Surface characteristics of Zinc-TiO$_2$ coatings prepared via micro-arc oxidation

Quan-ming Zhao$^a$, Li Cheng$^a$, Zhong-tang Liu$^b$ & Ji-jun Zhao$^a$

$^a$Department of Orthopedic Surgery, Wuxi People’s Hospital, Nanjing Medical University, Wuxi City 214023, Jiangsu Province, P.R. China

$^b$Department of Orthopedic Surgery, Changhai Hospital, The Second Military Medical University, Shanghai 200433, China

Published online: 15 May 2014.

To cite this article: Quan-ming Zhao, Li Cheng, Zhong-tang Liu & Ji-jun Zhao (2014) Surface characteristics of Zinc-TiO$_2$ coatings prepared via micro-arc oxidation, Composite Interfaces, 21:6, 585-593, DOI: 10.1080/15685543.2014.914377

To link to this article: http://dx.doi.org/10.1080/15685543.2014.914377

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &
Surface characteristics of Zinc–TiO₂ coatings prepared via micro-arc oxidation

Quan-ming Zhao¹, Li Cheng²*, Zhong-tang Liu²* and Ji-jun Zhao¹

¹Department of Orthopedic Surgery, Wuxi People’s Hospital, Nanjing Medical University, Wuxi City 214023, Jiangsu Province, P. R. China; ²Department of Orthopedic Surgery, Changhai Hospital, The Second Military Medical University, Shanghai 200433, China

(Received 17 December 2013; accepted 27 March 2014)

Titanium (Ti) and its alloys are widely used as metallic biomaterials for fabrication of dental and orthopedic implants due to their favorable biocompatibility and corrosion resistance in a body environment. However, the thin oxide layer (TiO₂) on Ti substrate formed naturally in air or in many aqueous environments is bioinert and surrounded by fibrous tissues without producing any chemical or biological bond to bone when implanted. In the present work, Zinc-incorporated porous TiO₂ coatings (Zn–TiO₂) were prepared on Ti substrate by micro-arc oxidation (MAO) technique in the zinc gluconate-containing electrolyte. The surface morphology, cross-sectional morphology, composition, and phase of the coatings were analyzed using scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffractometry, respectively. Surface topography and roughness of the coatings were investigated by atomic force microscopy operated in tapping mode. The results showed that Zn was successfully incorporated into the porous TiO₂ coatings, which did not alter apparently its surface topography and phase composition. In conclusion, the formation of porous Zn–TiO₂ coatings endow Ti with potential bioactivity and antibacterial activity, and we believe that the porous Zn–TiO₂ coatings on Ti by MAO technique might be promising candidates for orthopedic and dental implants.

Keywords: micro-arc oxidation; zinc; coating; titanium; biomaterials

1. Introduction

Titanium (Ti) and its alloys are well considered to be the most attractive substitutes for hard tissues that have been extensively used for dental and orthopedic implants over the past several decades due to their low density, high strength and toughness, good biocompatibility, and corrosion resistance in a body environment.[1–3] However, Ti and Ti alloys are still not sufficient for clinical use because the compatibility must be improved.

It is well known that the properties of the surface oxide layer (TiO₂) formed naturally in air or in many aqueous environments, involving topography, roughness, and composition, play an important role in the biocompatibility of a Ti implant.[4] However, the thin oxide layer on Ti is bioinert. If they were directly implanted into human bodies, there would be a number of problems, such as poor bioactivity, low bond-strength, and a long time needed to heal, etc.[5,6] Therefore, compositing with bioactive materials may be an effective way to improve the surface properties of Ti implants by surface modifications.

*Corresponding authors. Email: abc8385@163.com (L. Cheng); xiazaiguke@163.com (Z.-t. Liu)
Micro-arc oxidation (MAO) is a novel method to prepare an in situ ceramic coating on valve metals such as such as Ti, magnesium (Mg), aluminum (Al), and their alloys.[7] During MAO treatment, the valve metal substrate is used as anode and a stainless steel plate is used as a cathode in an electrolyte cell. When the applied voltage to the substrate immersed in electrolyte is increased to a certain point, a micro-arc occurs on the surface and a ceramic coating is formed. MAO coatings are usually porous and nanostructured, which has been proved to be beneficial to osteoblast adhesion and proliferation. Moreover, it provides strong adhesion and satisfactory mechanical strength for modifying metal substrates. More importantly, it is a relatively convenient and effective wet-chemical method for producing various functional coatings by tailor- ing the components of the electrolytes on metal surface.[8,9]

Recently, effects of trace elements on biological role have become an important topic in the research fields of bone formation and organism essential elements. It is well established that Zn is an important trace element in human bone, and Zn species play diverse roles in biological functions, such as DNA synthesis, enzyme activity, nucleic acid metabolism, biomineralization, and hormonal activity, while they also possess excellent antibacterial qualities.[10–12] Zn incorporated in bioactive glasses, calcium phosphates, or in other ceramics has been investigated as a potential material to stimulate bone formation and inhibit bone resorption with promising results.[13,14]

It is an interesting way that bioactive compositions or antibiotics can be incorporated into the coating during the MAO process by adjusting the composition of the electrolyte solution. For example, Ca and P ions have been incorporated successfully into the TiO2 coating using an electrolyte solution containing Ca and P sources, which results in a significant improvement in the osseointegration ability of the implant in in vivo tests.[15] A Si-incorporated TiO2 coating with enhanced cyocompatibility and corrosion resistance was prepared using the MAO method by adding sodium silicate in electrolytes.[16] However, it is a pity that the antibacterial activity and bone formability of Zn-related materials are rarely investigated together. Zn-incorporated TiO2-based biomaterials have not been explored, and the effects of Zn incorporation on the composition, microstructure, and biological responses of TiO2 coating are not clear by now.

In this work, Zn–TiO2 coatings were fabricated on the surface of pure Ti by MAO method in the zinc gluconate-containing electrolyte. The morphologies, topography, elemental compositions, and phase components of the coatings at different stages were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), EDX, and X-ray diffraction (XRD).

2. Experimental

2.1. Sample preparation

In the experiment, commercially pure Ti (Baoji Yide Metal Materials Co., Ltd, Baoji, China) were processed into disks (25 mm diameter and 2 mm thickness). They were mechanically polished with 100#, 200#, 400#, 800#, 1000#, and 1500# abrasive papers and then ultrasonically washed with acetone, ethyl alcohol, and distilled water, and dried at 60 °C.

2.2. Preparation of Zn-incorporated TiO2 coatings

A home-made high power-pulsed single-polar electrical source with a power of 20 kW was used for MAO under different working voltages in two different electrolyte
systems and a pure Ti disk was used as an anode, while a stainless steel column of the same size was used as a cathode in an electrolytic cell. One electrolyte was prepared by the dissolution of reagent grade chemicals of zinc gluconate, trisodium phosphate anhydrous, sodium hydroxide, sodium citrate, and a small amount of ethylenediaminetetraacetic acid disodium salt into deionized water, and the other electrolyte contained no zinc gluconate as a control. In the MAO process, the voltage was elevated rapidly from 180 to 360 V under a fixed current density. The frequency, duty cycle, and oxidizing time were 600 Hz, 20%, and 10 min, respectively.

2.3. Characterization of the coatings
Morphology images of the prepared coatings were studied with SEM (Hitachi S-3000N, Japan). The topography of coating was imaged with (AFM, Nanoscope IIIa, Digital Instruments, USA). Cross-sections of the coatings were observed and thickness was measured by SEM after it was coated with a thin Au film. The relative contents of elements in the coatings were investigated by energy-dispersive spectroscopy (EDS), and the average relative contents of elements were obtained from three measurements at different positions. The phase composition of the sample surfaces was determined by XRD using a Cu Kα radiation with a continuous scanning mode at a rate of 8°/min under an accelerating voltage of 40 kV and current of 30 mA. The coating thickness was measured using an eddy current-based thickness gage (CTG-10), and the average thickness of each sample was obtained from 10 measurements at different positions.

3. Results and discussion
3.1. Characteristics of Zn–TiO2 coatings
The difference between the Ti substrate and Zn–TiO2 coating was mainly color. Ti substrate was silvery white, while Zn–TiO2 coatings were gray black, and the color change of the surface mainly attributed to TiO2 coatings. The thickness of the coatings in zinc system was approximately 6–10 mm or so, and there was no significant difference between zinc system and non-zinc system. According to the calculation with the Image Pro Plus 5.0 software (Media Cybernetics, Bethesda, MD, USA), the porosity of the coatings was 15%.

Figure 1 was the surface morphologies of the Zn coatings prepared in zinc system and non-zinc system. Panel 1(a) showed that there were a large amount of micro-holes distributed evenly on the surface of the coatings prepared in zinc system, panel 1(b) was the partial enlarged picture of panel 1(a). Similarly, panel 1(c) was the surface morphologies of the coatings prepared in non-zinc system, panel 1(d) was the partial enlarged picture of panel 1(c). We could see that both coatings are porous and well separated and homogeneously distributed over the coating surfaces. Obviously, no significant differences in the morphology and micro-structure between the Zn-incorporated and Zn-free coatings were observed, which indicated that zinc gluconate in the electrolyte does not affect the structure of the coatings.

Surface properties including morphology and chemistry can generate preferential interactions with a biological system at protein and cellular levels, such as cell proliferation, differentiation, and gene expression. In the study, it could be seen that both coatings exhibited a porous structure which was the characteristic of the coatings grown by MAO process. In fact, during the MAO process, the coating formation and growth take place as follows. Initially, numerous micro-arc discharge channels are formed on the anodic surface. Ti is melted out of the substrate and participates in the plasma chemical
reactions to form the oxidation products because of the high temperature in the discharge channels. When the oxidation products are ejected out of the discharge channel, they leave a pore on the coating surface. So, the MAO coatings usually show a porous surface structure. Subsequently, the ejected oxidation product will come in contact with the surrounding electrolyte, get quenched, and finally deposited over the surface of the already-grown coating and the thickness of the coating increases in situ.[17]

Clinical studies demonstrated that surface properties including morphology and chemistry are of great significance in deciding the response of tissue to implants, as shown in the Figure 1, the MAO coating had relatively high porosity on the surface and the molten oxide particles with different sized pores were uniformly distributed on the coating, and the diameters of most of the pores were about 1–3 μm. The micro-scale topographical features could promote cell adhesion, bone ingrowth, and the formation of mechanical interlocking between the implant surfaces and bone tissue, which was important to prevent loosening of the implant and forms false joints. Besides, According to the above study, the pores were formed by the molten oxide and gas bubbles were emitted out of the micro-arc discharge channels. Although the molten oxide was rapidly solidified from the temperature of several thousand degrees in the relatively cooling electrolyte, we found that there was no micro-crack detected in the study, which demonstrated the electrolyte-containing zinc gluconate could improve the coating performance.

Figure 1. The surface morphologies of the coatings prepared in zinc system ((a) and (b)) and non-zinc system ((c) and (d)).
Figure 2 showed a three-dimensional view of the surface of MAO coatings formed in the electrolyte-containing Zn gluconate. The conclusion expressed the formation of a coarse surface with mean roughness of 0.519 μm. The growing coating was locally melted by the micro-arc discharge taking place on the anode surface, and molten oxides flowed out of discharge channels due to high temperature and high pressure in the channels, then oxides were rapidly solidified by cooling of the electrolytes when spark was quenched. These successive meltings and solidifications made the coatings roughened.

Figure 3 showed the cross-sectional morphologies of the MAO coatings formed on pure Ti. Panel 3(b) was an enlarged picture of panel 3(a). Obviously, the coatings were
relatively uniform in thickness. There was no apparent discontinuity in the interface of the coatings and the substrates, which indicated that the coatings could bond tightly to the Ti substrates.

Bonding strength of the coating and substrate is very important for implants and high-bonding strength is beneficial to adhesion of cells and tissues. Compared with sol–gel method, the coating prepared by MAO has a higher bond strength because of the characteristic of in situ growth of the coatings, and growth is indented, which is extremely important to prevent implant loosening clinically.

3.2. EDS analyses of the Zn–TiO₂ coatings of MAO

Figure 4 showed the results of the EDS analysis of the coatings prepared in the zinc gluconate electrolyte. It was clear that the coating was mainly composed of Ti, O, and Zn, which indicated that the Zn element in electrolytes could incorporate into MAO coatings. Figure 4(a) showed elemental content when MAO was 2 min, while Figure 4(b) was the elemental content when MAO was 10 min. As shown in the Table 1, the content of Zn

![Figure 4](image-url)

Figure 4. The results of the EDS of the Zn–TiO₂ coatings prepared in the zinc gluconate electrolyte: (a) 2 min and (b) 10 min.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Zn</th>
<th>Ti</th>
<th>O</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.13</td>
<td>28.12</td>
<td>68.55</td>
<td>2.21</td>
</tr>
<tr>
<td>5</td>
<td>1.45</td>
<td>27.47</td>
<td>69.58</td>
<td>1.51</td>
</tr>
<tr>
<td>10</td>
<td>1.65</td>
<td>30.05</td>
<td>67.45</td>
<td>0.84</td>
</tr>
<tr>
<td>20</td>
<td>1.64</td>
<td>30.43</td>
<td>67.15</td>
<td>0.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zinc gluconate (g/L)</th>
<th>Zn</th>
<th>Ti</th>
<th>O</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.07</td>
<td>26.35</td>
<td>70.07</td>
<td>1.50</td>
</tr>
<tr>
<td>5</td>
<td>2.89</td>
<td>26.61</td>
<td>68.86</td>
<td>1.63</td>
</tr>
<tr>
<td>6</td>
<td>4.36</td>
<td>25.63</td>
<td>67.06</td>
<td>2.95</td>
</tr>
</tbody>
</table>
elevated from 1.13 to 1.65%, which indicated that Zn content in the coatings increased with extension of time during the MAO process.

In this experiment, an electrolyte containing zinc gluconate was used for preparing the MAO coatings with Zn on the surface of pure Ti. The EDS result showed that the Zn element was compounded into the coatings during MAO process. Although some studies have reported the incorporation of electrolyte species into the MAO coating, specific mechanism remains unclear. As an active metal element, Zn incorporation could be a complex process, involving in ion electro-migration, adsorption, and diffusion, detailed mechanisms need further study.

### 3.3. Phase composition of the Zn–TiO₂ coatings

XRD patterns of the Zn–TiO₂ coatings are shown in Figure 5. The coatings mainly consist of anatase, rutile, and Ti phase, and the anatase form is the predominant phase in the coatings. According to Figure 5, it could be observed that the diffraction peaks of Ti were very strong. We concluded that it should come from the substrate due to the fact that the coatings formed in so short a period of oxidation were too thin. As shown in the Figure 5, no phase containing Zn was found from XRD in the MAO coatings, which indicated that the phase composition of the TiO₂ coatings was not altered apparently after the incorporation of Zn. At the same time, Zn could be seen from the EDX spectra, which indicates that Zn should exist in the coatings in an amorphous form. Some previous research also showed that MAO coatings prepared in an electrolyte containing Zn, contain amorphous phases made up of Zn, etc.[18]

![Figure 5. XRD patterns of the Zn–TiO₂ coatings.](image-url)
3.4. Effects of technique parameters on the concentration of Zn

Our study showed that the reaction time for the adjustment of the content of Zn in the coatings was suitable for the electrolyte. Clearly, with increasing of the MAO time, the relative content of Zn in the coatings was increased gradually. However, when the reaction time reached 20 min, the relative content of Zn stalled, which was related to slow growth of the coating in the final stages. At the same time, our study found that the concentration of the zinc gluconate could be a more important factor. Table 1 showed the relative contents of the Zn in the coatings prepared under different concentrations of zinc gluconate in electrolyte solution, with the increase of zinc gluconate in the electrolyte solution, the contents of the Zn in the coating were increased accordingly. Especially for the coatings prepared in the electrolytes with zinc gluconate of 6 g/L, the content of Zn reached 4.36.

Based on the above results, it can be easily found that the content of Zn can be controlled by the adjustment of the technique parameters like the concentration of zinc gluconate, the MAO time, etc. Surely, besides the MAO time and concentration of the zinc gluconate mentioned above, the voltage, current density, and duty ratio are also important parameters for the MAO process, which is bound to influence the content of Zn, which needs our further research to get an insight in it.

According to above study, the new work introduced a novel idea adding Zn to the composite coatings in order to improve the bioactivity of the coatings, and the results also proved the realizability. However, there are also many works needed to be done in depth. Although the EDS spectrum revealed that the deposited coatings were composed of Ti, O, and Zn, no crystalline Zn was detected by XRD. The chemical status and location of the Zn are not clearly understood yet. Does Zn exist as an ion, atom, or other valence state in the coating? Further studies are needed to answer these questions.

4. Conclusion

Zn was successfully incorporated into porous TiO₂ coatings by the MAO technique using a novel Zn-containing electrolyte. The surface of the coatings on Ti substrate produced a network structure without apparent interface to the Ti substrates. Moreover, it can be easily found that the content of Zn can be controlled by the adjustment of the technique parameters like the concentration of zinc gluconate, the MAO time, etc. Besides, surface characteristics of the Zn-containing TiO₂ coatings such as the surface morphology and phase were not altered apparently as compared to Zn-free TiO₂ coatings. More importantly, Zn–TiO₂ coatings endow Ti with potential bioactivity and antibacterial activity. Therefore, Zn–TiO₂ coatings are thought to be promising candidates for orthopedic and dental implants.

Funding

This work was supported by the National Natural Science Foundation of China [grant number 81171738], [grant number 81371936].

References


