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Surface modification of CP-Ti metallic implant material by plasma electrolytic oxidation

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Abstract. Plasma electrolytic oxidation (PEO) is a relatively new and environmentally friendly process for development of thick and adherent oxide coatings on conventional and nanostructured metallic implant materials. The PEO process involves anodic oxidation of metals or alloys in aqueous solutions at voltages higher than the breakdown voltage of the oxides present on its surfaces. Currently, the PEO process is gaining increased attention as a novel technique for the fabrication of corrosion resistant, bioactive and functionally modulated composite coatings on commercial pure titanium (Cp-Ti) and Ti based alloys for orthopedic and dental applications. The PEO process coupled with the electrophoretic deposition (EPD) technique is used for the fabrication of TiO₂/hydroxyapatite (HA) composite coating on a Cp-Ti implant material in a single step. This paper briefly reviews the properties of the coatings produced on Cp-Ti by PEO and PEO coupled EPD processes.

1. Introduction

Metallic materials are the most common synthetic materials used for biomedical implants nowadays. Owing to their high strength and toughness, they are mostly used for the load bearing implant applications [1]. In addition to the strength and toughness, the necessity of the implant material to be non-toxic and corrosion resistant to the body fluid environment, resulted in the usage of stainless steels, Ti and its alloys, Cobalt-chromium alloys [2, 3]. Among the metallic implant materials, Titanium is gaining a lot of attention, due to its low elastic modulus and better biocompatibility, compared to other metallic implant materials [4, 5]. The low elastic modulus (nearly equal to that of the natural bone, i.e., ~ 10 – 30 GPa) of CP-Ti and titanium alloys, results in the lesser stress shielding effects caused due to the mismatch of the elastic moduli of the bone and the implant material [6]. Titanium and titanium alloys are widely used as hard tissue replacements in artificial bones, joints and dental implants [7, 8]. Titanium and its alloys are often used in artificial hip joints, knee joint replacements [9].

Besides artificial bones and joints, titanium and titanium alloys are often used in osteosynthesis, such as maxillofacial implants, bone fracture fixation parts like bone screws and bone plates, etc. [10]. Because of their higher strength, inertness and non-magnetic properties, Ti and its alloys are widely used for cardiovascular implants like heart valves, pacemaker cases [11]. Titanium and its alloys are



also used for dental applications such as implants, crowns, bridges and overdentures. Besides having these many advantages, implants made of Ti and its alloys experience corrosion in the body fluid environment, which can be overcome by the surface modification techniques. This article provides a brief review of the usage of CP-Ti as an implant material and the existing ways of improving its corrosion resistance, biocompatibility and antibacterial properties.

2. CP-Ti as an implant material

Owing to the higher biocompatibility with the living tissues along with the absence of toxic elements, CP-Ti is a promising material for the implant applications. In spite of the good biocompatibility, CP-Ti lags in the strength perspective compared to other implant materials like Co-Cr alloys and 316L stainless steel, which limits the usage of CP-Ti in load bearing implant applications [12]. The enhancement in the mechanical strength can be achieved either by the alloying or by the grain refinement. The enhancement of the strength by alloying can be attributed to the secondary phase formation or solid solution strengthening by the addition of alloying elements like Al and V, which might lead to the release of the corresponding ions into the body after prolonged exposure to the body fluid, which causes various long-term health problems [13]. The grain refinement of materials by severe plastic deformation (SPD) techniques is gaining attention nowadays, owing to the attainment of fine nanosized grains, thereby enhancing the strength [14]. In addition to the strength, severe plastic deformation enhances the biocompatibility of CP-Ti by enhancing the osseointegration process [15]. Equal channel angular pressing (ECAP) is the most widely used SPD technique for the grain refinement, thereby achieving the strength. But, the plastic deformation of Ti has been a challenge due to its limited plasticity, which can be surmounted by the technique of warm ECAP, in which Ti is worked at an elevated temperature around 400-500 °C [16]. A further increase in strength can be achieved by a combination of techniques like cold rolling, cold extrusion and thermo-mechanical treatments [14, 17, 18]. The production of nanostructured long length rods and sheets suitable for commercial applications can be achieved by a relatively new technique - ECAP-conform. Various researchers reported that nanostructured Ti obtained by ECAP, exhibits an enhanced corrosion resistance, compared to unprocessed Ti, attributing to the rapid formation of strong oxide films and the absence of impurity segregation, as in the case of unprocessed Ti [19, 20]. However, the enhancement in corrosion properties is limited. Further enhancement in the corrosion can be achieved by the surface modification of SPD CP-Ti. This can also improve the cell adhesion, thereby reducing the osseointegration time.

3. Surface modification of CP-Ti

CP-Ti is a bio-inert material, the cell adhesion property can be improved by various surface modification techniques. Surface modification techniques like grit blasting followed by acid etching, selective laser melting, 3-D printing of porous implants, electrochemical modification by forming nanotubes, plasma immersion ion implantation, bioabsorbable polymeric coatings have been reported to enhance the osseointegration [21]. Among these techniques, electrochemical modification methods like anodization and plasma electrolytic oxidation are the most effective and easiest surface modification techniques. The porous nature of the oxide coating formed by the PEO process provides a higher surface area for the cell adhesion.

3.1. Plasma electrolytic oxidation

Plasma electrolytic oxidation is a technique used to form hard, corrosion resistant ceramic coatings on valve metals, which can easily form passive oxide films like Al, Ti, Nb, Zr, Mg etc. [22]. PEO is an anodic oxidation process occurring at higher potentials than the breakdown voltage of the formed thin oxide layer [23, 24]. PEO is a 3-stage process as shown in figure 1, in which the valve metal connected to the positive terminal of a power source gets oxidized during the initial stage. The oxidized metal reacts with the anions approaching electrolyte, thereby forming the metal oxide. The oxide layer further grows at the expense of the metal by the diffusion process, and the increased oxide layer thickness resists the current flow and the diffusion of the anions and metal cations will become sluggish. The oxide layer

will resist the current flow, till the breakdown of the formed oxide layer is evident. The breakdown of the oxide layer further promotes electrochemical oxidation. The continuous repetition of the breakdown, followed by molten metal oxide ejection and quenching of the molten metal oxide provides rough and porous morphology, which is beneficial for the cell adhesion, along with the better corrosion resistance and increased interlocking between implant material and the tissue. The characteristics of the formed oxide layer will depend on electrical parameters like current density, pulse duty cycle and frequency, along with the electrolyte chemistry.

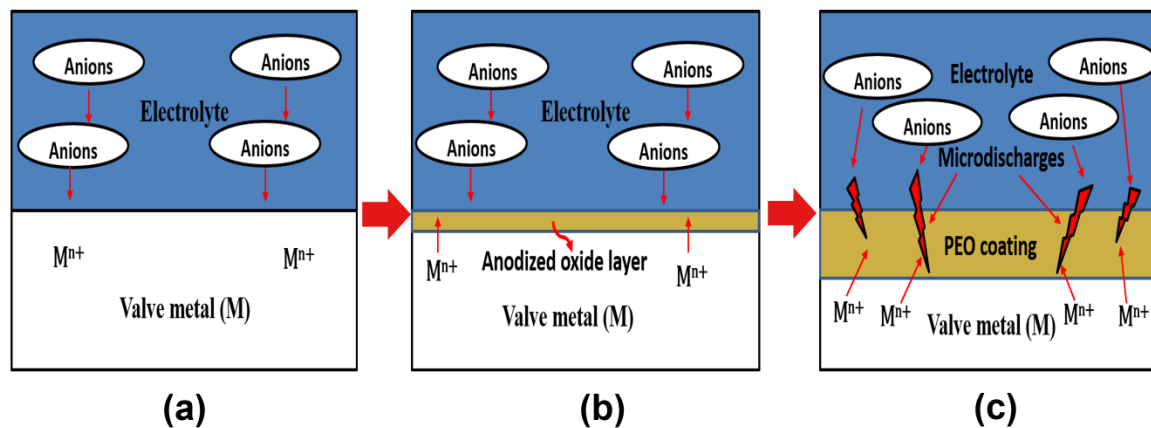


Figure 1. (a) Initial stage of PEO process (b) Anodized oxide layer formation (c) PEO coating formation by the microdischarges.

3.1.1. Effect of electrical parameters. Duty cycle and frequency have a considerable effect on the PEO coating characteristics developed on CP-Ti as reported by Gowtham et al. [25]. The coating produced at a higher duty cycle (95%) and a higher frequency (1000 Hz) exhibited a higher coating thickness ($\sim 9 \mu\text{m}$). The coatings produced at a higher frequency are relatively less porous than that obtained at a lower frequency (50 Hz), attributed to the short time period available for each cycle. The coating produced at a higher duty cycle and higher frequency exhibited the dense coating with a higher thickness, which provided the better corrosion resistance ($i_{\text{corr}} = 1.9 \text{ E-4 mA/cm}^2$) and scratch resistance along with the improved bioactivity. Current density affects the coating characteristics and properties of the coatings as reported by Khan et al. [26]. The PEO coating produced at higher current density (20 Adm^{-2}) possess higher coating thickness ($\sim 9 \mu\text{m}$). The amount of rutile phase content is observed to increase with an increase in the current density, along with a higher porosity. The high porosity and the rutile phase content observed in the sample with a higher current density was attributed to the increasing intensity of the discharge events with an increase in the current density.

3.1.2. Effect of electrolyte chemistry. Additives such as (Borate ($\text{B}_4\text{O}_7^{2-}$), Citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$) and Silicate (SiO_3^{2-})) show a considerable effect on the coating characteristics in the phosphate electrolyte system as reported by Venkateswarlu et al. [27]. Additives increased the rutile content, porosity, thickness and corrosion resistance. The coatings obtained with the citrate electrolyte system, exhibited highest rutile content (41.6 wt.%), along with the highest thickness ($\sim 11 \mu\text{m}$) and relatively less porous morphology, which resulted in the highest corrosion resistance ($i_{\text{corr}} = 3.1 \text{ E-9 Acm}^{-2}$). Sodium sulfate, Tris (hydroxymethyl) aminomethane, di-ammonium hydrogen phosphate and ammonium acetate additives affect the PEO coating characteristics, developed on CP-Ti as reported by Hari et al. [28]. The additives improved the corrosion resistance, and it is observed that the coating obtained with Tris (hydroxymethyl) aminomethane exhibited a rutile phase content (25.2 wt.%), along with higher corrosion resistance ($i_{\text{corr}} = 3.71 \text{ E-4 } \mu\text{Acm}^{-2}$), attributed to the fine pore morphology and dense inner barrier layer. Higher bioactivity and human osteosarcoma cell adhesion was also observed to be higher in the PEO coating

with Tris (hydroxymethyl) aminomethane additive. The zirconate additive can influence the PEO coating characteristics on CP-Ti, as reported by Babaei [29]. The increase in the zirconate level from 0 to 4 g/l, increased the pore size and roughness of the coating on the account of increased conductivity. On the other hand, the thickness of the coatings increased up to 5 μm . The higher (4 g/l) zirconate content, decreased the corrosion protection against the environment at 1000 Hz frequency, indicating the presence of through pores in the coating. The optimized zirconate additive content was reported as 2 g/l for the best corrosion resistant coating. The addition of electrolyte additives, such as, sodium carbonate (Na_2CO_3), sodium nitrite (NaNO_2) and urea ($\text{CO}(\text{NH}_2)_2$), resulted in the alteration of the PEO coating characteristics on CP-Ti, as reported by Venkateswarlu et al. [30]. The PEO coatings obtained in the electrolyte systems containing sodium carbonate exhibited the highest rutile content (54.4%), along with higher thickness ($\sim 55 \mu\text{m}$) and least porosity (11.6 %), thereby improving the corrosion resistance ($i_{\text{corr}} = 2 \text{ E-}2 \mu\text{Acm}^{-2}$). Fluoride ion also impacts the characteristics of the coatings as reported by Venkateswarlu et al. [31]. The PEO coatings obtained with four different fluorine precursors i.e., NH_4F , KF , NaF and K_2TiF_6 exhibited superior properties. A higher rutile phase content (37%), along with less porous surface structure was observed in the coating with K_2TiF_6 additive, which resulted in the better corrosion resistance ($i_{\text{corr}} = 8 \text{ E-}2 \mu\text{Acm}^{-2}$). Thus, the electrical parameters and electrolyte chemistry of the PEO process, greatly influence the coating thickness, morphology and phase composition, thereby increasing the corrosion resistance in the body fluid and making the coated samples more suitable for the bio-implant applications.

3.2. Plasma electrolytic oxidation coupled with electrophoretic deposition

Electrophoretic deposition (EPD) is the mechanism by which the charged nanoparticles suspended in an electrolyte move towards the anode due to its surface charge (zeta potential) and get deposited into the coating formed by the PEO process, thereby producing composite coatings. The suspended nanoparticles should have a sufficiently higher negative zeta potential to get incorporated into the coating [30]. The incorporation of the nanoparticles by the EPD mechanism occurs at higher voltages, which were observed at later stages of the PEO process [32]. The nanoparticle incorporation can be of a reactive or nonreactive type, depending upon the properties of the nanoparticles, such as a particle size, melting point temperature, etc., and the discharge characteristics observed during the PEO process [33, 34].

The electrolyte composition influences the nanosized ZrO_2 particle incorporation into the oxide coating developed by the PEO process, as reported by Gowtham et al. [35]. The increase in KOH levels from 0 g/l to 6 g/l, decreased the incorporation of nanoparticles, attributed to the reduction the velocity of the migrating particle in the electrolyte, which in-turn depend on the decreased potential difference attributed to the increase in the conductivity of the electrolyte. The nanoparticles are found to be incorporated partially reactive and partially inert, which was substantiated by the presence of both m- ZrO_2 and ZrTiO_4 phases. The m- ZrO_2 phase content is observed to decrease with the increase in the KOH content, corroborating with the decrease in the particle migration. The thickness and porosity of the coatings are found to be increasing with the KOH levels. The high corrosion resistance ($i_{\text{corr}} = 5.18 \text{ E-}8 \text{ mA/cm}^2$) is found to be offered by the coating with intermediate KOH level (4 g/l), correlating to its higher thickness along with the thick inner barrier layer. The addition of carbon nanotubes (CNT) is also found to affect the PEO coating characteristics on CP-Ti as reported by Yazici et al. [36]. The increase in the amount of CNT increased the formation of Al_2TiO_5 , by suppressing the TiO_2 rutile phase formation. The CNT content is observed to increase the pore size of the coatings. At 300 V, the coating thickness is found to be higher for the 2 g/l CNT added sample, then the sample without CNT addition, and as the CNT amount increased to 4 g/l, the coating thickness is found to be decreased. On the other hand, at 375 V, the coating thickness found to be decreased by increasing the CNT content from 0 to 4 g/l. Rare earth oxide nanopowders like CeO_2 addition to the PEO coatings, has been found to grab the attention of the researchers. The amount of CeO_2 addition, influences the coating properties produced on the CP-Ti as reported by Di et al. [37]. The increase in the CeO_2 content (0 g/l to 6 g/l), is found to enhance the anatase to rutile phase transformation up to 4g/l, and further increase in the CeO_2 , lead to

the formation of CeO₂ phase. The increase in the nanoparticle content decreased the pores size and number by the incorporation of nanoparticles into the pores formed during the PEO process. The thickness of the coatings is found to be increased with the increase in the nanoparticle content. The corrosion resistance of the coatings was also found to be increased by the increase in the CeO₂ content, up to 4 g/l and further increase lead to the decrease in corrosion resistance ($i_{\text{corr}} = 2.295\text{E-}6$), attributing to the decrease in the rutile content. Doping of Cu nanoparticles into the TiO₂ coatings, developed on CP-Ti, results in the enhancement of the antibacterial properties was reported by Yao et al. [38]. Cu nanoparticle addition doesn't significantly influence the coating thickness and morphology along with the phase composition. The antibacterial culture test conducted over a period of 24 h, concluded that Cu doping significantly increased the antibacterial activity by killing E. coli and S. aureus bacteria. The antibacterial activity along with the phosphatase activity of the bone marrow stem cells (BMSC) has found to be increased by the addition of Zn nanoparticles, during the PEO coating formation as reported by Hu et al. [39]. Zn addition does not show any significant changes in the morphology, thickness and phase composition. The antibacterial activity of the Zn doped coatings was attributed to the generation of reactive oxygen species. The Zn nanoparticles played an important role in the adhesion and proliferation of the BMSC's, which were the ideal seed cells for the tissue engineered bone. Ag-HA addition into the TiO₂ coatings prepared on CP-Ti results in the coating antibacterial performance as reported by Venkateswarlu et al. [40]. Better corrosion resistance was offered by the Ag-HA/TiO₂ composite coating along with the antibacterial property. The Ag-HA/TiO₂ coated sample exhibited the zone of bacterial inhibition in the E.coli atmosphere.

4. Conclusions

The characteristics of the PEO and PEO-EPD coatings, namely thickness, surface morphology, phase composition, antibacterial properties, cell adhesion, cell growth, corrosion resistance, are found to be influenced by various process parameters like electrical parameters, electrolyte chemistry, treatment time and nanoparticle additions. Precise control of various parameters has to be maintained for obtaining the biocompatible coatings on CP-Ti with better corrosion resistance along with the cell adhesion and proliferation along with the antibacterial properties.

Acknowledgments

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