

Urania

Jurnal Ilmiah Daur Bahan Bakar Nuklir

Beranda jurnal: <https://ejournal.brin.go.id/urania>



IMPROVEMENT OF PLASMA ELECTROLYTIC OXIDATION (PEO) COATING ON ZIRCONIUM ALLOYS USING ADDITIVES FOR NUCLEAR FUEL CLADDING APPLICATION

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(Naskah diterima: 22–11–2024, Naskah direvisi: 17–12–2024, Naskah disetujui: 23–12–2024)

ABSTRACT

IMPROVEMENT OF PLASMA ELECTROLYTIC OXIDATION (PEO) COATING ON ZIRCONIUM ALLOYS USING ADDITIVES FOR NUCLEAR FUEL CLADDING APPLICATION. This study explores the improvement of Plasma Electrolytic Oxidation (PEO) coatings on zirconium alloys using additives for pressured water reactor (PWR) fuel cladding application. PEO is a promising surface treatment for zirconium alloys, offering improved corrosion and wear resistance, essential for applications in extreme environments, such as nuclear reactors. Various types of stable particle and dissolved additives were incorporated into the electrolyte during PEO process to modify the coating's microstructure, phase composition, and mechanical properties. The incorporation of stable particle such as Al_2O_3 , CeO_2 , and Y_2O_3 not only reduces surface porosity and roughness but also increases the presence of the tetragonal zirconia phase ($t\text{-ZrO}_2$), leading to enhanced corrosion and wear resistance. Additionally, the use of dissolved additives, including complex agents and salts, positively affected plasma characteristics and further improved coating density and durability.

Keywords: Plasma Electrolytic Oxidation, zircaloy, additives, corrosion.

ABSTRAK**PENINGKATAN LAPISAN PLASMA ELECTROLYTIC OXIDATION (PEO) PADA PADUAN ZIRKONIUM MENGGUNAKAN ADITIF UNTUK APLIKASI KELONGSONG BAHAN BAKAR NUKLIR.**

Kajian ini mengeksplorasi peningkatan lapisan Plasma Electrolytic Oxidation (PEO) pada paduan zirkonium melalui penggunaan aditif untuk aplikasi kelongsong bahan bakar nuklir reaktor air tekan. PEO merupakan perlakuan permukaan yang menjanjikan untuk paduan zirkonium, dengan peningkatan ketahanan korosi dan aus, yang sangat penting untuk aplikasi pada lingkungan ekstrem, seperti reaktor nuklir. Berbagai jenis partikel stabil dan aditif terlarut ditambahkan ke dalam elektrolit selama proses PEO untuk memodifikasi struktur mikro, komposisi fasa, dan sifat mekanik lapisan. Penambahan partikel stabil seperti Al_2O_3 , CeO_2 , dan Y_2O_3 tidak hanya dapat mengurangi porositas dan kekasaran permukaan, tetapi juga meningkatkan keberadaan fasa zirkonia tetragonal ($t-ZrO_2$), yang mengarah pada peningkatan ketahanan korosi dan keausan. Selain itu, penggunaan aditif terlarut, termasuk agen kompleks dan garam, berdampak positif pada karakteristik plasma dan lebih lanjut meningkatkan densitas serta ketahanan lapisan.

Kata kunci: Plasma Electrolytic Oxidation, zirkonium, aditif, ketahanan korosi.

INTRODUCTION

PEO (Plasma Electrolytic Oxidation), also known as Micro Arc Oxidation (MAO), is a surface treatment technology capable of producing a strong and highly adherent oxide layer with improved mechanical properties, as well as wear and corrosion resistance [1], [2]. PEO is derived from the anodizing process, where a metal workpiece is placed in an electrolytic bath and voltage is applied between the workpiece and an inert cathode [3]. In the PEO process, the metal workpiece is immersed in an environmentally friendly alkaline electrolyte, as shown in Figure 1. PEO can also coat metals with complex shapes and large sizes [4]. The applied voltage in the PEO process must exceed the dielectric breakdown of the oxide formed.

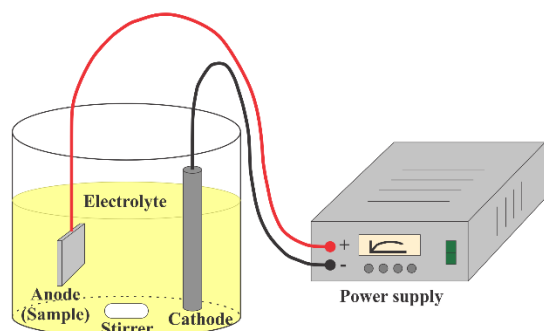


Figure 1. Schematic of PEO process.

PEO is typically performed on valve metals such as Al, Mg, Ti, and Zr [2], [5]. Valve metals refer to types of metals that, under anodic conditions, form a metal oxide where electrons encounter resistance as they flow through the oxide. An electric field forms in the oxide as voltage increases, eventually reaching a point where the dielectric strength of the oxide is exceeded, causing discharge [6]. The PEO process is appealing as a coating alternative due to its relatively low cost, simple process, low operating temperatures, environmental friendliness, strong ceramic coating adhesion, and its ability to coat complex surfaces [1], [7]. This technology has found applications not only in the nuclear industry but also in biomedical, aerospace, electronics, and automotive sectors. For example, PEO is employed in biomedical implants to mechanical properties and corrosion resistance [5], [8]. In aerospace application, PEO is used to improve solar absorptance of the thermal control flat absorber [9], or to improve the corrosion

resistance of various lightweight components [10]. In automobile application, PEO is used to enhanced hardness and wear resistance of surface load-bearing components [11]. In electronics, PEO is used to produce electrically insulating ceramic coating with good temperature resistance and thermal conductivity [12]. These diverse applications highlight the broad potential of PEO coatings to enhance material performance in demanding environments.

In the context of nuclear fuel cladding application, since the Fukushima accident, significant efforts have been dedicated to improving the integrity of nuclear fuel cladding. Researchers and engineers have focused on developing advanced materials and coatings that enhance the cladding's resistance to high-temperature oxidation and mechanical failure under severe accident conditions. These efforts include the investigation of innovative surface treatments such as PEO to improve the durability and safety performance of existing zirconium-based cladding [13], [14], [15], [16], [17]. The goal is to enhance the resilience of nuclear fuel cladding, reducing the risk of failure during extreme operational scenarios in nuclear reactors. Furthermore, the corrosion resistance of PEO coatings at high temperatures and/or pressures has been extensively studied. Under superheated steam condition (400 °C, 10.3 MPa) for 105 days, PEO-coated Zr alloy exhibits a 35.9 mg/dm² lower corrosion weight gain compared to bare Zr alloy due to its compact inner layer, which acts as a barrier against the penetration of corrosive media into the substrate [18], [19]. The PEO coating has been reported to enhance corrosion resistance of Zr at temperatures up to 1100 °C, due to lower oxygen diffusion coefficient of the ZrO₂ phase compared to bare Zr. However, at temperatures above 1100 °C, PEO-coated and bare Zr alloys exhibit nearly identical weight gain [20]. In addition to oxidation resistance, PEO coatings have also been reported to improve the nitridation resistance of Zr alloys [21].

The properties of PEO coatings are generally influenced by the coating composition and microstructure, which are determined by electrical and electrolyte parameters [17], [22], [23], as shown in Figure 2. The composition and concentration of the electrolyte can affect the composition and microstructure of the PEO coating. Various

types of electrolytes have been studied to enhance the quality of the oxide layers produced from the PEO process. For Zr alloys, the PEO process is commonly performed using silicate, aluminate, and phosphate electrolytes, either individually or in combination [24]. KOH or NaOH can be added to enhance electrolyte conductivity [25].

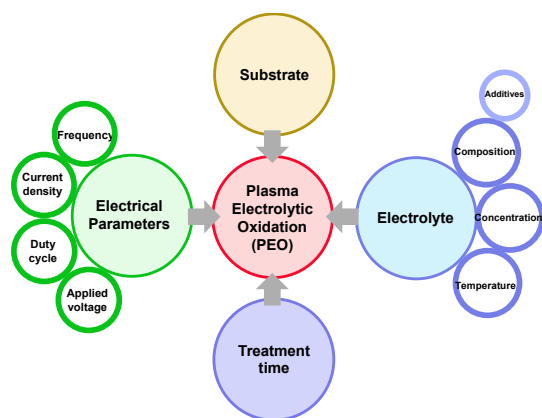


Figure 2. Factors affecting properties of PEO coatings.

Adjusting electrical parameters, including current mode, magnitude, frequency, and duty cycle, significantly influences the breakdown behavior, as well as the size, density, and intensity of discharges during the PEO process. Different types of current pulsation have been studied to enhance the quality of oxide layers formed through PEO, as these parameters can optimize the discharge characteristics. However, the effectiveness of this approach is limited, where the formation of cracks and porosity in the oxide layers are unavoidable.

To mitigate these issues, researchers have implemented further modifications to the electrolyte, particularly through the addition of various additives. These additives serve a dual purpose: they help seal micro-cracks that may develop within the PEO coating, and they can also alter the characteristics of the oxide layer. There are two primary categories of electrolyte additives: stable particles and dissolved additives. By carefully selecting and incorporating these additives, it is possible to achieve a more robust and high-quality PEO coating that meets specific performance requirements. This review aims to provide a detailed overview of PEO processes and mechanism on Zr and its alloys for nuclear fuel cladding application. It also delves into the mechanism and effects of solid

micro/nanosized particle and dissolved additives incorporation on the coating's properties. Notably, the dissolved additive which has not been widely used in Zr has the potential to be applied in nuclear applications.

MECHANISM OF PEO PROCESS

During the PEO process, several complex reactions occur, including electrochemical reactions, plasma chemical reactions, metallurgical reactions, and reactions related to thermal diffusion of oxygen [26]. These reactions produce acoustic emission, luminescence, and heat release [1]. Gas emissions and plasma discharges lead to the formation of micro-pores, discharge channels, and micro-cracks that are visible on the surface or throughout the thickness of the coating layer. PEO coating formation involves two growth mechanisms, namely the internal and external growth mechanisms. External growth is the movement of the layer from the substrate to the electrolyte, where the ejected species undergo melting, oxidation, and solidification. Internal growth occurs due to a strong electric field, allowing O^{2-} to penetrate the layer and react with the substrate metal cations, resulting in the formation of an oxide layer. Rapid cooling due to the cold substrate causes the rapid solidification of the molten oxide at the layer-substrate interface, forming a thin crystalline layer [1].

The mechanism of oxide layer growth during the PEO process has been reported [27], [28]. Initially, a passive oxide layer forms rapidly on the surface of the substrate within the first few seconds. As the voltage increases, an insulation layer with columnar structure grows, oriented perpendicular to the metal substrate. The growth of the oxide layer occurs at the metal-oxide and oxide-electrolyte interfaces, with O^{2-} and cations migrating in opposite directions along the layer. Due to the high voltage, dielectric breakdown occurs in relatively weak areas (thinner regions) of the oxide layer, resulting in the formation of numerous fine white sparks on the anode surface. Once the breakdown strength is exceeded, an avalanche of electrons occurs along the oxide film, forming discharge channels with high local temperature and pressure. The ions present in the discharge channels induce the formation of plasma, initiating plasma chemical reactions. Anionic species from the electrolyte

and substrate alloy are drawn into the discharge channels and oxidized by the strong electric field between the cathode and anode. The liquid products of the plasma chemical reactions condense and rapidly solidify into a solid form due to cooling by the electrolyte, forming solid blockages in the columnar structure primarily composed of crystalline oxides. Eventually, the discharge channels release gases generated during the process, resulting in the formation of volcano-like structures [4], [7], [27]. Sobrinho et al. [29] reported four stages of PEO coating development. The first stage is anodic oxidation (anodization), which results in the formation of a solid oxide layer. This layer increases the resistance of the metal substrate, ultimately causing a stable increase in voltage. As the voltage slowly exceeds the breakdown point, plasma discharge occurs, indicating the second stage of layer formation. This stage involves cycles of breakdown and regeneration or reformation of the layer, where the layer is regenerated at a rate that exceeds its dissolution rate. During this period, the outer layer exhibits porosity. In the third stage, voltage continues to increase. However, no increase in layer thickness is observed during this stage. The high temperature of the electrolyte may accelerate the dissolution of the layer, balancing the rates of regeneration and dissolution, even though the porous layer expands and covers a larger surface area of the substrate. The fourth stage presents two different release mechanisms. The first is the breakdown of the porous layer, primarily occurring in the thin barrier layer at the bottom of the large pores, where the probability of dielectric breakdown is higher compared to other sites on the surface. The second

mechanism is the breakdown in the voids between the substrate and the oxide, which is electrically connected to the electrolyte through cracks [30].

Hussein et al. [31] suggested that there are three types of plasma discharges during the PEO process, namely type A, B, and C, as shown in Figure 3. Discharge types A and C occur at the metal-oxide interface, specifically near the surface and within the pores of the oxide layer, respectively. Electrolyte species tend to enter the oxide layer through these types of discharges. Strong discharge type B occurs at the substrate-oxide interface. This type of discharge releases metal ions into the electrolyte and predominantly facilitates the incorporation of species from the substrate into the layer [31], [32].

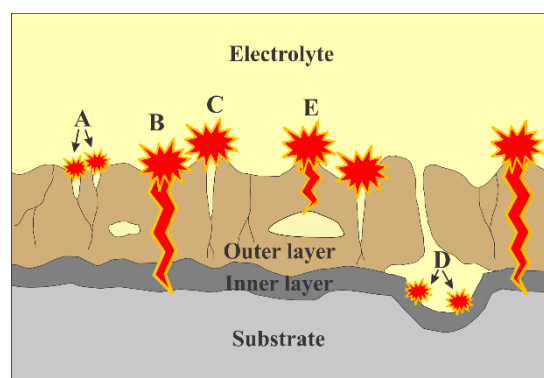
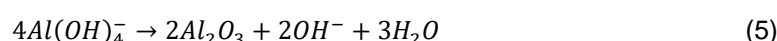
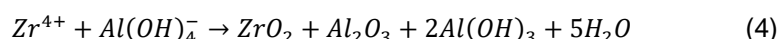
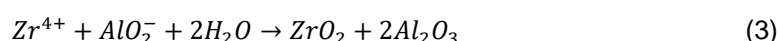
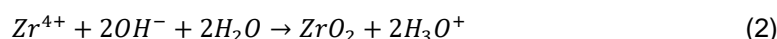


Figure 3. Types of plasma discharges during PEO process.

Anionic species from the electrolyte are deposited into the coating, as reported by Zhang et al. [33], [34] in the PEO of Zr using NaAlO_2 electrolyte, which resulted in formation of composite of ZrO_2 and Al_2O_3 PEO coating through the following reactions.



MICROSTRUCTURE OF PEO COATINGS

The PEO process produces a layered oxide coating with a pancake-like structure that is porous and contains micro-cracks. The oxide from the metal substrate is the main constituent of the PEO coating, making ZrO_2 the primary composition of the PEO coating on

Zr metal and its alloys. The morphology of the PEO coating generally consists of two layers: an outer amorphous layer with a porous and rough morphology, and an inner crystalline layer with numerous fine pores [35]. Some studies also report that there are three layers in the PEO coating: a barrier layer near the

substrate, an inner layer, and an outer layer [36]. Lateral pores (pore bands) may be present between the inner layer and the outer layer. The microstructure of the PEO coating is related to the characteristics of plasma discharges during the PEO process, such as intensity, size, and distribution of plasma on the anode surface [32]. A significant amount of high-energy plasma discharge generates a high thermal gradient, melting (re-melting) of oxides, as well as rapid cooling and solidification. This process not only facilitates layer growth but also results in defect formation. The discharges occurring during electrolytic oxidation cause the expulsion of liquid oxide and gas bubbles from the discharge channels, resulting in pore formation. The size of the pores in the layer is significantly influenced by the size and characteristics of the generated plasma. The pancake structure is produced by type B discharges with strong intensity, while micro-pores are generated by types A and C discharges [32]. Cheng et al. [37], [38] further suggested discharge type D and E, as shown in Figure 3. Discharge type D occur within the internal pores near the interface between the inner and outer layers and contribute to the growth of inner layer. Discharge type E penetrate the outer layer, leading to the development of large pores under the pancake-like structure.

There are two types of pores in the PEO coating: open pores located on the surface and closed pores located within the layer [7]. Additionally, the morphology of the PEO coating on Zr alloys is also reported to be influenced by electrolyte concentration, where low aluminate concentrations produce pancake structures, while high aluminate concentrations yield porous structures [38]. Micro-cracks can also form due to stress relief caused by layer growth [39] and thermal stress when liquid oxides rapidly solidify in relatively cooler electrolyte areas [40]. At atmospheric pressure, ZrO_2 has three types of polymorphs, regard to the temperature: monoclinic phase ($m-ZrO_2$), tetragonal phase ($t-ZrO_2$), and cubic phase ($c-ZrO_2$). The $m-ZrO_2$ is stable at temperatures below 1170 °C and at room temperature. The $t-ZrO_2$ is stable within range of 1170-2370 °C. The $c-ZrO_2$ exists at higher temperature, from 2370 °C up to its melting point at 2680 °C [41]. The crystal structure of $m-ZrO_2$, $t-ZrO_2$, and $c-ZrO_2$ are shown in Figure 4. The detailed phase diagram for Zr

and O showing those phases can be found elsewhere [42]. During the PEO process, the high temperatures generated by plasma melt the substrate and oxides which then undergo a rapid solidification in the vicinity of the cooler electrolyte, leading to the formation of mixture of $t-ZrO_2$ and $m-ZrO_2$ [43]. The rate of transformation can determine the ratio of those phases [34]. It has been reported that the difference of thermal condition throughout the coating results in different dominant phases in the inner and outer layer [44]. The discharges with very high temperature that primarily occur on the surface, combined with low conductivity of the coating, results in higher temperature in the outer layer of the coating. In contrast, the inner layer has a lower temperature due to heat dissipation into the metal substrate. Consequently, high temperature phases of $t-ZrO_2$ tend to form in the outer layer, while low temperature phases of $m-ZrO_2$ tend to form in the inner layer.

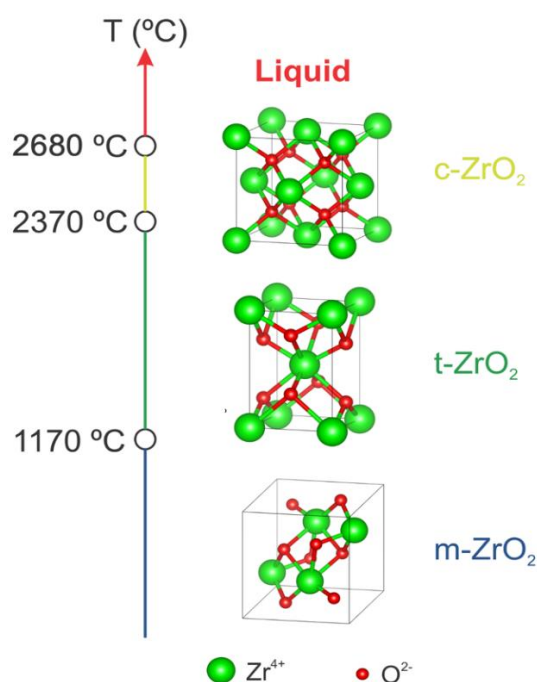


Figure 4. The crystal structure of $m-ZrO_2$, $t-ZrO_2$, and $c-ZrO_2$ at corresponding temperature. The crystal structures were modeled using VESTA software.

The phase transformation of $t-ZrO_2$ to $m-ZrO_2$ during cooling and solidification of liquid ZrO_2 is accompanied by shear strain of approximately 0.16 and a volume expansion of about 4%, which subsequently causes

cracking in the layer [39], [45]. Reducing the PEO process time can produce a thinner layer with fewer defects [46]. Conversely, pores and micro-cracks increase with prolonged PEO process time, leading to decreased corrosion resistance of the thicker PEO coating.

IMPROVEMENT OF PEO COATING QUALITY WITH ADDITIVES

Additives serve a dual purpose: they seal micro-cracks that may develop within the PEO coating, and they can also alter the characteristics of the oxide layer. For instance, it has been reported that particle incorporation to the PEO coating decreases porosity and surface roughness and increases the hydrophobicity of the coating, subsequently improve the corrosion resistance [47], [48]. In addition to particles, additives can also be added in the form of dissolved substances or salts. The addition of dissolved additives influences the characteristics of the generated plasma. The mechanism and effect of stable particle and dissolved additive to the PEO process are discussed below.

a. Improvement of PEO coating quality with the addition of stable particle additives

Mechanism of stable particle incorporation during PEO process

When particles exist in the electrolyte and an electric current is applied, the particle surfaces acquire an electric charge. The movement of charged particles in a liquid under the influence of an external electric field is known as the electrophoresis effect [49], as shown in Figure 5. Positively charged particles are attracted to the cathode, while negatively charged particles are attracted to the anode [50]. The electrophoretic force is determined by the charge behavior at the solid-liquid interface, which is influenced by the zeta potential (ζ). During plasma discharge, nanoparticles are absorbed and integrated into the PEO coating through various pathways such as micro-cracks, micro-pores, and channels [7]. The incorporation of particles into the PEO coating occurs through a combination of physical adsorption, electrophoretic deposition, and electrophoretic forces, along with physical or mechanical mixing by molten oxide [7], [51]. Particles with higher ζ in electrophoresis are more stable, less prone to agglomeration, and have a higher movement rate [35]. The pores in the

PEO coating can serve as entry pathways for particles during the PEO process. However, on another study, O'hara et al. [52] suggested that although electrophoretic forces are present near the PEO surface, they are relatively weak due to the low electric field strength (~ 100 V/m) in the electrolyte, with most of the applied potential being dropped across the oxide layer. Using the Smoluchowski relationship, it's estimated that the terminal velocity of particles is about $7 \mu\text{m/s}$, but this is an upper bound. Given the short period (~ 5 ms) in which a substantial electric field is active (due to the 50 Hz supply frequency), the resulting particle motion would be minimal—a small fraction of a micron [52]. Thus, electrophoretic forces are unlikely to significantly contribute to particle incorporation during PEO. Instead, convective forces from the electrolyte pump and rapid gas bubble movement during discharge cycles, which occur at much higher velocities (~ 10 m/s), are more influential in particle incorporation. The author suggested that the incorporation of particles during PEO occurs when the plasma bubble collapses, causing electrolyte to flow back into the pores or depressions on the coating surface. This backflow of electrolyte sweeps fine particles into these regions, as shown in Figure 6.

Based on their effect on the layer, the particle additives can be classified as inert, partially reactive, or reactive particles [51]. Inert incorporation occurs when particles are incorporated without any reaction or formation of a new phase. These particles can be easily traced and identified within the layer. The others are reactive or partially reactive incorporation, that occurs when particles are melted by the high-energy discharges during PEO process, allowing them to react with components from the matrix and electrolyte. This complex process is influenced by various factors, such as the substrate, electrolyte composition, particles concentration and Zeta potential (ζ), melting point, and the energy provided by the discharges [35], [53]. Particles with a high melting point are typically embedded in a partially reactive or inert manner, regardless of the particle size. In contrast, particles with low melting points (ranging from 1000 to 1200 °C) are likely embedded in a reactive manner [54].

Furthermore, nano-sized particles, being smaller than discharge channels, can penetrate deeply into the coating, unlike larger

micro-sized particles which are mostly embedded near the surface through large discharge channels at the end of the PEO process [54]. Therefore, large pores can facilitate the uptake of more particles [55]. However, nanoparticles tend to agglomerate in the electrolyte, especially during prolonged PEO [52]. To prevent this, procedures such as surfactant addition and ultrasonic treatment are often employed [56].

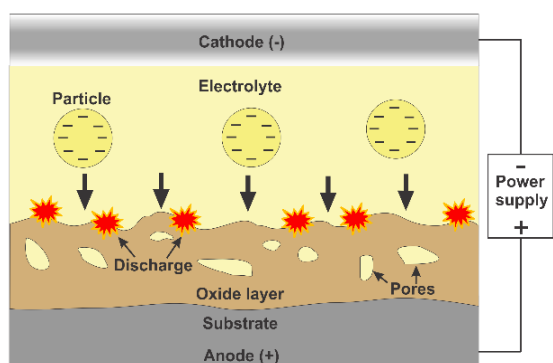


Figure 5. Mechanism of particles electrophoretic movement during PEO process.

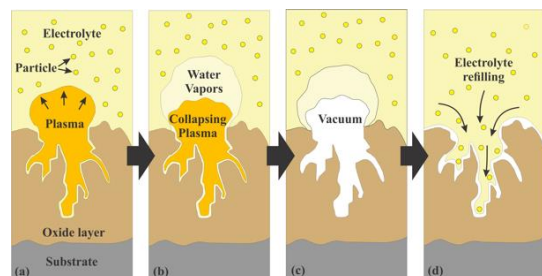


Figure 6. Mechanism of particles incorporation into the PEO coatings: (a) plasma formation and expansion; (b) collapsing of plasma; (c) condensation of vaporized electrolyte; (d) electrolyte refilling due to vacuum created by vapor condensation.

Effect of stable particle addition to the PEO coating

Introducing particles into the electrolyte influence the PEO process by modifying the solution's properties, such as viscosity, pH, and conductivity, which can influence the morphology and characteristics of the resulting coating [35]. Lower conductivity in a PEO electrolyte generally results in a higher breakdown voltage [57]. This is because lower conductivity reduces the

current flow, making it more difficult to initiate the plasma discharges, thus requiring a higher voltage to reach the breakdown point. Arun [47] reported that the addition of oxide particles of Al_2O_3 , CeO_2 , and ZrO_2 increased the breakdown voltage compared to the base electrolyte. The author also attributed this effect to the increased resistance of the layer due to particle incorporation. However, a different situation is observed with particles that have high electrical conductivity, such as GO, where the addition of 1 wt% GO to the Na_2AlO_4 based electrolyte increases the electrolyte conductivity from $15.6 \mu\text{S/cm}$ to $26.3 \mu\text{S/cm}$, subsequently lower the breakdown voltage [48]. The particle size can also influence the magnitude of the breakdown voltage, as reported in another study by Arun et al. [40] who investigated the effect of graphite particle size addition to Na_3PO_4 electrolyte on the PEO coating of pure Zr. Addition of nano-sized particles resulted in a slightly higher breakdown voltage compared to micron-sized particles [40]. Due to their advantageous size, the nano-sized particles are easily absorbed into the coating through discharge channels compared to micron-sized particles, increasing the thickness of the oxide layer.

The particle additives can fill the pores within the PEO coating by settling inside them during the discharge process, leading to a reduction in surface roughness and porosity, affecting the microstructure and morphology, as well as the coating thickness. It has been reported that the PEO on Zr in Na_3PO_4 (5 g/L) electrolyte and current density of 150 mA/cm^2 produced coating thickness of $\pm 6 \mu\text{m}$, while the addition of particles results in a PEO coating thickness of $\pm 8 \mu\text{m}$ [47]. Similar results concerning the increase in thickness with higher particle concentrations have also been reported [58]. On the other hand, the study by Roknian et al. [59] showed that the addition of ZnO particles up to 15 g/L in the PEO of Ti did not significantly affect the thickness of the PEO coating. However, the pore size in that study decreased with the addition of particles due to the increased conductivity of the electrolyte, which reduced the breakdown potential. Similar results were also reported by Bordbar-Khiabani et al. [60]. Furthermore, the arrangement of the particle additive within the oxide layer can be tailored by conducting a two-step PEO process [61]. For particles with a low melting point and that are reactively

incorporated, the coating phase is also affected. For instance, in PEO process of Mg with the addition of hydroxyapatite (HAp), the presence of a new phase, $\text{Na}_2\text{CaMg}_7(\text{PO}_4)_6$, is observed, which is not found in PEO without HAp particles [62].

In PEO of Zr metal, it has been reported that the addition of particles to the electrolyte can enhance the t-ZrO₂ phase in the PEO coating on Zr. Several research [16], [47], [63] have reported that addition of particle such as Al₂O₃, CeO₂, and Y₂O₃ to the electrolyte during the PEO of Zr can incorporate into the PEO coating and increase the t-ZrO₂ phase. Apelfeld [58] reported that the t-ZrO₂ phase in the PEO coating of Zr-1Nb alloy increased with the rising concentration of Y₂O₃ particles in the electrolyte. Additionally, compared to micron-sized particle, the nano-sized particles are more easily absorbed into the coating through discharge channels, resulting in thicker and denser PEO coating [40].

The decrease in porosity of the PEO coating due to particle incorporation can block the pathways for corrosive media to penetrate, thereby enhancing the corrosion resistance of the PEO coating [8], [63]. The Tafel extrapolation method is employed to determine corrosion characteristic parameters, including corrosion current density (i_{corr}) and corrosion potential (E_{corr}). The PEO coating of Zr-1Nb alloy with addition of CeO₂ particle has i_{corr} of 1.38×10^{-6} $\mu\text{A}/\text{cm}^2$, which is three orders of magnitude lower than the PEO coating in base electrolyte

without particle additive (1.97×10^{-3} $\mu\text{A}/\text{cm}^2$) [47]. Karimi [48] reported that as the concentration of GO additive particles increases, it not only raises the thickness of the PEO coating but also reduces the i_{corr} and increases the E_{corr} . This may also be due to the increased hydrophobicity with the decrease of surface roughness and porosity of the coating [47], [48].

The addition of particles in the PEO process can enhance wear resistance. Scratch test results indicate that the scratch grooves in the PEO coating without additive particles are deeper and wider compared to the PEO coating with particles addition under identical load parameters [47], [63]. Additionally, the GO sheets particles in PEO coating of Zr provided self-lubricating properties and improved wear resistance by transferring a thin layer of material to the abrasive pin surface during wear, creating a lubricating layer. In PEO coating containing GO particles, the wear mechanism was identified as delamination wear, while in PEO coatings without GO particles, the primary wear mechanism was adhesive due to insufficient lubrication [48]. Therefore, the smaller (nano)-sized particles in PEO coating can result in a better lubricant property. Their small size allows them to fill in the gaps between larger particles, reducing the surface roughness and, consequently, friction [40].

Table 1 shows several particles that have been used in the PEO process of Zr metals and their alloys, along with the characteristics of the resulting coatings.

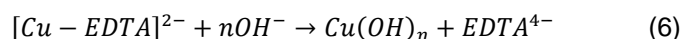
Table 1. Particle additives used in several PEO process in Zr metal and alloys.

Particle	Incorporation	Substrate	Characteristics of PEO Coatings	Ref
Al ₂ O ₃	Inert	Zr	Reduced surface roughness, increased corrosion resistance, increased scratch resistance, and increased t-ZrO ₂ phase	[47]
Graphite	Inert	Zr	Reduced pores in the PEO coating (especially with nanoparticles), with no change in phase structure	[40]
Graphene oksida (GO)	Inert	Zr-1Nb	Improved corrosion resistance, excessive addition inhibits layer growth.	[48]
CeO ₂	Inert	Zr	Reduced surface roughness, improved corrosion resistance, increased scratch resistance, and enhanced t-ZrO ₂ phase	[47]
MoS ₂	Inert	Zr	Improved wear resistance, reduced friction coefficient	[63]
SiC	Inert	Zr	Excellent adhesion strength and corrosion resistance	[64]
Y ₂ O ₃	Inert	Zr-1Nb	Increased t-ZrO ₂ phase, improved scratch resistance, excess Y ₂ O ₃ may form inclusions.	[58]
Y ₂ O ₃	Inert	Zr-4	Increased t-ZrO ₂ phase, improved high-temperature corrosion resistance.	[16]
ZrO ₂	Inert	Zr	Improve corrosion resistance, increased t-ZrO ₂ phase	[47]

b. Improvement of PEO coating quality with the addition of dissolved additives

Mechanism of Dissolved Additives Incorporation During the PEO Process

The addition of dissolved additives can be used to influence the PEO process as well as the plasma characteristics during the PEO process. For instance, Aubakirova et al. [65] reported that addition of boric acid to acetate-phosphate-based electrolyte in the PEO coating of Zr-1Nb alloy reduced pore size in the coating and increased coating density, which subsequently improved corrosion and wear resistance. The presence of boron was reported to reduce the melting point and viscosity of the oxide layer during plasma



CuO and Cu₂O, which have higher dielectric constants, can withstand stronger electric fields before reaching breakdown. The presence of copper oxides inhibits the formation of high-intensity plasma, while EDTA reduces the plasma size, resulting in a coating with low surface porosity, leading to improved corrosion resistance.

Hussain et al. [67] achieved porosity reduction in PEO coating of Al-Mg-Si through the formation of soft plasma using organic additives of sodium citrate and sodium oxalate, both individually and in combination, in the electrolyte. They reported that the combination of oxalate and citrate provided superior corrosion resistance compared to when each additive was used individually. The oxalate and citrate ions acted as strong Lewis bases during PEO process, interacting with the Al³⁺ ions at the interface, which serve as strong Lewis acids. This interaction led to the formation of a thick adsorbed electrochemical double layer that acts as a barrier and creates a complex ligand structure. The protective effect of this layer, along with its rapid reformation, facilitated the development of a defect-free coating, resulting in an enhanced corrosion resistance compared to other samples.

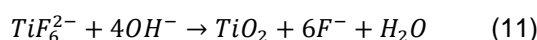
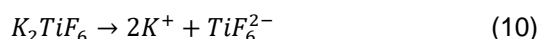
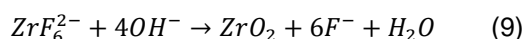
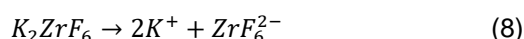
Effect of Dissolved Additives Incorporation on the PEO Coating

The addition of dissolved additives can be used to incorporate specific elements into the PEO coating. For instance, Li et al. [68], [69] incorporate Ti and Zr into PEO coating of

formation, resulting in slower solidification and easier pore filling. Dissolved additives can also enter the PEO coating through reactive mechanisms.

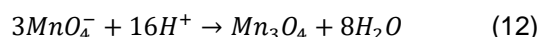
Kamil et al. added the complexing agent ethylenediaminetetraacetic acid (EDTA) and Cu-EDTA to the KOH (6 g/L) + Na₂SiO₃ (4 g/L) electrolyte for the PEO of Al-1.1Mg alloy [66]. EDTA can form complex ions with transition metals, facilitating the incorporation of transition metals into the PEO coating due to the formation of negatively charged ions. The addition of Cu-EDTA resulted in the incorporation of CuO and Cu₂O through the reaction:

Mg AZ91D alloy using dissolved additive method. They reported that addition of K₂TiF₆ and K₂ZrF₆ (5 g/L each) to electrolyte of KF (15 g/L) + NaH₂PO₄ (5 g/L) on the PEO process increased electrolyte conductivity, reduced breakdown voltage, and produced a finer plasma. PEO with K₂TiF₆ additive resulted in lower porosity compared to PEO with K₂ZrF₆. Ti and Zr cations were incorporated into the PEO coating through reactions:



Many studies have revealed that in-situ incorporation offers several advantages compared to the particle route. For instance, Kaseem et al. [70] compared PEO coatings of Al alloy that used particle additives of V₂O₅ (3 g/L) with those using salt additives of NH₄VO₃ (3 g/L) for incorporating V₂O₅ to enhance catalytic performance. The dissociated additive in salt method increases the conductivity of the electrolyte and lowered the breakdown voltage of the PEO process. They also reported that the salt-containing electrolyte covered a larger area compared to molten particles during the PEO process, incorporating more V₂O₅, resulting in a thicker PEO layer and subsequently providing better

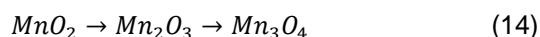
corrosion resistance compared to the particle method. Similarly, Bahrampour et al. [69] incorporated Mn_3O_4 into the PEO coating of Mg-Zn-Ca alloy using two approaches: adding $KMnO_4$ salt (4.5 g/L) and adding Mn_3O_4 nanoparticles (4.5 g/L) into the $K_3PO_4 \cdot 3H_2O$ (5 g/L) + KOH (2 g/L) electrolyte [69]. Both additives resulted in reduced surface porosity and increased layer thickness. The addition of $KMnO_4$ salt lowered the breakdown voltage, while Mn_3O_4 particles increased the breakdown voltage. During the PEO process, $KMnO_4$ salt decomposes to produce MnO_4^- and K^+ ions. MnO_4^- ions migrate to the discharge channel at the Mg anode under the influence of the electric field in the alkaline electrolyte. MnO_4^- reacts with H^+ in the electrolyte, resulting in the formation of Mn_3O_4 , which is incorporated in situ into the PEO coating, according to the reaction:



Meanwhile, redox reactions between molecules occur in the discharge channel:



MnO_2 then undergoes a series of redox reactions to produce Mn_3O_4 according to the reaction:



Where Mn_3O_4 subsequently enters the coating, reducing porosity and enhancing corrosion resistance.

CONCLUSIONS

Incorporation of additives during the PEO process significantly enhances the quality and performance of oxide coatings on zirconium alloys. Additives help reduce the formation of cracks and porosity, which are common challenges in PEO coatings. By optimizing PEO process parameters and selecting appropriate additives, it is possible to achieve coatings with superior mechanical properties and corrosion resistance. For Zr metal and alloy, particle additives such as Al_2O_3 , Y_2O_3 , and CeO_2 contribute to improved corrosion resistance, enhanced scratch resistance, and an increased presence of the t-ZrO₂ phase. Meanwhile, dissolved additives, aside from incorporating specific elements to alter the coating's properties, also aid in refining plasma characteristics, resulting in denser and more uniform coating structures. These

advancements can be applied to improving PEO coatings for Zr alloys, particularly for nuclear fuel cladding materials, to enhance their integrity and safety, especially under high-temperature and severe operational conditions. Future research should focus on further exploring dissolved additives for zirconium substrates to continue improving coating properties. Furthermore, the neutronic performance of the PEO coatings, particularly their impact on the moderation, absorption, and reflection of neutrons in nuclear applications still needs to be evaluated. Experimental studies on the irradiation performance of PEO-coated Zr alloys under simulated operational conditions still also remain limited. Addressing these gaps will provide critical insights into the feasibility and reliability of PEO coatings for nuclear applications, ultimately advancing their potential as a protective technology for Zr alloys.

ACKNOWLEDGEMENT

The author expresses sincere gratitude to the Degree by Research Program of BRIN for funding the master's education in Materials Science at the University of Indonesia

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