Surface Characteristic of Pure Titanium Sandblasted with Irregular Zirconia Particles and Acid-Etched

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Irregular alumina (IAI_2O_3) is widely used in the procedure of sandblasting with large grit and acid-etching (SLA) which has been confirmed as a favorable surface treatment for implant to improve osseointegration. However, IA_2O_3 with cytotoxic has been found residual on implant surfaces after modification and thought to be a potential threat to implants’ long-term survival. Due to its similar shape and excellent biocompatibility, irregular zirconia (IZrO_2) was used as sandblast particle in the present study to compare the different characteristic between IZrO_2SLA and IAI_2O_3SLA surfaces. SEM, optical profilometry and XRF analysis were performed for comparison of surface characteristic. Combined with acid-etching, IZrO_2 could generate suitable primary and secondary roughness with, respectively, 10–30 µm pits and 1–3 µm micro pits. Three-dimensional roughness parameters (S_a, S_z, S_d, and S_0) revealed that because of the lower Vickers hardness and higher specific gravity of IZrO_2, IZrO_2SLA surface was less rough than IAI_2O_3SLA surface. Meanwhile, resulted from its different physical properties, IZrO_2 (0.13 ± 0.07%) was detected significantly less on IZrO_2SLA surface than IAI_2O_3 (6.74 ± 0.74%) on IAI_2O_3SLA surface. Therefore, IZrO_2SLA could easily prepare titanium surface with suitable multi-level morphology and moderate roughness for osseointegration. Furthermore, fewer sandblast particles residual on IZrO_2SLA surface, worries from harmful residue could be greatly reduced due to the biocompatibility of IZrO_2.

Keywords: titanium, irregular zirconia, sandblast, acid-etch, surface characteristic

1. Introduction

Titanium has been widely used for orthopedic and reconstructive implants in oral and maxillofacial region due to its excellent mechanical properties and biocompatibility since osseointegration was confirmed by researches.1,2) The functional capacity of implant depends mainly on the quality of interface between the implant and bone. Hence, the characteristic of implant surface plays an important role on the progression towards osseointegration. Titanium surface with moderate roughness has been considered to be suitable for osteoblast to attach, proliferate and differentiate on in order to obtain a relatively rough titanium surface which has an affinity to osteoblast for rapid osseointegration, various surface modification techniques, such as grit blasting, chemical etching, anodic oxidizing and plasma spraying, are employed in optimizing the physical and chemical properties of implant surfaces.3–6) 

Sandblasting with large grit and acid-etching (SLA) treatment is one of the most common methods to improve implant surfaces in clinic. The SLA surface with multi-level pores has been demonstrated enhancement of bone deposition in histomorphometric studies and higher removal torque values in biomechanical testing.7–10) Customarily used as sandblast particle, alumina (AI_2O_3) with excellent material properties and suitable shape can effectively prepare the primary roughness with micro scale pits while acid-etching is employed in clearing the residual sandblast particles and generating the secondary roughness. However, a certain amount of AI_2O_3 particles could still be found remaining on titanium surface after the manufacture procedure.1,2) The contamination on the surface has been reported to be a potential threat to long-term stability of osseointegration. In vitro cytotoxicity research showed that osteoblast-like MG63 cells phagocytosed AI_2O_3 particles and exhibited ultra structural changes, as well as biochemical changes such as decrease of proliferation rate and levels of alkaline phosphatase (ALP) activity and TGF-β1.11–14) In addition, experimental animals exposed to AI_2O_3 nonmaterial had been found to be at potential risk of being genetic damaged.15) For the sake of avoiding the potential risk of contamination which would threaten the interface between implant and host tissue, various kinds of sandblast materials with biocompatibility, such as titanium dioxide (TiO_2), hydroxyapatite (HA) and biphasic calcium phosphate (BCP), can be used to rough titanium surface and increase surface area.16–18)

Similar to the mechanical properties of AI_2O_3, zirconia (ZrO_2) has been widely used as ceramic material in different industries. In vitro osteoblast-like cell cultivation with zirconia particles exhibited increase of proliferation rate and ALP specific activity instead of cytotoxicity.14) Due to its excellent biocompatibility, ZrO_2 implants have been successfully applied in reconstruction of dentition defect and displayed ability to achieve stable osseointegration.19) Titanium surface sandblasted with round ZrO_2 beans and acid-etched induced human mandible osteoblast a faster

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proliferation rate with a high phenotype differentiation.²⁰
In vitro experiment indicated that implants sandblasted with round ZrO₂ beans had the highest significant bone ingrowths at two weeks compared with the other treated implant.²¹

However, the physical and chemical properties of titanium surfaces sandblasted with irregular ZrO₂ particles and acid-etched and the residual rate of sandblast materials have never been assessed before.

The purpose of the present study was to evaluate the characteristic of titanium surface treated with irregular ZrO₂ particles sandblasting and acid-etching compared with that of irregular Al₂O₃ particles-treated and acid-etched surface. Also, the residual rates of these two different sandblast materials on respective surfaces after acid-etching procedure were compared.

2. Materials and Methods

2.1 Preparation of sandblast particles and titanium specimens

Round yttria-stabilized ZrO₂ particles (RZrO₂) (Ø = 0.1 mm, ZirPro®, Saint-Gobain, France) were directly applied in sandblasting while RZrO₂ with a diameter of 2.3 mm were shivered into irregular particles (IZrO₂) and sieved to a size of 90–250 µm. Irregular Al₂O₃ particles (IAI₂O₃) (90–250 µm, White Dove®, China) were produced and provided by the factory using a proprietary process. The chemical composition and physical properties of sandblast particles and titanium material used in the present study were compared in Table 1.

The titanium specimens (8 × 8 mm²) were cut from a commercially pure titanium sheet (grade 2) with 2 mm thickness. All titanium surfaces were polished with silicon carbide sandpaper No. 280, 360, 400, 600, 800 and 1000 grits in series to eliminate surface irregularities and washed with acetone, absolute alcohol and deionized water (Milli-Q Ultra-Pure, Millipore, Billerica, MA, USA) in an ultrasonic cleaner, respectively, for 15 min. Subsequently, the specimens were dried at room temperature for 24 h and stored in an airtight titanium container. All these procedures above were carried out with an autoclaved titanium forceps to avoid heterogeneous elements pollution.

2.2 Scanning electron microscopy (SEM)

The morphology of sandblast particles and titanium specimens were observed using a scanning electron microscopy (S-3000N, Hitachi, Tokyo, Japan). The SE mode with an acceleration voltage of 20 kV and emission current of 85 µA was selected for analysis and the vacuum pressure was maintained below 1.3332 × 10⁻³ Pa. For the direct comparison of surface morphology, the same magnifications of 500× and 3000× were selected for observation of the modified specimens while 150× pictures were taken for the comparison of the sandblast particles.

2.3 Optical profilometry analysis

The three-dimensional characteristics of surfaces treated with different modifications were analyzed using an optical profilometer (Wyko NT9300, Veeco, USA) in white light vertical scanning interferometry mode. Three-dimensional images of the surfaces were reconstructed using a 20× magnification over a 228 × 300 µm area. In order to evaluate the topographical roughness as objective as possible, quantification of roughness parameters including height (such as S₁ and S₂), spatial (such as the density of summits-Sₐ), and hybrid (such as developed surface area-Sₐ) parameters was performed by software (Vision 4.20, Veeco, USA) at minimal magnification of 10× with the maximal scanning area of 456 µm × 600 µm. Ten specimens from each group were measured.

2.4 X-ray fluorescence (XRF) analysis

A wavelength-dispersive X-ray fluorescence spectrometer (Axios PW4400, PANalytical, Almelo, The Netherlands)
with a semiconductor detector was applied for the semi-quantitative test of chemical composition of different titanium surface under He flow protection. A rhodium target was used at 60 kV and 60 mA. The probing depth was several micrometers. The XRF spectra were obtained and qualitative and semi-quantitative analyses were performed by the software (Measure and Analyse 5.0D, PANalytical, The Netherlands) included with the instrument. Five specimens from each group were measured.

2.5 Statistical analyses
The experimental data is expressed as the mean ± standard deviation (SD). Statistical analysis was carried out by SPSS v17.0 software (SPSS Inc., Chicago, USA). After checking for normal distribution and homogeneity of variances, data was analyzed using one-way analysis of variance (ANOVA) followed by post hoc Bonferroni tests for multiple comparisons. When variances were not homogeneous or observed values were not distributed normally, non-parameter analysis of Kruskal–Wallis H test and Nemenyi multiple comparison test were used to compare data among groups. Probabilities (p) < 0.05 were considered to be statistically significant and p < 0.01 was considered to be highly statistically significant.

3. Results

3.1 SEM analyses of different surfaces
Figure 1(a) showed that RZrO2 particles with a diameter of approximate 100 µm, 150×, bar = 300 µm; (b) IZrO2 particles and (c) IAl2O3 particles ranged from 90 to 250 µm, 150×, bar = 300 µm; (d) Machined surface with shallow parallel scratches, 1000×, bar = 30 µm; (e) RZrO2SL surface composed of overlapped shallow pits without any residual; (f) and (g) show the multi-level pores of IZrO2SLA and IAl2O3SLA surfaces and the residual sandblast materials, 500×, bar = 100 µm. The inset images in (f) and (g) display the micro pits resulted from acid-etching procedure, 3000×, bar = 10 µm.

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generated the primary roughness had a diameter of about 10–30 µm. At 1000× magnification, micro pits resulted from acid-etching procedure had been found to be about 1–3 µm and formed the secondary roughness. Microscopic evaluation displayed that certain amount of sandblast materials were residual on the rough surfaces. The residual ZrO₂/Al₂O₃ particles with an approximate size of 20–50 µm were found to be embedded firmly in the titanium substrate although the surrounding was etched to pits and micro pits.

### 3.2 Roughness analyses of different surfaces

Three-dimensional reconstructed images of different surfaces were showed in Fig. 2. Different from Machined surface [Fig. 2(a)] with shallow parallel scratches, RZrO₂SL surface [Fig. 2(b)] was composed of relatively homogeneous micro pits, while IZrO₂SLA and IAl₂O₃SLA surfaces [Figs. 2(c) and 2(d)] were characterized with irregular wavy peaks and valleys. Depth was marked by differences in color. Roughness parameters of different surfaces were summarized in Table 3 and Fig. 3. The comparison of parameters Sₐ and Sₙ among four experimental groups showed statistically highly significant difference between each two groups. The parameters above of IZrO₂SLA surface were significantly higher than those of Machined and RZrO₂SL surfaces but lower than those of IAl₂O₃SLA surface. The Sₙ value of Machined surface (0.80 ± 0.05%) was statistically significantly lower than those of IZrO₂SLA (25.04 ± 1.03%) and IAl₂O₃SLA (30.57 ± 1.77%) surfaces and also significant difference of Sₙ value was found between RZrO₂SL (10.16 ± 0.68%) and IAl₂O₃SLA surfaces. For the parameter

![Fig. 2](image_url) Three-dimensional reconstructed images of different surfaces (20×). Depth was marked by differences in color. (a) Machined surface, (b) RZrO₂SL surface, (c) IZrO₂SLA surface, (d) Al₂O₃SLA surface.

![Fig. 3](image_url) Comparison of roughness parameters among different surfaces. (***) indicates a highly statistically significant difference (p < 0.01).

<table>
<thead>
<tr>
<th>Group</th>
<th>Resume</th>
<th>Sₐ (µm)</th>
<th>Sₙ (µm)</th>
<th>Sₙ (%)</th>
<th>Sₙ/₁₀₀(µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Machined</td>
<td>0.25 ± 0.02</td>
<td>3.15 ± 0.57</td>
<td>0.80 ± 0.05</td>
<td>1622.75 ± 109.36</td>
</tr>
<tr>
<td>2</td>
<td>RZrO₂SL</td>
<td>1.26 ± 0.05</td>
<td>12.81 ± 1.23</td>
<td>10.16 ± 0.68</td>
<td>764.32 ± 26.26</td>
</tr>
<tr>
<td>3</td>
<td>IZrO₂SLA</td>
<td>2.16 ± 0.06</td>
<td>22.80 ± 1.48</td>
<td>25.04 ± 1.03</td>
<td>1379.34 ± 47.15</td>
</tr>
<tr>
<td>4</td>
<td>IAl₂O₃SLA</td>
<td>3.44 ± 0.10</td>
<td>28.97 ± 0.95</td>
<td>30.57 ± 1.77</td>
<td>987.11 ± 49.06</td>
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Sₐ: arithmetic mean height deviation from the mean plane; Sₙ: arithmetic average of the maximum peak-to-valley height of the five greatest values; Sₙ: the ratio of the developed surface area from a flat reference area; Sₙ/₁₀₀: the number of summits of a unit sampling area.
Machined surface (1622.75 ± 109.36 mm²) had significantly higher value than those of IAl₂O₃SLA (987.11 ± 49.06 mm²) and RZrO₂SL (764.32 ± 26.26 mm²) surfaces. However, there was no statistically significant difference between the Sds values of IZrO₂SLA and IAl₂O₃SLA surfaces. Furthermore, RZrO₂SL surface owned the lowest Sds value among groups.

3.3 Chemical composition analyses of different surfaces

Chemical composition of surfaces with different modifications was summarized in Table 4. Accompanied with the spectra in Fig. 4, XRF analyses indicated that Machined and RZrO₂SL surfaces composed of 100% Ti were clean without any contamination [Figs. 4(a) and 4(b)]. However, ZrO₂ and Al₂O₃ were found residual, respectively, on IZrO₂SLA and IAl₂O₃SLA surfaces [Figs. 4(c) and 4(d)]. With trace of Y₂O₃, IZrO₂SLA surface was made up of 0.13 ± 0.07% ZrO₂ and 99.86 ± 0.07% Ti. For IAl₂O₃SLA surface, the composition percentage of residual Al₂O₃ was significantly higher than that of ZrO₂ on IZrO₂SLA surface and up to 6.74 ± 0.74%. It was considered that IAl₂O₃ particles were more easily remained than IZrO₂ particles after sandblasting and acid-etching procedures.

4. Discussion

It has been confirmed that osteoblast prefer to adhere, proliferate and differentiate on titanium surface with moderate roughness and suitable topography in comparison with the smooth one. Customarily, sandblasting is used to efficiently obtain the primary roughness while acid-etching can be employed in creating the secondary roughness in the form of micro pits that could preferably active osteoblast. Materials used in the sandblasting procedure should have suitable shape, hardness and superior biocompatibility.

Similar to the shape of IAl₂O₃ particles, IZrO₂ particles utilized in the present study had sharp edges and angles [Figs. 1(b) and 1(c)] to efficiently generate pits on titanium surface with the help of compressed air. After the acid-etching treatment, the pits produced by sandblast particles were ached to be 10–30 μm and micro pits ranged from 1 to 3 μm were obtained [Figs. 1(f) and 1(g)]. It could be found that, similar to the SLA surface of famous Straumann® implants on commercial, such IZrO₂SLA and IAl₂O₃SLA surfaces owned favorable topography structures which were suitable for early osseointegration. But shallow pits resulted from RZrO₂ sandblasting on RZrO₂SL surfaces [Fig. 1(e)] did not seem to be deep enough to form suitable primary roughness and were easily etched away. Therefore, different from Machined and RZrO₂SL surfaces, both IZrO₂SLA and IAl₂O₃SLA surfaces could produce suitable surface topography with primary and secondary roughness which was characterized with multi-level pores.

Roughness parameters derived from optical profilometry analysis can indirectly reflect the topography characteristic of material surface. Sₘ and Sₚ indicate the average height and maximum peak-to-valley height, respectively, of the surfaces, while Sₖ expressing the spatial density is a hybrid parameter.
revised (material)
5. Conclusions

Accompanied with acid-etching, IZrO\textsubscript{2} particles which had similar shape with IAl\textsubscript{2}O\textsubscript{3} particles could easily prepare titanium surface with suitable multi-level structure morphology (10–30 \textmu m pits and 1–3 \textmu m micro pits) and moderate roughness for osseointegration. As a result of the lower Vickers hardness and higher specific gravity, IZrO\textsubscript{2} particles could generated relatively shallower and smaller pits which contributed to lower \( S_a \) (2.16 ± 0.06 \textmu m), \( S_z \) (22.80 ± 1.48 \textmu m), \( S_{3d} \) (25.04 ± 1.03\%) values and higher \( S_{3a} \) (1379.34 ± 47.15 mm\textsuperscript{2}) value in comparison to those of IAl\textsubscript{2}O\textsubscript{3}/SLA surface. The significantly lower residual rate indicated that less IZrO\textsubscript{2} was residual due to its higher fracture toughness. At the same time, residue could be more easily cleared since that IZrO\textsubscript{2} had different physical properties and was not embedded as IAl\textsubscript{2}O\textsubscript{3} residue in titanium surface when sandblasting under the same condition. Hence, fewer sandblast particles residual on IZrO\textsubscript{2}/SLA surface, worries about the harmful residue could be greatly reduced due to the excellent biocompatibility of IZrO\textsubscript{2}. In summary, IZrO\textsubscript{2} could be a novel choice of sandblast material for SLA modification.

Acknowledgements

Shaobing Li and Jia Ni contributed equally to this work and should be considered co-first authors. This research was financially supported by National Natural Science Foundation of China (No. 81170998).

REFERENCES