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Microstructure and thickness of the resin cement layer at zirconia crown over titanium base interfaces: an *in vitro* study

Jorge Miguel Carneiro Souto

Dissertação conducente ao Grau de Mestre em Medicina Dentária (Ciclo Integrado)

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Trabalho realizado sob a Orientação de Júlio Souza

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To all those who accompany me on this journey to the succession of my professional achievement.

Thank you all!

Abstract

Background: After a cementation procedure, the resin matrix cement layer can vary at the zirconia to titanium base interface of implant-supported prosthesis. Also, the roughness of the inner zirconia and titanium base surfaces do affect such resin-matrix cement layer variation.

Purpose: The main aim of the present project was to evaluate the microstructure and the thickness of the resin-matrix cement layer on zirconia to titanium base interfaces over dental implant abutment.

Materials and method: At first, a literature search on PubMed (via National Library of Medicine) was conducted on the articles published in the last ten years using the following search terms: "zirconia" AND "cementation" AND "titanium base" OR "titanium link" AND "abutment" AND "resin-matrix cement" OR "resin cement" AND "thickness" OR "layer". Zirconia crowns were produced by CAD-CAM and surfaces of titanium abutment base were prepared by different techniques, namely: grit-blasting, anodization, or grit-blasting plus anodization. Details on the roughness and morphological aspects were evaluated by optical and scanning electron microscopy for the zirconia and titanium base surfaces after the surface treatment. Zirconia crowns were cemented over titanium base after the surface modification under 1kg following the manufacturer's instructions. Groups of specimens were cross-sectioned for morphological evaluation. Then, the microstructure and thickness of the resin-matrix cements at the zirconia to titanium base interfaces was carefully analyzed by microscopic inspection.

Results: The surface of the titanium based was significantly modified by grit-blasting or anodization procedures leading to an increased roughness and therefore retention for cementation using resin-matrix cements. The thickness of resin-matrix cement ranged from around 15 up to 150 µm within the crown-to-titanium base interfaces. The margin of the zirconia crowns showed the lowest mean values of resin-cement thickness than those recorded along the restoration. Macro-scale defects such as voids and pores were detected at the resin-matrix cement layer as well as thick layers of adhesive.

Conclusions: The surface modification of titanium base abutment increase the roughness and retentive area for cementation. Nevertheless, the thickness of the resin-matrix cement and adhesive layers significantly varies at the titanium base to zirconia crowns manufactured by CAD-CAM. Defects in the resin-matrix cement layer can be spots for failures by propagation of cracks and catastrophic fracture.

Key words: zirconia, titanium base, fitting, cementation, resin cement

Resumo

Fundamentação: Após um procedimento de cimentação, a camada de cimento de matriz resinosa pode variar ao longo da interface entre a coroa de zircônia e a base de titânio implanto-suportada. Além disso, a rugosidade das superfícies de cimentação da coroa de zircônia e base titânio afetam essa variação da camada de cimento matriz-resina.

Objetivo: O objetivo principal do presente projeto foi avaliar a microestrutura e a espessura da camada de cimento de matriz resinosa após cimentação de coroas de zircônia sobre bases de titânio implanto-suportada.

Materiais e Métodos: Inicialmente, foi realizada uma pesquisa bibliográfica no PubMed (via National Library of Medicine) dos artigos publicados nos últimos dez anos usando os seguintes termos de busca: "zirconia" AND "cementation" AND "titanium base" OR "titanium link" AND "abutment" AND "resin-matrix cement" OR "resin cement" AND "thickness" OR "layer". Em seguida, coroas de zircônia foram produzidas por CAD-CAM e as superfícies da base de titânio foram preparadas por diferentes técnicas, nomeadamente: jateamento, anodização e jateamento combinado com a anodização. Detalhes sobre a rugosidade e aspetos morfológicos foram avaliados por microscopia ótica e eletrônica de varrimento para as superfícies de base de zircônia e titânio após o tratamento das superfícies. As coroas de zircônia foram cimentadas sobre as bases de titânio com aplicação de um peso de 1kg seguindo as instruções do fabricante. Grupos de espécimes foram seccionados para avaliação morfológica. A microestrutura e a espessura dos cimentos de matriz resinosa nas interfaces de base de zircônia e titânio foram cuidadosamente analisadas por inspeção microscópica.

Resultados: A superfície da base de titânio foi significativamente modificada por procedimentos de jateamento ou anodização, levando a um aumento da rugosidade e, consequentemente, aumentando a área retentiva para cimentação com cimentos de matriz resinosa. A espessura do cimento de matriz resinosa na interface protética variou entre 15 a 150 µm. A margem das coroas de zircônia apresentou os menores valores médios de espessura de cimento quando comparado a outras regiões. Defeitos em escala macroscópica, como vazios e poros, foram detetados na camada de cimento de matriz resinosa. Também foi detetada uma elevada espessura de camada de adesivo em algumas regiões das interfaces.

Conclusões: A modificação da superfície de bases de titânio aumenta a rugosidade e a área de retenção para cimentação de coroas protéticas. No entanto, a espessura do cimento de matriz resinosa e das camadas de adesivo varia significativamente ao longo das interfaces. Defeitos na camada de cimento de matriz resinosa podem ser pontos de concentração de tensões e falhas catastróficas oriundos da propagação de fissuras.

Palavras-chave: zircônia, base de titânio, adaptação, cimentação, cimento resinoso

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Lista de abreviaturas, siglas e acrónimos:

CAD - computer-aided design

CAM - computer-aided manufacturing

3Y-TZP - tetragonal zirconia polycrystals stabilized with 3%mol of yttria

MPa - Megapascal

HV – Vickers Hardness

GPa - gigapascal

Bis-GMA - bisphenol A-glycidyl methacrylate

Bis-EMA - ethoxylated bisphenol A glycol dimethacrylate

TEGDMA - triethylene glycol dimethacrylate

UDMA - urethane dimethacrylate

SiC - silicon carbide

SEM - scanning electron microscopy

EDS - energy dispersive spectroscopy

BSE - backscattered electrons

ANOVA - Analysis of variance

1. Introduction

The advances in computer assisted design and computer assisted machining (CAD-CAM) technology have promoted the development of aesthetic all-ceramic restorations including zirconia-based restorations. CAD-CAM is currently used in both dental office and laboratory for the manufacturing of inlays, onlays, veneers, crowns, fixed dentures, implant abutments, and orthodontics. Nowadays, tetragonal zirconia polycrystals stabilized with 3%mol of yttria (3Y-TZP) is the most used material to manufacturing dental prostheses, due their properties, such as high chemical stability, high biocompatibility, flexural strength (1200 MPa), hardness (1250 HV), Young's modulus (240 GPa), and fracture toughness (11 MPa $m^{1/2}$) [1-3]. Additionally, the color and translucency of zirconia-based materials are proper to mimic enamel and dentin structures providing adequate esthetic outcomes [3-5].

The polycrystalline microstructure of the yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) and the increase in thickness negatively affect the light curing of resin-matrix cements [6-10]. Indeed, low transmittance is expected through thick layers of 3Y-TZP, which explains the relatively light irradiation procedures used when cementing light-activated resin-matrix compounds [6-10]. Over the years, several types of resin-matrix cement materials have been developed for the adhesion of ceramics, and therefore, methacrylate-based cements are the first-choice material for joining dental structures and ceramic restorations [11-14]. The chemical composition of resin-matrix cements involves the presence of Bis-GMA, Bis-EMA, TEGDMA, and UDMA embed- ding inorganic fillers such as colloidal silica, ytterbium, or barium glass [15-17]. The resin-matrix composites possess the following properties which are important for cementing ceramic restorations: low solubility, translucency, flowability, easy handling, and elasticity [16,17]. Also, the solubility of the resin-matrix cement is lower than those recorded for conventional cements that promote a long-term sealing at the marginal region of the restoration [16,17].

Regarding the polymerization, there are three types of resin- matrix cements: light-curing, self-curing, and dual-curing [7,8,14,15]. Light-curing and dual-curing methods are used for prosthetic adhesion with resin-matrix cements, and therefore, the light-curing method has the main advantage on the working time for cementation and removal of remnant cement at the restorative margins [7,8,14,15]. Nevertheless, a solely light curing procedure cannot guarantee a high degree of conversion of the resin-matrix cement considering other factors such as ceramic type and thickness, type of resin-matrix cement, and polymerization pathways [9,10,13-17]. On the other hand, dual-cure resin-matrix cements combine the desirable properties of chemical and light-curing materials to guarantee the degree of conversion of monomers in the case of insufficient light transmission [6-8, 11, 13]. The major problem of having an inadequate polymerization is the low degree of conversion leading to a decrease in physical properties and color stability [7,8,15,16]. The degree of conversion of the organic matrix of resin-based cements must be enhanced that corresponds to an efficient polymerization of resin-matrix materials. As a result, the strength of the prosthetic interface is increased leading to a long-term performance of zirconia- based restorations [3, 11- 15].

2. Objectives and hypotheses

It was hypothesized that the resin-matrix layer varies around the zirconia to titanium base interface after cementation of the zirconia crown.

The main aim of the present project was to evaluate the microstructure and the thickness of the resin-matrix cement layer on zirconia to titanium base interfaces over dental implant abutment. The specific objectives can be drawn such as:

-evaluating the modification of the zirconia and titanium base surfaces by grit-blasting and acidic etching processes namely anodization;

-evaluating the microstructure and thickness of the resin-matrix cements at the zirconia to titanium base interfaces.

3. Materials & Methods

3.1. Search and selection of previous studies

A literature search on PubMed (via National Library of Medicine) was conducted using the following search terms: “zirconia” AND “cementation” AND “titanium base” OR “titanium link” AND “abutment” AND “resin-matrix cement” OR “resin cement” AND “thickness” OR “layer”. The inclusion criteria involved articles on the cementation of zirconia crowns over dental implant abutments published in English language from January 2012 up to December 2022. The eligibility inclusion criteria used for article searches also involved in vitro studies, meta-analyses, randomized controlled trials, and prospective cohort studies. A hand-search was performed on the reference lists of all primary sources and eligible studies of this systematic bibliographical for additional relevant publications. Studies based on publication date were not restricted during the search process. The present search of studies was carried out in accordance with previous integrative or systematic review articles (1–4).

3.2. Preparation of specimens

Twenty titanium base (ZZ base™, Zirkonzahn®,) for implant abutment were divided in four groups depending on the surface treatment, as follow: (A) untreated; (B) grit-blasted; (C) anodized; (D) grit-blasted plus anodized. The description of the groups is shown in Table 1 and data on the titanium base materials is described in Table 2. Thus, half of the specimens were grit-blasted by using airborne-particle abraded with 50 µm aluminum oxide (Al_2O_3) at 0.2 MPa, 20 mm away from the nozzle, for 10 s (Figure 1).

Table 1. Groups of the present study depending on the titanium base treatment.

Groups	Titanium base treatment	n
Control	Untreated	5
Test 1	Grit-blasted	5
Test 2	Anodized	5
Test 3	Grit-blasted plus anodized	5

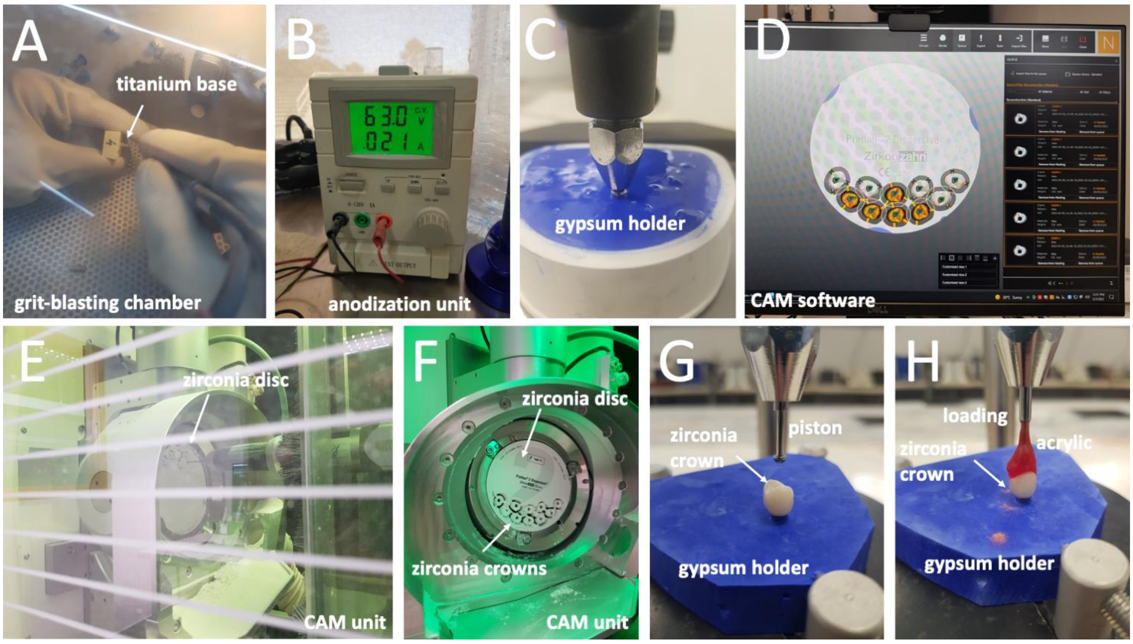

Figure 1. Preparation of specimens. (A) Grit-blasting and (B) anodization of titanium base surfaces. (C) Positioning of titanium base in gypsum-based plaster. (D) Computer aided designing and (E) computer aided manufacturing (Zirkonzahn®). (F) Milling of zirconia disc to produce prosthetic crowns. (G) Positioning and (H) cementation of zirconia crowns onto the titanium base surfaces.

A rotatory acrylic apparatus was developed for controlling the grit-blasting on each side of the titanium base (Figure 1A). And half of the specimens was modified by anodization on 63 V in $MgSO_4.7H_2O$ solution (Sigma-Aldrich, USA) for 3 s (Figure 1B). The surfaces were cleaned with sterile distilled water in an ultrasonic bath for 2 min. All surfaces were dried with oil-free air steam at room temperature and then conditioned with othoxisilane (Proclinic Products, Spain) for 60 s. The titanium base specimens were partially embedded in a gypsum-based holder and therefore exposing the cementation area (Figure 1C). Then, a universal adhesive (Futurabond™, VOCO, Germany) was applied on the surfaces by rubbing using a micro-brush for 20 s.

Twenty prosthetic crowns composed of 3Y-TZP (Prettau 2™, Zirkonzahn®) were produced by computer-aided design and computer-aided manufacturing (CAD-CAM) to ensure accurate placement over the titanium base surfaces (Figure 1D-F). The inner surfaces of the zirconia crowns were conditioned with othoxisilane for 60 s followed by a universal adhesive (Futurabond™, VOCO, Germany) for 20 s. The universal adhesive was applied on the surfaces by rubbing using a micro-brush for 20 s. At last, a resin-matrix cement (Bifix™, VOCO, Germany) was applied onto each conditioned surface and then each crown was placed over the corresponding titanium base surface (Figure 1G and H). The dental inspector apparatus (Ney surveyor, Germany) was used to align the crown with the long axis of the titanium base as seen in Figure 1G. The excessive cement layer was removed and the resin-matrix cement was light-cured at 420-480nm wavelength using a light curing unit (LY- A180, Anyang Zongyan Dental Material Co, Ltd, China) for 120 s (Figure 1H) [25]. Specimens were then assembled with a self-curing acrylic resin (Ortho resin™ Dentsply, USA) in a short length of polyvinyl chloride mold.

Table 2. Data of the materials used in this study.

Material (brand, country)	**Chemical composition**	**Elastic modulus (GPa)**	**Flexural strength (MPa)**
Titanium base (ZZ base™, Zirkonzahn®)	Ti6Al4V alloy	150	980
3Y-TZP (Prettau 2™, Zirkonzahn®)(5–7)	4-6wt% Y_2O_3, <1%Al_2O_3 ZrO_2 (3Y-TZP)	160-270	900-1050

Universal adhesive system (Futurabond™, VOCO, Germany)	2-Hydroxyethyl methacrylate, Bis-GMA, HEDMA, methacryloyloxy propyl dihydrogen phosphate, urethane dimethacrylate	5-6	N/A
Resin-matrix composite cement (Bifix™, VOCO, Germany)	0–25% Bis-GMA, 10–25% 1,6-hex-anediylbismethacrylate, ≤ 2.5% catalyst	7-9	125

3.3. Microscopic analyses

After cementation, zirconia to titanium base specimens were embedded in a self-curing acrylic resin (Ortho resin™ Dentsply, USA) and then cross-sectioned at 90 degrees relative to the plane of zirconia to titanium base specimens to resin-matrix cement interface. Surfaces were wet ground down to 1200 Mesh using SiC abrasive papers and then polished with 1µm Al_2O_3 particles. Then, surfaces were ultrasonically cleaned in isopropyl alcohol for 10 min and then in distilled water for 10 min [25].

Surfaces of the cross-sectioned specimens were sputter coated with a AgPd thin layer for scanning electron microscopy (SEM) analyses by using SEM unit JSM-6010 LV™ (JEOL, Japan) coupled to energy dispersive spectroscopy (EDS). The resin-matrix cement thickness and microstructure of the specimens were evaluated at high magnification ranging from x1000 up to x2000 under (SE) secondary and (BSE) backscattered electrons [25]. A number of three micrographs were acquired at x500 magnification, for each specimen (n = 15). The software Adobe Photoshop™ (Adobe Systems Software, Ireland) was used to analyze black and white images, with the black regions representing the pores and the white regions representing the bulk material. Image J™ software (National Institutes of Health, USA) was used to quantify the thickness dimensions and porosity percentage of the cross-sections.

3.4. Statistics

Results were statistically analyzed by normality test Shapiro-Wilk and two-way ANOVA to determine statistical differences in the resin-matrix cement thickness values between groups.

The t student test was used to compare the resin-matrix cement thickness results regarding the surface treatment of the titanium base. A probability value <0.05 was considered significant. The power analysis was performed by t student test or ANOVA, to determine the number of samples for each group (n), and to reveal a test power of 100% in the present study. Statistical analyses were carried out using Origin Lab statistical software (Origin Lab, Northampton, MA, USA).

4. Results

Scanning electron microscopy (SEM) images of the surfaces of the titanium base specimens free of treatment and after grit-blasting with alumina particles.

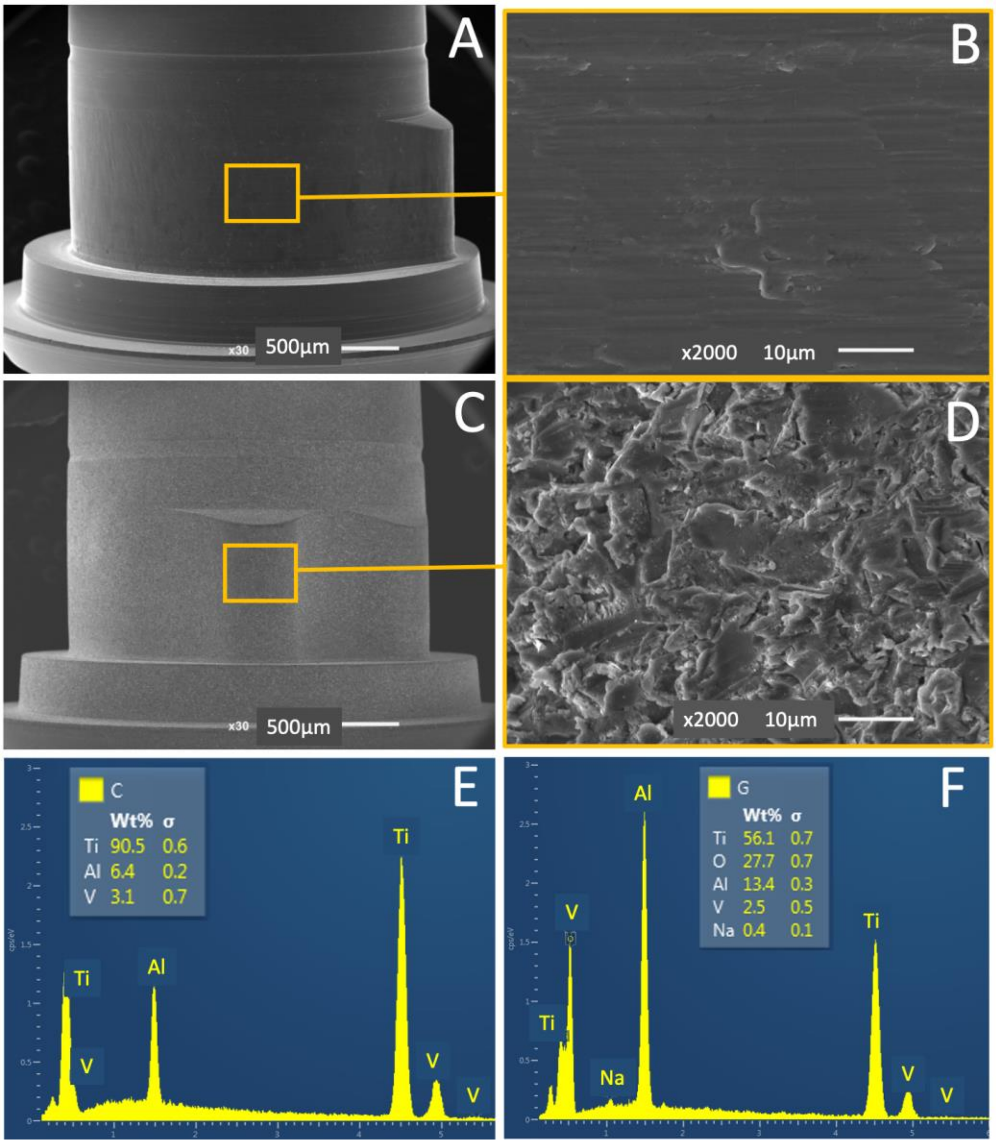

Figure 2. SEM images of the titanium base specimens (A,B) free of treatment (control group) and (C,D) grit-blasted with alumina (Al_2O_3) particles with 50 µm. Secondary electrons (BSE) mode and 15 kV. EDS spectra for (E) untreated and (F) grit-blasted titanium base.

Titanium base provided by manufacturer showed a smooth surface as expected (Figure 2A and B). Elemental analyses by EDS on untreated titanium base surfaces revealed around Ti (90wt%), Al (6wt%), and V (3wt%) that corroborate with the chemical composition indicated by the manufacturer. However, the surface was significantly modified after grit-blasting with alumina particles as seen in Figure 2C and D. Elemental analyses by EDS on grit-blasted titanium base surfaces detected around Ti (56wt%), Al (13wt%), V (2.5 wt%) and O (27.7wt%). The high content of Al and O revealed the presence of remnant Al_2O_3 particles entrapped on the surfaces after the grit-blasting even though the ultrasonically cleaning was performed in isopropyl alcohol followed by distilled water.

Also, surfaces modified by grit-blasting followed by anodization revealed a rough morphological aspect as shown in Figure 3. Elemental analyses by EDS on titanium base surfaces which were grit-blasted and anodized revealed around Ti (43.7 wt%), Al (15 wt%), V (1.5 wt%) and O (40wt%). The high content of Al and O revealed the presence of remnant Al_2O_3 particles entrapped on the surfaces. Titanium base surfaces modified only by the anodization procedure revealed a smooth surface aspect although the elemental analysis showed a high content of oxygen (~27wt%) due to the surface modification.

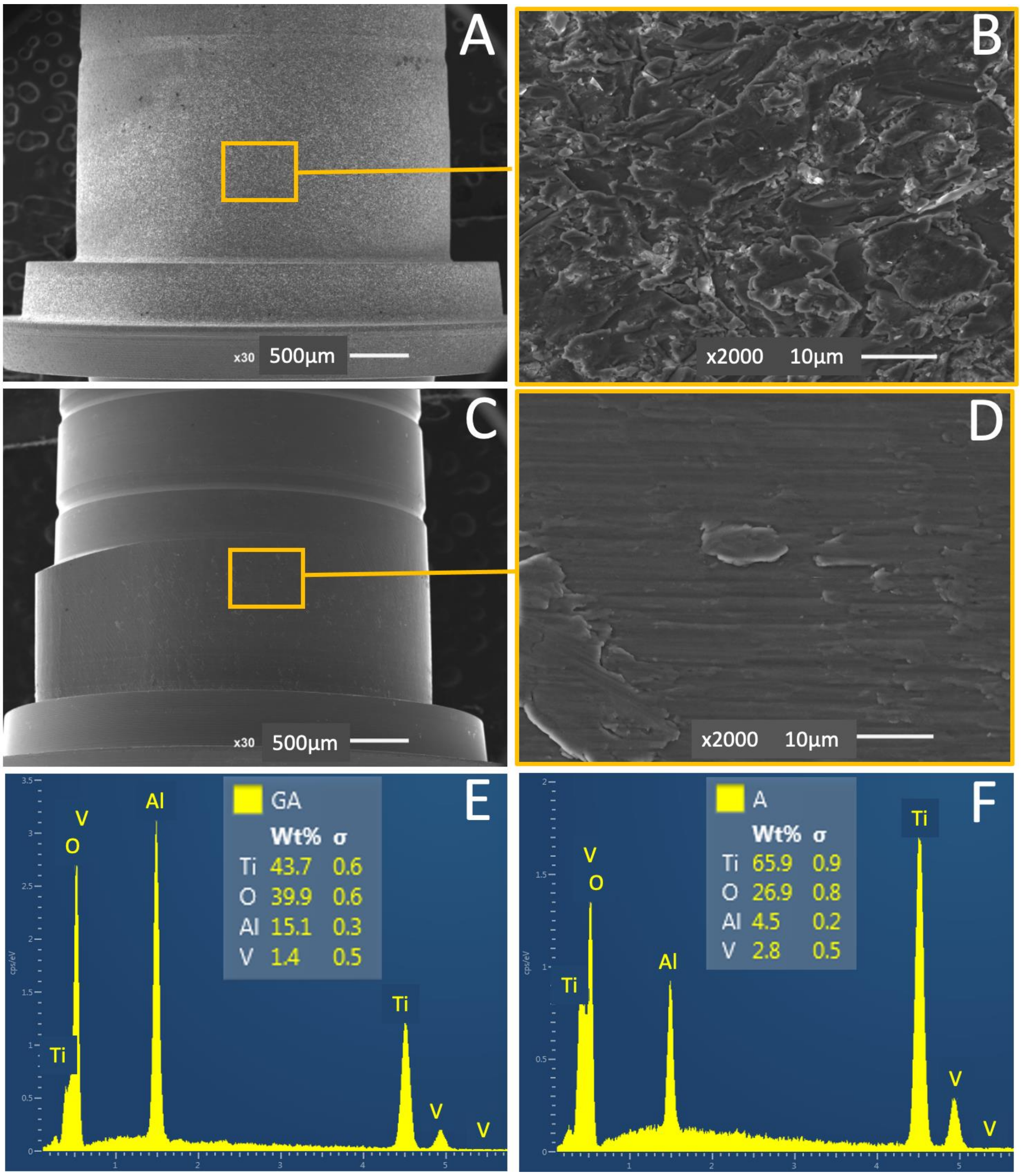

Figure 3. SEM images of the titanium base specimens (A,B) grit-blasted with alumina (Al_2O_3) particles with 50 µm followed by anodization and (C,D) only anodized. Secondary electrons (BSE) mode and 15 kV. EDS spectra for (E) grit-blasted plus anodized and (F) solely anodized titanium base.

SEM images of the inner surface of the zirconia crown are shown in Figure 4. Scratches from the milling process of the zirconia crown can be noticed in Figure 4B. After the cleaning procedure, any further surface modification was performed on the inner surfaces of the zirconia crowns.

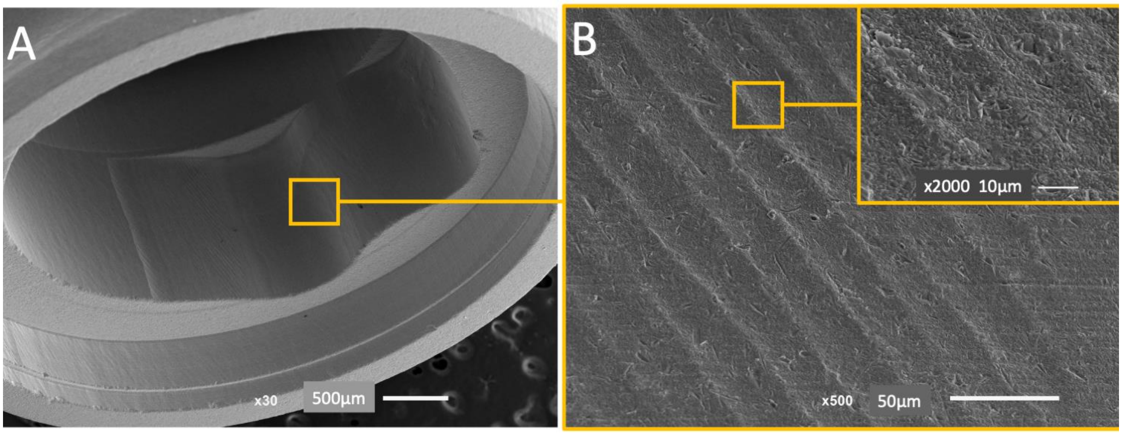

Figure 4. SEM images of the inner surface of the zirconia crown. Secondary electrons (BSE) mode and 15 kV.

SEM images of the interfaces established after cementation of zirconia crowns onto titanium base with resin-matrix cements are shown in Figure 5, 6, 7, 8, and 9. In Figure 5, it is noticed a detailed morphological analysis of the standard titanium base to resin-matrix cement and zirconia crown.

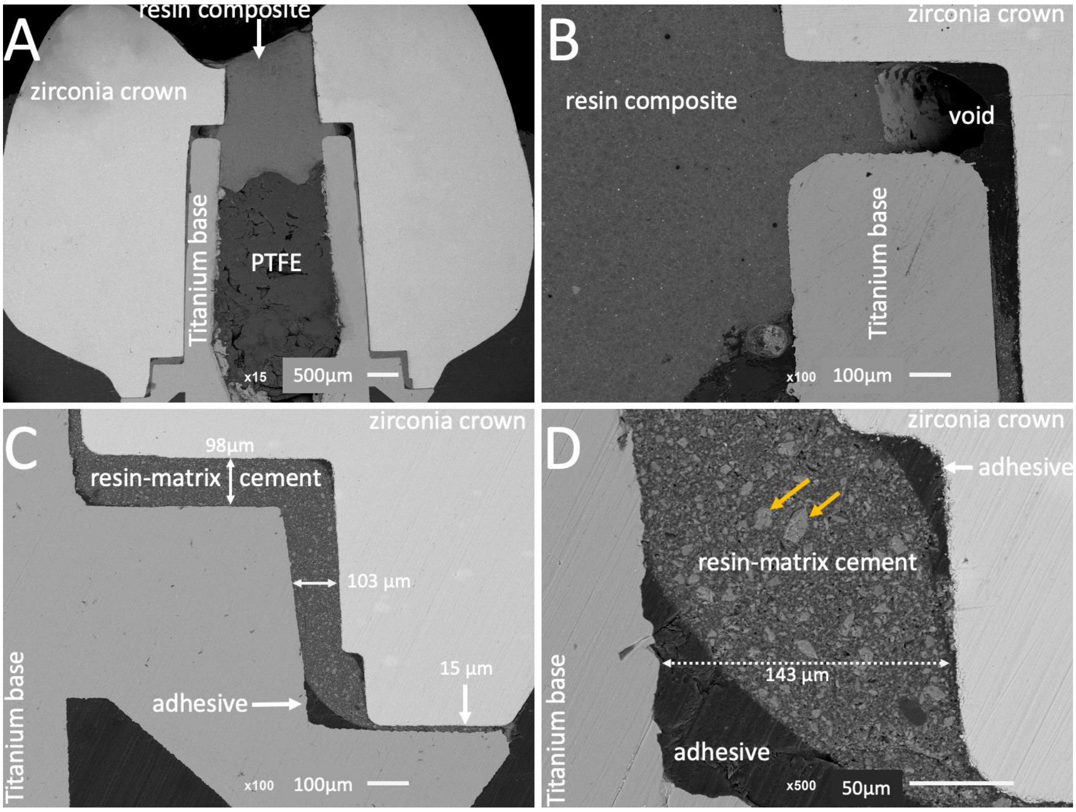

Figure 5. SEM images of the standard titanium base to resin-matrix cement and zirconia crown interfaces. Inorganic fillers were identified by yellow arrows. Magnifications at (A) x15, (B,C) x100, and x500 (D) at backscattered (BSE) mode and 15 kV.

Defects such macro-scale voids were detected at the resin-matrix cement microstructure as seen in Figure 5B. The thickness of the resin-matrix cement varied from 15 up to 143 µm depending on the interface region (Figure 5C and D). Also, a thick layer of the universal adhesive was noticed at the angle regions of the titanium base (Figure 5C). Inorganic fillers can be seen in Figure 5D.

Interfaces of the grit-blasted titanium base to matrix cement and zirconia crown are shown in Figure 6.

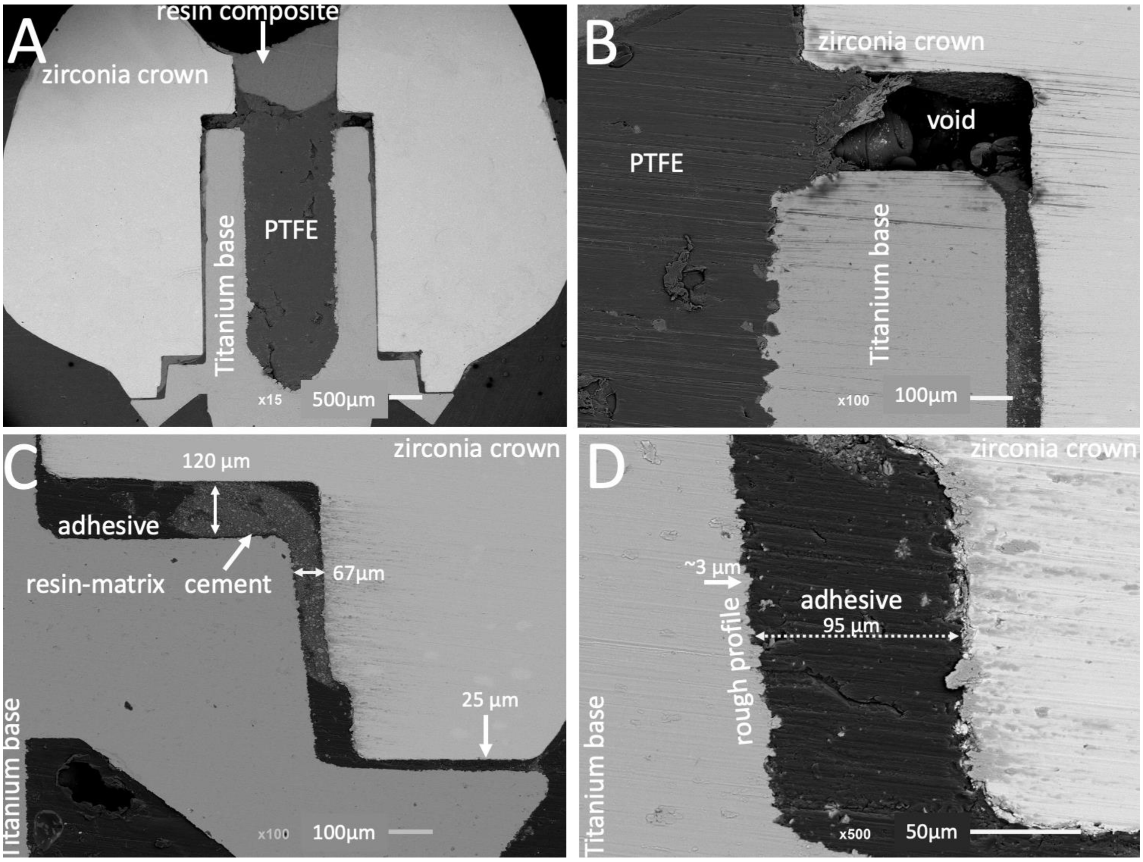

Figure 6. SEM images of the grit-blasted titanium base to resin-matrix cement and zirconia crown interfaces. Magnifications at (A) x15, (B,C) x100, and x500 (D) at backscattered (BSE) mode and 15 kV.

In Figure 6B, defects such macro-scale voids were also noted at the edge of the titanium base. The thickness of the resin-matrix cement varied from 25 up to 95 µm depending on the interface region (Figure 6C and D). Also, an excessive and thick layer of the universal adhesive was noticed at the angle regions of the titanium base (Figure 6C and D). The low volume of resin-matrix cement is noticeable in Figure 6C.

Interfaces of the grit-blasted plus anodized titanium base to matrix cement and zirconia crown are shown in Figure 7.

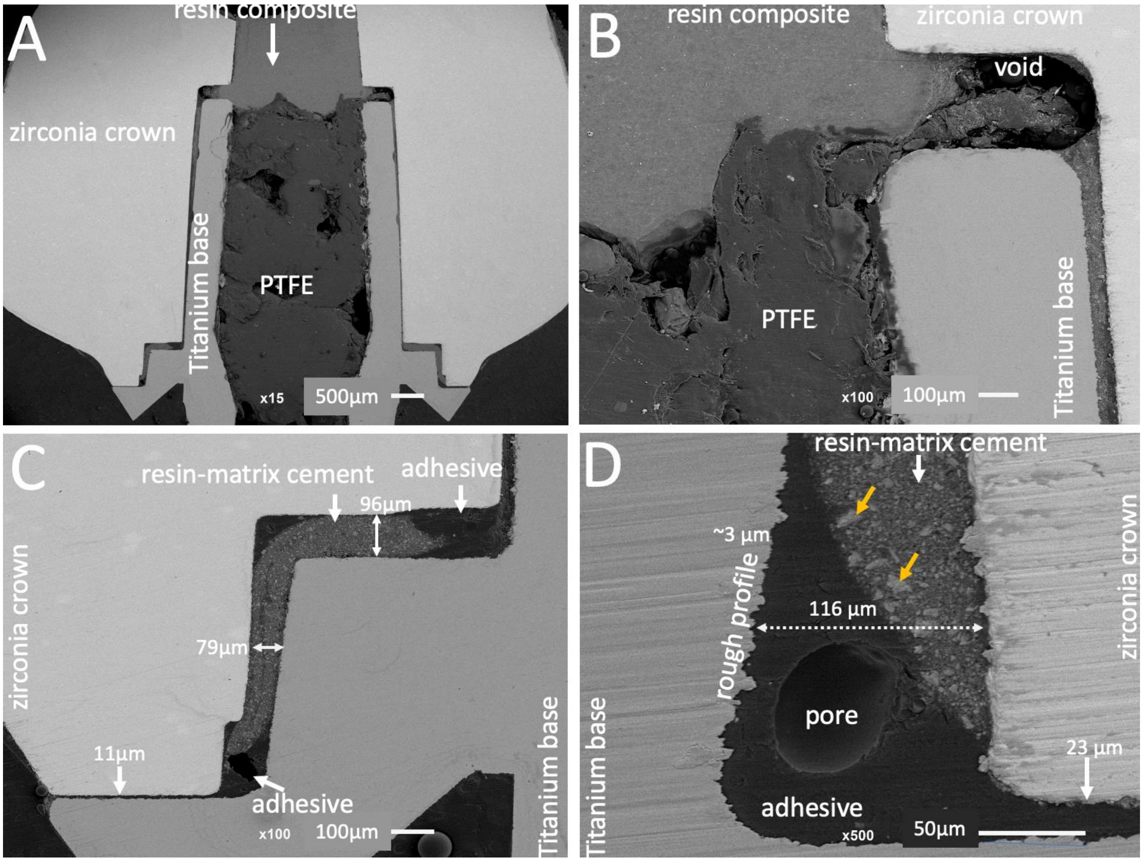

Figure 7. SEM images of the grit-blasted and anodized titanium base to resin-matrix cement and zirconia crown interfaces. Inorganic fillers were identified by yellow arrows. Magnifications at (A) x15, (B,C) x100, and x500 (D) at backscattered (BSE) mode and 15 kV.

Defects such macro-scale voids were detected at the edge of the titanium base (Figure 7C). Additionally, a macro-scale pore can be seen in the resin-matrix cement micro-structure (Figure 7D). The thickness of the resin-matrix cement varied from 23 up to 116 µm depending on the interface region (Figure 7C and D). Also, an excessive and thick layer of the universal adhesive was noticed at the angle regions of the titanium base (Figure 7C and D).

Interfaces of the anodized titanium base to matrix cement and zirconia crown are shown in Figure 8.

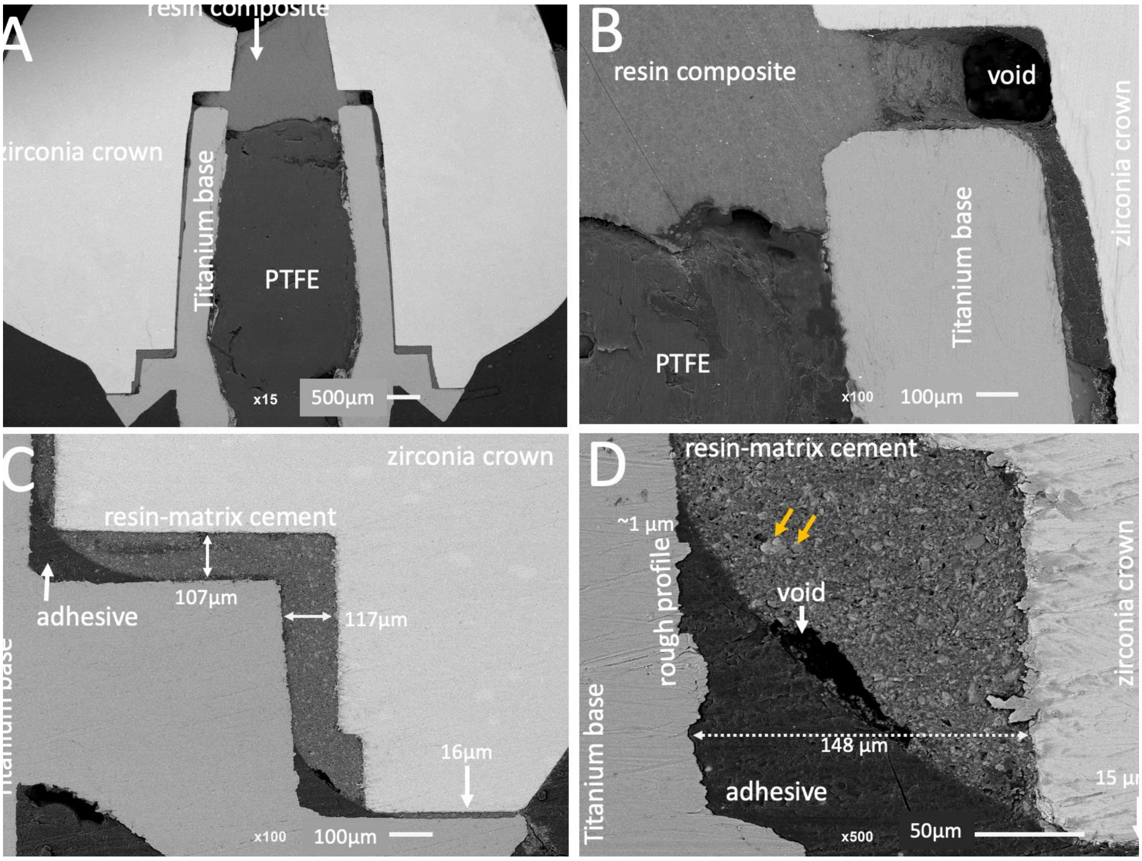

Figure 8. SEM images of the anodized titanium base to resin-matrix cement and zirconia crown interfaces. Inorganic fillers were identified by yellow arrows. Magnifications at (A) x15, (B,C) x100, and x500 (D) at backscattered (BSE) mode and 15 kV.

Defects such macro-scale voids were detected at the edge of the titanium base (Figure 8C). The thickness of the resin-matrix cement varied from 16 up to 148 µm depending on the interface region (Figure 8C and D). A thick layer of the universal adhesive was noticed at the angle regions of the titanium base (Figure 8C and D).

The roughness profile of the titanium base after cementation can be seen in Figure 9.

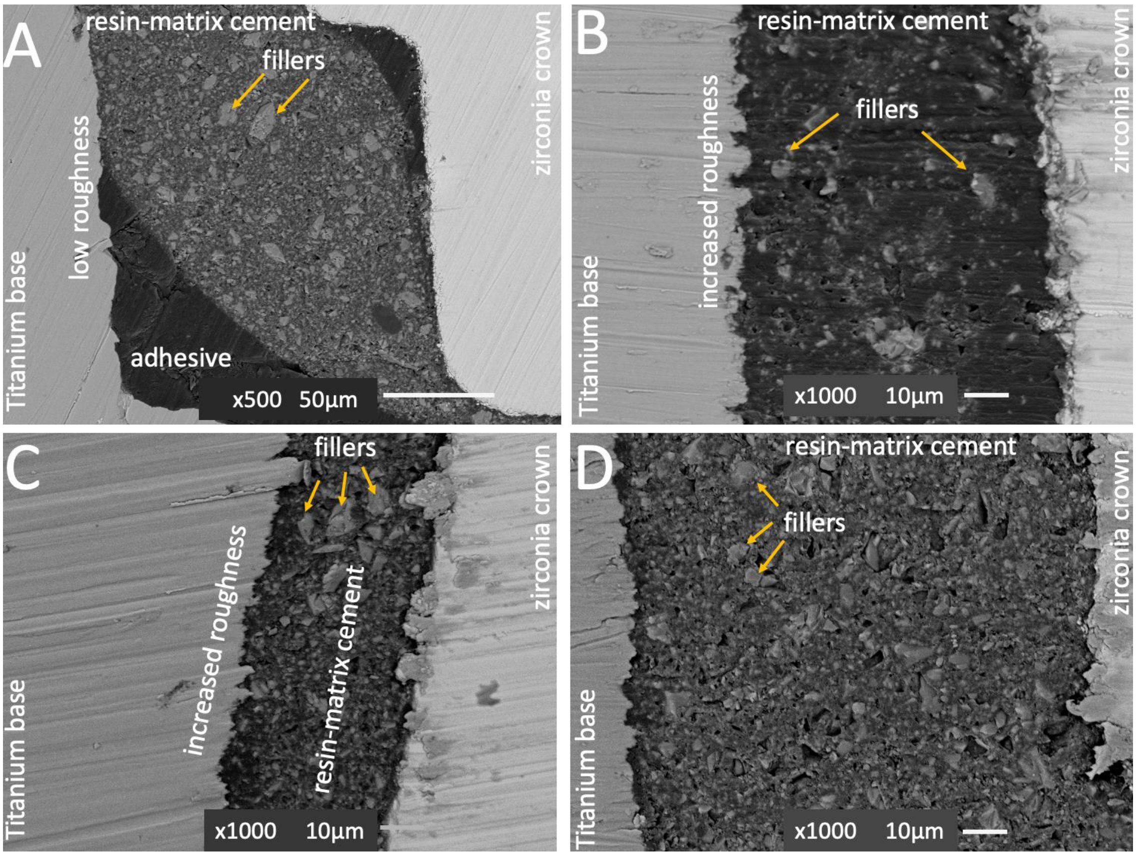

Figure 9. SEM images of the base to resin-matrix cement and zirconia interfaces. (A) free of treatment (control group). (B) grit-blasted with alumina (Al_2O_3) particles with 50 µm. (C) grit-blasted and anodized. (D) Anodized surfaces. Inorganic fillers were identified by yellow arrows. Secondary electrons (BSE) mode and 15 kV.

Indeed, the grit-blasted surfaces revealed a higher roughness profile when compared to untreated and anodized surfaces (Figure 9). The surfaces which were grit-blasted and anodized also revealed an increased roughness profile considering the SEM images of the titanium to resin-matrix cement interfaces. The dimensions of inorganic fillers were detected ranging from 1 up to 10 µm in the microstructure of the resin-matrix cement.

5. Discussion

The present study reported a detailed evaluation of titanium base surfaces after surface modification by grit-blasting and anodization as well as a measurement of the thickness of resin-matrix cements after cementation of zirconia crowns onto titanium base surfaces. The surface of titanium base was significantly increased after grit-blasting and anodization. The resin-matrix cement layer revealed an irregular layer thickness and presence of defects such as macro-scale voids and pores. Thus, the findings validate the hypothesis of this study. A detailed discussion on the main factors affecting the surface modification of titanium base and changes of the titanium base to resin-matrix cement layer is important to guide professionals in choosing the type and mode of cementation.

As seen in Figure 2, the titanium surface provided by the manufacturer revealed morphological aspects of a smooth surface that is adequate to decrease the biofilm accumulation. The roughness of titanium abutment surfaces after the industrially machining and finishing processes has been found at around 0.1-0.3 µm (8–12). However, the low roughness of titanium decrease the bonding strength to resin-matrix materials as reported by previous studies (11,13,14). In the present study, the increase in roughness is achieved by using grit-blasting with alumina (Al_2O_3) particles, as seen in Figure 2. Thus, the impact of high hardness alumina particles onto titanium surfaces removes titanium bulk material at micro-scale leading to a rough surface. That depends on the size, pressure, time, and distance of the grit-blasting process using alumina particles. A previous study reported an increase in roughness from 0.17 up to 1 µm after grit-blasting with 50-µm alumina particles on 0.25 MPa at 10-mm away from the surface for 10 s (11). Grit-blasting with alumina or silica particles has been assessed by several studies (9,11,13–17) and therefore it is the major procedure to enhance the retentive area of abutment and framework surfaces in prosthetic laboratories. Nevertheless, the presence of remnant alumina particles entrapped into the titanium surfaces due to the grit-blasting decrease the mechanical stability of the interface. Alumina particles are only mechanically retained onto the surfaces and therefore they can move out under tensile and shear stresses from occlusal loading. After grit-blasting, a functionalization of the surfaces by using silane and methacrylate-based adhesive coatings provide a high integrity interface with the resin-matrix cements (11,15,16,18–20). At first, the silane coating increase the surface wettability of zirconia or titanium surfaces by condensing SiO_2 and hydroxils groups onto the titanium oxide (Ti_xO_y) thin film. Then, a chemical bonding occurs through SiO_2 and hydroxils groups on the titanium abutment surface. On the resin-matrix cement application, a chemical reaction takes place between free radicals in the monomers' matrix and the SiO_2 and hydroxils groups to establish a chemical bonding (21).

Micro-scale valleys on the titanium and zirconia surfaces can be filled by conditioning with low-viscosity methacrylate-based adhesives such as universal adhesive used in the present study. After polymerization, rough surfaces are coated with the adhesive layer establishing a mechanical interlocking (14,22). Otherwise, a relatively viscous resin-matrix cement could not reach the deepest micro-scale valleys on the surface leading to the lack of mechanical retention and the presence of pores or voids. An absence of adhesive systems between zirconia structures and resin-matrix cements could decrease the bond strength of the interface. However, another issue is based on the application of low-viscosity adhesive that is carried out by using a hand-held micro-brush under reciprocating sliding (rubbing movement) onto the surfaces for 10, 15 or 20 s. Such procedure has an intrinsic sensitivity considering operator-induced factors such as: load, movement, time, air drying, and amount of adhesive. The, the layer thickness of adhesive varies depending on the application mode and the surface region. As seen in Figure 5, a thick layer of low-viscosity methacrylate-based adhesive was accumulated at the angles of the abutment surfaces. Also, defects such as macro-scale pores and voids can emerge from the methacrylate-based adhesive application as seen in Figures 5, 6, 7 and 8. The elastic modulus and strength values of the adhesive are lower when compared to the resin cement, abutment, and zirconia (Table 1). Considering the physical properties, the adhesive layer is the most mechanically susceptible material at the interface and therefore mechanical failures can take place by stresses under mastication loading (1-500 N), polymerization shrinkage, or thermal oscillations (i.e, 5- 50º C).

In this study, zirconia crowns manufactured by CAD-CAM showed an accurate fitting to titanium base at the gingival margins without vertical or horizontal discrepancies. The lowest thickness values of resin-matrix cements at the gingival margins were recorded at around 15 µm. Such thickness is expected when there is optimum fitting of prosthetic crowns and therefore it should provide a minimum space to accommodate the adhesive and resin-matrix cement. Thus, the inorganic fillers and organic matrix of the resin-matrix cement fill the space between the crown and substrate. The thickness of the resin-matrix cement can increase also depending on the size of inorganic fillers and flowability of the resin-matrix cement (2,23). Nevertheless, there is little information about the ideal luting space thickness for 2-piece zirconia abutments. Nevertheless, the fitting at the axial inner surfaces of zirconia crowns and titanium base resulted in higher thickness of resin-matrix cement recorded from 60 up to 148 µm (Figures 5, 6,7, and 8). A macro-scale large space for the luting agent can affect the prosthetic crown seating accuracy, causing occlusal interferences, horizontal marginal discrepancies, and low overall retention. The increased thickness of the resin-matrix cement also increases the probability of defects (pores, cracks and voids) in the microstructure of the resin-matrix cement. The defects become spot of concentration of stresses from the polymerization shrinkage, cyclic loading from mastication, and thermal oscillations. The variation of thickness and presence of defects at the resin-matrix cements were also found in a previous study (20). The propagation of cracks leading to fracture depends on those factors that can promote the mechanical failure of the prosthetic interface (20,22,24,25). Considering the physical properties of the materials, the resin-matrix cement is the second material with low elastic modulus and flexural strength in Table 1. It means the resin-matrix cement has a low stiffness and fractures can occur at lower forces when compared to zirconia or titanium (5,7,9,22,26). Indeed, the adhesive layer and resin-matrix cement are the weakest materials at the crown to titanium base interfaces.

The present in vitro study revealed a detailed microscopic analysis of zirconia crowns cemented to titanium base surfaces although limitations are related to the processing, selection, and number of materials. For instance, the study focused on the use of zirconia crowns prepared by using a standard CAD-CAM protocol. The assessment of lithium disilicate or resin-matrix blocks could be interesting for comparison with zirconia regarding the prosthetic fitting, surface conditions, and the thickness of the resin-matrix cement. The treatment of the zirconia crowns was performed only by silanization followed by conditioning with methacrylate-based adhesives. The increase of roughness of the inner surface of the prosthetic crowns also increases the mechanical interlocking of the adhesive and resin-matrix cement. Considering the cementation, several types of adhesives and resin-matrix cements should be assessed since their chemical composition and physical properties determine the mechanical interlocking, the resin-matrix cement thickness, and the mechanical integrity of the interfaces. The polymerization mode is also a key factor since the loading and mode of cementation depends on the operator. In fact, the cementation procedures of prosthetic crowns onto titanium base are not well-designed and the all the above-mentioned variables do affect the long-term success of the restorations.

6. Conclusions

Surfaces of zirconia crowns and titanium base manufactured by CAD-CAM revealed only scratches although those can be modified by physicochemical methods. Titanium surfaces modified by grit-blasting revealed morphological aspects within retentive area for cementation with resin-matrix cements. The chemical analyses showed the presence of alumina particles which maintained adhered to the titanium surfaces after grit-blasting. Alumina particles can negatively affect the bonding of adhesive and resin-matrix cement since those particles are not effectively bonded onto the titanium surfaces. In this way, failures at the interfaces might occur under occlusal loading and fatigue. The anodization procedure did not reveal a significant modification of the titanium surfaces. On the cementation interface, macro-scale defects such pores and voids were detected concerning the high sensitivity of the cementation procedure. Also, thick layers of adhesive and resin-matrix cements were detected along the interfaces. The lowest values of resin-matrix cement layers were noticed at the margins of the restorations since the fitting of the zirconia crown was well-designed at such regions.

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