Adherence of Porcelain Veneered on Titanium with an Intermediate Plasma-Sprayed Zirconia Layer

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Porcelain veneered on pure titanium with an intermediate plasma-sprayed ZrO$_2$ bond coat layer was investigated in this study. The pure porcelain coating veneered on Ti was used as a control. The specimens were subjected to four-point bending test to measure the bonding strength. The fractograph, microstructure, surface roughness, and phase of plasma-sprayed ZrO$_2$ bond coat were examined. The phase constituents at the location of adhesive failure of the fractured specimens were investigated by thin-film X-ray diffractometry. Experimental results reveal that the bonding strength of the coating with the intermediate layer was increased by 55.7% that was accompanied by a significant decrease of the area of adhesive failure in the fracture. The ZrO$_2$ results reveal that the bonding strength of the coating with the intermediate layer was increased by 55.7% that was accompanied by a significant constuituents at the location of adhesive failure of the fractured specimens were investigated by thin-film X-ray diffractometry. Experimental strength. The fractograph, microstructure, surface roughness, and phase of plasma-sprayed ZrO$_2$ porcelain coating veneered on Ti was used as a control. The specimens were subjected to four-point bending test to measure the bonding strength.

1. Introduction

Titanium is being developed in recent years as a metal substrate material for metal-porcelain restorations in dentistry. The interest in titanium is due to the consideration of biocompatibility, physical and chemical properties, and cost. During the firing of porcelain on Ti at high temperature, however the chemical reaction of metal with oxygen is violent and the reaction causes to form the Ti oxides layer that thickens and apparently weaks the bonding of the interface between porcelain and Ti.$^{1-3)}$ To alleviate the embrittled interface, Wang et al.$^{9)}$ deposited a Cr single layer and Cr/Cr oxide bi-layer coatings by the technique of physical vapor deposition, and the coatings served as an oxygen diffusion barrier on the Ti substrate prior to veneering of porcelain. Similarly, Sadeq et al.$^{5)}$ applied a thin gold coating on the surface of Ti to limit the Ti oxidation during firing cycles. It can be concluded that those processes apparently reduces the tendency of the formation of metal oxides, however the reactivity of the metals still remains a concern.

Recently, calcium phosphate biomaterials are plasma sprayed onto the titanium substrate as implants for orthopaedics and dentistry. According to the study by Chou et al.$^{5)}$ who indicated that the bonding strength between hydroxyapatite top coating and Ti substrate could be promoted by introducing a plasma-sprayed ZrO$_2$ bond coat. It was known that the higher surface roughness provided by the substrate resulted in a mechanical interlocking and a larger interfacial bonding.$^{7,8)}$ In addition, the tensile strength of as-sprayed ZrO$_2$ on Ti seemed unaffected by heat treatment at high temperature.$^{9)}$

The aim of this study was to study the adherence of porcelain on Ti with the introduction of an intermediate layer of plasma-sprayed zirconia as bond coat on Ti prior to porcelain overcoat and firing. Previous in vivo test has classified ZrO$_2$ as an bioinert material without the evidence of adverse tissue response.$^{10)}$ Since the plasma-sprayed ZrO$_2$ bond coat should result in a rougher surface$^{6,11)}$ it is very likely that this intermediate layer could promote the mechanical bond of ZrO$_2$ with porcelain. This is the merit probably not attainable by Cr or Au metallic intermediate layer produced by PVD, although the intermediate ZrO$_2$ layer is neither an efficient oxidation diffusion barrier$^{12)}$ as the Cr or Au metal. However, if the ZrO$_2$ coating can provide a sufficient oxygen protection to the underneath Ti during firing, the proposed composite system might be viable for metal-porcelain restorations in dentistry. The single-layer porcelain veneered on Ti substrate was also experimented as a control.

2. Experimental Procedure

2.1 Specimen preparation and characterization

Porcelain powder (Opaque type) and ZrO$_2$ powder stabilized with 8 mass% Y$_2$O$_3$ were obtained from the commercial suppliers (Ducera and Plasma Technik, respectively). The plates of pure Ti (ASTM Grade II) were machined to dimension of 6 mm ($l$) x 8 mm ($w$) x 3 mm ($t$) as substrate. Table 1 shows the chemical composition of experimental porcelain powder measured by inductively coupled plasma optical emission spectrometry (Spectro-P). The structure of porcelain consists of crystalline SnO$_2$ dispersoids in an amorphous phase made of SiO$_2$, Al$_2$O$_3$, K$_2$O and Na$_2$O.

Before plasma spraying of ZrO$_2$ (Plasma Technik M-1100C, using the parameters as shown in Table 2) and veneering of porcelain, the surface of Ti substrates was grid-blasted with SiC particles of an average of 650 µm and etched in a mixed-acid solution of 6 mL HF and 9 mL HNO$_3$ in.

Table 1 Chemical composition of porcelain powder.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>SnO$_2$</th>
<th>Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (mass%)</td>
<td>50.2</td>
<td>9.8</td>
<td>9.9</td>
<td>9.3</td>
<td>20.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

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Keywords: porcelain, titanium, zirconia (ZrO$_2$), bonding strength, adhesive failure, cohesive failure, diffusion barrier

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Table 2 Plasma-spraying parameters employed for the deposition of ZrO$_2$ bond coat

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ZrO$_2$ bond coat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of primary gas (Ar), (L/min)</td>
<td>41</td>
</tr>
<tr>
<td>Flow rate of secondary gas (H$_2$), (L/min)</td>
<td>10</td>
</tr>
<tr>
<td>Flow rate of powder carrier gas (Ar), (L/min)</td>
<td>3</td>
</tr>
<tr>
<td>Powder feed rate (g/min)</td>
<td>20</td>
</tr>
<tr>
<td>Ampere (A)</td>
<td>625</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>42</td>
</tr>
<tr>
<td>Stand-off distance (cm)</td>
<td>7.5</td>
</tr>
<tr>
<td>Surface speed (cm/min)</td>
<td>7500</td>
</tr>
<tr>
<td>Transverse speed (cm/min)</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3 Firing procedures for porcelains veneered on Ti substrate with and without ZrO$_2$ bond coat

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum (Pa)$^a$</td>
<td>6.67</td>
</tr>
<tr>
<td>Start temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Heating rate (°C/min)</td>
<td>55</td>
</tr>
<tr>
<td>Firing temperature (°C)</td>
<td>800</td>
</tr>
<tr>
<td>Holding time (s)</td>
<td>286</td>
</tr>
<tr>
<td>Cooling</td>
<td>in air</td>
</tr>
</tbody>
</table>

$^a$Vacuum was applied through the whole firing procedure until the holding time was reached.

85 mL distilled water for 60 seconds to produce an average surface roughness about 5.0 μm ($R_a$). For the porcelain/ZrO$_2$ specimens, the ZrO$_2$ powder was plasma sprayed onto the treated Ti plates to produce an intermediate layer about 30 μm in thickness, which was followed veneering with 270 μm thick of porcelain to produce a thickness about 300 μm bi-layer coating on the Ti substrate. The control single-layer specimens were produced by veneering with a porcelain coating about 300 μm in thickness on the Ti substrate. The firing procedures as shown in Table 3 for all the specimens were carried out in a quartz tube. The morphologies of as-etched Ti substrate and as-sprayed ZrO$_2$ bond coat were examined by scanning electron microscopy (SEM) (XL-40 FEG, Philips). The phase identity of as-sprayed ZrO$_2$ bond coat on the Ti substrate was determined by X-ray diffractometry with CuK$_α$ radiation, operated at 40 kV, 100 mA, and a fixed angle of 0.5°, with a scan speed of 1°/min (Rigaku Rint 2000) to determine the phase ingredients. To further investigate the fracture behavior, the location of AD failure of delaminated porcelain side and corresponding Ti side for PT and PZT were analyzed by thin-film X-ray diffractometry with CuK$_α$ radiation, operated at 40 kV, 100 mA, and a fixed angle of 0.5°, with a scan speed of 1°/min (Rigaku D-MAX IIB) to determine the phase ingredients. However, as will be shown in the experimental result, the AD failure of PZT specimen at Ti side is not only very small but also located in a basin of fractured surface with the surrounding higher terrace of cohesive failure of porcelain. To allow the low-angle beam of X-ray to get an access to the location of AD failure, the fractured fragment corresponding to the Ti side of PZT specimen was ground slightly to remove the surrounding porcelain around the location on the specimens. Unfortunately, the removal of surrounding porcelain on the Ti substrate resulted in the exposure of the underneath Ti substrate that was detected by thin-film X-ray as an artifact of Ti peak as shown later.

2.4 Effectiveness of ZrO$_2$ as the oxygen diffusion barrier

To study the effectiveness ZrO$_2$ as an oxygen diffusion barrier to protect the underneath Ti from oxidation for PZT specimens, the minute Ti oxides that might form at the interfaces of ZrO$_2$ and Ti, as compared with porcelain and Ti for PT specimen, need to be explored. For the purpose of more efficiently detecting the oxides at the interface by thin-film X-ray technique that usually requires smoother surfaces, extra specimens were prepared. The Ti substrate was ground and polished instead of grid-blasting and acid-etching before applying the porcelain coating and firing. The specially produced PT and PZT specimens were then immersed in a corrosive solution of 10 mL Br$_2$ and 90 mL methanol to dissolve the Ti substrates and thus free the porcelain and porcelain/ZrO$_2$ coatings associated with the PT and PZT specimens, respectively. These specimens were then analyzed from the bottom of specimens by thin-film X-ray diffractometry to detect the Ti oxides.

3. Experimental Results

3.1 Coating characterization

Figure 1 shows the SEM cross-sectional microstructure of single porcelain coating and bi-layer porcelain/ZrO$_2$ coating

$$\sigma_b = 3PL/4bh^2$$ (1)
on Ti. It reveals that the surface of plasma-sprayed ZrO$_2$ bond coat exhibits more conspicuous apophysis and cavities than the Ti substrate. It is found that the surface roughness increases from 5.0 ± 0.1 μm for the grit-blasted and acid-etched Ti substrate to 6.5 ± 0.2 μm for the as-sprayed ZrO$_2$ bond coat. Each value is the average of 6 tests and the values are given as mean ± standard deviation. The ZrO$_2$ bond coat has the rougher surface than the grit-blasted and acid-etched Ti substrate and the former should contribute to a higher mechanical bond.

The SEM surface morphologies of grit-blasted and acid-etched Ti substrate and as-sprayed ZrO$_2$ bond coat are shown in Fig. 2. It is evident that the surface of Ti substrate (Fig. 2(a)) is flatter than that of ZrO$_2$ bond coat (Fig. 2(b)). Figure 3 shows the X-ray diffraction pattern of as-sprayed ZrO$_2$ bond coat that exhibits a tetragonal crystal structure.

### 3.2 Bonding strength

The data of bonding strength measured by four-point bending test are listed in Table 4. It is found that the bonding strength increases from 23.0 ± 2.1 MPa for PT specimens to 35.8 ± 5.7 MPa for PZT specimens. The results indicate that the bonding strength of PZT specimen is significantly higher than that of PT specimen. The bonding strength of porcelain veneered on Ti is evidently reinforced by the introduction of ZrO$_2$ bond coat.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Bond strength (MPa) ± S.D.</th>
<th>AD failure (%) ± S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
<td>23.0 ± 2.1</td>
<td>55.5 ± 6.7</td>
</tr>
<tr>
<td>PZT</td>
<td>35.8 ± 5.7</td>
<td>27.7 ± 3.7</td>
</tr>
</tbody>
</table>

Each value is the average of 6 tests and values are given as mean ± S.D.
3.3 Fractography

3.3.1 Optical fractography on the fracture surface

The typical optical morphology of fracture surface of the delaminated porcelain fragment and the Ti substrate subsequent to four-point bending test is shown in Fig. 4. In this figure the white area represents the cohesive failure of porcelain coating, while the dark area represents the adhesive failure between porcelain and Ti substrate for PT specimen (Fig. 4(a)), and between porcelain and ZrO$_2$ bond coat for PZT specimen (Fig. 4(b)). The dispersed white spots within the location of adhesive failure in Fig. 4 might be the events of cohesive failures. The figure reveals that the fracture is a mix of cohesive (within the coating itself) and adhesive failure (coating to substrate). In addition, the corresponding AD adhesive failure in each specimen was calculated by the image analysis and the results are also shown in Table 4, which shows that the AD failure decreases from $55.5 \pm 6.7$ for PT specimen to $27.7 \pm 3.7$ for PZT specimen.

3.3.2 Cross section of the fractured specimens

The cross sectional images of fractured fragments glued together are shown in Fig. 5. The image seen in Fig. 5(a) for PT specimen shows that the fracture in the location of adhesive failure occurred near the interface between porcelain and Ti substrate. The detailed path of crack propagation cannot be explored by the cross sectional fractograph at the magnification, and should be investigated by thin-film X-ray as shown below. Figure 5(b) shows the border between adhesive failure and cohesive failure, where it is also seen that the ZrO$_2$ bond coat was adherent to the Ti substrate firmly, and no major pieces of ZrO$_2$ were detached to the porcelain side.

3.3.3 Thin-film X-ray diffraction analysis on the location of AD failure

The thin-film X-ray diffraction patterns analyzed on the location of AD failure of fracture surface for both PT and PZT is shown in Fig. 6. Comparing Fig. 6(d) on the Ti side of PZT with Fig. 3 shows that the diffraction pattern of ZrO$_2$ for the PZT specimen subjected to sintering heat treatment for porcelain at 800°C is identical to the pattern of as-sprayed ZrO$_2$ bond coat. The observation of failure inside the location of AD failure for PT specimen by comparing Figs. 6(a) and Fig. 6(b) with the technique of thin-film X-ray diffractometry indicates the following. In the delaminated porcelain side as shown in Fig. 6(a) very strong peaks of SnO$_2$ were detected with strong Ti apparently detached from the Ti substrate to the porcelain during fracture. While in the Ti side as shown in Fig. 6(b) very strong peaks of Ti with weak SnO$_2$ were observed. For both Figs. 6(a) and (b) no occurrence of TiO$_2$ was found.

The observation of failure inside the location of AD failure for the PZT specimen by comparing Fig. 6(c) and Fig. 6(d) with the technique of thin-film X-ray diffractometry indicates the following. The fracture surface of delaminated porcelain side (Fig. 6(c)) show strong peaks of SnO$_2$ and very weak ZrO$_2$, while in Fig. 6(d) very strong peaks of ZrO$_2$ with weak
SnO₂. This indicates that the fracture inside the area of AD failure for PZT occurred mainly through the interface between porcelain and ZrO₂, with some incidence of porcelain detached to the ZrO₂ bond coat but less chance of ZrO₂ being detached to the porcelain side. It must be emphasized that the spectra of Ti in Fig. 6(d) (as marked by T⁺) is an artifact caused during specimen preparation for thin-film X-ray analysis by removing the higher terrace of porcelain surrounding the location of AD failure in the Ti side specimen of PZT that unfortunately exposing the underneath Ti as explained before. This point is also supported by the cross sectional fractography as explained. Furthermore, if Ti should have existed in the Ti side of Fig. 6(d), usually there should also have some fragments of Ti attached to the porcelain side of Fig. 6(c), which however was not found. Hence the Ti peak in Fig. 6(d) is deemed as an artifact.

The oxides formation at the interface of porcelain/Ti, or ZrO₂/Ti, was observed from the bottom of free porcelain for PT specimen and free porcelain/ZrO₂ for PZT specimen, using thin-film X-ray diffractometry. This was made possible by dissolving the Ti substrate prior to X-ray irradiation. If the crack did occur at the exact interface between porcelain and Ti oxides or inside the Ti oxides, then the peak of Ti oxides should have been detected in Fig. 6(a) and Fig. 6(b). However, this was not evidenced. The thickness of Ti oxides in the present PT specimen was measured as 0.3 μm thick by cross sectional SEM micrograph. It might be that the quantity of Ti oxides is not sufficient to render a detectable peak in the thin-film X-ray diffraction pattern as shown in Fig. 6(a) and Fig. 6(b). This question must be further studied. The evidence that the crack propagated inside the Ti substrate is evident as shown in Fig. 6(a) and Fig. 6(b) for PT specimen, in which the peaks of Ti were detected. This result is in agreement with a previous study by XPS technique.²)

Attention is now paid to the interface between ZrO₂ bond coat and Ti substrate. It can be concluded that the ZrO₂ bond coat is bonded adherently to the Ti substrate and no Ti substrate is exposed on the fracture surface by examining the SEM cross sectional image of the fractured PZT specimen as shown in Fig. 5(b). As shown in Fig. 7(b) no oxides formed at the interface between ZrO₂ bond coat and Ti substrate. This infers that the ZrO₂ bond coat effectively reduces the diffusion of oxygen from the atmosphere or porcelain or form TiO₂ at the interface between ZrO₂ and Ti. If otherwise allowing oxygen to diffuse through the porcelain to oxidize the Ti substrate as shown in Fig. 7(a) for PT specimen, the Ti substrate could be embrittled and the fracture occurred within the embrittled Ti (Fig. 6(a) and Fig. 6(b)).

With the introduction of the ZrO₂ intermediate layer, the experimental result reveals that the fracture on the location of AD failure for PZT occurred slightly inside the porcelain near the interface between porcelain and ZrO₂ bond coat as suggested in Fig. 6(c) and Fig. 6(d). Only a minute ZrO₂ was detached to the porcelain side as shown in Fig. 6(c), gaged along the interface of porcelain and Ti oxides.¹,¹⁵,¹⁶)

The present study employed the thin-film X-ray diffractometry that allows to probe more properly to the thin layer less than 1 μm thick of the fracture surface.¹⁷) If the crack did occur at the exact interface between porcelain and Ti oxides or inside the Ti oxides, then the peak of Ti oxides should have been detected in Fig. 6(a) and Fig. 6(b). However, this was not evidenced. The thickness of Ti oxides in the present PT specimen was measured as 0.3 μm thick by cross sectional SEM micrograph. It might be that the quantity of Ti oxides is not sufficient to render a detectable peak in the thin-film X-ray diffraction pattern as shown in Fig. 6(a) and Fig. 6(b). This question must be further studied. The evidence that the crack propagated inside the Ti substrate is evident as shown in Fig. 6(a) and Fig. 6(b) for PT specimen, in which the peaks of Ti were detected. This result is in agreement with a previous study by XPS technique.²)

Attention is now paid to the interface between ZrO₂ bond coat and Ti substrate. It can be concluded that the ZrO₂ bond coat is bonded adherently to the Ti substrate and no Ti substrate is exposed on the fracture surface by examining the SEM cross sectional image of the fractured PZT specimen as shown in Fig. 5(b). As shown in Fig. 7(b) no oxides formed at the interface between ZrO₂ bond coat and Ti substrate. This infers that the ZrO₂ bond coat effectively reduces the diffusion of oxygen from the atmosphere or porcelain or form TiO₂ at the interface between ZrO₂ and Ti. If otherwise allowing oxygen to diffuse through the porcelain to oxidize the Ti substrate as shown in Fig. 7(a) for PT specimen, the Ti substrate could be embrittled and the fracture occurred within the embrittled Ti (Fig. 6(a) and Fig. 6(b)).
suggesting that the ZrO₂ was fracture resistant at the interface of porcelain and ZrO₂. Moreover, the SEM cross sectional image of the fractured PZT specimen shows the evidence that the fracture didn’t occur through the thickness of ZrO₂ bond coat. All the above findings suggest that the ZrO₂ bond coat might be a relatively tough material.¹⁸,¹⁹ There existed apparent cavities at the interface of porcelain and ZrO₂ bond coat as shown in Fig. 1(b), and this should underline the fracture resistance at the interface. However, Fig. 2(b) and the surface roughness measurement show that the surface of ZrO₂ bond coat as the substrate for veneering porcelain in PZT specimen was rougher than the grit-blasted and acid-etched Ti substrate in PT specimen. The previous investigators have proposed that the roughened interface resulted in a mechanical interlocking and a larger interfacial area for the interfacial adherence.²⁰,²¹

The results of this study reveal that the specimen with ZrO₂ bond coat (PZT) possessed the higher bonding strength than the one without (PT). The bonding strength increases from 23.0 ± 2.1 MPa for PT specimen to 35.8 ± 5.7 MPa for PZT specimen, an increase of 55.7% (Table 4). Correspondingly, the fractography shows that the AD failure decreases from 55.5 ± 6.7% for PT specimen to 27.7 ± 3.7% for PT specimen, a decrease of 50.1% (Table 4). From the present study, the correlation between bonding strength and AD failure can be established, and the introduction of ZrO₂ intermediate layer reduces the AD failure and hence increases the bonding strength of the system.

5. Summary

The study has demonstrated that the adherence of porcelain veneer on Ti can be significantly improved by the introduction of the intermediate ZrO₂ layer, which is associated with the decrease of adhesive failure in the fractured specimen. The decrease of adhesive failure is summarized as follows. The phase constituents at the location of adhesive failure of the fractured specimens investigated by thin-film X-ray diffractometry revealed that the ZrO₂ bond coat was bonded adherently to the Ti substrate. No oxides was found to form at the interface between ZrO₂ bond coat and Ti substrate, indicating that the ZrO₂ bond coat effectively reduced the diffusion of oxygen from the atmosphere or porcelain to the interface between ZrO₂ and Ti. The ZrO₂ itself is a tough material, and it might strengthen the interfaces of porcelain/ZrO₂ based on the fact that the fracture on the location of AD failure for PZT occurred slightly inside the porcelain near the interface between porcelain and ZrO₂ bond coat. The use of ZrO₂ is justified that the fracture of PZT specimen didn’t occur across the ZrO₂ bond coat. The interface between porcelain and ZrO₂ is further strengthened by the rougher surface of ZrO₂. Moreover, ZrO₂ retarded the oxidation of the underneath Ti at 800°C and hence strengthened the interface between ZrO₂ and Ti.

Acknowledgments

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