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Research Article

Investigation of the Effectiveness of Titanium Dioxide Nanotube Coating on Titanium–Resin Cement Bond Strength

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ABSTRACT

Objective: The aim of this in vitro study was to investigate the effect of the titanium dioxide formed by anodization process on the titanium–resin cement microshear bond strength.

Methods: Forty titanium cylinders (9 × 11 mm) were randomly divided into 4 groups according to the surface treatment methods: Control group, no treatment; airborne-particle abrasion group, 120 μm Al_2O_3; primer group, 120 μm Al_2O_3 + metal primer; and titanium dioxide group, titanium dioxide nanotube (n-TiO_2) formed by anodization process. Scanning electron microscope analysis was performed to determine the surface alterations of the specimens. Then, dual-polymerizing resin cement was applied on the specimens by using Tygon tubes, and microshear bond strength tests were performed by using a universal testing machine. The obtained data were analyzed by using 1-way analysis of variance and the Tukey post hoc test ($\alpha = 0.05$).

Results: Each surface treatment application increased the titanium–resin cement bond strength ($P < .05$). The highest bond strength value was obtained by titanium dioxide nanotube application, and the difference between groups was statistically significant (control group: 4.91 ± 1.10; airborne-particle abrasion group: 5.66 ± 1.90; primer group: 6.700 ± 2.05; and titanium dioxide group: 9.44 ± 1.20) ($P < .05$). All groups showed an adhesive failure mode.

Conclusion: The formation of titanium dioxide nanotube on titanium by anodization process increased the microshear bond strength significantly higher than that of the airborne-particle abrasion group or the metal primer group.

Keywords: Titanium, resin cement, TiO_2, microshear bond strength

INTRODUCTION

Full ceramic restorations meet more esthetic expectations of patients; however, the advantages of less complexity in the manufacturing process, low production costs, and ease of application made the metal–ceramic restorations still preferable in dentistry.[1] Noble metal alloys have superior mechanical properties, higher metal–ceramic bond strength, and good biocompatibility; however, the increased cost of these alloys limits the preference. In order to reduce the manufacturing cost, the preferred metal alloys to fabricate framework are nickel, chromium, or cobalt components. Among dental alloys, titanium (Ti) is the most suitable metal due to high corrosion resistance, exceptional mechanical properties, excellent biocompatibility, and light weight.[2] However, the chemical reaction with oxygen forms a thick oxide layer at high temperature while casting and that deteriorates the metal–ceramic bond strength. After introducing the computer-aided design and computer-aided manufacturing processes, prosthetic restorations are manufactured from prefabricated and homogeneous blocks with precise and accurate marginal fit.[3]

The life span of the prosthetic restorations not only depends on the metal–ceramic bond strength but also relays on the durability of adhesion performance of cement to restoration,[4] which is related to the cement type and to the surface characteristics of the framework.[5]

Due to the superior physical and mechanical properties, resin cements which can be categorized as non-adhesive

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and adhesive are the most suitable luting material than glass ionomer and zinc phosphate cements.[6,7] The difference between adhesive and non-adhesive cement is the adhesion mechanism. The adhesive cements form mechanical and chemical bonds, while the non-adhesive cementsonly bind mechanically.[8]

Different surface treatments such as airborne-particle abrasion (APA),[9-11] acid etching,[5] laser applications,[12] and chemical bonding agent applications[3,13] have been using for changing surface characteristics in order to enhance the adhesion of resin to Ti. Among these surface treatments, APA is the most common method used to create roughness at microscale to enhance mechanical interlocking; however, Gilbert et al[14] mentioned that the embedded sand particles after APA process on metal surface contaminate the Ti surface and deteriorate the bond strength between metal and ceramics. Furthermore, Miyakawa et al[15] emphasized that the surface contamination of Ti by sand particles diminishes the biocompatibility and corrosion resistance.

Chemical bonding agents with different functional monomers [urethan dimethacrylate, 10-methacryloyloxyethyl diphosphate monomer (MDP), thiophosphoric methacrylate, methylmethacrylate, and 6-methacryloyloxyhex yl-2-thiouracil-5-carboxylate] have been introduced to apply on metal surface before cementation to increase the bond strength of metal–resin, and each monomer was mentioned to be effective.[16,17]

Although the alteration of microscale topography of Ti substructure is essential and the effects were investigated in several studies, nanoscale topography is the basic structure that forms the microscale basis.[18] Current surface characterization processes are now focused on nanoscale applications. In implantology, titanium dioxide nanotube

MAIN POINTS

- It has been observed that the titanium dioxide (TiO_2) nanotube coating process increases the surface area and roughness.
- As expected, the surface treatments performed had a positive effect on the bond strengths in each group and ensured that the values were higher than those of the control group.
- The TiO_2 group, which haven't been studied before, The TiO2 group, which made our study different, made our study more valuable by having the highest value among all groups when the bond strength values were examined.
- Although it is thought that the current study will contribute to the literature, such studies should continue to increase the bond strengths.

(n-TiO_2) coating by anodization technique on the Ti surface to enhance the surface characteristics that improves bone formation and osteointegration was investigated in some research, and the findings showed that nano-topographic alterations formed a rough surface and directly increased cell differentiations and osteointegration.[19-22]

Anodization, a form of electrochemical surface treatment, is a novel and an encouraging method to enhance the surface roughness, wettability, and the corrosion resistance of the Ti via forming n-TiO_2 layers on the surface.[23-25] In addition to all these advantages, n-TiO_2 applications using anodization process are easy to perform, and also the result is always the same if the same parameters were used.[24-26] Furthermore, by varying the anodization voltage and dwelling time,[27] n-TiO_2's dimensions and alignment can be adjusted for the use of different purposes, and this makes the n-TiO_2 application by anodization attractive for dentistry.[28,29]

Although the effects of n-TiO_2 coating on osseointegration of implant have been investigated,[23,30] the effects on bond strength between Ti and luting cement on fixed partial denture have not been clarified, yet. Just as in implantology, achieving the appropriate surface topography is an indispensable factor to increase bond strength between metal and luting cement, and this study aims to decide the feasibility of the n-TiO_2 application on microshear bond strength (μSBS) between Ti and resin cement and to compare its effect with APA and metal primer application. In prosthodontic dentistry, n-TiO_2 coating by anodization process has not been used for this purpose, and the tested hypothesis was that the n-TiO_2 coating had a positive effective on μSBS between resin cement and Ti.

METHODS

Forty grade V Ti (Ti-6Al-4V) (ITI; Straumann, Basel, Switzerland) cylindrical specimens with a diameter of 9 mm and a height of 11 mm were cut from a Ti rod. The machined surfaces of the specimens were polished with 300, 600, and 1200 silicon carbide abrasives (English abrasives; Atlas, Ankara, Türkiye), respectively, and then finally polished with rubber burr (Metal polishing kit CA; Shofu dental, Kyoto, Japan). All specimens were randomly divided into 4 groups (control, APA, primer, and n-TiO_2) (n=10). One specimen from each group was examined under scanning electron microscope (SEM) (LEO 440; Zeiss, Oberkochen, Germany) at ×100K magnification to determine the surface characteristics.

In the APA group, polished Ti specimens' surfaces were abraded with 120 μm aluminum oxide (Al_2O_3) (Korox; Bego, Bremen, Deutschland) for 10 seconds. The nozzle was placed 20 mm away from the specimens and the pressure was at 0.4 MPa. Specimens' surfaces were ultrasonically cleaned with distilled water for 10 minutes after APA application.

In the primer application group, the first metal primer (Alloy primer; Kuraray, Hattersheim am Main, Germany) layer was applied slightly from the center of the specimens to the margin and then the second primer layer was applied to ensure the coverage of the complete surface. The metal primer applications were performed after APA as it was mentioned in the manufacturer's instructions.

In the n-TiO_2-coated group, the polished surfaces of the 10 Ti specimens were ultrasonically cleaned in acetone and methanol and rinsed with deionized water for 10 minutes. The anodization process was performed in a 2-electrode cell withTi foil used as a working electrode (anode) and platinum foil as a counter electrode (cathode). The specimens were immersed in an electrolyte containing 1 wt% ammonium florid (NH_4F) (Merck, Darmstadt, Germany) and a solvent of 3 wt% water and 96 wt% glycol (Merck) at 30°C.

At first, a voltage set (5-40 V range with increments of 5) was applied for 40 minutes to 8 specimens to determine the effects of voltage on n-TiO_2 formation. The SEM examination for each specimen was performed to decide the experimental group, and according to the SEM images the voltage was set to 40 V (Figure 1). After anodization, the Ti specimens were carried out from the electrolyte and washed with a large amount of deionized water to remove precipitated titanium oxides and then left to dry at room temperature.

The μSBS tests were performed on only 40 V applied specimens, as described in Shimada's research.[31] Thirty cylindrical Tygon tubes (Tygon tubing TYG-030; Saint-Gobain Performance Plastic, Courbevoie, France) with an internal diameter 0.8 mm and 0.5 mm height were placed on Ti specimens' surfaces which were APA, APA+°Cprimer, and n-TiO_2 coated. Dual-polymerized resin cements (Panavia F 2.0; Kuraray) were loaded into the tubes using a syringe compatible with the inner diameter of Tygon tube in a light-proof radiographic developing room in order to protect the specimens from light to avoid light polymerization and ensure the chemical reaction (Figure 2A). After 30 minutes without any intervention, the specimens were stored in distilled water at 37°Cfor 24 hours. The μSBS tests were performed by using universal testing machine (Lloyd LF Plus; Ametek Inc., İzmir, Türkiye) with a 0.5 mm/min crosshead speed (Figure 2B). Stereomicroscope (Stemi DV4; Carl Zeiss) examinations were performed to evaluate the failure mode of specimens. The failure modes were classified as follows:

Type A: Adhesive failure (on the interface)
Type C: Cohesive failure (within resin cement)
Type AC: Combined failure.

The obtained data were analyzed by using 1-way analysis of variance and the Tukey post-hoc test by Statistical Package for the Social Sciences software (IBM SPSS Statistics, v22; IBM Corp., NY, USA). The significance level was set at $\alpha = 0.05$ for statistical procedures.

RESULTS

The μSBS test results obtained in this study are depicted in Table 1. The highest bond strength between Ti and luting cement was obtained in n-TiO_2 groups (9.44 ± 1.20 MPa). The APA group presented the lowest bond strength (5.66 ± 1.90 MPa). In the primer group, the μSBS value was determined (6.70 ± 2.05 MPa). All surface treatments improved the bond strength, and the differences among all groups were statistically different ($P < .05$). The failure modes in all groups were determined as adhesive.

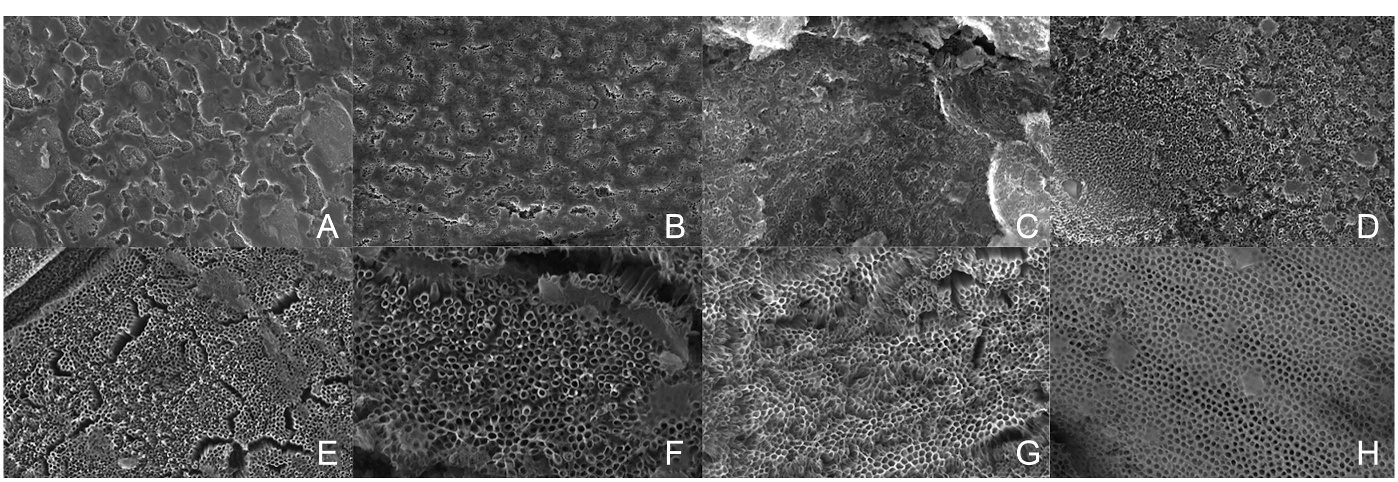

Figure 1. Scanning electron microscope images of titanium specimens anodized at different voltages (×100K): (A) 5 V, (B) 10 V, (C) 15 V, (D) 20 V, (E) 25 V, (F) 30 V, (G) 35 V, and (H) 40 V.

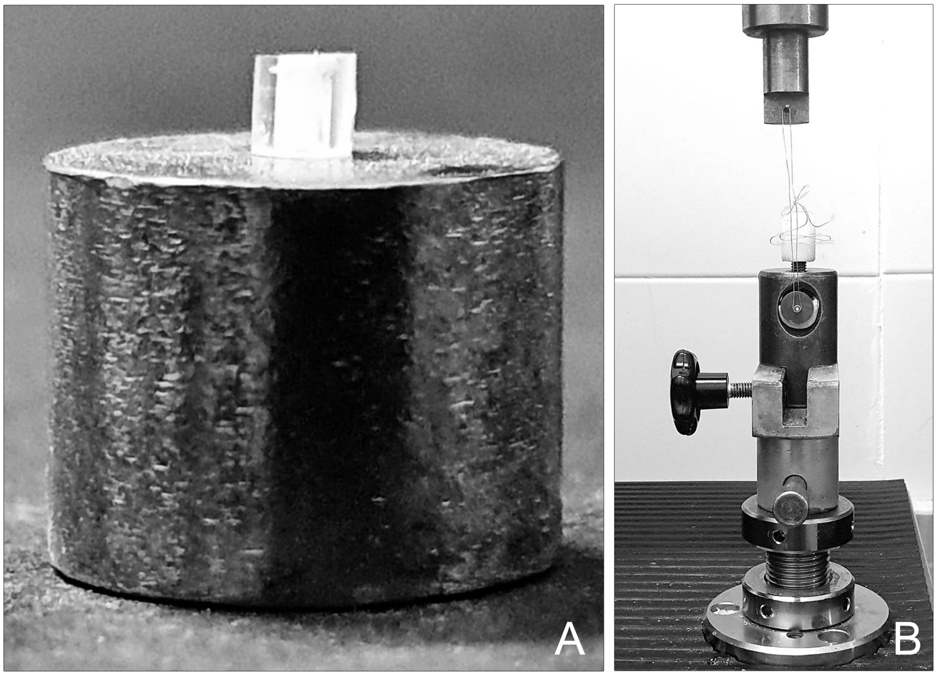

Figure 2. (A) Specimen with Tygon tube. (B) Microshear bond strength testing apparatus.

Table 1. Mean Microshear Values, SDs, and Failure Modes

Groups	Control	APA	Metal Primer	TiO_2
Micro shear (MPa)	4.91 ± 1.10[a]	5.66 ± 1.90[a]	6.70 ± 2.05[a]	9.44 ± 1.20[a]
Failure mode	A (10)	A (10)	A (10)	A (10)

APA, airborne-particle abrasion; TiO_2, titanium dioxide.
[a]Adhesive failure at resin cement–titanium interface; same superscript means statistically significant difference ($P < .05$).

The SEM images of the specimens after surface treatments are presented in Figure 3. According to these images, APA (Figure 3B) and n-TiO_2 applications (Figure 3C) improved the surface characteristics. The uniform alignment of n-TiO_2 and micropits resulting from APA were determined and exhibited a roughened surface compared to the control group (Figure 3A).

DISCUSSION

This study attempts to contextualize the effect of n-TiO_2 coating, primer application, and APA which is the most common technique to increase bond strength between Ti and cement. The results obtained from the tests suggested that all surface treatments significantly increase the μSBS ($P < .5$); therefore, the null hypothesis which advocates the application of n-TiO_2 coatings would enhance Ti–resin μSBS was accepted.

The increased wettability and surface roughness are crucial factors for successful metal–ceramic restorations. Therefore, recently, many surface treatment methods have been used for obtaining the adequate bond strength between metal and ceramic. The APA application as a surface treatment to improve the shear bond strength between Ti and resin cement is preferred in some researches, and there is no doubt on the agreement of the effectiveness.[10,16] The APA cleans the applied

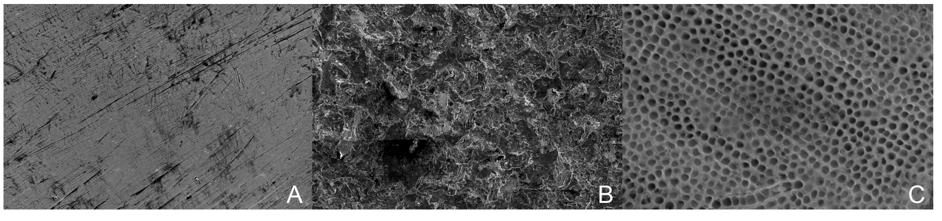

Figure 3. Scanning electron microscope images of surface treated specimens (×100K). (A) Surface polished specimens, control group; (B) airborne-particle abrasion specimens, airborne-particle abrasion group; and (C) titanium dioxide nanotube group.

surface, diminishes the surface tension, and increases wettability and surface area. The studies generally used 50 μm Al_2O_3 for APA, and all mentioned the enhancement of bond strength between Ti and resin cement; however, there is no report in the literature on the preference of grain size in these studies.[16,17] The most comprehensive study on the investigation of the effects of different Al_2O_3 particle size on Ti was carried out by Abi-Rached et al[11] who reported that 120 μm Al_2O_3 was effective than 250 μm and showed that the least effective particle size on Ti was 50 μm. In this research, the grain size of Al_2O_3 was decided according to Abi- Rached's manuscript, and the choice of 120 μm was made.

In recent research, the applied alloy primer contains both MDP and 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithiol (VBATDT) as functional monomers. The mechanism of alloy primer is based on the chemical bonding of the phosphoric acid group of MDP to the base metal atoms, while the sulfur atom of VBATDT chemically bonds to the noble metal atoms[13]. For alloy primer, the guidelines of the manufacturer recommend APA before the primer application. However, Egoshi et al[17] investigate the effect of APA, phosphate primer, HCl, and H_2SO_4 etching on the adhesion of resin composite on Ti and mentioned that the alloy primer could be applied irrespective of additional surface treatments. However, according to the preliminary tests and unpublished data of this research, with the use of alloy primer without APA, the adhesion of resin to Ti was very low. For this reason, in recent research, the alloy primer application was performed according to the manufacturer's instruction after APA process.

When comparing the effect of surface treatments according to the SEM images of the specimens, surface topographic changes could be detected clearly. After APA application, an enlarged rough surface full of microscale pits and fissures required to increase Ti–resin μSBS was obtained. This kind of bond strength is based upon mechanical interlocking. In addition to the mechanical bonding obtained by the APA process, the primer application forms a chemical bond between resin and Ti which explains the greater bond strength of the primer group (6.70 ± 2.05 MPa) than the APA group (5.66 ± 1.90 MPa) and works as a justification of chemical bonding. In the literature, on the use of different primers, Di Francescantonio et al[16] previously mentioned that all kind of primers containing different adhesive monomers increase the bond strength of Ti–resin and emphasized the importance of primer application after APA.

The n-TiO_2 application in prosthetic dentistry is an untested methodology. So far, there is no publication in the literature on the efficiency of TiO_2 tubes application at nanoscale (10^{-9} m) in order to increase the bond strength of resin or ceramic to Ti. The first n-TiO_2 applications in dentistry were on the Ti surface to investigate the effects on osteointegration and mentioned that the n-TiO_2 formed by the anodization process on the implant surface increased osteoblastic activity.[30] The alignment of n-TiO_2 varies with the applied voltage. At a voltage higher than 20 V, the structure of the n-TiO_2 formed on the Ti surface is crystalline (alignment in a regular fashion) and amorphous (alignment in an irregular fashion) at lower voltage.[29] With the increase in applied voltage, the amount of fluoride (F–) released from NH_4F in the electrolyte increases. These fluorides cause more Ti ions to be released by chemical dissolution from the Ti plate used as an anode which forms n-TiO_2 on the Ti specimen surface.[25] This research clarifies the effect of different voltages on the formation of n-TiO_2 on Ti. Eight different voltages were used, and SEM examinations were performed. According to the SEM images (Figure 1A,B,C,D) below 20 V applications, the distribution of the tubes is localized as a heap, amorphous, and there are gaps between these n-TiO_2 heaps, however, above this voltage the nanotube formation is crystalline (Figure 1E,F,G,H). Because of the most regular and homogeneous sequence of n-TiO_2, 40 V was used within these 8 groups for shear tests. Other groups may have positive effects on μSBS because of the irregularities in the alignment of the n-TiO_2, but this was planned as a further study.

Wettability or in other words contact angle which expresses the degree of hydrophilicity of the material shows the surface energy and surface topography. Contact angle decreases (hydrophilic) with the increase of surface roughness. Eliasa et al[23] compared the machined, APA, acid-etched, and anodized Ti surfaces by means of wettability and mentioned that the anodized surface exhibited the smallest contact angle (high wettability). In addition, Çırak et al[25] mentioned that the diameter and length of n-TiO_2 and surface roughness increased with increasing anodization voltage. In this research, the application of n-TiO_2 on Ti increased the resin μSBS, and this result may be attributed to the fact that the high surface area, high surface energy, and high wettability are obtained by nanoscale topographic changes via n-TiO_2.[21]

In recent research, the applied 3 different surface treatments (120 μm Al_2O_3, metal primer, and n-TiO_2) on Ti improved the μSBS of resin. The mean values of all 3 groups were higher than 5 MPa which was reported as a minimum requirement of the shear bond strength at the resin substrate interface to obtain clinically acceptable results,[7] and according to the findings of this research, the n-TiO_2 coatings can be used as a surface treatment alone.

Regarding the failure modes, all specimens in all groups showed adhesive failure, and the reason for such a result might be the small application area of resin cement.

In order to investigate the effects of surface treatments on Ti–resin bond strength, studies in the literature compare either one kind of application or in combination with different surface treatments; however, as the applied protocol increases, the procedure becomes more complicated, requires more precise application, and takes longer time. The main purpose of all these researches was to get the highest bond strength and in majority of these research, the highest bond strength is gained using both mechanical and chemical adhesion mechanism.[9-11,17] However, with the use of n-TiO_2 coating by the anodization technique, the obtained μSBS is high enough and simple to perform and always gets the same result.

Limitation of the Study

The limitation of the study is determining of the surface roughness of the TiO_2 applied samples. For future projects, non-touch surface roughness device will be used to determine the effect of different voltages of anodization.

Ethics Committee Approval: Our study was carried out in vitro in a laboratory environment. The methods and dental materials used have not been applied to any living creature. Therefore, an ethical committee was not required and no application was made in this direction

Peer-review: Externally peer-reviewed.

Author Contributions: Concept – T.A.; Design – M.E.C.; Supervision – T.A.; Resources – M.E.C.; Materials – T.A., M.E.C.; Data Collection and/or Processing – T.A., M.E.C.; Analysis and/or Interpretation – T.A.; Literature Search – M.E.C.; Writing Manuscript – T.A.; Critical Review – T.A., M.E.C.

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