**UNIVERSIDADE FEDERAL DE SANTA MARIA**
**CENTRO DE CIÊNCIAS DA SAÚDE**
**PROGRAMA DE PÓS- GRADUAÇÃO EM CIÊNCIAS ODONTOLÓGICAS**

# ADESÃO À CERÂMICA Y-TZP: ESTUDO DA DEPOSIÇÃO DE NANOFILMES DE SÍLICA NA SUPERFÍCIE DA Y-TZP

**DISSERTAÇÃO DE MESTRADO**

**Carolina Ceolin Druck**

**Santa Maria, RS, Brasil**
**2013**

# ADESÃO À CERÂMICA Y-TZP: ESTUDO DA DEPOSIÇÃO DE NANOFILMES DE SÍLICA NA SUPERFÍCIE DA Y-TZP

**Carolina Ceolin Druck**

Dissertação de Mestrado apresentada ao Curso de Mestrado do Programa de Pós-Graduação em Ciências Odontológicas, Área de Concentração em Odontologia, ênfase em Prótese Dentária, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para a obtenção do grau de
**Mestre em Ciências Odontológicas.**

**Orientador: Prof. Dr Luiz Felipe Valandro**

**Santa Maria, RS, Brasil**
**2013**

**Universidade Federal de Santa Maria**
**Centro de Ciências da Saúde**
**Programa de Pós-Graduação em Ciências Odontológicas**

A Comissão Examinadora, abaixo assinada,
Aprova a Dissertação de Mestrado

**ADESÃO À CERÂMICA Y-TZP: ESTUDO DA DEPOSIÇÃO DE NANOFILMES DE SÍLICA NA SUPERFÍCIE DA Y-TZP**

elaborada por
**Carolina Ceolin Druck**

como requisito parcial para obtenção do grau de
**Mestre em Ciências Odontológicas**

**COMISSÃO EXAMINADORA:**

**Luiz Felipe Valandro, Dr.**
(Presidente/Orientador - UFSM)

**Liliana Gressler May, Dra. (UFSM)**

**Lucio Strazzabosco Dorneles, Dr. (UFSM)**

Santa Maria, 15 de agosto de 2013.

Dedico esta dissertação:

***Aos meus pais, Marlice e Rogério, pelo amor incondicional, apoio e suporte para que eu seguisse em frente.***

***Aos meus avós, Mário e Norma, sempre presentes em meu pensamento.***

## Agradecimentos

Agradeço a Deus, que me permitiu ter o esclarecimento necessário para seguir por este caminho, me deu saúde e a força para enfrentar todos os momentos difíceis.

Aos meus pais, que não medem esforços para realizar meus sonhos. Agradeço pelo carinho e apoio constantes. Amo muito vocês!

À minha irmã, Letícia, agradeço pelas conversas, pela amizade, pelas risadas e por todo o apoio. Te amo pra sempre.

Ao meu namorado, William, meu amor e meu melhor amigo. Muito obrigada por compreender os momentos que estive que estar ausente, por apoiar todas as minhas decisões, pela paciência e por tornar essa etapa da minha vida mais leve e feliz.

Ao meu orientador, professor Luiz Felipe Valandro, por me proporcionar esses 5 anos de crescimento pessoal e profissional. Obrigada pela confiança depositada em mim. Muito obrigada pelos ensinamentos, conselhos, conversas e por estar sempre presente e disposto a ajudar. É um exemplo para mim de dedicação, competência e sabedoria. Muito obrigada por tudo!!!

À todo o nosso grupo orientado pelo professor Luiz Felipe Valandro: Andressa, Gabriel, Vinícius, Dagma, Catina, Rafaela, Gabriela, João, Taiane, e também aos que já foram do grupo: Marina, Marília, César, Manuela, Aline, Ariele, Emília, Mateus e Mariane. Muito obrigada pela amizade, pelas discussões científicas e pelas jantas. Foi muito bom conviver com vocês.

Ao grupo de discussões orientado pela professora Liliana: Ana Maria, Iana, Priscila, Sara e professora Liliana, muito obrigado pelos momentos de crescimento intelectual e descontração.

Ao César Bergoli, pela orientação e ajuda nos trabalhos desde a minha iniciação científica, pela amizade e apoio.

Ao João Luiz Pozzobon, pela amizade, contribuição no trabalho, pelas horas que ficamos no laboratório trabalhando e pela dedicação.

À Ana Maria Marchionatti, pela companhia nas viagens, ajuda nos trabalhos e momentos de descontração.

Ao Vinícius Wandscher, por estar sempre disposto a ajudar a qualquer momento, pelas conversas, pela parceria e por todo o apoio.

À todos os professores do PPGCO, em especial à Karla Kantorski, Carlos Heitor Cunha Moreira, Liliana Gressler May, Thiago Ardenghi e Osvaldo Kaizer por todo o conhecimento transmitido, colaborando para o meu crescimento intelectual e profissional.

Ao professor, Lucio Strazzabosco Dorneles, professor do curso de Física e da Pós-Graduação em Física da UFSM, por ter me recebido e dado todo o suporte para o desenvolvimento desse trabalho, muito obrigada pelo conhecimento transmitido e pela paciência nas explicações sobre a deposição de filmes.

Ao pessoal do Laboratório de Magnetismo e Materiais Magnéticos da UFSM, em especial ao Gustavo Luiz Callegari e Manoela Adams, pelo auxílio e explicações sobre a deposição de filmes.

Aos colegas Andressa Venturini, Gabriel Pereira e Guilherme Freitas pela amizade, pelas conversas descontraídas e por tornar esses 2 anos de mestrado muito mais divertidos.

Aos momentos agradáveis no laboratório com os colegas: Luciana Friedrich, Marcos Paulo Marchiori e Patrícia Henke.

À todos os meus colegas do mestrado, muito obrigada pelas discussões científicas em aula e pelos momentos de descontração.

Ao professor Walter Blaya, pela confiança, pelo carinho, pela amizade e por todo conhecimento compartilhado.

Ao professor Claudio Figueiró, pela amizade, confiança e por sempre, desde a graduação, contribuir substancialmente com meu crescimento profissional.

Aos professores do curso de especialização, Manuel Pimenta e Henrique Hollweg, por terem contribuído com meu aperfeiçoamento profissional, pela dedicação aos alunos e pela amizade.

As minhas amigas, Larissa de Abreu, Marina Londero e Patrícia Schneider, que mesmo com a distância, se fizeram sempre presentes me dando apoio, carinho e amizade. Amo vocês.

À minha querida amiga Michele Miriam May, meu maior presente da especialização. Muito obrigada pela amizade, pelas conversas, pelos momentos de descontração e pelos momentos de trabalho, por tudo.

À Raquel Menezes, pela amizade, troca de experiências, conversas descontraídas e confiança.

À secretária do PPGCO, Jéssica Dalcin da Silva, por ser uma excelente profissional, sempre pronta a ajudar e resolver os “problemas”. Muito obrigada também pela amizade e pelas conversas, que muitas vezes me deram força para ir em frente.

A CAPES e ao CNPq pela concessão de suporte financeiro durante estes dois anos de mestrado.

A todas as pessoas que de alguma maneira ajudaram e participaram da realização dessa dissertação.

*"É impossível progredir sem mudança, e aqueles que não mudam suas mentes não podem mudar nada".*

*George Bernard Shaw*

**RESUMO**

Dissertação de Mestrado
Programa de Pós-Graduação em Ciências Odontológicas
Universidade Federal de Santa Maria

**ADESÃO ÀCERÂMICA Y-TZP: ESTUDO DA DEPOSIÇÃO DE NANOFILMES À BASE DE SÍLICA NA SUPERFÍCIE DA Y-TZP**
AUTORA: CAROLINA CEOLIN DRUCK
ORIENTADOR: LUIZ FELIPE VALANDRO
Data e Local da Qualificação: Santa Maria, 15 de agosto de 2013.

O presente trabalho avaliou, *in vitro,* a influência da deposição de filmes à base de sílica sobre a superfície da Y-TZP na durabilidade da resistência de união entre essa cerâmica e um cimento resinoso. Foram confeccionados oitenta blocos (5x5x4 mm) de Y-TZP, estes foram incluídos em resina acrílica e divididos em 4 grupos de acordo com o tratamento de superfície (n=20): (TBS) tratamento triboquímico (Cojet, 3M/ESPE); (F-5) filme de $SiO_2$ de 5 nm e silanização; (F-500) filme de $SiO_2$ de 500 nm e silanização; (F-500HF) filme de $SiO_2$ de 500 nm + HF + silanização. Sobre os blocos de Y-TZP foram cimentados (RelyX ARC) cilindros feitos com resina composta confeccionados com uma matriz metálica. Metade dos espécimes (n=10) de cada grupo foi testada após 24h de cimentação (S- sem envelhecimento) e a outra metade (n=10) foi submetida ao envelhecimento (TC, armazenagem por 90 dias e $10^3$ ciclos térmicos). Então, os espécimes foram submetidos ao teste de cisalhamento (1min/min). Após o teste, as superfícies foram analisadas por Microscópio Óptico e MEV para categorizar o modo de falha. Também foram feitas análises adicionais em EDS. Os dados foram analisados estatisticamente pelo teste de Kruskal-Wallis/Mann Whitney ($\alpha$=0,05). A resistência adesiva foi influencida pelo tipo de tratamento de superfície, nas condições S (p=0.0001) e TC (p=0.0000). Em ambas condições de armazenagem, os tratamentos TBS e F-5 promoveram mais alta resistência adesiva, significativamente. Médias (DP) de RU (MPa) foram: TBS/S: 10,2(5,1)$^{AB}$; F-5/S: 12,0(3,9)$^{A}$; F-500/S: 14,9(4,7)$^{A}$; F-500HF/S: 4,1(5,6)$^{B}$; TBS/TC: 9,1(4,4)$^{a}$; F-5/TC: 7,8(5,3)$^{a}$; F-500/TC: 0,01(0,0)$^{b}$; F-500HF/TC: 1,4(2,3)$^{b}$. Concluiu-se que a adesão a zircônia pode ser potencializada se a superfície receber a deposição do filme de $SiO_2$ de 5 nm ou for submetida a jateamento com partículas de sílica, seguida de silanização.


**Palavras-chave:** Resistência de união. Tratamento de superfície. Y-TZP. Zircônia. Filme.

**ABSTRACT**
Master's Degree Dissertation
Post Graduate Program in Dental Science
Federal University of Santa Maria

**ADHESION TO THE Y-TZP CERAMIC: STUDY OF SILICA NANO-FILM COATING ON THE YTZ-P SURFACE**
AUTHOR: CAROLINA CEOLIN DRUCK
ADVISER: LUIZ FELIPE VALANDRO
Date and Local of Defense: August 15, 2013, Santa Maria.

This study in vitro proposed to evaluate the influence of silica-based film coated on the Y-TZP surface on the durability bond strength (BS) between ceramic and resin cement. Eighty Y-TZP blocks (5x5x4 mm) were obtained, included in acrylic resin and were divided into four groups according to the surface treatments treatments (n=20): (TBS) tribochemical silica coating (Cojet, 3M/ESPE), (F-5) 5 nm $SiO_2$ nanofilm and silanization, (F-500) 500 nm $SiO_2$ nanofilm and silanization, and (F-500HF) 500 nm $SiO_2$ nanofilm + HF + silanization. Specimen of composite resin were made with a metal matrix and cemented with resin cement (Relyx ARC) to Y-TZP blocks. Half of the specimens (n=10) of each treatment was tested 24 hours after adhesion (dry), and another half (n=10) will be subjected to the aging (storage for 90 days and $10^3$ thermal cycles). The specimens were submitted to shear test (1min/min). After debonding, the surfaces will be analyzed by optical microscopy and scanning electron microscopy (SEM) to categorize the failure modes and the micro morphology of treated surfaces. Additional analyzes were made in X-ray dispersive energy analysis (EDS). Data were statistically analyzed for Kruskal-Wallis/Mann Whitney (α=0,05) tests. The surface treatment showed significant differences in conditions D (p=0.0001) and A (p=0.0000). In both test conditions , TBS and F-5 promoted the highest bond strength, significantly. Means (SD) for BS data (MPa) were: TBS/D: 10.2 $(5.1)^{AB}$; F-5/D: 12.0 $(3.9)^{A}$; F-500/D: 14.9 $(4.7)^{A}$; F-500HF/D: 4.1 $(5.6)^{B}$; TBS/A: 9.1 $(4.4)^{a}$; F-5/A: 7.8 $(5.3)^{a}$; F-500/A: 0.01 $(0.0)^{b}$; F-500HF/A: 1.4 $(2.3)^{b}$. The adhesion to zirconia can be improved if the surface receives a 5 nm layer of $SiO_2$ nanofilm or is subjected to sandblasting with silica particles, followed by silanization.

**Key-words:** Bond strength. Surface treatment. Y-TZP. Zirconia. Film.

# SUMÁRIO

# 1. INTRODUÇÃO

Ao longo dos últimos anos houve um aumento na demanda por procedimentos mais estéticos na clínica odontológica. Apesar da casuística e do sucesso das restaurações metalocerâmicas, a odontologia sempre buscou substituir materiais metálicos, principalmente em função da estética e da biocompatibilidade. A confecção de próteses em cerâmica livre de metal tornou-se possível graças ao surgimento das cerâmicas reforçadas.

Dentre as cerâmicas reforçadas, a zircônia policristalina estabilizada por ítria (Y-TZP) é a que possui as melhores propriedades mecânicas entre todos os tipos de cerâmicas e pode ser comparada ao metal (PICONI et al., 1999; BLATZ et al., 2004), tanto que foi chamada de "*ceramic steel*" ou cerâmica de aço (GARVIE et al., 1975). Por esses motivos, foi gradativamente incorporada à prática odontológica para a confecção de infraestruturas de próteses livres de metal, implantes e pinos intrarradiculares. Além disso, a zircônia é um material inerte biologicamente e possui durabilidade a longo prazo (ABOUSHELIB et al., 2006).

Estudos clínicos têm mostrado uma excelente taxa de sobrevivência de próteses parciais fixas e coroas feitas com infraestruturas de zircônia, entretanto, esses estudos relatam que um tipo de falha que ocorre é a descimentação da prótese pela falta de uma adequada adesão entre a zircônia e o cimento resinoso. (TINSCHERT et al., 2008; MOLIN et al., 2008, RINKE et al., 2013)

A falta de adesão é atribuída ao alto conteúdo cristalino na sua composição e ausência de uma fase vítrea, ou seja, indisponibilidade de sílica na superfície da cerâmica Y-TZP. Por não ser condicionável por ácido fluorídrico, é classificada como uma cerâmica ácido-resistente, além disso, é uma cerâmica muito estável quimicamente e pouco reativa (DERAND & DERAND, 2000).

Com o intuito de aumentar a resistência de união entre a zircônia e os cimentos resinosos, numerosas técnicas de tratamento de superfície vêm sendo propostas na literatura. O tratamento de superfície destina-se a dois propósitos fundamentais que podem ocorrer simultânea ou separadamente, dependendo do procedimento adotado: produzir microrretenções superficiais que serão preenchidas pelo cimento resinoso criando uma grande área de imbricamento micromecânico (BORGES et al., 2003), e ampliar a reatividade química da superfície com os agentes de união para união química (BLATZ et al., 2003).

A técnica mais tradicional de tratamento de superfície é o jateamento da superfície da cerâmica com partículas de óxido de alumínio recobertas com sílica, denominado tratamento triboquímico (THOMPSON et al., 2011). Estudos laboratoriais já comprovaram que esta técnica é capaz de promover um aumento na resistência de união entre a cerâmica e o cimento resinoso (MAY et al., 2010), porém pode gerar defeitos na superfície da cerâmica Y-TZP, através de micro-trincas prematuras que podem provocar fraturas nas restaurações, levando a um insucesso clínico (ZHANG et al., 2006).

Outros estudos têm desenvolvido técnicas de condicionamento da zircônia via vitrificação da sua superfície, com o objetivo de tornar a superfície microrretentiva e reativa quimicamente, semelhante aos mecanismos de união da cerâmica feldspática (KITAYAMA et al., 2009; NTALA et al., 2010; CURA et al., 2011; VANDERLEI et al., 2013). Entretanto quando a camada de vitrificação é próxima de 100 µm pode influenciar o assentamento de próteses fixas, ocasionando o desajuste marginal (MCLEAN et al., 1971; BEUER et al., 2009; VANDERLEI et al., 2013).

Além da técnica de vitrificação, outros tratamentos também são descritos na literatura, como a técnica do condicionamento por infiltração seletiva (ABOUSHELIB et al., 2007), *primers* específicos para zircônia (MATINLINNA et al., 2006), fluoração da superfície da zircônia (PIASCIK et al., 2012), entre outros.

Dentro deste contexto, este estudo avaliou um novo método de tratamento de superfície para a cerâmica Y-TZP, através da deposição de nanofilmes de sílica, que por meio da união química entre a sílica, o agente de união silano e o cimento resinoso, resultaria em um aumento da resistência de união sem causar danos à cerâmica. Além disso, foi usado um método de envelhecimento (armazenagem em água e ciclagem térmica) para verificar da durabilidade dessa união a longo prazo.

## 2. OBJETIVOS

No presente trabalho propôs-se avaliar:

1. A influência dos filmes à base de silício, depositados por plasma sobre a superfície da cerâmica Y-TZP na resistência de união a um cimento resinoso.

2. A durabilidade de união entre Y-TZP e cimento resinoso.

# 3. ARTIGO - ADHESION TO THE Y-TZP CERAMIC: STUDY OF SILICA NANO-FILM COATING ON THE Y-TZP SURFACE

Este artigo será submetido à publicação no periódico *Journal of Biomedical Materials Research Part B: Applied Biomaterials*.

**Adhesion to Y-TZP ceramic: study of silica nano-film coating on the surface of Y-TZP.**

Carolina Ceolin Druck[a] / João Luiz Pozzobon[b] / Gustavo Luiz Callegari[c] / Lucio Strazzabosco Dorneles[d] / Luiz Felipe Valandro[e*]

[a] Carolina Ceolin Druck, MSciD/PhD Graduate Programs in Oral Science (Prosthodontics Unit), Faculty of Odontology, Federal University of Santa Maria, Santa Maria, Brazil.

[b] João Luiz Pozzobon, Faculty of Odontology, Federal University of Santa Maria, Santa Maria, Brazil.

[c] Gustavo Luiz Callegari, Graduate Program in Physics, School of Physics, Federal University of Santa Maria, Santa Maria, Brazil

[d] Lucio Strazzabosco Dorneles, MSciD/PhD Graduate Program in Physics, Physics Department, Federal University of Santa Maria, Santa Maria, Brazil.

[e] Luiz Felipe Valandro, MSciD/PhD Graduate Programs in Oral Science, Prosthodontic Unit, Faculty of Odontology, Federal University of Santa Maria, Santa Maria, Brazil.

**Short title: Adhesion to Y-TZP: study of silica nanofilm**

***Corresponding author**
**Luiz Felipe Valandro**, D.D.S., M.Sci.D., Ph.D., Associate Professor,
Federal University of Santa Maria
Faculty of Odontology
Head of Ph.D.-M.Sci.D. Graduate Program in Oral Science
Prosthodontics Unit
R. Floriano Peixoto, 1184, 97015-372,
Rio Grande do Sul State, Santa Maria, Brazil.
Phone: +55-55-3220-9276, Fax: +55-55-3220-9272
E-mail: lfvalandro@hotmail.com (Dr LF Valandro)

**ACKNOWLEDGEMENTS**
The authors thank support from CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), CAPES (Coodenação de Aperfeiçoamento de Pessoal de Nível Superior), and FAPERGS (Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul).

**Adhesion to Y-TZP ceramic: study of silica nano-film coating on the surface of Y-TZP.**

Carolina Ceolin Druck[a] / João Luiz Pozzobon[b] / Gustavo Luiz Callegari[c]/ Lucio Strazzabosco Dorneles[d]/ Luiz Felipe Valandro[e*]

ABSTRACT

This study evaluated the influence of silica-based film coatings on the surface of Y-TZP, in particular on the durability of the bond strength between the ceramic and resin cement. Eighty Y-TZP (In-Ceram YZ, Vita) blocks (4x4x3mm) were obtained and divided into 4 groups according to the surface treatments (n=20): (TBS) tribochemical-silica-coating (Cojet,3M/ESPE), (F-5) 5nm $SiO_2$ nanofilm and silanization, (F-500) 500nm $SiO_2$ nanofilm and silanization, and (F-500HF) 500nm $SiO_2$ nanofilm + hydrofluoric-acid-etching + silanization. Specimens of composite resin (3.25mm in diameter and 3mm in height) were cemented to Y-TZP blocks using resin cement (Relyx ARC). Half of the specimens from each group were tested 24 hours after adhesion (B- baseline condition), and the other half were subjected to aging (A- storage for 90 days and 10,000 thermal cycles). The specimens were subjected to shear testing (SBS) (1mm/min). After testing, the surfaces were analyzed with a stereomicroscope and SEM. Micro-morphologic and elemental chemical analyzes of the treated Y-TZP surface were made by EDS. Bond strength data were statistically analyzed by Kruskal-Wallis/Mann Whitney tests ($\alpha$=0.05). The surface treatment showed significant differences for B (p=0.0001) and A (p=0.0000) conditions. In both storage conditions, TBS and F-5 promoted the significantly highest bond strength. The most of the specimens presented adhesive failure. The EDS analysis depicted the highest peak of silica in the TBS and F-500 groups. The adhesion to zirconia can be improved if the surface receives a 5nm layer of $SiO_2$ nanofilm or is subjected to sandblasting with silica particles, followed by silanization.

Key-words: adhesion, zirconia, bond test, resin cement, silica deposition.

# INTRODUCTION

The use of ceramic restorations, combining the aesthetics of veneering porcelain with the resistance of infrastructure ceramic, became popular in the last decade.[1] Among the ceramic materials available for fixed partial denture frameworks, zirconia offers the highest mechanical properties to be used as framework of metal-free restorations. This material is characterized by high flexural strength, fracture toughness and fatigue resistance.[2-4] However, some clinical studies have reported restoration decementation as a type of failure, due to the difficulty in adhering a zirconia substrate to resin cements.[5-7]

Y-TZP zirconia (yttrium-stabilized tetragonal zirconia polycrystal) is a polycrystalline ceramic composed of a polymorphic material that occurs in three crystalline forms: monoclinic (m), tetragonal (t) and cubic. The yttrium oxide is added to control the volume expansion and to stabilize the tetragonal phase at environmental temperatures.[2] A relevant property which differentiates the Y-TZP ceramic from other ceramics is that, once a crack starts and spreads during the application of an external load, the tetragonal phase can change to a monoclinic phase around the edge of the crack. This located volumetric expansion (3-5%), caused by phase transformation, creates a compressive stress layer at the crack origin, which actively prevents crack propagation.[4,8,9]

As YTZP is a chemically and biologically inert material, a commonly observed problem on the clinical use of zirconia is the difficulty in forming adequate adhesion.[3,4] The porcelain (glass ceramic) surface is etched with 10% hydrofluoric acid associated with a silane coupling agent, resulting in a high resin bond strength.[10] However, the traditional adhesive technique utilized for silica-based ceramics is not effective in zirconia, due to the high crystalline content in its composition, creating a non-reactive surface which is resistant to etching with hydrofluoric acid.[11] Therefore, zirconia requires mechanical methods to promote adhesion, such as sandblasting, grinding, or abrasion with diamond rotatory instruments, to increase the surface roughness and activate its surface with adhesion promoters (*primers*) to obtain chemical adhesion.[4]

To improve the bond strength between zirconia and resin cements, several techniques have been proposed in the literature. The most commonly used method is tribochemical silica coating,[12-18] which involves blasting the surface with aluminum oxide particles coated by silica, followed by the application of a silane primer. However, some studies show that sandblasting particles can cause phase transformation, from tetragonal to monoclinic, causing micro cracks on the Y-TZP surface and leading to catastrophic fracture.[19-21]

Another method that has been studied is the use of specific zirconia primers. However these primers have shown low and unstable bond strengths after water storage and thermocycling.[22-24]

More recently, zirconia conditioning techniques have been studied, with the objective of making a micro-retentive and chemically reactive surface, similar to the bond mechanisms, which occur for feldspathic ceramics. Aboushelib et al.[25] developed a technique called '*selective infiltration etching*': a thin layer of an infiltration agent composed of a low temperature melting glass is applied on the zirconia surface and then is completely removed by hydrofluoric acid etching to promote nano retentions surrounding the zirconia crystals. Kitayama et al.[11] proposed the "*internal coating technique*": the application of a silica-based ceramic layer (approximately 100 µm thick) on the surface of Y-TZP. Piascik et al.[16] researched a technique that consists of the molecular vapor deposition (MVD) of a chloro-silane gas combined with steam to deposit thin $Si_xO_y$ films on the zirconia surface. Ntala et al.[26] and Cura et al.[27] developed different glass materials, based on lithium disilicate and specific feldspathic ceramic to zirconia, respectively, to improve adhesion to the zirconia substrate.

Vanderlei et al.[28] researched a similar technique to that presented by Kitayama et al.[11], Ntala et al.[26] and Cura et al.[27]. For this treatment, a low-fusing porcelain glaze is applied on the surface of the Y-TZP and is heat sintered. Then, the glazed Y-TZP surface is etched by hydrofluoric acid and silanized. Vanderlei et al.[28] noted a stable resin bond strength when the Y-TZP received that treatment. However, the glass layer application on the intaglio surface of Y-TZP crowns promoted marginal misfit of up to 100 µm, which was higher than when the layer was not applied.[28-31]

Queiroz et al.[32] tested a method of silica deposition on Y-TZP, through the physical vapor deposition (PVD) using magnetron sputtering. With this, $SiO_2$ nanofilms are deposited on the Y-TZP surface through the processing plasma. This method is only based on chemical adhesion, where the silica film deposition, associated with silanization, results in increased bond strength, without damage to the Y-TZP surface.[32] Furthermore, this method forms a homogeneous film and good adhesion to the substrate.[33]

Nevertheless, no studies are currently found in the literature that have evaluated the deposition of silica nanofilms with different thicknesses and the resulting zirconia-resin adhesion durability.

Thus, the aim of this present study was to evaluate the effect of $SiO_2$ nanofilm thickness on zirconia surface on the adhesion durability between zirconia and resin cement, and compare it to tribochemical silica coating (gold standard). The hypotheses tested were: 1) the surface treatment with silicon-based film deposition would improve the adhesion and 2) the water storage/ thermocycling would decrease the bond strength.

# MATERIALS AND METHODS

## Y-TZP Specimen Production

Yttria-stabilized tetragonal zirconia polycrystalline ceramic blocks (Y-TZP) (VITA In-Ceram 2000 YZ cubes for inLab) were prepared using a cutting machine (IsoMet® 1000/ Buehler, Illinois, USA), resulting in 80 blocks with an adhesive surface area of 5x5x4 mm. The samples were standardized using Sof-Lex disks (3M ESPE, Seefeld, Germany) and sanded with 1200-grit sandpaper. The specimens were sintered according to the manufacturer's guidelines, and were then divided into 8 groups, considering the surface treatment factors and thermocycling (Table 1).

## Y-TZP Surface Conditioning Methods

*Tribochemical silica coating*

The TBS group was sandblasted by air-borne particle abrasion with silica-coated aluminum oxide particles (30µm) (CoJet-Sand®, 3M ESPE, Seefeld, Germany) from a distance of 10 mm perpendicular to the surface for 10 seconds at a pressure of 2.8 bar. An adapted device was used to standardize the application.[34]

*Silica nano films*

The $SiO_2$ thin films were deposited in the Magnetism and Magnetic Materials Laboratory, UFSM; Santa Maria, Brazil, using the magnetron sputtering PVD process, as follows: the Y-TZP blocks and the silicon dioxide target were positioned in a vacuum chamber. The atmosphere inside the chamber was pumped down to ~ $10^{-7}$ Torr. Argon gas was admitted into the chamber at a flow rate of 20 sccm, keeping the pressure at 5.2 mTorr. A pre-sputtering of the target was performed. After pre-sputtering, the substrate holder was placed over the target, thus initiating the deposition process, and controlling the time required for exposure of the substrate to the plasma to the desired film thickness. The deposition process consisted of accelerating argon ions against the silica target, depositing the ejected material on the substrate (zirconia surface) located in front of the bombarded target.

Two $SiO_2$ nanofilm thicknesses were deposited: 5nm, corresponding to 90s of deposition and 500 nm, corresponding to 2h of deposition. For the F-500HF group, after 500nm of $SiO_2$ deposition occurred, the surface was etched with 10% HF for 5 s.

After conditioning, all specimens from all groups received the application of the MPS (methacryloxypropyltrimethoxy-silane) silane coupling agent (ESPE-Sil Silane, 3M ESPE, Seefeld, Germany), using a microbrush, waiting 5 min for solvent evaporation (ethanol), before cement application.

**Bonding Procedure**

Each Y-TZP block was embedded in a plastic cylinder (h=14 mm, Ø=25 mm) with chemically activated acrylic resin, keeping the bond surface free from contamination.

The composite resin specimen cylinders (Opallis, FGM, Joinville, Brazil) were produced immediately before cementation, using a bipartite cylindrical metallic template with a 3.25 mm diameter and 3 mm height. Thus, the base area for adhesion was 8.30 $mm^2$.

For cementation, a dual-cure resin cement (RelyX ARC, 3M/ESPE, Seefeld, Germany) was manipulated as recommended by the manufacturer, applied on the bonding surface of the composite resin cylinder and then cemented to the Y-TZP surface. The cement was light-cured (Radii-cal, SDI, EUA) for 20s from the top and the cement excess was removed. Photo activation was performed at the 4 lateral marginal regions for 40s.

All specimens were stored for 24 hours in distilled water at 37 °C.

## Aging process and SBS Test

After 24 h, 10 specimens from each group were submitted to the SBS test ("baseline" groups).

The other specimens were submitted to thermal cycling (10,000 cycles, 5°C/55°C, 30 seconds per bath; Ethic Technology, Vargem Grande Paulista, Brazil) and storage for 90 days in water (the "aging" groups).

The specimens were mounted in the jig of a universal testing machine (EMIC, São José dos Pinhais, Brazil) for shear testing and a wire loop (Ø= 0.12 mm) at a crosshead speed of 1.0 mm/min was used to load the adhesive interface until failure occurred. The bond strength ***R*** (MPa) was calculated according the formula R=F/A, in which ***F*** is the load for specimen failure (N), and ***A*** is the cross-sectional interfacial area ($mm^2$).

## Failure Analysis

All of the tested specimens were analyzed under a stereomicroscope at 15x magnification to determine the failure type (Discovery V20, Carl Zeiss, Alemanha). The failure types were classified according to the following criteria: (A) at the ceramic-cement interface; (B) cohesive in the resin cement; (C) cohesive in the ceramic; and (D) mixed (A+B). Moreover, representative failures were selected and analyzed under SEM (Scanning Electron Microscopy, JSM-6360, JEOL, Tokyo, Japan).

## x-ray Energy dispersive spectroscopy (EDS)

EDS (QUEST, Thermo Noran, Middleton, USA) was performed to evaluate the elemental chemical composition of the Y-TZP surfaces submitted to the surface treatments to identify the elements found on the surfaces.

## Micro-morphologic analysis

Two additional Y-TZP samples from each surface treatment were evaluated under a scanning electron microscope (SEM) (Jeol-JSM-T330A, Jeol Ltd, Tokyo, Japan) (1000x-10000x magnification).

## Data Analysis

Statistical software was used for data analysis (Statistix 8.0 for Windows, Analytical Software Inc, Tallahassee, FL, USA). The bond strength data were not parametric; therefore, the data were submitted to Kruskal-Wallis and Mann Whitney multiple comparison tests (5%).

# RESULTS

Means and standard deviations of the bond strength data are summarized in Table 1. The Kruskal-Wallis of the bond strength data showed that the surface conditionings had a significant influence for both the baseline (p=0.0001) and aging (p=0.0000) conditions.

The 5 nm silica nanofilm deposition and tribochemical silica coating promoted the highest and most stable bond strengths to Y-TZP, which were both statistically significant. The bond strength of the F-500 group (A) decreased drastically after aging (specimens failed during aging). The F-500HF group also significantly decreased in bond strength after aging.

Thus, the first hypothesis was partially accepted, since only the F-5 group improved bond strengths. The second hypothesis was also partially accepted, because aging only decreased the values of bond strength for the F-500 and F-500HF groups.

With regards to the failure modes (Table 2), adhesive failures at the ceramic-cement interface were the predominant failure type. No cohesive failures of the ceramic or composite failures were found. Figure 1 provides micrographs of representative fractured specimens.

The elemental chemical analysis (EDS) depicted the highest peak of silica in the TBS and F-500 groups (Figure 2).

The micrographs from the untreated and treated Y-TZP surface (Figure 3) show the air-abrasion with silica particles (silica-coating process) promotes relevant surface modifications of the surface, while the nano-film coating from magnetron sputtering PVD process (F-5, F-500, and F-500HF groups) generates none topographic alterations (resulting in nano-film deposition for chemical bond particularly).

## DISCUSSION

The current study did not compare the Y-TZP surface conditionings to an untreated group (without Y-TZP surface treatment) because several previous studies have already demonstrated the weak adhesion between untreated Y-TZP and resin cements.[28,35-37]

Another consideration regarding the current methodology involves using a resin cement without MDP (10-methacryloyloxydecyl-dyhydogen phosphate), in view of the fact that resin cements containing MDP increase the adhesion to the Y-TZP surface.[15,35,38-40] Thus, the potential for bond improvement of the Y-TZP surface treatments were evaluated more precisely, without the influence of MDP bonds.

Shear bond strength testing was chosen for the simplicity and facility for assessing the adhesion to a Y-TZP substrate. This material presents high mechanical properties, which makes the microtensile test difficult. However, a limitation of the shear bond strength test is the development of non-homogeneous stress distribution at the bonding interface, especially when the knife device is used. Interestingly, the shear test using the wire-loop approach, as used in the current study, generates better stress distribution than the knife approach.[41-43] As a consequence of non-homogeneous stress distributions, the shear tests increase the possibility of cohesive failure of the substrates, which is a limitation of the testing methodology.[43,44] In the present study, the F-500/D group was the only one that presented a cohesive failure, probably due to the test configuration.

The failure analysis from this present study showed a predominance of adhesive failures, followed by some mixed and one cohesive failure, as previously mentioned. The F-500(A) and F-500HF(A) groups presented a high incidence of spontaneous debonding during the storage/thermal cycling period due to their weak bonding, which confirms the weak bond to the Y-TZP material. These pre-test failures were arbitrarily assigned the value of 0.01 MPa to each specimen for the statistical analysis.

The study of adhesion to Y-TZP ceramics became a topic of great interest in recent years, as the microstructure and chemical composition makes it resistant to conditioning by hydrofluoric acid. Different surface treatment methods of Y-TZP are being developed to improve the bond strength to resin cements.[11,16,24-26] Within this context, the current study proposed to evaluate the effect of depositing a thin silica film on the Y-TZP surface and compare it to tribochemical silica coating, which is considered the ‘gold standard’.

The deposition of a thin silica film on the ceramic surface allows for chemical bonding between the deposited silica, silane and resin cement. The silane molecules react with water, forming silanol groups (–Si–OH) from methacryloxy groups. The silanol groups react with the silica deposited on the material surface to form a siloxane network (–Si–O–Si–O–). The monomeric ends of silane react with the methacrylate groups of the resin material.[45-47] This bonding mechanism occurs when the Y-TZP surface receives silica oxide layers by airparticle abrasion and by sputtering systems, since the silica oxides are available to adhere to silanes.

Another Y-TZP surface treatment method that has been extensively studied, with promising results, is the application of a thin layer of low-fusing glass porcelain on the Y-TZP surface .[11,16,27,28,48]

The advantages of the silica film deposition on Y-TZP ceramic, when compared to the application of a glass-ceramic, is that the deposition is rapid and can be performed at low temperatures. The thickness and the chemical composition of the film can also be controlled. Furthermore, this coating does not interfere with the clinical marginal adaptation of crown, because the film has a nanometric thickness. The film deposition is conducted at a temperature reaching a maximum of about 70 °C inside the deposition chamber, so it does not subject the ceramic to high temperatures. The disadvantages of silica film deposition include the requirement of special equipment, high cost and specific training for equipment use.

The literature [15,17,49-51] shows that aging has an important role on the longevity of composite to Y-TZP bonding and is fundamental for assessing the real capacity for bond improvement of any pretreatment of the Y-TZP surface. Water storage and thermal cycling resulted in a reduction in bond strengths for the F-500HF(A) group and spontaneous debonding for all specimens of the F-500(A) group. However, stable and higher bond strength values were found in the F-5(A) and TBS (A) groups. Although the tribochemical silica-coating method has been shown to be an effective treatment for zirconia, the literature reports that this method induces the tetragonal to monoclinic transformation. The presence of the monoclinic phase on the zirconia surface may result in surface alterations that compromise the establishment of reliable micromechanical adhesion.[52] Moreover, this conversion may induce defects on the zirconia surface, which may serve as crack initiation sites, decreasing the long-term survival of all-ceramic crowns.[36]

Two films thicknesses were used in this current study: 5 nm and 500 nm. Before aging, both films showed statistically similar bond strengths; however, all specimens of the F-500(A) group had spontaneous failure before shear test after aging, indicating a weak bond from this treatment. This spontaneous failure can be attributed to thermal cycling, as materials with different values of thermal expansion coefficients may lead defects at the interface.[53] In the F-5(A) group, the values of bond strength remained stable after aging. This film has a very thin thickness and probably mitigated the thermal expansion of the interface materials, ceramic or resin cement. Moreover, the 5 nm $SiO_2$ film mimics the zirconia surface morphology forming very small structures, as seen in the SEM images. When comparing this image with the image from an untreated zirconia surface, it cannot be determined if the surface is completely covered, and small voids may be present. However, the surface is uniformly covered with silica, making it more chemically reactive. These small grain structures would have a less rigid nature (especially if small voids are indeed present) when compared to a thicker film, which absorb expansion during thermal cycling without cracking.

The SEM images from the much thicker 500 nm $SiO_2$ film indicate larger silica grains, definitely covering the entire zirconia surface, which are less able to absorb expansion due to thermal cycling due to its more rigid structure. Piascik et al.[16] also found high bond strength results for a ceramic-based Y-TZP treated with $SiCl_4$ by vapor deposition, resulting in a $Si_xO_y$ film with a thickness of approximately 2.6 nm. The relation of film thickness with the bond strength was attributed to the chemical bonding between the film layers, whether the film is thick may lead to a lack of chemical bonding between the layers formed during deposition.

For the F-500HF (film deposition of 500nm) group, the treated surface was quickly etched with HF to create nano retention and increase the bonding area. However, low bond values were depicted for the "dry" condition, suggesting the most of the silica film was removed by hydrofluoric acid etching or that a non-uniform film remained on the surface, resulting in a ‘quasi Y-TZP untreated surface’, which may explain the low adhesion results both before and after aging. The EDS analysis showed a small silica peak from this group, indicating a small amount of silica on the Y-TZP surface.

## CONCLUSIONS

- the deposition of a 5 nm silica film on the surface of Y-TZP, followed by silane application, appears to be promising for the improvement of resin bonding (stable bonding) to the Y-TZP surface;

- the surface treatment of Y-TZP with 5 nm silica film deposition can be an alternative method to tribochemical silica coating.

# TABLES

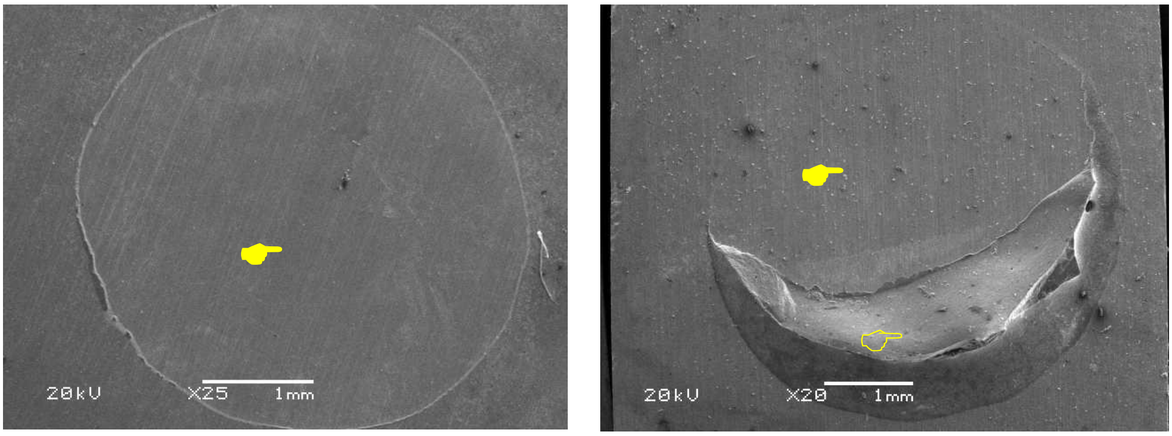
**Table 1.** Testing groups for bond strength evaluation. Considering the 2 studied factors (Y-TZP surface conditioning [in 4 levels] and storage condition [in 2 levels]). *Means (±SD) of the bond strength data (MPa) and Kruskal Wallis test are presented (comparison was made among groups from the same storage condition). **P values for comparison (Mann Whitney test) between the groups submitted to the same Y-TZP surface conditioning under different storage condition (P value < 0.05 represents the means of bond strength have significant difference; ns= no difference).

| Groups | YTZP surface conditionings (n=10) | Aging | Bond results* | Mann Whitney** |
|---|---|---|---|---|
| TBS | Tribochemical silica coating | Baseline (no-aging) | 10.2 (5.1)$^{AB}$ | 0.9097ns |
| F-5 | 5 nm $SiO_2$ nanofilm | | 12.0 (3.9)$^{A}$ | 0.1212ns |
| F-500 | 500 nm $SiO_2$ nanofilm | | 14.9 (4.7)$^{A}$ | 0.0002 |
| F-500HF | 500 nm $SiO_2$ nanofilm + etching with 10% hydrofluoric acid | | 4.1 (5.6)$^{B}$ | 0.0452 |
| TBS(TC) | Tribochemical silica coating | Aging | 9.1 (4.4)$^{a}$ | |
| F-5(TC) | 5 nm $SiO_2$ nanofilm | | 7.8 (5.3)$^{a}$ | |
| F-500(TC) | 500 nm $SiO_2$ nanofilm | | 0.01 (0.0)$^{b}$ | |
| F-500HF(TC) | 500 nm $SiO_2$ nanofilm + etching with 10% hydrofluoric acid | | 1.4 (2.3)$^{b}$ | |

**Table 1**. Failure mode classifications after shear bond strength (B- baseline condition; A- aging condition).

| Groups | Failure Mode | | |
|---|---|---|---|
| | Adhesive (%) | Mixed (%) | Cohesive (Cement) (%) |
| TBS(B) | 40 | 60 | 0 |
| F-5(B) | 50 | 50 | 0 |
| F-500(B) | 50 | 40 | 10 |
| F-500HF(B) | 90 | 10 | 0 |
| TBS(A) | 60 | 40 | 0 |
| F-5(A) | 50 | 50 | 0 |
| F-500(A) | 100 | 0 | 0 |
| F-500HF(A) | 70 | 30 | 0 |

## FIGURES




A B

**Figure 1**. Representative micrographs (SEM) of the failure modes after SBS testing. Image (A) shows the adhesive failure mode at the ceramic-cement interface and image (B) shows the mixed failure mode. The indicator (☛) represents the Y-TZP surface free of resin cement, while the pointer (☞) indicates the resin cement surface.

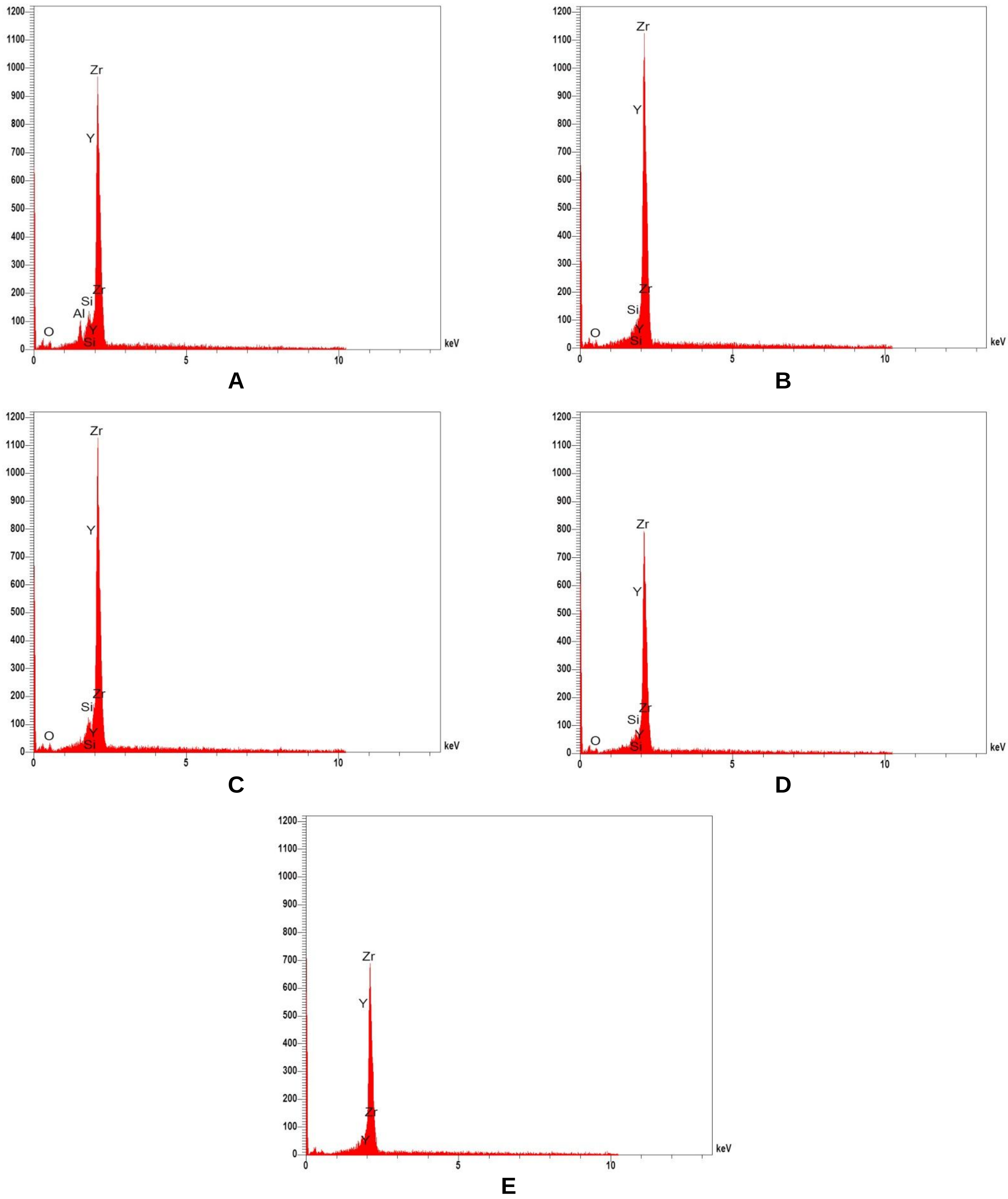
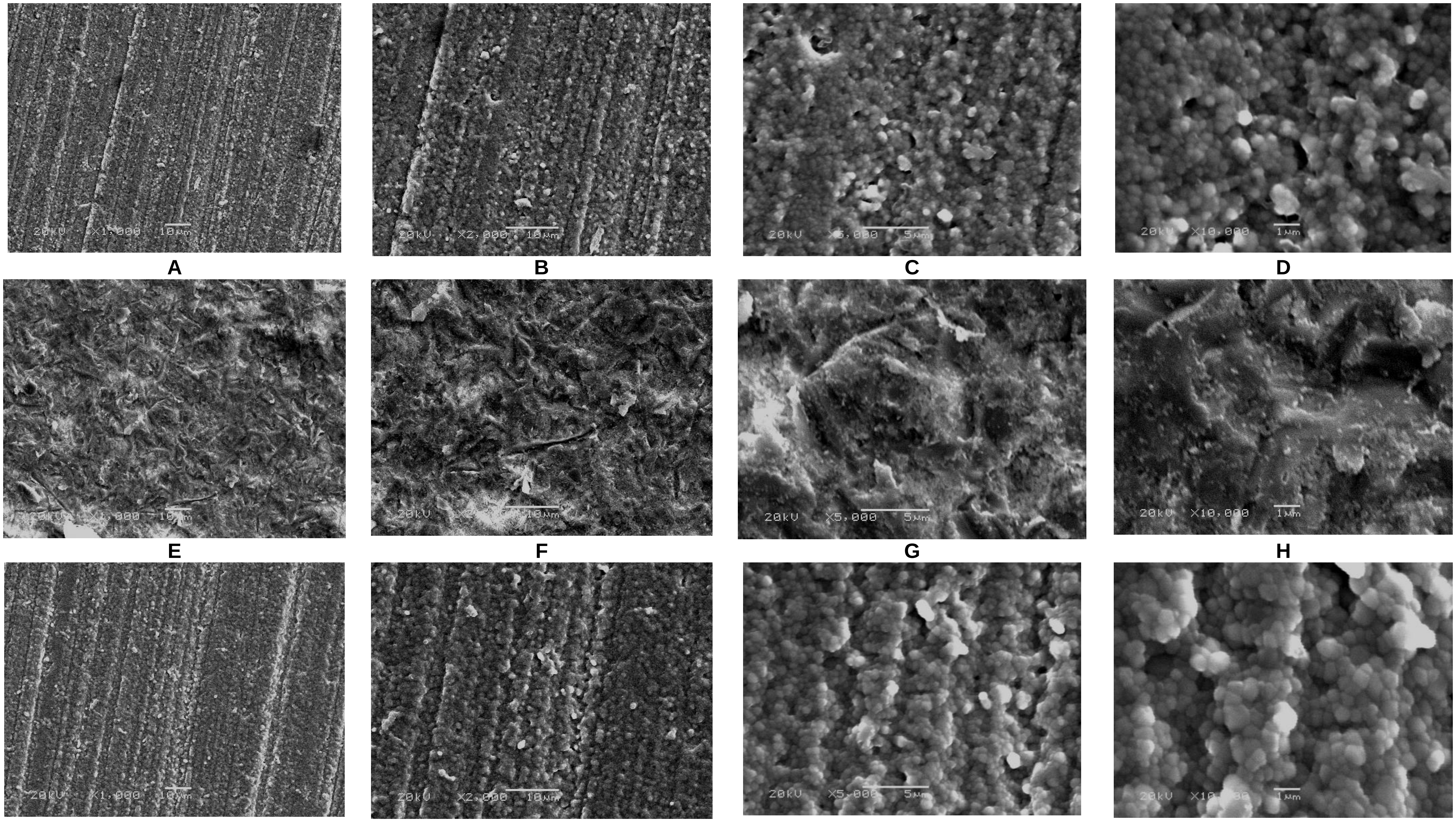



**Figure 2**. EDS spectra show the presence of silica (Si) in (a), (b), (c) and (d) corresponding the groups TBS, F-5, F-500, F-500HF, respectively. On contrary, it notes absence of silica on the untreated zirconia sample (e) (Abbreviation: Si, silica; Al, aluminum; Zr, zirconia; O, oxygen; Y, yttria).


A
B
C
D
E
F
G
H

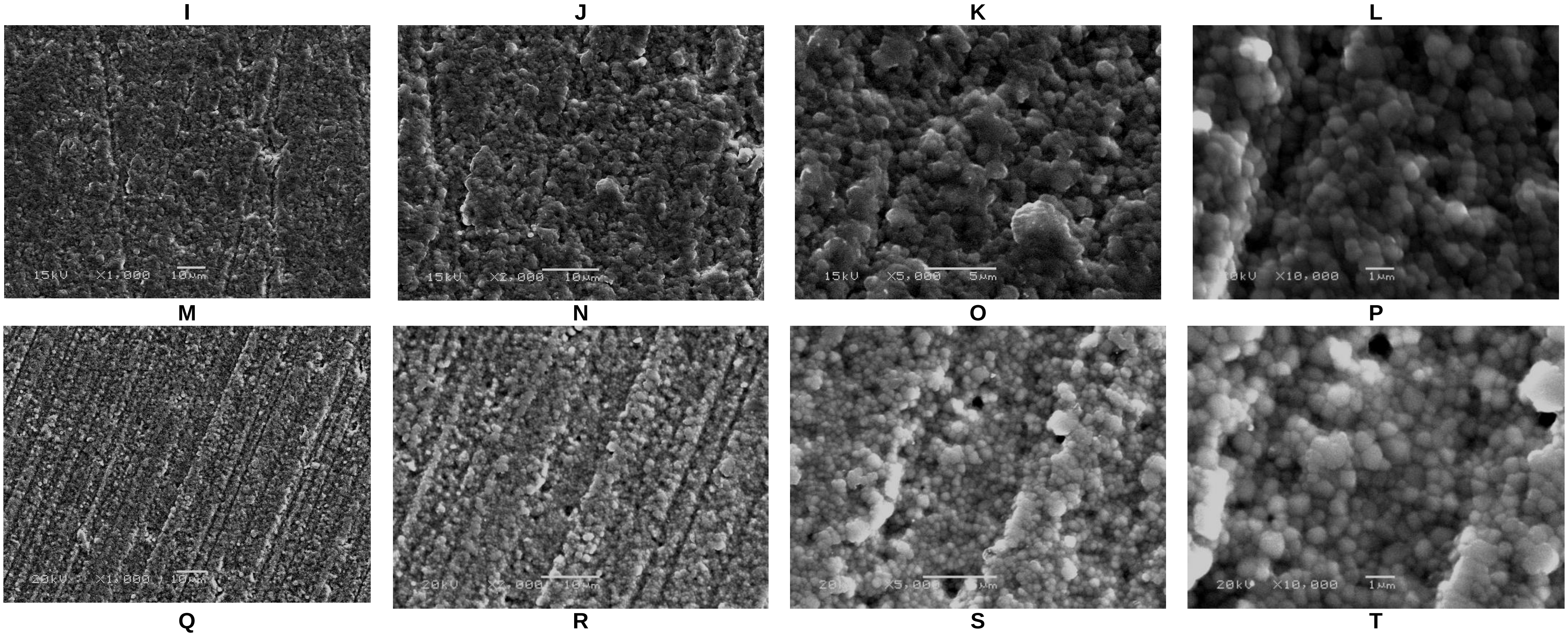



**Figure 3**. Representative micrographs of Y-TZP surface after different surface treatments compared to untreated surface (left to right: 1000x, 2000x, 5000x, and 10000x magnifications. (A-B-C-D): untreated surface; (E-F-G-H) tribochemical silica coating (TBS group); (I-J-K-L) 5 nm film deposition (F-5 group); (M-N-O-P) 500 nm film deposition (F-500 group); (Q-R-S-T) 500 nm film deposition + hydrofluoric acid etching (F-500HF group). It notes that the air-abrasion with silica particles (TBS group) promotes silica coating and increased rough. The silica depositions by sputtering (F-5, F-500 and F-500HF) promote none relevant surface modifications.

**REFERENCES**


1. Heather JC, Seong WJ, Pesun IJ. Current ceramic materials and systems with clinical recommendations: A systematic review. J Prosthet Dent 2007; 98: 389-404.

2. Luthardt RG, Sandkuhl O, Reitz B. Zirconia-TZP and alumina-advanced technologies for the manufacturing of single crowns. Eur J Prosthodont Restor Dent 1999; 7: 113-119.

3. Ferraris M, Verne E, Appendino P, Moisescu C, Krajewski A, Ravaglioli A. Coatings on zirconia for medical applications. Biomater 2000; 21: 765–773.

4. Thompson JY, Stoner BR, Piascik JR, Smith R. Adhesion/cementation to zirconia and other non-silicate ceramics: Where are we now?. Dent Mater 2011; 27: 71-82.

5. Tinschert J, Schulze KA, Natt G, Latzke P, Heussen N, Spiekermann H. Clinical behavior of zirconia-based fixed partial dentures made of DC-Zirkon: 3-year results. Int J Prosthodont 2008; 21: 217-222.

6. Molin MK, Karlsson SL. Five-Year Clinical prospective evaluation of zirconia-based Denzir 3-unit FPDs. Int J Prosthodont 2008; 21: 223-227.

7. Rinke S, Gersdorff N, Lange K, Roediger M. Prospective evaluation of zirconia posterior fixed partial dentures: 7-year clinical results. Int J Prosthodont 2013; 26: 164–171.

8. Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. Dent Mater 1999; 1: 426-433.

9. Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. Biomater 1999; 20: 1-25.

10. Chen JH, Matsumura H, Atsuta M. Effect of different etching periods on the bond strength of a composite resin to a machinable porcelain. J Dentistry 1998; 26: 53-58.

11. Kitayama S, Nikaido T, Maruoka R, Zhu L, Ikeda M, Watanabe A. Effect of an internal coating technique on tensile bond strengths of resin cements to zirconia ceramics. Dent Mater J 2009; 28: 446–453.

12. Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. J Prosthet Dent 2003; 89: 268–274.

13. Blatz MB, Chiche G, Holst S, Sadan A. Influence of surface treatment and simulated aging on bond strengths of luting agents to zirconia. Quintessence Int 2007; 38: 745-753.

14. Valandro LF, Özcan M, Bottino MA, Bottino MC, Scotti R, Della Bona. Bond strength of a resin cement to high-alumina and zirconia-reinforced ceramics: the effect of surface conditioning. J Adhes Dent 2006; 8: 175–181.

15. Ozcan M, Nijhuis H, Valandro LF. Effect of various surface conditioning methods on the adhesion of dual-cure resin cement with MDP functional monomer to zirconia after thermal aging. Dent Mater J 2008; 27: 99-104.

16. Piascik JR, Thompson JY, Swift EJ, Grego S, Stoner BR. Surface modification for enhanced silanization of high strength ceramics. Dent Mater 2009; 25: 1116–1121.

17. Passos SP, May LG, Barca DC, Ozcan M, Bottino MA, Valandro LF. Adhesive quality of self-adhesive and conventional adhesive resin cement to Y-TZP ceramic before and after aging conditions. Oper Dent 2010; 35: 689-696.

18. Attia A. Bond strength of three luting agents to zirconia ceramic-Influence of surface treatment and thermocycling. J Appl Oral Sci 2011: 388-395.

19. Zhang Y, Lawn B. Long-term strength of ceramics for biomedical applications. J Biomed Mater Res Part B Appl Biomater 2004; 69: 166–172.

20. Zhang Y, Lawn B, Rekow ED, Thompson VP. Effect of sandblasting on the long-term performance of dental ceramics. J Biomed Mater Res Part B: Appl Biomater 2004; 71: 381–386.

21. Curtis AR, Wright AJ, & Fleming GJP. The influence of simulated masticatory loading regimes on the bi-axial flexure strength and reliability of a Y-TZP dental ceramic. J Dent 2006; 34: 317-325.

22. Matinlinna JP, Lassila LVJ, Vallittu PK. The effect of a novel silane blend system on resin bond strength to silica-coated to substrate. J Dent Res 2006; 34: 436–443.

23. Matinlinna JP, Lassila LV, Vallittu PK. Pilot evaluation of resin composite cement adhesion to zirconia using a novel silane system. Acta Odontol Scand 2007; 65: 44-51.

24. Matinlinna JP, Heikkinen T, Ozcan M, Lassila LV, Vallittu PK. Evaluation of resin adhesion to zirconia ceramic using some organosilanes. Dent Mater 2006; 22: 824-831.

25. Aboushelib MN, Kleverlaan CJ, Feilzer AJ. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. J Prosthet Dent 2007; 98: 379-388.

26. Ntala P, Chen X, Niggli J, Cattell M. Development and testing of multi-phase glazes for adhesive bonding to zirconia substrates. J Dent 2010; 38: 773-781.

27. Cura C, Ozcan M, Isik G, Saracoglu A. Comparison of alternative adhesive cementation concepts for zirconia ceramic: glaze layer vs zirconia primer. J Adhes Dent 2012; 14: 75-82.

28. Vanderlei A, Bottino MA, Valandro LF. Evaluation of resin bond strength to yttria-stabilized tetragonal zirconia and framework marginal fit: comparison of different surface conditionings. Oper Dent 2013; 38.

29. McLean JW, & von Fraunhofer JA. The estimation of cement film thickness by an in vivo technique. British Dent J 1971; 131: 107-111.

30. Beuer F, Aggstaller H, Edelhoff D, Gernet W, Sorensen J. Marginal and internal fits of fixed dental prostheses zirconia retainers. Dent Mater 2009; 25: 94-102.

31. Boening KW, Wolf BH, Schmidt AE, Kästner K, & Walter MH. Clinical fit of Procera all ceramic crowns. J Prosthet Dent 2000; 84: 419-424.

32. Queiroz JRC, Duarte DA, Souza ROA, Fissmer SF, Massi M, Bottino MA. Deposition of $SiO_x$ thin films on Y-TZP by Reactive Magnetron Sputtering: influence of plasma parameters on the adhesion properties between Y-TZP and resin cement for application in dental prosthesis. Mater Res 2011; 14: 212-216.

33. Ohring M. The Materials Science of Thin Films. London: Academic Press, 1992.

34. Amaral R, Ozcan M, Valandro LF, Bottino MA. Effect of conditioning methods on the microtensile bond strength of phosphate monomer-based cement on zirconia ceramic in dry and aged conditions. J Biomed Mater Res Part B: Appl Biomater 2008; 85B: 1-9.

35. Miragaya L, Maia LC, Sabrosa CE, Goes MF, Silva EM. Evaluation of self-adhesive resin cement bond strength to yttria-stabilized zirconia ceramic (Y-TZP) using four surface treatments. J Adhes Dent 2011; 13: 473-480.

36. Lorenzoni FC, Leme VP, Santos LA, Oliveira PCG, Martins LM, Bonfante G. Evaluation of chemical treatment on zirconia surface with two primer agents and an alkaline solution on bond strength. Oper Dent 2012; 37: 625-633.

37. Cristoforides P, Amaral R, May LG, Bottino MA, LF Valandro. Composite resin to yttria stabilized tetragonal zirconia polycrystal bonding: comparison of repair methods. Oper Dent 2012; 37: 263-271.

38. Wegner SM, Gerdes W, Kern M. Effect of different artificial aging conditions on ceramic-composite bond strength. Int J Prosthodont 2002; 15: 267–272.

39. Aboushelib MN, Matinlinna JP, Salameh Z, Ounsi H. Innovations in bonding to zirconia-based materials: Part I. Dent Mater 2008; 24: 1268-1272.

40. Denry I, Kelly J.R. State of the art of zirconia for dental applications. Dent Mater 2008; 24: 299-307.

41. DeHoff PH, Anusavice KJ, Wang Z. Three-dimensional finite element analysis of the shear bond test. Dent Mater 1995; 11: 126-131.

42. Placido E, Meira JBC, Lima RG, Muench A, Souza RM, Ballester RY. Shear versus micro-shear bond strength test: a finite element stress analysis. Dent Mater 2007; 23: 1086-1092.

43. Braga RR, Meira JBC, Boaro LCC, Xavier TA. Adhesion to tooth structure: A critical review of “macro” test methods. Dent Mater 2010; 26: e38-e49.

44. Aboushelib MN, Feilzer AJ, Kleverlaan CJ. Bonding to zirconia using a new surface treatment. J Prosthodont 2010; 19: 340-346.

45. Plueddemann EP. Adhesion through silane coupling agents. J Adhes 2 1970; 184-201.

46. Valandro LF, Ozcan M, Amaral R, Vanderlei A, Bottino MA. Effect of testing methods on the bond strength of resin to zirconia-alumina ceramic: microtensile versus shear test. Dent Mater J 2008; 27: 849－855.

47. Lung CYK, Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: An overview. Dent Mater 2012; 28: 467–477.

48. Valentino TA, Borges GA, Borges LH, Platt JA, Correr-Sobrinho L. Influence of glazed zirconia on dual-cure luting agent bond strength. Oper Dent 2012; 37: 181-187.

49. Wolfart M, Lehmann F, Wolfart S, Kern M. Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods. Dent Mater 2007; 23: 45-50.

50. Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M, Osorio R. Effect of water aging on microtensile bond strength of dual-cured resin cements

to pre-treated sintered zirconium-oxide ceramics. Dent Mater 2009; 25: 392-399.

51. May LG, Passos SP, Capelli DB, Ozcan M, Bottino MA, Valandro LF. Effect of silica coating combined to a MDP-based primer on the resin bond to Y-TZP ceramic. J Biomed Mater Res Part B Appl Biomater 2010; 95B: 69-74.

52. Perdigão J, Fernandes SD, Pinto AM, Oliveira FA. Effect of artificial aging and surface treatment on bond strengths to dental zirconia. Oper Dent 2013; 38: 168-176.

53. Castro HL, Corazza PH, Paes-Júnior TA, Della Bona A. Influence of Y-TZP ceramic treatment and different resin cements on bond strength to dentin. Dent Mater 2012; 28: 1191-1197.

# 4. CONSIDERAÇÕES FINAIS

- O envelhecimento foi um fator fundamental para avaliar a durabilidade da união entre a cerâmica e o cimento resinoso.
- A deposição de um nanofilme de sílica com 5 nm de espessura na superfície da cerâmica Y-TZP parece ser uma alternativa promissora para aumentar a resistência de união entre a cerâmica e o cimento resinoso.
- Mais estudos devem ser feitos testando diferentes espessuras de nanofilmes de sílica, essas espessuras devem ser próximas a 5 nm.
- Estudos com deposição de nanofilmes utilizando coroas protéticas devem ser conduzidos, a fim de avaliar a plausibilidade clínica deste método de tratamento de superfície.

## REFERÊNCIAS

ABOUSHELIB M.N.; KLEVERLAAN C.J.; FEILZER A.J. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia - based materials. **Journal of Prosthetic Dentistry**, v.98, n.5, p.379-88, 2007.

ABOUSHELIB M.N.; KLEVERLAAN C.J.; FEILZER A.J. Microtensile bond strength of different components of core veneered all-ceramic restorations: Part II: Zirconia veneering ceramics. **Dental Materials**, v. 22, p.857-63, 2006.

BEUER F.; AGGSTALLER H.; EDELHOFF D.; GERNET W.; SORENSEN J. Marginal and internal fits of fixed dental prostheses zirconia retainers. Dental Materials, v.25, p.94-102, 2009.

BLATZ M. B.; SADAN A.; KERN M. Resin-ceramic bonding: a review of the literature. **Journal of Prosthetic Dentistry**, v.89, n.3, p.268-74, 2003.

BLATZ M.B.; RICHTER C.; SADAN A.; CHICHE G.J. Resin bond to dental ceramics, part ii: high-strength ceramics. **Journal of Esthetic and Restorative Dentistry**, v.16, p.324–328, 2004.

BORGES G. A.; SOPHR A.M.; GOES M.F.; SOBRINHO L.C.; CHAN D.C.N. . Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics. **Journal of Prosthetic Dentistry**, v.89, n.5, p.479-88, 2003.

CURA C.; OZCAN M.; ISIK G.; SARACOGLU A. Comparison of alternative adhesive cementation concepts for zirconia ceramic: glaze layer vs zirconia primer. **The Journal of Adhesive Dentistry**, v.14, n.1, p.75-82, 2012.

DERAND P.; T. DERAND. Bond strength of luting cements to zirconium oxide ceramics. **International Journal of Prosthodontics** v.13, n.2, p.131-135, 2000.

GARVIE R.C.; HANNINK R.H.; PASCOE R.T. Ceramic steel? **Nature**, v.258:703–704, 1975.

KITAYAMA S.; NIKAIDO T.; MARUOKA R.; ZHU L.; IKEDA M.; WATANABE A. Effect of an internal coating technique on tensile bond strengths of resin cements to zirconia ceramics. **Dental Materials Journal**, v.28, p.446–53, 2009.

MATINLINNA J.P.; HEIKKINEN T.; OZCAN M.; LASSILA L.V.; VALLITTU P.K. Evaluation of resin adhesion to zirconia ceramic using some organosilanes. **Dental Materials**, v.22, n.9, p.824-31, 2006.

MAY L.G.; PASSOS S.P.; CAPELLI D.B.; OZCAN M.; BOTTINO M.A.; VALANDRO L.F. Effect of silica coating combined to a MDP-based primer on the resin bond to Y-TZP ceramic. **Journal of Biomedical Materials Research Part B: Applied Biomaterials**, v.95 n.1, p.69-74, 2010.

MCLEAN J.W. & VON FRAUNHOFER J.A. The estimation of cement film thickness by an in vivo technique. **British Dental Journal**, v.131, p. 107-111, 1971.

MOLIN MK, KARLSSON SL. Five-Year Clinical prospective evaluation of zirconia-based Denzir 3-unit FPDs. **International Journal of Prosthodontics**, v. 21, p.223-227, 2008.

NTALA P.; CHEN X.; NIGGLI J.; CATTELL M. Development and testing of multi-phase glazes for adhesive bonding to zirconia substrates. **Journal of Dentistry**, v.38, n.10, p.773-81, 2010.

PIASCIK J.R.; SWIFT E.J.; BRASWELL K.; STONER B.R. Surface fluorination of zirconia: adhesive bond strength comparison to commercial primers. **Dental Materials**, v.28, p.604-08, 2012.

PICONI C.; MACCAURO G. Zirconia as a ceramic biomaterial. **Biomaterials**, v.20, p.1-25, 1999.

RINKE S.; GERSDORFF N.; LANGE K.; ROEDIGER M. Prospective Evaluation of Zirconia Posterior Fixed Partial Dentures: 7-Year Clinical Results. **The International Journal of Prosthodontics**, v.26, p.164–171, 2013.

TINSCHERT J.; SCHULZE K.A.; NATT G.; LATZKE P.; HEUSSEN N.; SPIEKERMANN H. Clinical behavior of zirconia-based fixed partial dentures made of DC-Zirkon: 3-year results. **International Journal of Prosthodontics**, v. 21, p.217-222, 2008.

THOMPSON J.Y.; STONER B.R.; PIASCIK J.R.; SMITH R. Adhesion/cementation to zirconia and other non-silicate ceramics: Where are we now?. **Dental Materials**, v.27, p.71-82, 2011.

VANDERLEI A.; BOTTINO M.A.; VALANDRO L.F. Evaluation of resin bond strength to yttria-stabilized tetragonal zirconia and framework marginal fit: comparison of different surface conditionings. **Operative Dentistry**, v.38, 2013.

ZHANG Y.; LAWN B.R.; MALAMENT K.A.; THOMPSON V.; REKOW E.D. Damage accumulation and fatigue life of particle-abraded ceramics. **International Journal of Prosthodontics**, v.19, p.442–8, 2006.

# ANEXOS

## ANEXO A- Normas para publicação no periódico *Journal of Biomedical Materials Research Part B: Applied Biomaterials*.

**Author Guidelines**

**Aims and Scope**

Journal of Biomedical Materials Research Part B: *Applied Biomaterials* is an official journal of the Society for Biomaterials, the Japanese Society for Biomaterials, the Australasian Society for Biomaterials, and the Korean Society for Biomaterials. It is a peer-reviewed journals serving the needs of biomaterials professionals who devise, promote, apply, regulate produce, and market new biomaterials and medical devices. Papers are published on device development, implant retrieval and analysis, manufacturing, regulation of devices, liability and legal issues, standards, reviews of different device areas, and clinical applications. Published manuscript fit into one of six categories: original research reports, clinical device-related articles, short research and development reports, review, special report, or columns and editorials. Manuscripts from all countries are invited but must be in English. Authors are not required to be members of a Society for Biomaterials.

**Types of Articles Considered for Publication**

**Original Research Reports:** Full-length papers consisting of complete and detailed descriptions of a research problem, the experimental approach, the findings, and appropriate discussion. Findings should represent significant new additions to knowledge.
**Clinical Device-Related Articles:** Full-length papers addressing such issues as material processing, device construction, regulatory matters, clinical trials, and device retrieval.
**Reviews:** Scholarly and critical topic-oriented reviews that present a state-of-the-art view. While most reviews are solicited, person sinterested in contributing may contact the Editor.
**Special Reports:** Reports of special topic-oriented symposia,device retrieval protocols, or other special reports not described in the above categories, yet of interest to the applied biomaterials research and development community. Potential contributors should contact the Editor before submitting special reports.
**Columns and Editorials:** While columns and guest editorials arepreponderantly solicited, persons interested in becoming columnists orcontributing editorials are encouraged to contact the Editor.

**Submission of Manuscripts**

**Online Submission:**
*Journal of Biomedical Materials Research Part B: Applied Biomaterials* is now receiving submitted manuscripts online at http://mc.manuscriptcentral.com/jbmr-b.

Submit all new manuscripts online. Launch your web browser and go tohttp://mc.manuscriptcentral.com/jbmr-b. Check for an existing user account. If you are submitting for the first time, and you do not find an existing account, create a new account. Follow all instructions.

At the end of a successful submission, a confirmation screen with manuscript number will appear and you will receive an e-mail confirming that the manuscript has been received by the journal. If this does not happen,please check your submission and/or contact tech support using the Get Help Now link in the right corner of any screen.

**Upon Acceptance:** Manuscript files will now automatically be sent to the publisher for production. It is imperative that files be in the correct format to avoid a delay in the production schedule.

*JBMR Part B* has adopted a policy that requires authors to make a statement concerning potential conflict of interest relating to their submitted articles. The Editorial Board asks authors of original reports and reviews to disclose, at the time of submission: (1) any financial or employment arrangements they may have with a company whose product figures prominently in the submitted manuscript or with a company making a competitive product; and (2) any grants or contracts from a government agency, a nonprofit foundation, or a company supporting the preparation of the manuscript or the described research. This information will be available to the reviewers of the manuscript. If the article is accepted for publication, the editor will discuss with the authors the manner in which such information may be communicated to the reader.

At the time of submission, *JBMR Part B* asks authors to certify that all animals utilized in their research were cared for according to the policies and principles established by the Animal Welfare Act and the NIH Guide for Care and Use of Laboratory Animals.

**Review Process:** All original reports and reviews receive critical review by at least two reviewers with expertise in the major subject area of the paper. Reviewers may recommend "Acceptance as is," "Acceptance with modification," or "Rejection." If modification is required, the manuscript is returned to the author(s). The revised manuscript is then re-reviewed by the original reviewers, and even re-revised if necessary. Differences in opinion are resolved by submission either to a third reviewer or the Editor.

**Organization and File Formats**

**Manuscript:** For optimal production, prepare manuscript text in size 12 font on 8-1/2 x 11 inch page, double-spaced, with at least 1-inch margins on all sides. Text files should be formatted as .doc or .rtf files. The results and discussion sections must be written separately and cannot be combined. Refrain from complex formatting; the Publisher will style your manuscript according tot the Journal design specifications. Do not use desktop publishing software such as PageMaker or Quark Xpress or other software such as Latex. If you prepared your manuscript with one of these programs, export the text to a word processing format. Please make sure your word processing programs “fast save” feature is turned off. Please do not deliver files that contain hidden text: for example, do not use your word processor’s automated features to create footnotes or reference lists. Manuscripts including references (but not figures or tables) should be no longer than 18 pages.

Please be sure to submit your illustrations and tables as separate files;the system will automatically create a pdf file of your paper for there viewers.

Original research and short reports should appear in the following order: title page (including authors and affiliations), abstract,keywords,introduction, materials and methods, results, discussion,acknowledgments,references, figure legends. Number pages consecutively starting with the title page as page 1. Abbreviations must conform to those listed in Council of Biology Editors' CBE Style Manual, 5th Edition.

When mentioning a material, chemical reagent, instrument, or other product, use the generic name only. If further identification (proprietaryname, manufacturer's name and address) is absolutely required,list it in parentheses.

***Title Page:*** List the full title of the paper and each author's full name (first name, middle initial(s), surname),department,institution, city, and state (and country if other than the United States).Indicate the name and address of the author to whom reprint requests should be sent.

***Abstract and Keywords:*** Include an abstract of about 200 words maximum summarizing the aims, findings, and conclusions of the paper. Below the abstract, list five keywords or phrases that best characterize the subject matter of the manuscript.

***Running Heads:*** Supply a short title of no more than65characters, including spaces and punctuations, to be used for running head copy.

***References:*** Number references consecutively as they appear in the text.Material accepted for publication but not yet published may be listed in the References, but unpublished observations, personal communications,and material submitted for publication but not yet accepted should be cited parenthetically within the text (and not included among the numbered references). Style references entries using the Council of Biology Editors Style Manual, 5th Edition formats:

*For journal articles:*

Alexander A, Green WS. Total hip replacements: A second look. JSocBiomater 1989;45:345–366.

*For books/chapters:*

Ricci JL, Guichet J-M. Total hip replacement: A third look.CindraAB, Franklin DE, editors. State of the art orthopaedics, vol 3, Hips.NewYork: Wiley; 1988:56–59.

*For abstracts:*

Davidson GRH. Total hip replacement: A fifth look. TransABCS1987;22-341–345.

*For presentations:*

Goodenough T. Total hip replacement: A sixth look. Presented atthe3rd Annu Mtg Orthop Res Soc, Boston, December 5–7, 1989.

**Figure Legends:** Please supply complete captions for all figures. Captions are to appear on a separate page at the end of the manuscript.

**Tables:** Please save Tables separately and supply numbers and titles for all. All table columns should have an explanatory heading. Tables should be submitted as doc or rtf files.