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Modern Conversion Layers as High-Performance Alternatives to Aluminum Anodizing and Its Alloys

Martin Chvojka (0000-0002-4279-924X), Viktor Kreibich (0000-0002-0238-5173), Jan Kudláček (0000-0002-9064-9350)
Czech technical university in Prague, Faculty of mechanical engineering, Department of manufacturing technology, Technická 4, Prague, Czech Republic. E-mail: martin.chvojka@fs.cvut.cz

The paper focuses on a novel and perspective surface treatment technology called Plasma Electrolytic Oxidation (PEO) applied to aluminium and its alloys. This innovative technology generates layers with specific properties, particularly suitable for tribological and heat-resistant applications. Plasma Electrolytic Oxidation technology represents an alternative to conventional oxidation methods, offering high utility properties and presenting a completely new approach to surface modification.

Keywords: PEO (Plasma Electrolytic Oxidation), Non-ferrous Metal Anodizing, Conversion Layers, Conventional Anodization

1 Introduction to the technology

1.1 About the technology

Plasma Electrolytic Oxidation (PEO), also known as Microarc electrolytic oxidation, is a relatively new method of surface modification for creating hard ceramic layers on the surface of substrates such as aluminum, magnesium, titanium, zirconium, and their alloys. PEO technology is essentially similar to conventional anodizing, but unlike anodizing, which is performed at electrical voltages ranging from 10 to 50 V, voltages in PEO are applied above the breakdown voltage of the original oxide layers, typically ranging from 400 to 800 V. By applying high-potential electrical voltages, plasma is generated through micro-discharges of the applied potential, which manifest optically as numerous sparking on the surface of the component's base material. Due to the localized thermal effects of the sparks, specific ceramic layers composed of substrate oxides and complex oxides containing elements from the electrolyte are formed.

Layers created by PEO technology exhibit excellent adhesion to the substrate, high hardness, significant wear resistance, short-term high-temperature resistance, specific electrical properties, and good corrosion resistance. Despite the creation of areas with numerous electrical discharges, the base material is not significantly thermally affected, thus there is no change in its properties. PEO technology is gaining increasing attention as a cost-effective and environmentally friendly surface treatment for forming thick and ultra-hard ceramic layers on lightweight non-ferrous metals and their alloys. Recently, there has also been interest in exploring the possibilities of using PEO in medicine and biomedical engineering, along with related testing for biocompatibility and cell growth integration.

1.2 The layer growt process

During the PEO process, a variety of phenomena occur, primarily involving physical and chemical processes. The process can be divided into several phases as illustrated in Figure 1. In the initial phase, there is a rapid increase in electrical voltage, leading to the formation of a highly thin insulating layer. This phase is characterized by the creation of layers similar to conventional anodizing technology, accompanied by significant gas evolution from the electrolyte around the component. This leads to the entire component's surface becoming illuminated with a high density of discharges, which is characteristic of the PEO process. In the second phase, there is a slow increase in electrical voltage over time, and the growth of the oxide layer slows down (despite significant layer growth, there is simultaneous local dissolution). In the third phase, there is again a gradual increase in electrical voltage over time. Micro-discharges are stronger, and arcs burn for a longer duration, but their frequency decreases. The color of the discharges gradually changes from white to yellow (2nd and 3rd phase) and finally to orange (4th phase). In the final fourth phase, there is a slight decrease in voltage, and the discharges are very strong with lower frequency, emitting a radiant orange color. Discharges play a crucial role in layer formation. Observing and explaining some chemical and physical processes occurring in the discharge channel are challenging, hence the ongoing debate and theoretical nature of their formation. [1], [2], [3]

Upon reaching the critical voltage, channels are created in the oxide layer with discharges. At one moment, a large number of such discharges occur over a small area, resulting in micro-regional instability. The theoretical temperature in the short-circuit area ranges from 4000 to 10000 K. The discharge temperature increases with layer formation. The regional plasma temperature around the discharge in the short-circuit channel is sufficiently high to excite everything in the immediate vicinity of the discharge, and the collapse of the discharge forces various materials to penetrate the layer. Anions from the electrolyte are drawn into the layer due to the large electromagnetic field created by the discharge. The high temperature and pressure in the short-circuit discharge area melt the substrate and the resulting layer, facilitating diffusion processes. The melted material is ejected to the layer/electrolyte interface due to the kinetic energy of the discharges, where it solidifies and contributes to further layer growth around the discharge channels. Gas escaping from the channels forms their shape into a circle at their outlet, creating an overall structure resembling craters. Essentially, there is continuous melting and enrichment of the oxide layer with its increasing thickness. The layer utilizing short-circuit discharges grows from its essence on both sides of the substrate/electrolyte. On the surface, material growth occurs due to melting and ejection, which solidifies around the channel. The substrate melts, and due to the presence of oxygen after the discharge, oxidation occurs at high temperature and pressure. Rapid cooling of the melted parts results in the formation of a crystalline structure with nanometric grains. [1], [3], [4]

During the process, three different types of discharges are also observed. These include gas discharges within individual micro-pores. Type A discharge penetrates the oxide layer material in small blind channels. Type C discharge penetrates deeper into the material layer. Type B discharge reaches the substrate itself and promotes layer growth from both sides. These discharges also generate the most heat. All three types of discharges melt and transfer layer material, shaping the resulting properties. [1], [4]

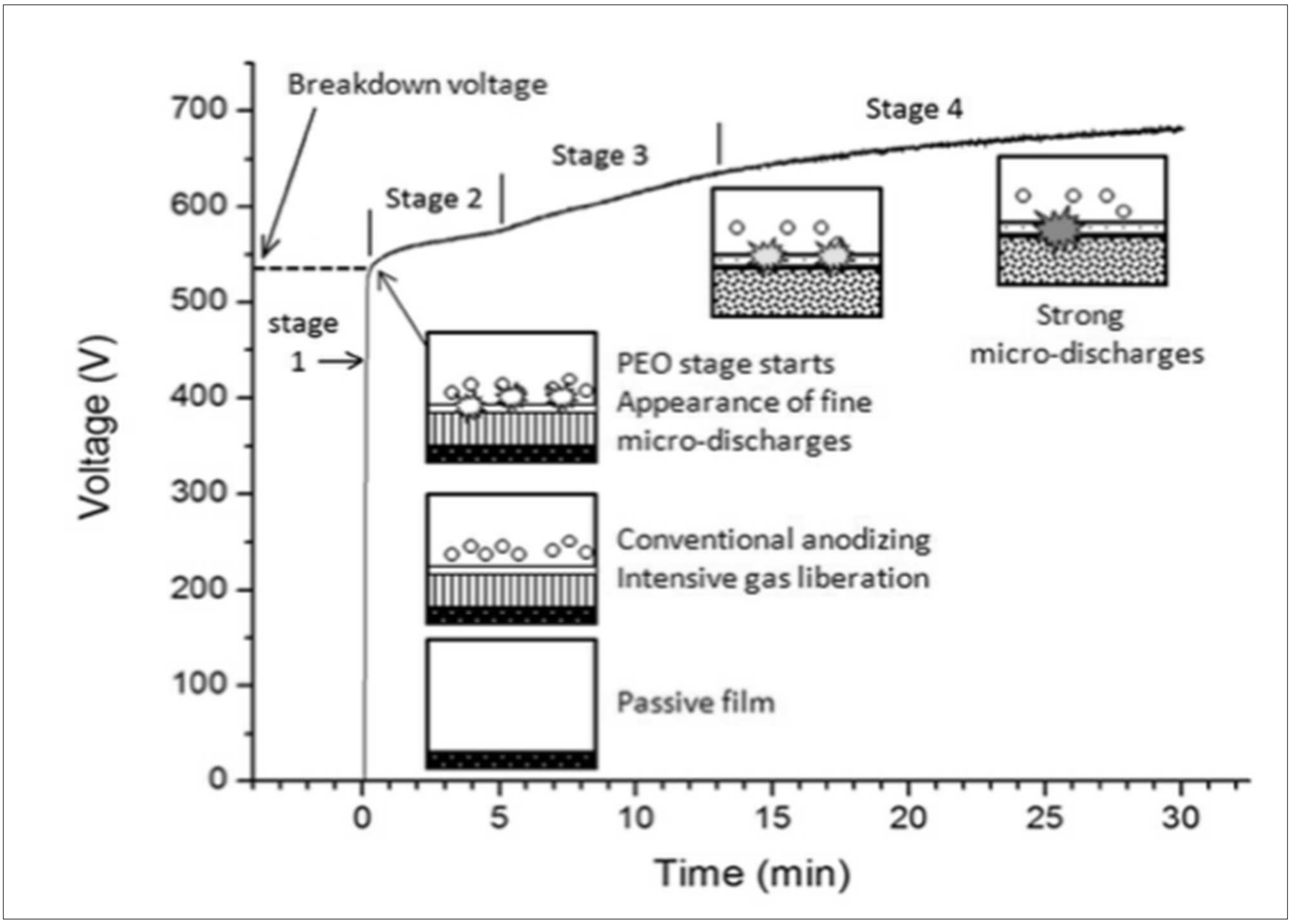

Fig. 1 *PEO layer formation in time* [1]

1.3 Technological equipment

The technological equipment for creating layers using PEO technology depends on many parameters such as electrical voltage, current characteristics, and the electrolyte used. The composition of the electrolyte also depends on the substrate used. PEO utilizes a very similar technology and device configuration to conventional hard anodizing but operates at much higher electrical voltages, typically ranging from 400 to 800 V. [4]

A created setup for creating layers using PEO technology is shown in Figure 2. Primarily, the equipment consists of a high-performance power supply and an electrolyser. The electrolyser is usually made of stainless steel or plastic and, in the case of stainless steel, also serves as the electrode (cathode). The system is connected to a cooling system to maintain the electrolyte temperature at the desired value. Cooling is achieved through electrolyte exchange or heat transfer through the tank. If the container is made of stainless steel, it must be placed on an insulating base, and other elements must be grounded for safety. Various types of direct current (DC) power supplies are used, including pulsed DC or alternating current (AC) power supplies. [4], [5], [6]

2 The realization of the workplace and the creation of initial samples

To verify the assumptions of the technology, development of own electrolyte, production of samples, and for properties verification of the created layers, a custom setup has been designed and assembled. [8]

Fig. 2 *Equipment setup with bath detail*

2.1 The proprietary process of manufacturing conversion layers and verifying the resulting properties

At the developed and assembled workstation, a set of samples was created from EN AW 1050 aluminium sheet to compare the observed properties with those of other basic anodic oxidation types. Electrolytic plasma oxidation (PEO) was performed using a 0.1g/L NaOH-based electrolyte solution and 800V pulsed monopolar current with a 300 μs pulse duration, which previous experiments had determined to be optimal. The PEO layer creation process is shown in Figure 3. [8]

The PEO layers were then compared to conventional anodic oxidation layers: decorative and hard (functional). These layers were created on the same base aluminium alloy to facilitate comparison between technologies. Decorative anodic oxidation samples were created using Rogal 3, and hard (functional) oxidation layers were created using Rogal 5 electrochemical solutions (manufacturer ELEKTROCHEM-PPÚ s.r.o.), both of which are sulfuric acid-based electrolytes (13-18 g/L). Neither the decorative nor hard anodic oxidation layers were infilled, for comparability with the PEO technology. [9]

Samples treated with the developed PEO process were tested and analysed to verify the layer and technology properties. These samples were also compared to those produced by conventional anodic oxidation technologies.

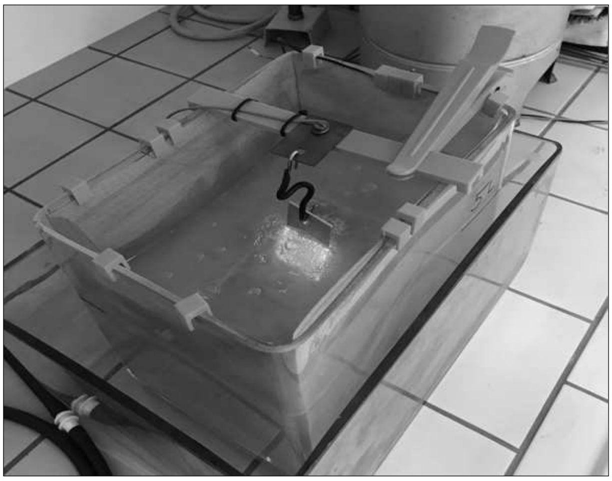

Fig. 3 *PEO layer development during the process*

The surface of the layer created by the PEO process is characterized by a unique surface topology, formed by individual discharges through the transformed base material, as can be seen in Figures 4 and 5. This topology determines the overall roughness of the layers and other tribological properties. The increased porosity is suitable as an adhesive base for anchoring other materials, such as coatings, composites, and polymers (Figure 6).

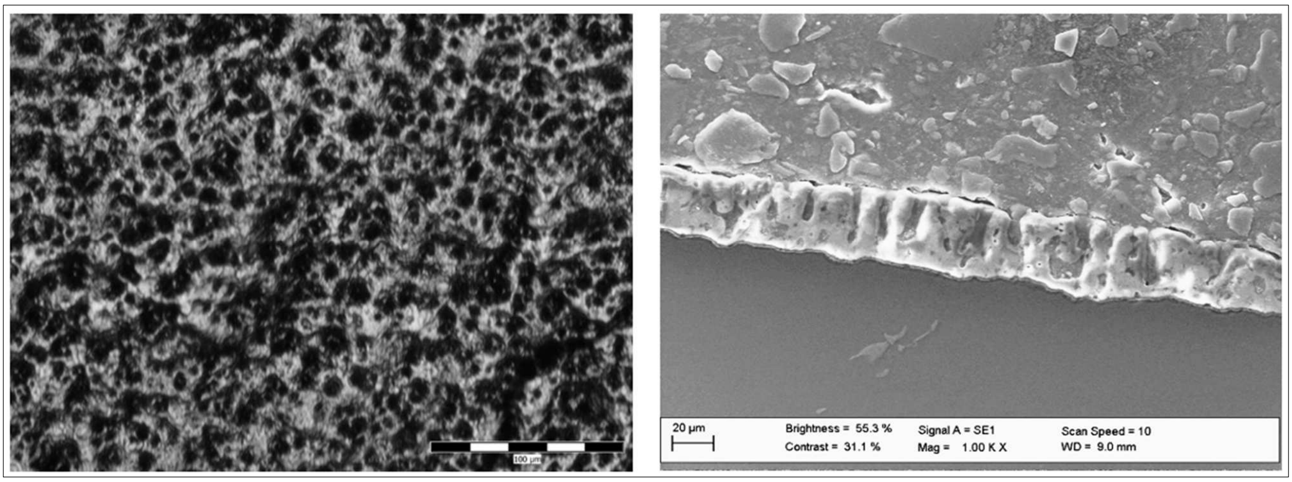

Fig. 4 *Optical microscopy (left) and SEM of the surface of PEO layer*

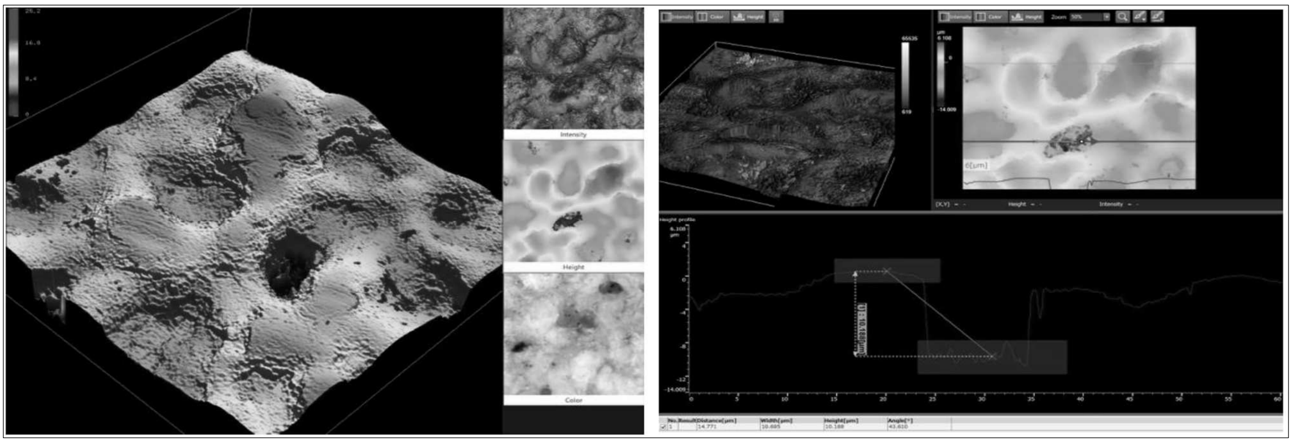

Fig. 5 *Topography of the surface of the PEO layer measured using confocal microscopy*

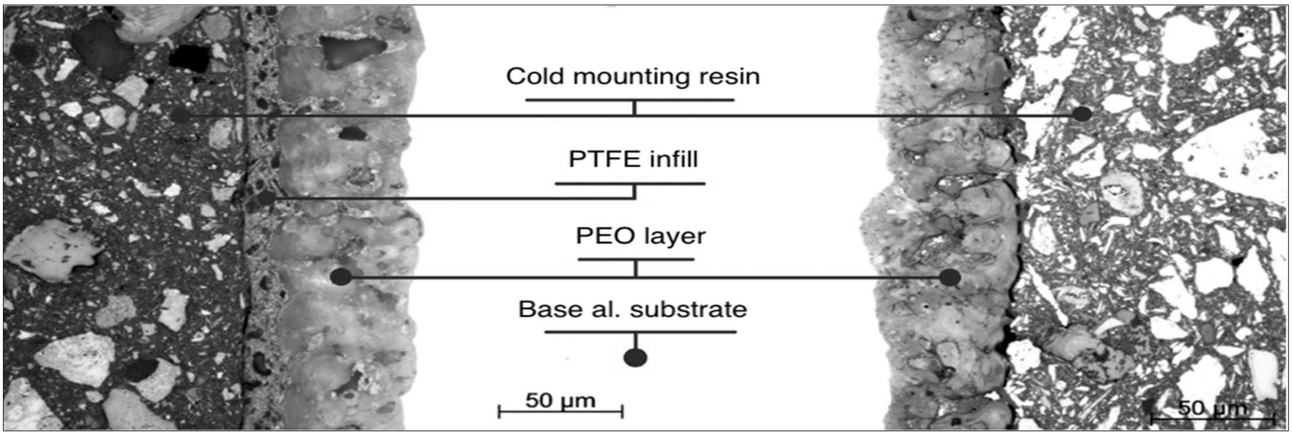

Fig. 6 *SEM and metallographic sample description of filled (left) and unfilled (right) PEO layer with PTFE polymer*

When applying PEO technology to aluminium alloys, the resulting layers consist of various phases of Al2O3. These primarily include the phases α-Al2O3 (with a strength of 26 GPa and temperature resistance up to 2600 °C) and γ-Al2O3 (with a strength of 17GPa and temperature resistance up to 1200 °C). The resulting strength and temperature resistance are primarily determined by the proportion of these prominent phases, with their proportion being influenced by the chemical composition of the base material. Theoretically, the metastable γ phase can be transformed into the stable α phase by annealing at temperatures above 1200 °C. However, these temperatures are challenging to apply considering the temperature resistance of the aluminium-based base material. The composition of the layers was confirmed using multiple EDS analyses and by determining the mechanical properties of the created layers. [4], [5], [6], [7]

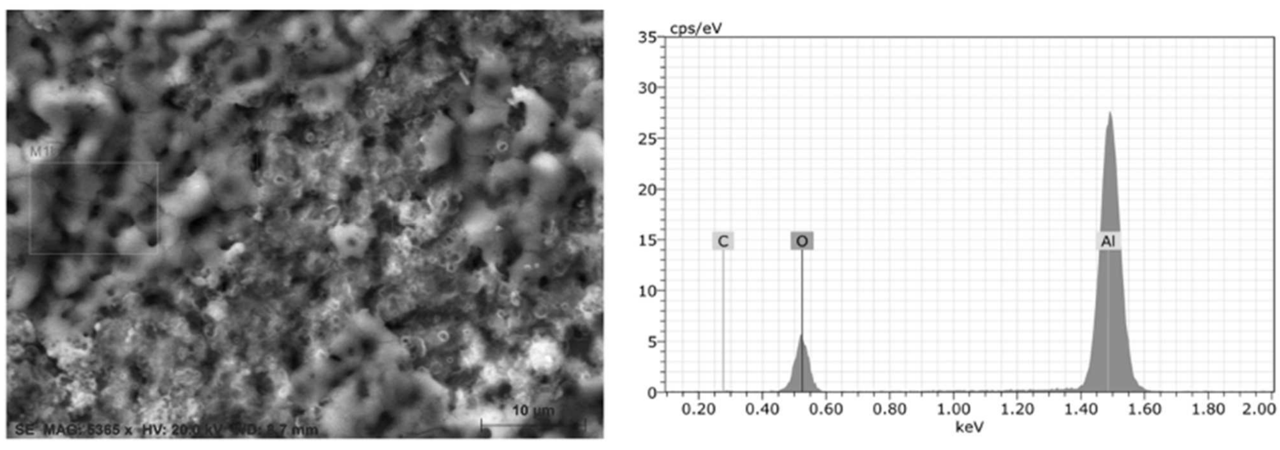

Fig. 7 *EDS of the selected area of the PEO layer*

3 Results

Thanks to the measurements and a set of tests on the properties of the created layers using both conventional technologies of regular anodic oxidation and PEO technology, their significant characteristics were described and compared.

It was found that the layers created by PEO technology developed at CTU are characterized primarily by (3.1, 3.2, 3.3 and 3.4):

3.1 Highier roughness

This is mainly due to the process of creating these layers. Due to the mechanism of layer growth in the presence of spark discharges, it is formed with a crater-like structure with higher surface roughness compared to anodic oxidation technologies. [9], [11]

Tab. 1 *Summary and comparison of roughness based on the parameter Ra for each technology*

Sample	Ra [µm]	
	In the direction of rolling of the base sheet	Perpendicular to the direction of rolling of the base sheet.
Decorative Anodic Oxidation	0.363	0.436
Hard Anodic Oxidation	0.505	0.632
PEO (CTU)	1.358	1.421

3.2 Highier mechanical resistance

Due to the composition of the resulting layers, the surfaces exhibit particularly high hardness compared to typical decorative and hard (functional) oxidation layers. [12]

Tab. 2 *Summary and Comparison of Hardness Values for Each Technology*

Sample	Nanoindentation Hardness [GPa]	Nanoindentation Hardness [HV]
Decorative Anodic Oxidation	6.11 ± 0.28	623 ± 28
Hard Anodic Oxidation	7.83 ± 0.89	799 ± 91
PEO (CTU)	13.14 ± 4.00	1353 ± 430

3.3 Suitable adhesive properties

Due to the specific relief character of the layer, the possibility of sealing/filling the layer for potential acquisition of additional properties was observed. Particularly for assessing the suitability of the synergistic effect of filling with lubricious polymers for further reduction of the coefficient of friction and enhancement of practical tribological properties. It was found that PEO layers exhibit suitable adhesive base for anchoring other materials such as coatings, composites, and other polymers. [7], [11]

3.4 Higher tribological properties

Tribological properties, especially coefficients of friction, were monitored using three independent devices. In two cases, static and dynamic friction coefficients were monitored using pin-on-plate (TOP 3) and pin-on-disk (MFT-500) type tribometers. Additional measurements were carried out on a custom-built coast-down machine to compare the friction coefficients of filled and unfilled layers. [10], [11]

Tab. 3 *Summary and Comparison of Friction Coefficient Values for Each Technology Using the TOP 3 Device*

Sample	Static coefficient of friction [-]	Dynamic coefficient of friction [-]
Decorative Anodic Oxidation	0.50 ± 0.09	0.38 ± 0.09
Hard Anodic Oxidation	0.50 ± 0.04	0.44 ± 0.09
PEO (CTU)	0.45 ± 0.07	0.30 ± 0.06

Tab. 4 *Summary and Comparison of Friction Coefficient Values for Each Technology Using the MFT-500 Device*

Sample	Coefficient of friction [-]
PEO – unfilled	0.39 ± 0.03
PEO + PTFE – filled	0.05 ± 0.1

Tab. 5. *Summary and comparison of the friction coefficient values for each technology using the "Coast-down machine"*

Sample	Dynamic coefficient of friction [-]	
	Rotational test	Linear test
Decorative Anodic Oxidation	0.5 ± 0.1	0.5 ± 0.1
Hard Anodic Oxidation	0.75 ± 0.1	0.5 ± 0.09
PEO (CTU)	0.15 ± 0.06	0.2 ± 0.08

4 Result discussion

Based on the results and measurements presented above, a significant increase in mechanical and tribological properties is evident. The twofold increase in PEO layer hardness compared to conventional anodic oxidation technologies is characteristic of the technology and determines many other mechanical and tribological properties. When values from tribological measurements are compared, the PEO layers show a slight decrease in the coefficient of friction and together with the high hardness of the layers, the technology is therefore very suitable for long-term tribological applications. If, in addition, the layer is sealed with a suitable filler, this coefficient of friction decreases even further and tribological applications extend even further.

5 Conclusions

Based on the measured data and determined properties, it can be unequivocally confirmed that the layers created by PEO technology exhibit superior functional properties compared to layers created by conventional anodic oxidation technologies, namely decorative and hard anodizing. Applications of PEO technologies encompass a wide range of industries. The technology is suitable for the aerospace and space industry, automotive manufacturing, electronics, biomedicine, and a variety of other possibilities.

The applications primarily relate to the following characteristic properties of these layers:

- a) High hardness (up to 2000 HV),
- b) Good tribological properties (wear resistance),
- c) Guaranteed adhesion of additional layers,
- d) High thermal resistance (the layer is used as a short-term thermal barrier up to 2,000°C),
- e) Biocompatibility for cell growth and implant integration,
- f) Dielectric properties (high electrical insulation),
- g) High corrosion resistance.

6 Summary

As evident from the individual results and images from the electron microscope, PEO layers are successfully applied to aluminium components. However, it is also possible to apply them to magnesium or titanium materials and their alloys. Recently, the PEO process has also been applied to zirconium and tantalum. Surface conversion layers can gain additional functional properties by subsequently filling the porous structures with functional polymers such as PTFE (polytetrafluoroethylene) or PEEK (polyetheretherketone). These surface treatments - layer formations are very promising, and we will increasingly encounter them in common engineering due to their advantageous properties. However, further research is needed to describe the process of creating these coatings. A better understanding of the process will enable us to further advance their applicability and potentially influence the resulting properties.

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