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Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty, Kazakhstan

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Kydyrmolla M.K.

“Institute of Metallurgy and Ore Beneficiation” JSC
Satbayev University, Almaty, Kazakhstan

E-mail: magzhank04@gmail.com

ORCID ID: <https://orcid.org/0009-0001-2988-7288>

Smagulov D.U.

“Institute of Metallurgy and Ore Beneficiation” JSC
Satbayev University, Almaty, Kazakhstan

E-mail: d.smagulov@satbayev.university

ORCID ID: <https://orcid.org/0000-0002-0599-8741>

Ybyraimkul D.T.

“Institute of Metallurgy and Ore Beneficiation” JSC
Satbayev University, Almaty, Kazakhstan

E-mail: d.ybyraimkul@satbayev.university

ORCID ID: <https://orcid.org/0000-0003-1506-6531>

Studying the influence of electrolyte composition on the structure and properties of the surface layer of aluminum alloys during plasma-electrolytic processing

Abstract: Plasma electrolytic oxidation (PEO) is a new processing process used primarily to produce a thick and dense surface layer of metal oxides, especially light metals, to improve wear and corrosion resistance. If we compare the surface layers obtained by the PEO method with the surface layers obtained by conventional anodic oxidation, then, first of all, they are more resistant to wear and corrosion. It is widely used in mechanical engineering, petrochemical, and biomedical industries. Many studies have been carried out to determine the characteristics of surface layers obtained by PEO. This review attempts to summarize and explain some fundamental aspects of the PEO process, the formation mechanism of the surface layer, the processing conditions affecting the process, the main characteristics of the process, and the mechanical and tribological properties. In addition, recent developments in nanocomposite surface layers and their applications are discussed with examples. It also highlights the importance of this process, its current trends, and the scope of future work. In this case, pay attention to the breakdown of dielectrics, which appears several times on the surface of the workpiece. These discharges play a central role in the process since it is mainly due to the associated plasma that the substrate is oxidized and the coating is formed. The details are complex because discharge characteristics are affected by a number of processing parameters. The relationship between electrical conditions, electrolyte composition, surface microstructure, and rate of discharge performance has become clearer in recent years, and these improvements in understanding are summarized here. There is a significant opportunity to more effectively control the process with specific objectives in terms of coating performance and energy efficiency, and efforts are being made to identify the key factors that contribute to this.

Keywords: plasma electrolytic oxidation, electrolyte composition, aluminum alloys, oxidation process, surface layer, corrosion resistance, mechanical properties, sulfuric acid, chromic acid, oxalic acid, wear resistance.

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Introduction

Plasma electrolytic oxidation (PEO) is one of the new methods of electrochemical treatment of surface layers. This method allows the processing of thick, hard, and dense surface layers of ceramics with layers of aluminum, titanium, and magnesium. The PEO process is known as micro-arc oxidation, plasma-chemical oxidation, and anodic oxidation. PEO uses environmentally friendly weakly alkaline and acidic electrolytes, in which oxide layers are formed under the influence of high electrical voltages (Lu et al., 2016; Kaseem et al.,). During this process, the thickness of the oxide surface layer on the packaging increases from tens to hundreds of microns, which can significantly improve corrosion resistance, wear resistance, and thermal strength properties. The PEO process has been studied for a long time and is considered a better approach for the

biomedical, electronics, aerospace and automotive industries than other traditional surface finishing processes (Rapheal et al., 2016). The phenomenon of electrolytic discharge in plasma was first discovered and described in article (Sluginov et al., 2012), and later this process was further studied in article (Simchen et al., 2020) in 1920 as a feature of the development of electrolytic capacitors. These phenomena were successfully studied by Brown and his colleagues in the early 1970s and used to create ceramic layers on aluminum alloy coatings in alkaline electrolytes (Brown et al., 1971). They called this method anodic spark deposition. Since then, researchers have continued to study this process, and it became practical after significant changes were made in the 1980s and 1990s (Kurze et al., 1986; Malyshev et al., 1984; Krysmann et al., 1984; Yerokhin et al., 1998). With the advent of industrial production and improvement of technology, this process was called PEO. This process has been developed and used commercially by companies such as Keronite in the UK; bioengineering companies such as Innovent, Cermanod, Meotec in Germany and Nobel Biocare in Switzerland; Keystone Dental in the USA; Research and practical use of Nano Prime in Poland continues.

The formation of surface layers by the PEO method is a complex process, since it involves three operations simultaneously: electrochemical reactions, plasma-chemical reactions, and oxygen thermal diffusion reactions. The layers produced by these reactions are typically three-layer structures with a porous outer layer, a dense intermediate layer, and a thin inner dense layer. Various methods have been developed for treating the surface of metals and their alloys intended for producing coatings. Examples of coating metals include chemical modification, anodizing, electroplating, organic cladding, laser cladding, vapor deposition (physical vapor and chemical vapor), and thermal/cold spraying (Seshan et al., 2001). Most of these methods use toxic or harmful chemicals to form the surface layer of the packaging and require proper care and monitoring during use. The above-mentioned surface layer formation processes may have some limitations related to the coating or substrate material, mainly caused by low adhesion forces, overlap of surface layers and the growth of pores and cracks, leading to potential equipment failure. In contrast, the PEO process is less complex because it typically uses non-hazardous and environmentally friendly solvents and achieves the highest performance oxide surface layer at low cost and long life.

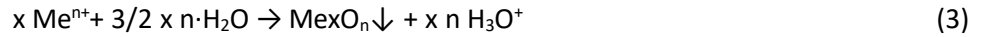
Anodization or anodic oxidation is a classical method of surface treatment of metals and their alloys in order to form a protective oxide layer (Chu et al., 2015). In this process, a uniform voltage or current is applied between two electrodes in an electrolytic solution to create a thick oxide layer on the metal substrate of the anode. Anodizing was first used on an industrial scale in 1923 to improve the protective properties of seaplane aluminum (Ebnesajjad et al., 2013). The oxalic acid anodizing process was patented in 1923 (in Japan) and was primarily used for architectural purposes. The anodizing process is typically carried out at low operating temperatures and high current densities. Here, the surface structure and chemical composition of the surface oxide layer can be changed by adjusting parameters such as electrolyte concentration and composition, electrical parameters, and substrate composition. The PEO process is an advanced version of the anodizing method, which uses the high potential to generate chemical, thermal, and plasma reactions in the substrate to form a thick and dense ceramic oxide surface layer. The PEO process also allows the formation of new surfaces of different colors and textures, providing wear and corrosion resistance, thermal stability, dielectric properties, good bioactivity and biocompatibility (Lu et al., 2016; Rizwan et al., 2018). A similar process to PEO is hard anodizing because it produces a thicker, stronger coating than conventional anodizing.

Literature review

1. The mechanism of formation of the surface layer in the PEO process

In the PEO process, changing the current mode between alternating current, direct current, bipolar, and unipolar current modes can lead to significantly different modifications of the surface layer. Key parameters such as current density, voltage intensity, pulse fluctuation, and positive/negative duty cycle influence the PEO procedure and the properties of the resulting surface layer (Martin et al., 2013). In addition, these parameters affect the characteristics of the PEO process, such as advanced stress fracture, local melting and oxidation of the coating, solidification, and recrystallization processes, and in turn significantly affect the microstructure and properties of the surface layer. The PEO process uses a wide range of voltages (95 to 750 V) with alternating or direct current between the cathode and anode. When the circuit is closed, the cathode and anode obey Faraday's and Ohm's laws. In this case, the metal coating together with a counter electrode (usually stainless steel or a graphite cathode) serves as a working electrode (anode) (Gao et al., 2014). Both electrodes are immersed in a slightly alkaline electrolyte. The electrodes are then connected to an external power source to begin the surface formation process. During the PEO process, electrochemical oxygen

evolution and metal oxidation reactions occur at the anode (equations (1) and (2)). In this case, due to a strong electric field, anodic generation of oxygen occurs, and oxygen anions (O_2^-) move to the anode and form metal oxide in the coating. Depending on the coating, electrolyte composition, and chemical activity, this may result in surface dissolution or the formation of an anodic oxide film (equation (3)). At the same time, intense evolution of hydrogen gas (equation (4)) and reduction of cations (equation (5)) occurs on the cathode surface. Due to gas evolution and the discharge reaction, the resulting layer may be more porous than the oxide layer formed during the solidification process. The general equations involved in the PEO process are:



where M is the metallic material required for the process, n is the number of electrons transferred, e is an electron, and Cat is a cation.

The article (Snizhko et al., 2007) reports that the Faradaic process is associated with traditional hard anodizing, but there have been cases where non-Faradaic phenomena were observed simultaneously with discharge reactions. It was later emphasized that the PEO process involves non-Faradaic processes such as thermal decomposition of water. Apart from these two processes, current PEO research mainly focuses on two hypotheses. Research is primarily being conducted to better understand the fundamentals of the PEO process, such as electrical discharge reactions, gas evolution (Snizhko et al., 2007), and acoustic emission (Arrabal et al., 2009; Boinet et al., 2005). The second assumption is different, such as the surface layer's resistance to corrosion and oxidation (Gu et al., 2011; Gu et al., 2012; Hwang et al., 2009; Barchiche et al., 2007), wear characteristics of the layer (Zhang et al., 2007; Yeshmanova et al., 2021), photocatalytic efficiency (Jiang et al., 2011; Kenzhaliyev et al., 2021; Yao et al., 2010), biological activity (Huang et al., 2005; Han et al., 2003) and thermal activity. and impact resistance (Clyne et al., 2019; Shokouhfar et al., 2012) regarding properties. All these assumptions are important for the emerging surface layer. General mechanisms in the PEO process: a) formation of an oxide layer at the interface of the metal and electrolyte, b) increase in the potential difference on both sides of the dielectric oxide layer; c) breakdown of the dielectric oxide layer (Lugovskoy et al; 2013). At the beginning of the oxidation process, there is an initial outward thickening of the oxide layer, followed by an inward thickening of the oxide layer (Darband et al., 2017).

The resulting oxide layer often has a solid crystalline structure because electrical discharges generate significant amounts of heat, leading to increased crystallization around the oxide layer (Wang et al., 2020). Surface layers treated with PEO have a higher level of porosity but are relatively more wear-resistant than anodized coatings (Clyne et al., 2019). Dielectric breakdown occurs between a thin oxide layer at the bottom of a deep pore in the coating. In the PEO process, high voltage and alternating current cause intense sparking due to microarc discharges, which leads to the formation of damaged oxide layers.

There are significant differences in the performance of PEO compared to the anodizing process. The layer formed as a result of anodization has a relatively uniform shape, and due to the low electrical conductivity of the oxide layer, the thickness of the resulting oxide layer is small. The resulting layer weakens the metal surface during anodization and limits its further growth (Fig. 1: Stages I-II). On the other hand, in the PEO process, high voltage causes intense sparking due to micro-discharge arcs that destroy the oxide layer (Fig. 1: stages I-III). High temperatures and pressures develop in the exhaust ducts, which cause complex phase transformation processes leading to the formation of a compact, thick and hard layer that is resistant to wear and corrosion. Despite the relatively high porosity of PEO layers, they can effectively protect the base metal from corrosion, since the pores formed during the discharge can be treated with molten oxides due to the high local temperature in the plasma discharge zone. Therefore, the surface layers of PEO do not allow aggressive environments to pass through.

The PEO process is influenced by various parameters such as the nature of the coating material, electrolyte components, current density, current type, voltage, frequency, duty cycle, additives, incorporated particles, coating time and operating temperature (Rapheal et al., 2016; Shokouhfar et al., 2012; Yerokhin et al., 2003; Li et al., 2013). Although this process is widely used for materials such as aluminum and its alloys (Yerokhin et al., 2003; Wielage et al., 2008; Patel et al., 2017; Loghman et al., 2018; Zhang et al., 2017) and

magnesium and its alloys (Narayanan et al., 2014; Lu et al., 2016; Apelfeld et al., 2017; Chen et al., 2018; Lu et al., 2018), recent research into PEO surface coatings has focused on other cladding metals such as titanium. (Luo et al., 2019; Han et al., 2018; Rokhian et al., 2018; Yavari et al., 2016; Jiang et al., 2016), tantalum (Wang et al., 2013; Gao et al., 2014; Rokosz et al., 2016; Zhao et al., 2017; Antonio et al., 2019), zirconium (Sandhyarani et al., 2014; Lu et al., 2015; Cengiz et al., 2017; Savushkina et al., 2017; Malayoglu et al., 2020), niobium and all their various alloys have been studied in (Rudnev et al., 2014; Stojadinović et al., 2016; Pereira et al., 2017; Pereira et al., 2018; Ge et al., 2019). Additionally, significant work on the modification of zinc using the PEO process has been reported by (Rocca et al., 2015; Stojadinović et al., 2016; Li et al., 2018; Yuan et al., 2018). Apart from the above-mentioned materials, several studies have been carried out with other rare metals such as hafnium (Stojadinović et al., 2017), beryllium (He et al., 2017) and brass (Cheng et al., 2020).

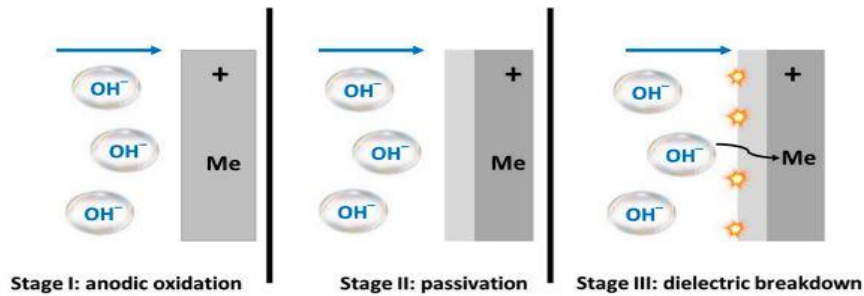


Figure 1. A schematic diagram explaining primary stages of an oxide layer generation in anodizing and PEO process (Yerokhin et al., 2003)

1.2. Processing conditions affecting the PEO process

In addition to the above parameters, there are other factors that affect the surface layer, such as the formation of gas bubbles, the development of soft plasma discharges in the late stages of the process, the emitted electromagnetic radiation, a phenomenon also known as galvoluminescence, plasma temperature, electrolyte in electrolyte when an electric field is applied, also known as electrophoresis. Mentioned in article (Kaseem et al., 2020) about the rapid movement of dispersed particles and the energy consumed in this process. The morphology, microstructure, and phase composition of the PEO layer ultimately determine the characteristics of the layer. Therefore, in the next section, we will briefly review studies analyzing the influence of technological parameters of PEO surface layers.

1.3. Action of electric current

The type of power used in the PEO process affects the morphology of the resulting surface layers, their structure, the rate of layer thickness growth, layer hardness, and porosity value (Denhavi et al., 2014). As mentioned earlier, the PEO process can use different electrical current modes: direct current and alternating current, as well as bipolar and unipolar current for specific applications. Although direct current can be used to form the PEO process, the process is more efficient when using alternating current. The use of direct current in applications requiring porous and thin surface layers is reported in (Khan et al., 2010). In addition, the constant current mode favors the formation of surface layers with a relatively low rate of oxide layer formation, which leads to the formation of highly porous structures. This current mode provides less control and less adjustable discharge characteristics, but if pulsed constant current mode is used, it allows better control of discharge duration and possibly reduced energy consumption (Khan et al., 2005; Jiang et al., 2010). Direct current is relatively cheaper and more convenient to use than alternating current. On the other hand, the advantage of using AC mode is that it stops the polarization of the electrode and helps control the process by interrupting the arc (Famiyeh et al., 2019). Bipolar pulsed current modes have been observed to produce taller and thicker coatings with higher corrosion resistance as they reduce the effects of high-intensity plasma discharges as well as high-temperature explosions when used in the PEO process (Denhavi et al., 2014; Hussein et al., 2011).

As for constant voltage modes, its effect on the PEO process with a zirconium (Zr) alloy in the presence of citric acid was studied (Stojadinović et al., 2014). They used optical emission spectroscopy (OES) to characterize microdischarges during PEO. The study showed that the optimal selection of experimental parameters, such as the type and volume of electrolyte, plays an important role in determining the

characteristics of the resulting surface layer. Other factors such as temperature and electron density have provided a more detailed understanding of the PEO process as well as the mechanisms involved.

Zhao et al. (2018) used direct current to improve the surface characteristics of several *Al-Zn-Mg-Mn-Zr* alloy samples in their research work. This process was characterized by the appearance of microdischarge sparks at four different stages. It was observed that in the first stage, the passivation film is formed under the action of a strong electric field, and in the remaining three stages, the passivation film is formed under the action of breakdown voltage. They found that the surface layer formed a thicker layer at lower current densities and with fewer internal defects. On the contrary, high current density had a detrimental effect on the composition and properties of the surface layer. (Sowa et al., 2018) studied the effect of direct current on the surface layer of pure *Zr* PEO in the presence of calcium acetate and calcium glycerol phosphate electrolytes. The process was carried out at voltages of 200, 300, and 400 V. At a voltage of 200 V, the appearance of the most corrosion-resistant surface layer without a porous structure was observed. This type of surface layer is ideal for biomedical equipment. When carrying out the process at 300 V and 400 V, in contrast to the 200 V process, a layer with less corrosion resistance was obtained. In addition, it was found that the thickness and roughness of the resulting layers increase with increasing stress. The influence of the electrolyte components on the surface characteristics was insignificant. Regardless of the parameters used, the pitting corrosion resistance of zirconium was found to improve after the application of PEO surface layers.

Another study (Akbar et al., 2017) analyzed the effect of the duty cycle on the surface layer thickness of bipolar direct current PEO. It was observed that the thickness of the surface layer decreases with increasing duty cycle and it was concluded that DC affects the surface layer of PEO differently and further research can be carried out to modify the surface layer.

Articles (Arrabal et al., 2009; Matykina et al., 2010; Guan et al., 2008; Matykina et al., 2009) write that PEO surface layers were applied to different metal coatings using different electrolytes under alternating current conditions. (Naeini et al., 2019) based on a research work investigated a biocompatible ceramic layer of *TiO₂* nanoparticles and hydroxyapatite (HA) deposited on pure titanium (*Ti*) using a PEO surface layer. In the experiment, a titanium sample was used as an anode, and stainless steel was used as a cathode. Five different types of electrolytes with different molar concentrations were used in the experiments, as shown in table 1. Initially, PEO surface coating was carried out on *Ti* samples in the presence of electrolytes without the addition of HA nanoparticles. Later, HA nanoparticles were added to the samples via an electrolyte. It was observed that surface layers in a solution containing electrolytes 1, 3 and 4 lead to better binding of HA nanoparticles due to the pores formed during the PEO process.

Table 1. Composition and concentration of electrolytes used

Electrolyte	Composition	Electrolyte concentration (M)
1	NaH ₂ PO ₄	0.030
	Ca(CH ₃ COO) ₂	0.020
2	NaH ₂ PO ₄	0.020
	Ca(CH ₃ COO) ₂	0.013
	NA ₂ (EDTA)	0.120
3	Ca(CH ₃ COO) ₂	0.055
	Na-Beta G	0.012
4	Ca(H ₂ PO ₄) ₂	0.020
	HMP	0.016
	NA ₂ (EDTA)	0.030
	Ca(CH ₃ COO) ₂	0.028
5	Ca(H ₂ PO ₄) ₂	0.050
	NA ₂ (EDTA)	0.045
	Ca(CH ₃ COO) ₂	0.0036

Among all the electrolytes, it was observed that 4 electrolytes give the greatest thickness of surface layers. Moreover, after reaching the breakdown voltage for all electrolytes, this led to a decrease in the thickness of the sample. This can be explained by the fact that local heat distribution and discharge generation in the PEO process affect the thickness of the sample (Aliasghari et al., 2016). It was also observed that the samples coated with HA nanoparticles showed less corrosion than the samples coated without HA

nanoparticles. From the results obtained in this study, it can be concluded that the addition of HA nanoparticles significantly improves the material properties of titanium samples.

In the PEO process carried out on alternating current, the formation of pores was observed during breakdown of the anode. These pores are regenerated by liquid oxides formed during the corresponding anodic pulse. In this case, the electrolyte near the sample is revived and the new oxide layers formed become homogeneous. Typically, the PEO process uses sinusoidal alternating voltages with a frequency of 50–60 Hz and a voltage of 100–600 V (Sah et al., 2012)[91].

It is assumed that PEO performed with alternating current goes through the following stages (Gao et al., 2014; Gu et al., 2011; Sah et al., 2012):

(a) During the first anodic half-cycle, a barrier oxide layer forms at the interface between the metal and the electrolyte.

b) The potential difference on both sides of the oxide layer increases with increasing anodic half-cycle.

c) electric sparks occur when the dielectric layer is damaged. A new volume of electrolyte is injected into the metal surface during fracture until the voltage is sufficient to induce a new fracture state, resulting in penetration and expansion of the oxide layers.

d) during cathodic half-cycles, relaxation of the metal and oxide layer and partial reduction of oxidized samples occur.

(e) The formation and destruction of gas bubbles during the process affects the growth of the oxide layer.

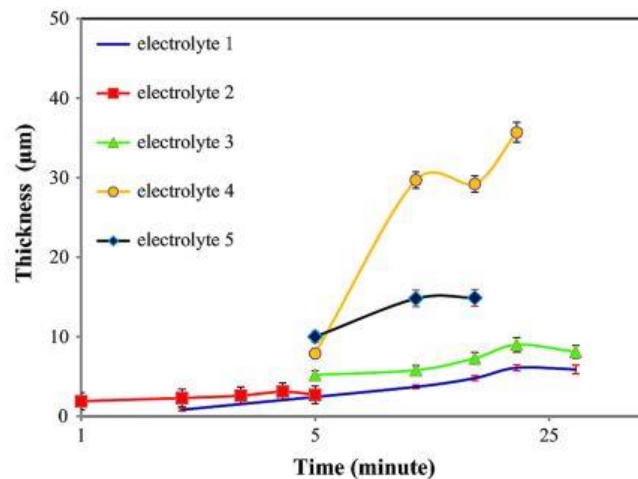


Figure 2. Time dependence of the thickness of the layer obtained from the electrolyte

To understand the importance of voltage and processing time characteristics associated with the PEO process, two studies are reported: (a) *AJ62 Mg* alloy using bipolar current mode and (b) *AM50 Mg* alloy operating in constant current mode (Chu et al., 2015). *AJ* alloys are magnesium-based casting alloys that provide optimum creep resistance at elevated temperatures. *AM* alloys containing aluminum and manganese, have good ductility and are used in the automotive industry for instrument panels, steering wheels and seat frames. There were four consecutive discharge periods for each study. Stage I: This stage is the initial phase of the PEO process where rapid electrochemical reactions occur in the resulting oxide film. Here the breakdown voltage has not yet been obtained. Stage II: At this stage, a decrease in the voltage level was observed, which was characterized by the appearance of several discharge sparks quickly moving along the surface of the sample. This phenomenon was characterized by a decrease in the rate of oxidation with increasing temperature in a process that was characterized by large numbers but slow discharge sparks. Stage IV: In this stage, the difference in stress rate was slower than in stage III. Here, intense discharges are formed in the form of relatively large and long-lasting sparks. In some cases, these powerful discharges can cause permanent damage to stage IV coatings.

1.4. Effects of electrolytes

The composition, nature (strong or weak) and concentration of electrolytes play an important role in determining the layer formed in the PEO process. Typically, the electrolytes used in the PEO process are

alkaline and weak. Electrolytes allow the movement of electrical charges to form a circuit and can regulate electrical conductivity as needed (Rogov et al., 2017). Aging of electrolytes is an important factor in the PEO process (Martin et al., 2015). In addition, the *pH* values of electrolytes play an important role in the PEO process, which can affect the microstructure and properties of the resulting layer.

In (Ghasemi et al., 2010), PEO surface layers were prepared on *AM50 Mg* alloys using *KOH* as an electrolyte with various additives such as silicate, phosphate and alumina, respectively. This alloy is widely used in automobiles, but its use is limited by low mechanical strength and corrosion resistance. The PEO process was found to produce the greatest silicate-based layer thickness of about 8 μm and the smallest alumina-based layer thickness of about 1 μm . In addition, it was found that the layer formed from these electrolytes has different phase components. In addition, PEO surface layers obtained in electrolytes with the same impurities but different concentrations may have different characteristics. It has been proven that increasing the electrolyte concentration increases the thickness of the total surface layers and affects its porosity.

In (Wang et al., 2020), the PEO process was carried out on *Al 1060* alloy in the presence of three electrolytes (permeability values may vary), namely silicate, phosphate and a mixture of silicate and phosphate. This alloy has excellent electrical conductivity, corrosion resistance and is widely used in electrical and chemical industries. It has been observed that the breakdown voltage is 240 V for silicate system, 300 V for phosphate system and 280 V for mixed electrolytes. The fastest and largest layer thickness was observed for the silicate system, followed by the phosphate and finally the mixed electrolyte system. The influence of electrolytes on the roughness of the resulting surface layers was determined. The surface shape formed by the silicate coating showed the greatest deviation, followed by the phosphate electrolyte and then the mixed electrolyte.

(Shin et al., 2011) studied the effect of two different electrolytes on a *Ti* layer using the PEO method. The model is intended for biomedical research. The electrolytes used were potassium pyrophosphate ($K_4P_2O_7$) and potassium triphosphate (K_3PO_4), both of which are harmless to the human body. Both electrolytes have the same *pH* value. Experiments using the PEO process were carried out at room temperature to study the role of surface roughness and the structure of oxide films on titanium. These surface layers were used to further investigate the formation of biomimetic apatite in a simulated body fluid. According to the research results, it was noticed that $K_4P_2O_7$ forms crater-shaped microporous structures, which leads to an increase in surface roughness. The smaller pore size resulted in easier development of the surface layer of apatite. X-ray analysis of the same data showed that $K_4P_2O_7$ forms more phases, resulting in a higher growth rate of biomimetic apatite. Therefore, it can be concluded that $K_4P_2O_7$ was the best electrolyte for titanium PEO process for biomedical applications.

1.5. Nanocomposite layers

The introduction of nanoparticles is an effective way to improve the quality of the PEO process. The PEO process of these nanoparticles incorporated into the surface layer formation structure allows the creation of composite surface layers. Although a significant number of embedded nanoparticles enter the inner fragments of the surface layers, most of them remain diffusely distributed near the outer layer of the surface layers (Bahramian et al., 2011). As a result, the structure of the layer changes. Nanoparticles embedded in the structure of the formation of the surface layer not only improve its corrosion and tribological characteristics, but also improve adhesion and hardness to the underlying metal. These nanocomposite layers are used in the automotive, petrochemical, biomedical, marine and electronics industries. In the research work (Arrunnellajappan et al., 2018), $\alpha\text{-Al}_2\text{O}_3$ and *m-ZrO*₂ nanoparticles were introduced into the *Al* alloy AA7075 by the PEO method in the presence of stearic acid, which led to the formation of nanocomposite layers. These nanoparticles were found to increase the thickness and corrosion resistance of the surface layer. The addition of stearic acid makes the coating hydrophobic in nature and further improves corrosion resistance. (Sharifi et al., 2016) used the processing of pure titanium PEO by adding $\alpha\text{-Al}_2\text{O}_3$ nanoparticles along with the non-toxic corrosion inhibitor ketoconazole to produce dense nanocomposite surface layers. The presence of ketoconazole promoted the absorption of nanoparticles, made the layer denser and reduced its porosity. It was found that the hardness and wear resistance of the surface layer of the nanocomposite were also improved. (Sharifi et al., 2016) investigated the effect of cerium nanoparticles (CeO_2) on *AM50 Mg* alloy to develop an aluminate-based PEO method in their research work. It was found that the introduction of cerium reduces the porosity and roughness of the surface layer of the nanocomposite.

2. Mechanical properties of surface layers processed by the PEO method

2.1. Tribological attributes

PEO coatings are required for many surfaces that require slip or abrasion resistance. It has been established that the surface layers processed by the PEO method are firmly bonded to the underlying metal and have low hardness. As a result, the energy release rate of such layers is low. Although PEO surface coatings have a lower hardness, they are harder than anodized coatings. Here tribological studies play an important role for PEO treated surface layers and will be explained with several examples in the next section.

In (Qin et al., 2015), the PEO process was carried out on Ti_6Al_4V alloy with laser surface structure (LST) coated with MoS_2 solid oil. Different samples were considered for this process: untreated Ti_6Al_4V , LST treated Ti_6Al_4V , PEO treated Ti_6Al_4V , and a combined PEO treated Ti_6Al_4V and PEO treated Ti_6Al_4V sample. Under the same inlet conditions, the LST and PEO treated samples showed a higher coefficient of friction, while the untreated samples had a lower coefficient of friction. When examining the wear rate in the same experiment with the same input parameters, the untreated sample showed the highest wear rate, while the LST and PEO treated sample showed the lowest wear rate.

(Pezzato et al., 2018) investigated the tribological effect of PEO-treated surface layers with and without graphite nanoparticles on *AZ91 Mg* and *AZ80 Mg* alloys. Dry sliding tests were carried out on two alloys with and without graphite additives on a steel counter surface at two different processing times: 1 and 3 minutes, respectively. The coefficient of friction for *AZ91* with and without additives was highest at 1 minute of treatment. This was due to the abrasive interaction of the counter surface of the hard and rough PEO treated *AZ91* sample with the steel surface. On the other hand, for *AZ80* alloy with and without graphite, the highest friction coefficient was observed at a processing time of 3 minutes. In wear roughness depth analysis, both *AZ91* and *AZ80* with graphite showed the least scar formation.

2.2. Effect of fatigue load

The resistance to cyclic fatigue loading was affected by the development of cracks and the initial stage of their growth. Since these phenomena occur at the surface, it is very important to analyze what increases or decreases the resistance to these surface changes. Corrosion can also affect these surface development processes. PEO surface layers are often compressive in nature and have relatively low residual stresses. The loss of compressive stresses in the metal itself leads to deterioration in surface quality, which is undesirable. Therefore, it is important to pre-treat surfaces before carrying out the PEO process.

(Winter et al., 2016) performed a PEO process on *Al 6082* alloy to understand the average stress sensitivity of the fatigue life of the alloy. *6082 Al* is a medium strength alloy with excellent corrosion resistance used in vehicles. Previous studies have shown that PEO-treated aluminum alloys have lower wear resistance compared to uncoated alloys. As the coating thickness increases, the wear characteristics of the existing aluminum alloy PEO surface layers are further reduced. The decrease in fatigue strength may be due to the porosity of the oxide film, which initiates early crack propagation. Three different applied load ratios (R) of -1, 0.0, and 0.1, respectively, were used to study the fatigue behavior of the aluminum alloy. The applied load factor is defined as the ratio of the minimum and maximum loads taken into account during the fatigue loading process. During the experiment, the PEO process time was reduced to produce a thinner film, which reduced the negative impact on fatigue strength. The maximum stress that can be applied to a material without failure for a certain number of cycles is called its fatigue strength. After completion of the process, the fatigue strength of the PEO-treated samples decreased significantly under all three loading factors. It was observed that the PEO process neutralizes the effect of mean stress on the fatigue life of the layer. Other studies have also been noted that indicate a decrease in the fatigue life of other *Al* and *Mg* alloys (Klein et al., 2017; Dejun et al., 2015; Němcová et al., 2014). However, the fatigue life did not change in the PEO process carried out on Ti_6Al_4V alloy (Petomati et al., 2012). After the PEO process is completed, there are residual electrolytes in the packaging. If this residual electrolyte is not completely washed away, corrosion can occur. Therefore, you must be very careful while performing this process and check each step.

2.3. Residual stresses

The surface layer produced by the PEO process is restructured several times under the influence of microdischarges, so the residual stresses generated during this oxidation process are constantly decreasing in magnitude. In addition, the relatively low hardness of PEO layers does not allow high stresses to occur. But in a number of cases, literature studies mention high residual stresses (Dehnavi et al., 2014; Ao et al., 2019).

However, there are differences in these results. These high residual stress values were obtained from X-ray diffraction patterns. This method is difficult to apply in PEO layers, since the microstructure of the layer consists of very fine grains, different phases and it is possible to significantly change the microstructure of the layer. To account for this limitation, a new method called curvature measurement was used. Using this method, the overall stress level in PEO treated layers was found to be about 50 MPa for *Al* and 150 MPa for *Mg* (Dean et al., 2015).

Conclusion

The PEO process has been a standard metal surface treatment technology in many studies. Its use has increased significantly and it has many unique characteristics that set it apart from other facial treatments. This review helps to understand the mechanisms and discuss the processes involved in the process, the processing conditions affecting the process, the main characteristics of the process, the mechanical attributes of the process.

The articles mentioned here explain the effect of electric current on the surface layer treated with PEO on a modern model. The importance of electrolytes used in this process is discussed in detail. In addition, the types of additives that can be used in PEO processes are listed, as well as their functional properties. The interesting nanocomposite layers formed using the PEO process are another highlight of this resume.

Because PEO-treated layers change the microstructure, it reduces residual stresses and creates an overall more uniform surface layer. For a deeper understanding, it is necessary to describe the microstructural properties of the resulting surface layers. No less important is the study of the mechanical and tribological properties of the treated layers.

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