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A further insight into coating-substrate interface of TiUnite implant by a novel coating detachment method

Zhen Wan[a,b,c,d,1], Ruitao Zhang[a,b,c,d,1], Li Xie[a,b,c,*], Suru Liu[a,b,c], Hao Wu[a,b,c,d], Yuan Tian[a,b,c,d], Weidong Tian[a,b,c,d,*]

[a] State Key Laboratory of Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu, Sichuan 610041, China
[b] National Clinical Research Center for Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu, Sichuan 610041, China
[c] National Engineering Laboratory for Oral Regenerative Medicine, West China Hospital of Stomatology, Sichuan University, Chengdu, Sichuan 610041, China
[d] Department of Oral and Maxillofacial Surgery, West China Hospital of Stomatology, Sichuan University, Chengdu, Sichuan 610041, China

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ABSTRACT

This work reports the development of a novel method to treat a commercially TiUnite® implant to detach its tightly bonded surface oxide layer. The implant was anodized in a fluorine-containing electrolyte (usually for TiO_2 nanotubes preparation) at 50 V for 2 h, which resulted in detachment of the coating. High-quality coating cross-sectional samples were prepared with detached coating fragments. Both the exposed titanium substrate and the detached coating were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). It was interesting to find that the coating-substrate interface exhibited a specific "mortise-tenon" anchorage structure. For comparison, focused ion beam (FIB) method was also conducted and the results revealed uneven bonding interface, specific internal pores distribution and varied coating thickness of the oxide coating. EDX results reported to existence of Ga^+ ion in the coating after FIB treatment while the novel method would increase the O element content. The novel method gave a brand new angle for detection of TiUnite implant and enhanced the understanding of its coating-substrate interface features unprecedentedly. It provides a novel and economy method for research, development and evaluation of coated titanium-based implant.

1. Introduction

Titanium dental implant is commonly used in the clinic due to its high specific strength, excellent biocompatibility and osseointegration ability [1]. To further enhance the osseointegration of the titanium implant, which was highly influenced by the implant surface characteristics, various surface coating and modification treatments have been developed [2–6]. Taking two representative commercial dental implant systems for example, NobelBiocare TiUnite® is coated by anodic spark oxidation with phosphorus-containing titanium oxide layer [7], and Bicon Integra-CP™ is treated by plasma spraying with hydroxyapatite coating [8,9]. Besides conventional detection of surface and coating properties, the detection of internal coating-substrate structure is also of great significance, which influences the mechanical properties [10], bioactivity [11], anti-corrosion ability [12], risks of coating peeling off [13], wear resistance [14] and so on. The characterization of internal structure of the coating is also required by Food and Drug Administration (FDA) regulations and international standards when a new dental implant system enters the market [15].

To obtain these information, the key task will be preparing high-quality and non-destructed cross-sectional samples. The small size (diameter 3–6 mm, length 6–18 mm), irregular shape (threaded, tapered) and the thin coating are typical characteristics of dental implants [16]. Thus, they place great difficulty to the cross-sectional sample preparation and following detection.

One of the usual means to prepare cross-sectional samples for subsequent SEM and related techniques is thawing and grinding method [7]. However, it requires hours to days of preliminary block sample preparation and mechanical sectioning. Moreover, coating diminishment is unavoidable during the preparation procedure and the structure of the coating can hardly be original [17]. In recent years, focused ion beam (FIB) has been progressively applied to specimen preparation in numerous scientific researches for site-specific ablation, analysis, and deposition of materials [18–20]. FIB systems use a finely focused beam of ions (usually Ga^+) to precisely ablate and expose the cross-section at micro-scale. In dental implant research field, FIB has already been

* Corresponding authors at: West China Hospital of Stomatology, Sichuan University, No.14, 3rd Section, Renmin South Road, Chengdu 610041, China.
E-mail addresses: samuel0121@163.com (L. Xie), drtwd@sina.com (W. Tian).
[1] These authors contributed equally to this work.

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Table 1
Dental implants information included in this study.

Information	1#	2#
Implant band	Nobelbiocare TiUnite	Nobelbiocare TiUnite
Type	Replace Select Tapered TiU NP 3.5 × 8 mm	Replace Select Tapered TiU NP 3.5 × 8 mm
Lot number	13000632	13031060
Cat number	85634-03	85634-04
Reference	36104	36104
Expiry date	2019-03	2021-03
Treatment method	FIB	TNT

commonly utilized in preparing site-specific cross-sections of the dental implant coatings as well as bone-implant interface for subsequent analysis [17,21,22]. However, it is a sophisticated technique and requires costly FIB workstation and trained testers. Besides, artifacts resulting from the high-energy ions contamination on the samples are inevitable [23,24].

Our previous work proposed an anodization method to detach coatings from titanium substrates. After anodizing the titanium samples in a certain F^--containing electrolyte, several kinds of coatings on titanium and titanium alloy substrates can be successfully detached. This method was used to prepare coating cross-sectional samples and non-destructive cross-sectional microstructures could be observed. Compared with traditional methods, preparing of coating cross-sectional samples could become rather convenient and less costly. And it was most significant that the coating cross-sectional morphology and structure were kept original and nondestructive. Since it was concluded that the TiO_2 nanotubes (TNT) formation at the coating-substrate interface led to this phenomenon [23], this method is therefore named TNT method in this work. But whether it would take effect on commercial titanium dental implants remains uncertain and needs further research.

Among numbers of dental implant systems, only a few of them are coated ones. As for moderately rough anodized surface, there is no doubt that TiUnite is one of the most widely studied clinical implant surface since its market launch in 2000 [25]. Therefore, TiUnite® implant was chosen as the research object in this work.

The main aim of this investigation is to evaluate the viability of the TNT method to detach the oxide layers from TiUnite implant for further detection. The traditional FIB method is therefore conducted as a comparison.

2. Material and methods

Two TiUnite® dental implants (Replace Select Tapered TiU NP 3.5 × 8 mm, Nobelbiocare, Sweden) were purchased and subsequently analyzed as shown in Table 1. The implants were moved from their storage boxes with tweezers and plastic gloves. Surface morphology and chemical components of the implant before the subsequent treatment were detected by SEM (Inspect F, FEI) and EDX (Oxford X-Max 80 EDX), respectively.

2.1. FIB method

Dual-beam focused ion beam and scanning electron microscope (FIB/SEM, Zeiss Auriga, the SEM instrument was equipped with an Oxford X-Max 80 EDX) were used in this study. Prior to insertion in the FIB equipment, one implant was sputtering coated with a thin film of Pt to protect the implant surface. The ion column utilized a Ga^+ source where the ions were accelerated at 30 kV to excavate trenches (9–16 μm in length) on the implant surface. Four sites were treated and analyzed (site 1: region near the implant neck, site 2: region in a thread valley, site 3: region on a thread top, site 4: region near the bottom of implant). The electron gun operated at 5 to 10 kV was used for SEM imaging. Furthermore, EDX analysis was performed on site 2.

2.2. TNT method

The TNT method proposed here was according to our previous literature [23]. The diagram of anodic oxidation apparatus is shown in Fig. 4A. An electrolyte containing NH_4F (5 wt%) + glycol (60 vol%) + glycerol (20 vol%) + H_2O (20 vol%) and a programmable DC

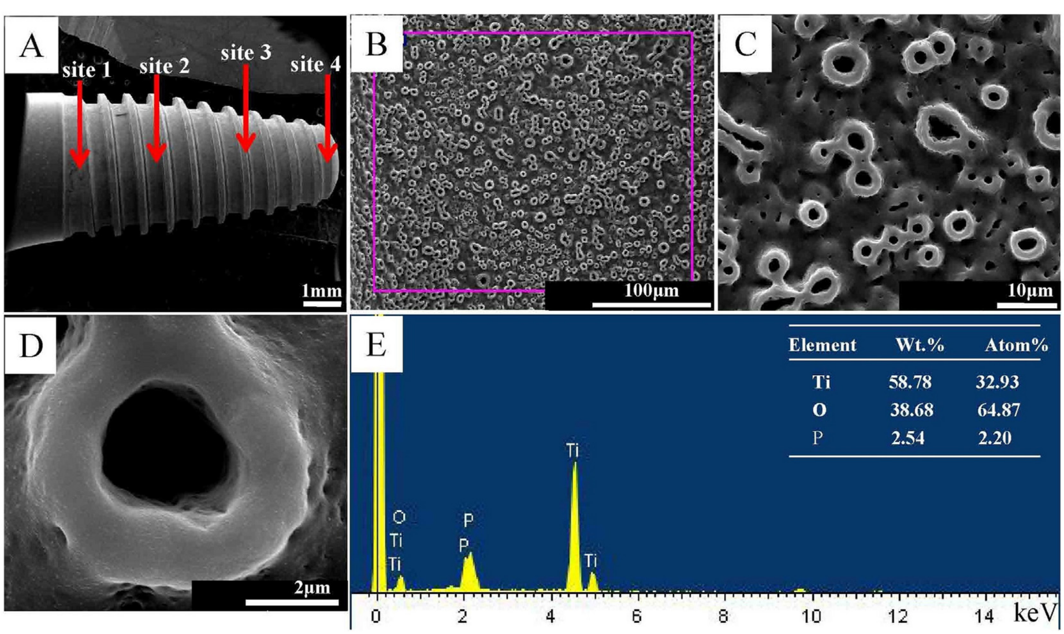

Fig. 1. (A) A low-magnification SEM image of a TiUnite® dental implant. Four sample sites for following FIB detection are marked by red arrows. Site 1: region near the implant neck, site 2: region in a thread valley, site 3: region on a thread top, site 4: region near the bottom of the implant. (B, C, D) Higher-magnification SEM images of the TiUnite® surface showed the characteristic volcanoes porous structure. (E) EDX analysis of the coating with presence of Ti, O and P. The scan area is marked by square frame in panel B. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)