Influence of Al Microstructure on Hard Anodising Quality – Profile Material

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IHAA Symposium, 25th of September 2014, New York
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  - Temperature Overview of Process Chain

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- Hard Anodising
  - Alkaline Etching
  - Formation of anodic oxide coating
Process Parameters vs. Quality

- The quality of hard anodised profile material is influenced by the various production / process parameters
  - Production parameters of Al profiles
  - Production parameters of the hard anodising process

- The key words through the whole process chain are temperature and time: It is important to control the time on temperature during the different production steps
Temperature overview of Process chain

Extrusion

Casting
Homogenisation
Preheating
Cooling
Forced air or water

Anodising
(anodic oxide thickness = 20 µm)

Degreasing
Etching
Desmutting
Anodising
Sealing

Temperature (°C)

~700°C
~580°C
20-200 °C/hr
440-490°C
185°C
5 hrs

0.5-1 min total
with ~5 sec in the
deformation zone

Critical temperature range in the
process route with respect to the
precipitation of coarse Mg₂Si
phase particles

T_solvus

TIME

5-15 min
10-15 min
2-3 min
40-60 min
60 min

5 hrs

(5) NEF 2008, 2008-05-20
Main Alloy Groups

- **Al + Mn**: 3000 (Manganese) - Good extrudability and formability
- **Al + Mg**: 5000 (Magnesium) - Marine corrosion resistant, Low extrudability
- **Al + Mg + Si**: 6000 (Magnesium + Silicon) - Good combination of extrudability and mechanical properties
- **Al + Zn**: 7000 (Zinc) - High strength
# Main Alloy Groups

**International nomenclature for Wrought Aluminium Alloys**

<table>
<thead>
<tr>
<th>1XXX</th>
<th>Aluminium of <strong>99%</strong> purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2XXX</td>
<td>Aluminium and <strong>copper</strong> alloys</td>
</tr>
<tr>
<td>3XXX</td>
<td>Aluminium and <strong>manganese</strong> alloys</td>
</tr>
<tr>
<td>4XXX</td>
<td>Aluminium and <strong>silicon</strong> alloys</td>
</tr>
<tr>
<td>5XXX</td>
<td>Aluminium and <strong>magnesium</strong> alloys</td>
</tr>
<tr>
<td>6XXX</td>
<td>Aluminium, <strong>Mg and Si</strong> alloys</td>
</tr>
<tr>
<td>7XXX</td>
<td>Aluminium, <strong>Zn and Mg</strong> alloys</td>
</tr>
<tr>
<td>8XXX</td>
<td>Other alloys</td>
</tr>
</tbody>
</table>

Each alloy is described by a 4 digit number + a letter and a number indicating its temper or condition
## Work and precipitation hardening

<table>
<thead>
<tr>
<th>Work hardening</th>
<th>Precipitation hardening</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1XXX</strong> Al</td>
<td><strong>Heat treatable</strong></td>
</tr>
<tr>
<td><strong>3XXX</strong> Al + Mn</td>
<td><strong>2XXX</strong> Al + Cu</td>
</tr>
<tr>
<td><strong>5XXX</strong> Al + Mg</td>
<td></td>
</tr>
<tr>
<td><strong>6XXX</strong> Al + Mg + Si</td>
<td><strong>6XXX</strong> Al + Mg + Si</td>
</tr>
<tr>
<td><strong>7XXX</strong> Al + Mg + Mg</td>
<td><strong>7XXX</strong> Al + Mg + Mg</td>
</tr>
<tr>
<td><strong>8XXX</strong> Al + other elements</td>
<td><strong>8XXX</strong> Al + other elements</td>
</tr>
</tbody>
</table>
## Temper designations

- Describes the basic heat treatment which influences material properties

### The most commonly used tempers for 6XXX extrusions

<table>
<thead>
<tr>
<th>Temper</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Extruded and air-cooled</td>
</tr>
<tr>
<td>O</td>
<td>Softened, annealed (350-500°C for 1-5 hrs)</td>
</tr>
<tr>
<td>T4</td>
<td>Solution heat treated and naturally aged (20°C for 5-10 days)</td>
</tr>
<tr>
<td>T5</td>
<td>Cooled from extrusion temperature and artificially aged (Typically 160-190°C for 4-10 hrs)</td>
</tr>
<tr>
<td>T6</td>
<td>Solution heat treated and artificially aged</td>
</tr>
</tbody>
</table>
AlMgSi extrusion ingot alloys used in Europe / USA

Only Si and Mg content shown
Principles for HA alloy designation system

- Based on Aluminium Association's (AA) four digit alloy code to describe alloy group + two digits to identify internal variants
- Last digit 0 or 5 is used for Hydro Aluminium (HA) standard alloys
- Letters in the AA alloy code are not included in the HA alloy code

- HA 6060 30
  - 4 digit AA alloy code
  - HA internal variant within 6060

- HA 6082 50
  - 4 digit AA alloy code
  - HA internal variant within 6082
## Alloys vs. Anodising quality

<table>
<thead>
<tr>
<th>HA Alloy</th>
<th>Protective Anodising</th>
<th>Colour Anodising</th>
<th>Bright Anodising</th>
<th>Hard Anodising</th>
</tr>
</thead>
<tbody>
<tr>
<td>1080</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>1060</td>
<td>E</td>
<td>VG</td>
<td>VG</td>
<td>E</td>
</tr>
<tr>
<td>1200</td>
<td>VG</td>
<td>VG</td>
<td>VG</td>
<td>E</td>
</tr>
<tr>
<td>2011</td>
<td>M-G</td>
<td>M-G*</td>
<td>U</td>
<td>G</td>
</tr>
<tr>
<td>2014</td>
<td>M</td>
<td>M*</td>
<td>U</td>
<td>G</td>
</tr>
<tr>
<td>2031</td>
<td>M</td>
<td>M*</td>
<td>U</td>
<td>G</td>
</tr>
<tr>
<td>3103</td>
<td>G</td>
<td>G</td>
<td>M</td>
<td>G</td>
</tr>
<tr>
<td>3105</td>
<td>G</td>
<td>G</td>
<td>M</td>
<td>G</td>
</tr>
<tr>
<td>4043</td>
<td>G</td>
<td>M*</td>
<td>U</td>
<td>G</td>
</tr>
<tr>
<td>5005</td>
<td>E</td>
<td>VG</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>5056</td>
<td>G</td>
<td>G</td>
<td>M</td>
<td>E</td>
</tr>
<tr>
<td>5083</td>
<td>G</td>
<td>G</td>
<td>M</td>
<td>G</td>
</tr>
<tr>
<td>5154</td>
<td>VG</td>
<td>VG</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>5251</td>
<td>VG</td>
<td>VG</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>5454</td>
<td>VG</td>
<td>VG</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>6061</td>
<td>VG</td>
<td>G</td>
<td>M</td>
<td>VG</td>
</tr>
<tr>
<td>6063</td>
<td>E</td>
<td>VG</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>6082</td>
<td>G</td>
<td>G</td>
<td>M</td>
<td>G</td>
</tr>
<tr>
<td>6463</td>
<td>VG</td>
<td>VG</td>
<td>VG</td>
<td>VG</td>
</tr>
<tr>
<td>7020</td>
<td>G</td>
<td>G</td>
<td>M</td>
<td>G</td>
</tr>
</tbody>
</table>

- **E** = Excellent
- **VG** = Very good
- **G** = Good
- **M** = Moderate
- **U** = Unsuitable
- ***** = only suitable for dark colours
Mechanical properties

Strength of different Al alloys

Ultimate Tensile strength (MPa)

Al 3003 6060 6082 7020 2015 7075
# Recrystallisation of 6000 alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Recrystallisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6060 F22</td>
<td>Normally full RX</td>
</tr>
<tr>
<td>6060 F25</td>
<td>Full RX for thin-walled profiles</td>
</tr>
<tr>
<td></td>
<td>Partly RX for thick-walled profiles</td>
</tr>
<tr>
<td>6005 F27</td>
<td>Full RX for thin-walled profiles</td>
</tr>
<tr>
<td></td>
<td>Partly RX for thick-walled profiles</td>
</tr>
<tr>
<td></td>
<td>(more prone to partly RX than 6060 F25)</td>
</tr>
<tr>
<td>6082 F31</td>
<td>Partly RX. Normally, the surface area recrystallises whereas the bulk material has a deformation structure</td>
</tr>
</tbody>
</table>
Grain structure in billet and profile

Grain structure in billet

Grain structure in profile, deformation/ fibre structure

Grain structure in profile, recrystallised structure
Recrystallised layer + fibre structure, alloy 608250

Profile with fibre structure in the middle

Profile without fibre structure in the middle; recrystallised layer through the whole profile wall
Casthouse Operation - Casting

- Important to ensure thin Inverse Segregation Zone (ISZ) or “billet skin” during casting

- Good control of the cooling intensity is necessary to achieve thin ISZ / billet skin

- TiB grain refiner is added to control the grain size in the billet material
Casting Equipment – Gas slip

- Hot-top
- Distribution pan
- Liquid metal
- Water cooled mould
- Oil
- Gas
- Solid metal
- Direct water cooling
- Starter block
Casting Mould (Table)

- Distribution pan
- Trough
- Throttle valve
- Water jacket
- Extrusion ingot
- Self centering starting block
Variation in chemical composition

Distance from the billet surface [mm]

Fe, Si, Mg (wt %)

AA6060

Average thickness for ISZ = 80 μm
Casthouse Operation - Homogenising

- Important to ensure good transformation degree of AlFeSi particles: From beta-AlFeSi to alfa-AlFeSi
- Good transformation degree has impact on the extrudability and anodising properties (etching response)
- The size / distribution of intermetallic particles (e.g. MgSi) is influenced by time on temperature in the homogenising furnace and the cooling intensity in the cooling chamber
- The residual stress after casting is removed in the homogenising process
Microstructure of 608250 alloy

Inverse segregation zone

Mid radius sample
Microstructure: As cast and after homogenising

Microstructure in a 608250 alloy
(Mid radius samples)

As cast

After homogenisation
Grain structure in 608250 alloy

(Mid radius samples, polarised light)

As cast

After homogenisation
Extrusion Operation – Press
Extrusion Operation – Tool stack
Extrusion Operation - Preheating

Preheating of the billet material is carried out to:

- Dissolve MgSi particles. Poor dissolution of MgSi particles will have a negative impact on the profile strength. The result is a difference in etching response prior to anodising as well.
- Soften Al to make it possible to extrude without ruin the extrusion die (low deformation resistance)
- Typical preheating temperatures:
  - 606035: 470-480 C
  - 608250: 490-500 C
Extrusion Operation – Die design

- The die design has a big impact on the quality of the profiles.
- The die design has influence on the microstructure:
  - Grain size
  - Grain orientation (texture)
  - Inflow of ISZ / billet skin (with a different chemical composition compared to Al matrix). Inflow is also caused by too short butt-end.
- For hollow dies, it is important to optimize the web height and length (webs are used to keep the mandrel in a fixed position).
- Too long / thick webs may result in streaks in the profiles.
- Streaks are made more prominent by the hard anodising process (etching step).
- In general, streaks are caused by variations in profile wall thickness due to variation in grain size.
Extrusion Operation – Die Design

Seam weld lines visible after anodising
Extrusion Operation – Die Design

Metal flow pattern

Porthole

Web

Weld chamber

Aluminium billet

direction of extrusion

Mandrel

Body

Die Plate

Seam Welds
Extrusion Operation – Die Design

Mandrel

Seam weld

Billet material

Billet material
Extrusion Operation – Metal Flow

Two main flow paths:

Flow (a):
- $D_{Tb-Tc}$ too small
- Unbalanced container temperature
- Poor alignment of the press
- Poor die design

Flow (b):
- Too short butt end

The blue arrows indicate that flow (a) is dependent on extrusion process parameters.
Extrusion Operation – Metal flow

Five rings and one strip are inserted into the billet. When etched, the inserted material becomes black, providing an excellent contrast to the base material.

Starting material
Extrusion Operation – Metal Flow

Dirt and particles from billet surface can enter the section through

- **Forward flow**
- Inflow from the back end of the billet at the end of the press

Butt ends at different percentages extruded

67 % 77 % 85 % 91 %
Extrusion Operation – Butt end size

- Butt ends with narrow and wide inverse segregation zones

Etching:
- 20% NaOH
- 80% H₂O (70° C)
- Soak for 2 to 3 min
Extrusion Operation - Cooling

- When the profile comes out of the die, cooling needs to be carried out.
- The cooling intensity is dependent on the alloy composition. To ensure optimum mechanical properties after artificial ageing, the MgSi particles must be kept in solid solution.
- Hard alloys (e.g. 6082) need faster cooling than soft alloys (e.g. 6060).
- When re-heating occurs during cooling, a phenomenon called black spots / soft spots is generated. Black spots / Soft spots are not visible direct after cooling. The defect appears after alkaline etching during anodising process.
- Fast / Even cooling along the extrusion length is necessary to avoid black spots / soft spots.
Extrusion Operation - Stretching

- Proper stretching of the profiles ensures release of stress in the material in combination with correct geometry.
- Poor stretching may give crazing (fine network of cracks) after hard anodising.
- Stabilising heat treatment is beneficial to release stress (and to stop natural ageing).
Extrusion Operation - Ageing

- Time on temperature during artificial ageing ensures optimum mechanical properties
- MgSi particles are transformed during the ageing, and temper changes from T4 to T6
- Profiles in T4 are more susceptible for grainy appearance than in T6
Process Order for Hard Anodising

1. Degreasing (Alkaline or acid)
   - Temp: 20-70°C
   - Time: 5-15 min
   - Air agitation

2. Rinsing (1 or more steps)

3. Alkaline etching (NaOH)
   - Temp: 60-70°C
   - Time: 10-15 min
   - Conc: 50-70g NaOH/l

4. Rinsing (1 or more steps)

5. Desmutting (HNO₃/H₂SO₄)
   - Temp: room temp.
   - Time: 2-3 min
   - Air agitation

6. Rinsing (1 or more steps)

7. Hard Anodising (Sulphuric acid)
   - Temp: -5 to +5°C
   - Time: min/μm
   - Conc: 160-200g/l
   - I: 2-10 A/dm²
   - U: 15-50V

8. Rinsing (1 or more steps)

9. Impregnation
Alloy composition vs. Etching response

● The etching tank is the most important process step to reveal differences in surface appearance between different Al-materials / profiles as a consequence of different alloys or differences in particle structure due to process conditions (size / distribution of AlFeSi and MgSi particles)

● Differences in chemical composition result in differences in types of particles (cathodic or anodic vs. matrix), but also size and distribution of these intermetallic particles. This gives differences in etching response.

● Differences in etching response generate variations in gloss and appearance after etching and anodising
Alloying elements influence on etching response

- Si: In AlFeSi and MgSi particles which influence etching response (size / distribution; cathode vs. anode). Much Si (4000 alloys) gives a grey / dull surface appearance.

- Fe: In AlFeSi particles. Low (<0.13 %) Fe content gives a high gloss surface appearance after anodising (oxide thickness < 10 µm)

- Cu: Adding Cu (0.12-0.15%) gives a high gloss surface appearance after anodising. Fe content must be low at the same time to obtain max effect. Too much Cu gives a matt surface (low gloss).

- Mn: Adding Mn influences degree of transformation of beta-AlFeSi to alfa-AlFeSi (from oblong particles to round particles). AlFeSi particles influence extrudability and etching response. Mn influences size and distribution of MgSi particles. In addition, Mn inhibits grain growth (see also Cr).
Alloying elements influence on etching response

- Mg: In MgSi particles which influence the etching response. A lot of Si and Mg gives grey / dull surfaces after etching and anodising (e.g. 608250). Much Mg (5000 alloys) results in a good anodising quality.

- Cr: Added together with Mn to inhibit grain growth, i.e. generate thin recrystallised layers in the profile surface.

- Zn: Too much free (not reacted) zinc (Zn2+) in the etching tank may give grainy appearance. The free zinc is coming from the zinc in the alloy.

- Ti: Ti influences the grain size together with B. TiB is added during casting to generate optimal (reduced) grain size and to avoid centre cracks in the billet.
Microstructure vs. Etching response

- Grain sizes: Recrystallised layers vs. Fibre structure layers

- Intermetallic particles: Cathodes and / or anodes in relation to Al matrix in alkaline etching solutions, pH:12-14

- Intermetallic particles: Size and distribution
Etching response vs. surface appearance after anodising

Matt surface appearance

Bright surface appearance
Effect of Mg and Si on gloss

Etching response of 6000 profiles is dependant on how Mg and Si exist prior to anodising:

- Mg and Si in solid solution => High gloss / Bright finish
- Reduction of Mg content => Gloss will increase
- Coarse MgSi particles => Low gloss / Matt finish
Gloss of anodised 6060 / 6063 profiles

% Si

Increasing gloss

% Mg

Preheating: 460 °C - Ageing 195 °C
Air/Water cooling after the press
Effect of Fe content on gloss after anodising

Anodised profile of alloy 6060 T6
Influence of Cu content on gloss

Anodised profile in alloy 6463 - T6

Precipitation of AlCu particles
Grainy appearance / Spangling
Effect of Zn: Grainy appearance
Topography (WLI) of selected grains
Inverse pole figures of the selected grains

Gray Scale Map Type: <none>

Color Coded Map Type: Inverse Pole Figure [001]

Aluminum

Boundaries: Rotation Angle

<table>
<thead>
<tr>
<th>Min</th>
<th>Max</th>
<th>Fraction</th>
<th>Number</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°</td>
<td>180°</td>
<td>0.666</td>
<td>1421</td>
<td>7.11 mm</td>
</tr>
<tr>
<td>5°</td>
<td>15°</td>
<td>0.071</td>
<td>117</td>
<td>666.00 microns</td>
</tr>
</tbody>
</table>

*For statistics - any point pair with misorientation exceeding 2° is considered a boundary.
Total number = 1640, total length = 8.20 mm
Zn-> Grainy appearance

Grainy appearance is most likely controlled by the following phenomena:

- Amount of free Zn (Zn2+) in the etching tank (from Zn in the alloy)
- Grain orientation in the surface of Al profiles
- Selective etching in the etching tank controlled by:
  - Grain orientation
  - Selective precipitation / plating of Zn on preferential grains (depending on grain orientation and amount of free Zn)
Summary:
Alloys vs. Etching response => Anodising appearance

Etching response is controlled by:

- Chemical composition: Amount of different elements
- Grain size
- Grain orientation
- Type of (intermetallic) particle
- Size and distribution of the different particles
- Amount of free Zn (Zn2+) in the etching tank
- Selective / Preferential etching (as a consequence of grain orientation)
- Selective precipitation / plating of Zn (as a consequence of grain orientation)
- Temperature and time in the etching tank
- Concentration of caustic (NaOH) and Al
- Type and amount of etch additive
Etching – Black Spots / Hot Spots

Black spots on both outer and inner profile surface

Consequence of current defect: 50% reduction in strength!
Black / soft spots – Cooling conditions

Consequence of current defect: 50% reduction in strength!
Black spots – Root causes and actions

- **Root causes:**
  - Variation in cooling intensity / re-heating on the run-out table or in the quench box during dead cycle

**Actions:**
- Ensure even / good cooling intensity along the extrusion length
- Avoid use of wet kevlar rolls on the run-out table
- Avoid leakage of water in the quench box during dead cycle
Crazing pattern in anodised profile surface
Crazing – Root causes

Root causes:

● Stress generated in the profiles during extrusion and cooling
● Stress introduced to the Al profile surface due to machining generates more susceptible material for crazing
● Stress produced in the anodic oxide coating when profiles are transferred between tanks with significant variation in temperature due to difference in thermal expansion coefficient between the anodic oxide coating and Al
● The defect is enhanced by high current densities, low electrolyte temperatures and thick oxide films (hard anodising conditions)
Crazing- Actions to avoid crazing

Actions:

- Cooling of profiles should be carried out without introducing stress in the material microstructure.
- Ensure proper stretching of the profiles after cooling.
- Carry out stabilising heating of the machined profiles to even out stress in the material (e.g. 130 °C for 40 minutes).