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Featured Letter

Hydrophilicity of bioactive titanium surface with different structure, composition, crystal form and grain size

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ABSTRACT

In this paper, the titanium (Ti) surfaces with different structure, composition, crystal form and grain size are prepared by micro arc oxidation and thermal treatment, and then their hydrophilicity and surface roughness are investigated. The experimental results show that there is no necessary relationship between hydrophilicity and surface roughness. For hydroxyapatite (HA) coatings with different surface structures, the structure with more HA amount has better hydrophilicity. And, with the same porous structure, HA surface endows better hydrophilicity than TiO_2. Anatase surface with small grain size has better hydrophilicity and rutile has better hydrophilicity than anatase. Combined with their biological properties which have been well reported, the dependent relationship of hydrophilicity and biological properties can be concluded, namely the good biological properties can be obtained by improving the hydrophilicity. This research work sheds light on the methods for optimization of biological properties of the implant materials.

1. Introduction

Titanium (Ti) is the most commonly used dental and orthopedic implant material due to its proper corrosion resistance, nonoxicity and biocompatibility. However, its bioactivity is not always satisfying, after implantation, it usually results in weak bonding with the bone tissues, and leads to poor osseointegration, raising the potential risk of loosening in the long-term usage [1]. Therefore, the researchers explored different methods to modify the Ti surface to achieve good bioactivity. For example, bioactive hydroxyapatite (HA) coatings are frequently prepared on Ti surface [2], micro-scale and nano-scale patterns are introduced [3], and titania coatings with different crystal form or grain size are also tried [4,5]. Fortunately, the methods really improved the bioactivity of Ti, however, their activation mechanism is not always the same, sometimes it is attributed to the surface composition and/or structure, sometimes attributed to the crystal form and/or grain size, and sometimes even some conflicting mechanisms are described. Considering that the activation mechanism endows the theoretical direction of surface modification of Ti implant, one valid and consistent activation mechanism should be obtained.

It is well known that, by adjusting the surface structure, composition, crystal form and grain size of Ti implant, the surface roughness and hydrophilicity can also be controlled. Therefore, some researchers also attributed the improved bioactivity to the enhanced surface roughness and/or hydrophilicity [6,7]. In our previous work, the surface hydrophilicity is thought to be a more important parameter than roughness, however, systematic research was not done and no reliable evidence was provided [8]. Therefore, in this work, several Ti implant surfaces with different structure, composition, crystal form and grain size were prepared by micro-arc oxidation (MAO) and post treatment, and their surface roughness and hydrophilicity were investigated. Combined with their biological properties which have been well reported, the effective factor which benefits the improvement of biological property might be confirmed, and thus a valid theoretical direction for surface activation of Ti implant would be achieved.

2. Materials and methods

2.1. Sample preparation

Commercially pure Ti (TA1, Tianjin, China) with the dimensions of 10 mm × 10 mm × 1 mm was polished with #1000 SiC sandpaper and ultrasonic cleaned in acetone, ethanol and deionized water, respectively, and then micro-arc oxidized in an electrolyte containing 0.2 mol/L calcium acetate ($(CH_3COO)_2Ca{\cdot}H_2O$) and 0.1 mol/L monosodiumorthophosphate ($NaH_2PO_4{\cdot}2H_2O$) for 3 min using a direct current (DC) power supply. Platinum electrode was

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Table 1
Parameters used to prepare the Ti surface with different composition, structure, crystal form and grain size (pulse frequency and duty cycle were separately set at 100 Hz and 50%).

Samples	Voltage (V)	Current (A)	Final treatment	
a	300	0.2		Different composition
b	360	0.4	ultrasonic clean	
c	360	0.2		Different structure
d	390	0.2		
e	360	0.6		
a	300	0.2	Kept at 900 °C for 2.5 h	Different crystal form
f				
a	300	0.2	Kept at 400 °C for 5 h and 10 h	Different grain size
g				

used as the cathode. The distance between anodic and cathodic electrodes was 50 mm. The pulse frequency and duty cycle were set at 100 Hz and 50%. The other parameters and corresponding samples are listed in Table 1. After MAO treatment, the samples were cleaned with deionized water and air dried. The experimental details can be seen in reference [9].

2.2. Surface characterization

Surface morphology and crystal structure of the samples were separately examined by scanning electron microscopy (SEM, HITACHI S-4800) and X-ray diffraction (XRD) analysis on a RIGAKUD/MAX2500 diffractometer with Cu Ka radiation. Atomic force microscopy (AFM, Agilent 5500) was used to detect the surface roughness, and the hydrophilicity was assessed from the measurements of the contact angle between the deionized water and sample surface at room temperature.

2.3. Statistical analysis

Samples were run in quintuplicate for each group. Statistically significant difference was determined by Students *t*-test. Difference with $p < 0.05$ was considered to be significant.

3. Results and discussion

Fig. 1 presented the different structures on Ti surfaces. It can be seen that, porous, flocculent and plate-like structures were formed on Ti surfaces. As voltage or current was increased, the floccules transformed into the plate-like structures (Fig. 1b–d). The porous structure (Fig. 1a) was achieved by peeling away the floccules precipitate by ultrasonic cleaning. Although different surface structures were obtained on these Ti samples, the XRD patterns (not shown here) detected the same composition of HA on Ti surface, and the different structures resulted from the different HA amount.

Fig. 2 showed the surface morphologies of the Ti samples with similar porous structures. Analyzing the two sample structures by image processing software, their pore density and diameters were about the same, separately 15 ± 3% and 1.5 ± 0.2 μm. However, the XRD patterns revealed that their surface composition was separately TiO_2 and HA, confirming the successful preparation of the similar structured Ti surfaces with different composition.

After heat treatment of the Ti samples at 400 °C for 5 h and 10 h, the same crystal form of anatase was detected as the original sample without heat treatment, however, as the heat preservation time was prolonged, the mean grain size of anatase increased from original 150 nm to 177 nm and 183 nm (XRD patterns not shown here). And when the Ti samples were heat treated at 900 °C for 2.5 h, only rutile was detected. During the heat treatment process, there is no obvious change in the surface morphologies, however the heat treatment ensured the achievement of the Ti samples with different crystal form and grain size.

Table 2 listed the surface roughness and contact angles of all the Ti samples obtained in this research work. It can be found that the Ti samples with similar surface structure (Sample a and b) showed similar surface roughness (0.324 μm and 0.321 μm), however contact angle of HA (Sample b) was about 34°, compared with the contact angle of TiO_2 (64°, Sample a), HA was proved to endow Ti samples with better hydrophilicity. While for the HA coatings with different structures (Sample b–e), as the HA amount was enhanced (Fig. 1), the surface roughness was increased from 0.321 μm to 0.601 μm, and the contact angles decreased from 34° to 0°, indicat-

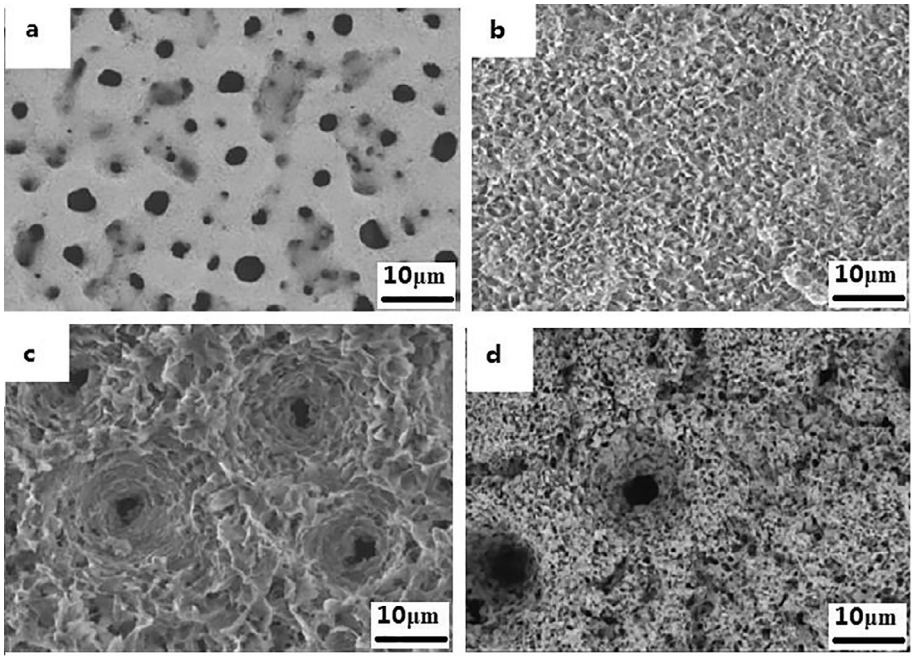

Fig. 1. Surface morphologies of the Ti samples with different surface structures: (a) sample b (360 V, 0.4A and then ultrasonic cleaned), (b) sample c (360 V, 0.2A), (c) sample d (390 V, 0.2A), (d) sample e (360 V, 0.6A).