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ELECTROLYTIC PLASMA PROCESSING for SURFACE MODIFICATION and ALTERNATIVE to ANODISING

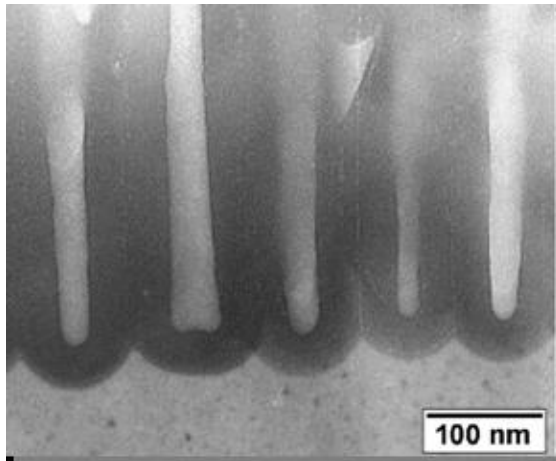
A.L. Yerokhin and A. Matthews

Contents

- Fundamentals of Electrolytic Plasma Processing as alternative to anodising
- Formation of structure and phase composition
- Mechanical properties (e.g. hardness and scratch adhesion)
- Tribological performance
- Corrosion performance
- Some application aspects

Thick Coatings on Light-weight Metals: Major Rivals (Al)

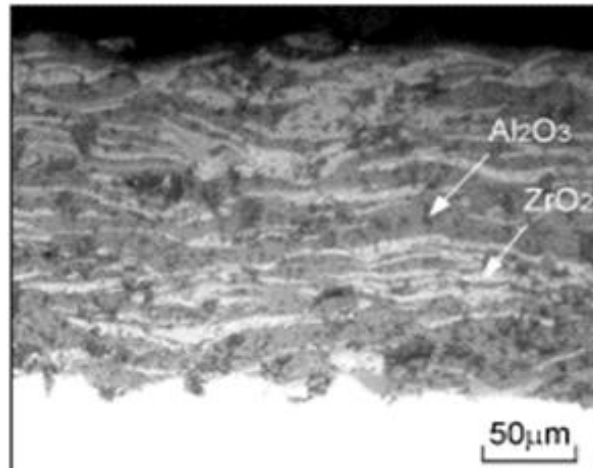
ANODISING



L. E. Fratila-Apachitei, et. al, *Electrochimica Acta*, 49 19 (2004) 3169

Thickness: 1 to 30 μm .
Phase composition: Mainly amorphous +hydrated alumina.
Morphology: Linear porosity + thin barrier layer.
Adhesion: Excellent

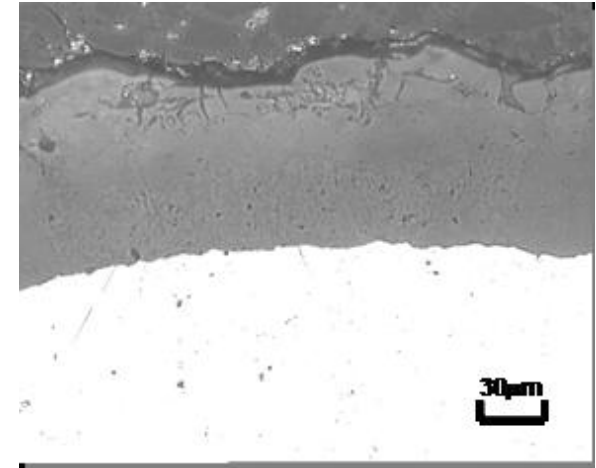
PLASMA SPRAY



T. Kuroda, *Vacuum*, 73 3-4 (2004) 635

Thickness: 0.05 to 2 mm.
Phase composition: α/γ - Al_2O_3 + toughening additions
Morphology: Lamellar layered structure with random porosity
Adhesion: Fair to good

PEO



A. Yerokhin, et al, *SCT*, (2004) to be published

Thickness: 10 to 300 μm .
Phase composition: Mainly α/γ - Al_2O_3
Morphology: Thin porous outer layer + dense functional inner layer
Adhesion: Excellent

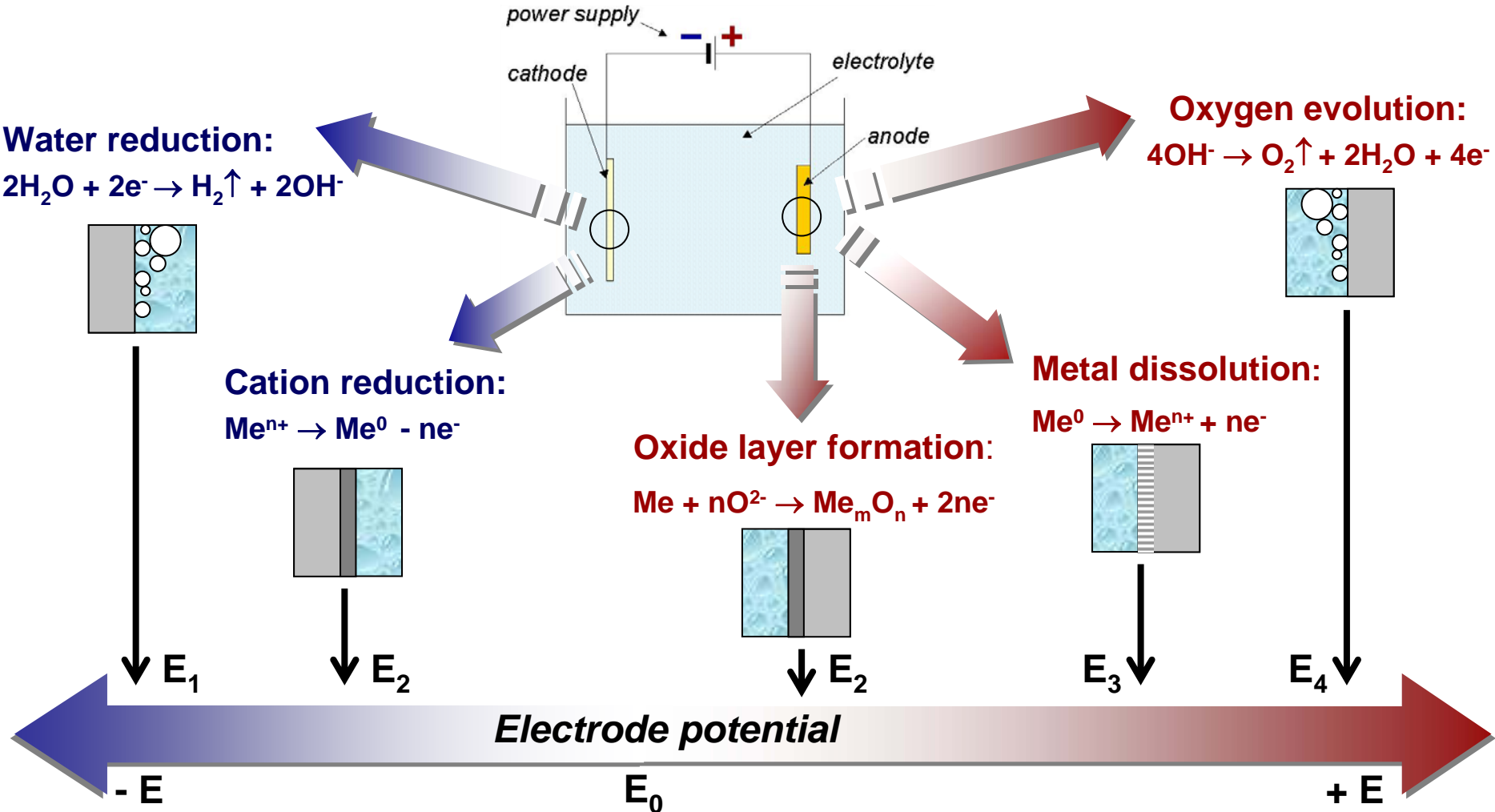
Definitions

- **PLASMA ELECTROLYTIC OXIDATION:** plasma-assisted electrochemical conversion of metal surface into oxide ceramic layer
- **METALS:** must be able to form semi-conductive surface oxide film ('valve' metals, e.g. Mg, Al, Ti, Zr, Nb, Hf, Ta, etc.)
- **ELECTROLYTES:** non-aggressive to the oxide film at PEO potentials (weak alkaline or acidic + passivating agents, e.g.:
 - silicates;
 - aluminates;
 - phosphates, etc.)
 - ✓ Ecologically friendly;
 - ✓ Inexpensive.

Definitions

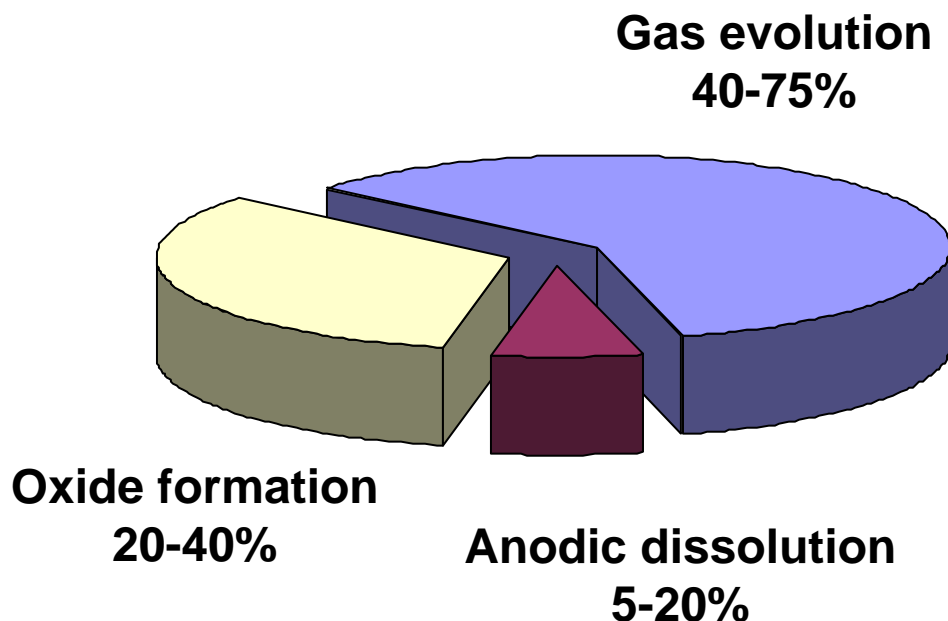
- **WORKING RANGES:** $I = 10^2$ to 10^4 A m⁻²
 $U = 10^2$ to 10^3 V
- **CURRENT MODES:**
 - **DC:** ($I = \text{const}$; $U = \text{const}$; $W = \text{const}$);
 - **AC:** amplitude modulated ($I^* = I$; $I^* \neq I$);
 - **Pulsed:**
 - unipolar (sine; square; triangular; trapezoidal)
 - bipolar:
 - Lower frequency (<10³ Hz)
 - Higher frequency (10³ to 10⁴ Hz)
- **PLASMA DISCHARGE:**
 - metal/electrolyte interface;
 - **$U > U_b$ ($\sim n \times 10^2$ V);**
 - moving discrete short-lived microdischarges (most often);
 - uniform glow;
 - surface discharge

Main electrode processes



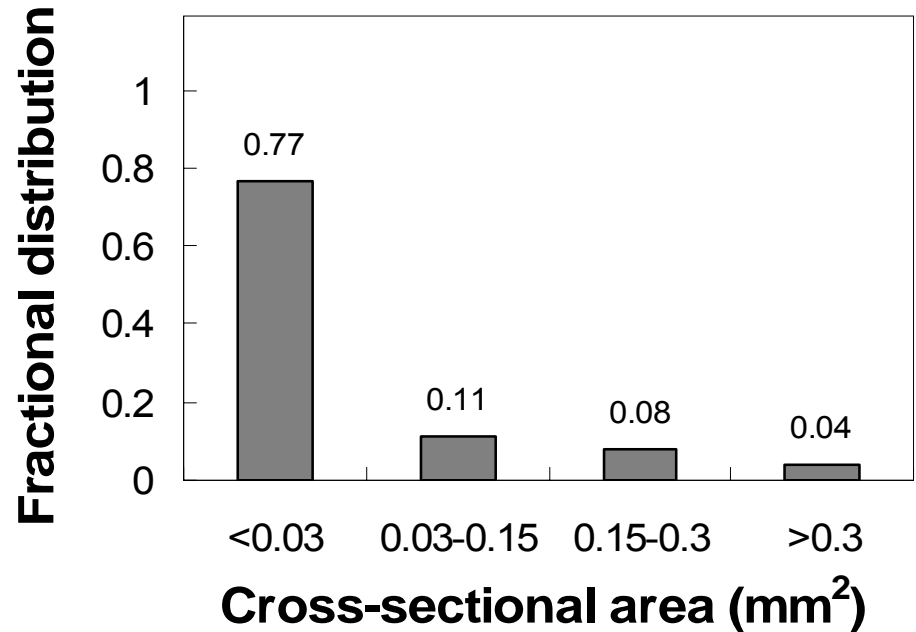
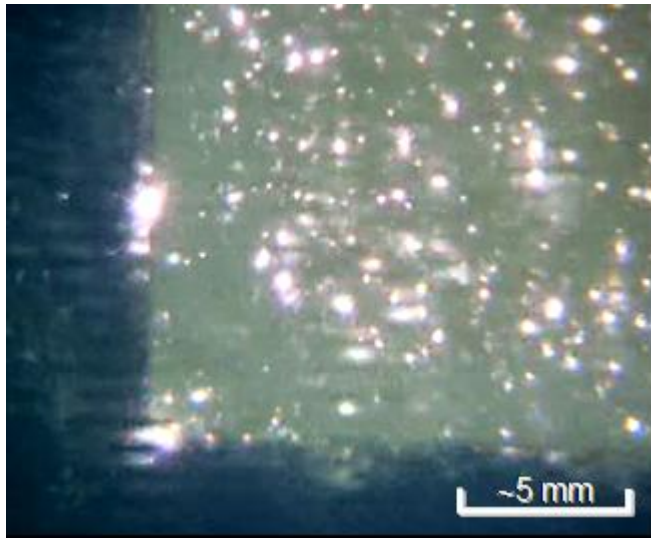
- Electrode processes provide charge transfer through metal/electrolyte interface.
- Each partial process commences at certain electrode potential.
- At high electrode potentials several electrode processes can run concurrently.

Current efficiency in PEO



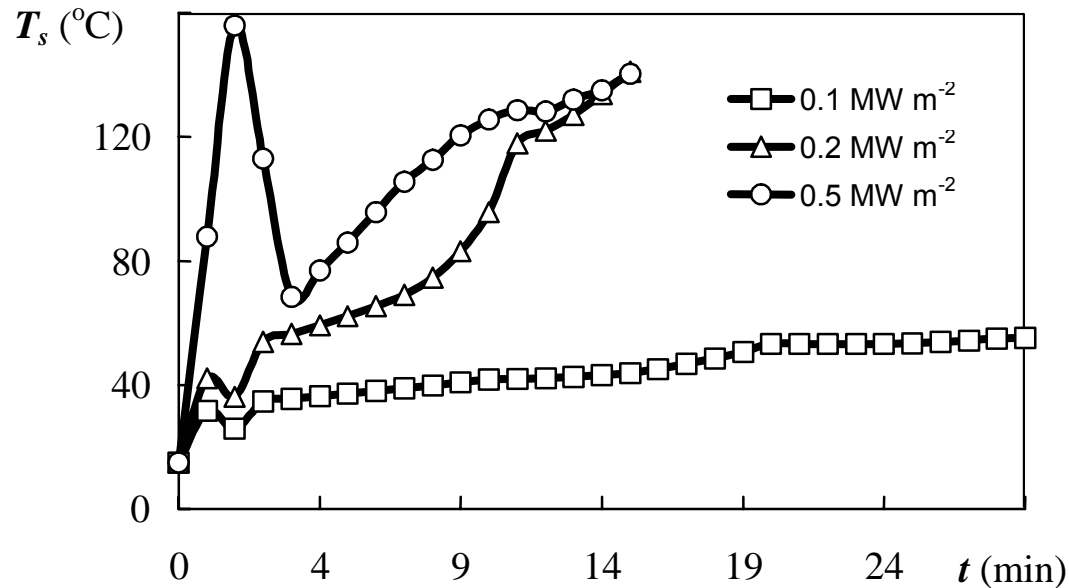
- Oxygen evolution is the major electrochemical process at the potentials of PEO.
- Only about 1/3 of net current is actually spent on oxide layer formation.
- Discharges however allow modifying the layer structure and phase composition to ensure superior properties.

Discharge Characteristics



- Diameter of light spot: 100 μm to 1.5 mm
- Discharge current density: 20 to 50 kA m^{-2}
- Duration of microdischarge event: 10^{-5} to 10^{-3} s
- Instantaneous local temperature: 10^3 to 10^4 K
- Surface structure greatly affected with intense localised heating-quenching cycles

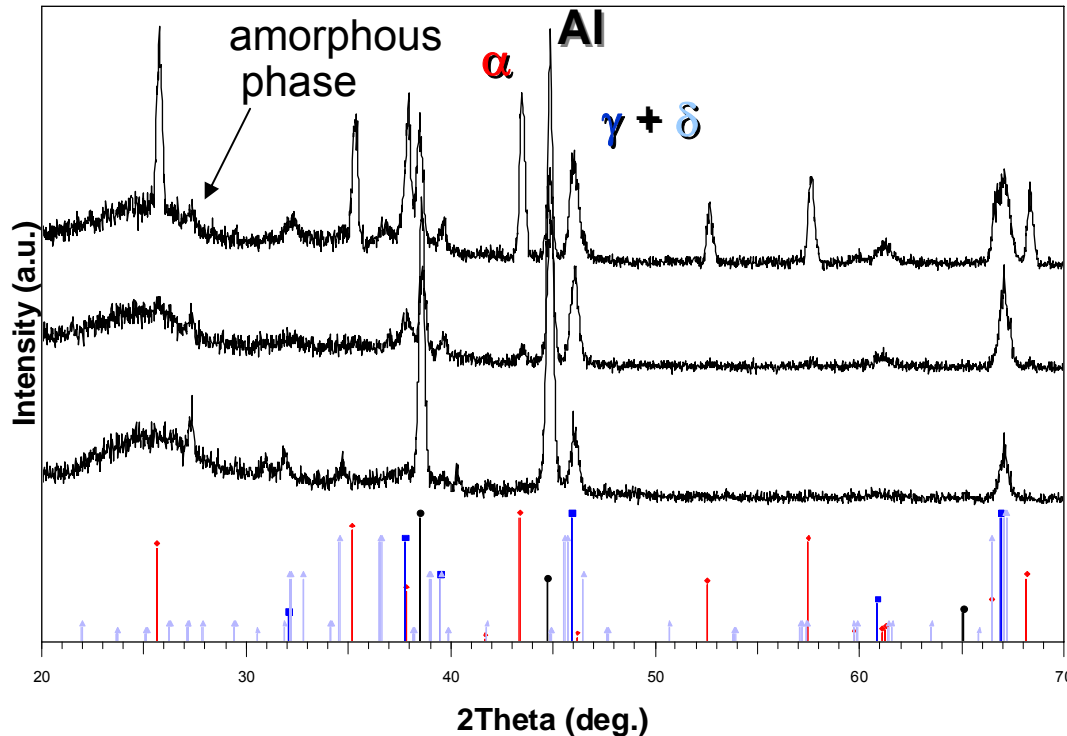
Bulk Substrate Temperature



- Bulk substrate temperature depends upon current regime and heat exchange conditions at the metal electrolyte interface.
- The temperature does not normally exceed 150 °C.

Phase Composition

Effect of Charge Density ($Q=I \cdot t$)



$$c_{[\text{KOH}]} = 1 \text{ g l}^{-1}$$
$$I = 700 \text{ A m}^{-2}$$

$$Q = 2800 \text{ kC m}^{-2}$$

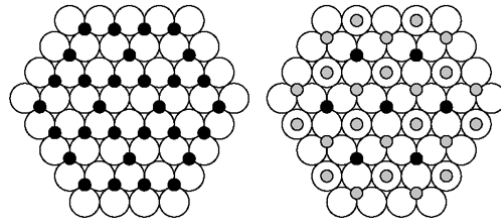
$$Q = 1400 \text{ kC m}^{-2}$$

$$Q = 700 \text{ kC m}^{-2}$$

- Coating mainly consists of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ and some amorphous phase.
- Minor $\delta\text{-Al}_2\text{O}_3$ indicates that microdischarges are appropriate to initiate $\gamma \rightarrow \delta \rightarrow \alpha$ transition around 1000 °C
- Content of $\alpha\text{-Al}_2\text{O}_3$ increases with coating growth

Properties of Alumina Polymorphs

Gamma alumina



Al coordination No:

4 (tetragonal)

O stacking:

ABCABC

Structure:

fcc (Fd-3m)
defect cubic spinel

Thermal stability:

Stable below 750-900 °C.
 $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ transformation
between 750 and 1100 °C

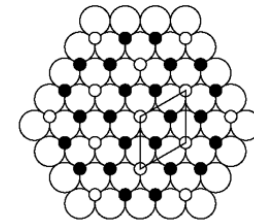
Chemical activity:

Reacts with atmospheric
moisture to form **Al(OH)₃**

Hardness:

10...15 GPa

Alpha alumina



6 (hexagonal)

ABAB

trigonal (R-3c)
close-packed

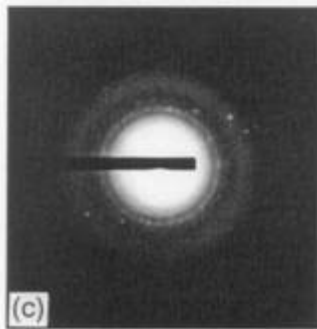
Stable at all
temperatures

Inert at $3 < \text{pH} < 10$

20...25 GPa

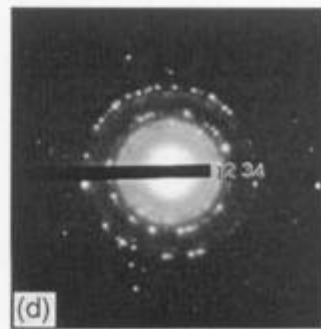
Quenching effect

Inner region
(near oxide/metal interface)



Amorphous-like
alumina

**Intermediate
region**



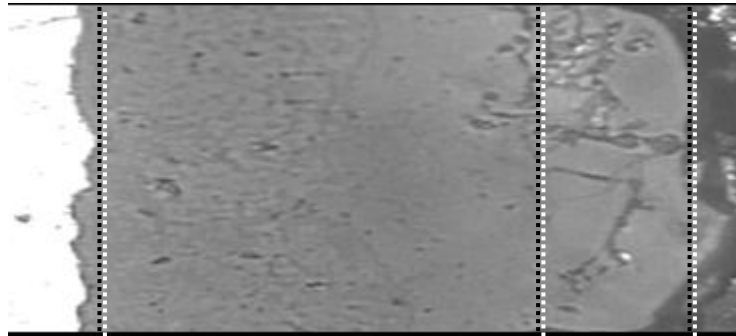
Nano-crystalline
 α -Al₂O₃

- Cross-sectional TEM reveals partly amorphous and nanocrystalline structure of PEO coating formed due to rapid heating and cooling of local surface areas.

- Fine crystals with typical grain size of 30 to 50 nm are formed in the intermediate region where cooling rate is relatively low.

- At the coating/metal interface cooling rate is particularly high. This promotes amorphisation of the oxide layer.

Hardness: Morphological aspect



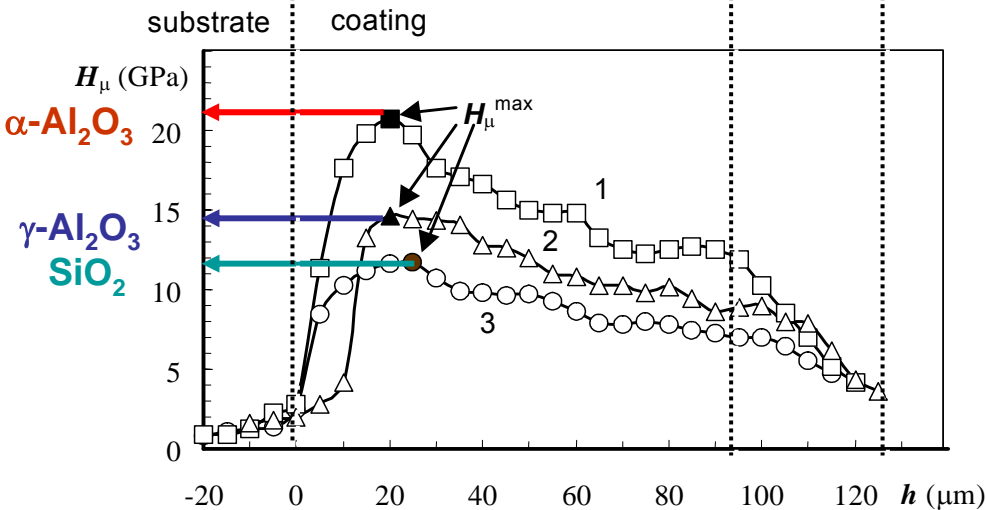
- Hardness profile correlate with coating phase composition and density.

- Maximum hardness corresponds to highest content of α -alumina in dense inner layer.

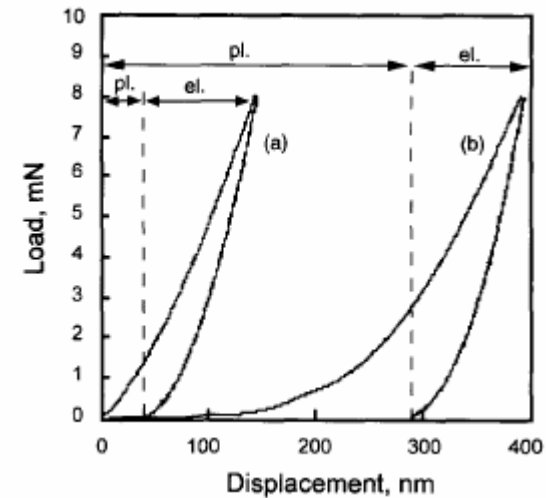
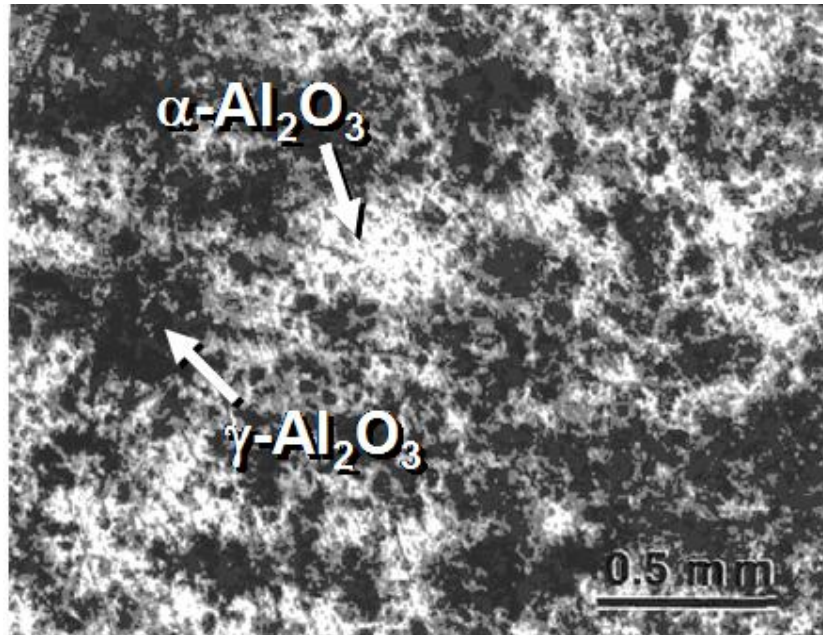
- Depending on phase composition, maximum coating hardness can vary in wide range

- Reduced hardness of outer porous layer facilitates finishing treatment and running-in.

- Gradient of mechanical properties in the dense layer particularly favourable for tribological applications



Hardness: Microstructural Aspects



- Bi-phase microstructure: high temperature $\alpha\text{-Al}_2\text{O}_3$ (bright areas) and mixed $\gamma\text{-Al}_2\text{O}_3$ /alumosilicate phases (dark areas)
- **Highly deconvoluted phase boundary!**
- Bright phase: $H = 18\text{...}23$ GPa; $E = 120\text{...}240$ GPa (tough and resilient)
- Dark phase: $H = 2\text{...}10$ GPa; $E = 40\text{...}120$ GPa (soft and ductile)

Effects of Alloying Elements

- Electrolyte species can be incorporated into oxide film, e.g.:

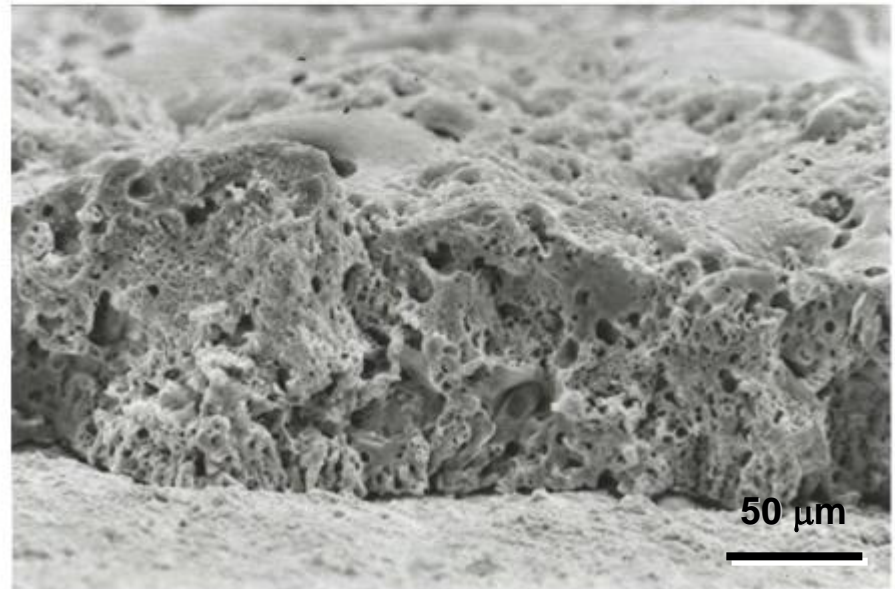
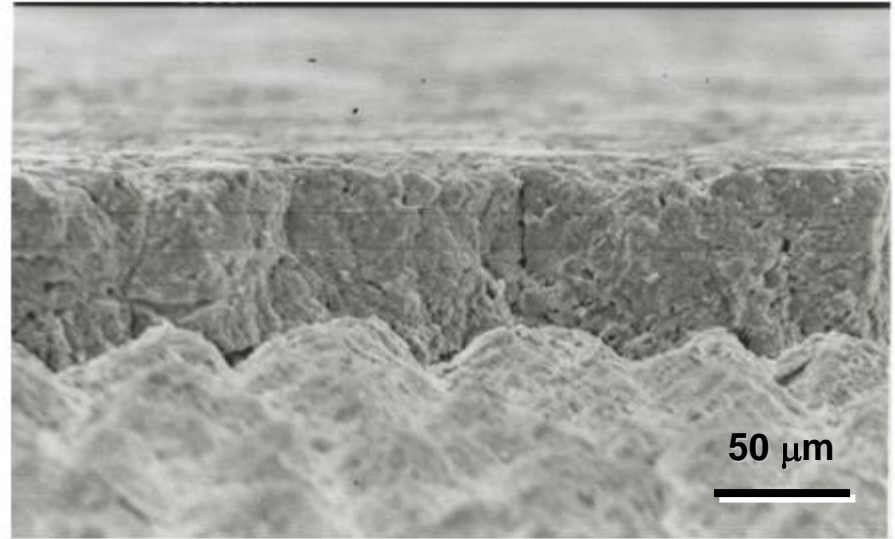
SiO_3^{2-} ; PO_4^{3-} ; WO_3^{2-} , MoO_4^{2-} , F^- , BO_3^{3-} , etc.

- Substrate alloying elements can be incorporated into the film, e.g.:

Mg, Cu, Mn, Zn, Si, Fe, Ti, etc.

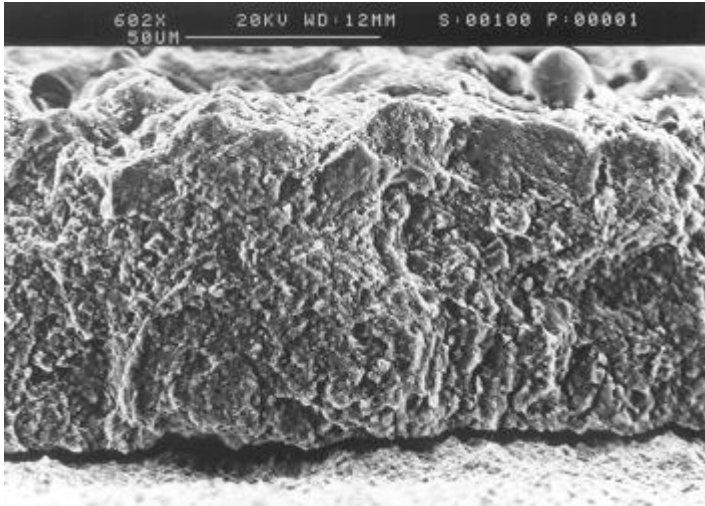
- **Converted surface layers** are formed if oxide phases of substrate metal prevail in the coating. These layers are normally dense and well-adhered to the substrate.

- **Precipitated coatings** are formed due to predominant precipitation of oxide/hydroxide phases from electrolyte. These coatings are thicker and more porous

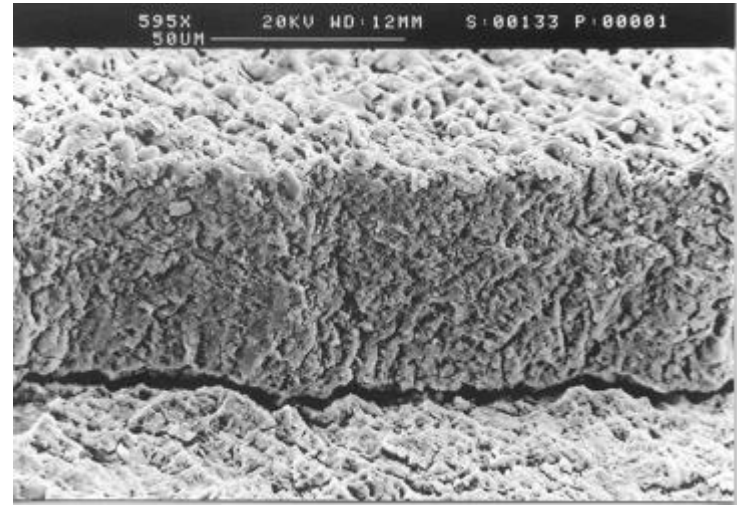


Effect of current mode

Amplitude modulated AC (50Hz)

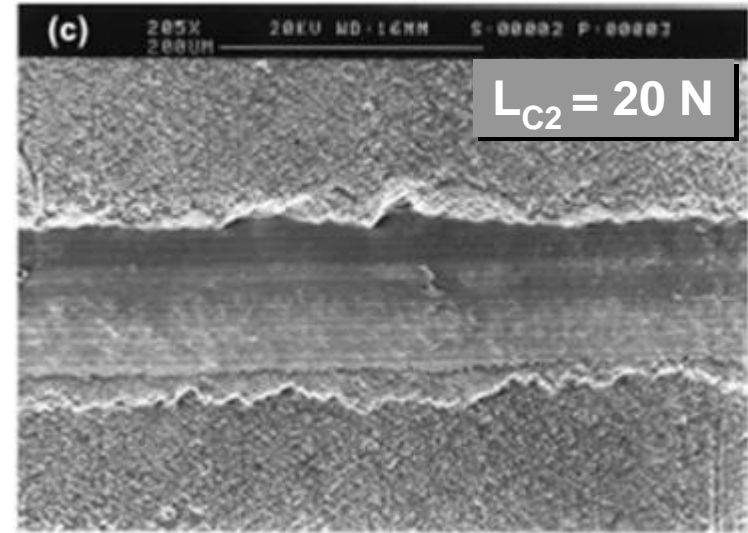
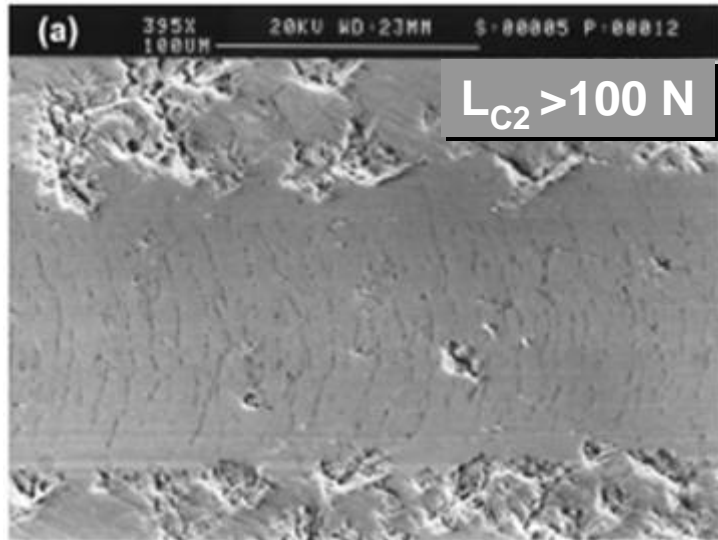


Pulsed bipolar current (1-3kHz)



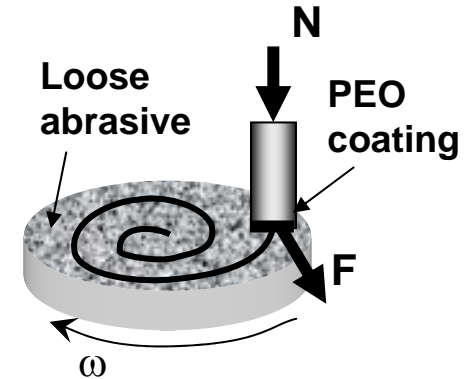
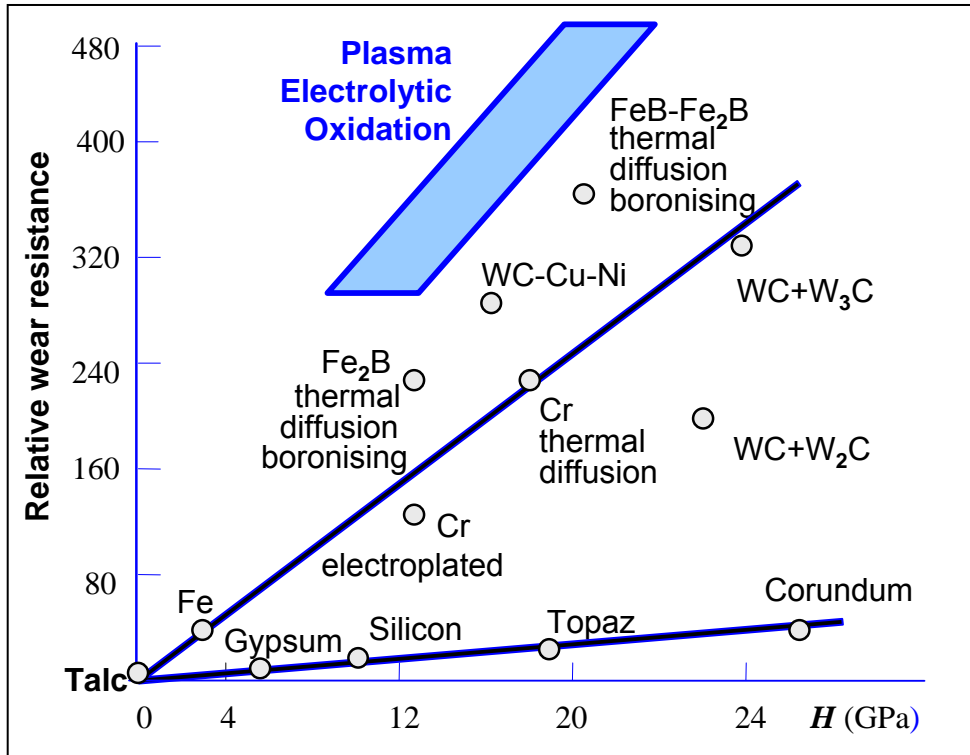
- Current mode provides effective control over discharge duration and intensity.
- Direct Current leads to formation of coarse coatings due to appearance of large long-lived microdischarges.
- Amplitude modulated (50 Hz) AC mode substantially improves coating morphology though some brittle phases could still appear in the structure (left).
- Higher frequency (1-3 kHz) pulsed bipolar current provides further refinement of both coating structure and phase content (right).

Scratch Adhesion



- Scratch adhesion test provides good model for ploughing conditions during wear
- Coating adhesion depends on Thickness, Structure, and Internal Stress
- If the above characteristics are adequate (left micrograph), coating adhesion increases with layer thickness, which is due to formation of graded transition from oxide film to substrate metal.
- Thick oxide layers provide excellent load support for soft light alloy substrates.

Abrasive Wear

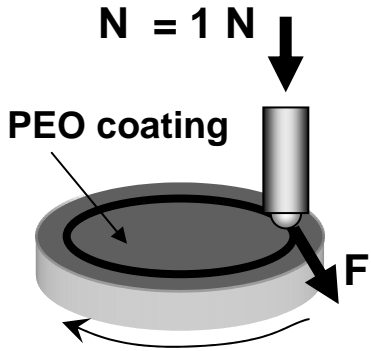


250 μm PEO coatings
vs
Silicon carbide

- Abrasive wear resistance of PEO coatings is higher than that of natural Al_2O_3 (corundum) and comparable to WC-based materials.
- Excellent load support from PEO coating to Al substrate
- Although abrasive wear resistance of PEO coating is primarily defined by hardness, structure also plays important role!

Sliding Friction:

Evaluation of Molecular Component



PEO (18...23 GPa)

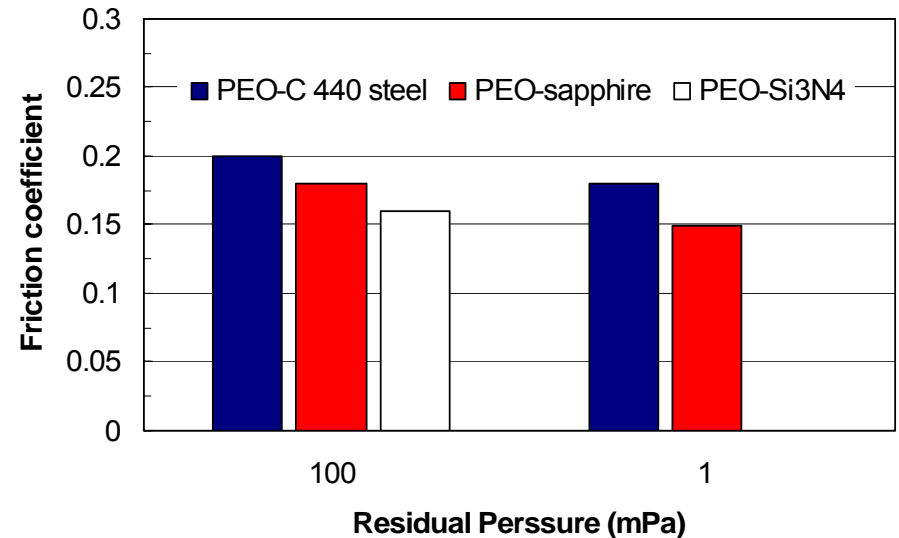
VS :

C 440 steel (8 GPa)

Al₂O₃ (18 GPa)

Si₃N₄ (16 GPa)

Friction in Vacuum



Components of Friction :

- **Adhesion**

- Molecular
- Environmental

- **Ploughing**

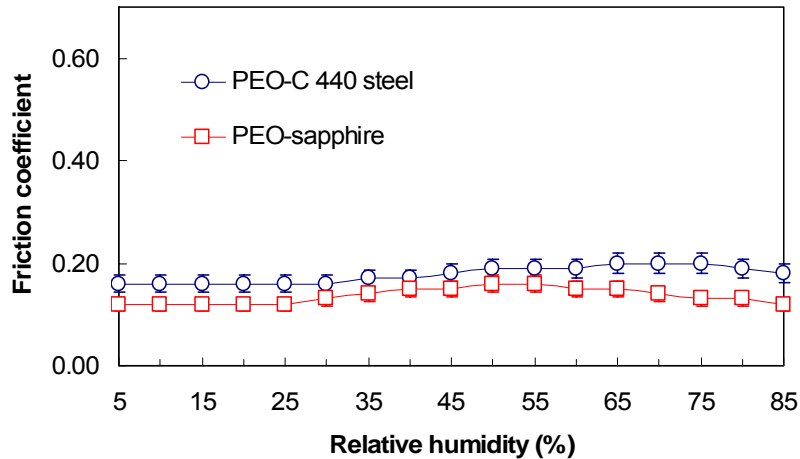
- **Deformation**

- Tests in vacuum provide a reference point for studies of tribochemical effects associated with atmosphere and lubrication.

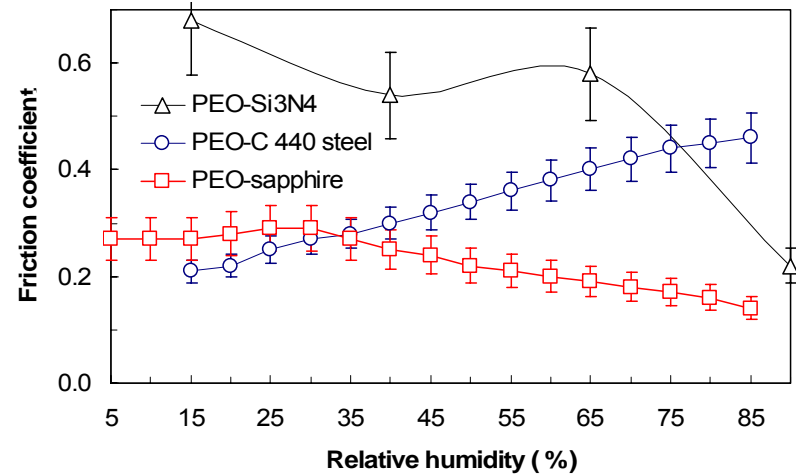
- PEO coatings show low intrinsic (molecular) friction ($f = 0.17...0.15$), particularly in pairs with ceramic materials, indicating their good potential for tribological applications.

Effect of Environment

Nitrogen

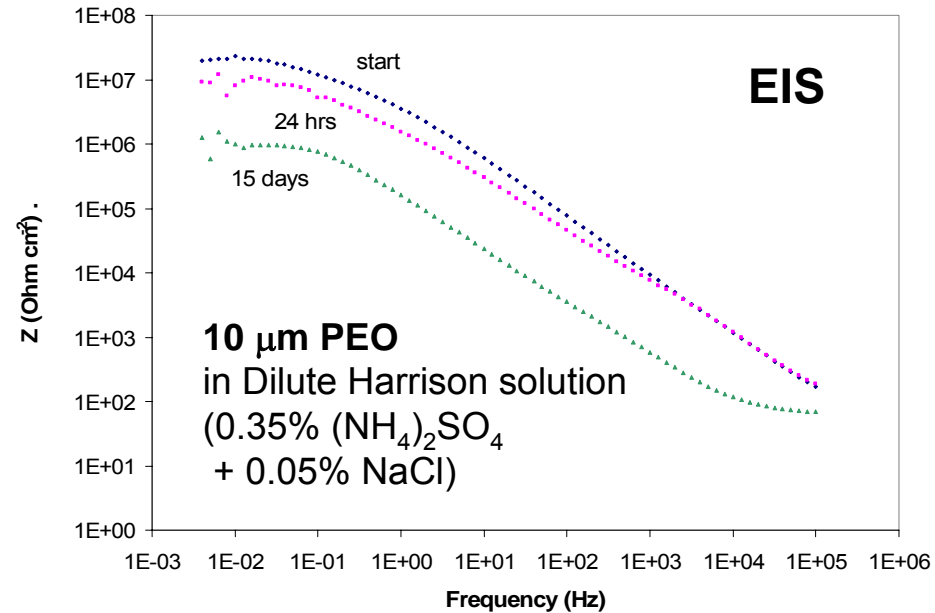
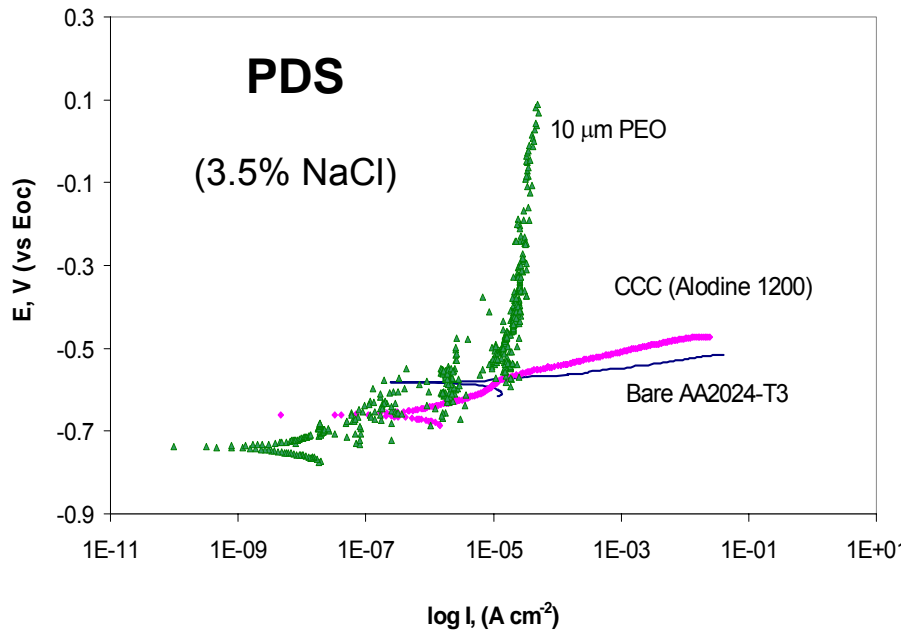


Air



- Friction behaviour of PEO alumina is affected environmentally induced chemical (adhesive) interactions.
- These interactions strongly depend on nature of both counter-face material and environment.
- Medium-humid air enhances chemical interaction between PEO alumina and iron or Si₃N₄, facilitating material transfer and associated adhesive wear within the friction pair (right graph).
- High humidity promotes formation of lubricious hydroxide films, particularly in ceramic surfaces

Corrosion performance: Electrochemical Analysis

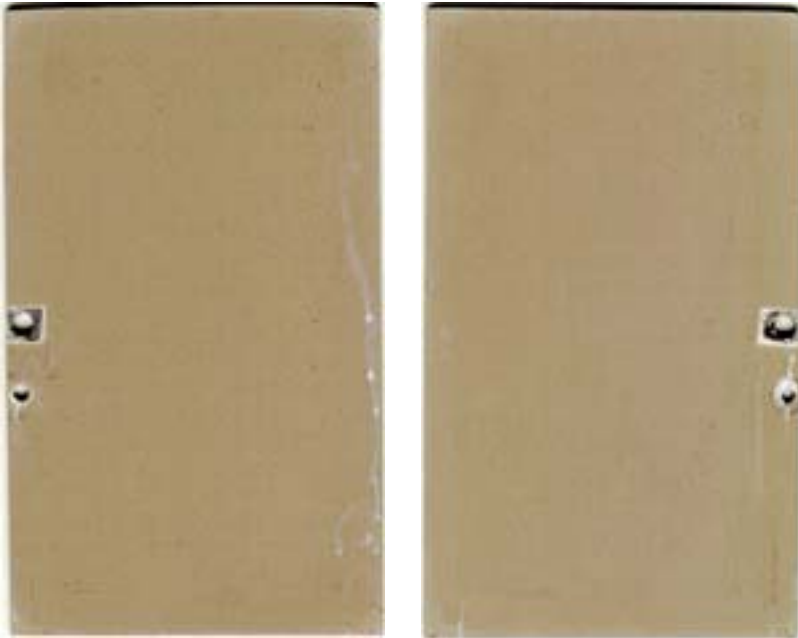


- **Potentiodynamic Scans (PDS)** show that PEO coating provides lower corrosion rate than commercial Chromate Conversion Coating (Alodine 1200) at high anodic potentials (>-0.5 V)
- **Electrochemical Impedance Spectroscopy (EIS)** reveals no significant changes in structure of the protective surface layer after 15 days-test

Corrosion performance:

Salt fog test (5% NaCl)

168 hrs

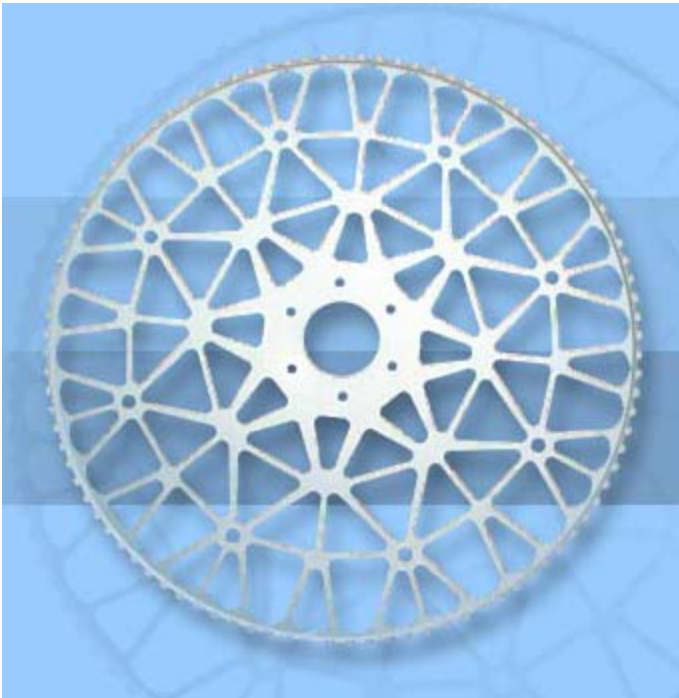


336 hrs



- PEO coatings show no signs of corrosion after 336 hrs exposure in 100% humid atmosphere with NaCl
- Thus, thin (10...20 μm) PEO coatings on Al can provide effective barrier against corrosion attack in chloride environments

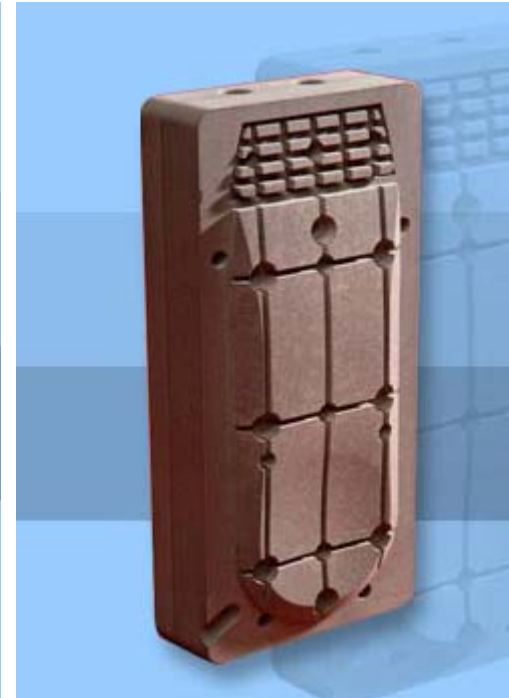
PEO applications for Al



Al wheels with PEO or PEO+PTFE coated teeth reduce wear against belts and chains.
No lubrication required.



Thermal barrier PEO coatings reduce temperature in the piston crown and improve overall engine performance.



Al moulds with PEO+PTFE coating reduce adhesive wear during casting. Tool production costs also reduced.

Conclusions

- Plasma Electrolytic Oxidation offers simple and ecologically friendly alternative to conventional anodising
- Although energy intense, the PEO process allows formation of thick, hard and well-adhered ceramic-like coatings on light alloys at near-to-ambient substrate temperature
- Mechanical properties and tribological performance of PEO coatings on Al alloys are superior of hard anodising films and similar to that of sintered ceramic alumina.
- Dense fused structure of PEO coatings provides excellent corrosion performance, superior of commercial Chromate Conversion Coatings.
- PEO coatings are considered promising in many applications