mA/cm\(^2\), to obtain the maximum adhesion strength 10N.

1. Introduction
Copper is one of the metals most extensively used in industry, either because of its intrinsic properties or as a base for further formation of metallic films. Electroplating is one of the methods most generally used to obtain metallic films of equal thickness, porosity-free construction and good adhesion [1–2]. Electroplating copper films have been widely investigated with regard to their structural characteristics, electrical properties and corrosion resistance [3-4] but less care has been yielded to their mechanical behaviour and its relation to Electroplating parameters. By controlling variables such as current density and bath concentration, a variety of pictures with different characteristics can be attained, therefore allowing to tailor the mechanical characteristics of the coatings for specific applications. One of the most important mechanical properties of the coatings is the adhesion strength, which is defined by The ASTM as the "condition in which two surfaces are held together by either valence forces or by mechanical anchoring or by both together" [1]. (Teer ST-30) Scratch test is one of widely used, fast, and effective methods to obtain the critical loads that are related to adhesion properties of the coating [5-6]. A survey in 2001 showed that the scratch test is the most common test method used for measuring the quality of the coatings in industries [7]. In most experimental studies of concentration process, conventional methods were used to determine the influence of operational parameters. When using the conventional methods to optimize the process, one parameter is changed while others are kept at a constant level. This should be repeated for all influencing parameters, resulting in a great number of experiments[8]. Its major disadvantage is that it does not include the interactive effects among the variables studied. To overcome this problem, using a second-order model is useful in approximating a portion of the true response surface with parabolic curvature. The second-order model includes all the terms in the first-order model, plus all quadratic terms and all cross-product terms. It is usually expressed as
\[ Y = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_3 + B_{11} x_{21} + B_{22} x_{22} + B_{33} x_{23} + B_{12} x_{12} + B_{13} x_{13} \] (1)

Where \( Y \) is the response (adhesion strength); \( x_i \) is the variables, \( B_0 \) is the constant coefficient; \( B_i \) and \( B_{ii} \) refer to the coefficients of linear and interaction terms, respectively.

The second-order model is flexible, because it can take a variety of functional forms and approximates the response surface locally. Therefore, this model is usually a good estimation of the true response surface. There are many designs available for fitting a second-order model. The most popular one is the central composite design (CCD). This design was introduced by Box and Wilson.

The aim of this paper is to create a second-order model for the parameters (\( \text{CuSO}_4 \) and \( \text{H}_2\text{SO}_4 \) concentrations and current densities) and the response (adhesion strength), also to determine the optimum settings of \( \text{CuSO}_4 \) and \( \text{H}_2\text{SO}_4 \) concentrations and current densities that result in the maximum adhesion strength over a certain region of interest. By using RSM to design the experiments and ANOVA to analysis the data.

2. Experimental

2.1. Material

The 316L stainless steel samples and the 99.91% pure copper were cut from 2 mm thickness sheets with 20 mm x 20 mm by EDM wire cutting machine were used as cathode and the anode respectively. All the stainless-steel samples were sanded up to 1000 SiC paper, and ultrasonically cleaned in acetone for 5 min before coated.

2.2. Experimental design

The copper thin film has been electroplated using a DC power source on a 316L stainless steel substrate with the electroplating parameters viz. \( \text{CuSO}_4 \) concentration (A), \( \text{H}_2\text{SO}_4 \) concentration (B), and current density (C). With \( \alpha = 2 \). The ranges and levels are shown in Table 1. In order to evaluate the effect of the factors on the response surface in the region of investigation, a three-factor-five-level CCD was performed.

Table 1. Experimental ranges and levels of the three independent variables used in RSM

| Coded value | \( \text{CuSO}_4 \) (g/L) | \( \text{H}_2\text{SO}_4 \) (g/L) | Current density (mA/cm\(^2\)) |
|-------------|----------------|-----------------|------------------|
| -1          | 100            | 100             | 40               |
| 0           | 150            | 150             | 60               |
| 1           | 200            | 200             | 80               |

The statistical software package `Design-Expert 10 (trial version)` was used to analyse the experimental design. The total number of experiments with three factors was 20 (2k+2k+6, when k=3, where k is the number of factors). In order to control the error bar, 20 runs were performed in a random order in which there were six replications at the centre points to evaluate the purity error. Every run was done with 20 min.

2.3. Characterization

The adhesion strength of the coatings was investigated by scratch testing (Teer ST-30 tester). The Teer ST-30 is a relatively simple apparatus in which the increasing load is obtained by the inclination of the sample respect to the indenter. In the present experiments, the load was increased from 0 to 20N with an inclination degree of 1° and an indenter speed of 25 mm/min. The morphology of the copper thin film has been studied using Scanning Electron Microscope (SEM, JSM-6380, JEOL).
3. Results and discussion

3.1. Results
Figure 1, shows the morphological details of the copper coating by SEM. The adhesion behaviour of the coating was assessed by analysing the representative images of the grooves left after the scratch tests shown in figure 2. In general, the adhesion behaviour was better for the C than A, B.

![Figure 1: SEM morphology of coatings produced in CuSO₄, H₂SO₄ concentrations and current densities respectively as A) 200 g/L – 106 g/L – 80 mA/cm². B) 200 g/L – 100 g/L – 57 mA/cm². C) 200 g/L – 100 g/L – 80 mA/cm².](image)

![Figure 2: The scratch adhesion tests on coating obtained in CuSO₄, H₂SO₄ concentrations and current densities respectively as A) 200 g/L – 106 g/L – 80 mA/cm². B) 200 g/L – 100 g/L – 57 mA/cm². C) 200 g/L – 100 g/L – 80 mA/cm².](image)

3.2. Statistical Analysis
The analysis of variance (ANOVA) was applied to study the effect of the input parameters on the adhesion strength. Table 2, gives the statistics for the model summary. The R-Squared of 0.9852 is closed to 1, and the Pred R-Squared of 0.9350 is in reasonable agreement with the Adj R-Squared of 0.9733; i.e. the difference is less than 0.2. It reveals that the quadratic model is the best appropriate model. So, for further analysis this model was used. Table 3, gives the Estimated Regression Coefficients of the adhesion strength for uncoded units. The value “p” for the model of <0.0001 is less than 0.05 which appear that the model terms are significant except C-current density with P-value more than 0.05 which is indicates that the current density as term C is less significant, but the terms AC and BC have a significant effect on the response.

| Source | Sum of Squares | df | Mean Square | F-value | P-value |
|--------|----------------|----|-------------|---------|---------|
| Model  | 11.80          | 8  | 1.47        | 82.93   | < 0.0001 significant |
| A-CuSO₄ | 4.04           | 1  | 4.04        | 226.97  | < 0.0001 |

Table 2. Model summary statistics.

Table 3. Estimated regression coefficients of the adhesion strength.
The effect of CuSO₄ and H₂SO₄ concentrations and the Current densities were investigated in order to serve as a tool for predicting final film adhesion strength. The quadratic equation for predicting the optimum point was obtained according to the Central Composite Design (CCD) and input variable, and then the empirical relationship between the response and the independent variable in the uncoded units was presented on the basis of the experimental results as follows:

\[
\text{Sqrt (Adhesion strength)} = 3.66237 - 0.023012 \text{ (CuSO}_4\text{)} - 0.012915 \text{ (H}_2\text{SO}_4\text{)} - 4.64939\times10^{-3} \text{ (Current density)} - 8.31768\times10^{-5} \text{ (CuSO}_4\text{)} \text{ (H}_2\text{SO}_4\text{)} + 3.02834\times10^{-4} \text{ (CuSO}_4\text{)} \text{ (Current density)} - 2.76441\times10^{-4} \text{ (H}_2\text{SO}_4\text{)}^2(2)
\]

This developed mathematical model can be used to predict the adhesion strength of copper electroplating. Also, accuracy of the model was determined by conducting conformity test runs using the same coating process. In this procedure, the process variables were assigned random values in order to carry out the validation test runs and the responses were measured and recorded as shown in Table 4. The results show that the model is accurate.

### Table 4. Comparison of predicted and actual values of adhesion strength

| No. | CuSO₄ (g/L) | H₂SO₄ (g/L) | Current Density (mA/cm²) | Predicted Adhesion strength (N) | Actual Adhesion strength (N) | Error % |
|-----|-------------|-------------|--------------------------|---------------------------------|-------------------------------|---------|
| 1   | 200         | 119         | 80                       | 6.83                            | 7                             | 2.5     |
| 2   | 200         | 100         | 57                       | 6.30                            | 6                             | 4.8     |
| 3   | 200         | 100         | 80                       | 10.01                           | 9.50                          | 5.1     |

### 3.3. Optimization

Based on analysing the equation, (2). With statistical experimental method, the optimal condition for adhesion strength of copper electroplating should be obtained for coating application. The adhesion strength of copper film, 10 N, can be obtained if the operation condition controlled at 200 g/L CuSO₄, 100 g/L H₂SO₄ and 80 mA/cm². As figure. 3. Validation experiments were performed and the results showed that the difference between the predicted values and the measured values is within 5.1%. Statistical optimization method overcomes the limitations of classic empirical methods and is proved to be a powerful tool for the optimization of copper film deposition.

### 4. Conclusions

The developed mathematical model equation (2) is accurate to predict the adhesion strength value at the ranges of CuSO₄ 100 to 200 g/L, H₂SO₄ 100 to 200 g/L and Current density 40 to 80 mA/cm². And it is found that, the maximum adhesion strength 10 N, could be obtained at operating condition 200 g/L CuSO₄, 100 g/L H₂SO₄ and 80 mA/cm².
Figure 3. Optimization of the adhesion strength

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