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*Full Paper*

# Optimization of Electroplating Conditions of Chromium(VI) Using Taguchi Experimental Design Method

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**Abstract**- In this study, Taguchi method has been used for optimization of chromium(VI) electroplating process and for this purpose brass materials have been electroplated under different conditions of the process to study their effects on throwing power of chromium deposit. Finally the results of main effects plot and analysis of variance showed that among the influential factors in this process, only current density of 4 A/dm$^2$ and time of 4 minutes have the most effects in the characteristics of the response. Also SEM images confirmed that the crack density on the surface of Cr-deposit is decreased under the mentioned conditions.

**Keywords**- Optimization, Electroplating, Chromium(VI), Taguchi method, Experimental design

## 1. INTRODUCTION

Chromium electrodeposits are widely consumed for improving and increasing the hardness, wear ability, corrosion resistance and decorative appearance of engineering instruments and components [1-2]. Usually, they are deposited from electrolytes based on chromic acid ($CrO_3$) which are highly toxic and oxidative in particular. With increasing environmental problems throughout the world, hexavalent chromium electroplating faces

possible extinction as a result of its serious health and environmental problems [3-4]. Chromium plating operations are divided based upon their thickness on the metal layers. It can be classified as "decorative chromium" and "hard chromium" electroplating. Decorative protective coatings are primarily used for adding an attractive appearance to some protective qualities. In this process, a layer of nickel is first electroplated over a metal substrate. Following this step, a thin layer of chromium is electrodeposited over the nickel layer in order to provide a decorative and protective finish. Chromium electroplating process is widely used on many mechanical parts and plastic molds due to its suitable mechanical property, good aesthetic appearance, and superior corrosion resistance [5].

Bayramoglu [6] studied the thickness and brightness of hard chromium electroplating by means of experimental design. Maria Cannio [7] performed a study of a hard chromium plating process using low concentrations of $H_2CrO_4$. In particular, the effect of different values of $CrO_3/H_2SO_4$ ratio on coating properties such as adhesion, apparent, surface roughness, hardness, and microstructure were studied. Spiridonov [8] considered the deposition of nickel-chromium coatings from chromium(III) Sulfate electrolytes. In this study, the effect exerted by the electrolysis mode and the pH of the electrolyte on the composition and quality of the obtained coatings was investigated.

In this study, Taguchi method [9-11] has been used to study the effect of process parameters such as concentration of chromic acid and sulfuric acid, time, and current density on throwing power (TP) of chromium deposit. Optimum parameters, which would provide the best throwing power values, were determined by using of the data obtained from the experiments. This method collects the necessary information to determine which factors have the most effects on the quality of the product with a minimum number of experiments. In this method, optimization of process parameters is the key step to achieve high quality without increasing cost and time.

## 2. EXPERIMENTAL

A Hull cell equipped with a mixer and air bubbler, plating tank of 267 mL, heating coil, digital thermostat, tin-lead anodes containing 7% tin and a programmable DC electrical power supply (rectifier), a ruler in order to measuring the throwing power in centimeter and an scanning electron microscope model LEO 1430 VP for the study of surface crack density of Cr-deposit were used during the chromium electroplating process.

### 2.1. Surface Preparation

Brass metal was used as a cathode (test specimens) material due to its outstanding plating characteristics as a base material for decorative chrome or similar coatings. The specimens were cut in plates with 7×10 cm and with a thickness of 2 mm. They were mechanically

abraded using SiC abrasive papers with five different grit sizes of 400, 600, 800, 1000 and 1200 mesh to obtain smooth surface on plated specimens. Then, very fine grades of silicon carbide polishing paste were applied to the test specimens by means of buff rotated by an electrical motor. After mechanical polishing finished, all specimens immersed in a tank which contained gasoline. Then, the specimens were cleaned by a soft brush for removing impurities formed on the surfaces during polishing. Finally, all specimens were rinsed by fresh water. Degreasing was carried out by immersing the test specimens in a plastic tank filled by carbon tetrachloride. They were kept in the tank for 10 min in order to complete removal of metal particles, abrasive and the residue of greases or waxes used for lubrication during polishing process. Following to degreasing process, the specimens were subjected to electrolytic cleaning process. A bath consisted of 80 g/L nitric acid was used for electro-chemical cleaning. The specimens were suspended to the anode of the cell and stainless steel cathodes were used for cathodic reaction. After immersing the specimens into the solution, 5 $A/dm^2$ of current density were applied to specimens for 5 min, and then specimens were rinsed. Chemical polishing process was applied to the specimens before the electroplating process. A hydrochloric acid solution at a concentration of about 15% was used for this operation. All of the specimens were immersed into the solution and kept for 5 min in the bath. Then, the specimens were rinsed as rapidly as possible in order to prevent further reaction of solvent retained on the surface of the specimens.

### 2.2. Electroplating

After completing surface preparation processes, all of the specimens were nickel plated in a Watts bath containing nickel sulfate ($NiSO_4.7H_2O$), nickel chloride ($NiCl_2.6H_2O$) and boric acid ($H_3BO_3$) with concentrations of 250, 60 and 40 g/L, and a set of additives of nickel bath such as nickel brightener, nickel leveler and nickel humidifier with the contents of 0.5, 12 and 12 mL/L respectively. The capacity of the bath was 250 mL and anodes with 99% nickel were used during this electroplating process. The bath temperature fixed at 50 $^{\circ}C$ and 4 $A/dm^2$ of current density was applied for 15 min. Nickel provided corrosion resistance and leveling effect of the substrate surface. Also on the basis of chromium plating, a hexavalent chromium bath was used for chromium plating in this study. For this purpose plating bath used $CrO_3$ as source of Cr(VI) ions, sulfuric acid as catalyst and a set of additives so called DC15 and DC16 (DC is an abbreviation of decorative chromium) built in Schlötter Galvanotechnik from German manufacturer company in order to improving the throwing power and quality of Cr-deposits. After mixing all components, the solutions were heated and stirred at 45 $^{\circ}C$. Then, by using of sulfuric acid, pH was adjusted to smaller than 1. Chromium electroplating was done with the aid of Hull cell which was a miniature plating unit designed to produce cathode deposits on substrates that correlates the characteristics of the electroplating unit being evaluated [12-13]. With the aid of Hull cell, rapid information about

brightness levels, irregular plate deposits, and uniformity of deposits, throwing power, impurities and chemistry of plating bath can be achieved. The experimental setup of the apparatus is shown in Fig. 1.

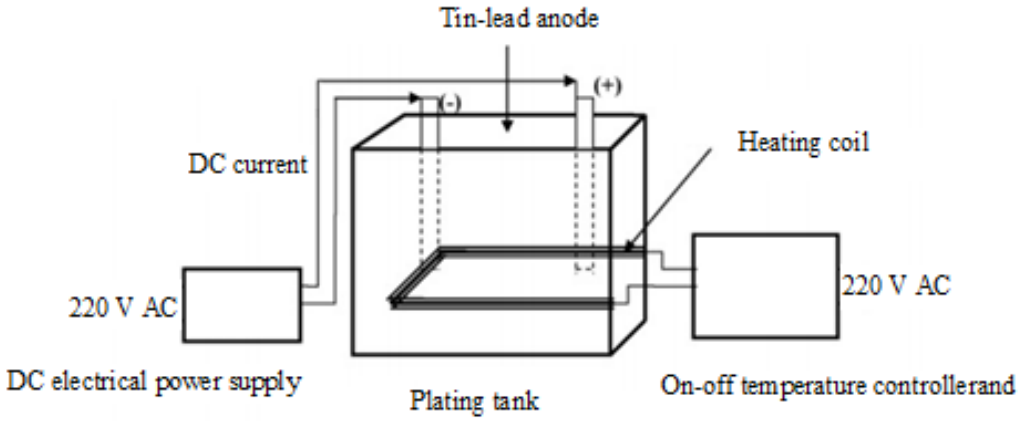


**Fig. 1.** The scheme of experimental setup of Hull cell

## 3. RESULT AND DISCUSSION

### 3.1. Orthogonal Array Experiment

In the present work, four parameters, i.e. amount of chromic acid (CA) and sulfuric acid (SA), current density (CD) and time (t) and each one in four levels were considered. The values of the electroplating parameters at the different levels are listed in Table 1. In complex manufacturing systems and nonlinear processes, the interaction effects of the process parameters become significant. However, in the present study, since orthogonal arrays do not test all variable combinations, the interaction effect of the electroplating parameters could not be taken into optimization process. As a result, the main effect of each plating parameter on the throwing power response was merely taken.

In this study, an $L_{16}$ ($4^4$) orthogonal array was employed. So, sixteen experiments are required to study the entire electroplating parameters space when the $L_{16}$ orthogonal array is used.

The experimental layout for the chromium plating process parameters using the $L_{16}$ ($4^4$) orthogonal array is shown in Table 2 and also the experimental results for measurement of throwing power for each run in terms of centimeter using the $L_{16}$ orthogonal array are shown in Table 2. In the present study, Minitab statistical software was used for the design and analysis of the experiments [14]. So, the main effects of process parameters for throwing power were investigated using this software. However, all of the trials were replicated two times for estimation of experimental error. The order, in which the experiments were carried out, was randomized to avoid any personal or subjective bias.

**Table 1.** Coding of factors and levels of orthogonal test

| Parameters | Level 1 | Level 2 | Level 3 | Level 4 |
|---|---|---|---|---|
| Time (min) | 2 | 4 | 6 | 8 |
| Amount of Sulfuric Acid (g/L) | 0.5 | 1.0 | 1.5 | 1.95 |
| Current Density ($A/dm^2$) | 2 | 4 | 6 | 8 |
| Amount of Chromic Acid (g/L) | 150 | 200 | 240 | 280 |

The optimum responses can be calculated using the following expression:

$$Y_{opt} = T/N + (A_{bar} - T/N) + (B_{bar} - T/N) + (C_{bar} - T/N) + (D_{bar} - T/N) \quad (1)$$

Where T is the grand total of all results, N is the total number of results and $Y_{opt}$ is the response under the optimum conditions. A, B, C and D are the mean responses of the time, amount of sulfuric acid, current density and amount of chromic acid at optimum levels, respectively. The effect of main process parameters, such as amount of $CrO_3$ and sulfuric acid, plating time and current density on the throwing power have been discussed in the following paragraphs.

In the Table 3 mean responses for throwing power are shown. Also in the Fig. 2 main effects plots for mean values of throwing power are shown.

### 3.2. Calculations of Signal to Noise Ratios

The signal to noise ratio (S/N ratio) was used to measure the sensitivity of the quality characteristic being investigated in a controlled manner. In Taguchi method, the term ‘signal' indicates the desirable effect (mean) for the output characteristic and the term ‘noise' represents the undesirable effect (signal disturbance, S. D) for the output characteristic which influence the outcome due to external factors namely noise factors. The S/N ratio can be defined as:

$$\text{S/N ratio, } \eta = -10 \log (\text{MSD}) \quad (2)$$

Where MSD: mean-square deviation for the output characteristic.

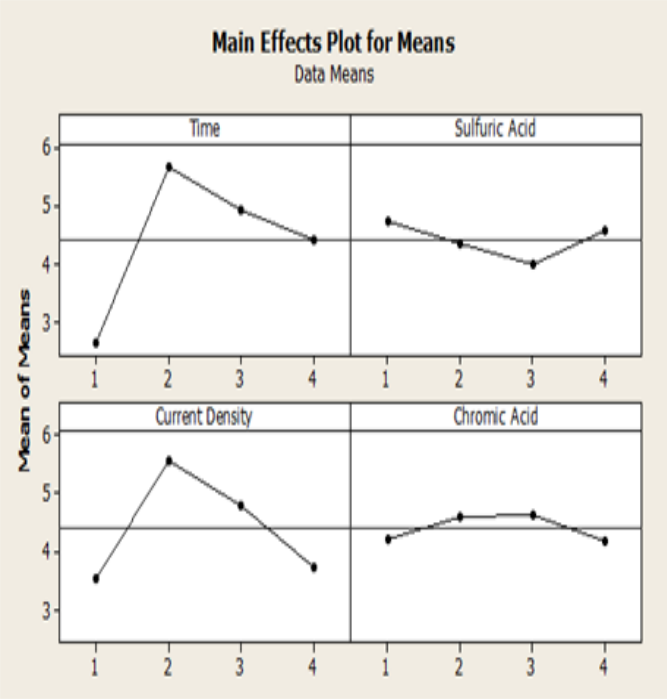


**Fig. 2.** Main effects plot for means of throwing power values

**Table 2.** The $L_{16}$ ($4^4$) array for optimization of electroplating conditions

| Run | t | SA | CD | CA | TP |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 2 |
| 2 | 1 | 2 | 2 | 2 | 3.5 |
| 3 | 1 | 3 | 3 | 3 | 3 |
| 4 | 1 | 4 | 4 | 4 | 2 |
| 5 | 2 | 1 | 2 | 3 | 7.5 |
| 6 | 2 | 2 | 1 | 4 | 4.7 |
| 7 | 2 | 3 | 4 | 1 | 4 |
| 8 | 2 | 4 | 3 | 2 | 6.5 |
| 9 | 3 | 1 | 3 | 4 | 5 |
| 10 | 3 | 2 | 4 | 3 | 4.5 |
| 11 | 3 | 3 | 1 | 2 | 4 |
| 12 | 3 | 4 | 2 | 1 | 6.2 |
| 13 | 4 | 1 | 4 | 2 | 4.4 |
| 14 | 4 | 2 | 3 | 1 | 4.7 |
| 15 | 4 | 3 | 2 | 4 | 5 |
| 16 | 4 | 4 | 1 | 3 | 3.5 |

**Table 3.** Mean responses for throwing power

| Factors | Level 1 | Level 2 | Level 3 | Level 4 |
|---|---|---|---|---|
| Time (min) | 10.5 | 22.7 | 19.7 | 17.6 |
| Amount of Sulfuric Acid (g/L) | 18.9 | 17.4 | 16 | 18.2 |
| Current Density (A/dm2) | 14.2 | 22.2 | 19.2 | 14.9 |
| Amount of Chromic Acid (g/L) | 16.9 | 18.4 | 18.5 | 16.7 |

The aim of any experiment is always to determine the highest possible S/N ratio for the result. A high value of S/N implies that the signal is much higher than the random effects of the noise factors or minimum variance. There are three categories of quality characteristics, i.e. the-lower-the-better, the higher-the-better, and the-nominal-the-better. In our experiment, the system is optimized when the response is as large as possible, so we deal with the S/N ratios and levels of the parameters that maximizing the S/N ratios. The mean-square deviation (MSD) for the higher-the-better quality characteristic can be expressed as:

$$S/N = -10 \log (\sum 1/Y_i^2)/n \quad (3)$$

Where, n :number of repetitions or observations

$Y_i$ : the observed data

The effect of each parameter on the S/N ratio at different levels can be separated out because the experimental design is orthogonal. The S/N ratio for each level of the plating process parameters is summarized in Table 3.

**Table 3.** Mean response S/N ratios for throwing power

| Factors | Level 1 | Level 2 | Level 3 | Level 4 |
|---|---|---|---|---|
| Time (min) | 8.116 | 14.811 | 13.733 | 12.793 |
| Amount of Sulfuric Acid (g/L) | 12.593 | 12.707 | 11.901 | 12.252 |
| Current Density (A/dm$^2$) | 10.596 | 14.552 | 13.303 | 10.999 |
| Amount of Chromic Acid (g/L) | 11.838 | 13.012 | 12.747 | 11.855 |

Fig. 3 shows the S/N ratios graphs taken from Minitab statistical software. Basically, the larger the S/N ratio the better is the quality characteristic for the throwing power. By means of S/N ratios graphs it is clear that among the influential variables in the process only current density and time of plating have the most effects on increasing the characteristics of the response.

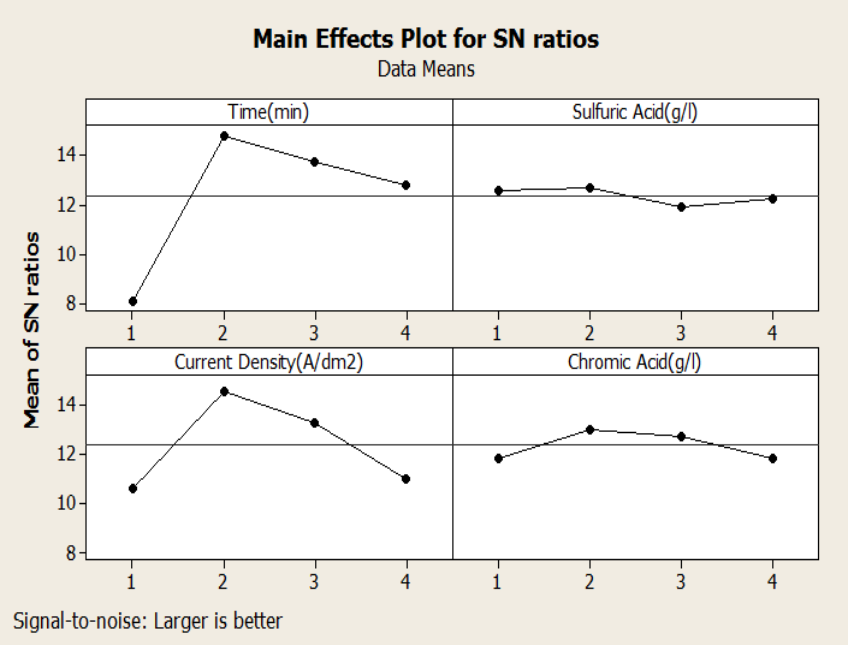


**Fig. 3.** Main Effect Plots for Signal to Noise Ratio for Throwing Power

### 3.3. Analysis of Variance (ANOVA)

The relative effect of the different parameters of electroplating on the throwing power was obtained by decomposition of variance, which is called analysis of variance or ANOVA. The relative importance of the electroplating parameters with respect to the throwing power was investigated to determine more accurately the optimum combinations of the electroplating parameters by using ANOVA. The results of ANOVA are presented in a table that displays for each factor the values of:

- DOF: degree of freedom which is the number of levels for each factor minus 1.
- SS: sum of squared deviations from the mean. For n values of $Y_i$ and the mean value $Y_{bar}$:

  $$SS = \sum_{i=1}^{n} (Y_i - Y_{bar})^2 \quad (4)$$
- MS: mean of squares.

  $$MS = SS / DOF \quad (5)$$
- F: F is the ratio between the mean of squares effect and the mean of squares error.

  $$F = MS_{effect} / MS_{error} \quad (6)$$

Statistically, F-test provides a decision at some confidence level whether these estimates are significantly different or not. Larger F-value indicates that the variation of the process parameter is significant.

- P: P is the probability value which gives the degree of confidence at which the factor is significant. If the P-value be smaller than 0.05, it means that the effect of experimental parameter on the TP is significant. The results of ANOVA for the electroplating data are shown in Table 4. According to ANOVA, the most effective parameters involved in the process are time and current density. Percent contribution presents the relative contribution of each factor on optimization of the response. For an electroplating factor with a high percent contribution, a small variation will have a great influence on the performance. According to the table, time of plating was the major factor affecting the response (61.7966%), whereas current density was found to be the second ranking factor (32.5458%).

According to Table 4, the F values of these factors is greater than tabulated F value for α (risk) = 0.05 (F = 3.29). This means that the variance of time and current density is significant compared with the variance of error and these factors have a significant effect on the response. In addition, P-values of these factors are smaller than 0.05 which means that the mentioned factors have the most effects on increasing the characteristic of the response.

**Table 4.** ANOVA for determination of throwing power (TP)

| Source | DOF | SS | MS | F | P | Contribution percentage |
|---|---|---|---|---|---|---|
| t | 3 | 20.2069 | 6.7356 | 22.66 | 0.015 | 61.7966 |
| SA | 3 | 1.1619 | 0.3873 | 1.30 | 0.417 | 3.5550 |
| CD | 3 | 10.6419 | 3.5473 | 11.93 | 0.036 | 32.5458 |
| CA | 3 | 0.6869 | 0.2290 | 0.77 | 0.582 | 2.1024 |
| Error | 3 | 0.8919 | 0.2973 | | | |
| Total | 15 | 33.5894 | | | | |

### 3.5. Surface morphology and crack density of the Cr-deposit

The morphologies of the deposited chromium coating were analyzed by LEO 1430 VP scanning electron microscope [15-16]. The study of the characteristics of chromium coating deposit on the substrate can be helpful in investigating the effects of influential factors on the microstructure morphology of chromium deposit. Fig.s 4 and 5 show the scheme of the specimen that had been electroplated under the best conditions of hexavalent chromium

electroplating process (for example run 5 in Table 2). As it is obvious from the figures with different views, the surface of Cr-deposited is smooth and approximately free of cracks.

Fig.s 6 and 7 depict the scheme of the specimens which have electroplated under undesirable conditions of the process (run 1 in Table 3). As it obvious from the scheme with different magnifications, crack densities on the Cr-deposit surface are very large with respect to the specimen with high throwing power.

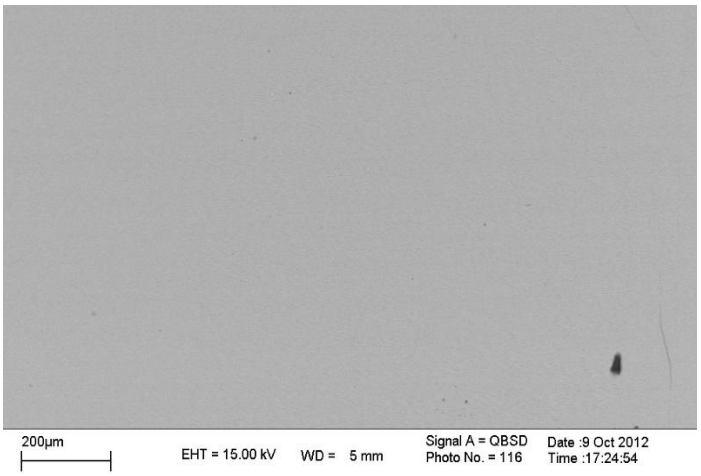


**Fig. 4.** SEM image of Cr-deposit with high TP and magnitude of ×200

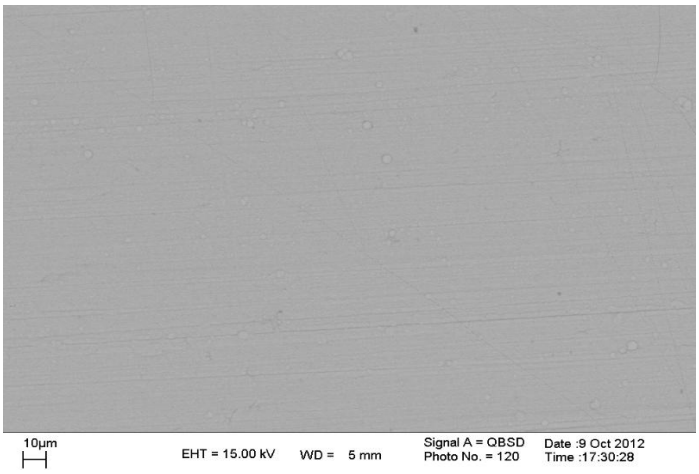


**Fig. 5.** SEM image of Cr-deposit with high TP and magnitude of ×1000

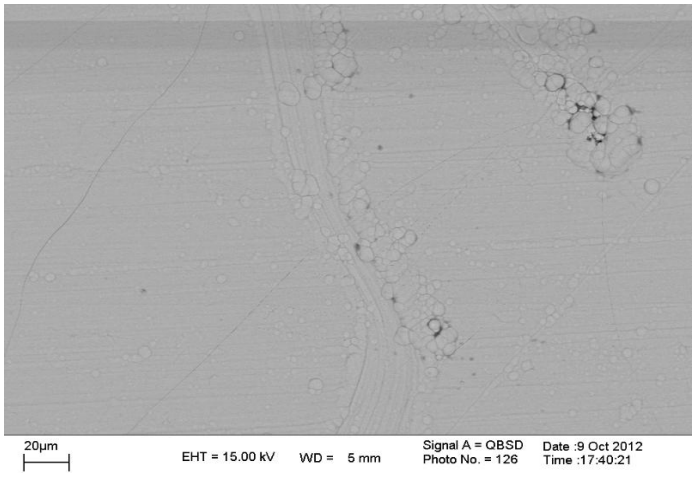


**Fig. 6.** SEM image of Cr-deposit with low TP and magnitude of ×500

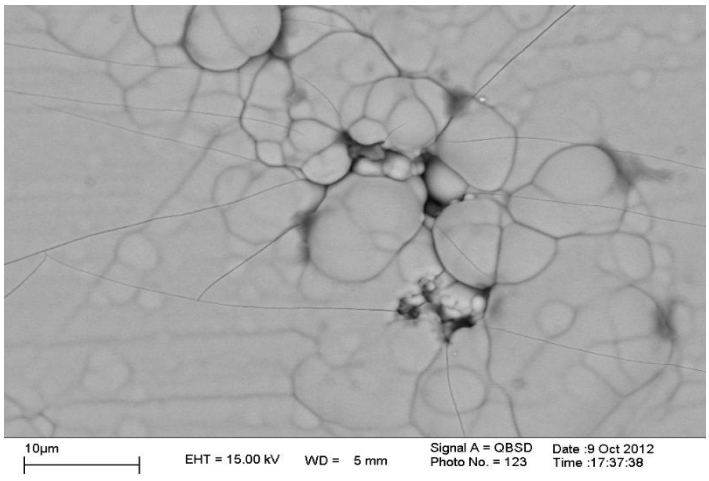


**Fig. 7.** SEM image of Cr-deposit with low TP and magnitude of ×1000

## 4. CONCLUSION

This paper has presented an investigation on the optimization and the effect of electroplating parameters on the throwing power of chromium in the brass sheets. The experimental studies were conducted under varying the time, sulfuric acid concentration, current density and chromic acid concentration. Here, Taguchi design method was used to optimize the parameter values for obtaining desired characteristics. The significance of the electroplating parameters on the response is determined by using ANOVA. Based on the ANOVA analysis, the highly effective parameters on throwing power were found as time and current density, whereas chromic acid and sulfuric acid concentrations were less effective factors so that the throwing power of coating reaches a maximum value while current density and time are 4 $A/dm^2$ and 4 minutes, respectively. The experimental results confirmed the

validity of the used Taguchi method for enhancing the throwing power and optimizing the plating parameters in chromium electroplating process.

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