Bonding of dental porcelain to non-cast titanium with different surface treatments

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This study investigated the bonding of dental porcelain to non-cast Ti surface with different treatments. Mechanically ground non-cast Ti strips, simulating surface conditions produced by CAD/CAM, were Al₂O₃-sandblasted, then subjected to different surface treatments, including immersion in HNO₃-containing acid, NaOH-containing alkaline, and NaOH-containing alkaline then HNO₃-containing acid. Ti-porcelain specimens preparations and their bend strength measurements were based on ISO 9693. Ti surface treatment changed not only surface roughness but also surface chemistry, leading to influence on bond strength. Bond strengths of all Ti-porcelain groups were higher than ISO 9693 minimum requirement. The sandblasted/acid-treated Ti surface showed the highest bond strength (34.60 MPa) with porcelain; no significant difference in bond strength (27.92–29.63 MPa) was found among other Ti-porcelain groups. All Ti-porcelain specimens showed adhesive bond failure. Bonding between non-cast Ti and dental porcelain was strengthened by a simple and practical sandblasting/acid-etching treatment of the Ti surface prior to porcelain sintering.

Keywords: Surface treatment, Non-cast titanium, Dental porcelain, Bond strength

INTRODUCTION

Titanium (Ti) tends to react with oxygen at high temperatures, which results in an overly thick oxidation layer. The oxidation layer is located on the Ti surface and influences the bond strength of the Ti-porcelain prosthetic appliance^{1,2}. It has been reported that dental porcelain-fused-to-metal (PFM) crowns can be produced with a thinner interfacial oxide layer that effectively promotes the bond between metal and porcelain³. Thus, several manufacturers have produced low-fusing dental porcelain that is suitable for sintering onto the Ti surfaces with thinner oxide layers⁴. However, the bond strength between low-temperature porcelain and Ti is only slightly higher than the minimum metal-porcelain bond strength prescribed by ISO 9693⁵. Relevant literature shows that the Ti-porcelain bond strength is still lower than the bond strength between porcelain and other noble or base metals^{6,7}. Consequently, there is a need for further investigation to improve the Ti-porcelain bond strength, which may be applicable to PFM dental crowns for long-term clinical application.

The strength of the bond between metal and porcelain can be influenced by several factors, including the metal and porcelain chemical compositions, metal surface treatment, porcelain sintering procedure and test method⁸. The bond strength primarily depends on the mechanical and chemical properties of the interface between the metal and porcelain^{9,10}. Although extensive studies have employed different surface treatments of Ti prior to porcelain sintering^{11–19}, a simple and practical technique to improve Ti-porcelain bond strength has not

been well determined, and the underlying mechanism for the bonding of Ti and porcelain is not well understood.

Chemical solution treatment is a method that can be used to treat and clean metallic surfaces for clinical applications²⁰. In industrial fields, an alkaline or acid solution has been successfully employed to clear superficial pollutants from Ti and Ti alloys²¹. Diniz *et al.*²² indicated that hydrofluoric acid can serve as an improvement agent and etchant of Ti, thus allowing a higher-quality metallic surface and the removal of pollutants produced during manufacturing. A previous study showed that the Ti surface hardness increases after immersion in a mixed nitric acid/hydrofluoric acid solution such that the Ti-porcelain bond strength is improved²³. Reyes *et al.*⁸ found that the bonding of Ti and porcelain can be improved by immersing the Ti in hydrochloric acid prior to porcelain sintering. Tróia *et al.*¹² studied the bond strength between porcelain and cast Ti with different surface chemical treatments. The Ti surface is immersed in acid solution, treated (or not treated) with alkaline solution, and finally sandblasted prior to porcelain sintering. There is no improvement in the Ti-porcelain bond strength when the Ti surface is only immersed in acid solution. The bond strength is enhanced when the Ti surface is first treated with an acid solution followed by an alkaline solution treatment, with a sandblast treatment as the final step. However, from a dental technician point of view, it should be noted that the sandblasting process is usually employed as the first treatment step for metallic prosthetic cast appliances following the casting process.

One of the problems for dental Ti cast made by

conventional lost-wax technique is the presence of a hardened alpha-case surface layer with a thickness of tens to few hundreds μm ^{24,25}. The alpha-case surface layer on Ti cast has much higher hardness than the internal structure. Therefore, the hardened alpha-case layer can hinder the grinding and polishing of Ti cast prostheses and is easy for crack initiation and propagation²⁶. Recently, computer-aided design (CAD)/computer-assisted manufacturing (CAM) has been clinically used to produce high-quality Ti prosthetic appliances²⁷. Through CAD/CAM procedures, Ti for fixed prosthetic appliances (dental crowns and copings) can be produced without the generation of a thick oxide layer on the Ti surface; this leaves a more homogeneous surface structure²⁸. The CAD/CAM-produced Ti surface is expected to have greater porcelain bond strength than the traditional Ti surface produced by the casting process^{29,30}. The bond strength of porcelain to the CAD/CAM-produced non-cast Ti surface is becoming more important in dentistry.

Although some researches have focused on the bonding properties between the porcelain and non-cast Ti surfaces without surface treatments^{6,31–33}, the mechanism of the bonding behavior is still not well understood. Previous studies seldom discussed the influence of chemical solutions on the bond strength between porcelain and non-cast Ti surfaces produced by CAD/CAM. The prevailing hypothesis is that the mechanical and chemical treatments of non-cast Ti surfaces prior to porcelain sintering can positively affect Ti-porcelain bond strength. The objective of this study was to determine a simple and practical procedure involving mechanical (e.g., sandblasting) and chemical (e.g., acid and/or caustic alkaline solution) treatments to increase the bond strength between the porcelain and non-cast Ti surface interface simulating CAD/CAM conditions.

MATERIALS AND METHODS

Specimen preparation

Commercially pure non-cast Ti strips (Grade 2 Ti, Ultimate Materials Technology Co., Hsinchu, Taiwan) after annealing treatment were used as test specimens; these were mechanically ground with silicon carbide paper to #240 (WTCC-S, Nihonkenshi Co, Osaka, Japan). The spontaneously formed surface thin oxide film, mainly as TiO_2 , on the ground, non-cast Ti strips was close to 10 nm, which was identified by X-ray photoelectron spectroscopy depth profile analysis (not shown here). The final test Ti strips had a size of 25 mm×3 mm×0.5 mm, which was confirmed using a digital caliper (Micrometer 193, Mitutoyo, Kawasaki, Japan). The ground, non-cast Ti surface without a thick hardened alpha-case layer simulated the surface conditions produced using the CAD/CAM milling process. The surface roughness (R_a) of the ground, non-cast Ti strip was 0.36 μm which was nearly the same as that of the Ti strip produced by commercial CAD/CAM milling system (DATRON D5, Datron Dynamics, Inc., Milford, USA). Forty Ti strips

were then divided into four groups (ten samples each) for the following surface treatments. The Ti strips sandblasted with 125 μm Al_2O_3 particles (WA, Rich Sou Technology Co., Kaohsiung, Taiwan) at a 4-bar pressure for 10 s in a sandblaster (BL-22, Fu Ming Co., Taichung, Taiwan) were used as the control (group SB), and the remaining three groups were experimental groups that were described as follows: for group SB-A, the SB specimens were immersed in an acid (35% HNO_3 +5% HF) solution; for group SB-C, the SB specimens were immersed in a caustic alkaline (50% NaOH) solution; and for group SB-CA, the SB specimens were immersed in a caustic alkaline solution followed by an acid solution. All chemical reagents were from Merck Chemicals (Merck KGaA, Darmstadt, Germany). The detailed steps for the surface treatments of Ti strips are shown in Table 1.

According to ISO 9693 specification⁵, a low-fusing porcelain (Vita Titankeramik, Vita, Bad Säckingen, Germany) was sintered on the center of the Ti strips of size 8 mm×3 mm×1 mm. In accordance with the sintering conditions recommended by the manufacturer (Table 2), as well as the actual operating sequence in the dental technology laboratory, the following porcelain sintering procedures were used: a thin (<0.1 mm) porcelain bond layer was first sintered on the Ti strips, followed by the sintering of opaque porcelain approximately 0.2 mm thick; the final sintering of dentin porcelain was approximately 0.8 mm thick. The porcelain layers (opaque and dentin) were applied with two different custom-made jigs which controlled the position and thickness of each. At the end, a glazing treatment was performed. The sintering processes were conducted in a dental vacuum porcelain furnace (Pro 100, Whipmix, Louisville, USA).

Bond strength of Ti-porcelain specimens

A universal test machine (EZ-L, Shimadzu, Tokyo, Japan) was used for the three-point bending test of the Ti-porcelain strip specimens according to the ISO 9693 specification. During the bending test, the porcelain surface faced downwards, and the load was applied to the center of the Ti surface at a rate of 0.5 mm/min. The *in situ* load vs displacement curves were recorded during the bending tests. The fracture load (or debonding load) was measured for specimens failing by a debonding crack occurring at one end of the porcelain layer⁵. The Ti-porcelain bond strength was then calculated with the following equation provided by ISO 9693⁵:

$$\text{Bond strength} = F \times k$$

where F is the fracture load; the coefficient k is a function of the thickness and elastic modulus of Ti strip according to ISO 9693 specification. The elastic modulus of Ti strip in bending test was determined according to the following equation³⁴:

$$E = L^3 \Delta P / 4bh^3 \Delta d$$

where E is the elastic modulus of Ti strip in bending, L

Table 1 Steps of surface treatments for Ti strips used in this study

Group	Description of surface treatment procedures
SB	Step 1: Sandblasting with 125 μm Al_2O_3 particles Step 2: Ultrasonic cleaning in distilled water for 3 min
SB-A	Step 1: Sandblasting with 125 μm Al_2O_3 particles Step 2: Immersion in 35% HNO_3 +5% HF containing acid solution for 3 min Step 3: Ultrasonic cleaning with distilled water for 3 min
SB-C	Step 1: Sandblasting with 125 μm Al_2O_3 particles Step 2: Immersion in 50% NaOH -containing caustic alkaline solution for 5 min Step 3: Ultrasonic cleaning with distilled water for 3 min
SB-CA	Step 1: Sand blasting with 125 μm Al_2O_3 particles Step 2: Immersion in 50% NaOH -containing caustic alkaline solution for 5 min Step 3: Immersion in 35% HNO_3 +5% HF containing acid solution for 3 min Step 4: Ultrasonic cleaning with distilled water for 3 min

Table 2 Porcelain sintering procedure conditions recommended by the manufacturer

Step	Initial temp. ($^{\circ}\text{C}$)	Final temp. ($^{\circ}\text{C}$)	Temp. rising rate ($^{\circ}\text{C}/\text{min}$)	Holding time (min)	Vacuum degree (bar)
1. Bonder	400	800	60	1	6
2. Opaque	400	790	110	1	4
3. First dentin	400	770	50	1	8
4. Second dentin	400	770	50	1	8
5. Glazing	400	770	100	1	4

is the distance between two supporting points (20 mm) for the Ti strip, b is the Ti strip width (3 mm), h is the Ti strip thickness (0.5 mm), and ΔP and Δd are the load and displacement increments, respectively.

Surface characterizations

After Ti strips underwent different surface treatments, X-ray photoelectron spectrometry (XPS) (Sigma Probe, Thermo VG Scientific Inc., West Sussex, UK) was used to analyze the surface chemical compositions of the Ti strips prior to porcelain sintering. Scanning electron microscopy (SEM) (JSM-6500F, JEOL Ltd., Tokyo, Japan) was used to observe the surface morphology of the Ti strips before porcelain sintering and the interfacial cross section between the porcelain and Ti after porcelain sintering. The surface arithmetic mean roughness R_a of Ti strips after surface treatments was measured using a surface profilometer (Dektak 3, Veeco Instruments Inc., NY, USA). After three-point bending tests, the fracture surfaces of the Ti and porcelain sides of the tested Ti-porcelain specimens were analyzed using SEM accompanied by energy dispersive spectrometry (EDS) (INCA Energy 300, Oxford Instruments, Oxfordshire, UK) to observe the surface topography and to analyze the surface chemical composition.

Statistical analysis

For the statistical analysis, a one-way analysis of variance (ANOVA) was used to analyze whether different surface treatment methods affect the surface roughness and Ti-porcelain bond strength. A $p < 0.05$ was considered to be statistically significant in all tests. Tukey's test was used as the post-hoc test. Ten samples were used in each test group.

RESULTS

After the grinding, the non-cast Ti strips underwent the different grinding surface treatments shown in Table 1. The corresponding surface topography and surface roughness were shown in Fig. 1: (a) SEM micrographs; (b) surface roughness R_a (mean $\pm$ standard deviation). Figure 1(a) shows a rough and sharp surface pattern that was produced on the group SB surface. The group SB surfaces were cleaned by immersion in caustic alkaline solution and/or acid solution, and the surface of the chemically treated Ti strips (groups SB-A, SB-C and SB-CA) visibly exhibited a different color. As shown in Fig. 1(b), the groups SB-A (R_a : $0.718 \pm 0.069 \mu\text{m}$) and SB-C (R_a : $0.703 \pm 0.078 \mu\text{m}$) had a significantly lower surface roughness than the control group SB (R_a : $1.048 \pm 0.042 \mu\text{m}$) (***: $p < 0.001$); there was no significant difference in

Fig. 1 (a) scanning electron microscope micrographs and (b) surface roughnesses R_a of the non-cast Ti strips after the different surface treatments described in Table 1 (error bar represented standard deviation; ***, $p < 0.001$).

R_a between groups SB and SB-CA.

Figure 2 shows the XPS chemical analysis results of $Ti2p_3$ spectra, corresponding to TiO_2 , on the outermost surface of non-cast Ti strips after the different surface treatments. The surface treatment appeared to have an influence on the surface chemistry of the Ti strips prior to porcelain sintering. Among the test groups, SB-A specimens showed the least amount of residual $Ti2p_3$ on the outermost surface of the Ti strip; the surfaces of SB-C and SB-CA specimens showed a greater amount of residual $Ti2p_3$ than the SB-A and SB specimens.

Figure 3 shows the SEM observations of the interfacial cross section of the Ti-porcelain specimens with different surface treatments: higher magnifications of (a) (as indicated by arrows) were shown in (b). The Ti-porcelain interface of the SB-C, SB-A and SB-CA

Fig. 2 X-ray photoelectron spectroscopy analysis of superficial $Ti2p_3$ spectra, corresponding to TiO_2 , on the non-cast Ti strips after the different surface treatments described in Table 1.

experimental groups was smoother than that of the SB control group.

The Ti-porcelain bond strengths of the various test groups in the three-point bending tests are shown in Table 3. The one-way ANOVA analysis results showed that only the acid treatment for the group SB surface before porcelain sintering had a significant influence on the bond strength of the Ti-porcelain specimens ($p < 0.01$). The SB-A specimens exhibited the maximum bond strength (34.60 MPa); the SB, SB-C and SB-CA specimens had bond strengths ranging from 27.92 to 29.63 MPa. The Tukey's post-hoc tests showed that no significant difference existed among the SB, SB-C and SB-CA test groups.

Figures 4 and 5 show the results of the SEM observation and EDS mapping analysis (Si and Ti elements) of the Ti and porcelain sides, respectively, of the fracture surface of the SB-A specimens after the three-point bending test. After the bending test, the Si and Ti elements were observed on the Ti and porcelain sides, respectively, of the fracture surface. The same results were also observed for the other three test groups, indicating that the Ti metal side of the fracture surface of the Ti-porcelain specimens after the bending tests had residual porcelain, and the porcelain side had residual Ti metal.

DISCUSSION

The experimental results conditionally supported our research hypothesis that the combined mechanical/chemical treatments of the ground, non-cast Ti surfaces can improve the bond strength between Ti and porcelain prior to porcelain sintering. Compared with the control group SB (bond strength 29.63 MPa), a sandblasting treatment followed by immersion in a HNO_3 -containing acid solution to treat ground, non-cast Ti surface (group SB-A) before porcelain sintering can significantly improve the bond strength of Ti-porcelain specimens (bond strength 34.60 MPa) ($p < 0.01$). However,

Fig. 3 Scanning electron microscopy of the interfacial cross section of Ti-porcelain specimens (M: Ti metal, P: porcelain; higher magnifications of (a) (as indicated by arrows) were shown in (b)).

Table 3 Means and standard deviations of bond strengths of Ti-porcelain strip specimens after three-point bending tests (note: mean values with different letters were significantly different ($p < 0.01$))

Group	Mean $\pm$ SD (MPa)
SB	29.63 $\pm$ 1.14 ^a
SB-A	34.60 $\pm$ 1.79 ^b
SB-C	28.43 $\pm$ 2.23 ^a
SB-CA	27.92 $\pm$ 1.34 ^a

sandblasting treatment followed by chemical immersion in NaOH-containing solution (group SB-C) or NaOH-containing solution and then in HNO₃-containing acid solution (group SB-CA) as the surface treatments for ground, non-cast Ti metal cannot improve the bond

strength of the Ti-porcelain specimens. It should be noted that regardless of the surface treatments, the bond strengths of all test groups were higher than 25 MPa, which was the minimum value suggested by the ISO 9693 specification⁵.

Previous studies^{4,20} have pointed out that the rough, cast Ti surface provides an important characteristic that increases Ti-porcelain bond strength. Different surface treatments for Ti produce dissimilar surface roughness, which may positively affect the mechanical bond properties between Ti and porcelain^{35,36}. In this study, the SEM observations show that mechanical sandblasting produced rough and irregular Ti surfaces (Fig. 1). The irregular and acute angles on the non-cast Ti surfaces produced during the sandblasting treatment were corroded (or smoothened) by chemical treatments in acid and/or caustic alkaline solutions. However, the bond strength of the experimental groups SB-C, SB-A and SB-CA with smoother surfaces was not statistically reduced when compared with the control group SB

Fig. 4 Scanning electron microscope observation and energy dispersive spectrometer mapping analysis (Si and Ti elements) of the metal side of the fracture surface of Ti-porcelain specimens (group SB-A) after the three-point bending test.

Fig. 5 Scanning electron microscope observation and energy dispersive spectrometer mapping analysis (Si and Ti elements) of the porcelain side of the fracture surface of Ti-porcelain specimens (group SB-A) after the three-point bending test.

with rougher surfaces, which implies that a decrease in the surface roughness of the non-cast Ti might not significantly affect the bond strength between Ti and porcelain. In the present investigation, the surface treatments changed not only the Ti surface roughness (Fig. 1) but also the Ti surface chemistry (Fig. 2), which

might also play a role in the Ti-porcelain bond strength.

Cai *et al.*²³⁾ used EDS to analyze the chemical compositions of the cast Ti surface after chemical solution treatments. The residual metallic chemicals (*e.g.*, Al and Zr) on the cast Ti after the surface treatments might increase the Ti-porcelain bond strength. In this study,

the SB-A specimens showed the least residual amount of Ti_2P_3 (corresponding to TiO_2) on the non-cast Ti surface before porcelain sintering (Fig. 2), which indicates that the HNO_3 -containing acid solution may thin and clean the surface Ti oxides (mainly as TiO_2) on the non-cast Ti before porcelain sintering and then increase the Ti-porcelain bond strength after porcelain sintering.

The EDS analysis results in Figs. 4 and 5 show that the Ti side of the fracture surface of the SB-A specimens exhibited the residual Si element derived from the sintering porcelain side; the porcelain side of the fracture surface revealed the existence of the Ti element derived from the Ti metal side. Similar results were also observed for the other test group specimens (SB, SB-C and SB-CA). This implies that the fracture mode of the Ti-porcelain specimen during the bending test was an adhesive bond failure; the interface between the non-cast Ti and porcelain had proper bond characteristics. Kimura *et al.*¹⁾ noted that a thick (approximately 5 μm) metallic oxidation layer created on a pure Ti surface cannot effectively adhere to Ti; thus, the Ti-porcelain bond failure occurs in the oxide layer. In this study, the sintering temperature of the low-fusing porcelain used in this research was lower than 800°C, which can inhibit the thickening of the oxide layer on the Ti surface during the porcelain sintering process³⁷⁾. Moreover, the ground non-cast Ti surface was roughened and cleaned using sandblasting and chemical solution treatments, respectively, prior to porcelain sintering. The abovementioned factors may significantly improve the bond property between the non-cast Ti and porcelain (e.g. group SB-A). Thus, the fracture mode between the low-fusing porcelain and the surface-treated Ti appeared to be of an adhesive type for all test Ti-porcelain specimens. Moreover, the bond strengths of all test specimens were higher than the minimum value (25 MPa) suggested in the ISO 9693 specification.

It should be noted that the metallographical grinding/polishing process, instead of the sandblasting process with Al_2O_3 particles, is used for Ti surface preparation prior to porcelain sintering in order to avoid the surface contamination of Al_2O_3 particles on the sandblasted Ti surface³⁸⁾. However, according to the manufacturer's advice, the sandblasting treatment with Al_2O_3 particles is usually employed as the first treatment step for Ti surface before porcelain sintering. In this study, based on the EDS analysis results, no significant contamination of Al_2O_3 particles was observed on the SB specimen surface which also showed a good bonding to porcelain (bond strength 29.63 MPa in Table 3).

For the ground, non-cast Ti surface without a hardened alpha-case layer, which simulated the surface conditions generated by the CAD/CAM procedure, the mechanical sandblasting treatment combined with the sequential chemical etching treatment using an HNO_3 -containing solution (group SB-A) significantly improved the Ti-porcelain bond strength as compared to the sandblasting treatment only (group SB). To increase the bond strength of the Ti-porcelain prosthetic appliance, it is simple and practical for dental technicians to apply

the sandblasting treatment first and then use the acid etching solution to treat the Ti surface prior to porcelain sintering. Although previous studies have suggested that the surface ceramic coatings (e.g. SiO_2 ¹⁵⁾, TiO_2 ¹⁶⁾, NbN ¹⁷⁾ and ZrN ^{17,18)}) may significantly improve the cast Ti-porcelain bond strength (>38MPa). On the other hand, some reports have shown that the surface modifications (e.g. electrical discharge machining¹¹⁾, SnO_x coating¹³⁾, ZrO_2 - Y_2O_3 - MgO coating¹⁴⁾ and SiO_2 coating¹⁹⁾) on cast Ti surface increase the Ti-porcelain bond strengths (<29 MPa) only a little higher than the minimum value (25 MPa) suggested by ISO 9693. The abovementioned surface treatments are rather complicated and more expensive than the proposed treatment in this study. Besides, no further information on the surface treatment for the CAD/CAM-produced non-cast Ti has been reported. Obviously, in this study, a simple and practical treatment combining sandblasting/acid solution treatment (group SB-A) significantly improved the non-cast Ti-porcelain bond strength to 34.60 MPa, which was about 1.4 times higher than the minimum value (25 MPa) specified in ISO 9693. The bond strength between the non-cast Ti and porcelain was related to not only the Ti surface topography but also the Ti surface chemistry.

CONCLUSION

The Ti surfaces treated with an HNO_3 -containing acid solution after sandblasting treatment showed a significantly improved Ti-porcelain bond strength (34.60 ± 1.79 MPa) compared with the Ti surfaces that were only sandblasted (29.63 ± 1.14 MPa). However, the sandblasted Ti surfaces treated with a caustic alkaline solution or caustic alkaline solution followed by acid solution did not show significant difference with regard to the Ti-porcelain bond strength. Regardless of the surface treatments used for non-cast Ti, the fracture mode of all test Ti-porcelain specimens after the three-point bending tests was of the adhesive type, and the bond strengths of all test Ti-porcelain specimens were higher than the minimum value (25 MPa) specified in ISO 9693.

The bond strength between the porcelain and the ground non-cast Ti surface, which simulates the CAD/CAM-produced conditions, can be significantly increased by applying the mechanical sandblasting treatment followed by the chemical acid treatment to the Ti surface prior to porcelain sintering. This simple and practical surface treatment procedure is provided as a reference for clinical practice in the dental laboratory.

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