Materials Science and Engineering C 42 (2014) 657–664

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Preparation and properties of plasma electrolytic oxidation coating on sandblasted pure titanium by a combination treatment

Hong-Yuan Wang [a,b,c], Rui-Fu Zhu [a,b,*], Yu-Peng Lu [a,b,**], Gui-Yong Xiao [a,b], Xing-Chuan Zhao [a,b], Kun He [a,d], Y.F. Yuan [d], Ying Li [e], Xiao-Ni Ma [e]

[a] School of Materials Science and Engineering, Shandong University, Ji'nan 250061, China
[b] Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Ji'nan 250061, China
[c] Jinan Vocational College, Ji'nan 250103, China
[d] Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI 49931, USA
[e] Stomatology Department, Affiliated Jinan Centre Hospital of Shandong University, Ji'nan 250013, China

ARTICLE INFO

Article history:
Received 6 July 2013
Received in revised form 13 April 2014
Accepted 9 June 2014
Available online 19 June 2014

Keywords:
Properties
Coating
Titanium
Combination treatment
Sandblasting
Plasma electrolytic oxidation

ABSTRACT

Plasma electrolytic oxidation (PEO) is one of the most applicable methods to produce bioceramic coating on a dental implant and sandblasting is a primary technique to modify metal surface properties. This study aims to deposit bioceramic Ca- and P-containing coatings on sandblasted commercially pure titanium by PEO technique to improve its bioactive performance. The time-dependent modified surfaces are characterized in terms of their microstructure, phase, chemical composition, mechanical properties and bioactivities. The results show that the combination-treated coating exhibits better properties than the PEO-treated one, especially in bioactivities, as evidenced by the HA formation after immersion in simulated body fluid (SBF) for 5 days and the cell viability after seeding for 1 or 3 days. The enhancement of the modified surface is attributed to a combination of the mechanical sandblasting and the microplasma oxidation.

1. Introduction

Titanium (Ti) and its alloys have excellent properties such as biocompatibility, corrosion resistance and lightweight, and have become the most striking metallic material for the purpose of orthopedic implants nowadays [1,2]. However, Ti together with its native oxide thin film is known to be bio-inert, and the ability of its surface to induce hydroxyapatite (HA) formation is rather poor. To overcome this drawback, many topological and chemical modification techniques have been applied on Ti surfaces to ensure the long-term osseointegration [3–5].

The surface properties of Ti and its alloys, as typical dental implants, play a key role. A roughened surface of Ti was shown to markedly increase osteoinduction, cellular differentiation and mechanical fixation [6,7]. To create the appropriate type of roughness, several techniques were developed, including sandblasting, acid etching and SLA (sandblasting, large-grit, acid-etching) [8]. Sandblasting is a common technique to modify mechanical properties of metal surface and near surface region through micromachining and inducing severe plastic deformation, leaving the treated region with a rough surface and a compressive residual stress state [9]. So it could create a coarse surface to facilitate adhesion of cells and growth of new bone. Nevertheless, the roughened surface is not completely identical and abrasive materials are often embedded into the treated surface, which might hinder osseointegration process [10,11]. The sandblasting method, by itself, might not be effective enough to achieve initial cell fixation and bone formation. Subsequently, additional surface modifications of the implant should be applied [12–15].

Compared with other modifications of producing bioactive coatings, plasma electrolytic oxidation (PEO) has been one of the most applicable methods to deposit bioceramic film on an implant and could provide the possibility for incorporating Ca and P ions, which can further improve HA's inducing ability and even facilitate its crystallization [16–20]. Moreover, PEO can form an oxide coating with a complex geometry, which is of importance for enabling the bone-bonding ability of the implant. However, to achieve a bioactive coating with high-quality performance, this technique demands to combine with other modifications [21–26].

In this study, bioceramic coatings on titanium substrate were synthesized by sandblasting and PEO treatments in a mixture of Ca- and

* Correspondence to: R.-F. Zhu, School of Materials Science and Engineering, Shandong University, Ji'nan 250061, China. Tel.: +86 531 86358503; fax: +86 531 86358603.
** Correspondence to: Y.-P. Lu, Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Ji'nan 250061, China. Tel.: +86 531 86358503; fax: +86 531 86358603.
E-mail addresses: ruifuzh@sdu.edu.cn (R.-F. Zhu), biosdu@sdu.edu.cn (Y.-P. Lu).

http://dx.doi.org/10.1016/j.msec.2014.06.005
0928-4931/

P-containing system under varied treating intensities, and the coatings' properties were examined. Since most PEO coatings were formed by sole technique in relevant literatures, the present study aimed at depositing a bioceramic PEO coating on sandblasting-treated titanium and having, thus, synergistic effects of the modified substrate with an oxide layer. These coatings were fabricated by the combination treatment which not only achieved their original morphology, but also possibly improved surface chemistry as well as characteristics due to the multiple functions of mechanical enhancement and electrochemical oxidation.

2. Experimental

2.1. Sample preparation

Commercially pure titanium TA2 discs (ZhiRui Metal Material Ltd., China) with a diameter of 8 mm and a thickness of 3 mm were used as the substrates. The surfaces of the discs were polished with #180-600 abrasive papers to a roughness of $R_a = 0.25$ μm, ultrasonically cleaned in acetone, distilled water respectively, and then dried in air.

2.2. Sandblasting

The polished discs were sandblasted by applying a jet of SiC particles in 200 μm size until the surface reached a uniform gray tone. In the treatment, the air pressure was set at 0.9 MPa, with the mass flow rate of 2.15 m/min and the treating time of 45 s; the impact angle was set at 75° with the distance between the nozzle and samples at 15 cm. Afterward, the treated samples were washed with distilled water and dried in warm air.

2.3. PEO treatment

The PEO treatment was carried out for 10–30 min in a water-cooled bath made of stainless steel, which served as a cathode, and the specimens were used as anode during the treatment. Bipolar electric rectangular pulses were applied to the specimens, fed from an AC-type high power supply, and the anodic power voltage was fixed at 500 V, with the current frequency of 400 Hz and the duty cycle ratio of 25%. In the experiments, aqueous solutions of electrolytes were prepared by mixing 30 mmol/l calcium acetate monohydrate ($(CH_3COO)_2Ca\cdot H_2O$, CA), 10 mmol/l β-glycerophosphate disodium salt pentahydrate ($C_3H_7Na_2O_6P\cdot 5H_2O$, β-GP) and 8 mmol/l sodium hydroxide (NaOH, CA), and the electrolyte was cooled to prevent heating over 40 °C during the oxidation process.

In this study, the PEO coupled with sandblasting pretreatment was defined as the combination treatment. For purposes of comparison, the polished discs of titanium substrates and the discs prepared by sandblasting were treated by PEO process, respectively, to obtain the PEO-treated group (P-group/control-group) and the combination-treated group (C-group) samples. After the treatment, the coated samples were flushed with distilled water, dried in an air oven, and labeled for analysis.

2.4. Immersion in SBF

The simulated body fluid (SBF) was prepared by dissolving the reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4\cdot 3H_2O$, $MgCl_2\cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 into distilled water sequentially and buffering at pH 7.40 with Tris (hydroxymethyl) aminomethane and dilute HCl at 37 °C. The ionic concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^{2-}, HPO_4^{2-} and SO_4^{2-} of SBF were 142.0, 5.0, 1.5, 2.5, 147.8, 4.2, 1.0 and 0.5 mmol/l, respectively [27]. Both the P-group and C-group specimens were soaked in 35 ml of SBF for 5 days to compare the results, and the SBF was refreshed every other day.

2.5. Cell experiments

2.5.1. Cell culture

In this survey, the fibroblast cell line L929 was selected to appraise the biological properties of the samples. L929 cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) with 10% fetal bovine serum (FBS) and 1% (10,000 units) penicillin/streptomycin and then were placed in incubator (37 °C, 5% CO_2 and 90% RH).

2.5.2. Cell attachment and adhesion assay

The P-group/control and C-group samples of 25 min (surface area: $\Phi 8 \times 3$ mm^3) were firstly placed in 6-well plates and sterilized by ultraviolet light for 2 h. 5×10^4 cells/μl culture medium were seeded on triplicate samples and then they were located in incubator for 3 h. When the cells have been adhered to the sample surface, 1 ml culture medium containing 10% FBS was poured on each sample, which was then kept in incubator for 24–72 h. Afterwards, each sample was removed from the culture medium and washed with phosphate buffer saline (PBS). 2.5% glutaraldehyde was used for fixation of the cells and then the samples were put in the refrigerator for 24 h. Eventually, the samples were washed with PBS, and 60%, 80%, 90% and 100% alcohol, respectively.

2.5.3. Cell proliferation assay

Cell viability was quantitatively analyzed by using the method of MTT assay, which has been widely used for appraising cytotoxicity and proliferation. After seeding for 24–72 h, the samples were incubated with a MTT solution at 37 °C for 3 h. The formazan product, which was obtained by the reduction of MTT in the mitochondria of viable cells, was measured using a microplate reader [28–35].

2.6. Characterization

The coating morphology was examined by SU-70 field emission SEM (FE-SEM). Because of the low conductivity, the sample was sputter-coated with Pt prior to the SEM. JXA-8800R electron probe microanalyzer (EPMA) with a Link ISIS300 energy spectrum analyzer was used to give the secondary electron (SE) image and the element analysis was conducted by energy dispersed spectroscopy (EDS). The phase analysis of the coatings was carried out using Bruker D8 Advance X-ray diffractometer (XRD), with a scan speed of 4°/min, operated at 40 kV and 40 mA. The thickness was measured through touching the FN sensor on the coatings non-destructively, using Mini Test 600B FN2 thickness meter. The microhardness was determined by indentation test on the HV-1000 Huayin microhardness tester, the load was fixed at 25 g and loading time of 15 s. The weight was tested through a TE214S Sartorius, with an accuracy of 0.1 mg.

3. Results and discussion

Treated bioceramic coating patterns were examined using a scanning electron microscope to characterize the mode of topography. Fig. 1 shows the surface morphology evolution of the polished, sandblasted substrates and their coatings formed by PEO and combination treatment, together with EDS spectra of the element contents. All the surfaces of both groups' sample coatings were characterized by micropores in different sizes and shapes, which depended on the treatment mode and conditions, and the elemental composition was detected from different proportions of oxygen, titanium, calcium and phosphorus by EDS. It could be identified clearly in Fig. 1(c) that little fine micropores less than 5 μm distributed randomly on the P-group sample coating, where some agglomerate islands could also be observed. Some particles were deposited beside the micropores on the C-group sample as shown in Fig. 1(d), and these were related to calcium phosphate by XRD test due to the electrophoresis process. With the proceeding of treatment, Fig. 1(e)–(h) shows that the micropore size increased strikingly in both