The History of Hard Coat

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International Hard Anodizing Association
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Agenda for presentation

- History
- Processes – from the beginning until today
- Various processes and their final properties
- General perspectives on how the Hard Coat process works
- Hard Coat vs. conventional anodizing
- Summary
History of Hard Coat

• Early work showed that cooling of sulfuric electrolyte could slow down dissolution creating thick coatings up to 10 mil (250 µm)

• Thickness is influenced by
  – Solution composition
  – Temperature
  – Current density
  – Composition of alloy

• Early 1950´s
  – M.H.C. process, Alumilite™, Hardas – followed by many others
Hard coating

- When a demand for combination of weight saving with high performance and wear resistance is found
- Primary characteristic
  - Hardness
  - Wear resistance

With courtesy of Öhlins
Hard coating

- Mechanical applications
  - Technical applications
- More complex aluminium alloys
  - Higher strength
  - Better machinability
- "Mis" coloring of the aluminium oxide
Anodizing Process

• Pretreatment
• Process Type III
  – Sulfuric acid based electrolyte
  – Any process operation to produce a heavy dense coating

• Green process
Hard Coat processes

- Martin M.H.C.
- Alcoa Alumilite
- Hardas
- Alcoa 225/226
- Alcoa 725/726
- Reynolds MAE
- High Copper Alloys I and II

All variations of sulfuric based electrolytes
<table>
<thead>
<tr>
<th>Process</th>
<th>Electrolyte</th>
<th>Current Density a.s.f (a.s.d.)</th>
<th>Voltage</th>
<th>Temp. F (°C) ±2</th>
<th>Time (Minutes)</th>
<th>Seal Options</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcoa Alumilite</td>
<td>7% (77 g/l) sulfuric acid + 1% - 4% oxalic acid</td>
<td>24 – 30 (2.6 - 3.9)</td>
<td>60 - 80 DC</td>
<td>30 - 35 (-1 to 2)</td>
<td>approx. 1.0 mil/hour</td>
<td>None required</td>
<td>Produces very hard, but relatively rough coatings.</td>
</tr>
<tr>
<td>Alcoa 225/226</td>
<td>12% (132 g/l) sulfuric acid + 1% (10 g/l) oxalic acid</td>
<td>36 (3.9)</td>
<td>40 - 50 DC</td>
<td>50 (10)</td>
<td>20 - 40</td>
<td>None required</td>
<td>Coating builds @ 1.0 mil/20 minutes. Higher dielectric obtained w/duplex seal of NiAc then, sodium dichromate.</td>
</tr>
<tr>
<td>Alcoa 725/726</td>
<td>Same as 225/226</td>
<td>Same</td>
<td>Same</td>
<td>Same</td>
<td>Same</td>
<td>Same</td>
<td>For cast alloys compatible with anodizing.</td>
</tr>
<tr>
<td>Martin (MHC)</td>
<td>15% (165 g/l) sulfuric acid</td>
<td>24 - 30 (2.6 - 3.9)</td>
<td>40 - 60 DC</td>
<td>32 (0)</td>
<td>1.5 mil / hour</td>
<td>None required</td>
<td>For thicker coatings on certain alloys than Alcoa Alumilite process. Higher dielectric obtained w/duplex seal of NiAc, then sodium dichromate.</td>
</tr>
<tr>
<td>Reynolds MAE</td>
<td>18% - 22% (200-240 g/l) sulfuric acid + 2% - 4% (vol) glycerine and glycolic acid</td>
<td>24 - 30 (2.6 - 3.9)</td>
<td>30 - 40 DC</td>
<td>70 (21)</td>
<td>1.0 mil/30 minutes @ 24 a.s.f.</td>
<td>Optional. Depends on application</td>
<td>Produces clear hard coatings capable of adsorbing dye. 1:1 mixture of glycerine and glycolic acid = 2 parts (vol) glycerine + 3 parts (vol) glycolic acid.</td>
</tr>
<tr>
<td>High Copper Alloys I</td>
<td>15% (165g/l) sulfuric acid</td>
<td>15 (1.6) 10 - 15 minutes, then 24-30 (2.6-3.9) balance</td>
<td>40 - 50 DC</td>
<td>50 (10)</td>
<td>2.0 mil in 90 minutes</td>
<td>None required</td>
<td>Many processing techniques and variables are possible to achieve desired results</td>
</tr>
<tr>
<td>High Copper Alloys II</td>
<td>23% (250 g/l) sulfuric acid</td>
<td>20 - 24 (2.2 - 2.6)</td>
<td>30 - 40 DC</td>
<td>30 - 50 (-1 to 10)</td>
<td>variable</td>
<td>As desired</td>
<td></td>
</tr>
<tr>
<td>Hardas</td>
<td>10% - 20% (110-220 g/l) sulfuric acid</td>
<td>Up to 90</td>
<td>25 - 30 (4 to -1)</td>
<td>&quot;Rapid film growth&quot;</td>
<td>None required</td>
<td>Used primarily in U.K.</td>
<td></td>
</tr>
</tbody>
</table>
Martin (MHC)

- **Electrolyte**
  - 15% (165 g/l) sulfuric acid
- **Current density**
  - 24 – 30 asf (2.6 – 3.9 asd)
- **Voltage**
  - 40 - 60 V DC
- **Temperature**
  - 32 F (0C)
- **Time**
  - 1.5 mil /hour
- **Seal option**
  - None required

For thicker coatings on certain alloys than Alcoa Alumilite process. Higher dielectric obtained w/duplex seal of NiAc, then sodium dichromate.
Alcoa Alumilite

- **Electrolyte**
  - 7% (77 g/l) sulfuric acid + 1-4% oxalic acid
- **Current density**
  - 24 – 30 asf (2.6 – 3.9 asd)
- **Voltage**
  - 60 - 80 V DC
- **Temperature**
  - 30 - 35 F (-1 - 2C)
- **Time**
  - 1 mil /hour
- **Seal option**
  - None required

Produces very hard, but relatively rough coatings.
Hardas

- **Electrolyte**
  - 10 – 20% (110 - 220 g/l) sulfuric acid

- **Current density**
  - 12 – 60 asf (1.3 – 6.5 asd) and 6 – 30 asf (0.6 – 30 asd) AC

- **Voltage**
  - 90 V DC

- **Temperature**
  - 25 - 30 F (-4 - -1C)

- **Time**
  - “Rapid film growth”

- **Seal option**
  - None required

Used primarily in U.K.
Alcoa 225/226 (Wrought alloys)

- Electrolyte
  - 12% (132 g/l) sulfuric acid + 1% (10 g/l) oxalic acid
- Current density
  - 36 asf (3.9 asd)
- Voltage
  - 40 - 50 V DC
- Temperature
  - 50 F (10C)
- Time
  - 20 – 40 min
- Seal option
  - None required

Coating builds @ 1.0 mil/20 minutes. Higher dielectric resistance obtained with duplex seal of NiAc compare to sodium dichromate.
Alcoa 725/726 (Castings)

- Electrolyte
  - 12% (132 g/l) sulfuric acid + 1% (10 g/l) oxalic acid
- Current density
  - 36 asf (3.9 asd)
- Voltage
  - 40 - 50 V DC
- Temperature
  - 50 F (10C)
- Time
  - 20 – 40 min
- Seal option
  - None required

For cast alloys compatible with anodizing.
Reynolds MAE

- **Electrolyte**
  - 18 - 22% (200 - 240 g/l) sulfuric acid + 2 – 4% (vol) glycerine and glycolic acid
- **Current density**
  - 24 – 30 asf (2.6 – 3.9 asd)
- **Voltage**
  - 30 - 40 V DC
- **Temperature**
  - 70 F (21C)
- **Time**
  - 1.5 mil / 30min @ 24 asf
- **Seal option**
  - Optional, depends on application

Produces clear hard coatings capable of adsorbing dye. 1:1 mixture of glycerine and glycolic acid = 2 parts (vol) glycerine + 3 parts (vol) glycolic acid.
High Copper Alloys I

- **Electrolyte**
  - 15% (165 g/l) sulfuric acid

- **Current density**
  - 15 asf (1.6 asd) 10 – 15 min, then 24 – 30 asf (2.6 – 3.9 asd)

- **Voltage**
  - 40 - 50 V DC

- **Temperature**
  - 50 F (10C)

- **Time**
  - 2 mil / 90 min

- **Seal option**
  - None required

Many processing techniques and variables are possible to achieve desired results.
High Copper Alloys II

- **Electrolyte**
  - 23% (250 g/l) sulfuric acid

- **Current density**
  - 20 – 24 asf (2.2 – 2.6 asd)

- **Voltage**
  - 30 - 40 V DC

- **Temperature**
  - 30 - 50 F (-1 - 10C)

- **Time**
  - Variable

- **Seal option**
  - As desired
Properties of Hard Coat

• Corrosion resistance
  – Higher than type II (NSS – 1000 hours type II/3000 hours type III)

• Wear resistance
  – Big improvement

• Adhesion
  – Depending on structure of the oxide layer
Properties of Hard Coat

- **Dielectric**
  - 2 mil hard coat will fail around 1.5-2.0 KV, sometimes higher

- **High temperature resistance**
  - Short period of time

- **Dyed**
  - Can be done but more difficult than coloring of type II
Defects and Deficiencies

- Crazing
- Blisters
- Surface Roughness
Defects and Deficiencies

- Corner Defects
- Dimension changes
Type III vs Type II

Sulphuric acid anodizing

- Type II (anodizing)
  - 15 – 20% Sulphuric acid
  - Porous layer
  - Thickness 0.2 – 1 mil (5 – 25 µm)

- Type III (hard anodizing)
  - Lower temperature
  - More compact layer
  - Thickness 1 – 2 mil (25 – 50 µm)
Meet specifications – type III

- MIL-A-8625F (new rev on its way)
- AMS 2468G (still in use)
- ISO 10074:2010 (replaced ISO 5599)
MIL-A-8625, F

- Type III coatings
  - Class 1 (non-dyed, no seal)
  - Class 2 (dyed and sealed)
- Thickness of coating
  - Nominal thickness 2 mils (50µm)
MIL-A-8625, F

- **Weight of coating**
  - Unsealed Type III coatings min. of 4320 mg/ft²

- **Abrasion resistance**
  - Max. wear 3.5 mg/1000 cycles Cu 2% or higher, 1.5 mg/1000 cycles for all other alloys
Sealing of Hard Coat

- **Class 1** shall be unsealed
  - To avoid decrease in wear and abrasion resistance
- **Class 2**
  - Improve corrosion resistance
  - Permitting reduced abrasion resistance
- **Solid film lubricants**
Some of the challenges

- Color variation
  - Light to dark gray
- Burning
- More compact
  - Higher voltage
Some of the challenges

• Brittle aluminum oxide
• Difficult to color
  – Narrow pores
• Base metal
  – High strength
Burning

- Pore
- Barrier layer
- Controlled formation
- Un-controlled formation
- Accumulation of heat
Pulse anodizing

- Different pulse anodizing methods
  - Low frequency
    - Seconds to minutes
  - High frequency
    - Milliseconds
  - Alternating frequencies
    - Cathodic and anodic
- Difficult to hard anodize certain alloys
  - Copper
  - Silicon
Effect of alloying elements on the thickness/coloring

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Thickness</th>
<th>Formation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi7Mg</td>
<td>46 µm</td>
<td>0.51 µm/min</td>
</tr>
<tr>
<td>AlSi5Mg</td>
<td>39 µm</td>
<td>0.43 µm/min</td>
</tr>
<tr>
<td>AlSi0.5Mg</td>
<td>50 µm</td>
<td>0.56 µm/min</td>
</tr>
<tr>
<td>AlCu4Ti</td>
<td>27 µm</td>
<td>0.30 µm/min</td>
</tr>
<tr>
<td>AlZn5</td>
<td>52 µm</td>
<td>0.58 µm/min</td>
</tr>
</tbody>
</table>
Assemble component

- Different alloy in same component
Summary

• Coloring of Hard Coat
• Certification
• Less energy consumption
• When to use the process
• Different properties
• Green process