

# Influence of Oxalate Concentration and Temperature on the Microstructure Morphology of Nano Anodized Copper Coating

M. H. Mahmood, Suryanto, Muataz H. F. Al Hazza and Farag I. Haider

*Department of Manufacturing and Material Engineering, IIUM, International Islamic University Malaysia, Kuala Lumpur, P.O. Box 10, 50728, Malaysia*

**Abstract:** Nanostructures anodized copper coating was successfully synthesized through electrochemical anodization method. Effects of oxalate concentration and temperature on the morphology and corrosion resistance of the anodized coating were investigated through the observation of the critical polarization current variations. The anodizing parameters were selected in the ranges of anodizing temperature 0-24 °C, oxalate concentration 0.1-0.5 M and applied voltage 7.5-9 V. Phase analysis of the anodized coating was carried out using XRD (X-ray diffraction). Resulted peaks of the X-ray diffraction referred to the formation of a monoclinic crystalline phase of nanostructure cupric oxide CuO. The results of critical polarizing current were analyzed to evaluate the charge transfer through the coating. The lowest critical polarizing current was obtained when the porosity of the coating was in its lowest values. The increasing of oxalate concentration increases solution conductivity leading to form coating of larger grain size with fewer pores. The decreasing of temperature decrease coating porosity. The highest resistance to charge transfer through the anodized coated surface was achieved in the highest oxalate concentration and lowest anodizing temperature.

**Key words:** Copper corrosion, copper oxide, anodization technique, corrosion protection.

## 1. Introduction

Development of copper oxide coating recently was demanded in many fields of scientific applications like gas detection sensors [1], hydrophobic surfaces [2], solar cells [3], energy storage [4], high temperature superconductors, magneto resistance materials [5] and memory devices [6]. Anodic polarization process is associated with electrochemical oxidation reactions that occur on the anode. The passive coating which formed on metals using anodic polarization supports the base metal from the surrounding environment corrosion by reducing the corrosion active potential. Copper is one of the active passive metals like chromium, aluminum, nickel, titanium, and many of their alloys. The active passive metals are the metals

that form an oxide conversion coating on the metal surface, which calls anodized coating. This coating protects the base metal from further corrosion. The corrosion protection behavior of the anodized coating results from its barrier effect, which is passive in many corrosive environments [7].

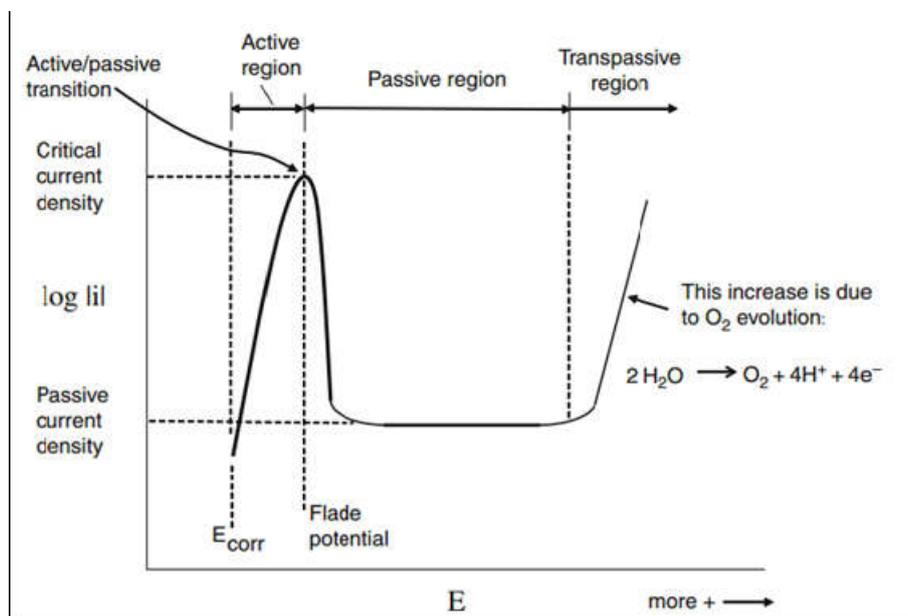
Anodization is one of the corrosion protection methods, which is industrially known as, the beauty of corrosion. In spite of being a kind of metal corrosion, it considered as a kind of corrosion protection for metal surfaces. So, it is possible to develop more effective corrosion protective metal oxides coating by a careful control of anodization parameters [8].

Fig. 1 illustrates a schematic for typical anodic polarization curve. It shows the electrochemical passivation behavior of metals. The active-passive polarization of metal in acid solutions is starting with the open circuit corrosion potential then it increases in the anodic direction and passing through a region of

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**Corresponding author:** Suryanto, Ph. D. in materials science technology, associated professor, research fields: materials science.

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**Fig. 1** Schematic for typical anodic polarization curve [9].

active corrosion in which the open-circuit corrosion rate can determine by the Tafel extrapolation method. Then at a specific potential, the increase in applied potential will cause decreased in anodic current density. As a result, of the formation of the passive film on the metal surface, the metal, in this case, is passively protected.  $E_{pp}$  and  $I_{cc}$  refer to the first passive potential and critical current respectively. The current after this potential drops sharply as the passive oxide film increases in thickness [9].

The polarization curve passed through three regions; active, passive, and trans-passive. The active region represents the anodic electrochemical reaction zone where metal is oxidized. The current and potential in this region are controlled by the kinetics of Tafel individual redox reactions. In the beginning, current is gradually increases with polarization, then it suddenly decreases at a specific polarizing potential ( $E_p$ ) which is called the passivation potential. The current that provides to the cell at this potential is called the critical current density ( $I_{crit}$ ). This current is sufficient to form a passive film on the metal surface. Therefore, the polarizing current is decreased after the critical polarization current [10].

The most important properties that control metal

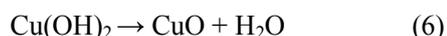
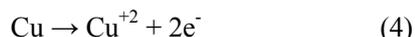
passivation process are the critical current density and the passivation potentials. After passivation, the trans-passive region starts by increasing the current because of the oxygen evolution or passive film breakdown [10]. In Fig. 1 the effect of solution environment on the anodization was illustrated. Anodization process is the electrochemical treatment that uses anodic polarization method to convert part of metal surface to anodized coating. Anodized coating consists of a converted metal oxide layer. Polarization resistance is the resistance to the transferring of charged electrons through the electrochemical cell at the corrosion current. High polarization resistance indicates low corrosion kinetics and low anodizing rate [10].

The maximum current in polarization process is known as critical current. It passes through the cell at the passivation potential. Critical current is the maximum current that passing through the passive film on the metal surface. The polarizing current after the critical current decreases as a result to the formation of the anodized passive coating that inhibit the rate of anodizing [10]. As example to the relation between polarizing current and the corrosion current. The increasing in the corrosion resistance of the iron alloys with high chromium content. This increasing is

due to the decreasing of the critical current of this alloy by adding the chromium [11].

The anodization is an electrochemical surface treatment used to grow an anodized coating of metal oxide film

Anodized coating was formed on a copper substrate using anodization method in oxalate containing solution. The successful coating was investigated by visual inspection when a uniform dark coating was formed on the copper surface. The electrical conductivity of anodized coating was also tested using an ohmmeter to confirm the coating formation because of the low conductivity of the anodized coating, which consists of copper oxide, as compared with the high electrical conductivity of copper. Anodization of copper occurs when copper atoms ionized by releasing electrons and reacts with the existing hydroxide ions near the surface to form a copper hydroxides as shown in the following Eqs. (1)-(6):



Anodization was conducted in oxalate containing solutions at various temperatures, concentrations, and applied voltages. The anodizing parameters were selected in the ranges of anodizing temperature 0-24 °C, oxalate concentration 0.1-0.5 M and applied voltage 7.5-9 V. The phases of anodized coating and its chemical composition were investigated using XRD (X-ray diffraction) and EDX (Energy Dispersive X-ray Spectroscopy) respectively. Moreover, the microstructures of the coating were investigated by using FESEM (Field Emission Scanning Electron Microscope). The investigations on the formation and microstructural characterizations of the coating are detailed in the following sections.

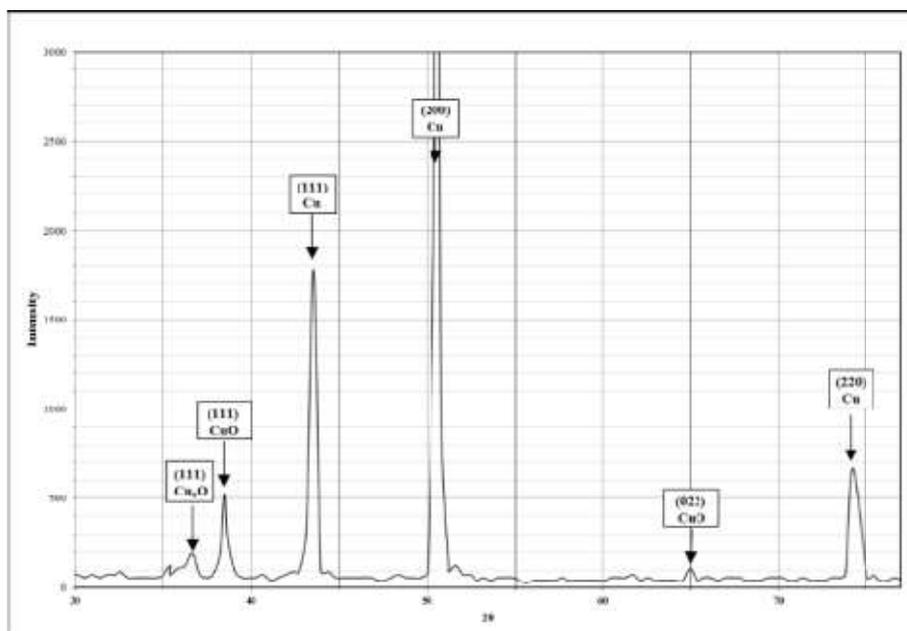
## 2. Materials and Methods

To study the effect of oxalate concentration in the solution on the anodic polarization of copper, the anodic polarization experiments were conducted on pure copper foil with thickness of 0.12 mm and dimensions 1 cm × 1 cm. The samples were polished, cleaned, and washed with distilled water, acetone. Finally, it dried in air at room temperature. Anodization bath solutions were prepared. Anodization electrolyte solutions were prepared with oxalate concentration range from 0.1 to 0.5 M. All anodization experiments were performed with Autolab Potentiostat/Galvanostat, using LSV (linear sweep voltammetry) at scan rate 0.02 V/s. The electrochemical cell was consisted of silver/silver chloride Ag/AgCl reference electrode (SSE) and Platinum foil as counter electrode. The experiments were conducted at operation temperatures 0, 8, 16, 24 °C.

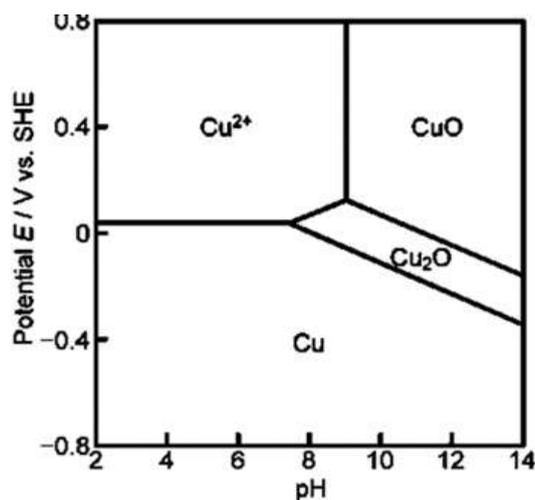
Phases of anodized coating were investigated using Bruker X-ray diffraction testing machine. The anodized sample was fixed on the sample's frame in the testing machine. The experiments were carried out using Cu- K $\alpha$  radiation,  $\lambda = 1.54\text{\AA}$  with a scanning rate of 0.02°/sec. The samples were scanned through the range of 20-80°. The X-ray diffraction pattern of the anodized coating is shown in Fig. 2.

By comparing the prominent peaks in the diffraction pattern with the Standards Diffraction card, JCPDS 05-0661 for cupric oxide, the peaks at 38 and 65° are referring to (111) and (022) planes. According to the Copper Standards Diffraction cards, JCPDS 00-04-0836, the peaks in the XRD spectrum at 43.3, 50.4 and 74.1° are referring to the metallic copper of (111), (200) and (220) planes respectively. Moreover, the other peak at 36.4° is suitable for cuprous oxide reflected from (111) plane, based on the Standards Diffraction cards JCPDS 00-05-0667.

The presence of copper ions at ambient temperature is shown in the potential-pH diagram Fig. 3 [12].



**Fig. 2** X-ray analysis of anodized coating.



**Fig. 3** Potential-pH diagrams of equilibrium copper ions at ambient temperature [12].

In oxalate solution of pH more than 12, stability of copper oxides was dominated in a wide range of potentials, as illustrated in the potential-pH diagram Fig. 3.

Presence of copper oxides  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  in the solution is an indication of the redox reactions  $\text{Cu}_2\text{O}/\text{Cu}$  and  $\text{CuO}/\text{Cu}^{+2}$ .

### 3. Results and Discussions

Micrographic results of the anodized coated samples showed that coating of nanostructures cupric

oxide was built on the hairy-like arrays of copper hydroxide nanowires, which formed at the initial stage of the anodization process, as shown in Fig. 4a. The diameters of copper hydroxide nanowires were varied between 30 to 60 nm. In the next stage of coating, a nanostructure of cupric oxide was grown from the edges of the hydroxides nanowires to cover all the surface area, as illustrated in Figs. 4b and 4c.

Previous results confirmed that uniform anodized coatings were successfully formed using anodization in oxalate containing solutions.

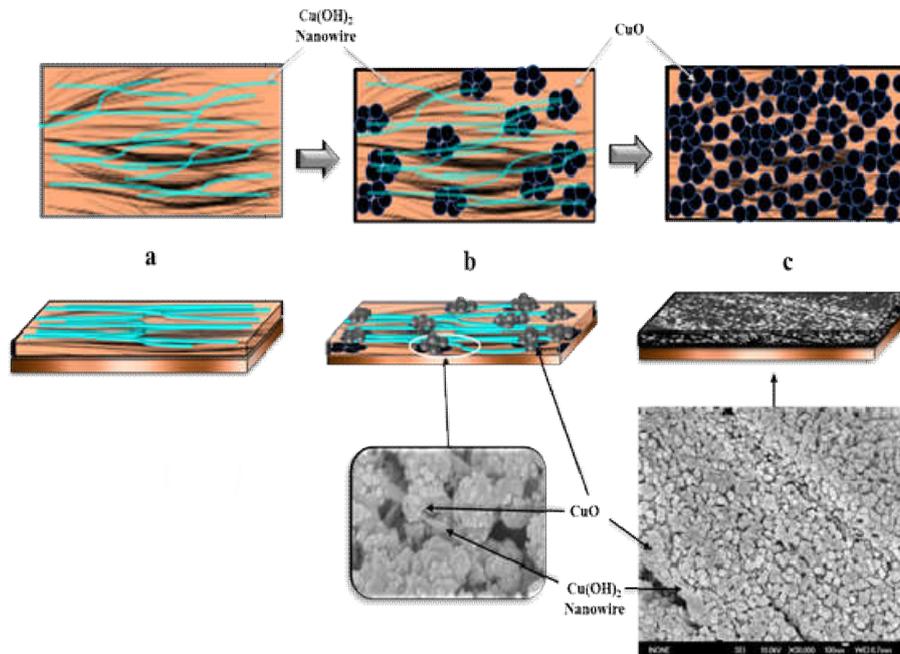


Fig. 4 Schematic of coating formation stages.

Taguchi method was applied to find the sequence of the dominance of parameters that control the coatings characteristics. The results of critical polarizing current were analyzed to evaluate the charge transfer through the coating. Taguchi L16 orthogonal array was employed using design expert DOE software for planning the design of experimental tests with three parameters and four levels. The anodizing rate of each anodization process was estimated according to the polarization resistance of coating. The transfer rate of the charged electrons through the anodized coating was estimated according to the critical polarizing current.

Effects of anodizing parameters on the polarization resistance and critical polarizing current were evaluated based on signal-to-noise (S/N) ratio. The results of the critical currents were analyzed using Taguchi method to find the sequence of dominance of anodizing parameters of oxalate concentration, temperature on the anodizing process. Taguchi L16 orthogonal array was employed with four parameters levels of 0.1, 0.23, 0.36, 0.5 M oxalate concentrations, 0, 8, 16, 24 °C anodizing temperatures, and 7.5, 8, 8.5,

9 V applied voltage.

The relation between the polarization results of polarization resistance and the critical polarizing current with the coatings microstructures of grain size and porosity was also analyzed.

Experimental runs used to test the effects of anodizing parameters over the critical polarizing current at various anodizing parameters. The critical polarizing current was considered as a characteristic quality response with the concept of the larger the better.

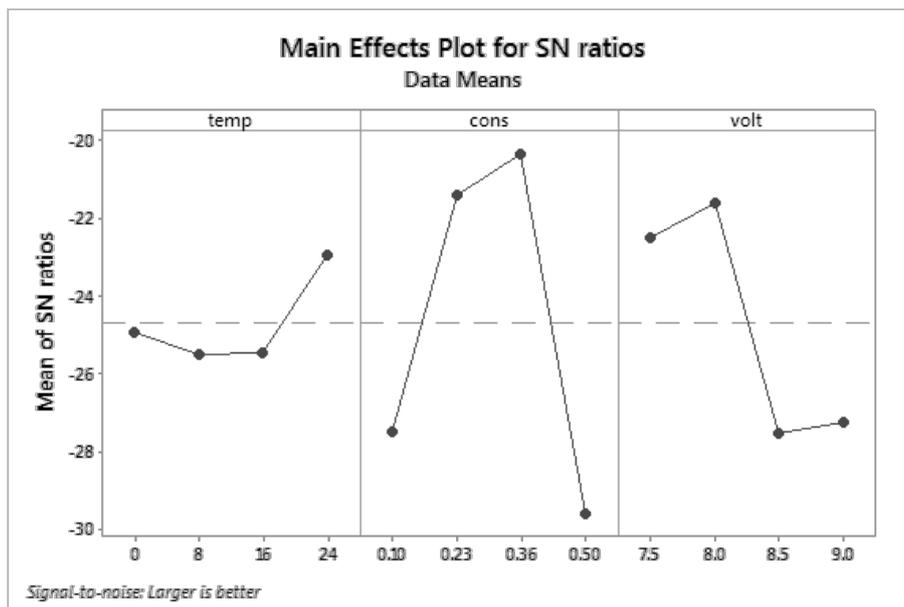
The values of critical polarizing current and their corresponding signal-to-noise ratio by factor level are listed in Table 1.

The effect of anodizing parameters on the critical polarizing current using the signal to noise ratio was illustrated in Fig. 5.

From these results, it was concluded that the oxalate concentration was the most affecting parameter on the critical polarizing current and the applied voltage was the second affecting parameter, while the less affecting parameter on the critical polarizing current was the anodizing temperature.

**Table 1** The values of S/N ratio considering critical polarizing current response.

Level	Temperature	Concentration	Voltage
1	24.92	27.50	22.47
2	25.51	21.39	21.58
3	25.47	20.32	27.54
4	22.93	29.63	27.24
Delta	2.58	9.31	5.96
Rank	3	1	2



**Fig. 5** Signal to noise ratio plots showing anodizing parameters effects over critical polarizing current.

### 3.1 Effect of Anodizing Temperature on the Critical Polarizing Current

The results obtained from signal-to-noise ratio showed that the anodizing temperature is the less affecting parameter on the critical polarizing current, as shown in Table 1 and Fig. 5. From this result, it was observed that the critical polarizing current was varied with the anodizing temperature. This variation is due to the effects of the obstacles that stand against the anodization process.

### 3.2 Effect of Oxalate Concentration on the Critical Polarizing Current

The results obtained from signal-to-noise ratio showed that the oxalate concentration of anodizing solution was the most affecting parameter on the critical polarizing current. As shown in Fig. 6, that

shows the relation between the critical polarizing current and the oxalate concentration.

From the previous result, it was observed that the lowest critical current and charge transfer through the coating were achieved at the lowest anodizing temperature and in the higher oxalate concentration.

### 3.3 The Relation of Critical Polarizing Current with Coating Microstructure

The results of grain size with its corresponding critical anodizing current were analyzed at various anodizing temperatures and oxalate concentrations, as shown in Figs. 7 and 8, respectively.

From the previous result, it was observed that coating with 43 nm grain size formed with lowest critical anodizing current. This result refers that this coating allows the minimum charge transfer through it.

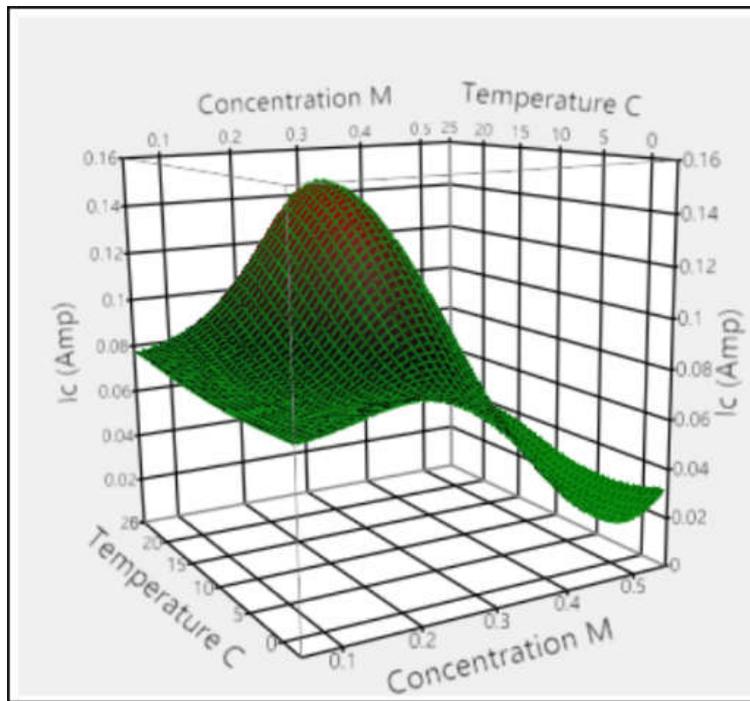


Fig. 6 Critical polarizing current as a function of the oxalate concentration at different anodizing temperatures.

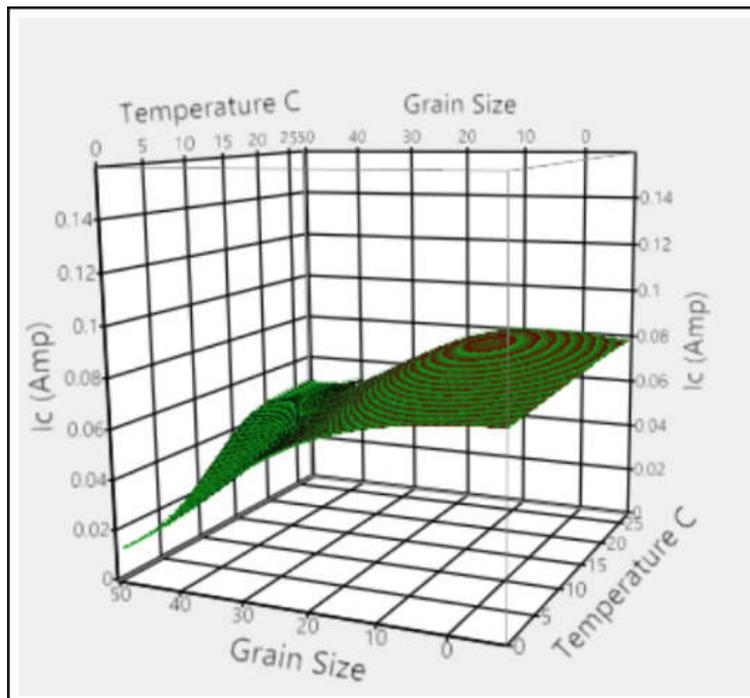


Fig. 7 The relation between the critical anodizing current and the grain size.

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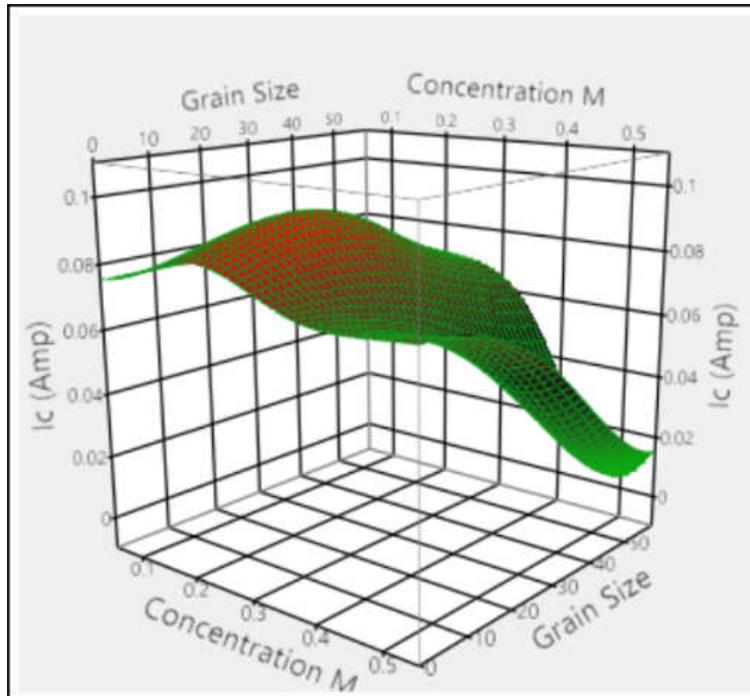


Fig. 8 The relation between the critical anodizing current with a grain size in various oxalate concentrations.

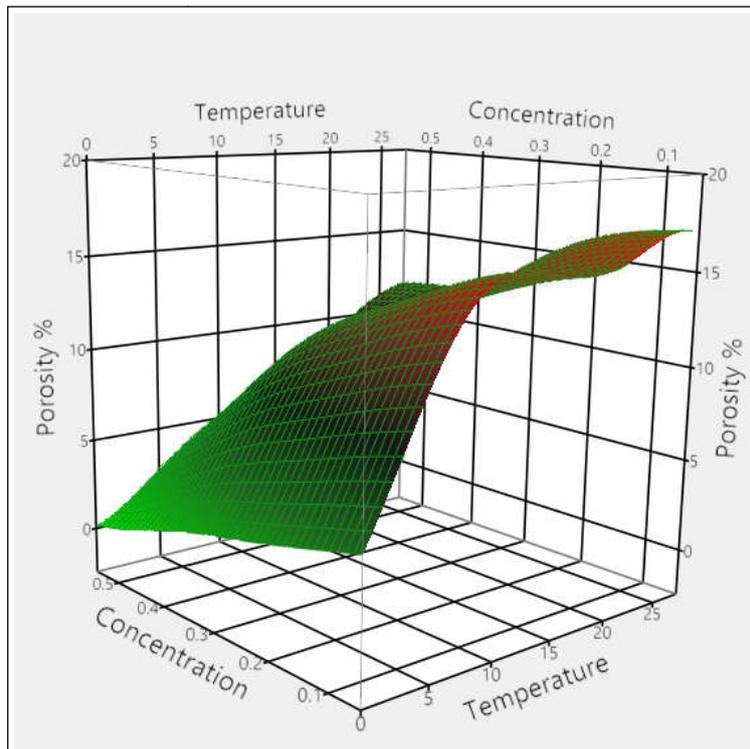


Fig. 9 Average porosity of anodized coating as a function of oxalate concentration and temperature.

Porosity of coatings anodized in different oxalate concentrations and various temperatures were analyzed to evaluate the effect of temperature and oxalate concentration on coating porosity. Fig. 9 showed the porosity of anodized coating as a function of the oxalate concentration and anodizing temperature.

From the previous results, it was observed that, the less porous coating was formed in the highest oxalate concentration and lowest anodizing temperature. From the previous results, it was concluded that the lowest charge transfer through coating was allowed under these conditions.

The results of porosity with its corresponding critical anodizing current were analyzed at various anodizing temperatures and oxalate concentrations, as shown in Figs. 10 and 11, respectively.

Fig. 12 illustrates a comparison between porosity of coatings anodized in various oxalate concentrations and temperatures showing the decreasing of coating

porosity with the increasing of the oxalate concentration and decreasing anodizing temperature. The increasing of oxalate concentration increases solution conductivity leading to form coating of larger grain size with fewer pores.

The increasing of grain size with the temperature is due to the increases of charging transfer through the anodizing solution. Hence increase the anodizing rate, which, leads to form larger grain sizes with more pores.

Moreover, the coating surface voids and pores effects on the corrosion properties of the of coating, where lower corrosion resistance expected for the higher coating pores. As a result to the increasing of the charge transfer through the pores of coating. The rates of corrosion reactions between the environment and the surface increases. Therefore, the highest resistance to charge transfer through the electrochemical cell was achieved in 0.5 M oxalate concentration at 0 °C and 9 V, where.

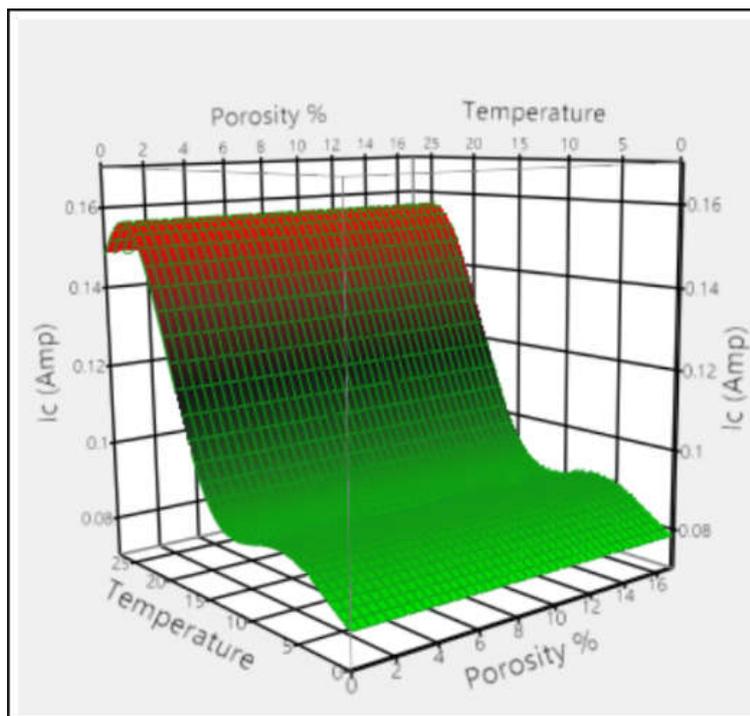
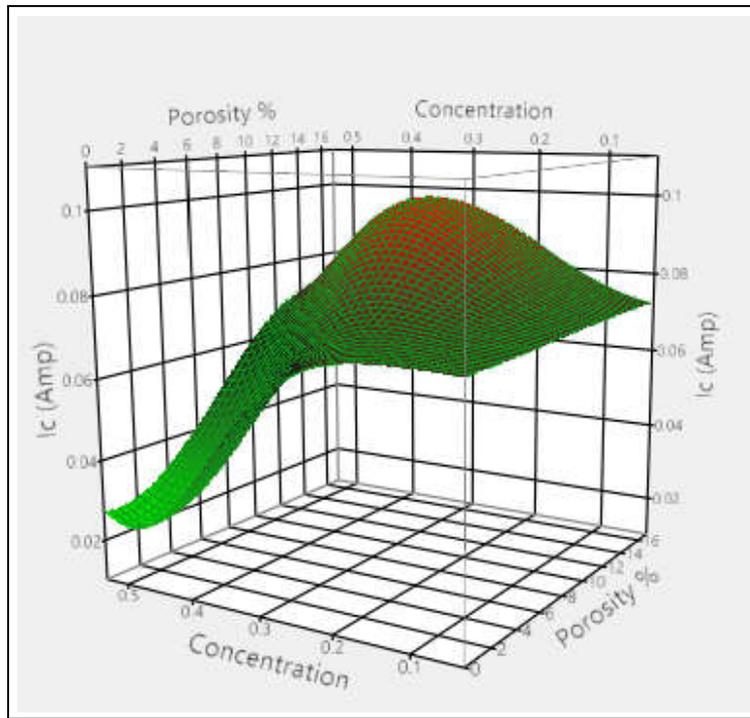
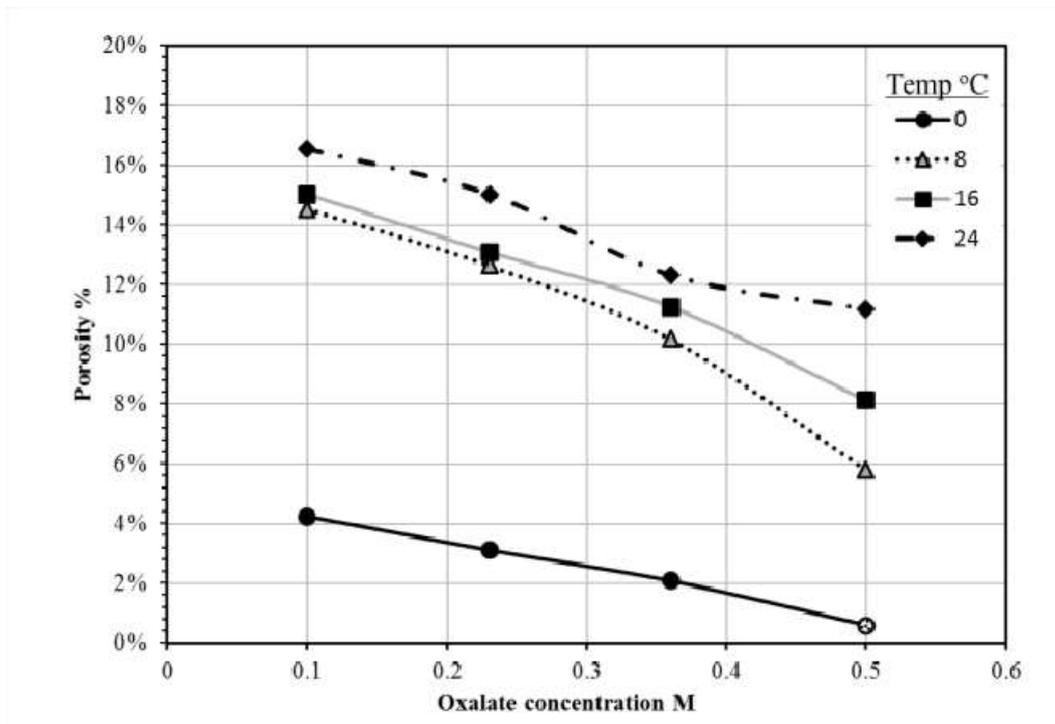


Fig. 10 Relation between critical anodizing current and porosity of coating anodized at various temperatures.

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**Fig. 11** Relation between critical anodizing current and porosity of coating anodized in various oxalate concentrations.



**Fig. 12** Porosity of coating anodized at various temperatures as a function of oxalate concentration.

#### 4. Conclusions

The main conclusions obtained from this research were:

The oxalate concentration was the most affecting parameter on the critical polarizing current and the applied voltage was the second affecting parameter, while the less affecting parameter on the critical polarizing current was the anodizing temperature.

The critical polarizing current was varied according to the oxalate concentration and anodizing temperature, where the lowest critical current was achieved at the lowest anodizing temperature of 0 °C and in the higher oxalate concentration of 0.5 M.

The lowest porosity of the coating was obtained when the critical polarizing current was in its lowest value.

Porosity of coating decreased with the increasing of oxalate concentrations and decreasing of temperature.

The increasing of solution conductivity increases the coating rate and forms coating with larger grain size and fewer pores.

The highest resistance to charge transfer through the electrochemical cell was achieved in 0.5 M oxalate concentration at 0 °C and 9 V, where.

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