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Investigation of the Effect of TiO_2 Nanotube Application on Titanium Ceramic Bond Strength

TiO_2 Nanotube Uygulamasının Titanyum Seramik Bağlantı Kuvveti Üzerine Etkisinin Araştırılması

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ÖZ

Amaç: Titanyum, korozyon direnci, hafifliği ve biyouyumluluğu nedeniyle sabit protezlerde altyapı materyali olarak tercih edilmektedir. Titanyum-seramik bağlanma dayanımının arttırması için yüzey işlemlerine ihtiyaç duyulmaktadır. Bu çalışmanın amacı anodizasyon yöntemiyle oluşturulan TiO_2 nanotüp uygulamasının makaslama bağlanma dayanımı üzerine etkisini araştırmaktır.
Gereç ve Yöntemler: Otuz adet titanyum silindir numunesi (12 mm çap, 10 mm yükseklik) hazırlandı ve yüzeyleri 300, 600 ve 1200 silisyum karbür aşındırıcılarla parlatıldı ve yüzey işlemlerine göre 3 gruba ayrıldı. Birinci grup kontrol grubu, ikinci grup 120 µm Al_2O_3 ile 75 psi' de 20 mm mesafeden 20 saniye boyunca kumlandı, üçüncü grup TiO_2 nanotüpleri oluşturmak için 40 V' da anodize edildi. Her gruptan bir numune taramalı elektron mikroskobu ve lazer profilometre cihazlarıyla incelendi. Üretici talimatlarına göre seramik (7x5 mm) numuneler üzerine uygulandı. Bağlantı testleri üniversal test makinesi kullanılarak gerçekleştirildi. Elde edilen veriler tek yönlü ANOVA ve Tukey testi ile analiz edildi.
Bulgular: En düşük bağlanma dayanım değeri kontrol grubundan elde edilmiştir (7,23±1,6 MPa). Ayrıca, TiO2 nanotüp uygulamasının (25,29±2,1 MPa) seramik bağ dayanımını arttırmada kumlama yönteminden (19,69±1,21 MPa) daha etkili olduğu bulunmuştur. Tüm gruplar arasındaki fark istatistiksel olarak anlamlı ($P<.05$) ve tüm gruplardaki kopmalar adeziv tip olarak tespit edilmiştir.
Sonuç: Uygulama sürecinde ek ekipmanlara ihtiyaç duyulsa bile, elde edilen daha yüksek bağlanma dayanımı TiO_2 nanotüp uygulamasını kumlamaya göre üstün kılmaktadır.
Anahtar Kelimeler: Titanyum, Seramik, Anodizasyon, Kumlama, Makaslama Bağlantı Dayanımı.

ABSTRACT

Objectives: Titanium is preferred as a framework for fix partial denture because of the corrosion resistance, light weight and biocompatibility. Surface treatments must be performed to increase the titanium-ceramic bond strength. The objective of this study was to investigate the effect of the TiO_2 application by anodization on shear bond strength between.
Materials and Methods: Thirty commercially pure titanium cylinder specimens (12mm diameter, 10mm height) were polished with 300, 600 and 1200 silicon carbide abrasives and divided into 3 groups according to the surface treatments. The first group is control group, second group was sandblasted (120 µm Al_2O_3 at 75 psi from a distance 20mm for 20 sec), the third group was anodized at 40V to form TiO_2 nanotubes. One specimen from each group was examined under scanning electron microscope and surface roughness by laser profilometer. Low fusing ceramic was applied (7x5 mm) onto the specimens according to the manufacture's instruction. Shear bond strength tests were performed using universal testing machine. The data was analyzed with One-way ANOVA and Tukey test.
Results: The lowest shear bond strength was obtained from the control group (7,23±1,6 MPa). Furthermore, TiO_2 nanotube application (25,29±2,1 MPa) was found to be a more effective than sandblasting method (19,69±1,21 MPa) to increase ceramic bond strength. The difference between all groups were statistically significant ($P<.05$) and the failure modes of all groups were adhesive.
Conclusions: Even if additional equipments are needed in the application process, the obtained higher bond strength made TiO_2 nanotube application superior to sandblasting.
Keywords: Titanium, ceramic, anodization, sandblasting, shear bond strength.

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INTRODUCTION

In modern dentistry, achieving a balance between aesthetic appearance and mechanical strength remains a critical challenge. Although the use of zirconium is more effective than metal-supported prostheses in meeting the aesthetic requirements, the use of a metal substructure in screw retained implant supported hybrid prosthesis, fix partial dentures, and crowns is still a method applied in many cases due to its resistance to the stresses caused by torquing the screw. Additionally, metal substructures offer simplicity in production, low costs, ease of application, and appropriate to all treatment plans (Adachi et al., 1990; de Almeida-Júnior et al., 2010; Al Hussaini et al., 2005).

Among metals used for fabricating dentures, titanium stands out as the first choice due to its high corrosion resistance, superior mechanical properties, excellent biocompatibility, and lightweight structure. However, the uncontrollable thick oxide layer formed on titanium after the casting process negatively impacts the metal-ceramic bond strength (Adachi et al., 1990).

The advent of computer-aided design (CAD) and computer-aided manufacturing (CAM) in dentistry has significantly advanced titanium substructure fabrication. By milling titanium from homogeneously produced blocks, these technologies enable the production of highly accurate restorations with precise marginal fits (Abduo et al., 2014).

The success and longevity of prosthetic restorations depend not only on the restoration's adhesion to the tooth but also on the bond strength between the substructure material and the applied ceramic (Aboushelib et al., 2005). This bond strength is closely related to the chemical compatibility of metal and ceramic as well as the surface treatments applied to the metal (Alkhadashi et al., 2020). Surface treatments aim to enhance the mechanical connection by increasing the ceramic-substructure contact area through the creation of a rough surface and undercuts areas for retention (Coskun et al., 2018; Shillingburg et al., 1997).

Common surface treatments that used for roughening are sandblasting, acid application, bur application, and laser roughening (Akar & Emre, 2023). Among these, sandblasting is the most widely used due to its simplicity. However, it requires a delicate balance. Airborne-particle abrasion (APA) at high pressure can cause abrasion and weaken the substructure material, while inadequate cleaning after the APA application, the embedded Al_2O_3 particles in metal structure reduce the metal-ceramic bond strength (Adachi et al., 1990).

Most surface treatments rely on creating roughness through an abrasive effect on material surface. Unlike abrasive methods, n-TiO_2 application by anodization process works by adding material rather than removing it. It was first applied as a surface treatment on titanium implants and its effects on osteointegration were examined and found to be biologically compatible and mentioned that n-TiO_2 application increase the wettability of the titanium and had positive effects on osteointegration (Von Wilmowsky et al., 2012). Furthermore, in different research it was mentioned that the application of n-TiO_2 increase the titanium-resin cement bond strength (Akar et al., 2023).

Anodization is an electro-chemical process used to form nanoscale titanium dioxide (n-TiO_2) tubes on the surface of titanium. This process is carried out by placing the titanium sample as an anode in an electrolyte solution.

Hydrofluoric acid (HF), ammonium fluoride (NH_4F) or other fluoride-containing solutions are usually used as a medium. It is possible to vary the diameter and length of the tubes with the applied voltage and application time. With the help of fluorine ions, a process of dissolution and re-deposition takes place on the titanium surface, forming a tube-like structure in the process (Lin et al., 2010; Von Wilmowsky et al., 2012; Zhao et al., 2015) In terms of biocompatibility, n-TiO_2 provide a biocompatible surface that promotes cell growth. The diameter and length of the tubes can be adjusted using different parameters according to the application requirements (Zhao et al., 2010, 2015).

This study specifically aims to evaluate the effects of n-TiO_2 formed by anodization process on titanium-ceramic bond strength and to compare these effects with APA, the most widely applied method. The hypothesis is that both methods will increase the bonding between the titanium ceramic and that APA will be more effective.

MATERIALS AND METHODS

Thirty titanium (Ti-6Al-4V) cylindrical specimens with a 9x11 mm dimension were cut from a grade V titanium rod (ITI; Straumann, Basel, Switzerland). The specimens' surfaces were polished manually with 600, 900, 1200 grits silicon carbide abrasives (English abrasives; Atlas, Türkiye), respectively and cleaned ultrasonically for 10 min with water.

The Ti specimens were divided into 3 groups of 10 each to received different surface treatments. In control group no surface treatment was performed, in sandblasting group specimens were subjected to APA, and the samples in TiO_2 group were treated with anodization method.

The samples in the control group were directly applied with low fusing ceramic (Ti22, Noritake, Japan) without any surface treatment.

In sandblasting group, the samples were treated with 120 µm Al_2O_3 (Metoxides, Dordmund, Germany) at 75 psi from a distance 20 mm for 20 sec. To clean the surface from Al_2O_3, the samples were cleaned ultrasonically for 20 min and then left in room temperature to dry.

The samples in TiO_2 nanotube group, first cleaned with acetone and methanol then rinsed with water for 15 minutes. The samples were immersed in a unit filled with a solution containing 1 wt % ammonium florid (NH_4F) and a solvent of 3 wt % water and 96 wt % glycol at 30 ^{0}C. This unit had 2 electrode cells, one was Ti foil served as an anode (working electrode), the other one was platinum foil serves as a cathode (counter electrode). The voltage was set to 40 V for 40 minutes. At the end of the duration samples were cleaned with water then left to dry at room temperature.

To determine the surface alterations after surface treatments one specimen from each group was examined at x100K under scanning electron microscope (SEM) (LEO 440; Zeiss, Germany) and to determine the surface roughness of the one specimen from each group was examined with profilometer (SPM-8100 FM, Shimadzu, Japan).

The ceramic application was performed according to the manufacture's instruction. First bonding agent applied and fired then opaquing agent application was performed. With the use of custom-made mold (5 mm internal diameter, 3 mm thick) low-fusing ceramic (Ti22, Noritake, Japan) was fired in a dental porcelain furnace (Programat P310, İvoclar Vivadent, Liechtenstein).

Shear-bond tests were performed using a universal testing machine (Lloyd LF Plus, Segensworth Fareham, England) with a speed 0.5 mm/min cross head speed. The failure modes were determined visually and classified into three groups:

Type A: Adhesive, at the interface.

Type C: Cohesive, within the ceramic.

Type AC: Combined

The obtained data were analyzed by using 1-way analysis of variance and the Tukey post-hoc test by SPSS (IBM SPSS Statistics, v22; IBM Corp., NY, USA). The significance level was set at α=0.05 for statistical evaluation.

RESULTS

The SEM image of the samples of all groups is presented in Fig. 1. From the images of air particle abrasion (b) and anodization group (c), surface modifications can be observed clearly. In anodization group TiO_2 nanotubes aligned properly, there is no space between the tubes and the holes located at the inner section of the tubes can be seen clearly.

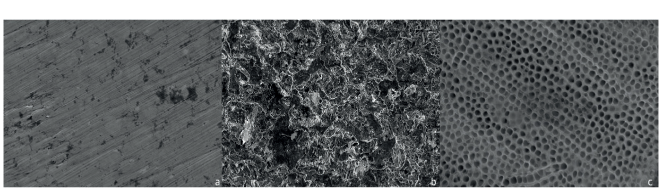

Figure 1: SEM images of all samples. (a) is control group, (b) is APA group, (c) is n-TiO2 group

The surface roughness values are presented in Table 1. The Ra values of the control group is 0.359 µm, air abrasion group is 0.263 µm, anodization group is 0.196. The lowest Ra value was obtained from the anodization group. The non-contact AFM image of control group is presented in Fig 2, APA group is in Fig 3, and the n-TiO_2 is in Fig 4.

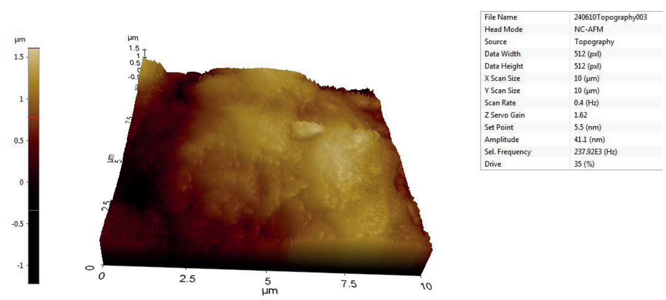

Figure 2: The non-contact AFM image of the control group.

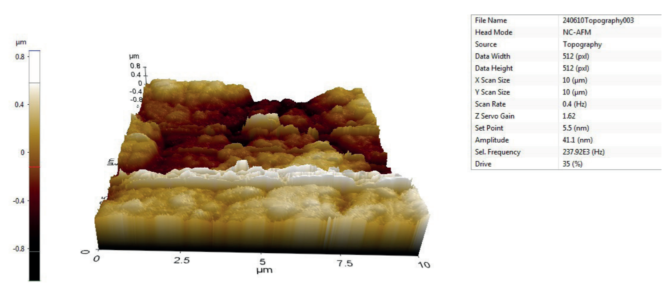

Figure 3: The non-contact AFM image of the sample after APA.

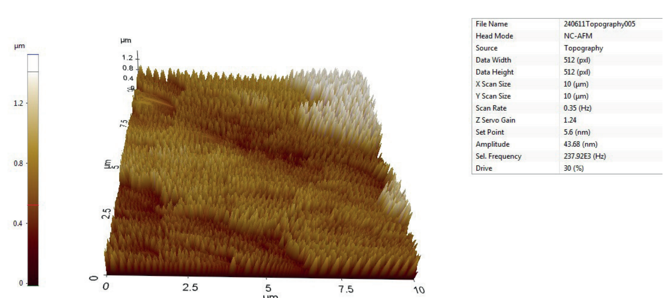

Figure 4: The noncontact AFM image of the sample after anodization.

Table 1. Surface roughness values (Ra)

	Control Group	APA Group	n-TiO_2
Surface Roughness	0.359	0.263	0.196

The shear-bond strength values obtained in this study are presented in Table 2. According to the SBS test the highest bond strength value between ceramic and titanium was obtained from anodization group (25.29±2.1 MPa). In APA group the SBS value was 19,69±1.21 MPa and the lowest SBS value was obtained from control group (7.23±1.6 MPa). The differences between groups are statistically significant (*P*<.05).

Table 2. Shear bond strength values (MPa)

	Control Group	APA Group	n-TiO_2
Shear Bond Strength	7.23	19.69	25.29

The failure modes of all samples in 3 groups showed adhesive failure which means the failure were on the interface between ceramic and titanium.

DISCUSSION

In this study, the effects of n-TiO_2 on the shear bond strength (SBS) between titanium and ceramic were investigated and compared with APA. The results demonstrated that the surface treatment methods significantly affect the bond strength between ceramic and titanium. The TiO_2 nanotube application by anodization process yielded the highest shear bond strength, followed by sandblasting, while the control group showed the lowest. These findings underscore the importance of surface treatments to improve the performance and longevity of titanium-ceramic restorations. According to the results obtained, the n-TiO_2 application proving more effective than the traditional airborne-particle abrasion method. Consequently, the hypothesis suggesting superior bond strength from APA treatment was partially supported.

APA increased the surface roughness which provides a larger contact area for the ceramic, thus strengthening the bond strength. However, the sandblasting process requires precise control over several factors. One of the most crucial aspects is the thorough cleaning of the titanium surface after sandblasting. Failure to remove residual Al_2O_3 particles can not only cause allergic reactions in patients but can also weaken the bond strength between the metal and ceramic (Al Hussaini & Al Wazzan, 2005). However, there is no need for additional cleaning after the anodization procedure. Unlike the APA, the anodization process changes the tomography by means of Ti tubes adhering to the surface which are biocompatible.

The parameters of the sandblasting process, such as Al_2O_3 particle size, pressure, and distance from the material, play a significant role in determining the quality of the bond strength. Furthermore, all these parameters must be rearranged for the material used as substructure because of the hardness difference (Śmielak & Klimek 2018). While some studies have searched the influence of these variables however, few have compared all parameters comprehensively, highlighting the need for more research to standardize the process for optimal results.(Abi-Rached et al., 2012; Coskun et al. 2018). In this research the parameters were chosen according to the Abi-Rached's research in which 50,120, and 250 µm Al_2O_3 were used and mentioned that the 120 µm was the most effective (Abi-Rached et al., 2012).

The superior bond strength achieved by the n-TiO_2 group can be attributed to the increased surface area and nanoscale roughness provided by the anodization process. The uniform and well-aligned nanotube structure observed in SEM image (Fig. 3) likely contributed to improved mechanical interlocking with the ceramic. This is consistent with studies indicating that nanoscale surface modifications enhance adhesion by creating a more effective interface for bonding between titanium and resin cement (Akar & Coskun, 2023).

According to the profilometric analysis, the roughness values created on the samples, n-TiO_2 creates a lower roughness value compared to the APA process. However, when the data were analyzed in terms of bond strength, it is determined that the highest values were obtained in the n-TiO_2 group. It could be attributed that of the preferred surface roughness detection method, the non-contact profilometer method allows only a limited area to be measured on the sample, while it does not provide complete information about the general structure of the samples. A second reason is that the oxide layer, which is the basis of the chemical bonding between ceramic and titanium, could be made more controlled by nanotube application. While the oxide layer on titanium is normally formed as a flat surface, the oxide layer is formed as a rough structure due to the F ion in the liquid medium in the anodization process (Çolak, 2008).

The findings of this study have significant implications for clinical practice. The higher bond strength achieved with TiO_2 nanotube application suggests that this method could enhance the durability and reliability of titanium-ceramic restorations. While the process requires additional equipment and expertise, the long-term benefits may outweigh the initial investment. Specifically, the enhanced adhesion could reduce the risk of debonding failures, which are a common cause of prosthetic restoration failure.

CONCLUSION

In conclusion, the TiO_2 nanotube application by anodization demonstrates significant potential as a surface treatment method for improving titanium-ceramic bond strength. Despite requiring additional equipment and expertise, its ability to achieve superior adhesion and biocompatibility makes it a promising alternative to conventional methods like sandblasting. Future studies should focus on optimizing the anodization parameters and evaluating its performance under clinical conditions to maximize its applicability in restorative and implant dentistry.

Conflicts of Interest

The authors declare that there is no conflict of interests.

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