

Surface modifications to improve Ti–porcelain bonding

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Abstract Investigations of surface modifications on cast titanium surfaces and titanium-ceramic adhesion were performed. Cast pure titanium was subjected to surface modification by preoxidation and introduction of an intermediate layer of SnO_x by sol–gel process. Surfaces only sandblasted with alumina were used as controls. Specimen surfaces were characterized by 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. However, a thin and coherent SnO_x film with small spherical pores obtained at 300 °C served as an effective oxygen diffusion barrier and improved titanium–ceramic adhesion. The SnO_x film changed the fracture

mode of the titanium–ceramic system and improved the mechanical and chemical bonding between porcelain and titanium, resulting in the increased bonding strength of titanium–porcelain.

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 [1, 2]. However, inferior bonding in titanium–ceramic systems compared to the conventional metal–ceramic systems is still a major problem for its application [3].

The bonding of ceramic to an alloy is attributed to van der Waal's forces, to a mechanical interlocking between both materials, and to chemical bonds between the ceramic and an oxide layer, which is built during the firing process on the surface of the alloy by oxidation of the base metals [4].

The main factors that affect the titanium–ceramic bond are (1) growth of an oxide layer on titanium 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 [5]. 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 [6, 7].

In a study [8], a thicker interfacial oxide layer between CP titanium and porcelain correlated with weaker porcelain bonding. The thickness of the oxide layer depended on the firing time and oxidizing atmosphere. Excessive oxygen

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dissolution into titanium resulted in fracture inside the titanium. The extent of titanium oxidation plays a very important role in titanium–ceramic bonding [9, 10].

An understanding of the structure and composition of the oxide layer between titanium and porcelain is therefore of vital importance in optimizing firing conditions in order to achieve successful metal–ceramic restoration [4]. It is reported that when the oxide film reaches 1 μm in thickness, a significant decrease in oxide adherence was observed [6].

Several studies have been carried out to prevent the formation of the nonadherent oxide layer involving the firing of porcelain in argon atmosphere [4], and an intermediate layer deposited on Ti prior to the application of porcelain. The intermediate layer must act as a barrier to the diffusion of oxygen, be strongly bonded to the Ti substrate and establish a strong bond to the porcelain [10]. The use of Si_3N_4 , chrome, SiO_2 and TiO_2 as intermediate layers to minimize Ti oxidation for Ti–ceramic restorations has been previously evaluated [5, 10–13]. It was hypothesized that SnO can be used as an intermediate layer to meet the criteria described earlier to improve the bonding of porcelain to titanium.

In spite of the variety of materials and processes available for intermediate layers, the literature lacks reports about how the oxide layer was affected and how it promote better bonding strength of ceramics to titanium. Understanding the reactions between porcelain and titanium, especially about the possible intermediate layers generated during firing, is important to elucidate the bonding mechanism [14].

The aim of this study was to optimize the surface treatment of titanium in regard to improve bonding strength. Further, the failure mode at the interface was investigated to gain insight into the possible mechanisms.

Materials and methods

ASTM grade II CP titanium was cast, ground with SiC paper and polished to prepare plate-shaped specimens ($25 \times 3 \times 0.5$ mm) for a three-point flexure bond test as specified in ISO 9693 [15]. Specimens were subsequently subjected to controls and one of the surface modification procedures (Table 1). Specimens were sandblasted for 15 s

with a dental sandblaster (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.

Preoxidation

Twenty-four specimens were preoxidized in order to investigate the influence of preoxidation on bonding strength. The specimens were (1) treated for 3 min at 800 $^\circ\text{C}$ in a Multimat 99 furnace (Dentsply, USA); (2) treated for 3 min at 800 $^\circ\text{C}$ in an air furnace, air cooled; and (3) treated for 3 min at 800 $^\circ\text{C}$ in an air furnace, furnace cooled.

The titanium surfaces and failed Ti–porcelain bonding interface were characterized by XRD and SEM/EDS. XRD was performed at room temperature using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) on an X-ray diffractometer (D/max-r, Rigaku Corp., Japan). The titanium surfaces were examined on a scanning electron microscope (JSM-6460, JEOL, Japan) coupled EDS apparatus (INCA-X-sight, Oxford, UK). Specimens were examined by SEM at the secondary electron image mode and EDS results were subjected to the ZAF correction.

SnO_x coating by sol–gel dipping process

Tin dichloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) was used as precursor, whilst ammonia was used as basic catalyst for the hydrolysis of the precursors. Tin dichloride was first dissolved in ethanol. Then the solution (0.8 mol/L) was stirred for 30 min at 60 $^\circ\text{C}$ with ammonia added drop-wisely until the pH was 3, after which it was allowed to cool to room temperature. A stable SnO sol was obtained.

The films were deposited by dip-coating (drawn speed of 1 mm s^{-1}) from the prepared colloidal suspension on titanium. After drying at 80 $^\circ\text{C}$ for 5 h, the films were treated for 10 min at 300, 400 and 500 $^\circ\text{C}$, respectively, in an air furnace.

SnO xerogels were prepared by drying a suitable amount of the above-mentioned sols at 25 $^\circ\text{C}$. Approximately 3/4 of the xerogels were fired at 300, 400 or 500 $^\circ\text{C}$ for 1 h

Table 1 Surface modifications for cast CP titanium

Method	Descriptions
Controls	Sandblasted with 120 μm Al_2O_3 particles, 0.4 MPa 15 s
Preoxidation	Treated for 3 min at 800 $^\circ\text{C}$ in different condition
SnO_x coating	SnO_x coating by sol–gel dipping process, treated for 10 min at different temperature

Table 2 Porcelain firing conditions of GG Titanium Porcelain (self-made)

	Start temperature (°C)	Heat rate (°C/min)	Final temperature (°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

(rate 4 °C min⁻¹) to produce membranes. The remaining 1/4 was used without further thermal treatment.

The fired and raw xerogels were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). IR spectra were recorded in the range 400–4500 cm⁻¹ on a Vector-22 FT/IR spectrophotometer (Bruker, German) using KBr pellets. The SnO_x films were characterized by SEM.

Porcelain application

The GG Titanium Porcelain (self-made) was fused in a Multimat 99 furnace (Dentsply, USA) according to the manufacturers' instructions (Table 2). A thin layer of bonding porcelain, opaque porcelain and dentin porcelain was fired at the central area (8 × 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 (α_{25-500}) 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).

Three-point flexural bond test

Each specimen was positioned on supports with a span distance of 20 mm in a universal testing machine (DSS-25T, Shimadzu, Japan) at a crosshead speed of 1.5 mm/min. The force was applied with the porcelain side opposite the center support until fracture. The three-point bonding strength was calculated according to the formula in ISO 9693 [15]. The bonding strength, τ_b , can be expressed as:

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

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

$$K = 54.78d_{\text{Ti}}^2 - 73.15d_{\text{Ti}} + 27.65 = 4.78 \quad (2)$$

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 failed Ti–porcelain bonding surface and cross section of the interface was characterized by SEM/EDS. These analyses were used to assess the mechanisms of failure, as well as the nature of the interface between the titanium and porcelain veneer.

Results and discussion

Effect of preoxidation on the bonding strength of titanium–porcelain

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 [13]. 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 [8].

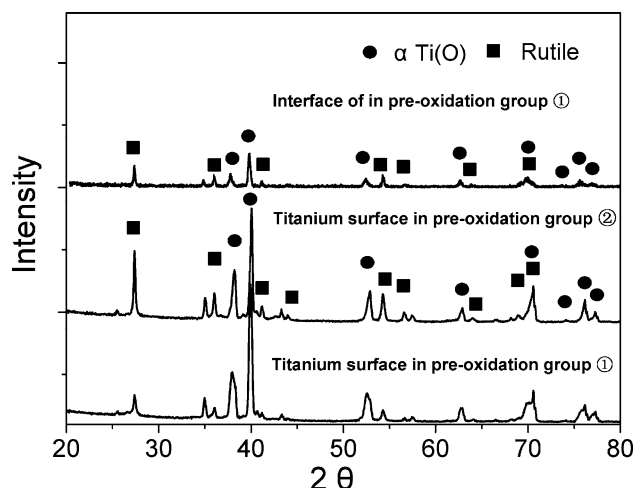


Fig. 1 XRD patterns of the titanium surface after oxidation treatment and the interface of Ti–porcelain

Fig. 2 SEM micrograph of a titanium surface after preoxidized for 3 min at 800 °C in a Multimat 99 furnace

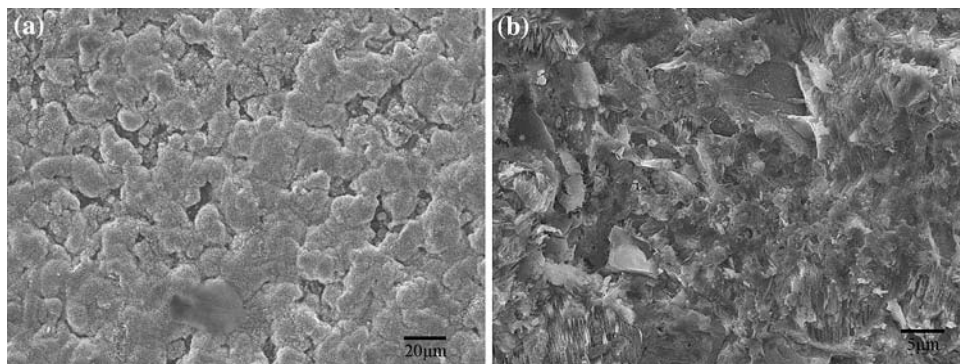


Figure 2a shows the SEM micrograph of titanium surface after preoxidized for 3 min at 800 °C in a Multimat 99 furnace. Figure 2a revealed many pores existed in the titanium surface. The pores increased the contact areas between the oxide and porcelain, and therefore increased the mechanical bonding. Figure 2b shows the SEM micrograph of titanium surface debonded from porcelain. The EDS results based on raster analysis showed that the titanium surface was composed of 36.0 wt% O, 60.8 wt% Ti, 2.7 wt% Al and 0.5 wt% Si. Aluminum came from the alumina particles embedded on the titanium surface as a result of sandblasting, and silicon came from the residual porcelain. This indicated failure of the titanium–porcelain predominantly occurred at the alloy–oxide interface [16, 17].

Figure 3 shows the SEM micrograph of titanium surface oxidized at 800 °C in an air furnace, air cooled. Figure 3a reveals the existence of microcracks on the titanium surface. Figure 3b shows the SEM micrograph of titanium

surface debonded from porcelain. The EDS results based on raster analysis showed that the titanium surface was composed of 19.7 wt% O, 78.4 wt% Ti, 1.8 wt% Al and 0.1 wt% Si. This was consistent with the results of Fig. 2b, which also indicated that failure of the titanium–porcelain predominantly occurred at the alloy–oxide interface. Figure 3b also exhibited a similar microstructure to that in Fig. 2b, which indicated that oxidation treatment did not affect the fracture mode of the titanium–ceramic system. In Fig. 3c, the oxide layer was visible at the interface of titanium–porcelain and was approximately 2 µm thick. Oxidation of titanium is generally believed to proceed by inward lattice diffusion of oxygen, with new oxide forming at the oxide–metal interface [5, 16]. The failure of TiO₂ to form a protective scale at high temperatures is thought to be due to stress build-up in the inwardly growing oxide scale. This stress build-up apparently exceeds the strength of the scale when the oxide layer becomes approximately

Fig. 3 SEM micrograph of a titanium surface oxidized at 800 °C in an air furnace, b titanium surface debonded from porcelain, and c the cross sections of the same sample

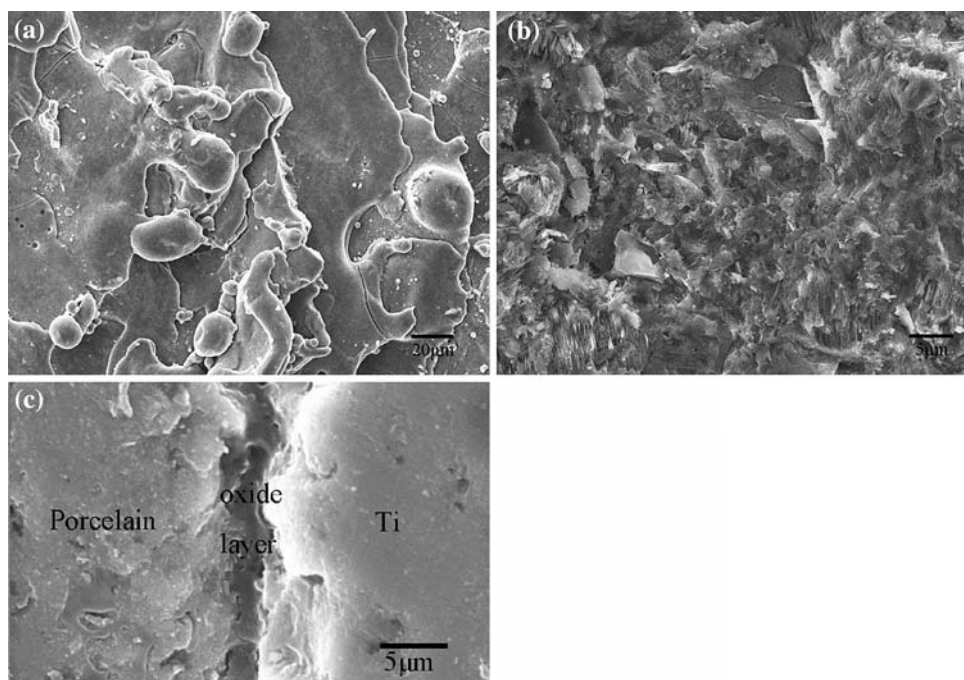


Table 3 Bonding strength of titanium–porcelain after oxidation treatment and the control

Groups	Control	1	2	3
Bonding strength (MPa)	35 ± 1.43	35 ± 1.53	27 ± 2.45	28 ± 1.73

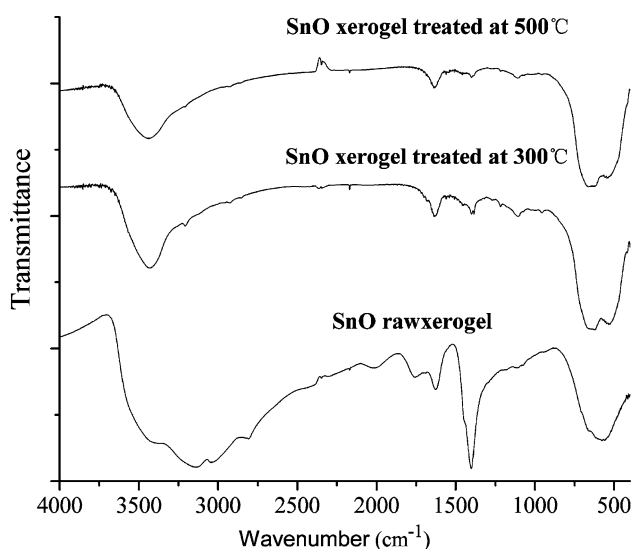
1 μm thick, causing the scale to fracture and expose new metal to the oxidizing atmosphere [16]. The results in Fig. 3a and c support this viewpoint.

The effect of oxidation on adhesion between titanium and dental porcelain is studied. The mean bonding strength data and standard deviations are presented in Table 3. The one-way ANOVA test indicated that there was no significant difference within the group oxidized at 800 °C for 3 min in a Multimatt 99 furnace and the control ($p = 0.286 > 0.05$), but a significant decrease after oxidized at 800 °C for 3 min in an air furnace ($p = 0.001 < 0.05$).

When the mechanical test results of oxidized at 800 °C in a Multimatt 99 furnace and in an air furnace groups were assessed with the SEM interface findings, it could be suggested that the presence of the thick oxide layer determined the bonding strength of titanium–ceramic systems. The results of this study supported others, which attributed lower bonding strength to the thick oxide layer on the metal surface [17–19].

Effect of SnO_x coating on the bonding strength of titanium–porcelain

Figure 4 shows the FT-IR spectra of SnO gel and SnO xerogels treated at 300 and 500 °C. In the FT-IR spectra, the feature at 550 cm⁻¹ corresponded to Sn–OH bounds, while the feature at 650 cm⁻¹ corresponded to Sn–O–Sn

**Fig. 4** FT-IR spectra of the raw xerogel and xerogel fired at 300 and 500 °C

bounds. As the firing temperature increased, the intensity of this feature decreased and another at 650 cm⁻¹, corresponding to Sn–O–Sn bounds, systematically increased. These changes indicated the loss of water of constitution. The IR features at 3400 and 550 cm⁻¹ indicated the presence of rudimental Sn–OH.

The IR features at 3050 and 1400 cm⁻¹ shown in Fig. 4 indicated the presence of ammonium (probably ammonium chloride) in the as-obtained xerogel. With the firing temperature increasing, the intensity of the features decreased, being almost negligible at 300 °C and disappearing completely at 500 °C. It indicated that most of the ammonium was eliminated at this temperature.

Figure 5 shows XRD patterns of the xerogel fired at different temperatures. In all cases, the typical pattern of SnO₂ was obtained. With the firing temperature elevated, the crystallinity of SnO₂ improved. It revealed the presence of SnO and SnO₂, which proved part of SnO oxidized to SnO₂.

The effect of SnO_x film on adhesion between titanium and dental porcelain was studied. The mean bonding strength data and standard deviations are presented in Table 4. The bonding strengths of samples with SnO_x film treated at 400 and 500 °C are significantly lower than the rest of the groups. Bonding strength of samples with SnO_x film treated at 300 °C is significantly greater than that without intermediate layer by independent-samples *t*-test using SPSS 10.0 for Windows ($p = 0.028 < 0.05$).

Figure 6 shows the SEM micrograph of SnO_x films fired at (a) 300 °C, (b) 400 °C and (c) 500 °C. Figure 6a reveals a coherent surface with small spherical pores. The pores increased the contact areas between SnO_x films and porcelain, and therefore increased the mechanical bonding. In

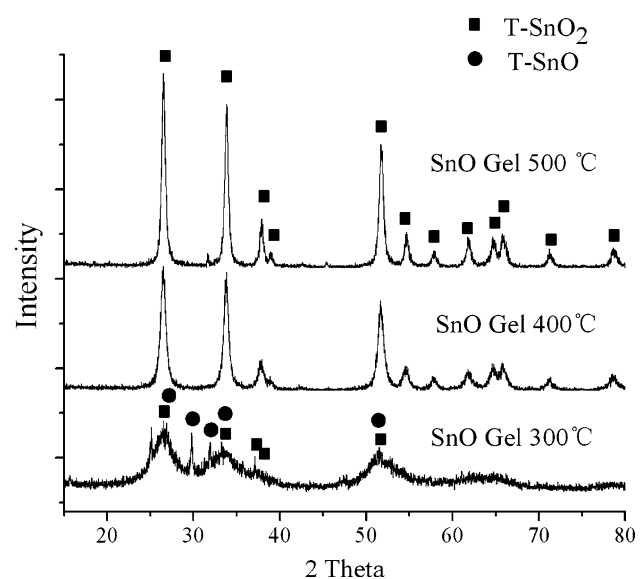
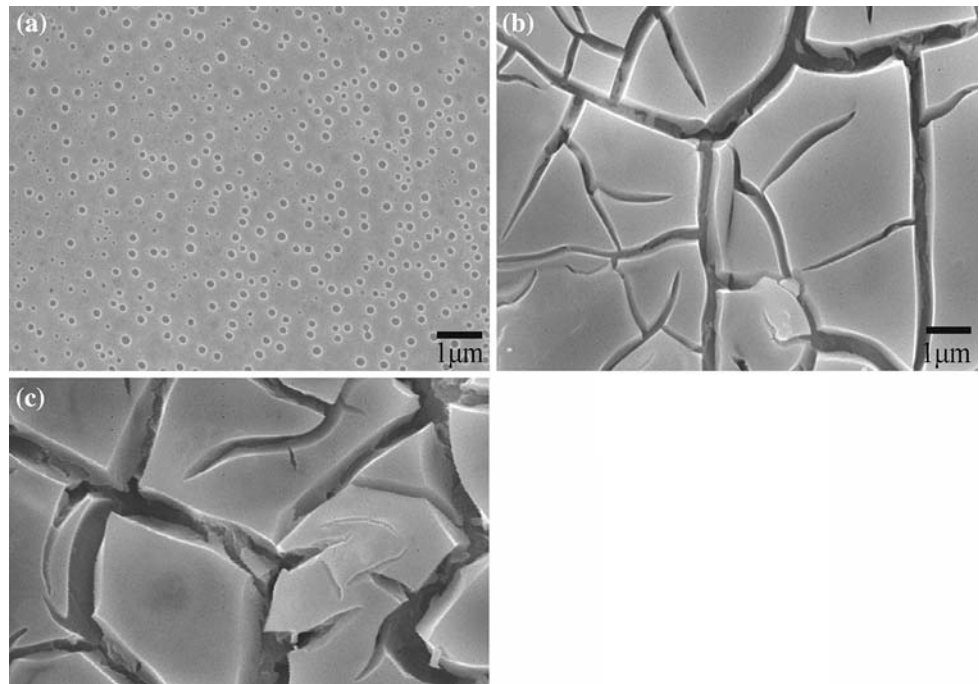
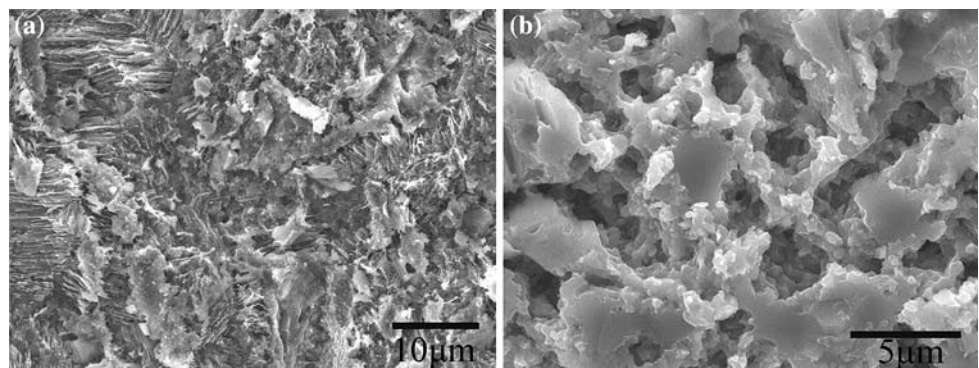
**Fig. 5** XRD patterns of the xerogel fired at 300, 400 and 500 °C

Table 4 Titanium–porcelain bonding strength with or without SnO film as intermediate layer

	No SnO film	SnO film 300 °C	SnO film 400 °C	SnO film 500 °C
Bonding strength (MPa)	35 ± 1.43	42 ± 1.48	26 ± 2.67	24 ± 3.41

Fig. 6 SEM micrograph SnO_x films treated at **a** 300 °C, **b** 400 °C, and **c** 500 °C**Fig. 7** SEM micrograph of titanium surface debonded from porcelain **a** without SnO_x films and **b** with SnO_x films treated at 300 °C

addition, coherent SnO_x films may prevent the formation of excessive, porous Ti oxides. Figure 6b and c reveals microcracks existed in the SnO_x films treated at 400 and 500 °C. During the porcelain fusion, minute amounts of oxygen were able to penetrate the cracks and cause localized oxidation of the Ti-substrate [4]. This resulted in the decrease of the titanium–porcelain bonding strength.

Figure 7 shows the SEM micrograph of titanium surface debonded from porcelain (a) without SnO_x films and (b) with SnO_x films treated at 300 °C. In Fig. 7a, only O and Ti elements were found at the interface. This indicated failure of the titanium–porcelain without SnO_x films predominantly occurring at the alloy–oxide interface [17, 18]. In

Fig. 7b, many pores are found at the interface. This porous structure resembled the structure of the SnO film. The EDS results showed that the debonded Ti–porcelain interface was composed of 30.1 wt% O, 2.6 wt% Ti and 67.3 wt% Sn. These results indicated that failure of the titanium–porcelain with SnO_x films treated at 300 °C predominantly occurred at the SnO_x layer.

Figure 8 shows the SEM micrograph of the cross sections of the sample with SnO_x films treated at 300 °C. In Fig. 8, a definite oxide layer (about 1.5 μm) was observed along the interface between SnO_x films (about 1 μm) and titanium. The two layers adhered to the titanium substrate and no crack was found between the layers and titanium.

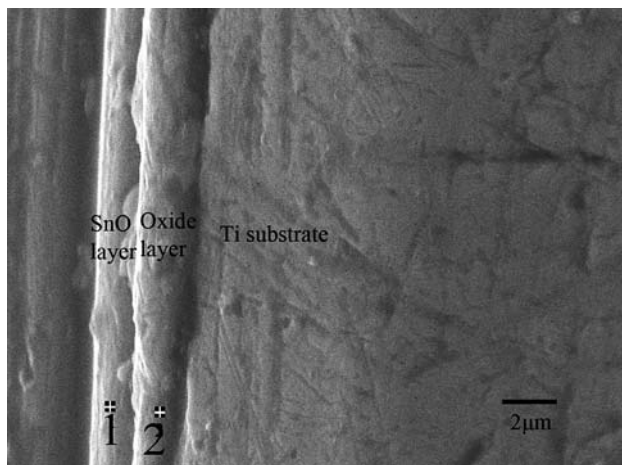


Fig. 8 SEM micrograph of the cross sections of the sample with SnO_x films treated at 300 °C. A definite oxide layer was observed along the interface between SnO_x films and titanium. EDS analyses of elements were performed on the position 1 and 2 in the micrograph

Table 5 EDS results of the cross section of the Ti–porcelain interface

Position	O (wt%)	Al (wt%)	Ti (wt%)	Sn (wt%)
1	30.4	0.4	6.50	62.7
2	36.2	0.5	60.1	3.2

Results of EDS analyses of the cross section of the Ti–porcelain interface are listed in Table 5. The EDS results showed that Sn diffused into the oxide layer. The Sn element reacted with titanium and changed the chemical composition of the oxide films, and therefore increased the chemical bonding between the oxide films to titanium. It also increased the chemical bonding between SnO_x films and titanium, and therefore increased the bonding strength of titanium–porcelain.

Wang et al. [5] used Si_3N_4 coatings as a protective coating on Ti substrate and fired Duceratin. In that study fracture had always occurred at multilayered Ti oxide. In our study, SnO_x film changed the fracture mode of the titanium–ceramic system and enhanced the titanium–porcelain bonding strength. The SnO_x film synthesized at 300 °C between titanium and porcelain served as oxygen diffusion barrier and improved the mechanical and chemical bonding between porcelain and titanium. Therefore, the titanium–porcelain bonding strengths increased.

There have been reports of patients suspected of exhibiting titanium allergy from implants [19]. Further investigation on the effect of the SnO_x film by the sol–gel dipping process on the surface of titanium on the corrosion resistance is in progress. In addition, a better understanding of SnO_x film on titanium–ceramic bonding will require techniques such as analytical transmission electron microscopy and X-ray photoelectron spectroscopy to

closely examine the metal surface and metal–ceramic interfaces.

Conclusions

There was no significant difference within the group oxidized at 800 °C for 3 min in a Multimatt 99 furnace and the control, but a significant decrease after oxidized at 800 °C for 3 min in an air furnace. 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 stress between the titanium–rutile interfaces resulted in the reduction of bonding strength of Ti–porcelain.

A thin and coherent SnO_x film with small spherical pores was synthesized at 300 °C by the sol–gel process. Failure of the titanium–porcelain with SnO_x film fired at 300 °C predominantly occurred at the SnO_x layer. The SnO_x film fired at 300 °C served as an effective oxygen diffusion barrier and improved the mechanical and chemical bonding between porcelain and titanium. SnO_x film was an effective intermediate layer to improve titanium–ceramic adhesion. When the temperature was elevated, SnO was oxidized to SnO_2 and the film microcracked. This resulted in the decrease of the titanium–porcelain bonding strength.

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