Electrochemical properties of anodized aluminum coated and/or sealed with p-Phenylenediamine based benzoazazines

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Introduction

Flycoat project: corrosion protection of aluminum alloys

Use of Cr VI: will be prohibited by REACH legislation

Today

Substrate of interest: AA2024-T3 (Cu)

Our research
Sulfo-Tartaric Anodizing

Structure of anodic layers (SEM-FEG) on different alloys

Anodized AA2024-T3

Anodized AA2024-T3

TSA = Tartaric-Sulfuric Anodising
Composition:
40 g/L sulfuric acid
80 g/L tartaric acid

Settings:
Voltage: 10 V
Duration: 25 min
Temperature: 40°C
Bath: TSA

Structure:
Pores: 12.2 nm (± 2.0 nm)
Porosity: 17.13 %
Thickness: 2.8 µm ± 0.1 µm
Benzoxazines

New type of thermosets: benzoxazine resins

- Low volume shrinkage during curing
- Low water absorption
- Great chemical resistance to almost every solvent
- High curing temperature needed
- Brittle material

Para-phenylenediamine-based benzoxazine:

Use of a diamine

- limiting thermal degradation
- Highly crosslinked network
**Benzoxazines**

Investigated benzoxazine monomers:

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>P-pPDA</td>
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<tr>
<td></td>
<td>Very hard to melt</td>
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<tr>
<td></td>
<td>Soluble into chloroform after 4 hours of heating</td>
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<tr>
<td></td>
<td>Curing from 140 up to 230°C for 6 hours</td>
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</tbody>
</table>

Extremely different behavior
P-pPDA
P-pPDA on anodized AA2024-T3

Spin coating: Dissolved in chloroform – 800 rpm

Curing: from 140°C up to 230°C

Almost no penetration of the resin inside the porous oxide layer

Favorable interface ➔ Excellent adhesion

GDOES profiling DSTC (Udine, IT)

Almost no penetration of the resin inside the porous oxide layer
P-pPDA on anodized AA2024-T3

Durable and highly capacitive

Coating

Metal surface

Brasher & Kingsbury \( \Rightarrow X_w < 0.4\% \)

2\( \mu \)m cured P-pPDA

AA2024-T3

Anodic layer:

Preventing delamination of the organic layer

2\( \mu \)m cured P-pPDA

3\( \mu \)m anodic layer

AA2024-T3

NaCl 0.1 M
Ref: \( \text{Ag}/\text{AgCl}/\text{KCl sat.} \)
CE: Pt wire
Area: 7cm\(^2\)
Amplitude: 30 mV
4EP-pPDA
4EP-pPDA on AA2024-T3

Dissolved in chloroform (10%w)
Deposited by spin-coating (800rpm)
Cured from 170 up to 210°C

Bare AA2024-T3
- Resin flows during curing
- Non-homogeneous coating
- Poor protection

Anodized AA2024-T3
- Resin seems to be « absorbed » by the anodic layer
- Homogeneous and reproducible coating
4EP-pPDA on anodized AA2024-T3

Importance of the curing step

Spin coating: 10%w in chloroform – 800 rpm

Curing: from 170°C up to 210°C for 4 hours

Before curing, a top layer of C (resin) is observed on top of Al (Al oxide)

After curing, C and Al are coexisting

EDX spectroscopy

Porous oxide layer

AA2024-T3

Resin deposit

Oxide layer

Metal

Uniform resin deposit

Oxide + resin

Nanoporous surface

Metal

AA2024-T3

Université de Mons

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4EP-pPDA on anodized AA2024-T3

**Not cured**

- AA2024-T3

**Fully cured (up to 210°C)**

- AA2024-T3

GDOES profiling DSTC (Udine, IT)

- **S** = marker of the anodic layer (coming from sulfuric acid)
- **C & N** = markers of the benzoxazine resin

4EP-pPDA present all along the anodic layer

→ Sealing rather than a coating

Sealing process during curing
4EP-pPDA on anodized AA2024-T3

**EIS ➔ Barrier properties**
- Area: 7 cm²
- Ref electrode: Ag/AgCl/KCl sat
- Electrolyte: NaCl (0.1M)
- Amplitude voltage: 30 mV rms
- Immersed in NaCl 0.1M for one month
- Thickness: 3µm

**Before curing:**
- Poor capacitance
- Strong changes over immersion time

**After curing:**
- Highly capacitive
- Stable over immersion time

**Curing = key step for obtaining good barrier properties**

**Materials Institute**

- 3µm AA2024-T3
- Thickness: 3µm
4EP-pPDA on anodized AA2024-T3: influence of the resin amount

10%w, Fully cured

The resin seems is fully absorbed by the oxide layer

20%w, Fully cured

Different electrochemical properties

Resin is absorbed by the oxide layer
The surplus forms an inhomogeneous top coat

-Modulus 1 day
-Modulus 1 week
-Modulus 1 month
-Phase 1 day
-Phase 1 week
-Phase 1 month

|Z| (Ohm.cm²)

Frequency (Hz)

-Phase angle (°)

Thickness: 3 µm
Immersed in NaCl 0.1 M

The resin seems is fully absorbed by the oxide layer

Different electrochemical properties

Resin is absorbed by the oxide layer
The surplus forms an inhomogeneous top coat
4EP-pPDA on anodized AA2024-T3: influence of the resin amount

10%w, Fully cured

- Anodic porosity on the whole surface
- Partial filling of the pores

20%w, Fully cured

- Anodic porosity partially visible
- Inhomogeneous top layer

Threshold around 15%w
4EP-pPDA on anodized AA2024-T3

What quantity of resin is necessary to reach good barrier properties?

- Three different « benzoxazine loadings » (full curing from 170°C up to 210°C):
  - 2.5% (10 g/dm²)
  - 5% (15 g/dm²)
  - 10% (25 g/dm²)

- Electrochemical Impedance Spectroscopy

- Modeling using Equivalent Electrical Circuits
4EP-pPDA on anodized AA2024-T3

What quantity of resin is necessary to reach good barrier properties?

After 1 day

- Phase angle (°)
  - 0
  - 20
  - 40
  - 60
  - 80

2.5% = corroded
5% = capacitive and stable
10% = Highest barrier

|Z| (Ohm cm²)

In NaCl 0.1M

Increasing loading ➔ More capacitive ➔ More durable

After 1 month

- Phase angle (°)
  - 0
  - 20
  - 40
  - 60
  - 80

2.5% = corroded

Increasing loading ➔ More capacitive ➔ More durable
4EP-pPDA on anodized AA2024-T3

Barrier properties as a function of the amount of resin

Calculation of the resistance of the resistive pathways

Used EEC:

\[ R_s, CPE_{bl}, CPE_b, R_p, R_b \]

\[ R_p (\text{Ohm cm}^2) \]

\[ \text{Immersion time (days): } 0, 5, 10, 15, 20, 25, 30 \]

\[ \text{Immersion in 0.1M NaCl} \]

\[ \text{Std = from 170°C up to 210°C for 4 hours} \]
4EP-pPDA on anodized AA2024-T3

Barrier properties as a function of the amount of resin

Calculation of the CPE admittance of the hybrid layer

Used EEC:

\[ Y = \frac{1}{CPE_{hl}} + \frac{1}{R_s} + \frac{1}{CPE_b} + \frac{1}{R_p} + \frac{1}{R_b} \]

- Immersed in 0.1M NaCl
- Barrier properties as a function of the amount of resin
- Calculation of the CPE admittance of the hybrid layer
- Used EEC:
  \[ Y = \frac{1}{CPE_{hl}} + \frac{1}{R_s} + \frac{1}{CPE_b} + \frac{1}{R_p} + \frac{1}{R_b} \]

Std = from 170°C up to 210°C for 4 hours
4EP-pPDA on anodized AA2024-T3

Hypothesis: resistive pathways = consequence of the very high curing temperature

- four different samples:
  - 5% cured with temperature limited at 170°C for 4 hours
  - 5% fully cured from 170°C up to 210°C for 4 hours
  - 10% cured with temperature limited at 170°C for 4 hours
  - 10% fully cured from 170°C up to 210°C for 4 hours

- EIS

GDOES:
Same behavior as for fully cured resin
= Full impregnation of the oxide layer by the resin
4EP-pPDA on anodized AA2024-T3

Impact of the curing temperature

After 1 day

In NaCl 0.1M

1 month

Limited curing temperature

- More capacitive
- Higher modulus
- More durable properties
- Only one time constant

Limits resistive pathways
Conclusion

• Both benzoxazine monomers show very good compatibility with the anodic layer

• Resulting electrochemical properties are strong and durable

• 4EP-pPDA plays the role of an organic sealant for the anodic layer rather than a proper coating

• Obtained barrier properties are directly related to the amount of resin loaded in the porous structure

• Limiting the curing temperature allows to reduce the formation of resistive pathways and increases the barrier properties
Thanks !