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Instituto de Ciência e Tecnologia

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**DEPOSIÇÃO DE HIDRETO DE SILÍCIO SOBRE A ZIRCÔNIA
EM DIFERENTES TEMPOS: análise química, microestrutural e
durabilidade da união ao cimento resinoso**

2018

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da união ao cimento resinoso**

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Orientadora: Pesq. III Dra. Renata Marques de Melo Marinho

Coorientador: Dr. Tiago Moreira Bastos Campos

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RESUMO

O objetivo deste estudo foi avaliar a Deposição Química na Fase Vapor Assistido por Plasma (PECVD) com hidreto de silício (SiH_4) em zircônia VITA YZ HT em diferentes tempos, bem como os seus efeitos nas características superficiais do material e na união ao cimento resinoso antes e após a termociclagem. Blocos de zircônia Vita YZ HT foram obtidos, polidos, sinterizados e divididos em 5 grupos, de acordo com o tempo de PECVD ($n = 31$): Zr-30 (30s), Zr-60 (60s), Zr-120 (120s) e Zr-300 (300s). O grupo controle (Zr-0) não recebeu deposição. Análises de DRX, FTIR, EDS, FE-SEM, XPS, goniometria e perfilometria foram utilizadas para caracterização química e topográfica. O silano Monobond N foi aplicado na superfície e um cilindro de cimento resinoso (Variolink N) foi confeccionado ($3 \times 3 \text{ mm}$). Metade dos espécimes de cada grupo foi armazenada por 24 h ou submetida à termociclagem (6×10^3 ciclos). Teste de resistência ao cisalhamento (SBS) foi realizado. Os resultados foram submetidos aos testes one-way Anova e Tukey ($\alpha = 0,05$). Para os grupos experimentais, o XPS mostrou que a formação de ligações Si-O contribuiu para o aumento da Energia Livre de Superfície (ELS). MEV-FEG e EDS mostraram que quanto maior o tempo de deposição, maior a quantidade de silício na superfície, apresentando apenas fase tetragonal. Zr-60 e Zr-300 apresentaram maior e menor rugosidade superficial, respectivamente. O silício penetrou na microestrutura, causando maior concentração de tensão. A resistência de união ao cimento resinoso foi melhorada após todos os tempos de deposição da PECVD. Portanto, a técnica de PECVD com o composto químico SiH_4 associada ao tratamento químico com primer universal baseado em metacrilato de silano é uma alternativa promissora para a manutenção da ligação entre cimento resinoso e zircônia HT.

Palavras-chave: Materiais dentários. Zircônia. Silício. Envelhecimento. Resistência ao cisalhamento.

Monteiro JB. Deposition of silicon hydride on the zirconia in different times: chemical, microstructural analyses and bond strenght with resin cement [tesis]. São José dos Campos (SP): São Paulo State University (Unesp), Institute of Science and Technology; 2018.

ABSTRACT

The aim of this study was to evaluate the effect of Plasma-enhanced Chemical Vapor Deposition (PECVD) with silicon hydride (SiH_4) on VITA YZ HT zirconia at different times, as well as its effects on material surface characteristics and bonding to resin cement before and after thermocycling. Blocks of VITA YZ HT zirconia were obtained, polished, sintered, and divided into five groups, according to PECVD time ($n = 31$): Zr-30 (30 s), Zr-60 (60 s), Zr-120 (120 s), and Zr-300 (300 s). The control group (Zr-0) did not receive deposition. XRD, FTIR, EDS, FE-SEM, XPS, goniometry, and profilometry analyses were used for chemical and topographic characterization. Monobond N silane was applied to the surface, and a cylinder of resin cement (Variolink N) was made (3×3 mm). Half of the specimens of each group were stored for 24 h or subjected to thermocycling (6×10^3 cycles). A shear bond strength (SBS) test was performed. Results were subjected to one-way ANOVA and Tukey's tests ($\alpha = 0.05$). For experimental groups, XPS showed that formation of Si-O bonds contributed to increased Surface Free Energy (SFE). FE-SEM and EDS showed that the longer the deposition time, the greater the amount of silicon on the surface, presenting only a tetragonal phase. Zr-60 and Zr-300 presented higher and lower surface roughnesses, respectively. The silicon penetrated the microstructure, causing higher stress concentrations. The bond strength to resin cement was improved after all PECVD deposition times. Thus, the PECVD technique with the chemical compound SiH_4 , associated with chemical treatment with universal primer based on silane methacrylate, is a promising alternative for maintaining bonding between resin cement and HT zirconia.

Keywords: Dental ceramics. Zirconia. Silicon. Aging. Shear strength.

1 INTRODUÇÃO

A busca constante por materiais restauradores totalmente cerâmicos que associam estética e alta resistência juntamente com a evolução dos sistemas CAD/CAM (*Computer-Aided Design/Computer-Aided Manufacturing*) contribuíram para o desenvolvimento de cerâmicas à base de zircônia Y-TZP (*Yttria Tetragonal Zirconia Polycrystal*) (Manicone et al., 2007; Denry, Kelly, 2008). A zircônia Y-TZP é um material polimórfico, existente em três formas cristalográficas distintas: monoclinica, tetragonal e cúbica (Garvie et al., 1975). Para a estabilização da zircônia em sua fase tetragonal, 3% de mol de óxido de ítrio foi incluído em sua composição (Piconi, Maccauro, 1999), garantindo uma alta resistência à flexão, alta tenacidade à fratura e melhor estabilidade química (Piconi, Maccauro, 1999; Adatia et al., 2009).

A seleção clínica dos sistemas cerâmicos se baseia nas propriedades mecânicas e ópticas dos materiais, dessa forma, a zircônia Y-TZP se tornou viável para utilização em tratamentos restauradores indiretos totalmente cerâmicos, como infraestrutura de coroas totais e próteses parciais fixas (Denry, Kelly, 2008; Koutayas et al., 2009), sendo ainda necessária a aplicação de cerâmicas de revestimento para a obtenção de uma estética adequada (Thompson et al., 2011). Contudo, fraturas e lascamentos são os problemas mais comuns que ocorrem no revestimento da cerâmica sobre a infraestrutura de zircônia (Raigrodski et al., 2006; Miyazaki et al., 2013), porque são materiais que apresentam grau de estresse interfacial gerado por diferenças de temperatura e incompatibilidade de expansão térmica e de temperatura de transição vítrea (Fischer et al., 2008; Thompson et al., 2011).

As zircônias altamente translúcidas (HT – *high translucency*) foram desenvolvidas para dispensar a necessidade de aplicação de uma cerâmica de

cobertura (Miyazaki et al., 2013; Tong et al., 2016) e essa propriedade de translucidez garantiu que fosse usada para restaurações monolíticas (Zhang et al., 2016), as quais podem ser indicadas em situações em que o espaço protético disponível é limitado, pois a espessura oclusal pode ser reduzida até um limite inferior de 0,5 mm, mantendo resistência suficiente para suportar as cargas oclusais (Rinke, Fischer, 2013a; Nakamura et al., 2015; Nordhal et al., 2015; Sorrentino et al., 2016) ou para casos estéticos, como a confecção de facetas laminadas ultrafinas, em que o fator adesão ao tecido dentário é primordial (Souza et al., 2018). O problema clínico das restaurações monolíticas à base de zircônia é a dificuldade em alcançar uma adesão adequada com os tecidos naturais e/ou os cimentos odontológicos, levando à perda de retenção na interface da restauração (Thompson et al., 2011; Rinke et al., 2013b; Güncü et al., 2015). Diferentes razões podem justificar essa falha, seja a microestrutura (material policristalino sem fase vítrea, o que a torna um material ácido resistente - não condicionável) e sua natureza hidrofóbica, a qual provoca baixa umidificação da superfície da zircônia pelos cimentos adesivos que são comumente usados (Manicone et al., 2007).

Atualmente, várias técnicas desenvolvidas *in vitro* ou clinicamente estão sob investigação para resolver o problema de união ao cimento resinoso e ao substrato dentário. A maioria concentra-se em modificações micromecânica e/ou química da superfície dessas cerâmicas, abrindo uma infinidade de opções de tratamento (Khan et al., 2017) em busca da durabilidade da união dessa cerâmica com os cimentos resinosos e o tecido dentário (Inokoshi et al., 2014; Tzanakakis et al., 2016). Portanto, mesmo com as técnicas sendo aplicadas associadamente, ainda não foram suficientes para gerar uma união duradoura em longo prazo entre cimento resinoso e zircônia (Da Silva et al., 2014; Khan et al., 2017). Existem relatos na literatura de que a associação entre o tratamento mecânico (jateamento de sílica) combinado com o químico (usando primer

cerâmico) forneceu a maior eficácia de ligação à zircônia mesmo com o envelhecimento térmico, porém, a superfície da zircônia pode sofrer mudanças significativas, tornando-a susceptível à falha (Inokoshi et al., 2013).

Até o momento, não há concordância quanto ao método não destrutivo e eficiente de tratamento de superfície para obter uma resistência de união ótima entre a zircônia HT e o cimento resinoso, por isso, faz-se necessário buscar um tratamento que tenha a capacidade de funcionalizar quimicamente a superfície da zircônia para se conseguir uma ligação adesiva, sem causar danos estruturais e mecânicos à superfície, mas que resulte na aderência química e no aumento da resistência de união entre os materiais, para que sucesso clínico em longo prazo dessas restaurações seja alcançado.

Diante do exposto, estudos têm mostrado que a técnica de Deposição Química na Fase Vapor Assistida por Plasma (PECVD – *Plasma-Enhanced Chemical Vapor Deposition*) com diferentes compostos químicos é um tratamento de superfície que resulta na aderência química e no aumento da resistência de união entre os substratos obtidos com a formação de uma nuvem de plasma (Piascik et al., 2009; Queiroz et al., 2011; Druck et al., 2015; Kaimal et al., 2017). Quando associada à aplicação de primer universal à base de metacrilato de silano, contribui com a promoção de uma adesão duradoura com o agente de cimentação (Da Silva et al., 2014), o que é desejável em muitas situações clínicas, como em dentes com preparações muito curtas ou finas e por isso, uma forte adesão química levaria a um aumento na resistência à fratura e fadiga em longo prazo (Thompson et al., 2011; Druck et al., 2015).

2 ARTIGO

2.1 Artigo – Monteiro JB, Prado PHCO, Campos TMB, Machado JPB, Trava-Airolti VJ, Melo RM. Caracterização microestrutural e análises química e de união de uma zircônia de alta translucidez após a deposição química na fase vapor assistida por plasma com hidreto de silício / *Microstructural characterization and chemical and bonding analyses of a high-translucency zirconia after plasma-enhanced chemical vapor deposition with silicon hydride**

RESUMO

O objetivo deste estudo foi avaliar a Deposição Química na Fase Vapor Assistida por Plasma (PECVD) com hidreto de silício (SiH_4) em zircônia VITA YZ HT em diferentes tempos, bem como os seus efeitos nas características superficiais do material e na união ao cimento resinoso antes e após a termociclagem. Blocos de zircônia Vita YZ HT foram obtidos, polidos, sinterizados e divididos em 5 grupos, de acordo com o tempo de PECVD ($n = 31$): Zr-30 (30s), Zr-60 (60s), Zr-120 (120s) e Zr-300 (300s). O grupo controle (Zr-0) não recebeu deposição. Análises de DRX, FTIR, EDS, FE-SEM, XPS, goniometria e perfilometria foram utilizadas para caracterização química e topográfica. O silano Monobond N foi aplicado na superfície e um cilindro de cimento resinoso (Variolink N) foi confeccionado ($3 \times 3 \text{ mm}$). Metade dos espécimes de cada grupo foi armazenada por 24 h ou submetida à termociclagem (6×10^3 ciclos). Teste de resistência ao cisalhamento (SBS) foi realizado. Os resultados foram submetidos aos testes one-way Anova e Tukey ($\alpha = 0,05$). Para os grupos experimentais, o XPS mostrou que a formação de ligações Si-O contribuiu para o aumento da Energia Livre de Superfície (ELS). MEV-FEG e EDS mostraram que quanto maior o tempo de deposição, maior a quantidade de silício na superfície, apresentando apenas fase tetragonal. Zr-60 e Zr-300 apresentaram maior e menor rugosidade superficial, respectivamente. O silício penetrou na microestrutura, causando maior concentração de tensão. A resistência de união ao cimento resinoso foi melhorada após todos os tempos de deposição da PECVD. Portanto, a técnica de PECVD com o composto químico SiH_4 associada ao tratamento químico com primer universal baseado em metacrilato de silano é uma alternativa promissora para a manutenção da ligação entre cimento resinoso e zircônia HT.

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Palavras-chave: Materiais dentários. Zircônia. Silício. Envelhecimento. Resistência ao cisalhamento.

ABSTRACT

The aim of this study was to evaluate the effect of Plasma-enhanced Chemical Vapor Deposition (PECVD) with silicon hydride (SiH_4) on VITA YZ HT zirconia at different times, as well as its effects on material surface characteristics and bonding to resin cement before and after thermocycling. Blocks of VITA YZ HT zirconia were obtained, polished, sintered, and divided into five groups, according to PECVD time ($n = 31$): Zr-30 (30 s), Zr-60 (60 s), Zr-120 (120 s), and Zr-300 (300 s). The control group (Zr-0) did not receive deposition. XRD, FTIR, EDS, FE-SEM, XPS, goniometry, and profilometry analyses were used for chemical and topographic characterization. Monobond N silane was applied to the surface, and a cylinder of resin cement (Variolink N) was made (3×3 mm). Half of the specimens of each group were stored for 24 h or subjected to thermocycling (6×10^3 cycles). A shear bond strength (SBS) test was performed. Results were subjected to one-way ANOVA and Tukey's tests ($\alpha = 0.05$). For experimental groups, XPS showed that formation of Si-O bonds contributed to increased Surface Free Energy (SFE). FE-SEM and EDS showed that the longer the deposition time, the greater the amount of silicon on the surface, presenting only a tetragonal phase. Zr-60 and Zr-300 presented higher and lower surface roughnesses, respectively. The silicon penetrated the microstructure, causing higher stress concentrations. The bond strength to resin cement was improved after all PECVD deposition times. Thus, the PECVD technique with the chemical compound SiH_4 , associated with chemical treatment with universal primer based on silane methacrylate, is a promising alternative for maintaining bonding between resin cement and HT zirconia.

Keywords: Dental ceramics. Zirconia. Silicon. Aging. Shear strength.

Microstructural characterization and chemical and bonding analyses of a high-translucency zirconia after Plasma-enhanced Chemical Vapor Deposition with silicon hydride

Objectives. The aim of this study was to evaluate the effect of Plasma-enhanced Chemical Vapor Deposition (PECVD) with silicon hydride (SiH_4) on VITA YZ HT zirconia at different times, as well as its effects on material surface characteristics and bonding to resin cement before and after thermocycling.

Methods. Blocks of VITA YZ HT zirconia were obtained, polished, sintered, and divided into five groups, according to PECVD time ($n = 31$): Zr-30 (30 s), Zr-60 (60 s), Zr-120 (120 s), and Zr-300 (300 s). The control group (Zr-0) did not receive deposition. XRD, FTIR, EDS, FE-SEM, XPS, goniometry, and profilometry analyses were used for chemical and topographic characterization. Monobond N silane was applied to the surface, and a cylinder of resin cement (Variolink N) was made ($3 \times 3 \text{ mm}$). Half of the specimens of each group were stored for 24 h or subjected to thermocycling (6×10^3 cycles). A shear bond strength (SBS) test was performed. Results were subjected to one-way ANOVA and Tukey's tests ($\alpha = 0.05$).

Results. For experimental groups, XPS showed that formation of Si-O bonds contributed to increased Surface Free Energy (SFE). FE-SEM and EDS showed that the longer the deposition time, the greater the amount of silicon on the surface, presenting only a tetragonal phase. Zr-60 and Zr-300 presented higher and lower surface roughnesses, respectively. The silicon penetrated the microstructure, causing higher stress concentrations. The bond strength to resin cement was improved after all PECVD deposition times. Thus, the PECVD associated with silane was able to increase bonding between zirconia and resin cement.

Significance. The PECVD technique with the chemical compound SiH_4 , associated with chemical treatment with universal primer based on silane methacrylate, is a promising alternative for maintaining bonding between resin cement and HT zirconia.

Keywords

Dental ceramics, zirconia, silicon, aging, bond strength.

1. Introduction

The constant search for fully ceramic restorative materials that combine esthetics and high strength, along with the evolution of CAD/CAM (Computer-aided Design/Computer-aided Manufacturing) systems, has contributed to the development of Y-TZP zirconia (Yttria Tetragonal Zirconia Polycrystal) [1,2]. Zirconia is a polymorphic material, existing in three distinct crystallographic forms: monoclinic, tetragonal, and cubic [3]. For the stabilization of zirconia in its tetragonal phase, a 3% mol of yttrium oxide was included in its composition [4], guaranteeing high flexural strength, high fracture toughness, and better chemical stability [4,5].

The clinical indication of ceramic systems is based on the mechanical and optical properties of the materials. Therefore, the Y-TZP zirconia has become viable for use in indirect ceramic restorations, such as total crowns and fixed partial dentures [1,6], where veneering ceramics must also be applied for suitable esthetics [7]. Fractures and chipping are the most common problems in the veneered zirconia core [8,9], mostly due to interfacial stress-generated thermal coefficient mismatches and zirconia's low thermal conductivity [7,10].

The high-translucency (HT) zirconia was developed to avoid the need for the application of a veneering ceramic [9,11], and this translucency ensured that it could be used in full-contour anterior and posterior restorations [12]. Those restorations are mainly indicated for situations where the interocclusal space is limited, since the occlusal thickness can be reduced to 0.5 mm while maintaining enough resistance to withstand occlusal loads [13–16], or for esthetic purposes, such as the manufacture of ultrafine laminated veneers [17]. The clinical issue arising from the use of monolithic zirconia restorations is its difficulty in achieving strong adhesion with dental cements and loss of retention at the restoration interface [7,18,19]. Several reasons may explain this type of failure, such as its microstructure (a polycrystalline material without a glassy phase, which makes it an acid-resistant material and thus non-etchable) or its hydrophobic nature, which causes low wettability on the zirconia surface by the adhesive cements [2].

Currently, several in vitro and clinical techniques are under investigation to solve the problem of bonding resin cements to ceramics. Most of them are focused on micromechanical and/or chemical modifications of the surfaces of those ceramics, opening a variety of treatment options [20] in search of durability of the bonding of the ceramic with resin cements and dental tissue [21,22]. However, even with the association of techniques, it has not been possible to obtain a long-term bond between resin cement and zirconia [20,23]. There are reports in the literature showing that the association between mechanical treatment (silica sandblasting) and chemical conditioning (with primer) provided the highest zirconia bonding efficiency, even with hydrothermal aging [24]. The favorable chemical bonding ability of primer to silica-blasted zirconia is due mostly to the phosphate-based functional monomer (MDP) [25] or to the universal primer containing silane methacrylate [26].

To date, there has been no agreement about a non-damaging and efficient surface treatment method to obtain optimal bond strength between HT zirconia and resin cement. Therefore, it is necessary to seek treatments with the ability to chemically functionalize the zirconia surface to achieve an adhesive bond without causing structural and mechanical damage, resulting in strong chemical adhesion and increased bond strength between the ceramic and the resin cement so that long-term clinical success of such restorations is achieved.

Studies have shown that the Plasma-enhanced Chemical Vapor Deposition (PECVD) technique containing silicon particles is a surface treatment that results in the chemical adhesion and increase of bond strength between the substrates [27–30]. When associated with primer application based on MDP or silane methacrylate, it promotes long-term adhesion with the cementing agent [23,26], which is desirable in many clinical situations, such as for teeth with minimal preparations. In addition, strong chemical bonding would lead to an increase in fracture resistance and long-term fatigue [7,29].

Therefore, the aim of this study was to characterize the surface topography of zirconia after the use of the PECVD technique at different times by SiH_4 gas, as well as to evaluate the influence of PECVD on the zirconia surface in shear bond strength (SBS) along with the resin cement after aging. The hypotheses tested were that: (1) the proposed treatment would chemically modify the zirconia,

and (2) the longest times of PECVD by SiH_4 would increase shear strength with the resin cement before and after aging.

2. Materials and methods

2.1. Specimen preparation

The largest non-sintered zirconia-based ceramic blocks (VITA YZ HT zirconia, Vita Zahnfabrik, Bad Säckingen, Germany; $39 \times 19 \times 15.5$ mm) for milling were prepared by means of a diamond disk at 100 rpm in a cutting machine (IsoMet 1000, Buehler, Lake Bluff, IL, USA) to obtain 155 smaller, square specimens ($4.6 \times 3.7 \times 3$ mm). The specimens were standardized by silicon carbide water paper (Norton Saint Gobain, São Paulo, Brazil) with decreasing granulation of #400, #800, and #1200 in a polishing machine (EcoMet 250 Grinder Polisher, Buehler). The cutting and polishing were performed under water cooling.

After being cut and polished, all blocks were washed with isopropyl alcohol for 5 min in an ultrasonic bath (Cristófoli Ultrasonic Washer, Campo Mourão). All specimens were sintered according to the manufacturer's instructions (VITA Zyrcomat, Vita Zahnfabrik; final sintering temperature, 1450°C , lasting approximately 4:40 h). After being sintered, all blocks were again cleaned with isopropyl alcohol in an ultrasonic bath for another 5 min.

2.2. Plasma-enhanced Chemical Vapor Deposition (PECVD)

Before PECVD was performed, the samples were stored in an oven (Olidef, Ribeirão Preto, São Paulo, Brazil) at 37°C for 24 h. For the chemical deposition of the SiH_4 gas on the surfaces of the samples, an in-house vacuum reactor was used. The specimens were randomly divided into five groups ($n = 31$), based on the times of PECVD: Zr-30 (30 s), Zr-60 (60 s), Zr-120 (120 s), and Zr-300 (300 s). The control group (Zr-0) did not receive deposition (0 s) (Fig. 1). The vacuum reactor chamber presents an

inlet tube for gases and an outlet tube with a vacuum pump, which eliminates remaining unreacted gases from inside the chamber. Prior to the experiment, the chamber was bombarded with argon for cleaning of both the chamber and zirconia samples under the following conditions: pressure of approximately 2.4×10^{-3} Torr and low voltage source (2 kV), for 5 min. The conditions for the deposition of SiH_4 gas were a high voltage source (10 kV), pressure of 2.4×10^{-3} Torr, and a pulse of 5 μs . A potential difference was generated and a plasma cloud arose to increase the gas reactivity. The pressure established inside the chamber, the applied voltage, the reactor configuration, and the thermodynamic equilibrium conditions led to greater effectiveness and homogeneity of silicon and hydrogen ions, which would be deposited on the surfaces of the zirconia samples. The thermodynamic equilibrium conditions contributed to the breakdown of SiH_4 bonds into silicon and hydrogen ions and the bombardment on the zirconia surface. The deposition time was controlled with the aid of a digital timer (Unilab, São Paulo, Brazil).

2.3. Zirconia surface analyses

One specimen per group ($n = 5$) was evaluated by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy with a Field Emission Gun (FE-SEM), Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS) (Fig. 1). X-ray diffraction (XRD) (X'pert Powder model, PANalytical, Westborough, MA, USA) was performed at $10-90^\circ$, with a scan step of 10.16° , at a 0.017° step size, with $\text{CuK}\alpha$ radiation. The infrared spectra were acquired by FTIR spectroscopy with a Universal Attenuated Total Reflectance sensor (FTIR-UATR) (Perkin Elmer Spectrum, Frontier model). The FTIR spectrum was an average of 16 scans at a speed of 2 s per scan at a range of $500-4000\text{ cm}^{-1}$. The resolution of the spectrometer was set at 4 cm^{-1} (Spectrum Search Plus program). EDS was performed by spectrometry with an energy-dispersive X-ray (Bruker Nano GmbH 410, Berlin, Germany) coupled to an SEM (Inspect S50, FEI Company, Brno, Czech Republic; Esprit 1.9 software, Bruker, Berlin, Germany). The FE-SEM (Tescan, Mira 3, Brno, Czech Republic), secondary electron

(SE), and back-scattered scanning electron (BSE) detectors were used. The samples were placed in a circular stub to obtain images at magnifications of 3000×, 5000×, 10,000×, and 15,000×. XPS analyses were performed in a spectrometer (Kratos Axis Ultra DLD) with the Al Mono monochromatic source (1486.6 eV) and 120 W power. The survey XPS spectra were recorded with pass energy (PE) of 160 eV and spectra in high resolution with PE of 40 eV. The spectra were calibrated relative to the O 1s peak at 529.2 eV, with a charge neutralizer at the ON position. All the measurements were performed in ultra-high vacuum less than 10^{-7} Pa pressure, 15 kV acceleration voltages, and 10 mA power emission.

In total, 10 remaining specimens per group ($n = 50$) were used for optical profilometry analysis and contact angle measurements. Surface roughness was analyzed by means of an optical profilometer (Wyko NT 1100, Veeco, Plainview, NY, USA; Wyko Vision 32 software, VSI mode, Veeco). Measurements of the three-dimensional parameters were performed with magnifications of 20.5×, in a $300 \times 230 \mu\text{m}$ area. Data were plotted and analyzed by one-way ANOVA ($\alpha = 0.05$). The total Surface Free Energy (SFE) and SFE of the polar and dispersive solids (in mN/n) were calculated from the mean contact angle ($n = 10$) by means of a goniometer and DROPimage Advanced software (Ramé Hart-Inc., Mountain Lakes, NJ, USA) with the sessile drop technique with distilled water and diiodomethane at room temperature.

2.4. Shear bond strength (SBS) test

Composition, manufacturer, batch, and expiration date of cementing materials are listed in Table 1. The 100 samples ($n = 20$) were included with autopolymerizable acrylic resin (Jet, Clássico Dental Articles, São Paulo, Brazil) in a PVC cylinder (Tigre, Brazil). A thin layer of silane (Monobond N, Ivoclar Vivadent, Schaan, Liechtenstein) was applied with a microbrush on the surface of the zirconia for 10 s, allowing the material to react for 60 s. A dual resin cement cylinder (internal diameter, 3 mm; height, 3 mm) (Variolink N Base and Catalyst, Ivoclar Vivadent) was built on the surface of each sample. The photopolymerization was carried out with the LED device (Valo, Ultradent Products,

South Jordan, Utah, USA; intensity of 1000 mW/cm², wavelength of 395 to 480 nm) for 20 s at each interface, simulating the occlusal, buccal, and lingual faces, totaling 60 s. The specimens were stored in distilled water in a greenhouse (Olidef, Ribeirão Preto, São Paulo, Brazil) at 37°C for 24 h.

The SBS test was performed in a universal testing machine (EMIC DL 1000, EMIC, São José dos Pinhais, Paraná, Brazil; 0.45 mm wire, 50 kgf load cell, speed of 1 mm/min). Half of the samples from each group were tested 24 h after cementation, while the other half were subjected to 6×10^3 thermal cycles (5°C - 55°C) in a thermocycler (Termocycle, Biopdi, São Carlos, SP, Brazil) before the test. Those thermocycling groups were identified according to the deposition time: Zr-0t (control), Zr-30t (30 s), Zr-60t (60 s), Zr-120t (120 s), and Zr-300t (300 s) (Fig. 1).

After the SBS test, the zirconia surface was evaluated on a binocular stereomicroscope (Discovery V20, Carl Zeiss, Göttingen, Germany) to determine the interfacial mode of failure (adhesive or predominantly adhesive - at the junction between cement and zirconia; cohesive - in cement or zirconia; and mixed - adhesive failure along with cohesive failure in cement). The SBS data obtained were obtained in MegaPascals (MPa) according to the formula:

Eq. A.1

in which the force is in N and the bonding area is given in mm², mathematically expressed by “ π ” (3.14) multiplied by “ r^2 ” (radius of the circumference = $1.5^2 = 2.25$). The mean and standard deviation of values of each group were analyzed with the Shapiro-Wilk test to verify the assumption of normality. One-way ANOVA followed by Tukey’s post hoc multiple-comparison test were used to compare SBS results, with a significance level of 0.05.

3. Discussion

This study evaluated the effect of the PECVD of SiH₄ on the surface topography of HT zirconia and chemical bonds with the resin cement, before and after aging, at different times (30 s, 60 s, 120 s, and

300 s) with high voltage and at low vacuum. According to the results, the hypotheses were accepted, since the proposed surface treatment modified the chemical characteristics of the HT zirconia and increased the SBS with resin cement at the different times of SiH_4 deposition, before and after the thermocycling, when compared with groups without deposition (Zr-0 and Zr-0t).

Several studies have attempted to apply plasma treatments to create a chemically functionalized surface – due to the reduction of carbon-based contaminants – eventually creating hydrophilic surfaces and increasing SFE [27, 38–40]. This is consistent with the findings of this study, which showed that the longer the deposition time of the ionized forms of the SiH_4 on the zirconia, the greater the amount of silicon on the surface (Table 2 and Fig. 7). However, some early studies [27, 38] were not concerned with the long-term bonding of the interfaces, which does not provide useful information about the real potential of new surface treatments for bonding zirconia.

The results obtained by XRD (Fig. 2) showed that, on the surface of the zirconia after PECVD, the interaction between silicon and zirconia did not form any crystalline phase, showing peaks indicative of tetragonal ZrO_2 alone [31–33]. In support of these results, the FTIR spectra presented a broad band between 500 cm^{-1} and 700 cm^{-1} in all samples (Fig. 3), a strong indication that the tetragonal phase was dominant [31,33,36]. Also, no signs of zirconia phase change were seen.

Fig. 3 further shows the variations in the shape and position of the center of the band as a function of silicon deposition times. The compressive stress shifts the center of the band to lower frequencies, and the tensile stress shifts the band to higher frequencies [31]. These data are in agreement with the results of XPS analyses showing that the Si $2p$ peak spectrum is at approximately 103 eV for Zr-30 and Zr-60 and 99 eV for Zr-120 and Zr-300 (Fig. 7). Therefore, the increased silicon on the zirconia surface forms chemical bonds with the oxygen (SiO_2) and surface compressive stresses (as observed for Zr-30 and Zr-60). For Zr-120 and Zr-300, a strong peak at 99 eV indicates a high percentage of Si. A plausible explanation for this finding is due to the continuous deposition of Si, forming SiO as a result of the interaction between Si and the SiO_2 already present on the zirconia surface [35]. The presence of SiO_2 and SiO may have been responsible for the increased surface

polarity [37] and the increased surface energy values when compared with those of the Zr-0 group, indicating an improvement in surface wettability and reactivity with resin cement (Table 4).

The PECVD also showed topographic changes on the zirconia surface. In the Zr-30 and Zr-60 samples, the bombardment and penetration of silicon in the microstructure generated zirconia grains with irregular polyhedral shapes and a previously non-existent volume on the surface, as observed in FE-SEM micrographs (Fig. 4g-i), and, as a consequence, a compressive stress was also present (Fig. 3). The formation of silicon islands and silicon cylinders occurred with the longest deposition times (Zr-120 and Zr-300), resulting in high tensile stresses (Fig. 3). The detachment of the zirconia grains and the silicon cylinders from the microstructure (Figs. 5 and 6) finally relieved surface tension (tensile stresses), and the bands were then displaced to higher frequencies (Fig. 3). Thus, the increase in SBS for Zr-120 and Zr-300 (before and after the thermocycling) was also possibly due to the microretentive surface caused by silicon grain detachments (Figs. 5 and 6). Apparently, this was the major contribution of stress variations in bond strength with increasing deposition time.

As previously stated, the combination of pre-treatments on the zirconia cementation surface can contribute to higher bonding with resin cements [21,41]. This is because enhanced performance of surface treatments of zirconia can be obtained from a microretentive cementation surface, as well as from silane application [42]. Thus, surface roughness is one of the factors that have a positive effect on bonding at the cementation surface [43]. This study showed that the mean values of surface roughness for all experimental groups were lower than those in the Zr-0 group (316.52 ± 16.34 nm), which indicates a general tendency for diminishing surface irregularities. This tendency was not confirmed on Zr-60 (376.11 ± 16.79 nm) (Table 3), since its SBS, before and after the thermocycling, was higher than that in Zr-0 (Table 5), which cannot be easily explained with only the findings of the present study.

In this study, the SBS test was used in spite of the arguments of unfavorable stress distributions at the bonding interface. This choice, however, was mainly because it is a common, rapid, and easy-to-execute joint force test [21,47], very useful when zirconia is the bonding substrate. According to the SBS test, two consecutive chemical treatments (PECVD and Monobond N primer

application) were able to produce a strong and durable joint with the resin cement, since the SBS was significantly higher for experimental groups compared with primer application (without PECVD - Zr-0 and Zr-0t). These results can be explained by: (1) the linking between the metal oxides (SiO bonds) on the zirconia and the universal primer containing silane methacrylate and (2) the methacrylate groups present in the resin cement reacting with the methacrylate termination of the silane molecule [26].

The bonding strength obtained with the Zr-0 group (14.91 ± 5.03 MPa) was higher than that with the Zr-0t group (0.95 ± 0.70 MPa), showing a weak bond at the zirconia-resin cement bonding interface with the use of universal primer only. The same occurred for the experimental groups, which, before thermocycling, had nearly identical SBS values but which, after aging, showed a clear drop but different bond strengths (Table 5). It is believed that the reduction in shear strength after thermocycling is caused by the degradation of the resin cement [50] and the hydrolytic effect caused by water at the resin cement-zirconia interface [50,51]. The post-thermocycling results showed that adhesion strength was approximately three times higher for the Zr-30t and Zr-60t groups and six times higher for the Zr-120t and Zr-300t groups, compared with that of the untreated group (Zr-0t). Therefore, the longer the deposition, the higher the long-term bond strength. Because the bond strengths were alike in the immediately tested groups, it is possible that additional bond strength was obtained with surface changes due to grain detachments, which warrants further investigation.

We are aware that clinical research points to chipping as the most common type of failure in zirconia restorations, but the trend for using low-retentive monolithic restorations must increase the need for more effective bonding. In general, the positive effects of PECVD on increasing the bond strength of zirconia with resin cement make it a promising alternative for HT zirconia bonding. However, further studies should be carried out to improve the process and to simplify coating procedures.

4. Results

4.1. Surface analyses

The XRD, FTIR spectroscopy, EDS, FE-SEM, and XPS results are presented in Figs. 2-7.

Fig. 2 shows the X-ray diffractograms of the control and experimental samples. The XRD spectra were identical for the different PECVD conditions and control group, showing that all diffraction peaks presented could be attributed to the plane of the tetragonal ZrO_2 phase [31-33]. These results showed that the interaction between silicon and zirconia did not form any crystalline phase.

In the FTIR spectrogram (Fig. 3), all samples had a broad band between 500 cm^{-1} and 700 cm^{-1} . The strong absorption peaks on these spectra correspond to the Zr-O vibrational modes. The shape and position of the center of the band shifts depend on the silicon deposition times. For Zr-30 and Zr-60, there was a shift toward lower frequencies, which means that the longer the time exposure, the higher the compressive stress on the zirconia, and the more the band tends to move to the left. This compressive stress can be caused by the penetration of silicon between the zirconia grains (Fig. 5). For Zr-120 and Zr-300, these bands returned to frequencies similar to Zr-0. This displacement can be associated with the stress that occurred during the PECVD process. With the detachment of the zirconia grains (Fig. 6), tensile stress relief leads to the change of position of the band, returning to its original position.

The specimens were chemically analyzed by EDS analysis (Table 2). The longer the deposition time, the greater the amount of silicon present on the zirconia surface. There was also an increase in oxygen.

Fig. 4 shows the micrographs of representative samples of all groups (control and experimental). In the surface micrographs of the Zr-0 sample, the zirconia grains are well-delimited, rounded, and homogeneous (Fig. 4a-c). In the experimental groups, darker islands formed in the BSE detector. EDS showed the presence of silicon, which has an atomic weight (28.0855 u) lower than that of zirconia (91.224 u). The deposition time is responsible for the greater number of silicon clusters present on the surface of the zirconia. The penetration of silicon covered the defects from processing, causing zirconia conformational change (resembling irregular polyhedral forms) (Fig. 4g-l) and the

compression stress on the surface, and therefore the infrared band was displaced (Zr-30 and Zr-60) (Fig. 3). For Zr-120 and Zr-300, there was a critical volumetric increase of zirconia grains until detachment (Fig. 5) and detachment of a silicon stick-like structure (Fig. 6b and 6c). The detachment can be better visualized in Fig. 6 and always occurred near processing defects. The 60-second deposition (Zr-60) caused silicon penetration and cylinder formation (Fig. 6a), which became clear and apparently detached from the silicon grains with 120-second deposition (Zr-120) (Fig. 6b), becoming fully detached from the surface of the zirconia with 300-second deposition (Zr-300) (Fig. 6c).

Fig. 7 shows XPS spectra from control and experimental samples. Only the Zr-0 group (without PECVD) exhibited the Zr 3*d* spectrum, where peaks were centered at approximately 180 eV, indicating peaks related to Zr-O-Zr bonds (ZrO₂). It was not possible to identify Zr-O-Zr bonds on the surface of any sample of the experimental groups (Fig. 7A). For the O 1*s* spectra, the peaks were centered at approximately 526-529 eV for Zr-0 and 529-533 eV for all experimental groups (Fig. 7B). Finally, for the Si 2*p* spectra, a centered peak was attributed to Si substrate at around 99 eV [34] for both Zr-120 and Zr-300 (Fig. 7C). The Si 2*p* peak between 102 and 103 eV for all experimental groups indicates Si-O bonds (SiO and SiO₂) (Fig. 7C) [35].

The surface roughness data are described in Table 3. One-way ANOVA showed that there was a statistically significant difference among all groups ($p < 0.05$). In Tukey's test, Zr-0 and Zr-120 were not statistically significantly different. Zr-0 presented a grooved surface, probably caused by polishing (316.52 ± 16.34 nm). The samples of zirconia with deposition time of 60 s (Zr-60) showed larger superficial roughness (376.11 ± 16.79 nm) in comparison with the other groups. The group that received the highest deposition time (Zr-300) presented the smoothest and most homogeneous surface, with the lowest values of surface roughness (241.04 ± 12.87 nm).

The means and standard deviations (SD) of the contact angles of the experimental groups in contact with distilled water and diiodomethane, the dispersive and polar energies, and the resulting free surface energy of each group are described in Table 4. All experimental groups presented

predominantly hydrophilic behavior, with the reduction of the contact angle with polar liquid (water) and increased polar component and SFE.

4.2. Shear bond strength

The failure analysis showed that for all samples, adhesive or predominantly adhesive failures occurred at the interface between zirconia and resin cement. Table 5 presents the descriptive and inferential statistical analyses, with the values of means, standard deviations (SD), and confidence intervals (CI) at 95% for the samples from the groups tested 24 h after cementation and after thermocycling for the "deposition time" parameter.

For the group subjected to the SBS test 24 h after cementation (non-aging), one-way ANOVA revealed a significant interaction effect, indicating that the shear strength of the material changed due to the deposition time ($p < 0.05$). Zr-0 had the lowest values of shear strength (14.91 ± 5.03 MPa), being statistically significantly different from the experimental groups Zr-30 and Zr-120 (24.79 ± 4.96 MPa and 23.02 ± 2.52 MPa, respectively). All experimental groups were statistically similar.

For the groups subjected to SBS after aging, one-way ANOVA also showed a significant interaction effect, indicating that the shear strength of the material changed due to the deposition time ($p < 0.05$). The results analyzed by the Tukey post hoc test showed differences between and among the groups. Zr-0t presented the lowest values of shear strength (0.95 ± 0.70 MPa), being statistically significantly different from the experimental groups. Zr-30t was statistically similar to Zr-60t as well as to Zr-120t and Zr-300t.

5. Conclusion

Within the limitations of this study, we can conclude that:

- The PECVD technique proposed in this work, with argon and SiH₄ gas, was able to form a more reactive zirconia surface with the universal primer containing silane methacrylate and with resin cement.
- The longer the deposition time of the SiH₄ on the surface of HT zirconia, the greater the amount of silicon present on the zirconia surface forming chemical bonds.
- Grain detachments and the absence of zirconia phase transformation were noticeable at longer deposition times.
- The PECVD technique proposed in this study, associated with primer application, was able to conserve a certain degree of bonding between HT zirconia and resin cement after thermocycling.
- The longer the deposition times (120 and 300 s), the more durable the bond strengths after thermocycling.

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Eq. A.1: $SBS = \text{Force} / \text{bonding area}$

Tables

Table 1 – Materials used in the study.

Material	Manufacturer	Composition	Batch No.	Validity
Zirconia YZ HT	Vita Zahnfabrik, Bad Säckingen, Germany	ZrO ₂ , Y ₂ O ₃ , Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃ , Na ₂ O	62700	Indeterminate
Monobond N	Ivoclar Vivadent, Schaan, Liechtenstein	Alcohol solution of silane methacrylate, phosphoric acid methacrylate, and sulphide methacrylate	U29879	07/2017
Variolink N Base	Ivoclar Vivadent, Schaan, Liechtenstein	Bis-GMA, urethane dimethacrylate, triethylene glycol dimethacrylate, barium glass, ytterbium trifluoride, Ba-Al-fluorosilicate glass, spheroid mixed oxide, initiators, stabilizers, and pigments	V00666	04/2018
Variolink N Catalyst			U48611	04/2018

Table 2 – Composition in percentage of weight (%) of control and experimental groups by EDS analysis.

Chemical element	Groups (percentage of weight %)				
	Zr-0	Zr-30	Zr-60	Zr-120	Zr-300
Zirconia	73.08	72.68	70.46	68.81	67.35
Oxygen	20.34	20.94	22.67	23.77	25.45
Yttrium	6.58	6.11	6.04	6.06	5.76
Silicon	-	0.28	0.83	1.37	1.44

Table 3 – Means, standard deviations (SD) in nm, and confidence intervals (IC) of values of surface roughness (Ra) of control and experimental groups.

Groups	Mean and SD (nm)	IC 95%
Zr-0	316.52 ± 16.34 ^a	(306.11; 326.93)
Zr-30	267.60 ± 11.43 ^b	(257.19; 278.01)
Zr-60	376.11 ± 16.79 ^c	(365.70; 386.52)
Zr-120	311.49 ± 22.14 ^a	(301.08; 321.90)
Zr-300	241.04 ± 12.87 ^d	(230.63; 251.45)

p = 0.05. Different lowercase letters mean statistically significant difference.

Table 4 – Mean contact angles and standard deviations for water and diiodomethane, polar (γ_p , in mN/m) and dispersive (γ_d , in mN/m) components, and respective SFE (γ_T , in mN/m) of the evaluated control and experimental groups of zirconia.

Groups	Mean contact angle		Components (mN/m)		
	Water	Diiodomethane			
	Mean (SD) (°)	Mean (SD) (°)	γ_p (SD)	γ_d (SD)	γ_T (SD)
Zr-0	75.76 (0.78)	38.02 (1.05)	10.11 (0.37)	41.05 (0.48)	52.16 (0.53)
Zr-30	50.33 (1.17)	35.38 (0.41)	22.15 (0.59)	42.21 (0.17)	64.36 (0.61)
Zr-60	50.56 (0.69)	38.55 (2.10)	22.37 (0.43)	40.82 (0.91)	63.19 (0.76)
Zr-120	59.15 (0.20)	36.66 (0.38)	17.85 (0.11)	41.66 (0.16)	59.51 (0.16)
Zr-300	56.74 (0.79)	33.61 (0.55)	18.77 (0.40)	42.96 (0.23)	61.73 (0.44)

Table 5 – Bond strength data between zirconia and resin cement. Descriptive statistics (Mean, SD, and IC, in MPa) and Tukey's test of the groups before (24 h) and after thermocycling.

Groups	Thermocycling	Mean and SD	95% IC
Zr-0	Absence	14.91 ± 5.03^B	(11.20-18.61)
Zr-30		24.79 ± 4.96^A	(21.09-28.49)
Zr-60		22.11 ± 8.45^{AB}	(18.41-25.81)
Zr-120		23.02 ± 2.52^A	(19.31-26.72)
Zr-300		20.13 ± 6.43^{AB}	(16.43-23.83)
Zr-0t	Presence	0.95 ± 0.70^c	(0.21-2.09)
Zr-30t		3.89 ± 0.69^b	(2.80-5.33)
Zr-60t		3.63 ± 0.81^b	(2.61-5.47)
Zr-120t		6.07 ± 1.78^a	(4.60-10.46)
Zr-300t		5.57 ± 1.80^a	(2.90-8.08)

p = 0.05. Different uppercase letters mean statistically significant difference between and among the groups after 24 h of cementation. Different lowercase letters mean statistically significant difference after aging.

Figure captions

Fig. 1 - Flowchart of experimental procedures.

Fig. 2 – X-ray diffractograms of Zr-0, Zr-30, Zr-60, Zr-120, and Zr-300. The peaks signaled by Zr-t correspond to tetragonal phases.

Fig. 3 – Representative FTIR spectra of control (Zr-0) and experimental groups (Zr-30, Zr-60, Zr-120, and Zr-300).

Fig. 4 – Representative micrographs of the zirconia surface (original magnification of 5000×, 10000×, and 15000×). (a-c) Zr-0 (after the polishing and without PECVD) and after PECVD (d-f) with 30 s (Zr-30), (g-i) 60 s (Zr-60), (j-l) 120 s (Zr-120), and (m-o) 300 s (Zr-300).

Fig. 5 - Micrographs of sample surfaces (3000×, 5000×, and 10000×) with PECVD by Zr-120 with silicon penetration and the beginning of zirconia grain detachment.

Fig. 6 – Micrographs of sample surfaces at the beginning of Zr-60 (60 s to 3000×), among Zr-120 (120 s – 5000×) and ending Zr-300 (300 s – 10000×) of the silicon cylinder detachment.

Fig. 7 – XPS spectra of (A) Zr 3d, (B) O 1s, and (C) Si 2p spectra for the control and experimental groups.

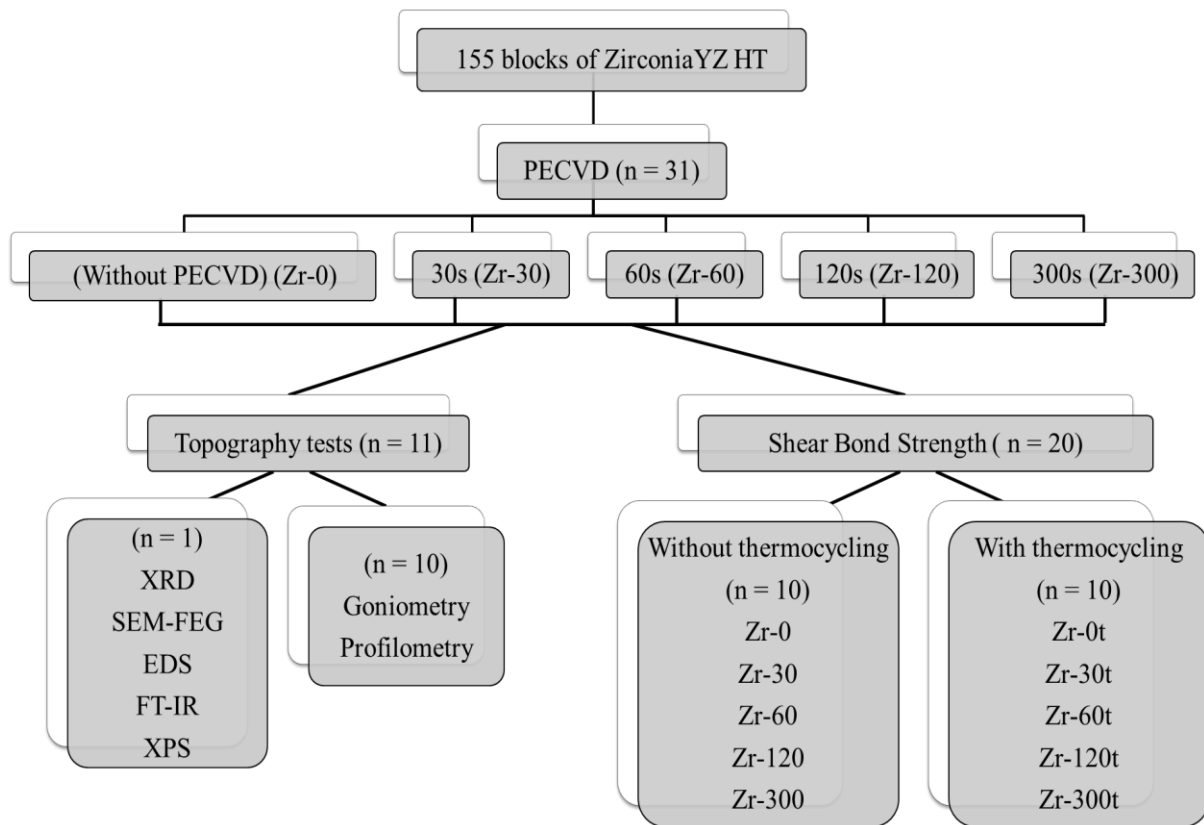


Fig. 1 - Flowchart of experimental procedures.

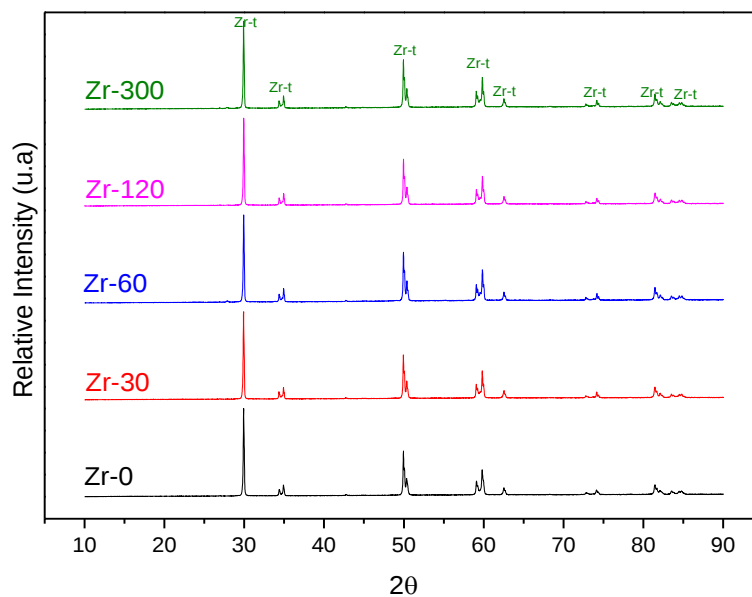


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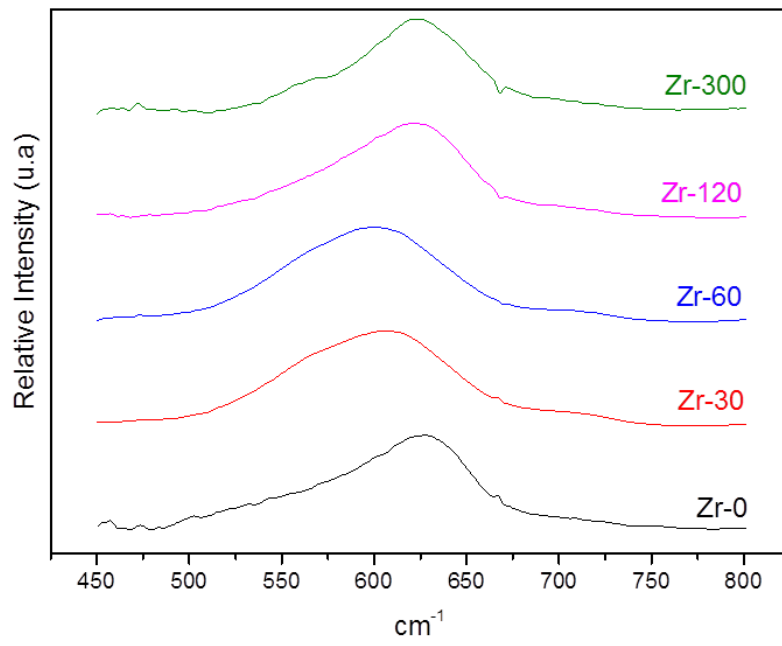


Fig. 3 – Representative FTIR spectra of control (Zr-0) and experimental groups (Zr-30, Zr-60, Zr-120, and Zr-300).

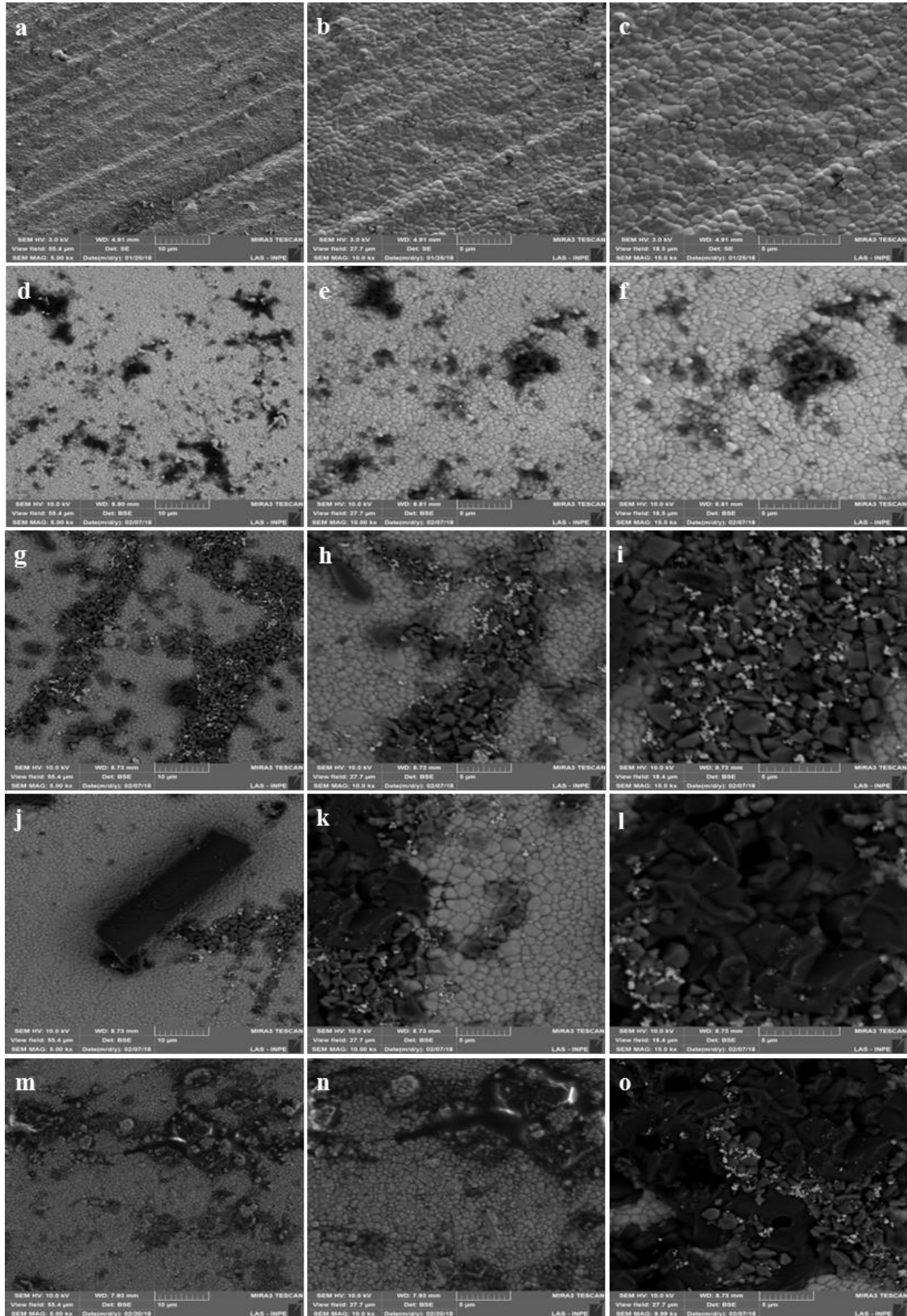


Fig. 4 – Representative micrographs of the zirconia surface (original magnification of 5000 $\times$, 10000 $\times$, and 15000 $\times$). (a-c) Zr-0 (after the polishing and without PECVD) and after PECVD (d-f) with 30 s (Zr-30), (g-i) 60 s (Zr-60), (j-l) 120 s (Zr-120), and (m-o) 300 s (Zr-300).

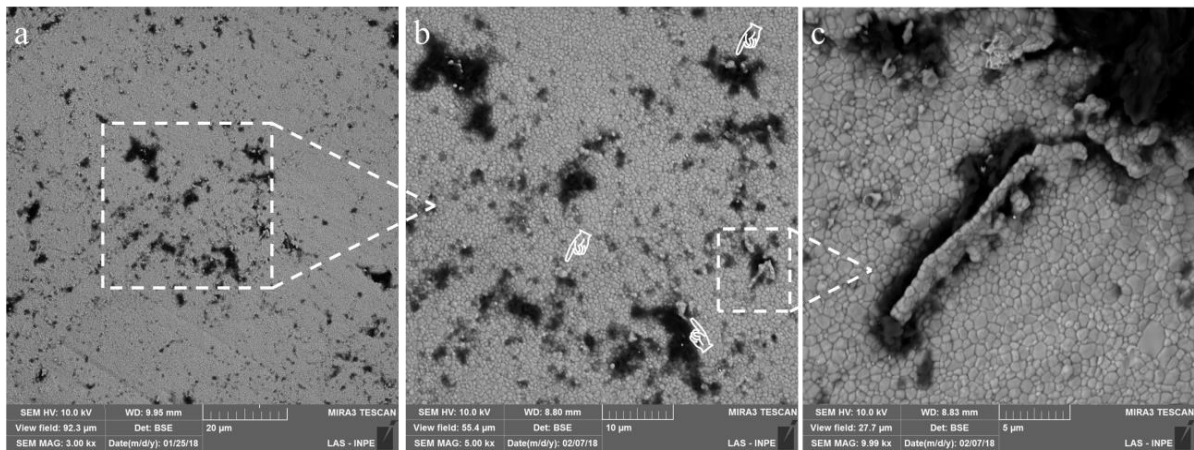


Fig. 5 - Micrographs of sample surfaces (3000×, 5000×, and 10000×) with PECVD by Zr-120 with silicon penetration and the beginning of zirconia grain detachment.

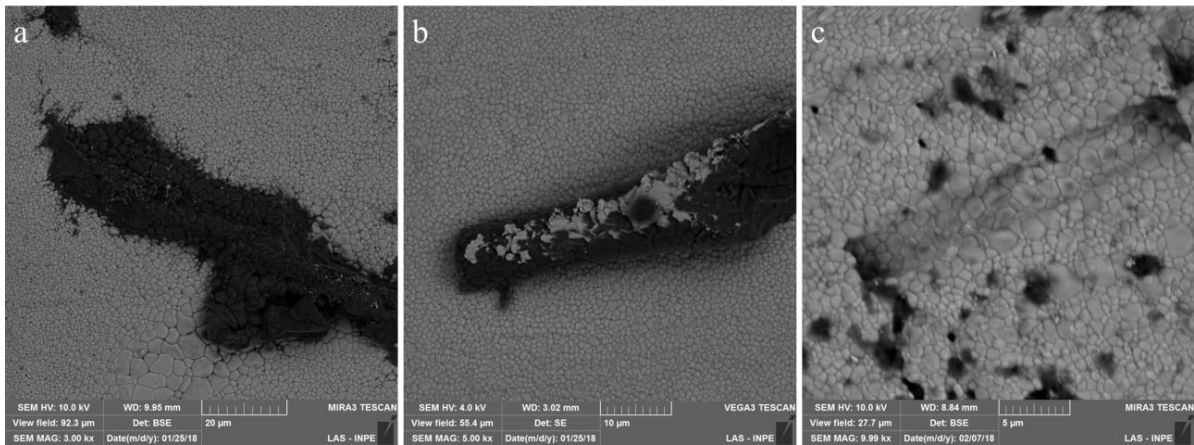


Fig. 6 – Micrographs of sample surfaces at the beginning of Zr-60 (60 s to 3000×), among Zr-120 (120 s – 5000×) and ending Zr-300 (300 s – 10000×) of the silicon cylinder detachment.

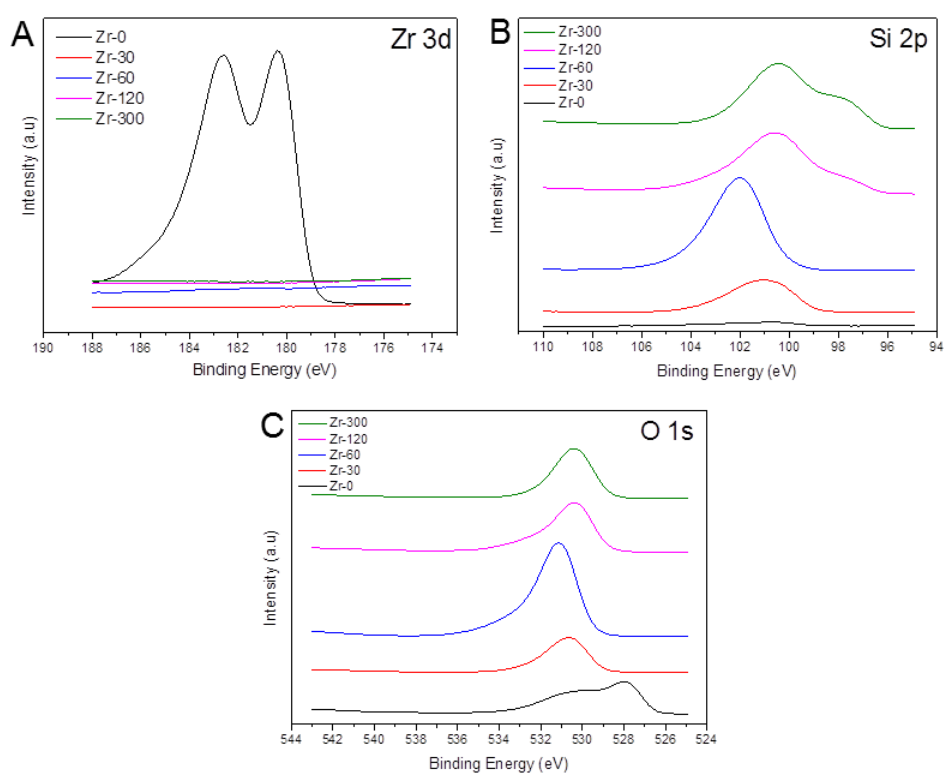


Fig. 7 – XPS spectra of (A) Zr 3d, (B) O 1s, and (C) Si 2p spectra for the control and experimental groups.

3 CONSIDERAÇÕES GERAIS

De acordo com os resultados encontrados nesse estudo e considerando as limitações de um estudo *in vitro*, é possível concluir que:

- A técnica de PECVD proposta neste trabalho, usando gás Argônio e gás SiH_4 , foi capaz de formar uma superfície de zircônia mais reativa com o primer universal contendo metacrilato de silano e cimento resinoso.

- Quanto maior o tempo de deposição do SiH_4 na superfície da zircônia HT, maior foi a quantidade de Silício presente na superfície da zircônia formando ligações químicas;

- Os destacamentos de grãos e a ausência de transformação da fase de zircônia foram perceptíveis em tempos de deposição mais longos.

- A técnica de PECVD proposta neste estudo, associada à aplicação de primer, foi capaz de conservar certo grau de ligação entre a zircônia HT e o cimento resinoso após termociclagem.

- Quanto maior o tempo de deposição (120 e 300 s), mais duráveis são as forças de adesão após a termociclagem.

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Jaiane Bandoli Monteiro <jaiane.monteiro@unesp.br>

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Title: Microstructural characterization and chemical and bonding analyses of a high-translucency zirconia after Plasma-enhanced Chemical Vapor Deposition with silicon hydride

Corresponding Author: Renata Marques de Melo

Co-Authors: Jaiane Monteiro, Pedro Henrique Condé Oliveira Prado, Tiago Moreira Bastos Campos, João Paulo Barros Machado, Vladimir Trava-Airoldi

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