Effect of Bonding Agent Application Method on Titanium-Ceramic Bond Strength

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Abstract

Purpose: Although milled titanium may be used as a substructure in fixed and implant prosthodontics, the application of the veneering porcelain presents particular challenges compared to traditional alloys. To address these challenges, some Ti ceramic systems incorporate the application of a bonding agent prior to the opaque layer. Vita Titankeramik’s bonding agent is available as a powder, paste, and spray-on formulation. We examined the effect of these three application methods on the bond strength.

Materials and Methods: Four titanium bars were milled from each of 11 wafers cut from grade II Ti using the Kavo Everest milling unit and a custom-designed milling toolpath. An experienced technician prepared the 25 × 3 × 0.5 mm³ metal bars and applied bonding agent using one of three application methods, and then applied opaque, dentin, and enamel porcelains according to manufacturer’s instructions to a 8 × 3 × 1 mm³ porcelain. A control group received no bonding agent prior to porcelain application. The four groups (n = 11) were blindly tested for differences in bond strength using a universal testing machine in a three-point bend test configuration, based on ISO 9693–1:2012.

Results: The average (SD) bond strengths for the control, powder, paste, and spray-on groups, respectively, were: 24.8 (2.6), 24.6 (2.6), 25.3 (4.0), and 24.1 (3.9) MPa. One-way ANOVA and Tukey’s multiple comparison tests were performed between all groups. There were no statistically significant differences among groups (p = 0.951).

Conclusion: Titanium-porcelain bond strength was not affected by the use of a bonding agent or its application method when tested by ISO 9693–1 standard.

Critics of metal ceramic restorations claim that conventional high-noble (HN) alloys are too costly, that predominately base (PB) alloys have compromised biocompatibility, and that casting procedures for all alloys are technique sensitive.¹ Of the many PB alloys that are less expensive than HN alloys, titanium has favorable mechanical properties² and exhibits superior biocompatibility, partly because of its stable oxide layer.³

Although cost and biocompatibility may favor the use of Ti over other HN and PB alloys for metal ceramic restorations, procedures for casting Ti restorations are significantly more technique sensitive than for other PB alloys. Casting investments for traditional alloys include gypsum and phosphate-bonded investments and contain components that form stable oxides at high temperature. But because titanium oxide is thermodynamically favored over those oxides formed in traditional investments, a magnesium oxide investment must be used to avoid excessive reactivity. Even using a magnesium investment, an unstable α-case layer is formed that must be eliminated before bonding to ceramic.⁴⁶ In addition, Ti reacts vigorously with oxygen at casting temperatures and must therefore be cast in an inert gas environment. These difficulties in casting have been circumvented by the development of CAD/CAM milling technologies. It was recently shown that these systems can produce copings that, after the addition and firing of porcelain, exhibit less marginal discrepancy than Ni–Cr cast alloy systems.⁷ Even though Ti copings can be milled accurately, the application of the veneering porcelain presents particular challenges. The quantity of the crystalline leucite phase must be altered...
from traditional formulations to obtain a compatible coefficient of thermal expansion. Additionally, Ti must be fired at a lower temperature than conventional metal ceramic alloys because it undergoes a phase change at 860 °C. Therefore, glass modifiers like boric oxide are added to decrease the firing temperature and control the oxide layer thickness and porcelain adherence.

The oxide layer also may be controlled via application of a bonding agent between the porcelain and the metal. Metal oxides are added to such bonding agents to scavenge oxygen and optimize the thickness and properties of the oxide layer. The composition of bonding agents varies widely between manufacturers and may lead to important differences in bond strengths. Titankeramic (Vita, Bad Sackening, Germany) bonding agent powder is estimated by energy-dispersive x-ray spectroscopy (EDS) to be composed of 71% SiO$_2$ and 7% Al$_2$O$_3$. It has a uniform particle size, and the particles are probably of single composition.

Bonding agents are supplied as powder/liquid systems, as pastes, and a unique commercial spray-on system (Vita Spray-On; Vita). A study employing a spray opaque and a PB alloy found that a more-even thickness was obtained with the spray application method, but bond strength was unaffected.

Recent studies have sought to document improvements in titanium–ceramic bond strength through various surface treatments, such as chromium electroplating of the Ti, airborne particle abrasion, acid or caustic treatments, nitridation, and silicon coating by magnetron sputtering. No studies demonstrate the effect of bonding agent application methods on metal-ceramic bond strength in Ti systems.

The three-point bending test proposed by Lenz et al commonly serves to facilitate comparison of materials and techniques involved in the metal-ceramic bond. Using this test, HN alloys with feldspathic porcelain systems demonstrate bond strengths averaging 50 to 60 MPa, while titanium-to-porcelain bond strengths average 20 to 40 MPa. A similar correlation is observed regarding clinical success. Walter et al showed 98% clinical success with HN metal-ceramic vs. 84% for titanium–ceramic systems over 6 years.

The primary aim of this investigation was to evaluate the effect of three application methods of the bonding agent on the strength of the metal-ceramic bond in low-fusing porcelain/grade II commercially pure titanium systems. Because it was suspected that the spray-on technique would produce a bond of bonding agent more uniform in thickness and in coverage than brush-on application, it was hypothesized that the strongest bond identified by the three-point bending test would be associated with spray-on, followed by paste, and then brush-on bonding agent. The null hypothesis was that there would be no significant difference in bond strengths between the three application methods.

**Materials and methods**

The experiment was designed to observe the effects of bonding agent application on the bond strength of the Ti-porcelain system. The application method was tested at four levels: no bonding agent, paste bonding agent, powder bonding agent brush-on, and powder bonding agent spray-on. Based on a priori power analysis, eleven specimens were used in each of four groups. The eleven specimens without bonding agent served as controls.

**Specimen preparation**

Specimen preparation resulted in a 25 × 3 × 0.5-mm$^3$-milled beam with porcelain applied to a central 8 × 3 × 1.0 mm$^3$ block in accordance with ISO 9693 KaVo Everest® T-B33/16 (Kavo, Biberach, Germany) Ti blanks in ASTM grade II cp Ti were machined into 3-mm-thick wafers using an industrial machining blade. These machined wafers were placed on a milled positioning jig and invested in acrylic resin for use in the Everest® milling unit. From each wafer, four Ti beams were milled to 3 mm wide × 0.5 mm thick (Fig 1). Each beam was standardized to 25 mm length using a thin carbide disc. Each set of four beams originating from a single wafer was randomized, received the assigned treatment, and underwent firing at the same time.

A custom milling toolpath was designed using DentMill dental CAD/CAM suit (Delcam, Salt Lake City, UT) to replicate the surface texture of a milled coping. Once the beams were milled, all further specimen preparation was done by the same experienced dental technician. The surface was prepared according to manufacturer instructions using airborne particle abrasion and steam cleaning. The beams were abraded with airborne particles of 120-$\mu$m aluminum oxide at a 2-bar pressure, a 3 to 5 cm distance, and an angle of approximately 45° to the surface. Each specimen was cleaned with pressurized steam before bonding agent application.

For beams in the brush-on powder/liquid groups, powder was mixed with the manufacturer’s supplied modeling liquid (Modeling liquid) and then applied using a sable brush. The paste bonding agent was applied in the same manner, using paste bonding agent liquid to maintain consistency. For those beams in the spray-on group, powder was mixed with the manufacturer’s solvent (Spray-on Liquid; Vita) in the jar of a HS #1 airbrush (Paache, Chicago, IL). Following the manufacturer’s instructions, the mix was standardized to 5 g of powder to 95 mL of liquid. It was sprayed at 6 to 8 cm from the surface,
at 1 bar pressure, and through a tip opening of 0.63 mm and then fired according to manufacturer’s instructions. The solvent contained 90% ethanol, which allowed the bonding agent to dry quickly once on the metal. Eleven Ti beams served as the control group and did not receive any bonding agent.

For all four groups, the opaque layer was applied next with a conventional brush-on technique. A device to facilitate the formation of the 1-mm-thick porcelain block (Fig 2) was made using three pieces of fluorocarbon resin (Teflon; DuPont, Wilmington, DE). The opaque layer was fired before 3D shade 2M2 dentin porcelain (Vita), and the corresponding EN2 shade enamel porcelain was next applied and fired simultaneously. The surface was then lightly ground using three strokes of a cylindrical diamond bur (S5117–023; Brasseler USA, Savannah, GA) to simulate a minor contour adjustment. The specimens were then fired in a calibrated Ney Centurion Qex oven (Denstply Ceramco; Burlington, NJ) according to manufacturer instructions24 (Table 1). Following bonding agent application, each set of four specimens was fired in the same oven for: (1) opaque; (2) body; (3) enamel; and (4) glaze (without addition of glaze material) firings.

### Table 1: Firing procedures used

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Temp (°C)</th>
<th>Hold (min)</th>
<th>Rate (°C/min)</th>
<th>Temp (°C)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste bonder</td>
<td>400</td>
<td>6</td>
<td>67</td>
<td>800</td>
<td>1</td>
</tr>
<tr>
<td>Powder bonder</td>
<td>400</td>
<td>2</td>
<td>67</td>
<td>800</td>
<td>1</td>
</tr>
<tr>
<td>Opaque</td>
<td>400</td>
<td>2</td>
<td>98</td>
<td>790</td>
<td>1</td>
</tr>
<tr>
<td>Dentin</td>
<td>400</td>
<td>6</td>
<td>53</td>
<td>770</td>
<td>1</td>
</tr>
<tr>
<td>Glaze without glaze</td>
<td>400</td>
<td>0</td>
<td>93</td>
<td>770</td>
<td>1</td>
</tr>
</tbody>
</table>

where \( k \) is a constant determined from an algorithm appended to the ISO standard derived from finite element analysis.19 The thickness and the modulus of elasticity of the Ti beam are used to determine normalized average shear stress. For the Ti beams in this study with thickness 0.43 to 0.54 mm, \( k \) ranged from 4.1 to 6.3 mm\(^{-2}\).

One representative specimen from each group was examined under SEM without undergoing mechanical testing. The specimens were mounted in epoxy resin (Epoxicure®, Buehler, Lake Bluff, IL) and finished and polished with silicon carbide paper and then with aluminum oxide to a final grit of 0.1 μm. The specimens were then carbon coated and examined at 5000× by SEM (Zeiss Sigma VP 4.0; Zeiss, Oberkochen, Germany).

One-way ANOVA with pairwise comparisons using least significant differences corresponding to this analysis was applied. Residuals were checked for homogeneity of variance and approximate normal distribution to assure the analysis assumptions were met. Based on the sample size of 11 and the pooled variance estimate of the treatment groups, there was a 0.80 power to detect a difference of 4.4 between two treatments at a two-tailed significance level of 0.05. Least significant difference pairwise comparisons were performed following the one-way ANOVA.

### Results

The average control, powder, paste, and spray-on bond strengths were calculated (Table 2). One-way ANOVA was performed, and no statistically significant differences between groups were identified. No post hoc test was indicated. Each
group had one adhesive failure (9.1%), with the remaining ten specimens (90.9%) failing in a mixed mode. Statistically, the null hypothesis was not rejected.

Examination of the interface using SEM is shown in Figures 3 to 6. Under standardized in vitro test conditions, the ISO test failed to distinguish bond strengths between bonding agent application methods.

Discussion

No increase in bond strength was observed when applying a bonding agent to the milled titanium surface, conflicting with previous findings using different titanium-porcelain systems. In the early Procera® Ti porcelain system (Nobel Biocare, Zurich, Switzerland), the bonding agent significantly improved bond strength. The Noritake product (Ti-22; Kuraray Noritake Dental Inc, Kurashiki, Japan) has also been tested, and the bonding agent shown to improve the bond strength. The GC bonding agent (GC Corp, Tokyo, Japan) improved (increased) the strain energy release rate in one study. But the Vita Titaneramic system has not been tested against its un-bonded control. Chakmakchi et al showed that the Titaneramic system contains 15% to 30% more silica and tin oxide than other bonding agents. Perhaps our finding that the bonding agent did not affect the bond strength may be attributed to the difference in chemical composition of the Titaneramic bonding agent.

In addition to the chemical factors attributed to the bonding agents, mechanical factors have been investigated and shown to affect the bond strength. Goeller et al and McLean and Sced showed a roughened metal surface increases bond strength. But Carpenter and Goodkind found that a roughened surface increases the oxide layer, which appears helpful in the case of other PB alloys, but may not be helpful in Ti. Of 37 previous in vitro studies on the titanium/porcelain bond, 13,26,31-41 cast the Ti; two reported milling the Ti surface or receiving manufacturer-supplied milled beams, 18,25,27,44-53 polished the beams, and four did not describe the Ti
surface preparation or roughness. Of nine clinical studies, only Kaus et al\textsuperscript{24} evaluated cast Ti; six studies\textsuperscript{22,57-61} evaluated the Procera\textsuperscript{R} milling/EDM process, and two\textsuperscript{62,63} evaluated the Everest\textsuperscript{R} milling process.

In this investigation, we tried to duplicate the surface roughness and topography of clinical specimens. The surface roughness of a typical milled Ti coping (Fig 7) was compared with that of the beams (Fig 8) using a noncontact surface profilometer (ContourGT; Bruker USA, Camarillo, CA). The Ra calculated for the coping was 0.69 and for the beams 0.48. Reproducing the same surface is important when evaluating milled vs. cast Ti, since the milling process may affect the overall bond strength.

Although we attempted to simulate clinical conditions, the results of this in vitro study should not compel a cautious clinician or technician to omit the application of bonding agent. Studies designed to elicit adhesive failures could provide additional insights and enhance the overall value of our data. In addition to better quantification of bond strength, additional studies could focus on a more objective analysis of the character
and dimension of the oxide layer formed using different application techniques.

Conclusion

In a three-point bend test of Titankeramic porcelain and bonding agents on milled ASTM type II commercially pure titanium, there was no statistically significant difference between a control with no bonder, spray-on bonder, powder-liquid bonder applied with a brush, and paste bonder. Qualitative examination of SEM images revealed a thicker oxide layer in those specimens without a bonding agent and a thinner, more uniform oxide layer in those using a spray-on bonding agent.

References