Original Article

Surface Treatment on the Shear Bond Strength of Dental Ceramics to Titanium Commercially Pure

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Abstract

Background: The aim of this study was to evaluate ceramic/titanium shear bond strength and microstructure of two commercially dental ceramics. **Materials and Methods:** Ceramic/titanium bond strength (6.0 mm × 2.0 mm) was measured using a universal testing machine. The load was applied with a crosshead speed of 0.5 mm/min until fracture. The titanium received different modifications for commercially pure titanium (airborne-particle abrasion and acid and thermic treatment). **Results:** All specimens showed different features within the interfacial area according to the different kinds of surface treatment. The tensile bond strength showed significant difference among the ceramics and surface treatment where the acid treatment groups had least means bond strength as differences between ceramic groups ($P = 0.03$). **Conclusion:** It was concluded that the use of acid solutions did not improve titanium-ceramic bonding strength values and the combination of airborne-particle abrasion and thermic treatment produced the most significant improvement in the titanium-ceramic bonding.

Keywords: Bond strength, ceramics, commercially pure titanium, surface treatment

INTRODUCTION

Titanium commercially pure (CP-Ti) has desirable properties that would recommend in dental use when they are comparable with dental gold alloys.[1] Recently, the use of CP-Ti and its alloys in implants and prosthesis has increased. However, problems with ceramic bonding are encountered when CP-Ti is used in metal-ceramic restoration.[2] The oxidation characteristics of titanium are the main problems, especially because casting titanium surface is susceptible to oxygen contamination.[2] Special low-fusing dental ceramics are necessary for titanium-ceramic bonding.[3] Relatively thick and nonadherent layers of titanium oxide tend to form at temperature above 800°C;[4] therefore, ceramic should be fired below this temperature since a thick oxide layer apparently minimizes metal-ceramic bond strength.[5,6] Other factors to be considered affecting titanium-ceramic bonding are adherence of the self-formed oxide to the titanium substrate; bonding by fusion of self-formed oxide to the ceramic; growth of an oxide layer on titanium at elevated temperatures;[1] and stress developed at the interface because of an imbalance in thermal coefficients that may affect the flexural bond strength of the titanium ceramic system.[7]

Several secondary factors may enhance the titanium-ceramic bond strength. These include alteration of the titanium surface using airborne-particle abrasion, acid etching,[8] and application of bonding agent before ceramic.[8,9] Some studies show that titanium surface nitridation[10] or thin chromium coating,[11] bonding agents,[8] argon atmosphere during ceramic firing,[8,12] and sputter-coated gold layer on titanium improved titanium-ceramic adhesion. The result is a highly activated surface that can be demonstrated by the wettability of the material.[13] Although airborne-particle abrasion of the titanium surface before ceramic application improves the adhesion of the ceramic to the titanium substrate,[9] this procedure remains technique sensitive. Dérand and Herø[4] observed that the use of larger alumina

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particles with a diameter of 250 μm, compared with 50 μm particles, significantly improved the bond between titanium and ceramic. It is possible that the small particles may embed in the titanium surface. In fact, Gilbert *et al.*[14] found that airborne-particle abrasion could contaminate the surface of titanium with alumina particles, which could weaken the mechanical interlocking of the ceramic and titanium. Contamination of the titanium surface might also decrease its corrosion resistance and biocompatibility.[15]

Galo *et al.*[16] evaluated the treatments based on airborne-particle abrasion (aluminum oxide [Al_2O_3]) of the titanium surface. The authors observed that specimens produced the highest mean repair bond strength values, dependent of the laser welded. Airborne-particle abrasion plays a critical role in composites bonding to CP-Ti by creating roughened surface and the combined between titanium and composite did increase the bond strength significantly when decreasing the aluminum particle. The objective of the present study was evaluating the effect of three different titanium surface treatments on the titanium-ceramic bond.

MATERIALS AND METHODS

Eighty specimens were cast with CP-Ti type I (Tritan; Dentaurum Inc., Pforzheim, Germany). Wax patterns were fabricated with dimensions of 6.0 mm × 2.0 mm, with cylindrical rods (2.0 mm diameter × 24.0 mm length) connected to the center of the disk.

Five patterns were sprued together and invested according to the manufacturer's instruction. Titanium casting was performed on the Rematitan Machine (Dentaurum, Pforzheim, Germany) by means of voltaic arc and injection through positive pressure of argon gas in the upper portion of the cylinder and negative through the vacuum in the lower cylinder. After casting, the CP-Ti specimens were divested and cleaned with carbide burs (702L; KG Sorensen Ind. Com. Ltda., Barueri, SP, Brazil) and airborne-Al_2O_3 abrasion was performed with particles of 110 μm in size for 20 s, under pressure of 30–40 psi, and distance of 3–5 cm.[16-18] Then, the specimens were divided into eight groups (*n* = 10) and subsequently submitted to one of the eight surface modification procedures [Table 1].

Two low-fusing ceramics were used: Noritake Ti22 (Noritake Dental Supply Co Ltda., Nagoya, Japan) and Triceran (Dentaurum, Pforzheim, Germany). The specimens in each group were further divided into two subgroups of 5 each. Then, ceramic-bonding agent powder and liquid were mixed. A thin layer was painted with a short bristle brush on the specimen's surface. The bonding agent was dried at the muffle entrance of the furnace and fired according to the manufacturer's instruction.

The entire process followed the manufacturer's instructions and began with application of 2 uniform coats of opaque ceramic, using a brush on each treated ceramic-bearing surface. After the opaque ceramic firing cycle, the area that should receive

the ceramic was demarcated and a 2.0 mm thick polyester spacer (Plexiglass; General Electric, Mt. Vernon) was used to obtain a standard dentin ceramic for each specimen. The firing shrinkage was compensated for by applying a second layer of body ceramic, yielding a final total thickness of 2.0 mm. A glazing procedure was not performed. In all specimens, a single investigator performed ceramic application.

Shear bond strength testing

For the shear bond test, a special stainless steel device was fabricated to enable the specimens to be held firmly during the shear bond test. The device containing the CP-Ti-ceramic specimen was placed in a universal testing machine (EMIC MEM 2000; EMIC Equipamentos e Sistemas de Ensaio Ltda, Sao Jose dos Pinhais, PR, Brazil). A perpendicular load as applied at a distance of 0.5 mm from the CP-Ti-ceramic interface using a crosshead speed of 0.5 mm/min.[19] The shear bond strength was calculated according to the following formula: T = F/S (MPa), where T = tensile strength; F = critical rupture load; and S = metal ceramic bond area.

Structure of dental ceramic

Specimens from each group were selected for examination of the CP-Ti-ceramic under scanning electron microscope (SEM) (PHILIPS/XL 30-FEG). These specimens were embedded in autopolymerizing acrylic resin. The specimens were sectioned in the midsection with a low-speed saw along their width so that the cross-sectional area could be examined. The sectioned specimens were ultrasonically cleaned for 10 min and manually polished with abrasive paper (Metprep, Coventry, UK) with grits up to 1000 followed by three polishing stages (1, 0.34, and 0.05 μm) with Al_2O_3 polishing paste (Arotec, São Paulo, Brazil). Before testing, specimens were immersed in Kroll's solution for 20 s. Then, the specimens were ultrasonically cleaned in ethanol for 10 min and in distilled water for 10 min. The samples were well dried with hot air and kept in the desiccator until the beginning of the test.

Another specimen from each group was selected for the examination of failed surfaces of the CP Ti-ceramic interface. These specimens were ultrasonically cleaned in distilled water during 10 min before the making of the SEMs.

Statistical analysis

Kruskal–Wallis and Mann–Whitney U-tests were used to compare results of the shear bond strength. All statistical analyses and calculations were at the 95% level of confidence using the SPSS statistical program (SPSS for Windows, SPSS Inc., Chicago, Ill, USA).

RESULTS

The means value and standard deviations of shear bond strength (MPa) for the experimental groups are presented in Figure 1. Statistical analyses showed that there were significant differences between the bond strengths of surface treatment and the ceramic groups (*P* = 0.03), and all the groups treated

Table 1: Surface modifications for commercially pure titanium

Group	Descriptions
Treatment 1 (TA1)	Step 1: Air abrasion with 110 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in ethanol
	(Triceran porcelain manufacturer's recommendation)
Treatment 2 (TA2)	Step 1: Air abrasion with 110 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in isopropyl alcohol
	Step 3: Thermal treatment (temperature 500°C-800°C)
Treatment 3 (TA3)	Step 1: Air abrasion with alumina 110 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in isopropyl alcohol
	Step 3: Immersion in 10% HF-5% HNO_3 aqueous solution at room temperature for 2 min
	Step 4: Ultrasonic cleaning for 15 min in distilled water
Treatment 4 (TA4)	Step 1: Air abrasion with 110 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in isopropyl alcohol
	Step 3: Immersion in 10% HF-5% HNO_3 aqueous solution at room temperature for 2 min
	Step 4: Ultrasonic cleaning for 15 min in distilled water
	Step 5: Thermal treatment (temperature 500°C-800°C)
Treatment 5 (TA5)	Step 1: Air abrasion with 50 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in ethanol
	(Triceran porcelain manufacturer's recommendation)
Treatment 6 (TA6)	Step 1: Air abrasion with 50 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in isopropyl alcohol
	Step 3: Thermal treatment (temperature 500°C-800°C)
	(Noritake porcelain manufacturer's recommendation)
Treatment 7 (TA7)	Step 1: Air abrasion with 50 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in isopropyl alcohol
	Step 3: Immersion in 10% HF-5% HNO_3 aqueous solution at room temperature for 2 min
	Step 4: Ultrasonic cleaning for 15 min in distilled water
Treatment 8 (TA8)	Step 1: Air abrasion with 110 µm Al_2O_3 particles
	Step 2: Ultrasonic cleaning for 10 min in isopropyl alcohol
	Step 3: Immersion in 10% HF-5% HNO_3 aqueous solution at room temperature for 2 min
	Step 4: Ultrasonic cleaning for 15 min in distilled water
	Step 5: Thermal treatment (temperature 500°C-800°C)

Al_2O_3 – Aluminum oxide

with acid had significantly lower bond strength than the groups treated without acid or based on the manufacturer's instructions.

Significantly, difference results were observed considering the ceramic and surface treatment factors as well as their interactions. For the groups were received Noritake ceramic treated with 110 and 50 µm airborne-particle abrasion without acid treatment demonstrated the higher mean values, but no significant differences between Triceran groups. The acid treatment groups had least means bond strength with differences between ceramic groups, except the groups received 110 µm airborne-particle abrasion with thermic treatment.

In addition, there were significant differences between the bond strength on Triceran groups ($P = 0.03$). There was a significant difference only between the groups was received acid treatment, where demonstrated lower values compared to no acid treatment.

The increases of shear bond strength were observed on Noritake groups. The Noritake group showed a significant difference in shear bond strength with respect to surface treatment ($P = 0.03$). The highest mean bond strength value was found in the 60 mesh airborne-particle abrasions with thermic and without acid treatment. Moreover, there were no differences in the bond strength values with the following groups: 110 µm airborne-particle abrasions with and without thermic treatment and then 60 mesh airborne-particle abrasions without thermic and acid treatment. However, there were differences statically with the other groups.

All specimens showed different features within the interfacial area according to the different kinds of surface treatment applied. A photomicrograph of the interface-bonded specimens showed black's spaces in the groups that were received acid treatment [Figure 2], and the photomicrograph of tested specimens demonstrated that the fracture line was located more often between ceramic and metal (CP-Ti) for all the groups. All of the experimental groups exhibited small of ceramic retained on the surface. This observation indicated that the mode of bond failure was primarily adhesive between the ceramic and CP-Ti.
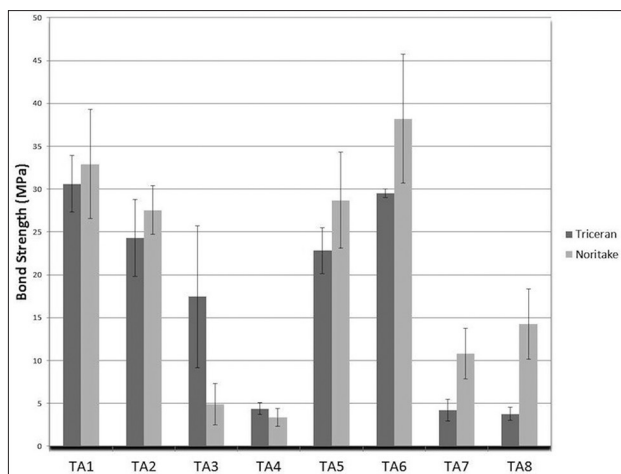
Figure 1: The means value and standard deviations of shear bond strength (MPa) for the experimental groups

Discussion

The use of surface airborne-particle abrasion and surface treatment enhanced the CP-Ti/ceramic bond. However, the assumption of better results for bond strength between CP-Ti and ceramic when acid treatments were used for the modification of the surface of the metal substrate was not confirmed. Paradoxically, the application of the manufacturer's protocol showed to be more effective in increasing the bond strength when compared to the all treatments. These observations demonstrated that the use of acid solution could cause a weakening of the bond strength mechanism when used on the titanium surfaces for 2 min. These results were not consistent with the findings from another study,[20] which acid treatment contributes to improve the CP-Ti/ceramic bond strength values. However, this result is similar with the other study,[3] where the acid treatment decreases the bond strength between CP-Ti/ceramic systems.

For the groups treated with thermic treatment only, the group treated with acid presented significantly lower bond strength values than the manufacturer's protocol and no acid treatment groups. The group treated with no acid treatment had lower values with no differences from group control. These observations demonstrated that the use of acid treatment could cause a weakening of the bond strength mechanism when used on the titanium surfaces. In addition, the use of thermic treatment did not improve Triceran ceramic adhesion to the titanium surface, when compared to the manufacturer's protocol.

The group treated by 110 μm airborne-particle abrasions did not produce significantly different on the shear bond strength than the 50 μm airborne-particle abrasion. Reyes *et al.* found that airborne-particle abrasion particles produced greater bond strength.[9] The study indicates that a modified titanium surface, when the surface receiving airborne-particle abrasion or thermic treatment, may lead to a satisfactory CP-Ti/ceramic bonding. This is in agreement with previous studies.[9,14] Wang
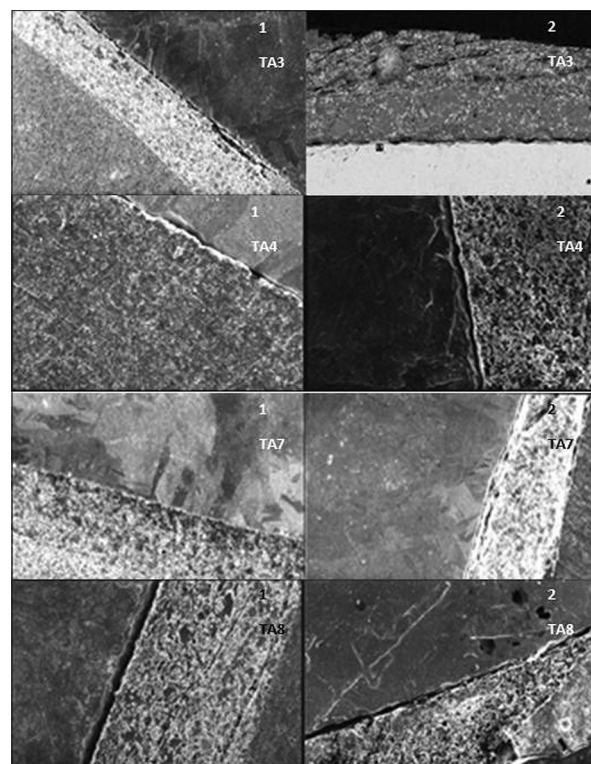

Figure 2: Scanning electron microscope showing the interface-bonded specimens with black's spaces in both groups (1 – Triceram and 2 – Noritake) that were received acid treatment (Treatment 3 - TA3; Treatment 4 - TA4; Treatment 7 - TA7; and Treatment 8 - TA8) (×200)

and Fung[11] have indicated that the surface treatment produces a strong, protective, and adherence oxide layer that is suitable for ceramic bonding.

Al Hussaini and Al Wazzan[21] observed that surface treatment with airborne-particle abrasion enhanced the bond strength of CP-Ti to ceramic and titanium surface treatment with acid produced no effect on the titanium/ceramic bond. In addition, Cai *et al.*[20] reported that combination of hydrofluoric acid with other treatment on CP-Ti surface increases the bond strength between ceramic and the metal substrate. However, these results are not consistent with the findings from these studies where the acid treatment of the surface improved decrease of CP-Ti/ceramic bonding.

Moreover, it is considered that such surface modifications changed the chemical natural of the CP-Ti surfaces and facilitated the adhesion of ceramic to the titanium through the chemical adhesion mechanism.[9]

SEM photomicrographs demonstrated the interface aspects of CP-Ti/ceramic before the rupture in all the groups. A photomicrograph of the interface-bonded specimens showed black's spaces in the groups that were received acid treatment [Figure 2], and the photomicrograph of tested specimens demonstrated that the fracture line was located more often between ceramic and metal (CP-Ti) for all the groups. These results are probably in agreement with Troia

et al.,[3] who observed the use of acid solutions did not improve CP-Ti/ceramic bonding strength values when compared to the control group. It has been shown that weak area of the CP-Ti/ceramic bond was the excessive and nonadherent oxide layer at the interface, and this problem must be solved to obtain greater bond strength.[22] The present study results suggest that use of surface airborne-particle abrasion along with an appropriate bonding agent will provide the highest bond strength of the ceramic to the titanium tested.

Photomicrographs showed that acid treatment produced a greater degree of roughness in the surface of titanium than the control group [Figure 2]. Furthermore, the surface roughness may increase the stress concentration at the CP-Ti/ceramic interface and generate steep reentrant angles that may prevent complete wetting and result in voids at CP-Ti/ceramic interfaces.[23]

The present study results suggest that the use of surface airborne-particle abrasion along with an appropriate surface treatment will provide the highest bond strength of the ceramic to the titanium tested. A limitation of this study was that only two brands of low-fusing ceramic and one brand of titanium were tested; the findings related to these three products may not be extrapolated to similar materials. Furthermore, if measuring the oxide layer thickness had been part of the study, helpful observations might have been obtained to better understand the behavior of the materials. Therefore, the impossibility of previewing the behavior of restorations in the oral cavity creates the expectancy for other studies corroborating in the development of new techniques that raise bond strength values between ceramic and titanium.

Conclusion

Within the limitations of this investigation and for the materials used in this study, the following conclusions were made:

1. The use of acid solutions did not improve titanium-ceramic bonding strength values when compared to the control group that represented the manufacturer's protocol
2. The Triceram ceramic bond strength decreased significantly with an applied thermic treatment in CP-Ti
3. The combination of airborne-particle abrasion and thermic treatment produced the most significant improvement in the titanium-ceramic bond
4. Titanium surface treatment with acid treatment, with or without bonding agent, produced no effect on the titanium-ceramic bond, as compared to the control specimens.

Conflicts of interest
There are no conflicts of interest.

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