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Review

Surface characterization and corrosion behavior of calcium phosphate-base composite layer on titanium and its alloys via plasma electrolytic oxidation: A review paper

A.R. Rafieerad [a,b], M.R. Ashra [a,*], R. Mahmoodian [a,b,c], A.R. Bushroa [a,b,**]

[a] Center of Advanced Manufacturing and Material Processing, Department of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] Department of Research and Development, Azarin Kar Ind. Co., Industrial Zone 1, 7635168361 Kerman, Iran

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ABSTRACT

In recent years, calcium phosphate-base composites, such as hydroxyapatite (HA) and carbonate apatite (CA) have been considered desirable and biocompatible coating layers in clinical and biomedical applications such as implants because of the high resistance of the composites. This review focuses on the effects of voltage, time and electrolytes on a calcium phosphate-base composite layer in case of pure titanium and other biomedical grade titanium alloys via the plasma electrolytic oxidation (PEO) method. Remarkably, these parameters changed the structure, morphology, pH, thickness and crystallinity of the obtained coating for various engineering and biomedical applications. Hence, the structured layer caused improvement of the biocompatibility, corrosion resistance and assignment of extra benefits for Osseo integration. The fabricated layer with a thickness range of 10 to 20 μm was evaluated for physical, chemical, mechanical and tribological characteristics via XRD, FESEM, EDS, EIS and corrosion analysis respectively, to determine the effects of the applied parameters and various electrolytes on morphology and phase transition. Moreover, it was observed that during PEO, the concentration of calcium, phosphor and titanium shifts upward, which leads to an enhanced bioactivity by altering the thickness. The results confirm that the crystallinity, thickness and contents of composite layer can be changed by applying thermal treatments. The corrosion behavior was investigated via the potentiodynamic polarization test in a body-simulated environment. Here, the optimum corrosion resistance was obtained for the coating process condition at 500 V for 15 min in Ringer solution. This review has been summarized, aiming at the further development of PEO by producing more adequate titanium-base implants along with desired mechanical and biomedical features.

Contents

* Corresponding author.
** Correspondence to: A.R. Bushroa, Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur, 50603, Malaysia.
E-mail addresses: Alireza5431.rafieerad@gmail.com (A.R. Rafieerad), nurulashra@gmail.com (M.R. Ashra), mahmoodian@um.edu.my, mahmoodian.reza@gmail.com (R. Mahmoodian), bushroa@um.edu.my (A.R. Bushroa).

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1. Introduction

During previous decades, the study of biomaterials as a specific field has been considered due to its direct relation to human health. A biomaterial is a nonviable matter used in a medical device intended to interact with biological systems [1]. Due to minimal tissue reactions, titanium and its alloys have been widely used in various biomedical applications, such as artificial joints, bone surgery and implant industries [2,3]. The attribution oxide layer, which is naturally formed on the surface of the considered metals, yields a favorable biological response [4].

According to recent research, Ti–6Al–4V has been utilized for most biomedical applications. However, this substance releases toxins and ions, and negative long-term effects are caused by vanadium as long as the substance remains inside the body. Modifications have been performed to minimize the undesired effects. These treatments improve the biocompatibility and increase the strength, Young's modulus (~100 GPa), yield strength (~650 MPa) and corrosion resistance [5–9].

Moreover, to produce high-strength and homogenous titanium-base substrates, severe plastic deformation (SPD) process, such as equal channel angular pressing[10,11], accumulative roll bonding (hot & cold) [12] and equal channel angular extrusion [13] have been used. Fig. 1 provides a schematic view of the abovementioned process.

Hence, the concept of biological improvements of titanium base implants has been considered via bioactive coatings. This represents the desired biological behavior related to the exact chemical composition of human bones [14–16]. Hydroxyapatite (HA), with the chemical structure of $Ca_{10}(PO_4)_6(OH)_2$, is composed of calcium phosphate and composes more than 65% of the bone tissue weight. It can be fabricated on a titanium surface by applying the mechanistic reaction of aqueous calcium hydroxide with orthophosphorous acid at room temperature, based on the present reactions from this study and Fig. 2[17,18]. Moreover, depending on the main conditions of the fabrication, HA displays a hexagonal symmetric structure from which various needle-shape and plate-shape structures may be obtained by applying the stoichiometric ratio of Ca:P = 1.67.

According to related publications, it has been proved that HA has the potential to endorse a new bone structure through osteoconduction without causing any local orsystemic toxicity or undesirable body effects. Although HA nanostructures are used as ceramic-base implants, the available carbonate apatite of the coated surface results in minimum stabilization and fixture of the implants to surround the tissues and, based on the chemical mechanistic features of HA particles, causes the inhibition of cancer cell growth [19–26] (Fig. 3).

HA nanoparticles with a grain size less than 100 nm are able to show a more appropriate stoichiometry, morphology and purity than do other HA structures and have been noted by the majority of researchers studying biomaterials [27–30]. Fig. 4 illustrates the various HA nanostructures that can be synthesized via the various abovementioned methods and schematic view of the PEO process.

Furthermore, HA and the other calcium phosphate-base composite layers can be coated on the titanium surface by various methods, such as electrophoretic (EPD), hydrothermal hot-pressing (HHP), high velocity oxygen fuel (HVOF), sol–gel, chemical vapor deposition (CVD), ion-beam assisted deposition (IBAD), physical vapor deposition (PVD), pulsed laser deposition (PLD), thermal spray and PEO, which also involves micro arc oxidation (MAO).

In this study, the increasingly widespread PEO method has been investigated as one of the best methods of placing the calcium phosphate-base composite layer on the biomedical grade of titanium. This process yields a substance of high adhesive strength, desirable mechanical and biomedical features, uncomplicated setup, and controllable chemical reaction methods. Hence, the surface characterization and corrosion behavior of HA, CA and the other calcium phosphate-base composite layers have been evaluated for this method.

2. Plasma electrolytic oxidation method

2.1. Calcium phosphate-base composite layer via PEO

Compared with the other coating processes, PEO is one of the most significant methods of depositing a bioactive layer, such as HA, on a biomedical-grade titanium surface. PEO can provide the condition to incorporate ions such as calcium, phosphor and titania to fabricate the composite layer, which would enhance not only the biocompatibility but also the mechanical characteristics of the coated layer by changing the coating's crystallinity and morphology [10–13,31,32].

Furthermore, the PEO method can form a layer on a substrate with various geometrical shapes, which increases the bonding strength. It is remarkable that the PEO method has often been combined with other methods to obtain optimum results and to fabricate bioactive coatings. In this review, the fabrication of a calcium phosphate-base layer and a composite type, such as HA, HA–TiO_2 and CA, on titanium base alloys has been investigated by PEO, not only achieving the desired morphology but also enhancing the chemical, physical and electrochemical characteristics [33–37].The plasma discharges cause high temperature adaptations of the coated layer by converting it into crystalline phases, which have a higher hardness strength.

The PEO method has the potential to form a coating layer with sufficient electrical conductivity. Furthermore, the method facilitates incorporating the ions of calcium and phosphor into Ti and its alloy surface by controlling coating parameters, such as the electrolyte composition, voltage, current density and times. Table 1 lists the results of applying

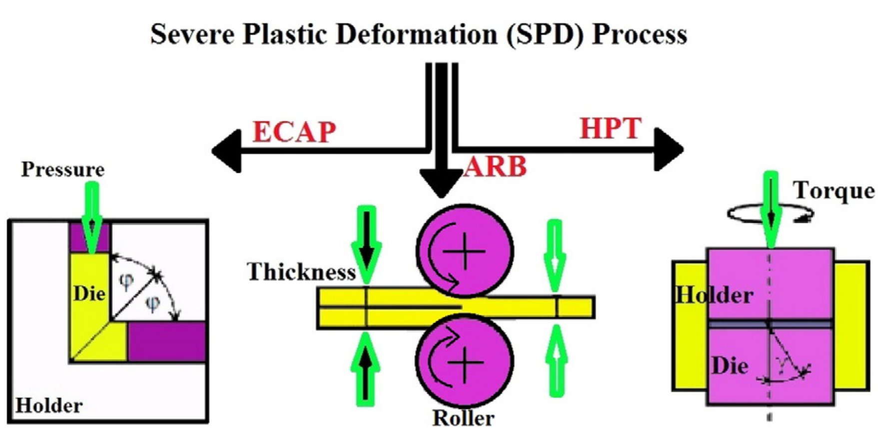

Fig. 1. Schematic view of the SPD process.