

White Paper

# What is Plasma Electrolytic Oxidation (PEO)?

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# Introduction

Plasma electrolytic oxidation (PEO) is a bath-based method of producing ceramic layers on the surface of light alloys. PEO surface coatings are characterised by their wear resistance, corrosion resistance and thermal and chemical stability. The method is suitable for alloys of high aluminium, magnesium and titanium composition, but can also be applied to other metals such as zirconium, tantalum, niobium, hafnium and cobalt.

Electrolytic oxidation without the use of plasma — anodising — has been the prevalent technique over many years. The introduction of plasma fundamentally alters coating and performance characteristics in stressful end-use applications.

The use of plasma introduces several benefits:

1. Development of harder ceramic phases (including crystallisation).
2. Chemical passivity - most PEO ceramics are chemically inert.
3. Incorporation of elements from the electrolyte into the ceramic to give different properties.
4. Reduced stiffness gives high adhesion under mechanical strain or thermal cycling.
5. Crack-free edges.



Surface coatings formed through plasma electrolytic oxidation can offer 2-4x more hardness than hard anodizing or steel, and provide increased wear resistance. The combination of these qualities and the comprehensiveness of protection has made PEO a breakthrough surface engineering innovation.

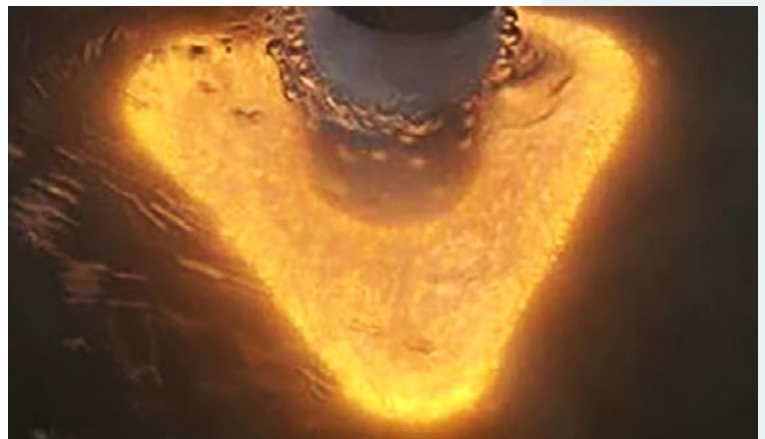
# The Plasma Electrolytic Oxidation Process

The process generally follows these three stages:

## 1. Oxidation of the substrate

As occurs during anodising, a component is submerged in a bath of electrolyte. Bath compositions differ based on the desired characteristics of the PEO coating, but is usually a proprietary dilute aqueous solution. This is free from chrome and other heavy metals. Additionally, the solution composition is disposable and clean, in contrast to hard anodising techniques which employ sulphuric acid ( $H_2SO_4$ ).

Depending on the desired coating characteristics, different electrical regimes can be employed. For example, alternating the polarity of an aluminium substrate can achieve variations of growth formation. Higher voltages are typically used to create plasma discharge.



*Figure 1. Plasma discharge around a component immersed in electrolyte*

## 2. Plasma Modification

In conventional anodising, the coating growth mechanism causes through-thickness cracks or fissures in the protective layer on corners or uneven surfaces. Additional seals or treatments are necessary to increase the corrosion resistance capabilities of hard anodised components for this reason. These also reduce the fatigue strength of a component, acting as stress raisers.

With PEO, plasma is used to modify the coating during the growth process. This alters the microstructure, resulting in no through-thickness cracks, and provide consequent benefits in corrosion resistance and fatigue strength.

In many cases, the plasma also causes crystallisation of the oxide layer, increasing hardness and potential for wear resistance. Micro and nanocrystals such as Al<sub>2</sub>O<sub>3</sub> corundum in aluminium, periclase on magnesium and anatase/rutile in titanium can be introduced into the ceramic layer for enhanced hardness.

Plasma modification creates other attractive features such as chemical passivity, low stiffness and thermal stability.



## Process Parameters

The processes involved in PEO are highly flexible, particularly when compared to alternatives such as hard anodising. This opens up a wide range of potential surface coating properties, which can be adapted and tailored to best suit the end use application of a component:

- Pre-treatment is simpler for PEO. In many cases, aluminium components may only require a light degrease prior to treatment. By comparison, most anodising and plating processes will need a cleaner surface, necessitating degreasing, etching and desmut steps to ensure a high quality coating.
- Applied electrical parameters can be adjusted based on a preferred surface morphology. Coating morphologies can be created with mean length scales from nanometer to micron range.

- Process chemistry can be developed to create different coatings and treat different metals and alloys.

When optimising a PEO layer for specific use, the ability to enhance certain coating characteristics is vital in the overall quality and sustainability of a component.

## Coating Characteristics

PEO's unique and flexible process produces highly protective layers that can be enhanced for performance in specific usage. With the added bonus of being a clean process, free of heavy metals, it's unsurprising that widespread interest has been sparked for the technique.

### Coverage

In general, PEO coatings are characterised by good coverage of the component compared to line-of-sight processes such as painting, powder coating and plasma or flame spray techniques. Also, the

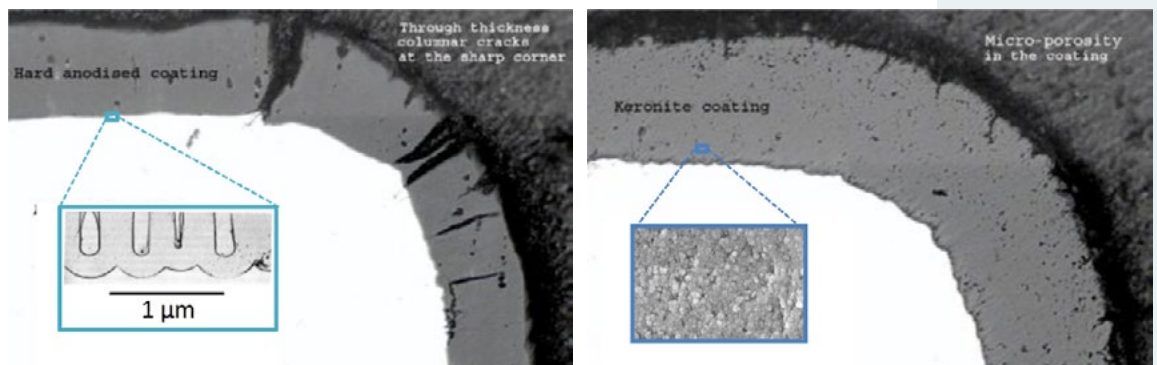


Figure 2. Comparative layer structures of Hard Anodising Coatings (left) and PEO (right)

insulating properties of the coating ensure good uniformity at corners and edges. Paints tend to thin at corners, whereas electroplating techniques tend to thicken at corners.

As illustrated in the SEM images in Figure 2, PEO layers are characterised by their complex microstructure. The presence of irregularly shaped microcrystals and other features provide more comprehensive protection on corners than through-thickness cracks clearly visible in hard anodised coatings.

## Extreme Hardness

As light alloys become more desirable to work with, both in terms of performance and cost, the need for innovative surface coatings has increased.

One such quality is the extreme hardness created in PEO. Typical coatings on aluminium are harder than steel (1600HV vs 500HV), yet the component itself could be up to 66% lighter. The performance enhancing characteristics of PEO coatings have enabled light alloys - even magnesium - to prominently feature in aerospace and automotive applications.

This extreme hardness is gained through a combination of crystallisation (of the oxides) and co-deposition of elements from the electrolyte in the ceramic layer. Aluminium, for example, can generate  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystalline phases on AA7075, with hardness up to 2000HV, which outperforms steels on pin-on-disc tests.

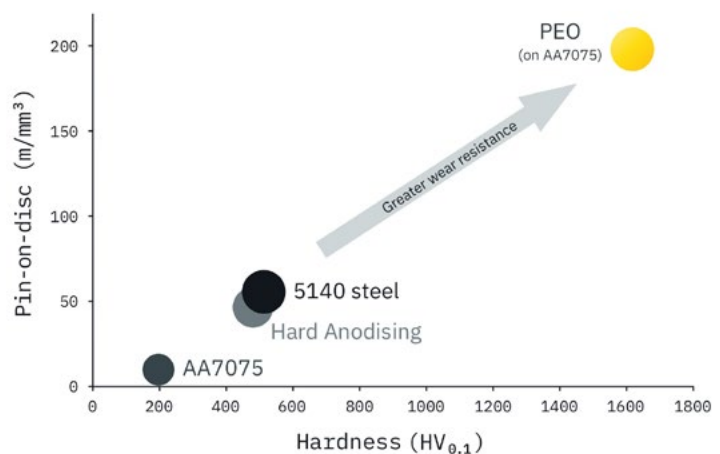


Figure 3. Hardness of PEO layers in pin-on-disc tests

## Corrosion Resistance

For optimal corrosion resistance performance, PEO works best as a pretreatment for subsequent sealers, paints and other polymers.

Figure 4 illustrates a polyester powder coat image applied to a PEO layer on a magnesium alloy substrate. The strong bond between the two layers enhances corrosion resistance capabilities, also forming scratch resistant qualities. The polyester coating effectively fills the pore architecture created during the formation of the PEO layer.

Generally, PEO is good for different types of bonding because its reticulated microstructure creates a physical 'key' and does not rely upon chemical compatibility between additional coats, unlike alternative coating mechanisms. The same principle applies to adhesion of oil and other lubricants in sliding wear applications.

Blanchard et al. (2005), in a study of 25 different surface treatments for Magnesium in terms of corrosion, found PEO to surpass the Chromium VI and Chromium-free alternatives tested. The results are illustrated in Figure 5, with F, G, H, I and J being derivatives of plasma electrolytic oxidation.

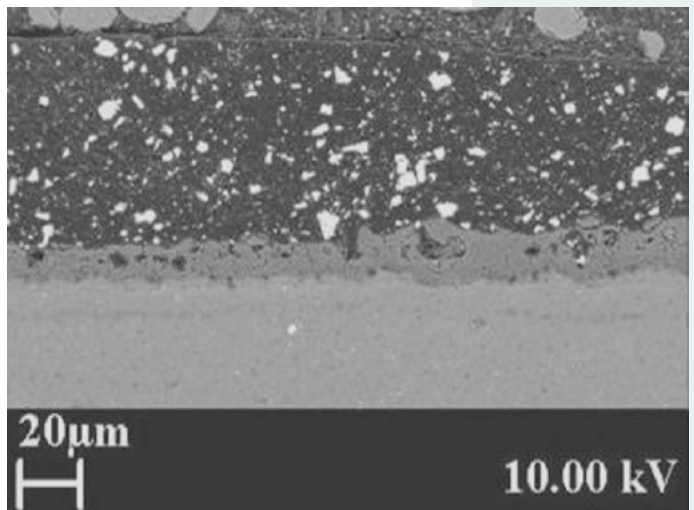


Figure 4. Polyester Powder Coat on a PEO coating on a Magnesium substrate

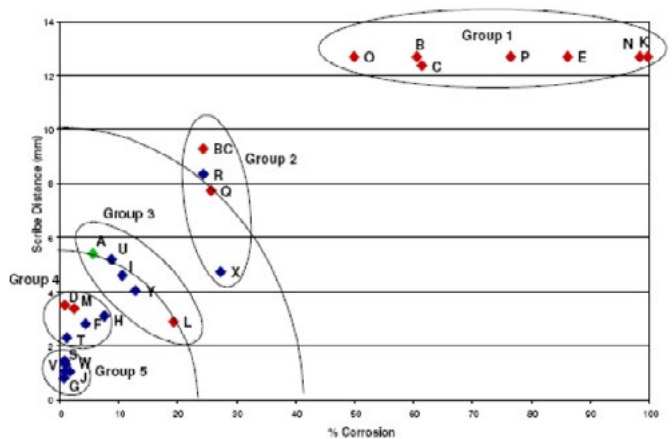


Figure 5. Evaluation of Corrosion Protection Methods for Magnesium Alloys in Automotive Applications Blanchard, P.J., Hill, D.J., Bretz, G.T. McCune, R.C., Magnesium Technology, TMS (2005).



## High Strain Tolerance

High hardness alone does not necessarily provide comprehensive wear resistance capabilities. Compliance is also a very valuable property, allowing for some deformation of the component under deflection or thermal expansion without placing undue stress into the coating-metal surface.

Hardness and appropriate levels of compliance combined increase the wear-resistance of a substrate.

Again, PEO's unique microstructure gives the material high fracture toughness, reducing the potential for cracking under force, which means ceramic surface coatings provide excellent performance in tribology applications.

## Environmental Friendliness

Coating and surface treatments that employ heavy metals (such as nickel, cobalt and frequently chromium) often involve high-hazard chemicals. Regulations surrounding the use of these are tightening, thus making them more difficult to work with. Conventional anodising employ strong acids, raising safety issues in use, transportation and disposal.

PEO is an environmentally safe option. Electrolytic baths are typically low concentration, chemically benign, aqueous solutions. Process waste streams can typically be discharged directly to drain after pH adjustment, so operating licenses are easily obtained. It is for this reason the technique has become popular in highly technical industries that require high performance surface coats in challenging environments.

# Learn more about PEO as a solution for internal automotive surfaces



In the grand scheme of a vehicle's mass, the internal components account for a significant portion of weight. Knowing this, automotive engineers have long been swapping out heavy carbon steels for aluminium – but this switch has been anything but straightforward.

Keronite's scientists set about developing a unique variation of plasma electrolytic oxidation (PEO). The coating—currently under the final stages of development—has exceeded manufacturer specifications by 200% across a variety of parameters.

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