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Effect of Oxidation and SiO_2 Coating on the Bonding Strength of Ti-Porcelain

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Investigations on the effect of oxidation on titanium-ceramic adhesion were performed. Cast pure titanium was subjected to surface modification by preoxidation and introduction of an intermediate layer of SiO_2 by sol-gel process. Specimens were characterized by TG-DSC, XRD, and SEM/EDS. The adhesion between the titanium and porcelain was evaluated by three-point flexure bond test. Failure of the titanium-porcelain with preoxidation treatment predominantly occurred at the titanium-oxide interface. Preoxidation treatment did not affect the fracture mode of the titanium-ceramic system and did not increase the bonding strength of Ti-porcelain. The SEM results revealed the existence of microcracks on the SiO_2 coating surface oxidized at 800 °C in an air furnace. During the porcelain fusion, minute amounts of oxygen were able to penetrate the cracks and caused localized oxidation of the Ti-substrate. Failure of the titanium-porcelain with SiO_2 coating predominantly occurred at the SiO_2 layer. The SiO_2 coating served as an effective oxygen diffusion barrier and improved the mechanical and chemical bonding between porcelain and titanium.

Keywords dental material, oxidation, SiO_2 coating, sol-gel process, titanium-porcelain bonding

1. Introduction

Titanium is an attractive dental restorative material for its excellent characteristics such as excellent biocompatibility, corrosion resistance, light weight, and high strength and low cost (Ref 1, 2). However, inferior bonding in titanium-porcelain systems compared to the conventional metal-porcelain systems is still a major problem for its application (Ref 3).

The main factors that affect the Ti-porcelain bond are: (1) growth of an oxide layer on Ti at elevated temperatures, (2) adherence of the self-formed oxide to the Ti-substrate, and (3) bonding of the self-formed oxide with the porcelain (Ref 4). It has been proposed that the poor bonding strength between porcelain and titanium was partly because of continual oxidation of titanium during the porcelain fusing and formation of a nonadherent oxide layer (Ref 5).

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Ti has a great affinity for oxygen, and its oxidation rate increases exponentially at elevated temperatures. Relatively thick and nonadherent layers of titanium oxide tend to form at above 800 °C; therefore, porcelain should be fired below this temperature (Ref 6). Special low fusing dental porcelains are necessary for titanium-porcelain bonding.

Several studies have been carried out to prevent the formation of the nonadherent oxide layer involving the firing of porcelain in argon atmosphere (Ref 7), and an intermediate layer deposited on Ti prior to the application of porcelain. The use of Si_3N_4, chrome, SiO_2, and TiO_2 as intermediate layers to minimize Ti oxidation for Ti-porcelain restorations has been investigated (Ref 4, 8-14).

In spite of the variety of materials and processes available for the intermediate layers, the literature lacks reports about how the oxide layer was affected and how the bonding strength of porcelain to titanium was improved. In this study, sol-gel dipping process was employed to produce a thin SiO_2 coating on the titanium substrate.

It was postulated in this study that a SiO_2 coating, which could be expected to serve as an oxygen diffusion barrier on titanium during the porcelain firings, could be effective in improvement of bonding between titanium and porcelain. The authors aimed to evaluate the effects of SiO_2 coatings on the bonding strength of porcelain to titanium and the mode of failure.

2. Materials and Methods

ASTM grade II CP titanium was cast, ground with SiC paper and polished to prepare plate-shaped specimens (25 mm × 3 mm × 0.5 mm) for a three-point flexure bond test as specified in ISO 9693 (Ref 15). Specimens were sandblasted for 15 s with a dental sand blaster (G5833, Tianjin Jing-Gong Medical Equipment & Technology Co., Ltd., Tianjin, China), using 120 μm Al_2O_3 powder. The air pressure for sandblasting

was maintained at 0.2 MPa, and the distance between the nozzle tip and surface was maintained at 10 mm. After sandblasting, specimens were ultrasonically cleaned for 15 min in deionized water, and dried in air. Specimens were subsequently subjected to preoxidation and sol-gel coating. The specimens without any treatment were used as control.

2.1 Preoxidation

Specimens were preoxidized to investigate the influence of preoxidation on bonding strength. The specimens were treated for 3 min at 800 °C in a Multimat 99 furnace.

2.2 SiO_2 Coating by Sol-Gel Dipping Process

The silica precursor solution was prepared by mixing tetramethoxysilane oligomer into ethanol. Then, the solution was stirred for 30 min at 60 °C with ammonia added dropwisely until the pH was 3, followed by cooling down to room temperature.

The coatings were deposited by dip-coating (drawn speed of 1 mm s^{-1}) from the prepared colloidal suspension on titanium. After drying at 80 °C for 5 h, the coatings were treated for 10 min at 300 °C in an air furnace. Silica xerogels were prepared by drying a suitable amount of the above-mentioned sols at 25 °C. Approximately, 1/2 was used without further thermal treatment. The remaining 1/2 of the xerogels were fired at 300 °C for 10 min (rate 4 °C min^{-1}).

The xerogels were characterized by TG-DSC. TG-DSC spectra were recorded in the range 0-800 °C at the rate of 20 °C/min in atmosphere.

2.3 Porcelain Application

The GG titanium porcelain (self-made) was fused in a Multimat 99 furnace (Dentsply, American) according to the manufacturers' instructions (Table 1). A thin layer of bonding porcelain, opaque porcelain and dentin porcelain were fired at the central area (8 mm × 3 mm) of the specimen, respectively. The thickness of the bonding porcelain and opaque porcelain together was 0.4 ± 0.02 mm. The total thickness of the fired porcelain was 1 mm. After the dentin porcelain firing, specimens were ultrasonically cleaned in deionized water for 5 min and dried in air.

The coefficient of thermal expansion ($\alpha_{25\text{-}500}$) of the bonding, opaque and dentin porcelains used in this study were 9.1, 8.9, and 8.1 ppm/°C, respectively, which were lower than that for pure titanium (9.5 ppm/°C).

2.4 Three-Point Flexural Bond Test

The three-point flexural bond test was performed in a universal mechanical testing machine (DSS-25T, Shimadzu, Japan). For each group, a set of six samples was chosen. The specimens were placed in the testing machine with the ceramic on the side opposite to the applied load with a span of 20 mm. A compressive load was applied at the midline of the metal strip at a cross-head speed of 1.5 mm/min. The three-point bonding strength was calculated according to the formula in ISO 9693 (Ref 15). The bonding strength, τ_b, can be expressed as:

$$\tau_b = KF_{fail}, \quad \text{(Eq 1)}$$

where F_{fail} is the applied load at failure, and K is a function of the thickness of the titanium (d_{Ti} = 0.5 mm), and the value of Young's modulus of titanium (E_{Ti} = 105.4 GPa). The coefficient K can be expressed as:

$$K = 54.78d_{Ti}^2 - 73.15d_{Ti} + 27.65 = 4.77. \quad \text{(Eq 2)}$$

The results were analyzed by one-way ANOVA and Student-Newman-Kuels test at $\alpha = 0.05$ using statistical software (SPSS 10.0 for Windows).

The titanium surfaces, SiO_2 coatings, and failed Ti-porcelain bonding interface were characterized by XRD and SEM/EDS. XRD was performed at room temperature using Cu K_α radiation (λ = 1.5418 Å) on an X-ray diffractometer (D/max-r, Rigaku Corp., Japan). The acceleration voltage was 60 kV with an 80 mA current flux. Scatter and diffraction slits of 0.5 mm and collection slits of 0.3 mm were used. Data were collected for 2θ in the range of 20-80°; with a counting rate of 8.0°/min. The titanium surfaces were examined on a scanning electron microscope (JSM-6460, JEOL, Japan) operating at 5.0 kV coupled EDS apparatus (INCAX-sight, Oxford, England). Specimens were examined by SEM at the secondary electron image mode and EDS results were subjected to the ZAF correction. These analyses were used to assess the mechanisms of failure, as well as the nature of the interface between the titanium and porcelain veneer.

3. Results and Discussion

Figure 1 shows the XRD patterns of the titanium surface after oxidation treatment and the interface of Ti-porcelain. The XRD results revealed the titanium oxide [α Ti(O)] [JCPDS 11-0218] as the major phase, the rutile [JCPDS 21-1276] as a secondary phase. It revealed that a rutile layer was formed on the titanium surface after oxidation treatment. The XRD results on the interface of Ti-porcelain revealed that the failure of the titanium-porcelain predominantly occurred at the titanium-oxide interface. The rutile layer was more strongly bonded to the ceramic than titanium. The poor adhesion of the rutile with substrate was due to the thermal stress arising from large lattice mismatch and the large difference in coefficient of thermal expansion between Ti and rutile during cooling (Ref 16). The XRD pattern of the titanium surface also revealed the existence of corundum phase [JCPDS 10-173], which revealed the

Table 1 Porcelain firing conditions of GG titanium porcelain (self-made)

	Start temp., °C	Heat rate, °C/min	Final temp., °C	Holding time, min	Vacuum, cm/Hg
Oxidation	500	50	800	3	74
Bonding	500	50	800	3	74
Opaque	500	50	780	3	74
Dentin	500	50	760	3	74

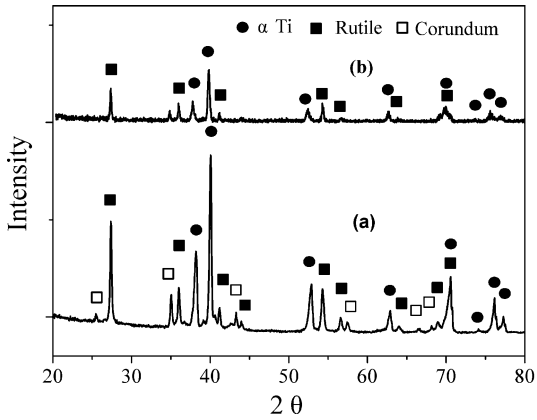

Fig. 1 XRD patterns of (a) titanium surface after oxidation treatment and (b) interface of Ti-porcelain

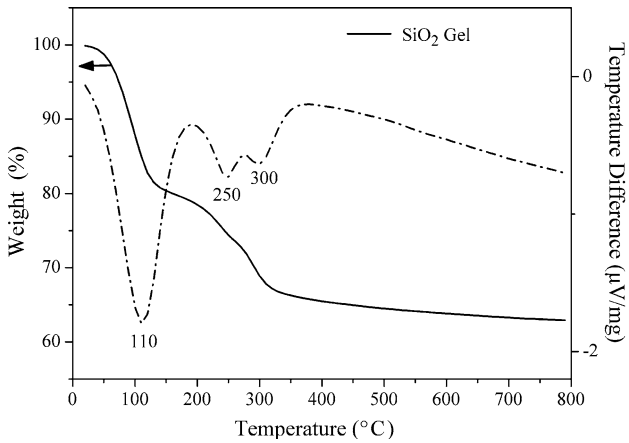

Fig. 2 TG-DSC patterns of the SiO_2 raw xerogel

alumina particles embedded on the titanium surface as a result of sandblasting.

Figure 2 shows TG-DSC patterns of the SiO_2 raw xerogel. The peak at about 110 °C corresponded to the loss of water of absorption, while the peaks at about 250 and 300 °C corresponded to the loss of water of constitution and the formation of SiO_2. Therefore, the SiO_2 coatings were heat-treated at 300 °C in this study.

Figure 3(a) shows the SEM micrograph of titanium surface after preoxidized for 3 min at 800 °C. Figure 3(a) revealed many grains and pores existed in the titanium surface. Figure 3(b) shows the SEM micrograph of titanium surface debonded from porcelain after oxidation. Figure 3(b) also exhibited a similar microstructure to that in Fig. 3(a). In addition, only O, Ti, and Al elements were found at the titanium surface and Ti-porcelain interface by EDS analysis based on raster analysis. This indicated failure of the titanium-porcelain predominantly occurred at the titanium-oxide interface. In addition, the one-way ANOVA test indicated that there was no significant difference within the group oxidized at 800 °C for 3 min in a Multimat 99 furnace (34 ± 1.81 MPa) and the control (35 ± 1.43 MPa, $P = 0.179 > 0.05$). Oxidation treatment did not affect the fracture mode of the titanium-ceramic system and the bonding strength of Ti-porcelain.

Figure 3(c) and (d) shows the SEM micrograph of SiO_2 coatings treated at 300 °C and titanium surface debonded from porcelain with SiO_2 coatings. Figure 3(c) and (d) revealed microcracks existed in the SiO_2 coatings and titanium surface debonded from porcelain with SiO_2 coatings. The EDS results based on raster analysis showed that the SiO_2 coating was composed of 46.9 wt.% O, 0.4 wt.% N, and 52.7 wt.% Si, and the titanium surface debonded from porcelain was composed of 51.2 wt.% O, 5.1 wt.% Ti, 0.2 wt.% N, and 43.5 wt.% Si. Nitrogen came from the ammonia used to adjust pH value. This indicated failure of the titanium-porcelain predominantly occurred at the SiO_2 layer. The one-way ANOVA test also indicated that there was a significant increase of the bonding strength of Ti-porcelain after SiO_2 coating treatment (38 ± 1.27 MPa) compared with the control (35 ± 1.43 MPa, $P = 0.021 < 0.05$). When the mechanical test results were assessed with the SEM/EDS findings, it could be suggested that the oxidation of the titanium surface determined the bonding strength of titanium-ceramic systems. During the porcelain fusion, minute amounts of oxygen were able to penetrate the cracks and caused localized oxidation of the Ti-substrate. The SiO_2 coating prevented the diffusion of oxygen to the titanium surface and improved the mechanical and chemical bonding between porcelain and titanium. Failure of the titanium-porcelain with SiO_2 coating predominantly occurred at the SiO_2 layer. The results of this study supported others (Ref 17-19).

The bonding strengths of Ti-porcelain coated and uncoated with SiO_2 coating in our study (ranged from 35 to 38 MPa) were all higher than those in the I. Özcan's study (ranged from 17 to 25 MPa) (Ref 12). In the standard ISO 9693, a lower limit of 25 MPa for bonding strength is fixed (Ref 15). In this investigation, all measured bond strengths were higher than 25 MPa.

There have been reports of patients suspected of exhibiting titanium allergy from implants. Further investigation on the effect of the SiO_2 coating by the sol-gel dipping process on the surface of titanium on the corrosion resistance is in progress. In addition, a better understanding of SiO_2 coating on titanium-ceramic bonding will require SEM images and EDS data on the cross section of coated and bonded samples to closely examine the metal surface and metal-ceramic interfaces.

Since dental restorations exposed to the oral environment may undergo repeated forces during chewing, thermal variations, and corrosion of the saliva, further investigation on thermal or mechanical cycling procedures and immersion in artificial saliva prior to mechanical testing will be done in the future (Ref 20, 21).

4. Conclusions

Failure of the titanium-porcelain with preoxdation treatment predominantly occurred at the titanium-oxide interface. Preoxidation treatment did not affect the fracture mode of the titanium-ceramic system and did not increase the bonding strength of Ti-porcelain. The SiO_2 coating synthesized at 300 °C changed the fracture mode of the titanium-porcelain system. Failure of the titanium-porcelain with SiO_2 coating predominantly occurred at the SiO_2 layer. The SiO_2 coating was an effective intermediate layer to improve titanium-ceramic adhesion.

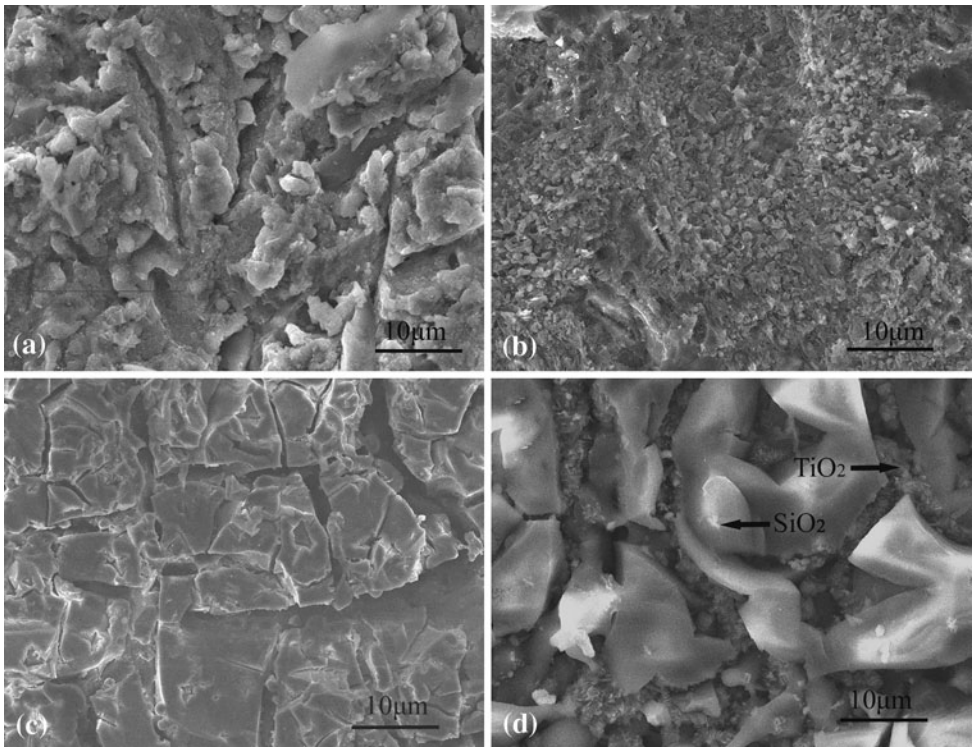

Fig. 3 SEM micrograph of (a) the titanium surface after preoxidized for 3 min at 800 °C, (b) the debonded titanium surface after oxidation, (c) SiO_2 coatings treated at 300 °C, and (d) titanium surface debonded from porcelain with SiO_2 coatings

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