Multiphysics Simulation of Localised Anodisation of Aluminium

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Abstract

For locally confined anodisation processes on aluminium substrates, usually masking techniques are required, which are mostly time-consuming and at the same time resource-intensive, since these processes are carried out in basins with large electrolyte volumina. Anodisation using a microcapillary cell or a continuous electrolyte jet provides resource-efficient alternatives for localised anodisation.

In this study COMSOL Multiphysics is used to simulate the localised anodisation process of aluminium using a microcapillary cell. The simulations were carried out in order to analyse the influences of processing parameters like voltage and to better understand this localised anodisation process. Based on the geometry of a microcapillary cell used in experimental investigations, a simulation model was build up. The oxidation process was simulated using the application modes “Electric Currents” and “Boundary ODEs and DAEs” of COMSOL Multiphysics.

As a result of the simulation, the calculated oxide height increases digressively over the anodisation time according to previous experimental results. Slight deviations from the experimental results indicate that a further adaption of the simulation model is required.

FEM Simulation, Localised Anodisation, Aluminium, Microcapillary Cell, Continuous Electrolytic Free Jet

1. Introduction

Anodisation of aluminium and its alloys is used e.g. to form oxide layers in order to improve the corrosion and wear resistance. Usually, anodisation processes are carried out in electrolyte baths to cover the whole work-piece surfaces. Due to the trends in component integration and multifunctionality, localised anodic oxidation is needed e.g. in medical and precision engineering applications. Up to now, localised anodisation processes are realized using masking techniques. Resource-efficient and economical alternatives to the deposition and removal of such masking layers are the creation of localised oxidations applying a microcapillary cell or using a continuous electrolyte jet. [1–3]

In macroscopic scale, the anodisation of aluminium is well-known and controllable. In contrast, the effect of anodisation in a determined area without using masking techniques is widely unknown. Recently, experimental investigations of localised anodisation with microcapillary cells have been carried out showing the applicability of this technique [1–3]. In addition to the experiments, multiphysics simulation using COMSOL Multiphysics 5.3 were executed. These simulations are used to analyse multiphysical phenomena during the process of anodisation which are hardly measurable.

In this study, multiphysics simulations are carried out to simulate the growth of oxide layers using a microcapillary cell. The simulation results will deliver the basis for transferring this technique to localised anodisation by help of a continuous electrolytic free jet.

2. Experimental Methods

For analysing local anodisation, a microcapillary cell was used in previous studies. The cell consists of 2 glass capillaries, whereas the smaller capillary is fixed concentrically inside the larger one. The electrolyte flows continuously through the cell, while the inner capillary is the electrolyte inlet and the outer capillary serves as electrolyte outlet. The capillary cell is placed on top of the work piece. The work piece is connected to the positive potential of a potentiostat. The counter electrode is a platinum wire, which is mounted inside the capillary cell. [1]

2.1. Model geometry and conditions

The design of the microcapillary cell is used as basis for the simulation model. Figure 1 shows the geometry used in the simulation.

Figure 1. Section of the Model geometry with highlighted domains

The model is based on a 2D axially symmetric geometry. Similar to the experimental setup [1], the geometry consists of
two glass capillaries mounted concentrically one inside the other. The electrolyte fills the inside of both capillaries. In general the glass capillaries only influence the shape of the electrolyte and have no influence on the electrochemical processes. Therefore, only the relevant contour of the glass capillaries is implemented in the geometry. The work piece is placed below the capillary cell. The counter electrode is situated on top of the inner capillary. The counter electrode is not implemented as solid object. Instead, the properties of the counter electrode are attached to the upper boundary of the electrolyte domain. The experimental conditions are based on the conditions in the previous study [2]. The relevant conditions for the domains and boundaries are listed in Table 1.

Table 1. Relevant domain and boundary conditions

<table>
<thead>
<tr>
<th>Domain/boundary</th>
<th>Condition</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work piece</td>
<td>Material</td>
<td>EN AW 7075</td>
</tr>
<tr>
<td></td>
<td>Electric potential</td>
<td>60 V</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Type</td>
<td>Oxalic acid</td>
</tr>
<tr>
<td></td>
<td>Conductivity</td>
<td>0.8 mol/l</td>
</tr>
<tr>
<td>Counter electrode</td>
<td>Electric potential</td>
<td>0 V</td>
</tr>
</tbody>
</table>

2.2. Used application modes

To simulate the growth of oxide layers in the microcapillary cell, two application modes available in COMSOL Multiphysics were chosen: “Electric Currents” and “Boundary ODEs and DAEs”. Since the driving force in electrochemical processes is the current density, the application mode “Electric Currents” is used for simulating the current flow or the current density distribution. The oxide layer is implemented as a “Contact Impedance” on the work piece surface. The growth of the oxide layer is implemented by a differential equation within the “Boundary ODEs and DAEs” module. Equation (1) describes the oxide growth and is based on Faraday’s law. Table 2 lists the coefficients of equation (1).

\[
\frac{h_{ox}}{t} = \frac{v_{ox}}{t} = \frac{M_{ox}}{F} = \frac{J}{(1 - V_F) \cdot \rho \cdot z \cdot F}
\]

(1)

Table 2. Coefficients of equation (1)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of the oxide ( h_{ox} )</td>
<td>[µm]</td>
</tr>
<tr>
<td>Time ( t )</td>
<td>[s]</td>
</tr>
<tr>
<td>Oxide growth rate ( v_{ox} )</td>
<td>[µm/s]</td>
</tr>
<tr>
<td>Current density ( J )</td>
<td>[A/cm²]</td>
</tr>
<tr>
<td>Constants</td>
<td>Value</td>
</tr>
<tr>
<td>Molar mass of the oxide ( M_{ox} )</td>
<td>101.96 g/mol</td>
</tr>
<tr>
<td>Pore fraction within the oxide ( V_F )</td>
<td>0.43</td>
</tr>
<tr>
<td>Density of the oxide ( \rho )</td>
<td>3.94 g/cm³</td>
</tr>
<tr>
<td>Valence number ( z )</td>
<td>6</td>
</tr>
<tr>
<td>Faraday constant ( F )</td>
<td>96485.3 As/mol</td>
</tr>
</tbody>
</table>

The two application modes interact with each other as follows: during the simulation the current density is calculated using the “Electric Currents” module. The current density is used to calculate the oxide growth. The oxide height is used for calculating the “Contact Impedance” on the work piece surface and as a consequence the current density, too.

3. Simulation results

Since the conductivity \( \sigma \) of the oxide layer cannot be determined exactly by experiments due to its complexity [1, 4], the following three possible values were chosen for the simulations, according to [5]: \( 1 \times 10^{-6} \) S/m; \( 5 \times 10^{-6} \) S/m and \( 10 \times 10^{-6} \) S/m.

According to the experimental processing time, the simulation time was set to 900 s. Figure 2 shows the simulated oxide height as a function of time for the three chosen values of the oxide layer conductivity.

![Figure 2. Simulated oxide height as a function of time](image)

It can be seen that the oxide height increases digressively at increasing processing time. The reason for the decreasing oxide growth rate is the increasing oxide height, which results in an increasing resistance and therefore leads to a decrease in current density. In comparison, the experimental result [1] is situated between the simulation results with oxide conductivities of \( 1 \times 10^{-6} \) S/m and \( 5 \times 10^{-4} \) S/m. Hence, a value between these two should be chosen in order to improve the simulation results.

4. Summary and conclusion

In this study the localised anodisation of aluminium using a microcapillary cell was simulated. Therefore, a simulation model was developed using COMSOL Multiphysics according to the experimental setup. The oxide height increases digressively over the processing time, which is also observable in the experimental results. The calculated oxide height at 900 s does not exactly match the experimental results, using the chosen oxide conductivities. Therefore, the simulation model needs to be improved in order to converge to the experimental results.

Thus, the simulation model will be adapted to build a reliable basis for the simulation of the localised anodisation process in order to transfer this technique to localised anodisation using a continuous electrolytic free jet.

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References