Surface Modification II *

*Modifications with changing composition of the surface

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- Chemical or electrochemical transformation processes which form phosphates, chromates and oxides on the surface (conversion coatings)
- Anodic oxidation (Anodizing)
- Micro arc oxidation (MAO)
- Thermochemical diffusion heat treatments: includes diffusion of C,N,B (interstitials), Al, Cr or Si elements through alloy surface at high temperatures.
- Ion implantation
- Laser melting + alloying

Phosphate chemical conversion coatings

Phosphate coating is a treatment of iron, steel, galvanized steel or aluminium with phosphoric acid and other chemicals. In this process there is a chemical reaction occurs between phosphoric acid and metal surface.

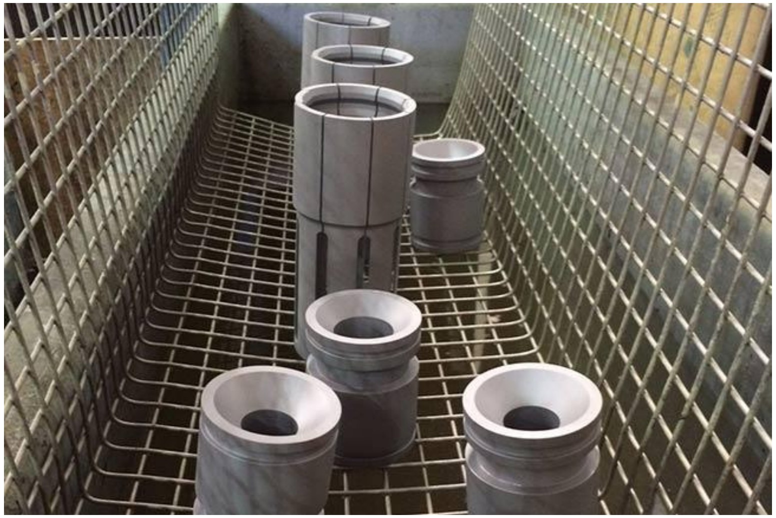
<u>A protective crystalline phosphate layer forms.</u>

Control factors on crystalline structure, weight and penetration thickness of phosphate coatings:

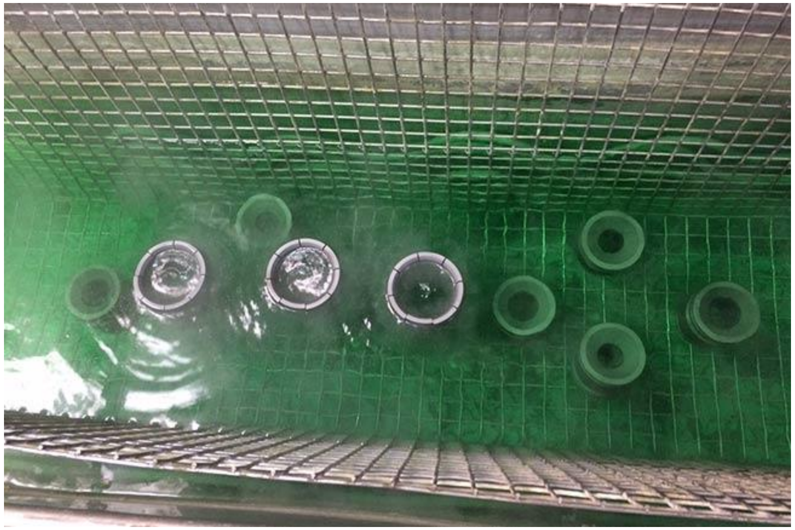
- Cleaning technique before the process
- Using activated rinse water which includes Ti and other metallic compounds
- Application technique of solution
- Temperature, concentration and process time
- Modification of chemical composition of phosphate solution

Properties of phosphate coatings

- Thicknesses of phosphate coatings are between 3-50 μm.
- It is especially used to provide a substrate for painting.
- To form substrates for anti-oil and anti corrosive (anti-rust) materials.
- Temporary resistance for non-severe corrosions.
- To form substrates for adhesives which are used in plastic-metal laminates or rubber-metal applications.



Before treatment



During treatment

After treatment

Chromate chemical conversion coatings

These transformation coatings occur with chemical and electrochemical processes of metals or metallic coatings in a solution which includes Cr^{+6} ions and other compounds.

It is applied for:

- Increase corrosion resistance of painted or unpainted surfaces.
- Improve adherence of paints (dyes) or other organic materials.
- Provide decorative appearance on metallic surfaces.

- Chromate chemical coating is used as finish process for Al, Zn, Steel, Mg, Cd, Cu, Sn, Ni, Ag and other substrates.

- Chromate coating can be applied with dipping and spraying. Electrostatic spraying or anodized deposition are also applied.

- Chromate conversion on aluminium is called alodine.

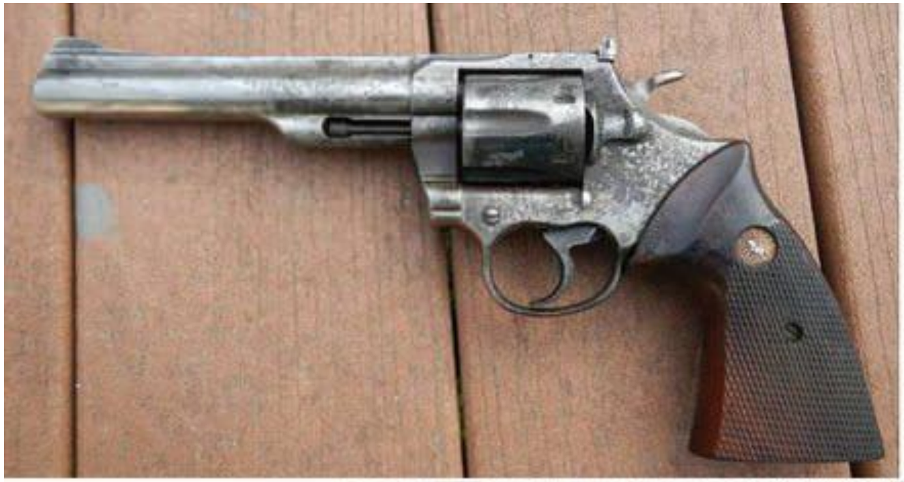
Zinc chromate ($ZnCrO_4$) conversion coating on small steel parts.

Oxide coating

<u>Gun-bluing:</u> Coating of gun parts with blue-black coloured oxides.

- These oxides somewhat increase corrosion and wear resistance of parts also provide decorative appearance

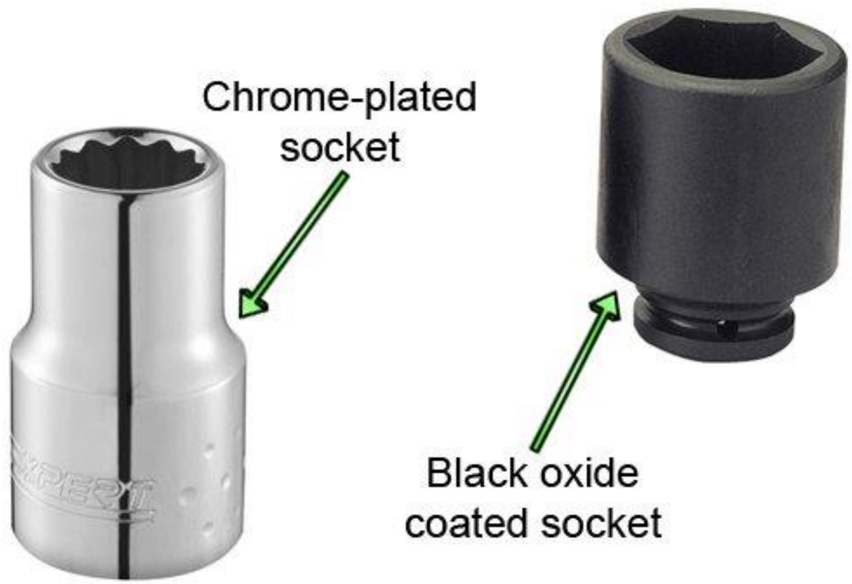
- It is a kind of passivation process for protect steels against to corrosion.




TROOPER MK V

Black oxide coating

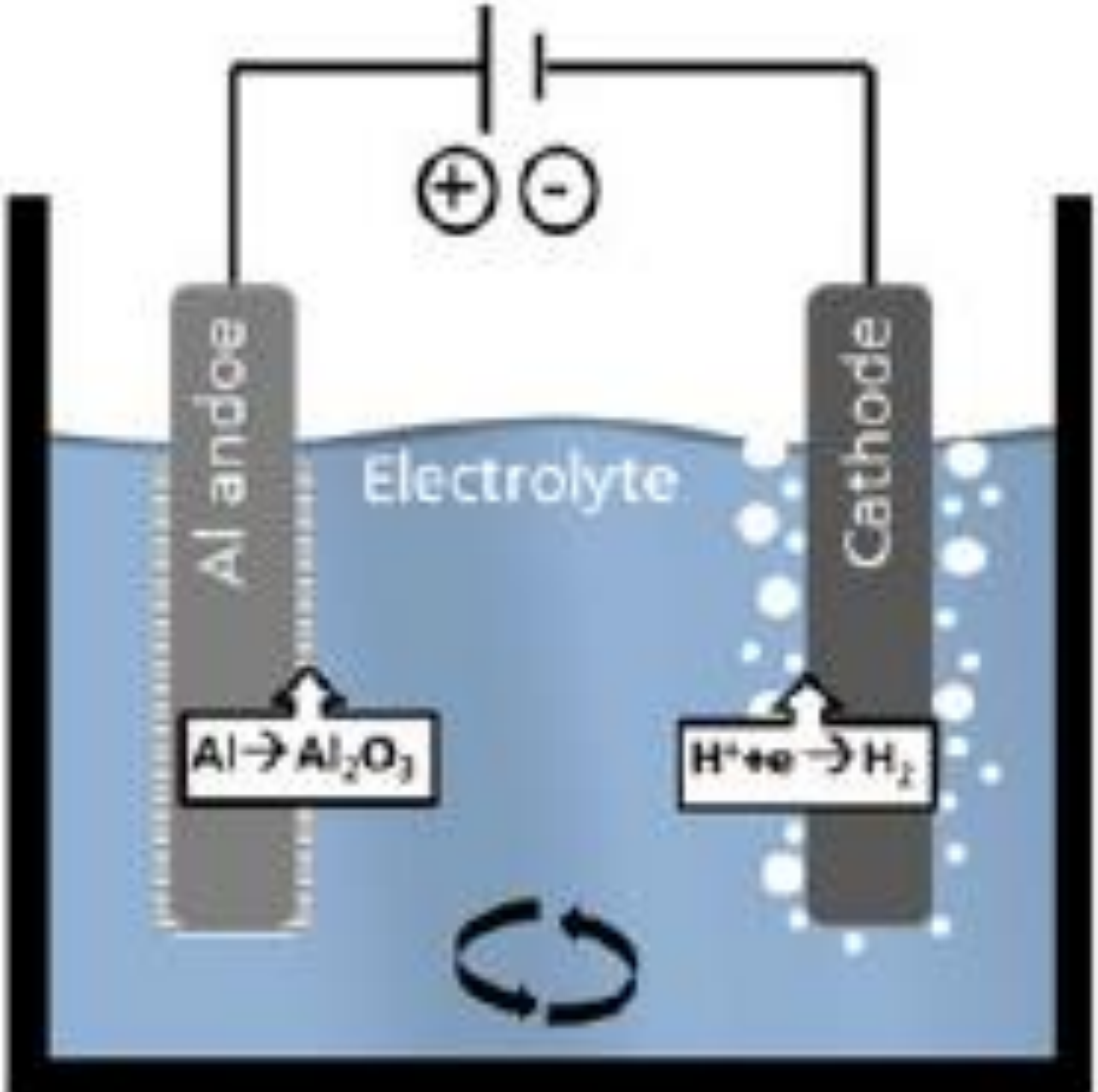
- Fe_3O_4 layer forms on the surface.
- Fe based materials are deep into sodium hydroxide or nitrides solution.
- To increase corrosion resistance, oil infiltration is carried out to this layer.
- It can be used for Zn and Ag soldering of Fe based, Cu and Cu based alloys.


Chrome-plated
socket
Black oxide
coated socket

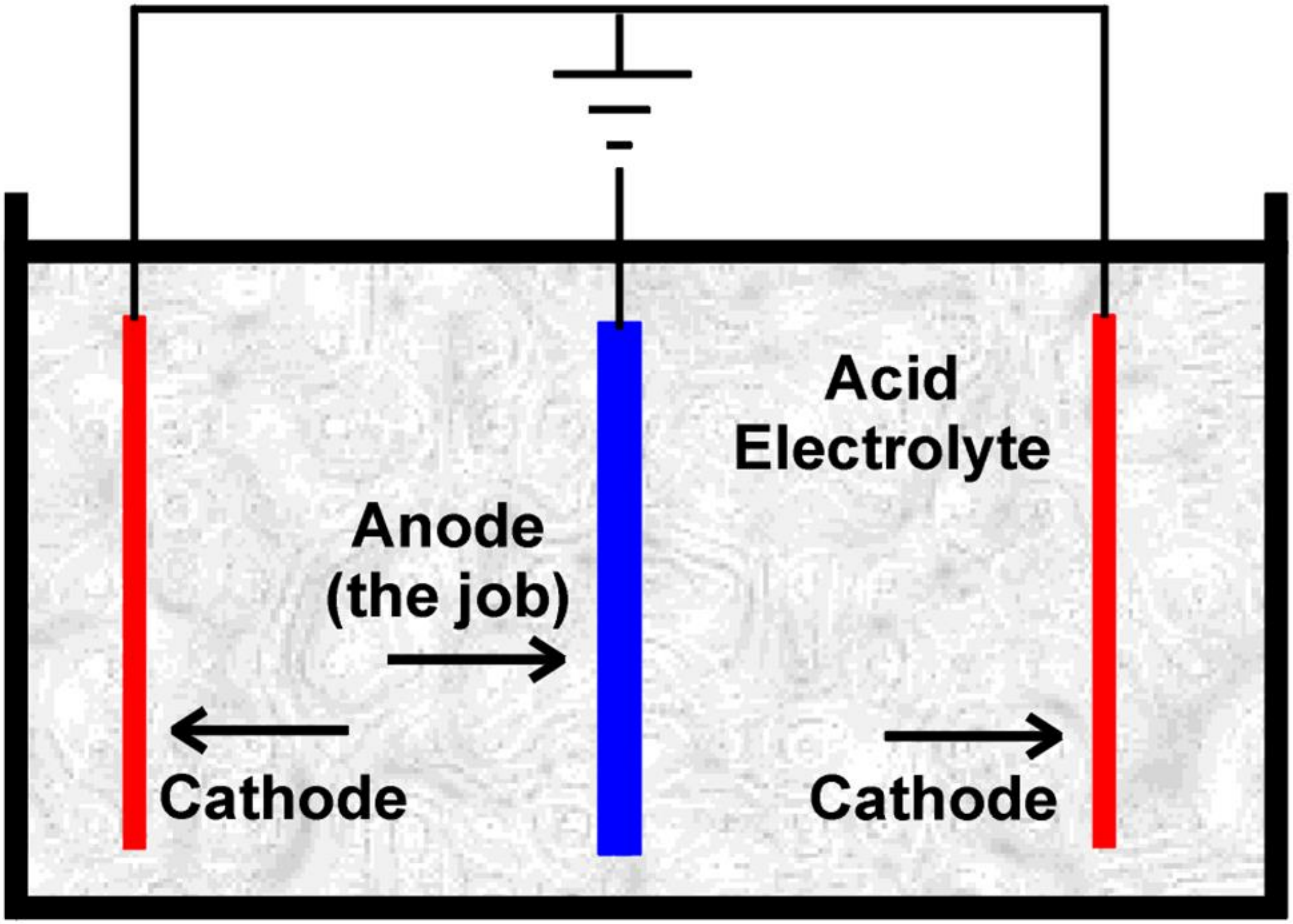
Anodic oxidation (Anodizing) (Eloxal* Coating)

- It is a process of formation oxide layer or stabilize and thicken existing oxide layer on metallic surfaces which are connected to electrolytic circuit as an anode.
- The most applicable metal is Al. Also it is applied to Cu, Ti, Cd, Fe, Mg, Zn, Zr.
- Anodizing causes wide range changings on surface properties of Al. Thus it is the most using metal for anodizing in industry.

** Electrolytic Oxidation of Aluminium*


Al andoe
Electrolyte
Cathode
$Al \rightarrow Al_2O_3$
$H^+ + e \rightarrow H_2$

Anodising



Properties of anodizing

- Formatted layer can be coloured, so it can be used in architectural applications.
- Protect surface against weather conditions.
- Increase wear resistance.
- Increase surface hardness.
- Improve adherence of paint, adhesive and lac layers.
- Improve insulation property.
- Change optical properties.

Anodizing processes

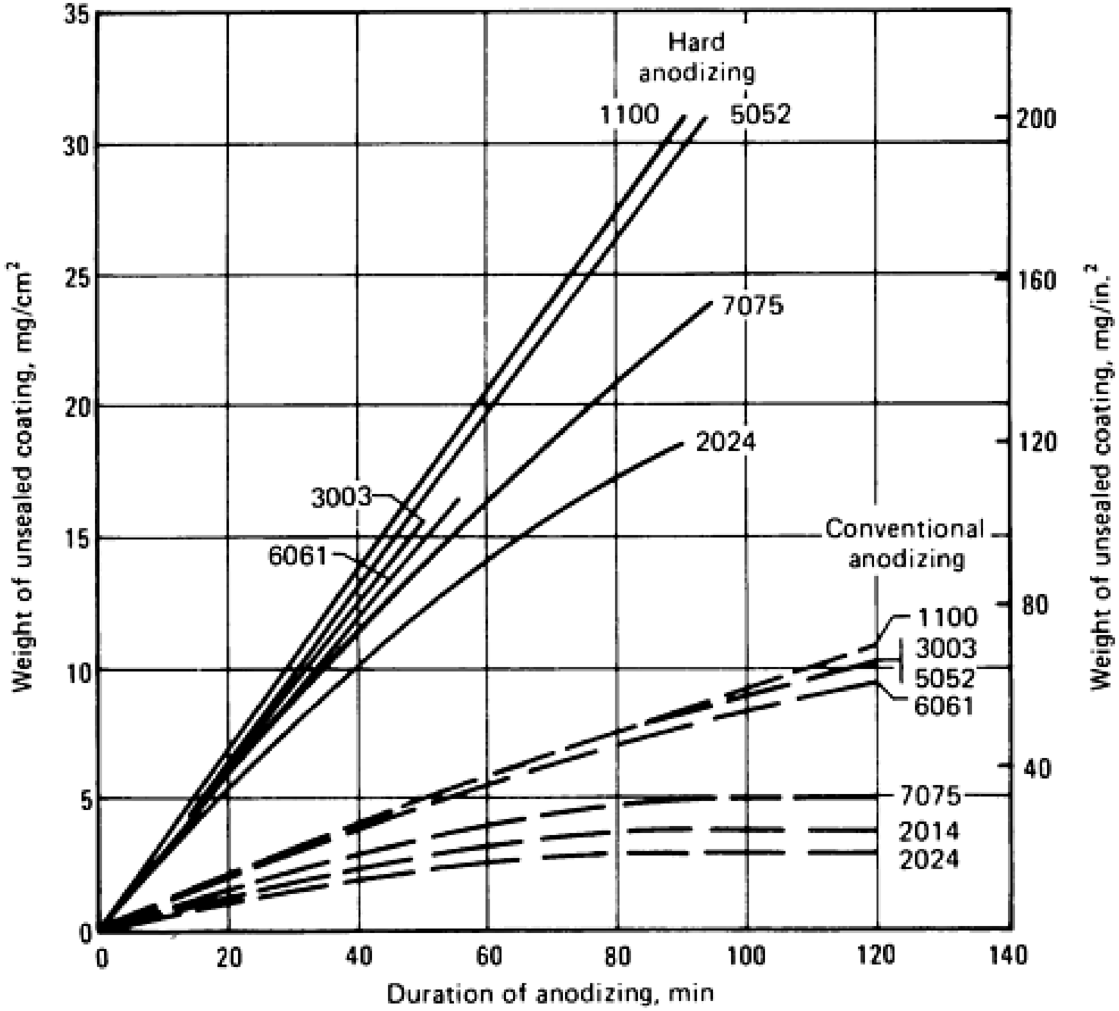
- There are three types of anodizing.

1. Chromic acid process: Use chromic acid (CrO_3) as electrolyte in 3 – 10 wt %. Due to the corrosive nature of sulfuric acid, chromic acid anodizing is the preferred process on components such as riveted or welded assemblies where it is difficult or impossible to remove all of the anodizing solution.

2. Sulfuric acid process: Use sulfuric acid as electrolyte in 1-20 wt %. Parts or assemblies that contain joints or recesses that could entrap the electrolyte should not be anodized in the sulfuric acid bath.

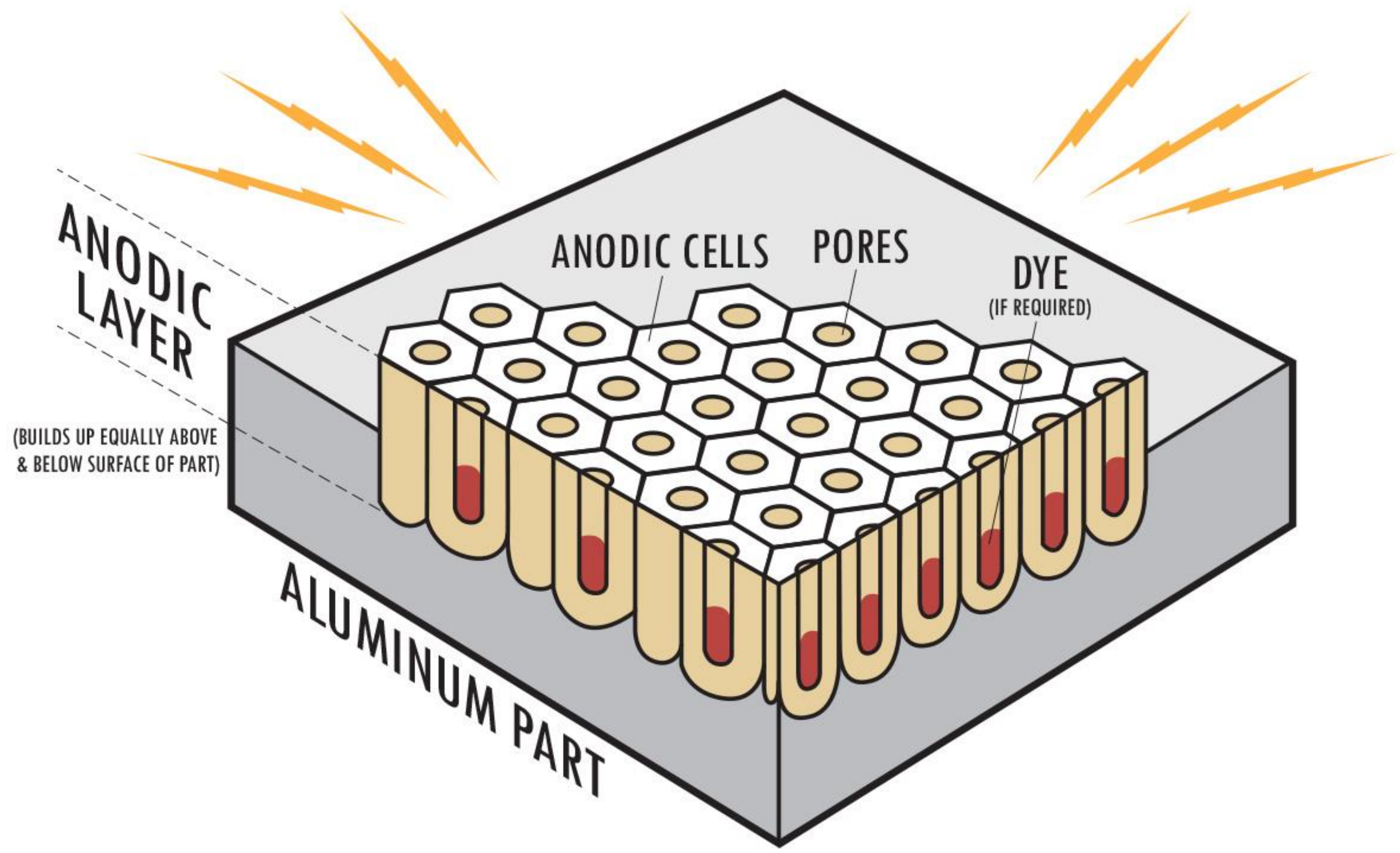
3. Hard anode process: Basically use sulfuric acid as electrolyte in 12-20 wt %. The primary differences between the sulfuric acid and hard anodizing processes are the operating temperature, the use of addition agents, and the voltage and current density at which anodizing is accomplished.

Hard anodizing, also referred to as hardcoat or type III anodizing, produces a considerably heavier coating then conventional sulfuric acid anodizing in a given length of time.

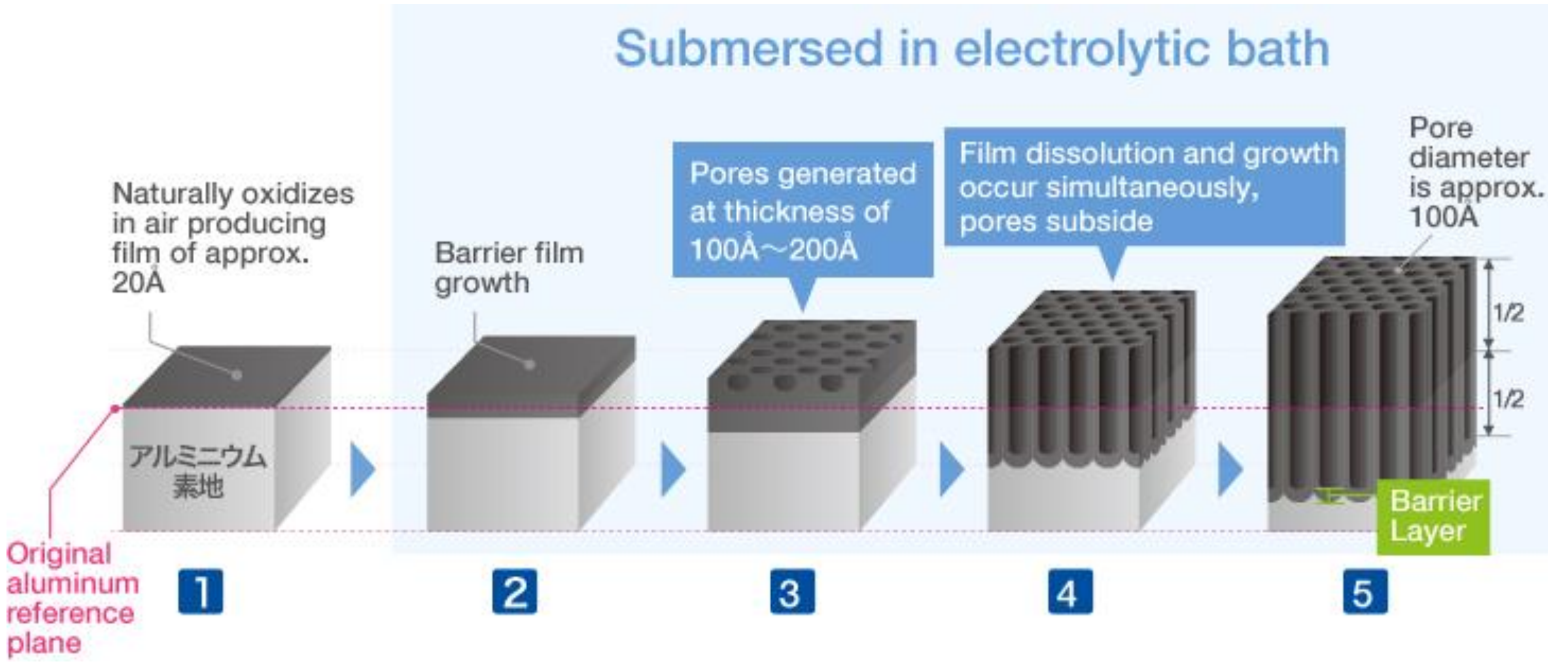


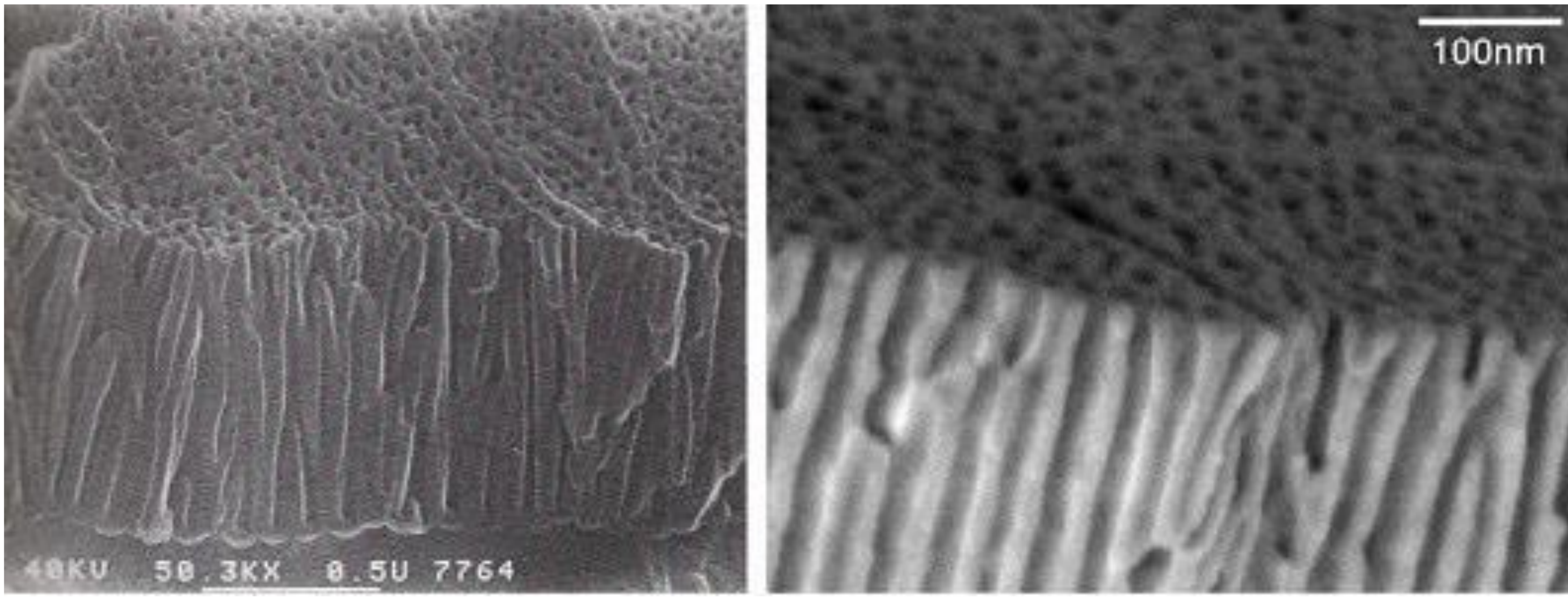
Effect of anodizing time on weight of hard and conventional anodic coatings. The hard anodizing solution contained (by weight) 12% H_2SO_4 and 1% $H_2C_2O_4$ (Oxalic acid) and was operated at 10 °C and 3.6 A/dm^2 The conventional anodizing solution contained 1% (by weight) H_2SO_4 and was operated at 20 °C and 1.2 A/dm^2

Structure of anodized aluminium surface



Formation of pore structure during anodizing





SEM images of anodic film section

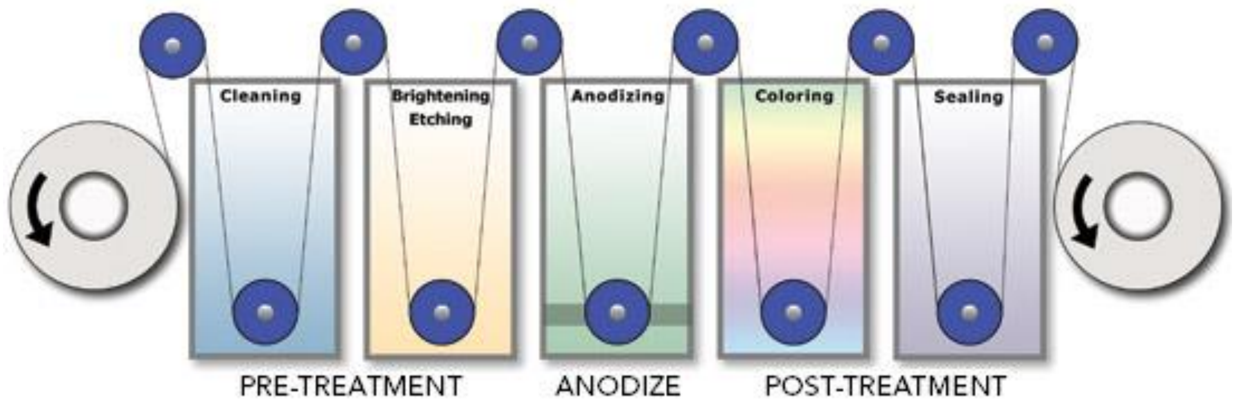
Sealing process: Closing the surface of cell cores.

- If planned, painting must be carried out before sealing.

Sealing techniques:

- Hot sealing (hydratation sealing): Parts are deep into water or vapour at 95 °C. Holding time is 2 minutes. per each μm thickness.
- Cold sealing (impregnation sealing): A solution is used at room temperature which includes deionized water, nickelsulphate and nickelchloride. Holding time is 1 minute per each μm thickness.
- Hot sealing is better than cold sealing.

ALUMINUM COIL ANODIZING LINE



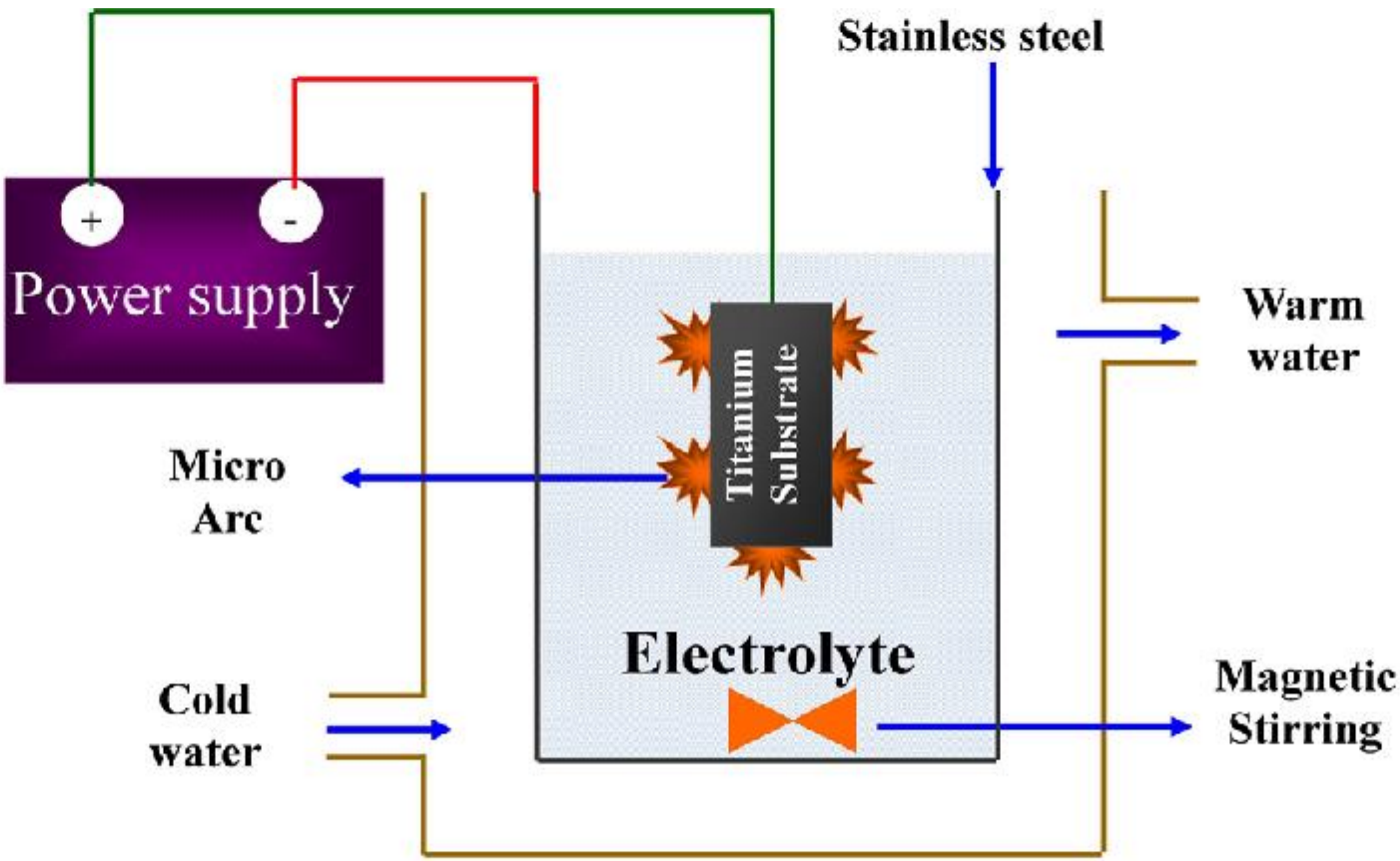
Micro arc oxidation (MAO)
Plasma electrolytic oxidation (PEO)
Electrolytic plasma oxidation (EPO)

- An electrochemical surface treatment process for generating oxide coatings on metals. It is similar to anodizing.
- But it employs higher potentials, so that discharges occur and the resulting plasma modifies the structure of the oxide layer.
- This process can be used to grow thick (tens or hundreds of micrometers), largely crystalline, oxide coatings on metals such as <u>aluminium, magnesium and titanium.</u>

- Because they can present high hardness and a continuous barrier, these coatings can offer protection against wear, corrosion or heat as well as electrical insulation.
- In addition, being a porous structure, this coating layer provides high bone ingrowth while formed on biomedical implants and fixations.
- The coating is a chemical conversion of the substrate metal into its oxide and grows both inwards and outwards from the original metal surface.
- Because it grows inward into the substrate, it has excellent adhesion to the substrate metal.
- A wide range of substrate alloys can be coated, including all wrought aluminum alloys and most cast alloys, although high levels of silicon can reduce coating quality.

The parameters affecting the coating quality:

- Voltage
- Current density
- Electrolyte type
- Process time
- Pulsate current
- Current type ie., AC or DC


Stainless steel
+
-
Power supply
Warm water
Titanium Substrate
Micro Arc
Electrolyte
Magnetic Stirring
Cold water

Video links

- https://www.youtube.com/watch?v=qFTYc8Bonl0
- https://www.youtube.com/watch?v=DsTI_eOOwc4
- https://www.youtube.com/watch?v=6zWed-NISUY
- https://www.youtube.com/watch?v=vuP4m6L95K4
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