Experimental Study and Modelling of Heat Transfer During Anodizing of Aluminum

Herman Terryn
Vrije Universiteit Brussel (VUB)
Research Group Electrochemical and Surface Engineering (SURF)
Department Materials and Chemistry, Pleinlaan 2, 1050 Brussels, Belgium
Tel:+ 3226293537 (secr 3255) Fax:+3226293200 hterryn@vub.ac.be
www.vub.ac.be/SURF
Part time TUDelft
Department of Materials Science and Engineering, Tu Delft
Surfaces and Interfaces Group, Corrosion Technology and Electrochemistry
Mekelweg 2,2628CD Delft,The Netherlands
the SURF brains

8 ZAP members
8 postdoc researchers
25 researchers
administrative staff
technical staff
SURF’s approach

Electrochemical and surface processes

Combined experimental and modelling approach

Experimental techniques
- Macroscopic and local electrochemical methods
- In-situ & ex-situ surface analysis techniques
- Reactors for electrochemical and surface engineering

Modelling techniques
- Reliable parameter estimation by fitting
- Numerical tools for electro-chemical system modelling
valorisation of SURF's research & expertise

Closely working with industrial partners
Anodizing of Aluminium – introduction

**Problem:**
depending on reactor configuration, convection anodizing conditions, ...

- non-uniform oxide thickness
- burning effects (high $J$)
- process optimisation by trial & error

**Improvement:**
process optimisation based on simulations

**Model:**
Non uniformity comes from $T$

Electrochemical Modelling

• Collaboration with Computational Electrochemistry Group of Johan Deconinck/ Elsyca (spinoff company VUB)
• Large project in Flemish community
• Based on Boundary Finite Element Calculations
• Different electrochemical systems considered
  – Cases
    • Gas Production (Cl gas production)
    • 3D micro nano electrodes (recovery solutions)
    • Electroplating mass transfer (Cu, Zn)
    • Anodizing heat transfer
    • AC Etching of Al (mass transfer+gas)
• Turbulent regime + Two phase systems (fraction of gas)

• Case Anodizing: local heat transfer
Introduction to anodizing - mechanism of porous oxide growth

Ionic migration through pre-existing film

| $E| \sim 10^9 \text{V/m}$

Incorporation of anions see lecture of Shoshan tomorrow

Effects of the morphology and composition on the adhesion
Considered strategy

1) gaining insight on temperature dependency

influence $T_{H_2SO_4}$ ?
- a) effect bulk temperature
- b) $\Delta$(convection)
  $\Rightarrow$ effect local temperature

local phenomena: burning
- characteristics ?
- influence heat transfer ?

influence of $T_{Al}$ ?
- experiments at applied electrode temperature
  $\Rightarrow$ setup ?
Considered strategy

2) modelling of the process

- influence $T_{H_2SO_4}$
- local phenomena: burning
- influence of $T_{Al}$

3) simulations of the process

\[ j = f(\eta, T) \]
Anodizing of Aluminium – general introduction

Temperature dependency:

- Heat production during Anodizing
  - Joule heating of oxide
  - exothermal oxide formation
- Significant influence $T$ on
  - electrochemical behaviour
  - film morphology
  - mechanical properties

- Important influence of *heat transfer*

- Requirements set-up for validation of simulated experiments:
  * known convection
  * access to local information
  * recording different parameters

wall – jet electrode reactor
Wall-jet electrode reactor

dydrodynamic flow pattern

- Non-uniform convection along electrode
  ⇒ non-uniform hydrodynamical, thermal, diffusion boundary layer
  ⇒ investigation influence local difference in $h_i(r)$, $h_m(r)$

Wall-jet electrode reactor

experimental set-up

- **local measurement** $T$ on electrode
- electrochemical quantities $i (j), U$
- flow rate, temperature of electrolyte

Microhardness, wear, porosity
20 µm anodized film in H2SO4 17 V

Wall-jet electrode reactor
hydrodynamic flow pattern

Flow field near W.E. (Re = 600)

Evolution of $h_T$ in function of radial position

Known conditions of convection and heat transfer

Quantitative approach possible!
Influence of variation of local temperature during anodizing*

**Scope**

Wall jet reactor

- Re = 500 \[
\text{heat transfer} \uparrow
\]
- 256°C/dm²
- Re = 5000

- Re = 5000 \[
\text{heat transfer} \downarrow
\]
- 256°C/dm²
- Re = 500

**Effect noticeable**
- ° electrochemical behaviour
- ° microstructure oxide

**h_r in function of radial position**

**Radial position (m)**

<table>
<thead>
<tr>
<th>Re = 500</th>
<th>Re = 5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>h_r (W/m²/K)</td>
<td>h_r (W/m²/K)</td>
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</table>
Influence of variation of local temperature during anodizing

Experimental conditions

AA 1050

Alkaline etched + desmutted

DC – anodizing in 145g/l H$_2$SO$_4$ + 5g/l Al$_2$(SO$_4$)$_3$.18H$_2$O

galvanostatic anodizing 1 → 16A/dm$^2$ - 25, 45°C - 512C/dm$^2$

Electrolyte flow rates $Re = 500 \rightarrow 5000$
Demonstration influence heat transfer - electrochemical behaviour

Local electrode temperatures

$Re = 800$

Higher $T(r,t)$ towards border electrode

In correspondence heat transfer

Similar evolutions at other $Re$

For comparison: $T(r, t_{final})$

Influence of variation of local temperature during anodizing

galvanostatic 8A/dm² 45°C

Re = 500 → 5000

Immediate or moderate but measurable effect
Influence of variation of local temperature during anodizing.

Galvanostatic 8A/dm² 45°C  
Re = 5000 → 500

Immediate but measurable effect.

\[ T_{W.E.}(r, t) \]

\[ U_{W.E.}(t) \]
strategy of the thesis

1) gaining insight on temperature dependency

- influence $T_{H_2SO_4}$?
  - a) effect bulk temperature
  - b) $\Delta$(concentration)
    - effect local temperature

- local phenomena: burning
  - characteristics?
  - influence heat transfer?

- influence of $T_{Al}$?
  - experiments at applied electrode temperature
  - setup?
Demonstration influence heat transfer - electrochemical behaviour

\[ d_{\text{oxide}}(r) \leftrightarrow T_{\text{electrode}}(r, t_{\text{final}}) \]

- reduced convection \( \rightarrow \) less uniform electrode
- incline from centre towards border

**influence heat transfer on anodizing:**

\( \text{heat transfer} \downarrow \Rightarrow \Delta T_{\text{electrode}}(r) \uparrow \quad \leftrightarrow \quad d_{\text{oxide}}(r) \uparrow \quad \text{where} \quad T_{\text{electrode}}(r) \uparrow \)

Demonstration influence heat transfer - strange observation

local oxide thickness $d_{\text{oxide}}(r)$

local electrode temperature

Incorrect measurement? no: burning

Local phenomena: *burning - oxide morphology*

- **normal oxide**
- **burning area**
- **“oxide hillocks”**

Local phenomena: *burning*

- **burning area**

- **oxide hillocks:**
  - base → normal pores
  - top → tubular structure

*characteristic for burning*

Local phenomena: burning

- burning area

oxide morphology

quenching of burning
Local phenomena: burning

- general evolution

pore development

healing
Influence of electrode temperature

Traditional approach:

- varying $T_{\text{electrolyte}}$
  - $T_{\text{Al}}$?
    - in-situ measurements
    - calculations (CFD)
    - *uncontrolled* …
Influence of electrode temperature

**presented approach:**

- **varying** applied $T_{anode}$

- $T_{Al}$ known and controlled

realized by in-house developed electrode holder

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Temperature applied anodizing

*T-controlling sample holder(s)*

Al heat sink

Water cooling

Influence of electrode temperature - $T_{Al} > T_{H2SO4}$

- electrode potentials
- oxide thickness & morphology
- anodizing ratio → ionic migration

Results – modelling of the process

proposed, optimized model:

\[ j = \frac{\eta \cdot j_{c,0} \cdot e^{B_1 \cdot T}}{(\eta_{c,0} + B_1 \cdot T)} - \eta \]

where:

\[
\begin{align*}
\eta_{c,0} & = 53.0 \text{ V} \\
B_1 & = -0.09823 \text{ V/K} \\
J_{c,0} & = 5.971 \times 10^{-8} \text{ A/m}^2 \\
B_2 & = 0.06957 \text{ K}^{-1}
\end{align*}
\]

experiments

- good correspondence
- in wide range of conditions:
  - 86%: \( |\Delta \eta| \leq 0.5 \text{ V} \)
  - 30%: \( |\Delta \eta| \leq 0.1 \text{ V} \)
Considered model

Hydrodynamics solution

\[
\begin{aligned}
\vec{\nabla} \cdot \vec{v} &= 0 \\
\rho \left( \frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \vec{v} \right) &= \mu \vec{\nabla}^2 \vec{v} - \vec{\nabla} p
\end{aligned}
\]

+ turbulent viscosity from low-\(Re\) \(k-\omega\) model

temperature distribution

\[
\begin{aligned}
c_{p,i} \rho_i \left( \frac{\partial T}{\partial t} + (\vec{v}_i \cdot \vec{\nabla}) T \right) &= \vec{\nabla} \cdot (\lambda_i \vec{\nabla} T) + Q_i \quad i=\text{electrolyte or Al}
\end{aligned}
\]

\[
Q_{Al} = Q_{\text{Ohmic}} + Q_{\text{loss}} + Q_{\text{anod}} = \rho_{Al} \cdot j^2 + \alpha \cdot S \Delta T + \eta \cdot j
\]
Considered model

Electrical potential distribution

$$\nabla \left( -\sigma_i \nabla U_i \right) = 0 \quad \Rightarrow \quad \vec{j}_i = -\sigma_i \nabla U_i \quad i=\text{electrolyte or Al}$$

Anodizing boundary condition (still working on this) empirical equations

Or Physical equation (High Field equation)

$$j = D.T^m.e^T \left( \frac{B}{e^{RT}} \left( \frac{\alpha z F \eta}{RT} - e \frac{(1-\alpha) z F \eta}{RT} \right) \right)$$

with

$$D = 9.86E-6$$
$$B = -2600$$
$$\alpha = 0.0116$$
$$z = 3 \quad \text{and} \quad m = 0.5$$

Oxide thickness

$$j(r) \quad \Rightarrow \quad d_{ox} = \varepsilon \frac{M \cdot j \cdot \Delta t}{z \cdot F \cdot \rho} \quad \text{(Faraday)}$$
Anodizing experiments vs. model

Followed approach

Consider:
- Wall-jet reactor set-up
- $T_{H2SO4}$
- $Re_a$
- $i - Q$

Simulation of anodizing process

$T(r,t_f)_{EXP} - d_{ox}(r,t_f)_{EXP}$

$T(r,t_f)_{NUM} - d_{ox}(r,t_f)_{NUM}$

experiments vs. model

Numerical $T(r,t_f)$

4A/dm$^2$

8A/dm$^2$


Simulations of the process - results

\[ T_{H_2SO_4} = 25 \, ^\circ C \quad j = 4 \, A/dm^2 \quad Re = 5000 \]

- Mutech model > reference model
- good correspondence Mutech \leftrightarrow exps
  - offset error remains
  - behaviour near border

Collaboration
Elsyca
Industrial Modelling

http://www.elsyca.com/
Model equations

Laplacian equation for ohmic drop in electrolyte

- Electrical field: $E = -\nabla U$
- Current density: $J = \sigma E = -\sigma \cdot \nabla U$
- Charge conservation: $\nabla \cdot J = 0 \Rightarrow \nabla \cdot (\nabla U) = \Delta U = 0$

Boundary conditions
- Anodic polarisation: $J_n = f_1(\eta) = f_1(V - U)$
- Cathodic polarisation: $J_n = f_2(\eta) = f_2(V - U)$
- Insulating walls / electrolyte meniscus $J_n = 0$
Case A: high density caliper part load

No anode shielding

120 parts per rack / flight bar

Flight bar Top View
Case A: high density caliper part load

<table>
<thead>
<tr>
<th>Porous layer thickness</th>
<th>$\Delta t$ [min]</th>
<th>Imposed $\Delta V$ main [V]</th>
<th>$I_{\text{main}}$ [A]/flightbar</th>
<th>Imposed $\Delta V$ aux [V]</th>
<th>$I_{\text{aux}}$ [A]/flightbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
<td>12.9</td>
<td>877</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Average value [micron]** 14.4

**Minimum value** 10.9

**Maximum value** 19.9

**Standard deviation** 1.8

**Minimum specification** 12.0

**Maximum specification** 18.0