Anodic electrodeposition of copper sulfide film on copper electrode in solution containing sulfides

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Abstract: The electrodeposition of the copper sulfide was studied. The temperature, applied current density and potential, time and sulfide concentration are optimized in order to improve a high-quality deposit film. The electrodeposition was assured using chronoamperometry and chronopotentiometry methods. The deposited film was characterized by the means of the scanning electron microscopy (SEM) and the X-ray diffraction. An adherent, homogeneous deposit was obtained for a potential of 800 mV, a temperature of 25°C and with 2000 or 12000 ppm of sulfides, during 30 min. The X-ray diffraction confirmed the cubic Cu₂S formation on the copper surface.

Keywords: Sulfide induced corrosion; copper sulfide; cathodic reaction; anodic electrodeposition, electrodeposition conditions.

1. Introduction

The sulfidation of metals and their alloys constitute an important field of study that grow more and more. Now days, it can be importantly similar as well as the interest given to metal oxidation or recovering processes. By investing different method to elaborate a sulfide metal, the formed film acquired a numerous applications for its huge application (Gennero De Chialvo and Arvia, 1985). In electrochemistry, the copper sulfide is one of the obtained sulfide films when a copper area is immersed in a sulfide medium. This film has a main role in many areas of applied chemistry and electrochemistry. The Flash Evaporation method is using to synthetize copper sulfide phases with improved thermoelectric properties, especially in its digenite phase (Amiri et al., 2022). On the other hands, two dimensional copper sulfide are synthetized for increasing the conductivity of textile substrates (Cho et al., 2023). In addition, the copper sulfide was formed and doped with carbon quantum dots to become an advanced photo-catalyst (Iqbal et al., 2022). In biological field, the nanoparticles of copper sulfide are covered by an antimicrobial lipid and display an enhanced bactericidal influence against Carbapenem-Resistant Acinetobacter Bahmani (Karnan Singaravelu et al., 2022). The porous copper (I) sulfide is also formed on copper surface using a sequential chemical modification. It is a simple method for obtaining highly conducting supercapacitors (Shaikh et al., 2022). Scheme 1 A series of corrosion studies improved that the sulfide ions modify and complicate the
electrochemical behavior of copper by the formation of a copper sulfide based layer (Guo et al., 2020, Nady et al., 2017, Zaafarany and Boller, 2010).

**Scheme 1.** Copper in solution containing sulfide

In our last published article, we have confirmed that the simultaneous presence of sulfides and dissolved oxygen increased the oxygen reduction reaction (ORR) and the cathodic current. Consequently, the electrodeposited copper sulfide enhanced the global corrosion process (El Mouaden et al., 2020). The aim of this work is the optimization of the formation conditions of the copper sulfide obtained by electro-deposition on the copper foam. Then, the formed film was characterized in order to confirm our purpose. The adopted method was the anodization of the copper electrode accordingly to the previous published works (Z. Qing-Gong et al., 2016) (Eqn. 1, Eqn. 2 and Eqn. 3):

**Anode:** \[ Cu \rightarrow Cu^+ + e^- \]  \textbf{Eqn. 1} \quad \text{and} \quad 2Cu^+ + S^{2-} \rightarrow Cu_2S  \textbf{Eqn. 2}

**Cathode:** \[ 2H^+ + 2e^- \rightarrow H_2 \] \textbf{Eqn. 3}

**Methodology**

The employed sodium sulfide nanohydrate was purchased from SIGMA-ALDRICH. The present electrolyte was of analytical grade purity and without any further purifications. The copper-foam was degreased using acetone and rinsed with distilled water. The electrodeposition of Cu$_2$S layer on copper surface is obtained via the immersion of Cu sample (working electrode) in the sodium sulfide solution in a thermostatic electrochemical cell. The platinum and saturated calomel electrodes as employed. The chronocamperometry and chronopotentiometry methods are used for the anodic electrodeposition by applying various potential values from 0 to 1000 mV and a current range from 1 to 20 mA/cm$^2$. The tested electrodeposition time is 30, 60 and 90 min. In addition, three temperature values are verified (25°, 40° and 50°). In order to evaluate the Na$_2$S concentration effect on the current synthetization, 2000 and 12000 ppm of Na$_2$S are studied. All the experiments are conducted under slow stirring. As results, a black film was formed on the copper foam. The samples were washed with distilled water and dried. The morphology characterization of the deposited films is obtained using a JEOL JSM-6480 LV scanning electron microscopy (SEM) and X-ray diffraction via X-ray diffractometer (Bruker D8 Advance) for the 2θ range of 20°-80° with Cu $\text{K}_\alpha = 1.5418$ and scan speed of 1 (°).s$^{-1}$. All the electrochemical tests are realized by the means of electrochemical workstation Versastat 3.

2. Results and discussion

3.1 Effect of deposition potential

The copper sulfide films are electro-deposited on a copper foam using chronocamperometry method by applying various potential values from 0 to 1000 mV for a deposition time of 30 min.
(Figure 1). The electrolyte solution is prepared by $\text{Na}_2\text{S}, 9\text{H}_2\text{O}$ (2000 ppm) as a precursor at 25 °C.

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Figure 2. Chronoamperometric deposition of copper sulfur at different applied potentials 
(t=30 min, T= 25° C, $[\text{S}^2^-]=2000$ ppm)

The figure shows, generally, that the current density tends to decrease and stabilize after about 500 s. The best stabilization is obtained for the applied potentials higher than 600 mV. The limit current density, which corresponds to a mass transfer, obeys to Cottrell law (A. J. Bard and Faulkner, 2001) (Eqn. 4):

\[ i = n F C \left( \frac{D}{\pi t} \right)^{1/2} \]  

(4)

Where $i$ is the currant density, $n$ is the exchanged electrons number, $F$ is Faraday constant, $D$ was the diffusion coefficient, $C$ designed the concentration of species at the studied volume and $t$ was elapsed time.

The Figure 2 presents the SEM images and corresponded EDS spectra for the sulfide copper deposition at different potential values after 30 min.

<table>
<thead>
<tr>
<th>Applied potential</th>
<th>SEM image</th>
<th>EDS spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mV : Unrequited deposit</td>
<td><img src="image1.png" alt="SEM Image" /></td>
<td><img src="image2.png" alt="EDS Spectra" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.02</td>
</tr>
<tr>
<td>O</td>
<td>0.42</td>
</tr>
<tr>
<td>S</td>
<td>19.47</td>
</tr>
<tr>
<td>Cu</td>
<td>86.30</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

200 mV:
Lift-off of the deposit

400 mV:
Trace of deposit

600 mV:
Lift-off of the deposit

800 mV:
Black and adherent deposit
3.2 Effect of the electrodeposition current

The chronoamperometric curves are acquired by applying different current values of 20, 10, 5 and 1 mA/cm² (Figure 3). The electrodeposition is realized using 2000 ppm of Na₂S, 9H₂O during 30 min, at 25 °C.

It is noted that the increase in the current applied, shifts the potential towards cathodic values reaching -1015 mV for 20 mA/cm². Nevertheless, the potential undergoes only a slight variation depending on the applied current.

The surface analyzes carried out (Figure 4) show an increase the % S and a decrease in that of copper by decreasing the applied current value. A maximum sulfur content of 21.30% is obtained with i= 1 mA/cm². While, SEM images let to observe a homogeneous covering on the surface of the electrode. However, the obtained deposits tend to peel off after the samples are dried. We conclude that the chronoamperometric technique gives more reliable and encouraging results than the chronopotentiometric technique.
Figure 5. SEM images and corresponded EDS patterns of the obtained depot by chronopotentiometric method (t=30 min, T= 25°C, [S²⁻]=2000 ppm)

3.3 Deposit time effect
The chronoamperometric technique is adopted with an optimized potential of 800 mV, a temperature of 25°C and a sulfide concentration of 2000 ppm. Three different deposits are
realized on the copper electrode during different immersion times. Figure 5 represents the chronoamperometric curves obtained for different deposition times.

![Figure 5](image)

**Figure 5.** Chronoamperometric curves obtained for different deposition times.

We observed a similar behavior of the curves by varying the deposition time from 30 to 90 min. The extension of time does not influence the variation of i. This result shows that the overall reaction implemented at the surface of the copper is not very influenced during this period. Figure 6 shows that the surface of the substrate has a different appearance depending on the deposition time. In addition, the EDS display the increase in the % S with the time, reaching 35.56 % after 90 min. However, the SEM identified that the deposited films in 60 and 90 min did not exhibit the properties of an adherent film.

![Figure 6](image)

**Figure 6.** Chronoamperometric deposition of copper sulfur during different deposit times (E= 800 mV, T= 25°C, [S²⁻] =2000 ppm).

<table>
<thead>
<tr>
<th>Deposit time</th>
<th>SEM image</th>
<th>EDS spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min : Black and adherent deposit</td>
<td><img src="image" alt="SEM image" /></td>
<td><img src="image" alt="EDS spectra" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
<th>% massique</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.30</td>
</tr>
<tr>
<td>O</td>
<td>0.74</td>
</tr>
<tr>
<td>S</td>
<td>16.53</td>
</tr>
<tr>
<td>Cu</td>
<td>78.53</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>
60 min:
Non-adherent deposit

90 min:
Swelling of the deposit

**Figure 7.** SEM images and corresponded EDS patterns of the obtained films at different deposition times (E= 800 mV, T= 25°C, [S²⁻]=2000 ppm)

### 3.4 Effect of the electrodeposition temperature

In order to study the effect of temperature on the deposition of copper sulfide, we carried out many deposits at different temperatures while keeping the other conditions constant (E= 800 mV, T= 25°C, t=30 min, [S²⁻] =2000 ppm).

**Fig. 8**: Effect of the temperature on the i-t curves of the copper sulfide deposit (t=30 min, E= 800 mV, [S²⁻]=2000 ppm)
Figure 7 shows that raising the temperature induced the increasing of the current density of the deposit and consequently the kinetics of the corresponding reaction.

<table>
<thead>
<tr>
<th>Deposit temperature</th>
<th>SEM image</th>
<th>EDS spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C: Sparsely distributed deposit</td>
<td><img src="image1" alt="SEM image" /></td>
<td><img src="image2" alt="EDS spectrum" /></td>
</tr>
<tr>
<td>40°C: Lifting off and swelling of the deposit</td>
<td><img src="image3" alt="SEM image" /></td>
<td><img src="image4" alt="EDS spectrum" /></td>
</tr>
<tr>
<td>50°C: Pointed deposit</td>
<td><img src="image5" alt="SEM image" /></td>
<td><img src="image6" alt="EDS spectrum" /></td>
</tr>
</tbody>
</table>

**Figure 9.** SEM images and corresponded EDS patterns of the obtained films at different deposition temperature (t=30 min, E= 800 mV, [S²⁻]=2000 ppm)

The obtained SEM images (Figure 8) show that the increase in the temperature of the electrolytic bath influences the morphology of the surface. For T= 40°C, a non-adherent deposit is formed which swells and peels off after the samples are dried. In the case of T= 50°C, the recovered film shows occasional deposits which are not uniformly distributed on the surface. However, the EDS analysis asserts that the sulfur peak increases with temperature.
### 3.5 Sulfide concentration effect on the deposit

The chronoamperometric technique was used to develop layers based on sulfides with an optimized potential of 800 mV, an optimum temperature of 25°C for a sufficient time of 30 min. In this case, the effect of sulfide concentration (2000 and 12000 ppm) was studied. Figure 9 summarizes the obtained results.

![Figure 9](image)

**Figure 9.** Effect of sulfide concentration on i-t curves of copper sulfide deposition (t=30 min, E= 800 mV, T= 25°C)

The curve in red color (Figure 9) denotes perfectly the theoretical diagram of the current-time curve appropriate for germination which includes three distinct zones (B. Trémillon, 1993):

- Zone I: Corresponds to the zone of the double layer during the necessary time to form the germs.
- Zone II: Corresponds to the growth of germs on the active surface on the electrode.
- Zone III: Corresponds to the diffusion of ions in the solution, constituting a limiting step for the growth reaction of the deposited film.

It is noted that the deposition curve with 12000 ppm of sulfides is in excellent agreement with the model of nucleation followed by a three-dimensional (3D) growth, which is controlled by diffusion. (B.R. Scharifker and G.J. Hills, 1983).

The acquired SEM micrographs (Figure 10) for the deposits show a close dependence on the concentration of sulfides in the electrolytic solution. It is observed that the concentration of 12000 ppm is recommended to obtain a surface composed of homogeneous and irregular agglomerate particles. The covering of the surface appears satisfactory and uniform compared to the deposit obtained with 2000 ppm. On the other hand, we noticed that the EDS spectra illustrate the increase in the percentage relative to S (from 16.53 to 32.57 %) and a decrease in that of Cu (from 78.53 to 66.47%) going from a concentration of 2000 to 12000 ppm.
Sulfide concentration | SEM image | EDS spectra
---|---|---
2000 ppm: Sparsely distributed deposit | ![SEM image](image1.png) | ![EDS spectra](image2.png) |
12000 ppm: Homogeneous and irregular deposit | ![SEM image](image3.png) | ![EDS spectra](image4.png) |

**Figure 11.** SEM images and corresponded EDS patterns of the obtained films for two sulfide concentration (t=30 min, E= 800 mV, T=25°C)

Therefore, we obtained adherent, homogeneous deposits for a potential of 800 mV, a time of 30 min, a temperature of 25°C and with 2000 or 12000 ppm in sulfides. These results are confirmed by X-ray diffraction analysis of the obtained films. The diffractograms are obtained in a range of 2θ 20° to 80° with Cu Kα radiation (K=1.5418) and a scanning speed of 1s per step. The selected spectra are represented in **Figure 11.** We note that samples (a) and (b) agree with the standard cubic Cu₂S file (00-053-0522). The diffraction of the (220) reticular plane of the deposited film exhibits a large intensity compared to the intensity recorded by the PDF file of the Cu₂S map. The increase in the concentration of sodium sulfides implies a relative increase in the intensities of the other peaks of the film. In addition, the two copper substrate peaks are also recorded and detected on the XRD spectra.
Conclusion

In conclusion, the electrodeposition of the layers of copper sulfides on the copper substrate have been carried out in this current work. The variation of the different experimental parameters made is realized in order to optimize the greatest conditions to obtain an electrodeposited film with good morphological properties. The good characteristics of the electrodeposited copper sulfide have been verified by XRD and SEM analyses.

Disclosure statement: Conflict of Interest: The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References


![Figure 12. X-ray diffraction patterns of deposited Cu₂S on the copper foam in (a) 2000 and (b) 12000 ppm of sulfide solutions (t=30 min, E= 800 mV, T=25°C)](image-url)


(2023) ; https://revues.imist.ma/index.php/ajmet/index