Si-based thin film coating on Y-TZP: Influence of deposition parameters on adhesion of resin cement

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ABSTRACT

This study evaluated the influence of deposition parameters for Si-based thin films using magnetron sputtering for coating zirconia and subsequent adhesion of resin cement. Zirconia ceramic blocks were randomly divided into 8 groups and specimens were either ground finished and polished or conditioned using air-abrasion with alumina particles coated with silica. In the remaining groups, the polished specimens were coated with Si-based film coating with argon/oxygen magnetron discharge at 8:1 or 20:1 flux. In one group, Si-based film coating was performed on air-abraded surfaces. After application of bonding agent, resin cement was bonded. Profilometry, goniometry, Energy Dispersive X-ray Spectroscopy and Rutherford Backscattering Spectroscopy analysis were performed on the conditioned zirconia surfaces. Adhesion of resin cement to zirconia was tested using shear bond test and debonded surfaces were examined using Scanning Electron Microscopy. Si-based film coating applied on air-abraded rough zirconia surfaces increased the adhesion of the resin cement (22.78 ± 5.2 MPa) compared to those of other methods (0–14.62 MPa) (p = 0.05). Mixed type of failures were more frequent in Si film coated groups on either polished or air-abraded groups. Si-based thin films increased wettability compared to the control group but did not change the roughness, considering the parameters evaluated. Deposition parameters of Si-based thin film and after application of air-abrasion influenced the initial adhesion of resin cement to zirconia.

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1. Introduction

Yttrium stabilized tetragonal zirconia polycrystal (Y-TZP) ceramic (hereon: zirconia) lately gained popularity for restorative applications as it presents mechanical properties superior to other available all-ceramics in dentistry [1]. The possibility of milling zirconia using CAD/CAM devices also increased its clinical indications. Unfortunately, the achieved roughness after milling procedures is not sufficient to adhere resin-based cements that consequently limit their potential use for minimal invasive reconstructions [2]. In addition, traditional adhesion protocols used for silica-based ceramic systems such as acid etching with hydrofluoric acid and subsequent silanization is not effective for generating physical and chemical changes on zirconia surface [3, 4]. Since good adhesion obtained at the cementation interface could promote prevention of microleakage [4], surface modification of zirconia is essential to achieve a stable adhesive joint with resin cements [3]. Thus, several surface conditioning methods have been suggested to condition zirconia surfaces physically and/or chemically, such as air-particle abrasion using alumina particles followed by application of ceramic primers, adhesive monomers or tribotechnical silica coating (Rocatec and Cojet Systems) followed by the application of silane coupling agents [3, 5]. Chairside air-abrasion protocols using alumina or alumina particles coated with silica (tribotechnical coating) is particularly favored to condition zirconia as it eliminates the organic contaminants on the surface, improve wettability, increase

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bonding area, roughness [6,7]. Air-abrasion protocols also promote micromechanical interlocking of the resin [8,9]. Furthermore, deposition of amorphous silica layers on the zirconia surface enables silane reactions by tribochemical coating [3,10].

The impact of particle deposition on zirconia using air-abrasion protocols could promote surface changes by local lattice distortions and/or by the emergence of a new phase by ferroelastic domain switching under stress [11] or yield to complete lateral cracks [12]. When alumina particles are used, subsurface damage can occur in zirconia and this influences the survival in the cyclic fatigue testing [12–14]. Instead, the use of alumina particles coated with silica (CoJet) was reported to reduce the impact induced surface flaws and not affect the survival under cyclic fatigue loading compared to non-air abraded control groups [11]. Yet, tribochemical conditioning and silanization is not always indicated for the cementation of inlay-retained fixed dental prosthesis (FDP) when chemical adhesion could be obtained with resin cements [15].

Since controversial opinions exist regarding to surface activation of zirconia with air-abrasion protocols, new approaches for surface conditioning that do not compromise the strength and marginal adaptation of crowns and FPDs have been suggested such as selective infiltration etching [16], glazing [17], alumina coating [18], the use of adhesive promoters with bifunctional monomers [2,19,20], strong acid etching [21,22], chemical vapor deposition using hexamethyldisiloxane [23], chlorosilane gas [4], or sulphur hexafluoride [24], physical vapor deposition using the magnetron sputtering technique [25,26], non-thermal plasma exposure [27] and laser irradiation [28]. Among these methods, it can be anticipated that Si-based film deposition process could improve adhesion between zirconia and resin cement [25,26] based on the fact that the silane coupling agent shows chemical affinity to silicon oxides [3,10,29]. Previous studies showed promising results using Si-based films [25,26]. However, adhesion was not optimum at the film-zirconia interface [26].

Using magnetron sputtering technique, thin films could be deposited on zirconia surface. This physical process functionalizes surfaces and improves the surface energy of the substrate [30]. The deposition rate of compounds depends on the material of the sputtered target, gas, electrical conductivity of the sputtered target and type of power supply used to grow the film. When parameters are optimized, uniform deposition, controlled film thickness and multilayer deposition of films could be achieved [30].

The objectives of this study therefore, were to evaluate the influence of surface texture and deposition parameters for Si-based thin films using reactive magnetron sputtering on coating zirconia, to characterize the functionality of these coatings and assess their effect on adhesion of resin cement compared to conventional surface conditioning methods. The tested hypothesis was that plasma parameters used for deposition of Si-based thin films would affect the chemical reactivity of zirconia and increase adhesion of resin cement compared to conventional conditioning methods.

### 2. Materials and methods

#### 2.1. Specimen preparation and experimental groups

The brands, types, chemical compositions, manufacturers and batch numbers of the materials used in this study are listed in Table 1.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Type</th>
<th>Chemical composition</th>
<th>Manufacturer</th>
<th>Batch number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cercon zirconia</td>
<td>Ceramic core</td>
<td>Zirconium oxide, yttrium oxide, hafnium oxide</td>
<td>Dentsply/Degudent, Hanau, Germany</td>
<td>318900-3</td>
</tr>
<tr>
<td>Oxide de Aluminio Monobond-S</td>
<td>Particle for air-abrasion (45 μm)</td>
<td>Alumina oxide, Ethyl Alcohol, 3-methacryloxypropyltrimethoxy, methylethyl ketone</td>
<td>Polidental, São Paulo, Brazil</td>
<td>20919</td>
</tr>
<tr>
<td>Metal/zirconia primer</td>
<td>Ceramic primer agent</td>
<td>Methyl isobutyl ketone, phosphonic acid, acrylate, benzoyl peroxide</td>
<td>Ivoclar Vivadent, Schaan, Liechtenstein</td>
<td>N011595</td>
</tr>
<tr>
<td>Multilink</td>
<td>Resin cement</td>
<td>Benzoyl peroxide, HEMA, inorganic fillers, ytterbium trifluoride, pigments</td>
<td>Ivoclar Vivadent</td>
<td>M68692</td>
</tr>
</tbody>
</table>

### Table 1

The brands, types, chemical compositions, manufacturers and batch numbers of the materials used in this study.

- **Zirconia ceramic** (Cercon Zirconia, Dentsply/Degudent, Hanau, Germany) blocks (N = 80) (6 mm x 6 mm x 3 mm) were prepared and sintered (Vita Zirconat furnace, Vita Zahnfabrik, Bad Säckingen, Germany) according to the manufacturer’s instructions. They were then randomly divided into 8 groups (n = 10 per group) and conditioned as follows:
  - **GC**: The ceramic surfaces were ground finished to 1200 silicon carbide (SiC) paper under water cooling in a polishing machine (DP-10, Panambr, São Paulo, Brazil) and cleaned in an ultrasonic bath (Vitasonic, Vita Zahnfabrik) in distilled water for 10 min.
  - **GP**: The specimens were prepared as described for group GC. Then, a ceramic primer (Metal/Zirconia primer, Ivoclar Vivadent, Schaan, Liechtenstein) was applied to the ceramic surface using a clean brush one layer and left to react with the surface for 180 s at room temperature (20 °C), 50% relative humidity. Next, the excess primer was removed by air spray (2.8 bar) free from oil contamination for 5 s.
  - **GS**: The specimens were prepared as described for group GC. The cementation surfaces were air abraded with 30 μm alumina particles coated with silica (CoJet Sand, 3M ESPE AG, Seefeld, Germany) using a chairside air abrasion device (CoJet-Prep, 3M ESPE AG) at pressure of 2.8 bar for 10 s. The distance between the ceramic surface and the nozzle was standardized at 10 mm, at an angle of 90°. The specimens were then ultrasonically cleaned in distilled water for 10 min and silane coupling agent (Monobond S, Ivoclar Vivadent) as described in group GP.
  - **GR**: Prior to sintering process, the cementation surfaces were air abraded with 45 μm alumina particles at pressure of 2.8 bar for 10 s. The distance between the ceramic surface and the nozzle was standardized at 10 mm, at an angle of 90°. After sintering, the specimens were ultrasonically cleaned in distilled water for 10 min and then ceramic primer (Metal/Zirconia primer) was applied as described in group GP.

- **GF1**: The specimens were prepared as described for group GC. Si-based thin film coating was achieved using Argon radio frequency magnetron discharge. A silica target (KurtJ. Lesker, Pittsburgh, USA) was sputtered on the cementation surface of the zirconia. Following film deposition, the specimens were ultrasonically cleaned in distilled water for 10 min and silane coupling agent (Monobond S, Ivoclar Vivadent) was applied as described in Group GP.

- **GF2**: The specimens were prepared as described for group GC. A direct current magnetron discharge, silicon target (KurtJ. Lesker), and argon/oxygen gases (8:1 in flux) were used to promote film growth on the zirconia surface. Application of the silane coupling agent was performed as described in GF1.
Table 2
Parameters used during Si-film deposition (target composition, Ar, O₂ gas flux, pressure, power supply type, power, target-substrate distance).

<table>
<thead>
<tr>
<th>Film</th>
<th>Target</th>
<th>Ar flux (sccm)</th>
<th>O₂ flux (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Power supply type</th>
<th>Power (W)</th>
<th>Distance (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF1</td>
<td>SiO₂</td>
<td>20</td>
<td>–</td>
<td>7</td>
<td>Radio frequency</td>
<td>120</td>
<td>8</td>
</tr>
<tr>
<td>GF2/GF2R</td>
<td>Si</td>
<td>20</td>
<td>2.5</td>
<td>7</td>
<td>Direct current</td>
<td>120</td>
<td>8</td>
</tr>
<tr>
<td>GF3</td>
<td>Si</td>
<td>20</td>
<td>1</td>
<td>7</td>
<td>Direct current</td>
<td>120</td>
<td>8</td>
</tr>
</tbody>
</table>

GF3: The specimens were prepared as described for group GC. A direct current magnetron discharge, silicon target ([Kurt. Lesker]), and argon/oxygen gases (20:1 in flux) were used to promote film growth on the zirconia surface. Application of the silane coupling agent was performed as described in GF1.

GF2R: The specimens were prepared as described for group GR. A direct current magnetron discharge, silicon target ([Kurt. Lesker]), and argon/oxygen gases (8:1 in flux) were used to promote film growth on the zirconia surface (as GF2). Application of the silane coupling agent was performed as described in GF1.

Deposition parameters for groups GF1, GF2, GF3, GF2R are presented in Table 2.

Additional 15 zirconia blocks (2 mm × 10 mm × 10 mm) were manufactured for the adhesion test and were randomly divided into three groups (n = 5): (a) GC, (b) GS and (c) GF2.

2.2. Silica film growth

The surfaces of zirconia specimens were coated with Si-based thin film by physical vapour deposition (PVD) method using a reactive magnetron sputtering (RMP) technique. For this process, high purity (99.99%) SiO₂ and Si-target ([Kurt. Lesker]) and the zirconia blocks were positioned in a tailor made vacuum chamber (Laboratory of Plasma and Process, ITA, Brazil) and evacuated to a background pressure of 5 × 10⁻⁵ Torr. A previous Argon discharge was performed for 10 min to remove surface contaminations on the targets. The depositions were performed at a working pressure of 7 mTorr (~2.7 Pa). A thermocouple evaluated the temperature on the specimen holder during deposition processes. All substrates attained a maximum of 95 °C.

For GF1, a silica target was sputtered by an argon radiofrequency magnetron discharge in order to deposit the films. For GF2, GF3 and GF2R, Si atoms sputtered from the Si-target reacted with oxygen plasma, forming silicon oxides (SiOₓ) that are deposited on substrate surface, producing a thin film. Deposition of stoichiometric and non-stoichiometric films (SiOₓ where 0 ≤ x ≤ 2) was obtained by altering the oxygen concentration in the plasma [31]. The deposition time was maintained constant at 30 min and the cathode voltage and electric current were measured every 5 min to control the process stability. Three additional silicon plate samples (n = 3) that were electrochemically polished (Ra < 15 nm) and partially covered with a mask, were submitted to each film deposition process and used for film thickness measurements.

Subsequently, the specimens were removed from the reactor, cleaned ultrasonically in distilled water for 10 min and dried by oil-free air spray for 30 s at 2.8 bar.

2.3. Bond strength test and failure analysis

Equal amounts of the base and catalyst paste of resin cement (Mutilink, Ivoclar Vivadent) were mixed for 20 s and bonded to the conditioned zirconia specimens using polyethylene molds (Ø: 2.4 mm; thickness: 3 mm). Following auto-polymerization for 24 h, the specimens were stored in distilled water (37 °C ± 1 °C; 48 h). Shear bond strength test was performed using a universal testing machine (DL-1000, EMIC, São José dos Pinhais, Brazil) (crosshead speed: 1 mm/min; 100 kg F load-cell) and the bond strength (MPa) was calculated (force (in N)/adhered area in mm²).

The debonded surfaces were examined using an optical microscope at 60× magnification (Measuring Microscope MFA, Mitutoyo, Kawasaki, Japan) and Scanning Electron Microscopes (SEM) (SSX-550, Shimadzu, Kyoto, Japan) at 35×−5000× magnification in secondary electron (SE) mode to characterize the failure mode. In order to verify the presence of Si on the ceramic surfaces after bond test, additional surface analysis was performed using SEM/Energy Dispersive Spectrometer (EDX, Shimadzu).

Failure types were classified as follows: A1: adhesive failure along the interfacial region between the film and the cement; A2: adhesive failure along the interfacial region between the film and the ceramic; C: cohesive failure in the resin cement; and M: mixed failure, adhesive failure between the cement and ceramic together with cohesive failure in the resin cement and/or ceramic.

2.4. Surface roughness and Rutherford Backscattering Spectroscopy (RBS) analysis

For roughness analysis (Ra) of the zirconia surfaces following surface conditioning, four additional specimens from each group were evaluated using an optical profilometer (Wyko NT 1100, Veeco, Plainview, USA) that was connected to a computer drive containing the Software Vision 32 (Veeco). Measurements were performed at 20× magnification on two random areas (301.3 μm × 229.2 μm) of each specimen.

The following roughness parameters were measured:

Ra: Arithmetical mean of the absolute values of the surface departures from the mean plane within the sampling area in μm.

Rz: The mean value (μm) of the absolute heights of the five highest peaks and the absolute value of the five deepest valleys within the sampling area. This parameter is sensitive to the changes of pronounced topography features.

Sdr (surfaces area ratio): This ratio expresses the increment of the interfacial surface area related to the area of the projected (flat) xy plane. For a totally flat surface, the surface area and the area of the xy plane were the same and Sdr was 0.

The silicon plate samples were evaluated to measure film thickness in order to calculate the deposition rate by determining the ratio between film thickness and deposition time.

In addition, specimens were further gold sputtered in a sputtering device and analyzed under an SEM (SSX-550, Shimadzu) at 20 kV to observe the topographic changes on the zirconia ceramic surface in different groups in secondary electron (SE) mode.

Rutherford Backscattering Spectroscopy (RBS) is an ion beam analysis with high sensitivity to detect chemical elemental concentration in depth. The atomic composition of the films as deposited on zirconia specimens was analyzed by RBS (Pelletron-tanden 5SDH, National Electrostatic Corporation, Middleton, USA). RBS studies were performed with a 1 mm diameter collimated beam of 2.2 MeV 4He⁺ ions. Backscattered ions were detected using Si(Li) detectors placed at 10° scattering angles. The resolution of detection was <15 atoms/cm².

2.5. Contact angle and work of adhesion analysis (WA)

Using a tailor made goniometer (Technological Institute of Aeronautics, São José dos Campos, Brazil), contact angle measurements were performed for all three groups (GC, GS and GF2). Based on the
sessile drop technique at controlled room temperature (20 °C) and humidity (40%), a drop of deionized water (15 μL) was applied on the specimen surface and allowed to flow until it reached equilibrium. Work of adhesion \( W_A \) was calculated by the Young-Dupré equation, using the mean of the measured contact angle values obtained for each group \((\theta)\) and the interfacial energy between liquid and solid \((\gamma LS)\).

\[ W_A = \gamma LS [\cos(\theta) + 1] \]

### 2.6. Statistical analysis

Statistical analysis was performed using one-way ANOVA and post hoc multiple comparisons were made between groups by the Tukey's post hoc test (SPSS 11.0 software for Windows, SPSS Inc., Chicago, IL, USA). \(P\) values less than 0.05 were considered statistically significant for all statistical tests.

### 3. Results

The RBS analysis of the Si-based thin film identified only silicon (Si) and oxygen (O) atoms with slight differences among the films. The Si and O concentrations for each film were GF1: 31.25% and 68.75%; GF2/GF2R: 33.3% and 66.7%; and GF3: 39.2% and 60.8%, respectively. The film thickness data (\(\mu m\)) and the deposition rates (\(nm/min\)) for each film were: GF1: 0.17 and \(-5\); GF2/GF2R: 0.23 and \(-8\); GF3: 0.35 and \(-11\), respectively.

SEM images showed similar smooth surface topography for GC, GP, GF1, GF2 and GF3. From these groups, representative SEM of GF2 is presented in Fig. 1a. Other groups presented different patterns of surface topography. For GS, sharp grooves and peaks were found with random distribution (Fig. 1b). For GR, air-abrasion before the sintering process created a new retentive surface with micro hollows the grain boundaries were visible in GC (Fig. 1c) that disappeared after film deposition to GF2R (Fig. 1d). SEM image to GF specimens showed grain boundaries under the film, suggesting a nano thickness of the film and micro spot defects at some areas on the Si-film (Fig. 2a and b).

Bond strength results were significantly affected by the surface conditioning methods \((p \leq 0.05\), one-way ANOVA\). The mean bond strength data obtained in GF2R was significantly higher than those of other groups \((p \leq 0.05\) (Table 3). Air-abrasion treatment increased the roughness but the film deposition process did not.

Failure analysis of the specimens under optical microscopy revealed mainly A1 type of failure in groups GC, GP, GS, GR (Table 4). GF2R group, where the highest bond strength was observed, demonstrated mainly M type of failures (Fig. 3a). In GF2 and GF2R where M type of failures were dominant, qualitative EDS analysis on the adhesive bonding area indicated traces of Si on the zirconia surface corresponding to adhesive failure between the Si film coating and zirconia (Fig. 3b).

**Table 3**

<table>
<thead>
<tr>
<th>Groups</th>
<th>Bond strength (MPa)</th>
<th>Tukey’s test</th>
<th>Ra ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>0.12 (&lt;0.1)</td>
<td>D</td>
<td>0.12 (&lt;0.1)</td>
</tr>
<tr>
<td>GP</td>
<td>2.42 (0.3)</td>
<td>D</td>
<td>0.12 (&lt;0.1)</td>
</tr>
<tr>
<td>GS</td>
<td>14.62 (3.2)</td>
<td>B</td>
<td>0.51 (0.1)</td>
</tr>
<tr>
<td>GR</td>
<td>8.29 (1.2)</td>
<td>C</td>
<td>0.62 (0.2)</td>
</tr>
<tr>
<td>GF1</td>
<td>6.85 (2.2)</td>
<td>C</td>
<td>0.11 (0.1)</td>
</tr>
<tr>
<td>GF2</td>
<td>10.51 (1.5)</td>
<td>C</td>
<td>0.10 (0.1)</td>
</tr>
<tr>
<td>GF3</td>
<td>2.77 (0.7)</td>
<td>D</td>
<td>0.12 (0.1)</td>
</tr>
<tr>
<td>GF2R</td>
<td>22.78 (5.2)</td>
<td>A</td>
<td>0.61 (0.2)</td>
</tr>
</tbody>
</table>

*The same letters in the bond strength column indicate no significant differences in the same column (Tukey's test, \(\alpha = 0.05\)).

**Fig. 1.** SEM images showing different morphologies of the groups (a) GF2 (\(\times 2000\)); (b) GS (\(\times 2000\)); (c) GR (\(\times 5000\)) and (d) GF2R (\(\times 5000\)).
Contact angle, $W_A$, and roughness parameters (Ra, Rz and Sdr) were significantly affected by the surface conditioning evaluated in groups GC, GS and GF2 according to one-way ANOVA ($p = 0.0$) for all results (Table 5). Both air-abrasion (GS) and film deposition (GF2) improved the wettabiliy compared to GC. The best results were found in the GF2 group. The mean values for surface roughness, contact angle and work of adhesion, calculated by Young-Dupré equation, showed significant differences between groups (Tukey’s test) Table 3.

4. Discussion

Durable adhesion of resin cement to zirconia could increase the minimal invasive applications for prosthetic rehabilitation. This study evaluated whether Si coating deposition parameters would change surface texture, and affect adhesion of the cement to zirconia. In addition, the effects of the film on the adhesion properties (roughness, contact angle, WA) of zirconia were verified. Based on the results of this study, it can be stated that the Si-based coating followed by a silane application could deliver acceptable initial chemical bond strength of the resin cement to zirconia. The promising effect of Si-based coating however was particularly effective in GF2R (film associated with a rough surface) but not in all groups. Therefore, the tested hypothesis that application parameter deposition of Si-based thin films would affect chemical reactivity of zirconia and increase initial adhesion compared to conventional conditioning methods could be partially accepted.
The success of adhesion in order to prevent degradation under aggressive environments depends on the chemical compatibility and durability of the interface between different materials. The surface properties of the materials involved and the study of adhesion mechanism are important issues for predicting the behavior of bonded interfaces through which bond strength could be optimized [32]. In this regard, surface wettability in particular is of importance and in this study, the Si-based thin film improved wettability. Physical and chemical properties of materials involved in cementation process affect the stability of the interface. An essential aspect in the cementation process is the cement choice. The cement chosen in this study (Multilink) is a bis-GMA based conventional resin composite luting agent that requires moisture control and application of a silane and a bonding agent to achieve effective adhesion to zirconia. This resin cement was chosen because bifunctional monomers are not present in its chemical composition. Functional monomers present in some resin cements increase bond strength to zirconia [26,33] and could have masked the real effect of novel surface treatments proposed in this study. The cement choice seemed to be not relevant according to the failure types observed in this study, since the weakest interface was between the Si-based film and zirconia. Previous studies have evaluated the bond strength of bis-GMA based resin cement to zirconia and reported that the use of adhesive promoters was not effective at promoting an increase in adhesion to zirconia [3,7,26]. In agreement with these studies, in this study, GC group presented exclusively pre-test failures and GP showed less chemical adhesion. On the other hand, GS presented better initial bond strength results compared to those of GC and GP. This indicates that surface activation through particle abrasion and in particular using silica-containing abrasives is essential to achieve better adhesion to zirconia with this cement. Yet, the results could still be considered weak. Using the plasma technique for film deposition as a conditioning strategy for better adhesion to zirconia, the effect of the nanofilm deposited on zirconia was reported to promote the chemical adhesion of the silane coupling agent [4]. This study showed that air-abrasion with 50 μm alumina abrasive followed by gas-phase chlorosilane pretreatment for depositing ultra-thin silica-like layers improved adhesion to zirconia using traditional silanation and bonding techniques. Thus, the response of an interface and its chemical interactions with other molecules may be obtained by superficial surface modifications using advanced techniques. It is well known that silane coupling agent shows chemical affinity with silicon oxides [3,10,29]. The use of silane is recommended for feldspathic ceramics to form a siloxane network with the silica in the glass phase of the ceramics to improve the bond strength. Due to the chemical stability of zirconia, adhesion of silane coupling agent was reported to be poor and presented a higher potential for hydrolytic degradation [10,34]. In a previous study, it was shown that Si-based film could improve bond stability when compared to solely air-abraded zirconia [26]. Thus, this study was conducted in order to grow different Si-based thin films using the magnetron sputtering technique at varying deposition parameters on flat zirconia surfaces.

When the mean bond results on flat surfaces are compared (GC, GP, GF1, GF2, and GF3), it was evident that chemical adhesion (GF2 and GF1) improved the results compared to the remaining groups. Even in the group GR, where the main adhesion mechanism used was based on micromechanical retention, no statistical difference was verified between this group and those of GF1 and GF2. Moreover, GF2R revealed statistically higher results compared to the silica coating and silanization method applied in GS. A rough surface presents a larger surface area, increasing bond sites, that eventually increases the bond strength by micromechanical retention and improves wettability for zirconia ceramics [7,8]. Despite of this, reports in the literature affirm that the original roughness produced by milling during fabrication is not sufficient to promote adhesion to resin cements zirconia [2]. This study showed that roughened surface produced before firing (green state) using the air-abrasion procedure (GR) was not sufficient to promote initially as good results as the group that received chairside silica coating (GS). This finding is in disagreement with a recent study [35]. It is known that air-abrasion of zirconia surface after sintering causes phase transformation from tetragonal to monoclinic [36,37]. As it is demonstrated in groups GS and GR, presenting higher roughness for the Ra parameter, indicates that monoclinic state may be more reactive than tetragonal polycrystals [2,38]. However, when a Si-based thin film was used on GR, forming the group GF2R, the initial bond strength was improved, increasing the frequency of mixed failures. In addition, surface roughness remained unchanged following the film deposition process, suggesting that the chemical modification promoted in GF2 and GF2R could be the mechanism used to increase bond strength compare to the same rough surface without film (GP and GR). The growth of a thin film on the surface using a cold plasma technique can modify surface chemical and physical properties without changing the properties of the bulk material [30]. However, the effect of treatment on the mechanical properties of zirconia applied in the group GR was not studied in this study but warrants future research.

Regarding film adhesion in zirconia substrate, the results for GF1, GF2 and GF3 occurred independent of the micromechanical adhesion mechanism as they were produced on a flat surface. Yet, the film detached from the zirconia surface together with the resin cement after debonding, suggests that chemical affinity of the Si-based films to the cement followed by silanization was higher than to zirconia surface. Consequently, the effect of this film on the bond strength with cement cannot be measured. The lowest bond values obtained in GF3 showed that the presence of Si-based thin film as interlayer between zirconia and resin cement in combination with the silane application, was not sufficient to promote strong initial bond strength as this film was not found to be attached to the zirconia surface after bond test. Reduced oxygen flux in GF3, diminishing the oxygen concentration in this film could change nucleation behavior of the film during deposition process, influencing the adhesion between the film and the ceramic surface [30]. For GF1, the reasons for the increase in oxygen concentration were not investigated in this research. Although elemental concentration could be expected to be similar to GF2, since the plasma used for GF1 was nonreactive (only argon gas), probably the sputtering of SiO2 target preferentially removed oxygen [30]. However, the results suggest that the increase of oxygen in the Si-based film (as in GF1) could promote higher internal stress on the Si-based film, diminishing adhesion to zirconia in this group. Although GF1 and GF2 presented statistically similar results, analysis of the failure types under SEM and using EDS, showed that the resin cement and the coating film remained on the zirconia surface after bond test only for the group GF2.

According to SEM images, Si-based thin film seems to be dense but micrometric flaws in the film integrity were still apparent. The localized pinhole defects in this film could be induced as a consequence of impurities on the zirconia surface, intrinsic film stress, low energy surface of zirconia or plasma sputtering on the film [30]. A recent study using the chemical deposition process to grow an ultra-thin silicate-layer suggested that porosities in the film would make it more susceptible to stresses eventually enhancing hydrolytic degradation [39]. The reason for the presence of these defects needs to be explored and improved in future studies. Such defects could be determinant on the adhesion of the film, reducing initial bond strength results. In addition, the use of sputtering on the ceramic surface prior to film deposition could improve the adhesion between film and zirconia [30].
The deposition rate for Si-based thin films decreased from approximately 11–8 nm × min⁻¹ as the oxygen flux increased from 1 to 2.5 sccm in the gas discharged for GF3 and GF2, respectively, influencing the film thickness. This is due to the process of target poisoning (oxidation) that reduces the sputtering yield off the target and, accordingly, the condensing atom flux toward the zirconia surface [25]. According to van Hattum and coworkers, as the oxygen flow rate increases, the gas discharge is characterized by a sudden decrease in silicon atoms toward the growing film, with a simultaneous increase in SiO₂ molecules, indicating coverage of the target and substrate by the compound [31]. Furthermore, the use of a silica target for GF1 reduced the deposition rate to 5 nm × min⁻¹ because the insulating aspect inherent to this target reduces the sputtering rate. This is the reason why a radio frequency was chosen to substitute direct current as the power supply in this group (GF1).

SEM and atomic force microscopy (AFM) analysis have been often used to evaluate the surface roughness in similar studies [2,40]. In this study, profilometry was used for qualitative and quantitative analyses of the roughness following surface conditioning methods. This is an optical technique for measuring surface roughness using optical interference, in which the light intensity of the fringes is related to the surface height. Profilometry presents a nanometric vertical resolution with a dynamic range (scan size) that greatly exceeds the microscope probes, providing quick images of the surface similar to SEM with the roughness parameter supported by 3D image as in AFM [29].

Adequate roughness parameter analyses and a large scan size to evaluate the effect of topography modification on adhesion can help to understand the behavior of a new surface conditioning method on bond strength and adhesion properties. Ra has been used frequently in order to express the topographic changes on the zirconia surface in the dental literature and considered as an important parameter for general use [40]. However, it is important to stress that the Ra parameter reduces the effects of odd scratches or non-typical irregularities. Instead, Rz presents additional information, revealing the possible presence of defects on the surface. If Ra and Rz parameters show similar amplitudes, a uniform standard of roughness is expected to be present on the surface. The large difference between the Ra and Rz parameters showed the presence of spot flaws on the conditioned zirconia, even on the flat surface.

Analysis of the roughness results of GC, GS, and GF2 showed that Ra increased by 0.4 μm when the surfaces were air-abraded, suggesting a better micromechanical interlocking between this surface with resin cements. The increase in the Rz parameter between GS and GC (3.5 μm) verified the energy effect produced by particle impact during air-abrasion producing morphological surface changes. The Sdr parameter indicated an increase in surface area of approximately 80% when the Y-TZP ceramic was air-abraded, increasing bonding sites available to react with an adhesive promoter. Thus, this procedure can improve bond strength results, affecting both physical (micromechanical interlocking mechanism) and chemical (adsorption mechanism) adhesion and at the same time increasing the wettability of the zirconia surface. However, several studies showed that additional chemical adhesion promoted only by martensitic transformation mediated by air-abrasion procedure with alumina particles but it was inefficient to resist hydrolytic degradation after aging of the interface [4,8,39]. The results of surface roughness for all three parameters (Ra, Rz and Sdr) in GF2 were not statistically significant compared to GC (control group), suggesting that the improved contact angle and $W_A$ in GF2 occurred due to chemical modification on the surface. $W_A$ plays a vital role in adhesion and is defined as the reversible work, required separating a unit area of interface between two different materials [32]. Even modest changes in their values can cause large differences in practical adhesion measurements [32]. The strong implication is that if spontaneous spreading does not occur, the interfacial contact could be incomplete. This study showed that $W_A$ for GF2 (calculation based on 20°) was improved compared to the other groups (GC and GS), implying that chemical modification on the surfaces provided by the Si-based thin film was more efficient than physical and chemical changes promoted by air-abraded surface regarding this property.

5. Conclusions

Overall, this study showed that the air-abrasion protocol used in GS improved the contact angle against the polished surface in GC. Likewise, the effect of the Si-based thin film on the surface was significant. Despite using a smooth surface for these groups, they exceeded the angle limit (20°) detected by the goniometer. There are two primary reasons for seeking methods to minimize the contact angle of the bonding agent against the zirconia surface: (a) minimum contact angle corresponds to maximum area and intimacy of contact between the bonding agent and ceramic surface and (b) minimum contact angle corresponds to a maximum thermodynamic work of adhesion ($W_A$). The Si-based thin films deposited on zirconia by reactive magnetron sputtering technique did not change the roughness, considering the parameters evaluated. The adjusted deposition parameters for Si-based thin films followed by silane application increased the initial bond strength results between resin cement and zirconia ceramic tested but the variation in deposition parameters seemed to play a role on improved adhesion with zirconia interface. Initially rough zirconia surfaces made it possible to achieve better deposition of Si-based thin films compared to smoother surfaces. Different sputtering parameters for Si-based thin film deposition affected the chemical properties of the zirconia surface and all conditioning methods tested improved wettability of the zirconia surface compared to the control group. Finally, adjustments in the parameters used for a more uniform film growth and for improving adhesion of the film on the substrate, using different deposition techniques, require further investigations. Irrespective of future research, the plasma technique is not a common process in dentistry and the cost of its implementation in a prosthodontics laboratory remains currently high.

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