Interfacial Characterization of Porcelain Veneered on the Pure Titanium under Vacuum Firing

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The interfacial characteristics between porcelain coating and titanium under vacuum firing at 800°C have not been well documented. The cross-sectional variations in microstructures and compositions at the porcelain/Ti interface were investigated with a SEM and an EPMA equipped with WDS. The phase constituents of the porcelain bulk coating and the nearby porcelain/Ti interface were analyzed by X-ray and thin-film X-ray diffractometry respectively. In addition, a TEM equipped with EDS was used to examine the porcelain/Ti oxide interface. The experimental results revealed that the oxidation of Ti occurred at the porcelain/Ti interface, and it is reasonable to deduce that the Ti reduces the SnO$_2$ and SiO$_2$ components of the porcelain and becomes Ti oxide. Furthermore, redox reactions and chemical bonding occur at porcelain/Ti interface during firing and thus prevent initiation of fracture from occurring at this interface. Subsequently, the fracture initiation tends to be located near the interface of newly formed Ti oxide and Ti substrate and/or slightly inside the Ti.

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1. Introduction

Porcelain-fused-to-metal (PFM) restorations are used in fixed prosthodontics for its esthetic considerations. During the past decade pure titanium has become one of the attractive base metals employed in PFM because of its practical advantages: high strength, good corrosion resistance, inert biocompatibility and rather low price compared to precious metals. However, the high reactivity of Ti with oxygen becomes severe at high temperature. The oxidation of Ti under high temperature and fairly long duration time results in Ti oxides growth that impairs the oxides adherence to Ti. Consequently, in the practical application of PFM, the growth of oxides causes a decrease in bonding strength when porcelain coatings are simply veneered on the Ti. A previous study reported that interfacial fracture often initiated from the uppermost Ti substrate near the Ti oxides and Ti interface. However, no fracture has been found inside Ti oxides or at the interface between the porcelain coating and Ti oxides. This phenomenon indicates that the bonding strength between the porcelain coating and the Ti oxides might be higher than that between the Ti oxides and the Ti substrate.

It is well known that the connection between the porcelain veneer and the Ti is often both mechanical and chemical, and that the chemical bond depends on the surface area of the metal substrate. Wagner et al. pre-oxidized the metal substrate before porcelaining, which resulted in improved bonding strength primarily due to the pre-oxidation caused rougher surface of the metal substrate. Accordingly, a higher contact area can be achieved by making the metal substrate with rougher surface and then using a fine wetting porcelain might result in an increase in interfacial reactions between the porcelain and the Ti. Furthermore, Pask et al. indicated that the presence of metal oxide is a necessary requirement for wetting, and Jach et al. concluded that the metal and the glass never came into contact without some sort of intermediate oxide layer. Though studies on the interfacial reactions between porcelain and Ti were recently published, however, more experimental evidence still needs to be collected.

According to our previous studies, the location of adhesive failure occurred near the Ti oxide/Ti interface and even slightly inside the uppermost Ti substrate. This revealed that the porcelain/Ti oxide interface possesses fairly high bonding strength, i.e. chemical bonding might occur, and thus the fracture tended to occur near the Ti oxide/Ti interface instead of initiating at the porcelain/Ti oxide interface. This study aims to investigate the interfacial reactions and bonding features between porcelain coating and Ti substrate. Speculations, based on observation of the microstructure, qualitative determination of compositional variations across the interface and thermodynamic analysis of the possible interfacial reactions between porcelain coating and Ti substrate, were made about the correlation between oxide formation and chemical bonding.

2. Experimental Procedure

2.1 Materials preparation and specimens fabrication

Experimental low-fusing titanium porcelain (Opaque type, Duceratin) powder and pure Ti (ASTM Grade II) were obtained from the respectively commercial manufacturers. Table 1 shows the chemical compositions of the porcelain powder measured by inductively coupled plasma optical emission spectrometry (Spectro-P). The porcelain powder comprises an amorphous phase made of SiO$_2$, Al$_2$O$_3$, K$_2$O and Na$_2$O with a dispersedly crystalline SnO$_2$. Pure Ti plates were machined to 10 mm(t) x 25 mm(w) x 1 mm(t) by a water-cooled diamond band saw. Before applying the

<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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porcelain, the surface of the Ti substrates were ground to 2000 grit with wet SiC papers and then polished with Al₂O₃ particles (5 and 1 μm) to eliminate the innate contaminants and to expose the smooth Ti surface. Afterward the porcelain powder was mixed with carving liquid to the slurry and a layer of porcelain coating was applied on the smooth Ti substrate. Subsequently, the composite specimen was baked in an oven and then fired in a quartz tube. Firing of the composite specimen was carried out under vacuum according to the firing procedures as shown in Table 2. After firing, the composite specimen with a porcelain coating had the thickness of about 300 μm.

2.2 Characterization of porcelain veneered Ti

A scanning electron microscope (SEM) (XL40 FEG, Philips) was used to examine the cross-sectional morphology of the as-fired specimen. First, the specimen was cut to 10 mm(l) × 1.3 mm(w) × 1 mm(t) and then mounted in epoxy resin. Subsequently, the mounted specimen was ground and polished perpendicularly to the veneered surface and coated with a carbon film. To identify the phase of the as-fired porcelain coating, a special specimen was prepared. The composite specimen was immersed in a corrosive solution (10 ml Br₂ and 90 ml methanol) to dissolve the Ti substrate and thus obtain the free porcelain bulk coating. The surface of the porcelain bulk coating that was originally next to the Ti substrate was then analyzed by thin-film X-ray diffraction (Rigaku Rint 2000, CuKα radiation). The opposite surface of the same porcelain bulk coating was subjected to X-ray diffraction (Rigaku D-MAX IIB, CuKα radiation) analysis for phase identification. In addition, an extra specimen was in accordance with the experimental procedure of our previous study¹³) to induce fracturing. The fractured specimens were observed cross-sectionally by SEM to examine the fracture status at the location of adhesive failure.

2.3 Interfacial examination

To investigate the variations of compositions across the interface between the porcelain coating and the Ti substrate, an electron probe micro-analyzer (EPMA) (JEOL 8900R) coupled with wavelength-dispersive spectroscopy (WDS) was used. The WDS line scan was used for preliminarily compositional study across the porcelain/Ti interface. The detailed analysis of chemical reactions and interfacial diffusion at the porcelain/Ti interface was identified with a transmission electron microscope (TEM) (JEOL 3010 AEM) coupled with an energy dispersive X-ray spectrometer (EDS). The preparation of the cross-sectioned specimen for TEM was made through the following process. The composite specimen was cut perpendicular to the coating interface into several pieces and each piece was glued to another one with the Ti substrates face to face. The as-glued pieces were inserted into a copper tube with dimensions of 20 mm(l) × 3 mm (outer diameter) and 2 mm (inner diameter), and mounted with G1 glue (Gatan Inc.) to fix the pieces inside the tube. The tube was cut to disks 0.5 mm in thickness and then ground until 5–10 μm remained. The ground specimen was fixed with a Cu holder and the cross-sectional area near the center of the disk was further thinned by using twin jet etching and ion milling thinner (Gatan DuoMill 600). The thinned specimens were then coated with a carbon film for electrical conductivity and examined at a voltage of 200 kV in the TEM.

3. Experimental Results

3.1 Metallographic observations and coating characterization

SEM cross-sectional images with low and high magnification of porcelain veneered on the Ti under vacuum firing are shown in Fig. 1. In Fig. 1(a), under low magnification, it can be seen that the porcelain coating is uniform and adheres to the Ti substrate without obvious variation of microstructure across the interface. However, under high magnification (Fig. 1(b)), a scale (about 600 nm) with white

![Fig. 1 SEM cross-sectional images of porcelain veneered Ti (a) at low magnification, and (b) at high magnification. (P: porcelain coating, T: Ti substrate, C: crevice, TO: Ti oxide)](image-url)
contrast can be seen between the porcelain and the Ti, and the scale is preliminary speculated to be composed of Ti oxides. A further magnification of the local area between porcelain and the scale in Fig. 1(b) will be analyzed by TEM. Fig. 1(b) also shows a crevice mark, the crevice is recognizable between Ti oxide and the Ti substrate even though the specimen only underwent pretreating grinding.

Figure 2 shows the X-ray diffraction spectra of the porcelain coating after vacuum firing. Figure 2(a) shows the result of the coating surface that was originally next to the Ti substrate and Fig. 2(b) shows the result of the bulk coating. In Fig. 2(b), it indicates that the porcelain coating only has the crystalline SnO\(_2\) phase that is the same as porcelain powder before firing. By comparing the results of Figs. 2(a) and (b), extra peaks in Fig. 2(a) including Sn, Ti and TiO\(_2\) are found. It is obvious that the phase change occurred at the porcelain/Ti interface during the vacuum firing process. The appearance of Sn might be due to the reduction of SnO\(_2\) by Ti which resulted in the formation of TiO\(_2\) at the porcelain/Ti substrate interface. However, residually metallic Ti was detected on porcelain coating after etching in corrosive solution and resulted in the appearance of Ti spectra in Fig. 2(a). The X-ray diffraction analysis preliminarily demonstrates that chemical reactions might be at the porcelain/Ti interface.

### 3.2 Fracture behavior and compositions analysis across the interface

The cross-sectional images of the fractured specimens in Fig. 3 show that there is a gray scale adhered to the porcelain coating (seen clearly in Fig. 3(b)). The scale contains the Ti ingredient\(^{13}\), which means that the fracture at the location of adhesive failure occurred near the Ti oxide/Ti interface and even slightlyly inside the Ti substrate. Thus it is speculated that there might be a strong bonding at the porcelain/Ti oxide interface. Figure 4 shows the back-scattered electron image (BEI) of EPMA examination, where the intermediate area consisting of a band-like zone that appears white contrast at the interface between porcelain and Ti substrate. According to the profile of WDS line scan across the porcelain/Ti interface, which is shown under the BEI, a significantly compositional variation of Sn element was detected. In addition, the BEI and the profile also reveal that the Ti element has a tendency to diffuse into the porcelain coating.

### 3.3 TEM examinations of microstructures

The cross-sectional microstructures examined by TEM across the interface of porcelain and Ti oxide are shown in Fig. 5. The TEM images of the bright field image, dark field image and selected area diffraction pattern (SADP) are shown in Fig. 5(a), Fig. 5(b) and Fig. 5(c), respectively. In Fig. 5(a), the Ti oxide and the porcelain coating can be seen easily, but the interface between them is not obvious to distinguish. There are also spherical particles near the Ti oxide, and these particles are determined to be the pure Sn crystal that will be further depicted later. The SADP (Fig. 5(c)) taken from one grain corresponding to the dark field image shown in Fig. 5(b) (white contrast particle about 150 nm × 100 nm) is indexed to TiO\(_2\) (rutile phase) with a tetragonal crystal structure (JCPD 86-0147). The other similar particles on the top of the cross-sectional microstructures in Fig. 5(b) (dark contrast) are also TiO\(_2\), which is consistent with the TiO\(_2\) spectra of X-ray diffraction as shown in Fig. 2(a). Furthermore, the scale with white contrast in Fig. 1(b) is also confirmed to be TiO\(_2\) with rutile phase. In addition, the SADP in Fig. 5(b), there is a circular particle
with white contrast below the uppermost TiO$_2$. It is a crystalline structure and can be deduced as a Sn phase.

In order to confirm the existence of pure Sn close to the porcelain/Ti oxide interface, the TEM results for SnO$_2$ and Sn in porcelain bulk coating are shown in Fig. 6. The bright field image of SnO$_2$ particles away from the porcelain/Ti oxide interface shows that the appearance of each SnO$_2$ crystal is a polyhedron. The SADP taken from each particle of the bright field image in Fig. 6(a) is shown in Fig. 6(b) and indicates that the SnO$_2$ crystal has a tetragonal crystal structure (JCPD 77-0451). However, the TEM observation of the area near the porcelain/Ti oxide interface (shown in Fig. 6(c)) shows that the polyhedral SnO$_2$ particles are absent, but dispersedly circular particles (less than 50 nm in diameter) are precipitated instead. Meanwhile, the SADP (nano-electron beam was used) (Fig. 6(d)) taken from each circular particle in Fig. 6(c) was identified as pure Sn with a tetragonal structure (JCPD 86-2265). The precipitation of pure Sn particles near the porcelain/Ti oxide interface (Fig. 6(c)) confirms the formation of the band-like zone found in the EPMA image as shown in Fig. 4. Moreover, the reduction of SnO$_2$ indicates that the chemical reaction occurs at the porcelain/Ti oxide interface.

Additional TEM observations and EDS analysis of the cross-sectional porcelain/Ti oxide interface were performed, and identified an additional chemical reaction and interfacial diffusion process. Figure 7(a) shows the bright field image of
the porcelain/Ti oxide interface, which reveals that there are arresting flake-like microstructures (indicated by the white arrows) found near the porcelain/Ti oxide interface in addition to circular Sn particles. In Fig. 7(b), the dark field image corresponding to Fig. 7(a), the flake-like microstructures appear as white structures, thus demonstrates that the flake-like structures are crystalline solids. The SADP taken from the left grain corresponding to the dark field image shown in Fig. 7(b) is identified as pure Si with a hexagonal structure (JCPD 80-0005) as shown in Fig. 7(c). Consequently, the SiO\textsubscript{2} reduced to Si confirming more that a chemical reaction occurs at the porcelain/Ti oxide interface. Fig. 7(d) shows the EDS analysis results of the area marked “×” in Fig. 7(a), which indicate that the quantity of Ti is rather high near the porcelain/Ti oxide interface. Since the Ti element is not a component of porcelain, the phenomenon results apparently from the dissolving of TiO\textsubscript{2} into the porcelain coating. It should be noted that the copper element was considered to be an artifact from the Cu holder by the secondary signal of the electron beam during EDS analysis.

4. Discussion

It is well known that Ti is highly reactive with oxygen especially at elevated temperatures above 500°C. In this study the Ti oxides formed at the porcelain/Ti interface (Fig. 1(b)) during firing. Considering the factors, there are two oxygen sources: one is the diffusion of oxygen from the atmosphere in the quartz tube, and the other is obtained from the oxides in the porcelain. According to previous study\textsuperscript{14} it should be noted that it is difficult for the porcelain to wet on the surface of the Ti substrate without the presence of a Ti oxide layer, i.e. the oxidation of Ti is necessary to take place at the porcelain/Ti interface during the initial stage of firing. Thus it could be argued that the oxygen was mainly provided by the surrounding atmosphere instead of by the oxides in the porcelain during the initial stage of firing, and that it is reasonable to suggest that the chemical reactions between porcelain and Ti are not noticeable before the formation of Ti oxide at the porcelain/Ti interface.

After the initial stage of firing, the Ti oxide would form continuously with relationship to the sinter and fuse of porcelain at high temperature; owing to the fusing porcelain wetted the surface of Ti oxide and consequently resulted in chemical reactions. It was theorized\textsuperscript{9} that a fused glass in contact with an oxidized metal surface attempts to increase its O/Si ratio by dissolving the oxide before the porcelain became saturated, which would result in the elimination of the porcelain/Ti oxide interface and thus a minimum energy state at the interface. Furthermore, because of the bonding similarities between the oxides in the porcelain and Ti oxide, the Ti oxide dissolves easily in the porcelain and promotes chemical bonding across the porcelain/Ti oxide interface. The EDS results (Fig. 7(d)) demonstrate that the quantity of Ti is rather high inside the porcelain (the area marked “×” in Fig. 7(a)) near the porcelain/Ti oxide interface due to the dissolution of Ti oxide. In addition, the dissolution of Ti oxide created the opportunity for the porcelain oxides to contact the Ti substrate. The contact between the porcelain oxides and Ti substrate plays an important role in the redox reaction and contributes to the oxidation of Ti. On the other hand, when Ti is in contact with a less stable oxides (as compared to TiO\textsubscript{2} according to the high negative Gibbs free energy of Ti oxidation shown in Table 3), it is reasonable to suggest that self-oxidation would occur and result in the reduction of oxides such as SnO\textsubscript{2} and SiO\textsubscript{2}.

In the later stage of firing, the oxidation of Ti was caused by the diffusion of oxygen from both the porcelain and the surrounding atmosphere. Subsequently, the Ti oxide would saturate the porcelain side within a very narrow layer between the porcelain and Ti oxide. TEM observation in the vicinity of the porcelain/Ti oxide interface reveals that the precipitation of pure Sn (Figs. 6(c) and (d)) and Si (Figs. 7(a) and (c)) was found to support this inference. It implies that the Ti element reacted with oxygen from the oxides (SnO\textsubscript{2} and SiO\textsubscript{2}) in the porcelain to form the Ti oxide at the porcelain/Ti interface. Consequently, partial oxygen might diffuse into the uppermost Ti substrate causing brittleness of the Ti. The above mentioned interfacial reactions (redox reactions) play an important role proceeded the chemical bonding between the porcelain coating and the Ti oxide.

<table>
<thead>
<tr>
<th>Formation of metal oxide</th>
<th>Free energy (kJ/mol O\textsubscript{2})</th>
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</thead>
<tbody>
<tr>
<td>Sn\textsubscript{0} + O\textsubscript{2(g)} → SnO\textsubscript{2},TiO\textsubscript{2(g)}</td>
<td>−375</td>
</tr>
<tr>
<td>Si\textsubscript{0} + O\textsubscript{2(g)} → SiO\textsubscript{2},TiO\textsubscript{2(g)}</td>
<td>−680</td>
</tr>
<tr>
<td>Ti\textsubscript{0} + O\textsubscript{2(g)} → TiO\textsubscript{2},TiO\textsubscript{2(g)}</td>
<td>−743</td>
</tr>
</tbody>
</table>
during firing.

The microstructural features of porcelain veneered Ti after vacuum firing are schematically shown in Fig. 8, where zone A is the solid solution of TiO$_2$ in porcelain coating, zone B is the Ti oxide scale, and zone C is the embrittled Ti. According to a previous study, the induced stress variations between Ti oxide and Ti during the oxidation processes will impair their adherence. In addition, with prolonged firing time oxygen dissolved into Ti caused brittleness in the uppermost Ti layer. Hence, the weak point of the porcelain/Ti specimen is near the interface between zone B and C and/or slightly inside zone C. When the precipitates (Sn and Si) formed in zone A, the major portion of their combined oxygen would then combine with Ti to form Ti oxide, i.e. zone B grew continuously. Furthermore, the remaining oxygen subsequently diffused into zone C as a solid solution state, which embrittled zone C. The evidence (Figs. 3(a) and (b)) indicates that fracture occurred at the weak point during fracture testing and even in the process of specimen grinding (crevice in Fig. 1(b)), demonstrating that the strength of chemical bonding between the porcelain and the Ti oxide is strong enough to prevent the fracture from occurring at the interface of zone A and B and causes failure to occur near the interface between zone B and C and even slightly in the embrittled zone C.

The results of the present study indicate that the interfacial reactions between the porcelain coating and the Ti substrate should be further clarified as different porcelains often result in different interfacial reactions.

5. Conclusions

Cross-sectional variations in the porcelain/Ti interface were investigated by SEM, EPMA, X-ray diffraction and TEM for porcelain veneered Ti after firing. The following results are obtained:

1. During vacuum firing at 800°C, experimental evidence confirms that the Ti oxide formed at the porcelain/Ti interface is related to the location of the fracture initiation site at the interface between the Ti oxide and the Ti substrate.

2. The presence of pure Sn and Si precipitates found by TEM observations implies that redox reactions occurred at the porcelain/Ti oxide interface. The chemical bonding at the porcelain/Ti oxide interface prevents fracture initiation from occurring at the porcelain/Ti oxide interface.

3. The Ti substrate near the Ti oxide/Ti interface might be embrittled by the oxygen from SnO$_2$ and SiO$_2$ during redox reactions and the embrittled Ti will be too weak to prevent fracturing.

Acknowledgments

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REFERENCES