Applied Surface Science 292 (2014) 204–212

Contents lists available at ScienceDirect

Applied Surface Science

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

Effect of sandblasting intensity on microstructures and properties of pure titanium micro-arc oxidation coatings in an optimized composite technique

Hong-Yuan Wang[a,b,c], Rui-Fu Zhu[a,b,*], Yu-Peng Lu[a,b,*], Gui-Yong Xiao[a,b], Kun He[a,d], Y.F. Yuan[d], Xiao-Ni Ma[e], Ying Li[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] Implant Dentistry Centre, Stomatological Hospital of Shandong University, Ji'nan 250033, China

ARTICLE INFO

Article history:
Received 21 July 2013
Received in revised form 4 October 2013
Accepted 20 November 2013
Available online 1 December 2013

Keywords:
Sandblasting
Microstructure
Property
Micro-arc oxidation
Coating
Pure titanium

ABSTRACT

Sandblasting is one of the most effective methods to modify a metal surface and improve its properties for application. Micro-arc oxidation (MAO) could produce a ceramic coating on a dental implant, facilitating cellular differentiation and osseocomposite on it. This study aims to deposit bioceramic Ca- and P-containing coatings on sandblasted commercially pure titanium by an optimum composite technique to improve the bioactive performance. The effect of sandblasting intensity on microstructures and properties of the implant coatings is examined, and the modified surfaces are characterized in terms of their topography, phase, chemical composition, mechanical properties and hydroxyapatite (HA)-inducing ability. The results show that a moderate sandblasting micromachines the substrate in favorable combination of rough and residual stresses; its MAO coating deposits nano-hydroxyapatite after immersion in simulated body fluid (SBF) for 5 days exhibiting better bioactivity. The further improvement of the implant surface performance is attributed to an optimized composite technique.

1. Introduction

Commercially pure titanium (CP Ti) has been widely used as dental and orthopedic implant materials owing to its excellent mechanical strength, chemical stability and biocompatibility [1,2]. The surface properties of implants are known as key factor for successful osseointegration, however, titanium together with its native oxide thin film is bio-inert, and the ability of its surface to induce bone formation is consequently rather poor [3–5]. To improve the clinical performance of titanium implants, various surface treatment technologies have been applied in attempts to modify the structure, composition, and chemistry of titanium surfaces including deposition of bioactive coatings [6–10].

The frequently applied commercial technique of surface treatment for dental implant involves sandblasting, acid etching and SLA (sandblasting, large-grit, acid-etching) [11]. Sandblasting is the most common method, which not only alters surface topography of an implant but also leaves the treated region in a compressive residual stress, and thus it greatly improves mechanical fixation and cellular differentiation due to the treated micro-scale or nano-scale texture [8,12]. However, the non-uniform surface roughness and embedded abrasive remnants potentially hinder osseointegration process, resulting in the poor bone bonding quality [13]. On its own, the sandblasting modification might not be effective enough to achieve early proliferation and bone formation [14–16].

Compared with sandblasting treatment, micro-arc oxidation (MAO) is a recently developed technique which could produce a porous and firmly adherent oxide coating on titanium surface [17,18]. In this process, metal substrate is oxidized with a microplasma treatment in an aqueous electrolytic bath which contains modifying elements to be incorporated into the resulting coating. Then the oxide titanium coating containing Ca and P ions usually appears to induce bone-like apatite in the simulated body fluid (SBF), and could enhance the bonding between implant and bone with a firm anchorage, resulting in a considerable improvement in the osseointegration ability of the implant [19–23]. To make further progress, it is still challenging to develop new methods that could allow the treatment of high voltage micro-spark on the modified substrate.

* Corresponding authors. 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).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.11.115

Table 1
Process conditions for the sample treatments.

Mode	Technical parameters	Values
Sandblsting pretreatment	Abrasive size (μm)	180
	Air pressure (bar)	7.0
	Flow rate (m/min)	2.15
	Impact angle (°)	75
	Nozzle distance (cm)	15.0
	Process time (s)	0, 15, 30, 45, 60
Micro-arc oxidation treatment	Voltage P/N (V)	400/0
	Frequency P/N (Hz)	500/0
	Duty cycle P/N (%)	20/0
	Treating time (min)	25
	$(CH_3COO)_2Ca{\cdot}H_2O$ (mmol/l)	35.0
	$C_3H_7Na_2O_6P{\cdot}5H_2O$, β-GP (mmol/l)	7.0
	KOH (mmol/l)	5.0

As most literatures reported forming bioactive coatings by sole MAO technique, the treatments were largely confined to the selection of electrical modes or adjustments of electrical parameters. In this study, bioceramic MAO coatings were deposited on sandblasted pure titanium, and the oxide coatings were fabricated on the variedly micromachined substrates to preferably join the electrochemical oxidation with the mechanical modification, taking optimum effect of the hybrid method. Thus, further improvement of titanium implants' bioactivities could be carried out by relying on the incorporation of Ca- and P-containing coating on sandblasting treated substrate optimally.

2. Experimental

2.1. Sample preparation

Commercially pure titanium TA2 discs with a diameter of 14 mm and a thickness of 2 mm were used as the substrates. The disks were polished with 180–800 grit abrasive sandpapers to a roughness of R_a = 0.2 μm, ultrasonically cleaned in acetone, subsequently in distilled water, and finally dried in an air oven.

2.2. Sample treatments

The polished discs were firstly sandblasted by applying a jet of SiC particles in micron size to modify its surface microstructure and mechanical properties. The technical factors that could influence the surface properties were: Abrasive size, compressed air pressure, mass flow rate, impact angle, processing time and distance from the nozzle to the sample, as listed in Table 1. Among them, the processing time was the key technical parameter, which determined the sandblasting intensity and was deliberately varied from 0 to 60 s to observe the influence of the treatment on MAO coatings. For purposes of comparison, the time-dependent sandblasted substrates were subsequently treated by MAO under the same experimental conditions: The process was carried out in a water-cooled bath made of stainless steel, which served as a cathode, and the specimen as an anode; bipolar electric rectangular pulses were applied to the specimen, fed from an AC-type high power supply; the technical parameters together with electrolyte solutions were also detailed in Table 1. The electrolyte was cooled to prevent heating over 40 °C during the oxidation process. After the treatment, the coated samples were flushed with acetone and distilled water respectively, dried in warm air, and labelled as the MAO-Sandblsting-treated group (MS-group): MS-0/Control sample, MS-15, MS-30, MS-45, MS-60 for analysis.

Table 2
Reagents and ionic concentrations for the preparation of SBF.

Order	Reagent	Amount (g)	Ion	Concentration (mmol/l)
1	NaCl	8.035	Na^+	142.0
2	$NaHCO_3$	0.355	K^+	5.0
3	KCl	0.225	Mg^{2+}	1.5
4	$K_2HPO_4{\cdot}3H_2O$	0.231	Ca^{2+}	2.5
5	$MgCl_2{\cdot}6H_2O$	0.311	Cl^-	147.8
6	1.0M-HCl	39 ml	$(HCO_3)^-$	4.2
7	$CaCl_2$	0.292	$(HPO_4)^{2-}$	1.0
8	Na_2SO_4	0.072	$(SO_4)^{2-}$	0.5

2.3. Immersion in SBF

The SBF was prepared by dissolving the reagent-grade chemicals into distilled water in order and buffering at pH 7.40 with tris(hydroxymethyl)aminomethane and dilute HCl at 37 °C. The reagents and ionic concentrations in SBF were listed in Table 2. All the MS-group specimens were soaked in 35 ml of SBF for 5 days to compare the results, and the SBF was refreshed every other day.

2.4. Characterization

The coating morphology was examined by SU-70 field emission SEM (FE–SEM), and the sample was sputter-coated with Pt prior to the observation because of its low conductivity. JXA-8800R electron probe microanalyser (EPMA) with a Link ISIS300 energy dispersive spectrometer (EDS) was used to analyze the elemental composition. The phase analysis was carried out using Bruker D8 Advance X-ray diffractometer (XRD), with a Cu*K*α radiation (λ = 0.154 nm) and a scan speed of 4°/min, operated at 40 kV and 40 mA. The thickness was measured by Mini Test 600B FN2 thickness meter. The microhardness was determined by indentation test on HV-1000 Huayin microhardness tester, the load was fixed 25 g and loading time of 15 s. Sample weight increase or loss during the treatments was measured by the evaluation of dry weight: The samples were rinsed in distilled water, dried at 20 °C to constant weight, and tested through a TE214S Sartorious, with an accuracy of 0.1 mg. The relative weight was calculated according to the following equation:

$$Rw = \frac{W_2 - W_1}{W_1} \times 100\%$$

where W_1 is the starting dry weight and W_2 is the dry weight after treatment.

3. Results and discussion

The sandblasted titanium patterns were examined using a scanning electron microscope to characterize the mode of material removal and morphology. The typical FE–SEM micrographs of the substrate surfaces sandblasted for 0, 15, 30, 45 and 60 s were presented in Fig. 1(a)–(e). Fig. 1(a) shows that the polished substrate surface without sandblasting was relatively smooth and covered with slight polishing tracks. Fewer and smaller microcutting or ploughing tracks were observed remaining on the 15 s-treated sample surface, where seldom polishing tracks could also be identified in some area. With an increase in treatment time, extensive and relatively large ploughing tracks were observed on the surfaces, and the total area or the individual size of the gouged region also increased. More ploughing and the resulting lip formation were evident in the micrograph of 30 s, and the remaining abrasive residues indicated in Fig. 1(c) were embedded due to the high velocity of abrasive particles. The particles ploughed the surface and pushed up ridges of material in front of them, however, some of these ridges were eroded during subsequent collisions. On subsequent