Effects of micro-arc oxidation on bond strength of titanium to porcelain

Jian-Xue Li, a,b, Yu-Mei Zhang a,⁎, Yong Han c, Yi-Min Zhao a,⁎

a Department of Prosthodontics, School of Stomatology, Fourth Military Medical University, Xi’an 710032, Shaanxi, People’s Republic of China
b Department of Stomatology, Lanzhou General Hospital, Lanzhou Command, PLA, Lanzhou 730050, Gansu, People’s Republic of China
c State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, Shaanxi, People’s Republic of China

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A B S T R A C T

Due to the pronounced oxidative nature of titanium at high temperatures, an excessively thick oxide layer may form on its surface. This oxide layer could adversely affect titanium–porcelain bonding. The aim of the present study was to investigate the effects of micro-arc oxidation on the titanium–porcelain bond strength which was relevant to the titanium oxide layer. Twelve cast titanium specimens were prepared following the protocol ISO 9693. The test group was treated with micro-arc oxidation and the control group was treated with sandblasting. Contact angle and surface roughness were detected. SEM, XRD, and SEM/EDS analyses were performed on the titanium surfaces to ascertain bond failure. The groups were compared for their bond strength. The results showed that: there are differences in the surface morphology and the phase components of two groups. In addition, compared with the control group, the contact angle of the MAO group is smaller, but the surface roughness is similar. In the MAO specimen, the oxide layer was thin, and it was compact bonding with titanium and porcelain. The mean bond strength of the micro-arc oxidation group and the control group were 46.46±4.35 MPa and 33.28±2.24 MPa, respectively. While the improvement in bond strength was 39.6% for micro-arc oxidation group, it was statistically significant for the control group. These results suggest that the micro-arc oxidation technique is significantly effective in improving the bond strength of titanium–porcelain.

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1. Introduction

Titanium is known as a useful biometal material for its excellent biocompatibility, corrosion resistance and mechanical properties. It is considered as an alternative substructure material for metal–ceramic restorations. However, titanium reacts strongly with gaseous elements such as oxygen, hydrogen, and nitrogen, and also dissolves them extensively. This high reactivity may cause problems when dental porcelain is fused to the surface of titanium [1–3].

The formation of weakly adhering oxide to titanium at porcelain firing temperatures leads to the bonding problems between titanium and porcelain [1,4–10]. The formation of a metal–ceramic bond at porcelain firing temperatures should be strong enough to resist both transient and residual thermal stresses and mechanical forces in function. The requirements which are to provide such a bond are discussed as chemical, thermal, and mechanical compatibilities, and have been reviewed in literature [1,8–11]. However, there are many pending problems on titanium–porcelain bonding. Some titanium–porcelain systems appear to be susceptible to oxide layer, which can cause weaker bond strength. Relatively thick and non-adherent layers of titanium oxide tend to form at temperatures above 800 °C. So porcelain should be fired below this temperature because a thick oxide layer apparently minimizes metal–porcelain bond strength [8,12,13]. Other factors affecting titanium–porcelain bond to be considered are listed as follows: (1) growth of an oxide layer on titanium at elevated temperatures; (2) adherence of the self-formed oxide to the titanium substrate; (3) bonding by fusion of the self-formed oxide to the porcelain; and (4) stress developed at the interface because of an imbalance in thermal expansion coefficients. In order to prevent the formation of a weak interface, a strategy is devised to prevent Ti oxide formation at dental porcelain sintering temperatures and to generate an adherent oxide. The procedure involves using an intermediate layer deposited on Ti prior to the application of porcelain. Such a layer must include a biocompatible material, acts as a barrier to the diffusion of oxygen, and can be strongly adherent to the Ti substrate. Also, it must be capable of establishing a strong bond to porcelain.

Various surface treatments and attempts to overcome oxidation problems associated with titanium–porcelain systems have been considered [9,10,14–22]. One of the approaches which involves covering the titanium with a layer to prevent the formation of excessive and weak adherent Ti oxide layer during porcelain firing improves the bond strength between titanium and porcelain by controlling oxidation [9]. Micro-arc oxidation (MAO) is a relatively new surface treatment method to form ceramic coatings on valve
metals such as aluminum, magnesium, titanium and their alloys in a suitable electrolyte by increasing the voltage to a high stage, usually accompanied with discharge phenomenon and intensive gas evolution [23–26]. An advantage of MAO process is that the formed coatings are not only porous but also uniformly coated on metal surfaces with complex geometry and strongly adherent to the Ti substrate. The presented results for MAO coating were encouraging.

We have assumed that ceramic coating formed by MAO, which could be expected to serve as an oxygen diffusion barrier on titanium during the porcelain firings, could be effective in forming an improved bond between titanium and porcelain. The purpose of this study was to evaluate the effects of MAO technique on the bond strength of titanium to porcelain. The mode of failure at the interface, the effect of the MAO coating on reducing titanium oxidation, and the influence of intermediate layers on the improvement of bond strength were investigated.

To our knowledge, this is the first report investigating the use of micro-arc oxidation for increasing the bond strength on titanium to porcelain.

2. Materials and methods

2.1. Surface treatment and interface analysis

Commercially pure titanium (CP-Ti) of ASTM Grade 2 (99.9 mass% Ti, Northwest Institute for Nonferrous Metal Research, China) was cut into 25 mm × 3 mm × 0.5 mm. The specimens were randomly divided into two groups: One group was treated with MAO (MAO group, MAO-100, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, China). For the MAO treatment, a pulse power supply was employed, and a Ti specimen was used as an anode, while a stainless steel plate was used as a cathode in an electrolytic bath. An aqueous solution containing 20 g/L Na2SiO3 was used as an electrolyte by increasing the voltage to a high stage, usually accompanied with discharge phenomenon and intensive gas evolution. An advantage of MAO process is that the formed coatings are not only porous but also uniformly coated on metal surfaces with complex geometry and strongly adherent to the Ti substrate. The presented results for MAO coating were encouraging.

We have assumed that ceramic coating formed by MAO, which could be expected to serve as an oxygen diffusion barrier on titanium during the porcelain firings, could be effective in forming an improved bond between titanium and porcelain. The purpose of this study was to evaluate the effects of MAO technique on the bond strength of titanium to porcelain. The mode of failure at the interface, the effect of the MAO coating on reducing titanium oxidation, and the influence of intermediate layers on the improvement of bond strength were investigated.

To our knowledge, this is the first report investigating the use of micro-arc oxidation for increasing the bond strength on titanium to porcelain.

2.2. Porcelain sintering, bond strength measurement and bond interface analysis

After the MAO treatment, for cast titanium specimens, a thin bonding porcelain was applied to the central portion (8 mm × 3 mm) of the specimen surface. After the bonding porcelain was fired, opaque porcelain was applied in a masking layer, as it was a common practice with the porcelain fused to metal technique, and fired. Dentin porcelain was applied onto opaque porcelain using a custom-made jig that controlled the position and the thickness of the porcelain. Low fusing porcelain for titanium Noritake (Superporcelain TITAN, Japan) was used and the sintering conditions were shown in Table 1. The vacuity was 0.37 × 10⁻² Pa. After firing, the bond strength test was performed with a three-point bending device on a universal testing machine (AGS, Japan) according to the protocol ISO 9693. The specimens were placed with the porcelain facing down in the bending apparatus with rounded supporting rods 20 mm apart, and loaded in the center with a rounded bending piston (radius 1 mm). Force was applied at a constant rate of (1.0 ± 0.5) mm/min and recorded until the disruption of the load–deflection curve occurred that indicated bond failure. The fracture force F (in N) was measured for failure of specimen by a debonding crack occurring at one end of the ceramic layer. The loads that resulted in bond failure were recorded digitally by computer with software program (Zwick testXpert ver. 8.0, Zwick GmbH Co, Ulm, Germany). The coefficient k was a function of the thickness of the metal substrate and the value of Young’s modulus of the used metallic material. To read the value k for a certain thickness, the curve for the proper value of Young’s modulus was first selected, then the value k could be read from the picked curve for the thickness. The debonding/crack initiation strength τ was calculated by the equation: τ = k × Fmin. The micrographs of the cross-section and the morphology of fracture face of titanium–porcelain were evaluated by SEM. The elemental analysis of the fracture face was evaluated by EDS.

2.3. Statistical analysis

The results were analyzed by one-way ANOVA to detect statistically significant differences. A p-value of less than 0.05 was considered statistically significant.

3. Results

During the MAO treatment process, numerous wandering sparks could be seen on the surfaces of the titanium specimens. The surface morphologies of oxide layers after different treatment methods are shown in Fig. 1. Fig. 1a shows the surface morphology of the oxide layer before measuring the contact angle with a probe liquid, the chamber was allowed to become saturated with the vapor of the liquid employed. Subsequently, the contact angles were obtained analysing the images captured by a computer.

The mean surface roughness of each type of specimen was determined using a portable surface roughness tester (TR240, Time Group Inc, Beijing). The roughness measurements were performed before the porcelain was applied. Four randomly selected specimens from each group were used for the measurements. Measurements were made on four different areas of each specimen.

Table 1

<table>
<thead>
<tr>
<th>Porcelain</th>
<th>Starting temperature (°C)</th>
<th>Sintering temperature (°C)</th>
<th>Sintering time (min)</th>
<th>Porcelain layer thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding</td>
<td>500</td>
<td>800</td>
<td>3</td>
<td>0.2</td>
</tr>
<tr>
<td>Opaque</td>
<td>500</td>
<td>780</td>
<td>3</td>
<td>0.2</td>
</tr>
<tr>
<td>Dentin</td>
<td>500</td>
<td>760</td>
<td>3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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formed by MAO. The surface was composed of micro-protrusions with pores. The pores were well separated and homogeneously distributed over the surface of the specimen, and the diameter of the pores was about 1–3 μm. Fig. 1b shows the surface of the titanium specimen after sandblasting treatment. The surface was scraggy with irregular laminar structure, but without pore. The phases of the oxide layers formed by the MAO process and the sandblasting treatment were characterized by XRD analysis, as shown in Fig. 2. The oxide layer prepared by MAO was composed of rutile and Ti, and the surface of sandblasting treatment consisted of anatase and Ti.

Before and after firing at porcelain sintering temperatures without porcelain applications, EDS line scanning spectrums of cross-sections of titanium specimens treated with different methods are shown in Fig. 3. Signals were integrated over the peak width using the Ti and O-lines. Line scanning method was used to determine the relative location and boundary of oxide layer. In Fig. 3a, segregation of Ti and O could be clearly identified before firing in the MAO group. By elemental analysis, the thickness of oxide layer was about 5–6 μm, which was similar to that after firing (Fig. 3a'). In Fig. 3b, in the control group, the thickness of oxide layer was very thin before firing, but there was about 10–12 μm-thick oxide layer after firing (Fig. 3b').

The static water contact angles of the MAO group and the control group are shown in Fig. 4. The contact angle on the control group was 74.4 ± 13.5°. In the MAO treatment group, the static contact angle decreased significantly to 55.4 ± 4.0° (p<0.05).

Table 2 shows the surface roughness values of the specimens of the MAO group and the control group. In the one-way ANOVA test, no significant difference was observed between two groups (p>0.05).

Fig. 5 shows the SEM micrographs of the cross-sectioned titanium/porcelain specimens. SEM micrograph of titanium specimen treated with MAO is shown in Fig. 5a. There was no distinct boundary in the cross-sectional image, no air bubble or micro-crack. It was compact bonding between titanium and porcelain. The thickness of oxide layer was about 5–6 μm. But in Fig. 5b, SEM micrograph of titanium/porcelain specimen treated with sandblasting showed a loose boundary with a few of voids or micro-cracks between titanium and porcelain. An approximately 10–12 μm-thick oxide layer was detected.

The bond strength of the titanium–porcelain system was determined by the Schwickerath crack initiation test according to ISO 9693. The mean values of two groups were presented in Table 3. Six specimens (n = 6) of each group were tested. Bond strength values of titanium–porcelain of the MAO group were 39.6% higher than that of the control group. T-test was performed to determine the statistical significance of the bond strength difference between two groups. A level of significance of 0.05 was chosen (p=0.05). A significant difference was found in the bond strength of ceramic fused to titanium between two groups (p<0.05).

The micrograph and the elemental analysis of the fracture face after the porcelain which has been stripped are shown in Fig. 6. Fig. 6a shows a SEM micrograph of titanium specimen treated with MAO. There was a piece of rough grey coating with lamellar crystal structure but without porous structure on the surface of the titanium. The elements of Ti, F, Zr, Si and Al were observed by EDS analysis (Fig. 6a'). Fig. 6b shows a SEM micrograph of titanium specimen treated with sandblasting. There was a piece of rough coating with lamellar structure on the surface of the titanium. The elements of Ti, F, and Al were observed by EDS analysis (Fig. 6b').

4. Discussion

The presence of the oxide layer on titanium surface can play an important role in bonding of titanium to porcelain. Compared to the bonding in typical metal–porcelain systems, the adhesion between titanium and porcelain is relatively poor [27], attributed to the forming of a thick titanium layer, known as the “α-case” on its surface [28,29]. This oxide layer forms during the casting of the titanium and the high temperature sintering of the porcelain. To solve this problem, some scholars suggest to introduce interlayer between titanium and porcelain [30,31]. Such a layer may shield titanium from oxygen to prevent over-oxidation on the surface of titanium, eventually increasing the bond strength of titanium–porcelain.

The MAO technique is a new method that produces ceramic coating on the surface of nonferrous metal in natural condition. One of
Fig. 3. EDS line scanning spectrums of cross-sections of the different surface treated specimens before and after firing at porcelain sintering temperatures without porcelain applications. In the MAO group: (a) before sintering, (a’) after sintering; In the control group: (b) before sintering, (b’) after sintering (Ti: titanium element; O: oxygen element).

Fig. 4. Contact angles of water: (a) MAO treatment; and (b) sandblasting treatment. The contact angle of the MAO treatment is smaller than that of sandblasting treatment.
the characteristics is that ceramic coating is produced from basal body, which enhances the tightness between basal body and ceramic coating. The bond strength of titanium to coating could reach up to 56.9 MPa [32]. The other characteristic is that the surface of basal body is porous. The porous structure can increase the rugosity of basal body and thus may enhance the bond strength of Ti–porcelain [10].

The SEM/EDS shows the different morphologies of the surface and the fracture face of two treatment methods. In the MAO group, there were some micro-pores on the surface of titanium specimen, but the SEM morphology of fracture face after stripping the porcelain shows that there is no micro-pore and only lamellar crystal structure, some elements of bonding porcelain were analyzed by EDS on the fracture face. It is implied that the melting porcelain may flow into the micro-pores during liquid phase sintering and the fracture face probably occurs inside the oxide layer or between the oxide layer and the porcelain. In the control group, there is no pore on the surface of titanium, and the fracture face is lamellar structure. The elements of the fracture face are no porcelain ingredients. Its fracture face probably takes place inside the oxide layer or between the oxide layer and the titanium substrate. The pore structures of the MAO group might take an active part in the bonding of titanium and porcelain, and such a pore surface also provides increased mechanical interlocking between titanium and porcelain. In addition, there is Si element in the electrolyte and the porcelain, which might have an effect on the bond strength of the titanium–porcelain.

It is well known that titania has three polymorphs in nature: rutile, anatase and brookite. Rutile is the only stable phase, whereas anatase and brookite are metastable at all temperatures and transfer to rutile when heated. The XRD results indicated that the TiO₂ with MAO treatment was rutile, that was to say, the oxide layer treated with MAO technique is an over-oxidized. Compared with the control group, the MAO specimens showed a bond strength improvement of 39.6%. This result may be relevant to the porous surface, the stable crystal structure and the surface hydrophilicity of the titanium. The porous surface would be in favor of mechanical interlock between the oxide layer and the porcelain. From the contact angle results of two groups, they further support the high bond strength of the MAO treatment of titanium to porcelain. This difference in surface hydrophilicity might trigger different responses of titanium and porcelain upon contact with the oxidized coating. In this study, although it is not significantly different in the surface roughness values of the MAO and the control groups, their bond strength values are generally different. Furthermore, this study shows a low bond strength value for the sandblasting titanium as a result of the thick oxide layer that formed during sintering. By contrast, the titanium treated with MAO exhibits enhanced bond strength to porcelain. This is achieved through the formation of oxide layer after treated with MAO. The MAO coating can prevent the forming of oxide layer by acting as a barrier to the oxygen diffusion which occurs during the porcelain firing. It is also assessed with the SEM, SEM/EDS line scanning of cross-section findings, it may be suggested that the correlation between the roughness and the bond strength in that the greater the roughness, the higher the bond strength.

Cross-sectional SEM/EDS line scannings of two groups show the different characterizations of the reaction zone at the interface. In the MAO group, there was no significant contrast of the thickness of oxide layer before and after firing without porcelain applications. After porcelain sintering, the oxide layer had no air bubble or micro-crack. The bonding was compact between titanium and porcelain. And especially, the thickness of the oxide layer was similar to that before. However, in the control group, the oxide layer became thicker after firing. After porcelain sintering, the oxide layer was loose with micro-cracks. It was not compact between titanium and porcelain. Thus, the different thickness and the characterization of the oxide layer observed in this study may explain the difference in their interfacial reaction behavior and bond strengths between titanium and porcelain. It is implied that oxide layer treated with MAO technique is an effective barrier to control the formation of excessive and non-adherent titanium oxide layer during porcelain firing, and may increase the bond strength of titanium to porcelain.

Fig. 5. SEM photographs (original magnification ×5000) of cross-sections of titanium–porcelain systems: (a) MAO treatment; (b) sandblasting treatment, and arrows stand for voids or micro-cracks between titanium and porcelain. The bar is 5 μm.

### Table 2

<table>
<thead>
<tr>
<th>Group</th>
<th>Ra in μm (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAO group</td>
<td>1.00 (0.05)*</td>
</tr>
<tr>
<td>Control group</td>
<td>0.99 (0.07)</td>
</tr>
</tbody>
</table>

* Denotes no statistically significant difference at the $p \leq 0.05$ level.

### Table 3

<table>
<thead>
<tr>
<th>Group</th>
<th>Young’s modulus (GPa)</th>
<th>k</th>
<th>Bond strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAO group</td>
<td>105</td>
<td>4.1</td>
<td>46.46 ± 4.35*</td>
</tr>
<tr>
<td>Control group</td>
<td>105</td>
<td>4.1</td>
<td>33.28 ± 2.24</td>
</tr>
</tbody>
</table>

* Denotes statistically significant difference at the $p \leq 0.05$ level.
presence of the oxide layer determines the bond strength of titanium–porcelain systems. The results of this study support others, which attribute lower bond strength to the thick oxide layer on the metal surface [5,7,10]. This study indicates that the bond strength values of titanium to porcelain are not significantly different from those of the base metal alloys and the noble alloys. The replacement of noble metals with titanium would lead to significant economic benefits.

Current density, working hours and ratio of electrolytic solution are important factors during MAO treatment. As these factors vary, the coatings produced are different. Therefore, it is necessary to control the MAO parameters to gain the favorable surface suitable biomedical applications.

5. Conclusion

The effect of porous, compact TiO₂ coating which was deposited by MAO technique, on bond strength between titanium and porcelain was studied. Oxidation experiments that simulated thermocycles of porcelain sintering were carried out in order to characterize the TiO₂ coating’s effectiveness in preventing the adverse oxidation of titanium and enabling the compact bonding of titanium and porcelain. The following conclusions can be drawn from this study: By micro-arc oxidation technique, bond strength of titanium–porcelain is improved about 1.4 times over that of sandblasting. The surface of titanium with porous, compact, and stable TiO₂ coating, and the high surface hydrophilicity result in higher bond strength of titanium to porcelain. The parameters of the MAO are: voltage 300 V, pulse frequency 500 Hz, duty cycle 0.04, and time 3 min. The bond strength value is excessively beyond the ISO standard 9693 and not significantly different from base or noble metal alloys. So the bond strength of titanium–porcelain is sufficient for clinical use.

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