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Editorial

Plasma Electrolytic Oxidation of Metals and Alloys

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1. Introduction

Porous oxide layers formed on metals and alloys via Plasma Electrolytic Oxidation (PEO) have been developed and used for decades in medicine and for technical purposes. The following metals—Ti, Ta, Nb, Zr, Al, and Mg—are now in focus for PEO treatment, which can help improve their biomedical and mechanical properties. Apart from single metals, selected two-, three-, and four-component titanium alloys, such as Ti-*x*Mo, Ti-*x*Zr-*x*Nb, and Ti-*x*Ta-*x*Nb-*x*Zr, are currently undergoing PEO processing. Differing from Ti-6Al-4V alloy, which has been routinely used in medicine, these new and advanced titanium alloys do not include vanadium. They are characterized by low Young's modulus and biocompatible alloy elements, and after PEO treatment may be used for medical applications, such as promising metallic implants to bone [1–6].

Lightweight designs in many industries, transportation, and aerospace require the application of light metals (Al, Mg) and alloys, enhanced by special surface treatments. The requirements, therefore, not only concern mechanical strength, but also significant protection of the materials against corrosion and wear resistance. Here, plasma electrolytic oxidation (PEO) comes into play to obtain hard and wear-resistant oxide coatings [7,8]. In comparison to the PEO treatments mentioned earlier that last 3 to 5 min, plasma electrolytic oxidation of aluminum and its alloys take one to three hours to obtain strong coatings with proper thickness and structure [7].

Magnesium (Mg) and its alloys are classified as biodegradable materials and are promising for medical implant engineering due to their biocompatibility, non-toxicity, mechanical properties, and biodegradation behavior. The corrosion products of Mg and its alloys are physiologically beneficial to humans. Unfortunately, their uncontrolled rate of degradation is a problem. Surface modification can improve the corrosion resistance of Mg alloys and decrease their degradation rate. The developed CaP coatings can be applied in the manufacturing of medical biodegradable implants and devices (fixators, screws, plates, scaffolds) from Mg alloys for orthopaedic and cardiology applications.

2. Contributions

The present Special Issue covers 10 papers: Six articles [1–6] discuss the Plasma Electrolytic Oxidation PEO of titanium [2,4,6] and its alloys [1,3,5], two papers talk about the PEO processing of aluminum alloys [7] and composites [8], and one on magnesium alloys [9]. The tenth paper is a review regarding soft sparking issues in PEO [10].

Technologically advanced two- and three-component titanium alloys—Ti-15Mo, Ti-13Nb-13Zr and Ti-6Al-7Nb—were anodized in suspensions, followed by treatment in alkali solutions by Kazek-Kęsik et al. [1]. After anodizing, the samples were immersed in NaOH or KOH solution with various concentrations and different process parameters. The purpose of such processing was to enhance metal surface bioactivity, cytocompatibility, and antibacterial properties [1]. The reported techniques were used for titanium alloy surface modification in view of obtaining a functional biomaterial surface for medical applications.

In paper [3], the authors propose surface modification for titanium Ti-15Mo, Ti-13Nb-13Zr, and Ti-6Al-7Nb alloys as a material for dental implants. Alkali treatment of Ti alloys appears to be a useful method to enable PEO layers to change their biological properties quickly and in a simple manner. The chemical composition obtained after the treatments strongly affected the final result of the titanium alloys' surface modification.

In paper [2], the results of CP Titanium Grade 2 after PEO treatment are displayed. New porous coatings enriched in calcium and phosphorus were obtained in an electrolyte based on concentrated phosphoric 85% H_3PO_4 acid and calcium nitrate tetrahydrate $Ca(NO_3)_2 \times 4H_2O$ under DC voltage conditions, with and without pulsation at 450 V. The same material was used in another work by Rokosz et al. [4] with the aim to study and determine the effect of voltage increasing from 500 V_{DC} up to 650 V_{DC} on the chemical and electrochemical properties of the porous coatings obtained with plasma electrolytic oxidation (PEO). It was found that porous coatings may contain elements originating from the electrolyte used, leading to a bone-like structure (phosphorus and calcium) and showing antibacterial properties (copper and zinc) with simultaneous high corrosion resistance. On the basis of GDOES studies, a four-sub-layer model of PEO coatings was elaborated upon. Analysis of the potentiodynamic corrosion curves noted that the best electrochemical repeatability was noted for magnesium- and zinc-enriched coatings obtained at 575 V_{DC}.

Engelkamp et al. in their work [4] reported on titanium PEO treatment using a technique with combined potentiostatic and galvanostatic control. They used sulfuric acid electrolytes of different concentrations, from 0.5 M up to 12.9 M, to study the effect on titanium oxide formation. The results revealed that the thickness, porosity and phase composition changed substantially. They found that the oxide layer produced by plasma electrolytic oxidation can be adjusted on request by tuning the periods of galvanostatic and potentiostatic control.

Banakh et al. [5] worked to obtain bioactive coatings on Ti-15Mo alloys using PEO treatment in electrolytes containing Ca and P compounds. The studies were performed to reveal the influence of the nature of the electrolyte, its concentration, and PEO process parameters on the properties of anodized layers. They found that despite the maximum Ca/P ratios in the coatings being low, equaling about 1, the anodized layers on Ti-15Mo alloy demonstrated good biological activity, comparable to pure microrough titanium.

Technically hard and wear-resistant oxide coatings on aluminum alloys were produced by plasma electrolytic oxidation (PEO); results of the studies are presented in [7]. During PEO, a conversion of the aluminum substrate to a ceramic oxide takes place. The widely used commercial high-strength alloys of Al with Cu/Mg (EN AW-2024), Mg/Si (EN AW-6082), and Zn/Mg/Cu (EN AW-7075) were tested with regard to their abrasive behavior according to ASTM G65. The corrosion studies performed indicated a decrease of the corrosion current density by approximately one order of magnitude compared to the bare substrate. The PEO layers obtained on technically pure aluminum resisted the testing regimes when an electrolyte with an elevated silicate content, without additional hydroxide ions, was employed for a prolonged period.

Alloyage of aluminum composites with copper (1–4.5 wt%) were treated by PEO; the results are presented in [8]. Coatings, with thickness of up to 75 μm, were formed on the surface. The electrochemical corrosion behavior of coated composites and uncoated ones was studied in 3% NaCl solution. It was found that after plasma electrolytic oxidation, corrosion current density was greatly reduced.

Sedelnikova et al. [9] studied biodegradable magnesium alloy Mg-0.8Ca after PEO/MAO (Micro-Arc Oxidation) treatment. Modification of the biodegradable magnesium alloy using the MAO in electrolytes with the addition of beta-tricalcium phosphate (β-TCP) particles was performed to improve its biocompatibility and corrosion resistance. The aim of the study was to control and decrease the corrosion degradation rate. The MAO process was carried out using an anodic potentiostatic regime under pulsed voltage that varied in the range of 350–500 V; the process duration was 5 min to 10 min. Microstructure, morphology, topography, composition, and physical and chemical properties of the CaP coatings containing β-TCP particles were investigated. The corrosion experiments showed that the biodegradation rate of the Mg-0.8Ca alloy, coated with calcium phosphate, is almost 10 times lower than that of the uncoated alloy.

A review of soft sparking issues on the metal–oxide–electrolyte interface in the PEO process was carried out by Tsai and Chou [10]. In their paper, they consider phenomena occurring in an electrolyte of sodium silicate and potassium hydroxide, when an Al-based sample is oxidized with an AC or DC pulse current preset with the cathodic current exceeding the anodic counterpart. In the process, to get a dense inner layer, a sufficient amount of oxide is required on the metal surface. Their studies show that the dense inner layer requires plasma softening to avoid discharge damages, while maintaining a sufficient growth rate. An optimum porous top layer ought to retain heat to sinter the amassed oxide, and proper timing to initiate the transition and end the surface processing after transition. They state that further studies are needed, as the current soft sparking knowledge on Mg- and Ti-based alloys is insufficient.

3. Conclusions and Outlook

Plasma electrolytic oxidation (PEO) is currently being used to modify metal surfaces and improve the essential properties of contemporary metals and alloys. The process engages micro arcs on the treated metal surface, such that the oxide film melts and mixes with electrolyte ions. To improve the performance of the coating, various additives may be used. This set of papers is presented to showcase advanced technology and recent knowledge, which could be used in the fields of medicine and technical/engineering.

Present studies on PEO processes are concerned with attempts at further optimization of the parameters and conditions concerning proper electrolyte candidates, time of the treatment, and final results with mechanical and surface properties on request. However, process repeatability is an issue that needs to be looked at before it can be introduced on an industrial scale. The results of relevant studies show that although a big step has been taken to introduce and develop this kind of treatment, there are several questions that need to be answered before it can be initiated into modern surface technology.

As a guest editor, I would like express my gratitude to the contributing authors for making this Special Issue a valuable reference source on the topic. I extend my special thanks to the *Metals* editorial team, in particular Natalie Sun, for their assistance and support during the preparation of this issue.

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