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Surface modification of severe plastically deformed ultrafine grained pure titanium by plasma electrolytic oxidation

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A B S T R A C T

Severe plastic deformation is the best method for processing ultrafine grained (UFG) high strength commercially pure titanium (CP Ti) without any toxic and harmful elements for biomedical implants. Besides, because of the vital importance of the surface bioactivity of a medical implant, this paper studies the effect of Plasma electrolytic oxidation (PEO) process of UFG CP Ti processed by equal channel angular pressing (ECAP). The aqueous electrolyte chosen for PEO process was prepared by mixing 0.15 M calcium acetate hydrate and 0.075 M sodium hypophosphite hydrate at a ratio of 1:1 wt%. The results showed that in PEO-coated coarse-grained (CG) CP Ti, the dominant components are oxygen and titanium, while the two principal elements in the coating of UFG CP Ti are oxygen and calcium. It was revealed from EDS and X-ray diffractometry analysis that the more HA and higher content of Ca and P is formed on the UFG Ti coated sample in comparison with those on coarse-grained Ti coated. The overall Ca/P ratio in the layer was determined as 1.65 and 1.70 for the cases of CG CP Ti and UFG CP Ti, respectively. Also, a few numbers of microcracks were obtained on the PEO-coated UFG CP Ti sample compared to those in PEO-coated CG CP Ti. The microhardness of PEO-coated UFG CP Ti was 3275 MPa which was noticeably higher than the microhardness of UFG CP Ti. The electrochemical impedance spectroscopy (EIS) tests were carried out at room temperature using Ringer's solution. EIS test results indicated that the corrosion resistance of PEO-coated UFG CP Ti was greater than non-coated CP Ti and UFG CP Ti. Furthermore, the PEO-coated UFG CP Ti showed more protection against corrosion compared to PEO-coated CG CP Ti. Finally, it is very promising that UFG Ti with PEO surface modification would be a suitable candidate for replacement of Ti-6Al-4V alloy implants containing toxic elements of Al and V.

1. Introduction

Due to the unique properties such as high strength to weight ratio, excellent biocompatibility, inherent ability to osseointegration, relatively low modulus, good fatigue strength, formability, machinability and exceptional corrosion resistance, titanium and its alloys are widely used in different industries especially in biomedical devices including surgical implements and implants [1–3]. The CP Ti and titanium alloy Ti-6Al-4V specified as grades 1 to 5 according to the American Society for Testing and Materials (ASTM) are the most prevalent alloys preferred for the manufacturing of titanium implants. Among Ti grades 1 to 4 of unalloyed CP Ti, grades 1 and 2 are most suitable for using in implants provided that the lower strength problem be solved. Although Ti-6Al-4V alloy has higher strength compared to grade 2 titanium, several reports indicate concerns relating to toxic long term effect of V and Al and its adverse reaction with body tissues [4–6]. From the other hand, grade 2 titanium has a lower elastic modulus than of Ti-64 which is more desirable in implants because of avoiding stress shielding and the associated bone resorption [7]. However, grade 2 titanium shows the low mechanical strength which stems from its original coarse-grained (CG) conventional form. This deficiency could be compensated by refining its grain structure through severe plastic deformation (SPD) methods. Equal channel angular pressing (ECAP) proposed by Segal is one of the most common SPD methods in which ultrafine grained (UFG) and nanograined structures are achieved by pressing the metal billet through an angular channel [8]. The schematic of ECAP process is illustrated in Fig. 1. To achieve optimal results, the process may be repeated several times which results in a uniform and ultrafine microstructure throughout the bulk of the metal [7]. The occurrence of cracking and segmentation during deformation brings about difficulties in the processing of titanium by ECAP at room temperature [9].

Several experimental and theoretical studies have been carried out to investigate the effect of ECAP parameters such as die angles, pressing speed, temperature, the number of passes and back pressure on the microstructure and mechanical properties of nanostructured titanium [10–14]. Gunderov et al. [10] studied the evolution of microstructure, macrostructure and mechanical behavior of pure Ti during the

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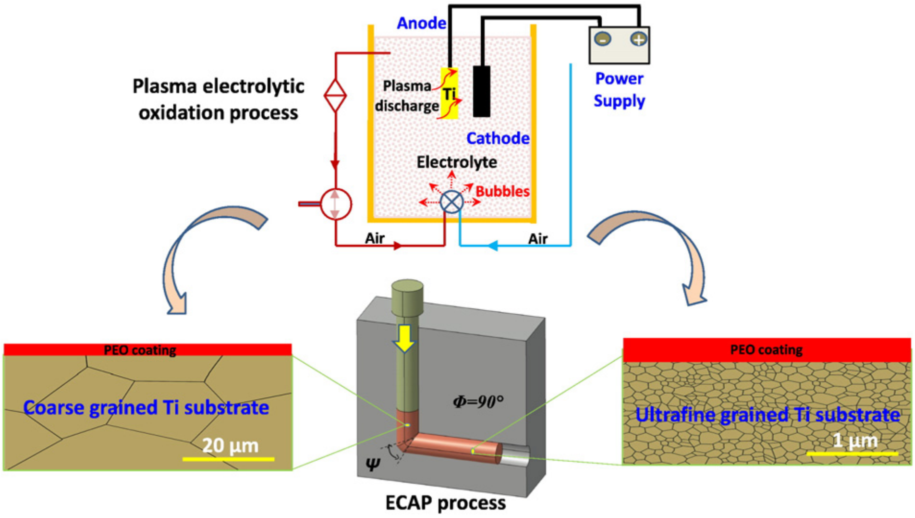

Fig. 1. Schematic illustration of ECAP and plasma electrolytic oxidation processes.

thermo-mechanical ECAP process via the conform scheme. They observed that the microstructure is more refined with increasing number of passes. Raab et al. [13] investigated the ECAP process of CP Ti at low temperatures. The results indicated that the decrease of ECAP temperature and the increase of hydrostatic pressure at the deformation zone would result in finer grains and enhanced mechanical properties.

In addition to mechanical strength, corrosion resistance is a major issue regarding dental implants. Although CP Ti and Ti alloys have high corrosion resistance, it could be enhanced by other techniques such as alloying titanium with other noble metals (platinum group metals), surface coating and microtexture and microstructure evolution [15]. There are several conflicting reports about the effect of grain refinement on the corrosion resistance behavior of CP Ti. The complicated relationship between grain refinement resulted from SPD methods, and corrosion resistance of achieved UFG CP Ti could be interpreted regarding a competition between the adverse effect of the inhomogeneous microstructure and the positive effect of the grain size reduction [16]. Also, it has been observed that in comparison with grain size, texture is the dominant factor controlling the corrosion properties of CP Ti [17].

Besides, because of the vital importance of the surface bioactivity of a medical implant, several surface modification techniques were investigated. In the last decades, surface anodization has attracted researcher's attentions as an effective method to provide the surface of Ti with a stable inert oxide film leads to enhancement of corrosion resistance. It should be noted that the surface characteristics of CP Ti such as roughness and morphology play a major role in increasing the lifetime of the implant and stimulating biocompatibility and osseointegration. Moreover, several techniques have been developed to fabricate a bioactive surface by applying Hydroxyapatite (HA) oxide coatings on the surface of CP Ti [18]. Advances in surface modification of Ti for implant application have led to the development of Plasma electrolytic oxidation (PEO) as an anodization technique being carried out in high voltage. The schematic of PEO setup was presented in Fig. 1. Compared with conventional anodization, PEO is a rapid and straightforward process in which metal surface is converted into a ceramic-like layer (rutile) [19]. It has been approved that coatings synthesized by PEO have superior characteristics such as excellent corrosion protection, favorable wear resistance, high hardness and enhanced bonding strength with substrate [20].

Different researches have been performed on surface modification of Ti and its alloys by PEO in literature. Simka et al. [21] incorporated Ca and P into the emerging passive layer during anodic oxidation on a titanium substrate, and it was proved that the modified titanium presents higher resistance to corrosion in the investigated environment than unmodified titanium. Shokouhfar et al. [22] studied the growth characteristics and corrosion behavior of the fabricated ceramic coating on titanium by PEO procedure in different electrolytes. They demonstrated that the spark voltage of oxide layer has the significant influence on the surface morphology, size and homogeneity of micro-pores. The effect of PEO pre-treatments on the adhesive bonding of titanium was investigated using lap-shear tests by Aliasghari et al. [23]. It was corroborated that the pre-treatments influence on the lap-shear strength is not noticeable.

To the best knowledge of the authors, though several studies were done on PEO coating of conventional alloys [24–26], a few studies have been allocated to apply PEO procedure on UFG CP Ti Grade 2. The main objective of this article is to remove the limitations of CP Ti application in the field of implant manufacturing. In the first stage of this research, four passes ECAP process is implemented to prepare UFG CP Ti with excellent mechanical strength from CG CP Ti. In the next stage, PEO process is employed to form a porous bioactive coating on the surface of UFG CP Ti. In this paper, several characterizations including the investigation of surface and cross-sectional morphologies, elemental and phase composition, microhardness, the corrosion resistance of the PEO-coated and non-coated CG and UFG CP Ti samples were carried out.

2. Materials and methods

2.1. ECAP procedure

Round bars 10 mm diameter CP Ti Grade 2 were used as the starting material. The impurity constituents in this material were 0.20 wt% Oxygen, 0.03 wt% Iron, 0.01 wt% Nitrogen, 0.02 wt% Carbon, 0.002 wt% Hydrogen. An ECAP die with 90° channel angle was manufactured from hot worked tool steel and hardened to 50 HRC. The ECAP process was conducted by pressing the bars through a die having two channels with the same circular cross-sectional areas intersecting each other at angle 90 degrees (Fig. 1). The Bc route was chosen in the deformation procedure to ensure yielding equiaxed grains in the microstructures of products. Four passes ECAP process via route B_c were applied to the Ti bars at a constant temperature of 400 °C. Namely, the Ti bars were rotated 90° clockwise around the pressing axis between the consecutive passes. A graphite-based slurry was used on ECAP channel as a lubricant to reduce the friction between Ti bars and die surfaces during deformation. The picture ECAP die and Ti sample during the process were shown in Fig. 2. To achieve a smooth surface finish; ECAPed sample was then machined to the diameter of 8 mm.