Study on Metal Anodic Dissolution

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This paper approaches the study of metal anodic dissolution process controlled by mass transfer. The theoretical study of this process under rotating disc conditions leads to a mathematical model that allows to calculate the mass transfer coefficient of ionic species formed at the anode. The mathematical model was experimentally verified. In this way there were employed aqueous solutions of sulphuric acid and copper sulphate (0.025 M CuSO₄ + 1.7 M H₂SO₄; 0.05 M CuSO₄ + 1.4 M H₂SO₄; 0.075 M CuSO₄ + 1.75 M H₂SO₄), and copper anodes. Based on the measured anodic polarization curves, current-limiting densities, mass transfer coefficients and anodic dissolution rates were determined. The obtained results show that the suggested mathematical model verifies well the experimental data corresponding to relatively low values of the anode rotational speed.

Keywords: anodic dissolution rate, rotating disc electrode, mass transport, binary electrolyte

Anodic dissolution is an electrochemical process frequently met in industry at metal refining, metal surface modeling and finishing, etc. In the last few years, these techniques have been more extensively employed in electronics and other high-tech industries in order to obtain microcomponents, thin films and foils of materials difficult to be achieved by using other methods.

The literature comprises several papers [1-4] approaching the study of electrode processes as components of an electrochemical process, from an engineering point of view. Due to the various practical applications of anodic dissolution processes, literature contains a high number of works [5-21] related to this kind of processes. In references [6-10] the authors used in their studies electrolytic continuous-flow cells for metal and alloys surface finishing. References [11-13] treat the mass transfer at copper dissolution in aqueous solutions of phosphoric acid by using the rotating disc technique, and in paper [14] the authors study the experimental dissolution of copper thin films in concentrated solutions of phosphoric acid. The obtained results point out how the rotating disc speed and current density influence the finishing degree of copper film surface.

References [18,19] present the results of an experimental study on mass transfer of anodic dissolution of copper in solutions of copper sulphate and sulphuric acid by using the rotating disc technique.

In this paper is established a mathematical model for anodic dissolution of metals under the conditions of rotating disc technique, when the dissolution process is diffusion controlled. The mathematical model leads to a criteria equation that allows to calculate the mass transfer at anodic dissolution of metals. This model is experimentally validated under rotating disc conditions using copper anodes and aqueous solutions of copper sulphate and sulphuric acid.

Mathematical model

In order to establish the mathematical model of the anodic dissolution process, a physical model was considered as shown in figure 1.

According to the model, the anode is a disc made of metal R (reduced oxidation state) and is fixed into a support that can be rotated with an ω angular speed. The support and metal disc are immersed into a liquid containing ions of metal O (oxidized state). On the anode surface contacting the liquid, the following electrochemical reaction takes place:

\[ \text{R} - z \cdot \text{e} \rightarrow \text{O} \]  

Ions formed on the anode surface diffuse to the liquid bulk, their concentration at the interface being \( C_o^d \) and in the liquid bulk \( C_o^\infty \). The liquid having Newtonian rheological properties moves towards the disc surface in axial direction, and the mass transfer of ions formed at the anode takes place by molecular and convective diffusion.

Under isotherm conditions and steady state, the diffusion-controlled process of anodic dissolution can be described mathematically through the following equation:

\[ \frac{D_O}{\nu_z} \frac{d^2 C_o^d}{dz^2} - \frac{d C_o^\infty}{dz} = 0 \]  

Limiting conditions are as follows:

\[ z = 0, \ C_o = C_o^d \]  

\[ z = \delta, \ C_o = C_o^\infty \]

Introducing the notation

\[ \varphi = \frac{\nu_z}{D_O} \]

equation (2) becomes:

\[ \frac{D_O}{\varphi} \frac{d^2 C_o^d}{dz^2} - \frac{d C_o^\infty}{dz} = 0 \]
\[
\frac{d^2 C_O}{dz^2} - \frac{\phi}{\delta} \frac{dC_O}{dz} = 0 \tag{6}
\]

Taking into consideration the limiting conditions, the solution of the differential equation (6) is:

\[
C_O = C_{Oi} + \frac{C_O^i - C_{Oi}}{1 - e^{\frac{-\phi}{\delta}}} \left(1 - e^{\frac{-\phi}{\delta}} \right) \tag{7}
\]

The specific mass transfer flux of O ions diffusing from the rotating disc surface is given by Fick's Law:

\[
n_O = -D_O \left. \frac{dC_O}{dz} \right|_{z=0} = -D_O \phi \left( C_{Oi} - C_{O}^i \right) \tag{8}
\]

Due to \( \phi \cdot \delta < 0 \), equation (8) can be written as:

\[
n_O = -D_O \phi \left( C_{Oi} - C_{O}^i \right) \tag{9}
\]

From equation (9) and mass transfer equation,

\[
n_O = k_i \left( C_{Oi} - C_{O}^i \right) = \frac{D_O}{\delta} \left( C_{Oi} - C_{O}^i \right) \tag{10}
\]

it can be obtained:

\[
\delta = \frac{1}{\phi} = \frac{D_O}{n_O} \tag{11}
\]

Mean velocity of the liquid is given by the relationship:

\[
\bar{v}_z = \frac{\delta}{\phi} \int_0^z v_z \, dz \tag{12}
\]

When it is used the relation proposed in [1] in order to calculate the axial component of the liquid velocity, \( v_z \):

\[
v_z = -0.51 \log^{1/2} \cdot \nu^{-1/2} \cdot z^2 \tag{13}
\]

equation (12) becomes:

\[
\bar{v}_z = -0.17 \cdot \omega^{3/2} \cdot \nu^{-1/2} \cdot z^2 \tag{14}
\]

Substituting the expression of \( v_z \) velocity in relationship (11), it is obtained the following relationship for the boundary layer thickness:

\[
\delta = \left( \frac{1}{0.17} \right)^{1/3} D_O^{1/3} \cdot \omega^{1/2} \cdot \nu^{1/6} \tag{15}
\]

Based on equation (10) and expression (15), it can be obtained:

\[
k_l = 0.55 \cdot D_O^{2/3} \cdot \omega^{1/2} \cdot \nu^{-1/6} \tag{16}
\]

Equation (16) for mass transfer coefficient can be also written in criteria form:

\[
Sh = 1.38 \cdot Re^{1/2} \cdot Sc^{1/3} \tag{17}
\]

From the mass transfer equation and Faraday’s law, it can be obtained the following relationship between the limiting current density, \( i_L \), and mass transfer coefficient, \( k_l \):

\[
i_L = \frac{z \cdot F}{M_O} \cdot k_i \cdot \Delta C_O \tag{18}
\]

**Experimental part**

In order to validate experimentally the mathematical model, the potentiodynamic polarization curves were measured by using the VoltaLab 32 (Radiometer Copenhagen) electrochemical system that is shown in figure 2.

This system is composed of a DEA-322 (Digital electrochemical analyzer) potentiostat, a three-electrode electrolytic cell provided with thermal coating and gas-sparging system, an IMT 102 data interface connected to a computer operated with Volta Master 2 acquisition and processing software. CTV 101 (Radiometer Copenhagen) was employed in order to operate the rotating electrode in the range of 0-5000 RPM. The thermostating system consisted of a 657 MTA Kutesz controlled by 1031 MTA Kutesz regulator. For removing air from the electrolyte solution, a nitrogen gas bottle was employed.

The electrolytic cell is composed of three electrodes according to a standard geometry, and is provided with thermal coating. There were employed discs of copper having a diameter between 1.5 and 2.5 mm as working electrode, a saturated calomel electrode as reference electrode, and as counter-electrode a copper wire of 2 mm in diameter immersed 1 cm in length in the solution. The high ratio between the cathode surface and anode surface allowed obtaining the limiting current at the anode. A volume of 30 mL of electrolyte solution was used in the experimental investigations.

There were processed electrodes of cylindrical shapes, each one being fixed into Teflon (polytetrafluoroethylene) supports for mechanical and electrical connection to the rotating device of the electrochemical system.

![Fig. 2 Experimental set-up](image-url)
Before each experimental determination, the planar surface of the electrode was polished in wet state using, firstly, SiC-240 abrasive paper, then SiC-2500 abrasive paper, degreased with alcohol ethylic and, finally, rinsed with distilled water.

Solutions of electrolyte were prepared by dissolving CuSO₄·5H₂O and H₂SO₄ 98% (Merck Analytical Reagents) in distilled water. The concentrations of the solutions employed in investigations were 0.025 M CuSO₄ + 1.7 M H₂SO₄, 0.05 M CuSO₄ + 1.4 M H₂SO₄, and 0.075 M CuSO₄ + 1.75 M H₂SO₄ respectively. Adjusted to room temperature, the electrolyte was deoxygenated for 10 min by bubbling nitrogen before each experiment.

The experimental conditions were as follows: solution temperature of 25°C; potential sweep range between –200 ÷ 3500 mV/ESC, potential sweep rate of 50 mV/s and resolution time of 0.08s.

Results and discussions

In figures 3-5 are shown the polarization curves measured with the experimental installation presented in figure 2, for three aqueous solution of copper sulphate and sulphuric acid with different concentrations (0.025 M CuSO₄ + 1.7 M H₂SO₄; 0.05 M CuSO₄ + 1.4 M H₂SO₄; 0.075 M CuSO₄ + 1.75M H₂SO₄), at the temperature of 25°C and rotational speed values of the copper electrode ranged between 200-2200 RPM.

As a function of the value of electrode potential, each polarization curve points out the presence of three distinct regions. When the electrode potential (E) has lower values than those corresponding to anodic peaks, the dissolution process is controlled by the electrode reaction. When the values of the potential E is in the mixed region that includes the anodic peak and minimum, and continues near the limiting current plateau, the dissolution process is controlled by both electrode reaction and mass transfer. Further, at high values of the electrode potential, the metal is passivated and the mass transfer of ions formed at the anode becomes the rate-determinant process. In this

![Fig. 3. Linear sweep voltammograms obtained at a potential sweep rate of 50 mV/s, \( \phi \) = 1.5 mm, in solution of 0.025 M CuSO₄ + 1.7 M H₂SO₄](image)

![Fig. 4. Linear sweep voltammograms obtained at a potential sweep rate of 50 mV/s, \( \phi \) = 2.5 mm, in solution of 0.05 M CuSO₄ + 1.4 M H₂SO₄](image)

![Fig. 5. Linear sweep voltammograms obtained at a potential sweep rate of 50 mV/s, \( \phi \) = 2.5 mm, in solution of 0.075 M CuSO₄ + 1.75 M H₂SO₄](image)

<table>
<thead>
<tr>
<th>Rotational speed, RPM</th>
<th>Limiting current density, ( A \cdot cm^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.2274</td>
</tr>
<tr>
<td>400</td>
<td>0.3248</td>
</tr>
<tr>
<td>600</td>
<td>0.4118</td>
</tr>
<tr>
<td>800</td>
<td>0.4898</td>
</tr>
<tr>
<td>1000</td>
<td>0.5794</td>
</tr>
<tr>
<td>1400</td>
<td>0.7185</td>
</tr>
<tr>
<td>1800</td>
<td>0.8380</td>
</tr>
<tr>
<td>2200</td>
<td>0.9419</td>
</tr>
</tbody>
</table>

Table 1

LIMITING CURRENT DENSITY AT COPPER ANODIC DISSOLUTION IN AQUEOUS SOLUTION OF COPPER SULPHATE AND SULPHURIC ACID
region, a limiting diffusion current, \( I_L \), is established on a wide range of potential of approximately 2V.

Using the polarization curves described in figures 3-5, the values of limiting current corresponding to a potential of 2V/ESC were determined at several values of the rotational speed of the copper electrode, and for the investigated electrochemical systems. Based on these data, the values of current density, \( i_L \), were obtained as shown in table 1.

As it can be noted, the limiting current density increases with electrode rotational speed. At low values of the rotational speed, \( i_L \) values corresponding to the three solutions are very close to each other.

Further, based on equation (18) and values in table 1, the values of mass transfer coefficient were determined for \( i_L \) as presented in table 2. Equilibrium data (C*CuSO₄) listed in table 3 were employed in order to calculate the driving force of the mass transfer process. In addition, experimental values in table 2 were compared with those calculated using equation (16) established by us, and with those obtained by Levich’s eq.:

\[
\text{Eq. (19)}
\]

As can be noted, equations (16) and (19) that allows the determining of the values of mass transfer coefficient are almost similar, the only difference between them being the value of the coefficient in the right hand side. Values obtained with equations (16) and (19) are also listed in table 2. Data in table 2 emphasize that at low rotational speeds, values of \( k_L \) obtained with equation (16) are very close to the experimental ones. At high values of rotational speed, values determined with equation (19) are close to the experimental ones. Hence, it can be stated that at low values of anode rotational speed, the equation suggested by us fits better the experimental data, while Levich’s equation is more proper for high values of the rotational speed.

In figures 6-8 are represented \( Sh = f(Re) \) functions corresponding to experimental values and those calculated with the aim of equations (17) and (20). Equation (20) was obtained from equation (19) and is written as follows:

\[
\text{Eq. (20)}
\]

Dependences presented in figures 6-8 show a good agreement between the experimental data and those calculated with equation (17) at low values of electrode rotational speed. The agreement is also very good at high values compared to data obtained with equation (20).

For the experimental data presented in figures 6-8 there were also achieved the following regression equations:

\[
\text{Table 2}
\]

<table>
<thead>
<tr>
<th>Rotational speed, RPM</th>
<th>( 0.025\text{M CuSO}_4 + 1.7\text{M H}_2\text{SO}_4 )</th>
<th>( 0.05\text{M CuSO}_4 + 1.4\text{M H}_2\text{SO}_4 )</th>
<th>( 0.075\text{M CuSO}_4 + 1.75\text{M H}_2\text{SO}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega ) s⁻¹</td>
<td>( 10^3 k_L ), m⁻¹</td>
<td>( 10^3 k_L ), m⁻¹</td>
<td>( 10^3 k_L ), m⁻¹</td>
</tr>
<tr>
<td>200</td>
<td>20.93</td>
<td>1.372</td>
<td>1.558</td>
</tr>
<tr>
<td>400</td>
<td>41.87</td>
<td>1.961</td>
<td>2.203</td>
</tr>
<tr>
<td>600</td>
<td>62.80</td>
<td>2.486</td>
<td>2.698</td>
</tr>
<tr>
<td>800</td>
<td>83.73</td>
<td>2.956</td>
<td>3.115</td>
</tr>
<tr>
<td>2200</td>
<td>230.27</td>
<td>5.686</td>
<td>5.166</td>
</tr>
</tbody>
</table>

\[
\text{Eq. (20)}
\]

\[
\text{Eq. (17)}
\]

\[
\text{Experimental data}
\]

\[
\text{Fig. 6. Sherwood number dependence on the Reynolds number at copper dissolution in aqueous solution containing 0.025 M CuSO}_4 + 1.7 M H_2SO_4
\]

\[
\text{Fig. 7. Sherwood number dependence on the Reynolds number at copper dissolution in aqueous solution containing 0.05 M CuSO}_4 + 1.4 M H_2SO_4
\]

\[
\text{Sh} = 2.0586 . Re + 32.195, \quad \text{Sh} = 1.2448 . Re + 56.372, \quad \text{Sh} = 1.0782 . Re + 79.534
\]

The values of the determination coefficients, \( R^2 \), of these three regression equations are 0.9898, 0.9908 and 0.9834 respectively.

Based on the data in table 3 and equation (10), the specific mass flux of ions formed at the anode was calculated. This flux is identified with the anodic dissolution
The results obtained, shown in table 4, supports those stated here above concerning the model validation.

Conclusions

In this paper is presented a study of mass transfer at metal anodic dissolution. A mathematical model was established to describe the anodic dissolution process under rotating disc conditions when the process is controlled by the rate of mass transfer of ions from the electrode surface to the liquid phase bulk.

The suggested mathematical model was experimentally validated using aqueous solutions of copper sulphate and sulphuric acid, and copper anodes respectively. Polarization curves were measured and based on them, limiting current density, mass transfer coefficient and anodic dissolution rate respectively. The experimental results obtained were compared to those calculated with the suggested model and Levich’s equation. It was found that at low values of anode rotational speed there is a very good concordance between the experimental data and those predicted by the suggested model. However, Levich’s model fits better experimental data corresponding to higher rotational speed values.

Table 3

<table>
<thead>
<tr>
<th>Solution of electrolytes</th>
<th>ν1, kg·m⁻³</th>
<th>η, Pa·s</th>
<th>ν, m²·s⁻¹</th>
<th>D_Cu²⁺, m²·s⁻¹</th>
<th>C_S₂O₄²⁻, mol·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 M CuSO₄ + 1.7 M H₂SO₄</td>
<td>1081</td>
<td>1.23·10⁻³</td>
<td>1.137·10⁻⁶</td>
<td>5.02·10⁻⁹</td>
<td>0.8835</td>
</tr>
<tr>
<td>0.05 M CuSO₄ + 1.4 M H₂SO₄</td>
<td>1069</td>
<td>1.186·10⁻³</td>
<td>1.109·10⁻⁶</td>
<td>4.46·10⁻⁹</td>
<td>0.9685</td>
</tr>
<tr>
<td>0.075 M CuSO₄ + 1.75 M H₂SO₄</td>
<td>1089</td>
<td>1.28·10⁻³</td>
<td>1.175·10⁻⁶</td>
<td>4.81·10⁻⁹</td>
<td>0.8780</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Rotational speed, RPM</th>
<th>ν, m·s⁻¹</th>
<th>ν₀, kg·m⁻³·s⁻¹</th>
<th>ν₀, kg·m⁻³·s⁻¹</th>
<th>ν₀, kg·m⁻³·s⁻¹</th>
<th>ν₀, kg·m⁻³·s⁻¹</th>
<th>ν₀, kg·m⁻³·s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>20.93</td>
<td>0.740</td>
<td>0.850</td>
<td>0.957</td>
<td>0.729</td>
<td>0.846</td>
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<tr>
<td>400</td>
<td>41.87</td>
<td>1.069</td>
<td>1.202</td>
<td>1.353</td>
<td>1.094</td>
<td>1.196</td>
</tr>
<tr>
<td>600</td>
<td>62.80</td>
<td>1.356</td>
<td>1.472</td>
<td>1.637</td>
<td>1.375</td>
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<tr>
<td>800</td>
<td>83.73</td>
<td>1.613</td>
<td>1.700</td>
<td>1.914</td>
<td>1.648</td>
<td>1.691</td>
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<tr>
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<td>104.67</td>
<td>1.908</td>
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<td>1.891</td>
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<td>1400</td>
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<td>2.532</td>
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<td>2.237</td>
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<tr>
<td>1800</td>
<td>188.40</td>
<td>2.759</td>
<td>2.549</td>
<td>2.871</td>
<td>2.726</td>
<td>2.537</td>
</tr>
<tr>
<td>2200</td>
<td>230.27</td>
<td>3.101</td>
<td>2.818</td>
<td>3.174</td>
<td>2.901</td>
<td>2.805</td>
</tr>
</tbody>
</table>

Nomenclature

C₀ - concentration of O ionic species, kg·m⁻³;
C₀, - concentration of O ionic species at interface, kg·m⁻³;
C_m, - concentration of O ionic species in the bulk of liquid phase, kg·m⁻³;
d - electrode diameter, m;
D₀ - molecular diffusion coefficient of oxidized species (ions), m²·ms⁻¹;
F - Faraday’s constant, C·mol⁻¹;
I₀ - diffusion limiting current, A;
I₀c - limiting current density, A·m⁻²;
kₐ - mass transfer coefficient, m·s⁻¹;
M₀, - molar mass, kg·kmol⁻¹;
n - rotational speed, rot·s⁻¹;
n₀, - ion species of O specific mass flux, kg·m⁻²·s⁻¹;
Re = ν · n · d² · η⁻¹ - Reynolds number, non-dimensional;
Sc = ν · D₀, - Schmidt number, non-dimensional;
Sh = kₐ · d · D₀, - Sherwood number, non-dimensional;
V₀ - mean flow speed of the liquid in the diffusion-limiting layer, m·s⁻¹;
z - axial coordinate, m;
δ - thickness of diffusion-limiting layer, m;
η - liquid dynamic viscosity, N . s . m⁻²;
ρ - liquid density, kg . m⁻³;
ν - liquid kinematic viscosity, m² . s⁻¹;
ω - angular speed, s⁻¹;

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Manuscript received: 4.05.2008